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## Unit 2-Instrumental Methods of Analysis

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### \* Introduction:

- Electrochemistry is a branch of chemistry which deals with the relationship between chemical reaction and electrical energy. The electrochemistry comprises - the study of chemical changes produced by the passage of an electric current and the generation of electric current from chemical changes. i.e. Electrochemistry deals with the transformation of electrical energy into chemical energy and vice-versa.

A chemical change produced by the passage of electric current, resulting in the chemical decomposition of a substance is known as 'Electrolysis'.

Electric current is a flow of electrons generated by a battery and taken out from the negative pole of the battery when the circuit is completed. A substance which allows electric current to pass through it, is called a Conductor. e.g. All metals, graphite, fused salts, aqueous solutions of acids, bases and salts. The conductors are of two types;

- ① Metallic Conductors - These are the substances which conduct electricity, but are not decomposed by it.  
e.g. Almost all metals, graphite etc.
- ② Electrolytic conductors / Electrolytes - These are the substances which allow the electric current to pass through them in their molten states or in the form of aqueous solution and undergoes chemical decomposition.  
e.g. Acids, bases & electrolyte salts.

On the other hand, the substances which do not conduct electricity either in their molten state or through their aqueous solutions are called non-electrolytes.

e.g. Alcohol, oils, starch solution, sugar solution, petrol etc.

Cellpage

• Instrumental methods of analysis are based on laws of electrochemistry, in which qualitative and quantitative analysis of the analyte is carried out using different scientific instruments like Conductometer, pH meter, Potentiometer, etc.

\* Types of Methods of Analysis:-

1. Classical methods of analysis - (a) Gravimetric analysis.

(b) Volumetric analysis.

2. Instrumental methods of analysis - (a) Conductometry.

(b) pHmetry.

(c) Potentiometry.

(d) Spectroscopy.

(e) Chromatography.

\* Advantages of Instrumental Methods of Analysis:-

• All these methods are giving accurate results.

• All results obtained by these methods are reproducible.

• Instrumental methods of analysis are very convenient to use.

• These methods are giving fast results.

## \* Reference Electrode:

### Definition -

The reference electrode is defined as the electrode which has stable and defined or reproducible electrode potential. It completes the cell, acting as half cell.

### Example : Calomel Electrode.

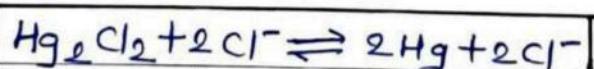
This is the most widely used reference electrode.

### Construction :-

- Calomel electrode consists of a narrow glass tube at the bottom of which is liquid mercury, above it is a paste of  $Hg - Hg_2Cl_2$  and remaining portion of glass tube is filled with saturated KCl solution.
- For making electrical contact, platinum wire is inserted in the pure Hg.
- A dipping type of calomel electrode has tapering lower end and the bottom is porous.
- In some calomel electrode, there is side tube filled with gel for acting as salt bridge and making the electrical contact.

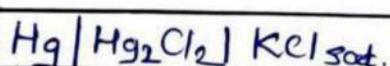
### Reaction :-

If the calomel electrode acts as cathode, reaction is-



and if it acts as anode, then the reaction is reverse.

- Cell Representation of Calomel electrode is -



- The reduction electrode potential is given by,

$$E_{cal.} = E^{\circ} - 0.0591 \log_{10} [Cl^-]$$

FOR EDUCATIONAL USE

Saturated KCl

KCl

Hg + Hg<sub>2</sub>Cl<sub>2</sub>  
paste

Hg

Calomel reference electrode

Pt Wire or Silver Chloride coated Silver wire

Glass tube

0.1 M HCl

Thin walled glass tube

Glass Electrode

### Advantages:-

- i) It is very handy, compact and easy to transport.
- ii) Its potential can remain constant and it can be easily reproduced.
- iii) Durable construction.

### Disadvantages:-

- i) It should not be used above  $50^{\circ}\text{C}$  as  $\text{HgCl}_2$  starts decomposing.
- ii) It involves handling of poisons Hg &  $\text{HgCl}_2$ .

## \* Indicator Electrode :

### Definition -

The indicator electrode is defined as the one of the electrode, in an electrochemical cell, whose potential depends upon the concentration of specific ion in the solution.

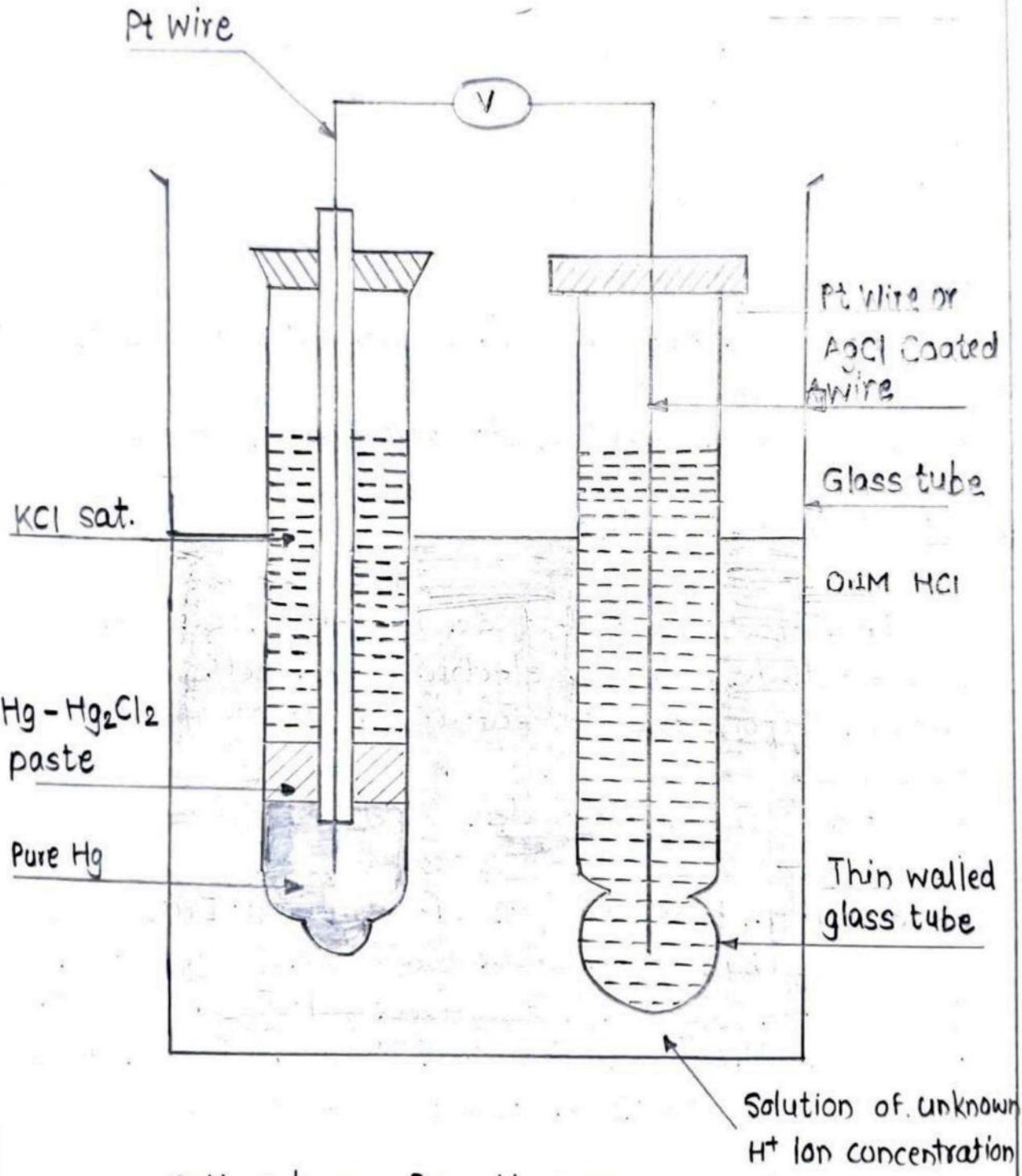
### Example : Glass Electrode.

### Principle :-

When two solutions of different  $[\text{H}^+]$  are separated by a thin glass membrane, a potential difference is developed at the two surfaces of membrane. The potential difference developed is proportional to the difference in  $[\text{H}^+]$  of the two solutions.

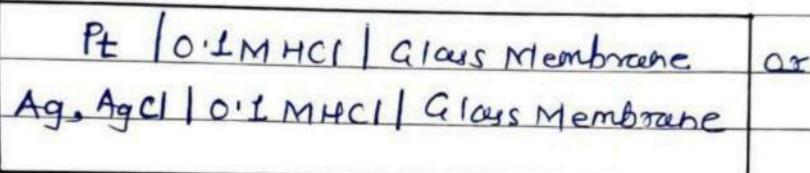
### Construction :-

- A glass electrode is made up of a glass tube with a thin-walled glass membrane bulb at the bottom.
- The glass bulb is made from doped glass having low



melting point and high electrical conductivity.

- The electrode is filled with 0.1M HCl solution.
- For making an external connection, platinum (Pt) wire or AgCl coated Ag wire is inserted inside the electrode.
- The glass membrane acts as an ion exchanger i.e. exchange of  $\text{Na}^+$  of glass with  $\text{H}^+$  of solution.
- The glass electrode may be represented as;



- Glass electrode before use requires soaking in water for some hours so that, glass membrane layer becomes hydrated, glass membrane surface becomes active and ion exchange can take place easily & equilibrium will be reached fast.

#### \* pH determination by using Glass Electrode :-

- In pH determination, two electrodes are used; the Calomel electrode (as a reference electrode) and the glass electrode (as an indicator electrode).
- When glass and calomel electrodes are placed in a test solution containing unknown  $\text{H}^+$  ion concentration, the potential development across the glass membrane is created because of the difference in concentration of  $\text{H}^+$  ions on both sides of the membrane.
- The potential is determined by connecting the saturated calomel electrode and glass electrode to the pH meter by constructing the cell.

Calomel electrode || H<sup>+</sup> unknown | Glass Electrode

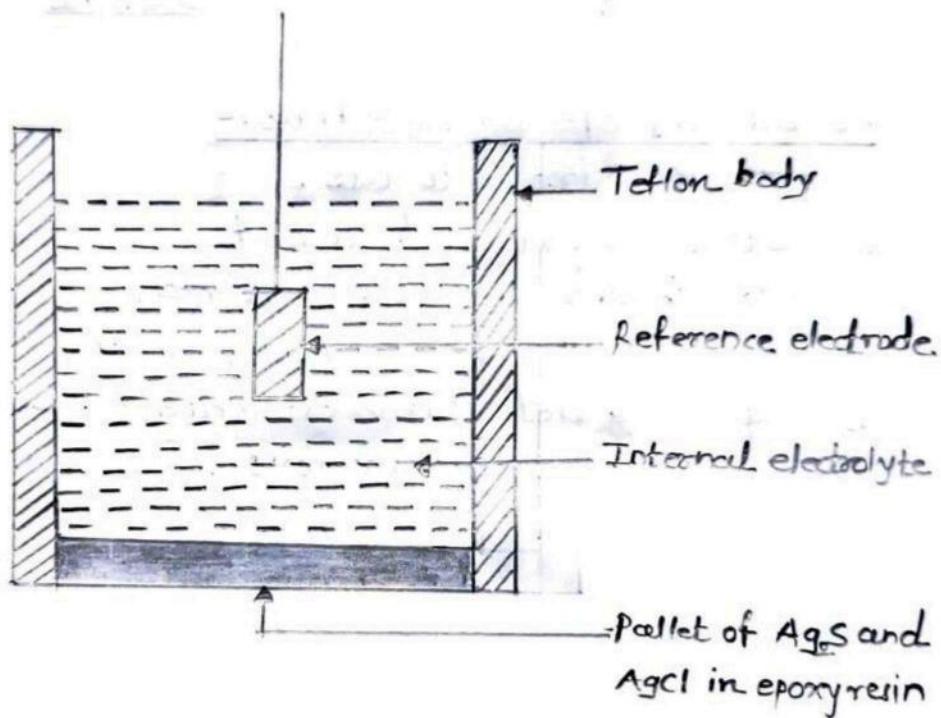
$$E_{\text{cell}} = E_{\text{cal}} - E_g$$

$$= 0.2422 - (E_g^{\circ} + 0.0591 \text{ pH})$$

$$\therefore \text{pH} = \frac{0.2422 - E_{\text{cell}} - E_g^{\circ}}{0.0591}$$

Advantages of Glass Electrode:-

- i) It is simple to use.
- ii) It is portable and compact.
- iii) Equilibrium is easily attained.
- iv) Gives accurate and quick results.
- v) It can detect and estimate H<sup>+</sup> ion concentration in the presence of other ions.



Chloride Ion Selective Electrode

## \* Ion Selective Electrode:

Definition:-

A membrane of a half cell is sensitive to particular ion in solution and ion exchange takes place between the membrane electrode and the solution containing specific ions and develops a potential which depends upon the concentration of that ion.

Example : Solid-state Membrane ISE.

In solid ion selective electrodes, ion selective membrane is made from a springly soluble and ion conducting substance, which is incorporated in polymeric material. One of the ions from the solid-state membrane is identical to the ion, to be analyzed from the sample.

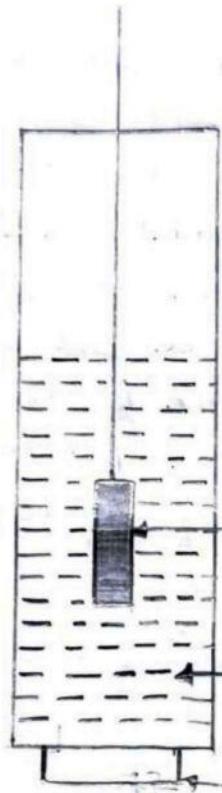
### ④ Fluoride Ion Determination:

Construction / Composition:-

- The membrane is made from Lanthanum trifluoride ( $\text{LaF}_3$ ) crystal doped with Europium fluoride ( $\text{EuF}_2$ ).
- The crystal is sealed at the bottom of the polymeric container containing internal reference solution ( $\text{NaF} + \text{NaCl}$  or  $\text{KF} + \text{KCl}$ ) and consists of  $\text{Ag}, \text{AgCl}$  reference electrode.

Working:-

- $\text{EuF}_2$  produces holes in the crystal lattice of  $\text{LaF}_3$  through which  $\text{F}^-$  ions can pass.
- When the electrode is in contact with the sample solution, a potential develops across the membrane which depends on the differences of  $\text{F}^-$  concentration on either side of the membrane.



Internal reference electrode  
 $\text{Ag} - \text{AgCl}$ .

Internal reference solution  
 $(\text{NaF} + \text{NaCl} \text{ or } \text{KF} + \text{KCl})$

Membrane,  $\text{LaF}_3$  doped with  
 $\text{EuF}_2$

### Fluoride Ion Selective Electrode

- Since the concentration of  $F^-$  in the internal solution is fixed, the potential developed across the membrane is related to  $F^-$  concentration in the sample solution.

B) Chloride Ion Determination :

- Chloride ion selective electrode is made up of a Teflon body and the membrane with the pellet of  $Ag_2S$  and  $AgCl$  is attached using epoxy resin.
- When electrode membrane is in contact with a solution containing chloride ions, an electrode potential develops. This potential is measured using a reference electrode.
- Chloride ion selective electrode gives fast measurement of chloride ion concentration in water. It is mainly used to measure chloride ion concentration in seawater and salts in food products.

## A] Conductometry:

### Introduction:-

- Conductometry is a method of electrochemical analysis, used to measure conductance of an electrolyte solution using a conductometer.
- It has wide applications in analytical chemistry. It measures the mobility of ions when an electric current is passed through the electrolyte solution using conductivity meter.

### Factors Affecting Conductivity:-

- a) Number of ions per ml: Greater the no. of ions per ml in a solution, greater is the specific conductance. At higher concentration of the solution, the number of ions per ml is higher.
- b) Concentration: In the case of weak electrolytes as concentration decreases i.e. is dilution increases the no. of ions increases and equivalent conductance increases, although specific conductance decreases.
- c) Mobility of Ions: Smaller the size of ion, greater is the mobility and the conducting ability.
- d) Charge on Ion: Higher the charge on an ion, greater is its conducting ability. e.g.  $Mg^{2+}$  and  $SO_4^{2-}$  having more conductivity than  $Na^+$  and  $NO_3^-$ .
- e) Temperature: At higher temperature, the conductance of an electrolyte is higher, because at higher temperature, the kinetic energy of ions is more, viscosity of water is lesser and interaction between ions is lesser.

### \* Ohm's Law:

Metallic conductors as well as electrolytes obey 'Ohm's Law' which states that:

The current flowing through a conductor is directly proportional to the potential difference applied across the ends of the conductor.

Thus, mathematically the Ohm's Law becomes;

$$I \propto V \text{ and } I = \frac{V}{R}$$

It is usually formulated as,

$$V = IR$$

Where;  $V$  = Potential difference or Voltage in Volts

$I$  = Current in amperes.

$R$  = Resistance of the conductor in ohms

- In electrochemistry, the term conductance ( $C$ ) is more commonly used instead of resistance ( $R$ ).
- Conductance is the ease with which the current flows through a conductor or solution and it is the reciprocal of resistance.

i.e.  $C = \frac{1}{R}$  unit: ohm<sup>-1</sup> mho or Siemens (S)

### \* Resistance and Specific Resistance:

- The opposition to the flow of current is known as resistance ( $R$ ). Unit of resistance is ohm ( $\Omega$ ).

The resistance ( $R$ ) of a conductor of uniform cross-section is directly proportional to its length ( $l$ ) and inversely proportional to the area of cross-section ( $A$ ).

$$\therefore R \propto \frac{l}{A}$$

where,  $R$  = Resistance in ohms.

$$R = \rho \frac{l}{A}$$

$l$  = Length in cm.

$A$  = Area of cross-section in  $\text{cm}^2$ .

- ' $\rho$ ' is a constant called resistivity or specific resistance which depends on nature of material of conductor.

If  $l = 1 \text{ cm}$  and  $A = 1 \text{ sq. cm.}$  then  $R = \rho$ .

- Therefore, specific resistance is defined as the resistance of uniform column of the material of the conductor having length of 1 cm & area of cross-section 1  $\text{cm}^2$ .

- Unit of sp. resistance ( $\rho$ )  $\Rightarrow$

We have a relation;  $R = \rho \frac{l}{A}$

$$\therefore \rho = R \frac{A}{l} = \text{Ohm} \frac{\text{cm}^2}{\text{cm}} = \underline{\underline{\text{Ohm.cm}}}$$

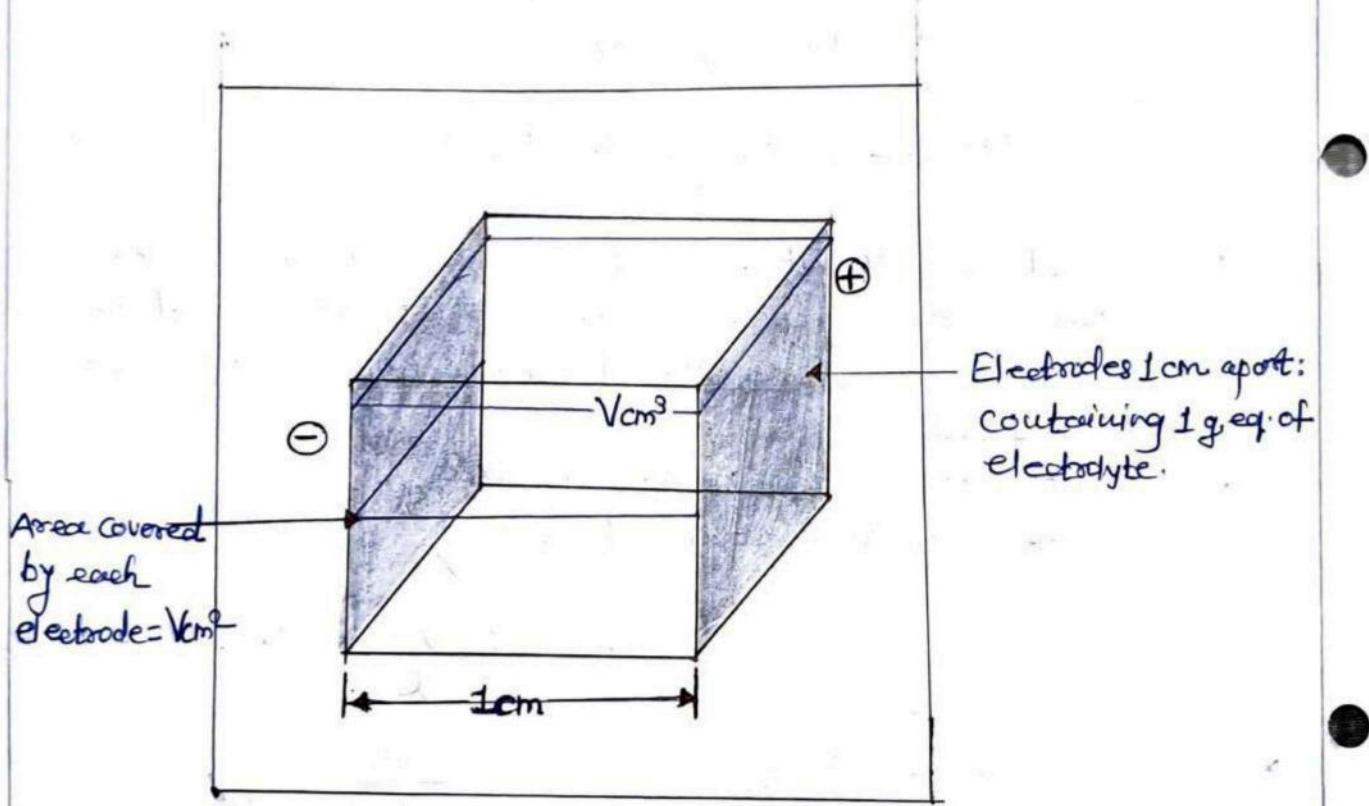
#### \* Specific Conductance / Sp. Conductivity ( $k$ ):

- The specific conductivity of conductor is the reciprocal of specific resistance (or resistivity) of a conductor.
- Generally it is represented by letter  $k$  (kappa).

Then,  $k = \frac{1}{\rho}$

$$\therefore k = \frac{1}{R \frac{A}{l}} = \frac{1}{R} \cdot \frac{l}{A} \quad \dots \quad (\because R = \rho \frac{l}{A} \text{ or } \rho = R \frac{A}{l})$$

If  $l = 1 \text{ cm}$ ;  $A = 1 \text{ cm}^2$ , then  $k = \frac{1}{R} = \text{Conductance}$ .



\* Relation between specific and equivalent conductivity \*

- Therefore, Specific conductance of a conductor is defined as the conductivity offered by a solution of length 1cm and area of unit cross-section.

In short, specific conductivity ( $k$ ) is the conductivity of 1 cm<sup>3</sup> of solution.

- Unit of sp. conductance  $\Rightarrow$   
It can be derived as follows;

$$k = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} = \underline{\underline{\text{ohm}^{-1} \text{cm}^{-1}}}$$

### \* Equivalent conductance ( $\Lambda_{eq}$ ):

- It is defined as the conductivity of a solution containing 1 gram equivalent of the electrolyte (or solute), when placed between two sufficiently large electrodes, which are 1 cm apart from each other.
- It is denoted by  $\Lambda_{eq}$  (Lambda)
- To understand the significance of the equivalent conductance, consider a rectangular tank with two opposite sides made up of metallic conductor and acting as electrodes exactly 1 cm apart. Now, 1 c.c. of solution is placed in the tank, and the conductivity is measured. If this one c.c. of solution contains 1 gram equivalent of the solute then the measured conductivity will be the equivalent conductivity.

$$\therefore \text{Equivalent conductivity} (\Lambda_{eq}) = \left\{ \begin{array}{l} \text{Volume (in cm}^3\text{) containing} \\ 1 \text{ gram equivalent of solute} \end{array} \right\} \times \left\{ \begin{array}{l} \text{Specific conductivity of} \\ \text{Solution (}k\text{)} \end{array} \right\}$$

$$\therefore \Lambda_{eq} = V \times k$$

- If  $C$  is the concentration of solution as gram-equiv. per litre (Normality), then volume  $V$  of the solution in ml containing 1 gram-equivalent will be  $1000/C$ .

$$\therefore \Lambda_{eq} = \frac{1000 \times k}{C}$$

- Unit of Equivalent Conductance  $\Rightarrow$  It can be obtained as follows;

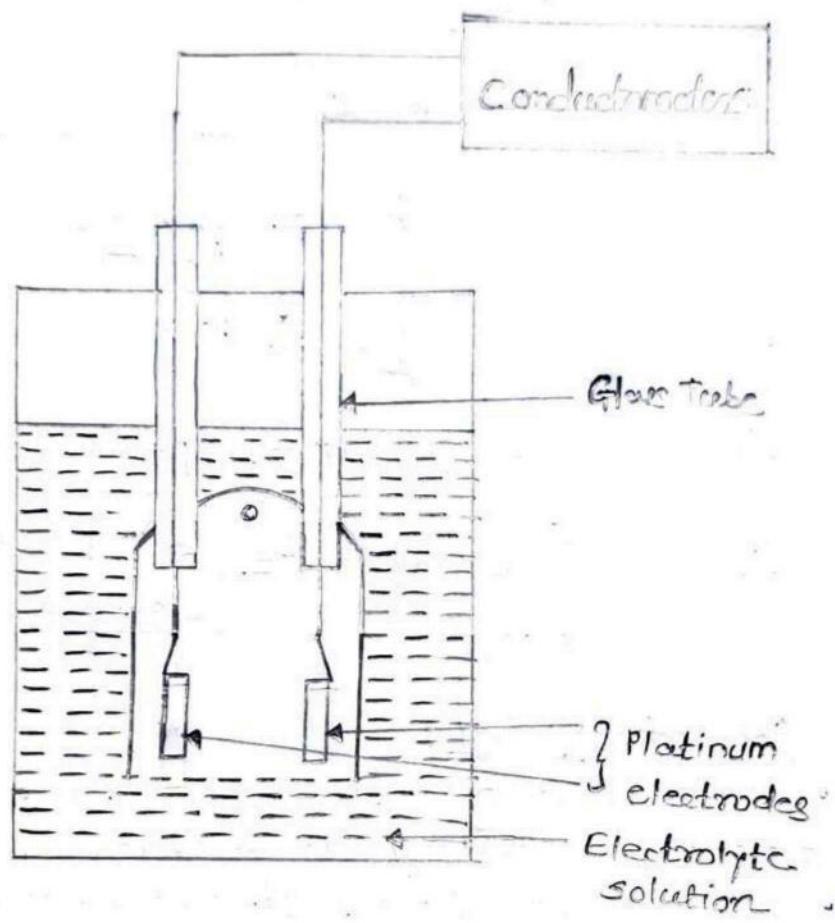
$$\begin{aligned}\Lambda_{eq} &= k \times V = \frac{1}{R} \times \frac{l}{A} \times V \\ &= \frac{1}{\text{Ohm}} \times \frac{\text{cm}}{\text{cm}^2} \times \frac{\text{cm}^3}{\text{equivt}} \\ &= \underline{\underline{\text{Ohm}^{-1} \text{cm}^2 \text{equivt}^{-1}}}.\end{aligned}$$

### \* Molar Conductance ( $\Lambda/m$ )

- Molar Conductance ( $\Lambda/m$ ) of a solution is defined as the conductance of all the ions present in one mole of electrolyte in the solution.
- If 'M' is the molar concentration in moles/lit, then:

$$\Lambda_m = \frac{1000k}{M}$$

- Unit of molar conductance  $\Rightarrow \underline{\underline{\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}}}$



Conductivity Cell

### \* Cell Constant:

Cell constant is the ratio of the distance between two electrodes ( $l$ ) to the area of the cross-section of the electrode ( $A$ ).

$$\text{i.e. Cell constant} = \frac{l}{A} = \frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}$$

And,

$$k = \frac{1}{R} \times \frac{l}{A}$$

$$\therefore \frac{l}{A} = k \times R$$

$$\therefore \text{Cell constant} = \frac{\text{Specific Conductance} \times \text{Observed Resistance}}{\text{Observed Conductance}}$$

### \* Conductivity Cell:

- A conductivity cell is a device used to measure the electrical conductivity of a solution.
- It typically consists of two electrodes made up of platinum, coated with platinum black, to increase their surface area and reduce polarization effects.
- These electrodes are dipped into the solution whose conductivity is to be measured.
- One common application of conductivity cell is in determining the concentration of an electrolyte solution.
- The conductivity of a solution is directly proportional to the concentration of ions present.
- By measuring the conductivity of a solution and knowing its cell constant, we can calculate the sp. conductance and from that, the molar conductivity of the solution.

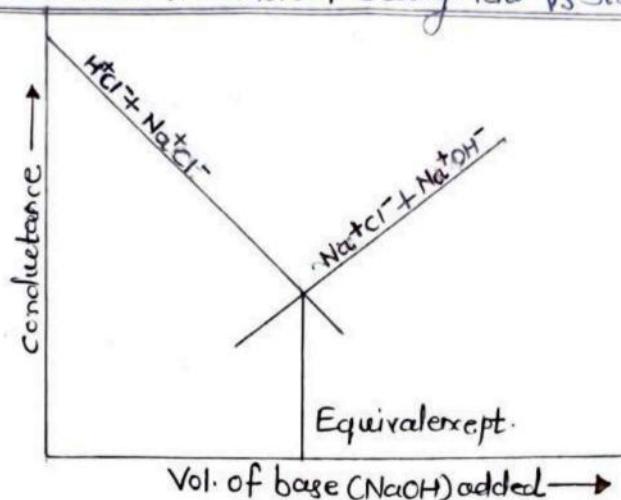
### \* Conductometric Titrations:

- The detection of the end point in the titration of an analyte with a titrant by monitoring the change in the conductance of the solution.
- The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration.
- The electrical conductance depends upon the no. of free ions in the solution and the mobility of ions in the solution.
- The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.
- Let us take a few specific cases to illustrate.

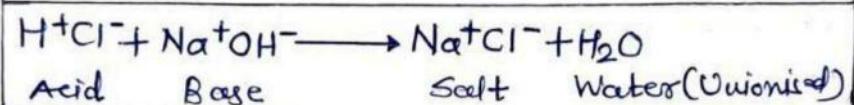
#### a) Strong Acid Vs Strong Base Titration.

- In the titration of strong acid like HCl against strong base NaOH from burette, the acid is taken in the conductivity cell. Initial conductance is high due to presence of highly mobile hydrogen ( $H^+$ ) ions.
- When the base is added, the no. of  $H^+$  ions of higher mobility will be replaced by slower moving  $Na^+$ . Hence, conductivity goes on decreasing, until the end pt./eqpt.
- At the equivalence pt., the solution contains only  $NaCl$ . Beyond this point, on adding  $NaOH$ , the conductance increases due to the large conductivity of triion.

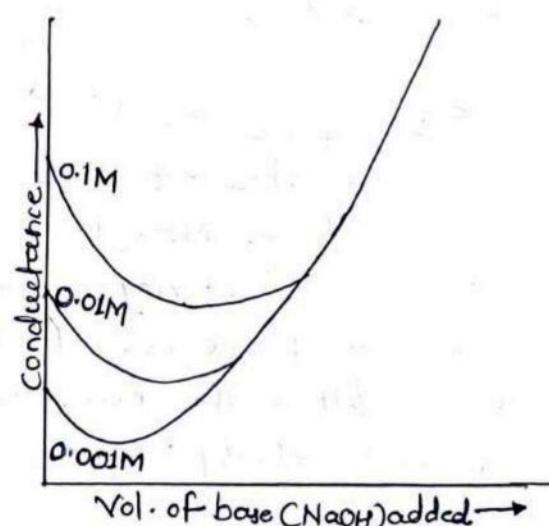
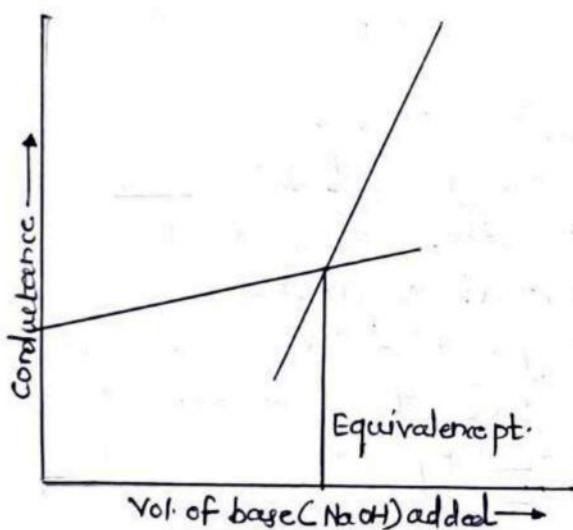
## a) Conductometric Titration of Strong Acid Vs Strong Base



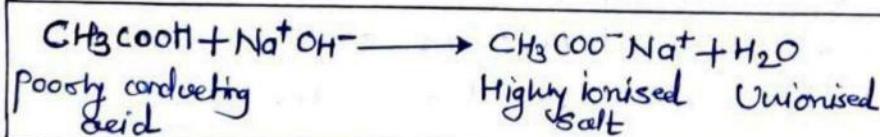
• Reaction:



b) Conductometric Titration of Weak Acid Vs Strong Base.



- Reaction:



- Equivalence pt. corresponds to the minimum conductance and this point is the intersection of the two lines.

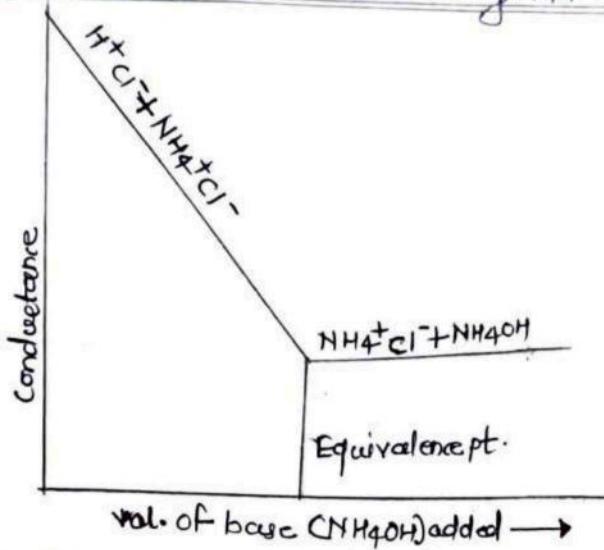
### b) Weak Acid Vs Strong Base Titration.

- Let us consider weak acid like CH<sub>3</sub>COOH titrating against a strong base NaOH. Initially the conductance is low due to the feeble ionization of acetic acid.
- On the addition of base, there is again decrease in conductance not only due to replacement of H<sup>+</sup> by Na<sup>+</sup> but also due to depression in its dissociation by the common ion-acetate formed during early stage of neutralization.
- But very soon, the conductance increases slowly on adding NaOH as NaOH neutralizes the undissociated CH<sub>3</sub>COOH to CH<sub>3</sub>COONa which is the strong electrolyte.
- This increase in conductance continues raise upto the equivalence point. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH<sup>-</sup> ions.

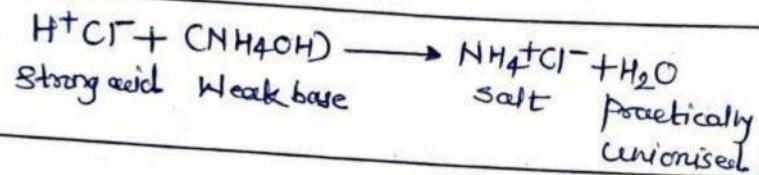
### c) Strong Acid Vs Weak Base Titration:

- Let us consider strong acid like HCl titrating against weak base NH<sub>4</sub>OH. Initially the conductance is high and then it decreases due to replacement of H<sup>+</sup> by NH<sub>4</sub><sup>+</sup> ions.
- The conductance in the beginning starts falling (due to the removal of H<sup>+</sup> ions) to form practically cationised water plus slow moving NH<sub>4</sub><sup>+</sup> ions.

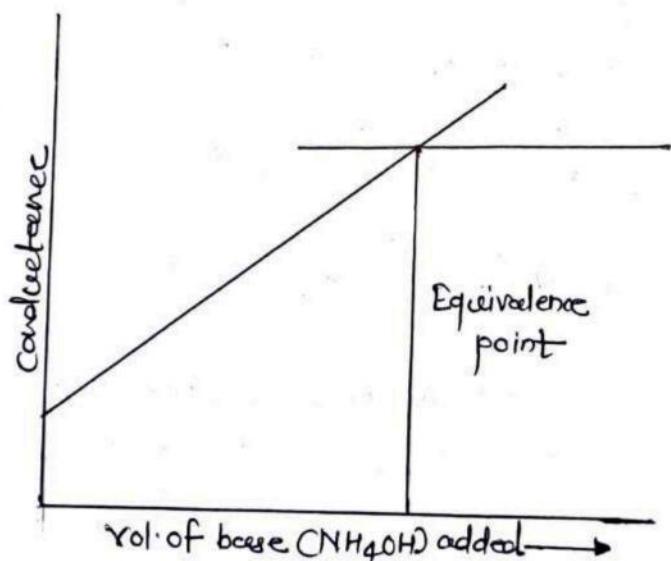
### c) Conductometric Titration of Strong Acid Vs. Weak Base



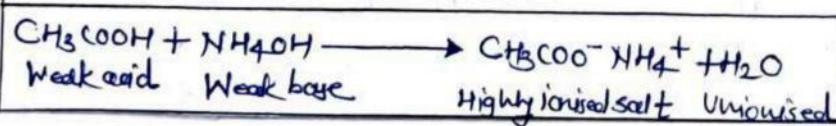
- Reaction:



d) Conductometric Titration of Weak Acid Vs Weak Base.



- Reaction:



- However, when the entire acid is neutralized, further addition of poorly ionised ammonium hydroxide does not cause any appreciable change in the conductance. The slope of the curve thus obtained is shown in the figure.

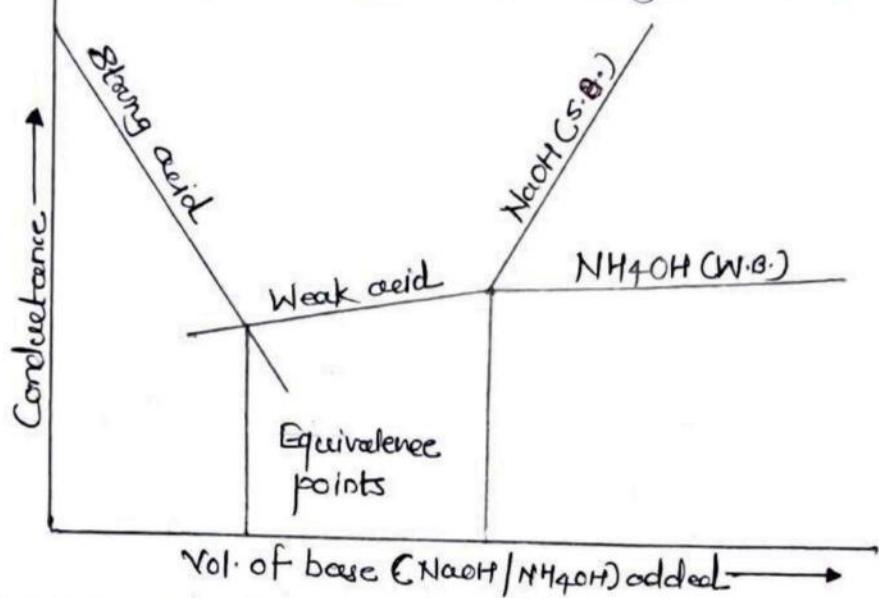
d) Weak Acid Vs Weak Base Titration.

- Let us consider weak acid like  $\text{CH}_3\text{COOH}$  titrating against weak base  $\text{NH}_4\text{OH}$ . The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base.
- Such a type of titration cannot be performed by using indicator, because there is no indicator available to note the end point accurately.
- Initially the conductance of acetic acid is low, because of its poor dissociation. As the titration proceeds, there is formation of strong electrolyte ammonium acetate and therefore, the conductance of titration mixture goes on increasing upto the equivalence point.
- After the equivalence point, there is no formation of ammonium acetate, and conductance is only because of added weak base. Hence, conductance increases negligibly after the equivalence point.
- The graph is plotted as conductance of titration mixture with ml of  $\text{NH}_4\text{OH}$  added from burette.

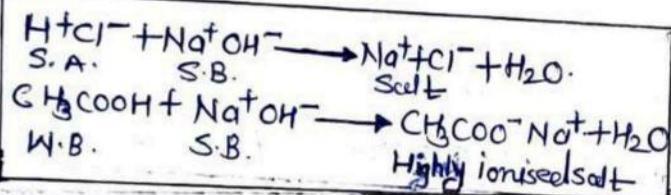
e) Mixture of Strong & Weak Acids Vs Strong Base or Weak Base

- Let us consider Strong acid  $\text{HCl}$  & Weak acid  $\text{CH}_3\text{COOH}$  mixture titrating, against Strong Base ( $\text{NaOH}$ ) or Weak Base ( $\text{NH}_4\text{OH}$ ).

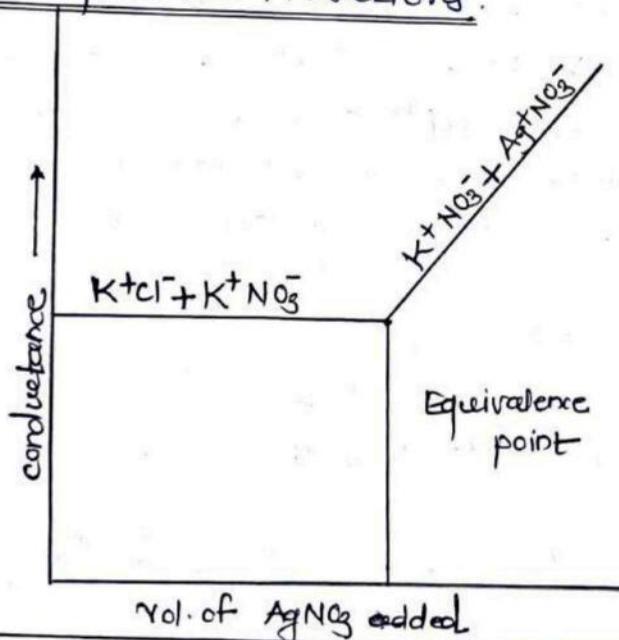
e) Cond. Titration of Mixture of Acids Vs. Strong/Weak Base.



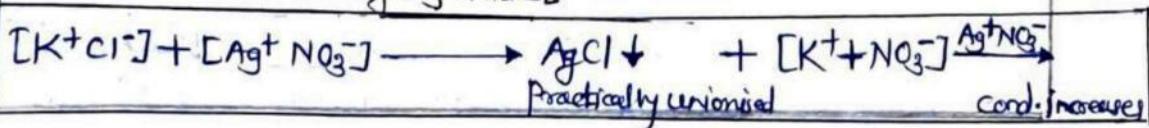
- Reaction:



## Precipitation Titrations



- Reaction



- As NaOH is added to the mixture of the acids, the stronger acid HCl is neutralized first. This leads to the decrease of conductance. Once all the HCl has been neutralized, that of CH<sub>3</sub>COOH begins.
- During the neutralization of this weak acid, there is a small increase in conductance. Beyond the equivalence point, the addition of excess NaOH increases the conductance steeply.
- However, when the titrant is a weak base (NH<sub>4</sub>OH), it remains almost constant after the eq.pt.

#### f) Precipitation Titration.

- Precipitation titrations can be carried out conveniently by conductivity measurements. Example- KCl versus AgNO<sub>3</sub> titration using conductivity meter.
- As AgNO<sub>3</sub> is added from a burette to KCl, no change in conductance occurs as KCl, a strong electrolyte, in the solution is replaced by another strong electrolyte KNO<sub>3</sub>.
- Beyond the equivalence point, the additional AgNO<sub>3</sub> (a strong electrolyte) steeply increases the conductance.

#### \* Applications of Conductometric Titrations.

- It is applicable to even, coloured reactants with which no indicator would work satisfactorily.
- It is suitable for the very low concentrations of the reactants, unlike with conventional titrimetry.
- It can be used for precipitation titration with precision.  
The end point, determined graphically is accurate & does not require any special precaution.

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## B) pH Metry:

### \* Introduction:

- The concept of pH was introduced by Danish biochemist Soren Peter Lauritz Sorensen in 1909. It is very convenient concept for representing the hydrogen ion concentration.
- pH is defined as the negative logarithm of hydrogen ion concentration and is expressed mathematically as;

$$\text{pH} = -\log_{10} [\text{H}^+]$$

- pH refers to the potential of hydrogen. The pH meter measures the potential between the electrodes and converts the results into the pH of the solution.
- pH meter is the instrument, we to measure the acidity or basicity of solution.
- pH measurements are important in chemistry, biology, agriculture, water treatment, food industry etc.

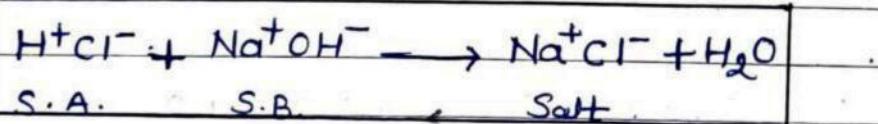
### \* Standardization of pH meter:

- Standardization of a pH meter refers to the process of adjusting and verifying the meter's accuracy to ensure reliable pH measurements.
- For precise working of the pH meter, it should be calibrated before and after each measurement because glass electrode does not give a reproducible emf over longer periods of time.
- The calibration process correlates the voltage produced by the probe with the pH scale.
- Buffer solutions of pH=4, p=7 and pH=9.2 are used for standardization / calibration of pH meters.

- A digital pH meter is standardized / calibrated as follows—
  - i) Connect the reference (calomel) and indicator (glass) electrodes to the pH meter and switch on the pH meter.
  - ii) Rinse the electrodes using distilled water.
  - iii) If the electrodes are dipped in buffers of  $\text{pH} = 7.0$  then display should show the same reading otherwise adjust the pH reading on display by using calibration knob.
  - iv) Similarly, pH meter is calibrated for  $\text{pH} = 4.0$  as well as  $\text{pH} = 9.2$  using respective buffer solutions.

### \* pH Metric Titration of Strong Acid versus Strong Base:

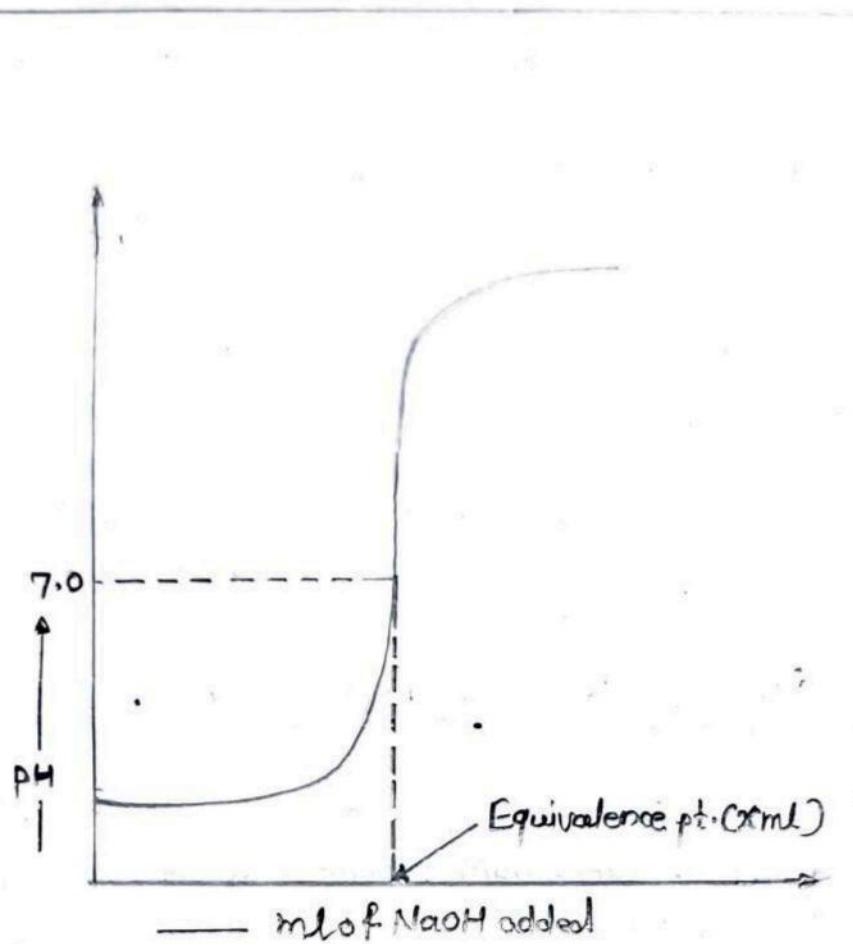
- The equivalence point in acid-base titration can be accurately determined using a pH meter.
- Consider the titration between strong acid and strong base ( $\text{HCl}$  vs  $\text{NaOH}$ ).
- As  $\text{HCl}$  is a strong acid and  $\text{NaOH}$  is a strong base, they undergo complete dissociation as—



- At equivalence point, equal amounts of  $\text{H}^+$  and  $\text{OH}^-$  combine to form water, resulting in a pH of 7.0.

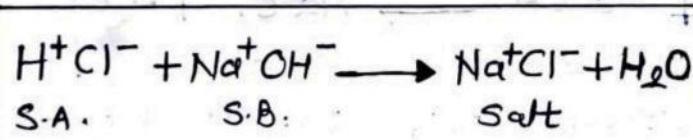
Procedure :-

- i) Standardize the pH meters using pH 4, 7 and 9.2 buffer solutions.
- ii) Take the known volume of the given acid soln. in a 100ml beaker and add about 30 ml of water.



Titration Curve for pH metric titration of S.A. Vs S.B.

Reaction:



- 21
- iii) Rinse the electrodes with distilled water and then place into the beaker. Electrodes should be properly dipped into the solution.
  - iv) Fill the burette with a known concentration of NaOH solution.
  - v) Measure the pH of the solution at zero ml addition of NaOH.
  - vi) Then, add a fixed volume of NaOH each time and stir the solution with a magnetic stirrer. Record the pH of the solution after each fix volume addition of NaOH, and continue the addition of NaOH solution until the end point exceeds by 2ml.
  - vii) The equivalence point in acid-base titration can be accurately determined using pH metric titration curve.

#### Observation:-

At the equivalence point, acid is undergoing complete neutralization. Therefore pH of the solution in the beaker will be 7. From the graph, ml of NaOH required for complete neutralization, corresponding to pH 7 is determined as 'x' ml.

#### Calculation:-

Using  $N_1 V_1 (\text{HCl}) = N_2 V_2 (\text{NaOH})$ , the concentration (Normality) of HCl and Strength is calculated.

i.e.  $\text{HCl Vs NaOH}$

$$N_1 V_1 = N_2 V_2$$

$$\therefore N_1 = \frac{N_2 V_2}{V_1}$$

$$\therefore \text{Normality of HCl} = N_1 = \frac{N_2 \times 'x'}{V_1} \text{ And, Strength of Acid} = \text{Normality} \times 36.5 \text{ g/l}$$

## \* Applications of pH Meter:

1. pH meters are used to measure the acidity of various food and beverage products to ensure quality and safety.
2. pH meters are used in agriculture to measure the pH level of soil, which helps farmers to know which crop will grow best in a particular field.
3. pH meters are used to monitor pH levels in various chemical reactions to ensure optimal conditions for the reaction to occur.
4. pH meters are used to measure pH levels in different water bodies, such as rivers, lakes and oceans to monitor environmental health.
5. pH meters are used in research and development to measure the pH levels of various materials and substances, including pharmaceuticals, cosmetics and plastics.
6. pH meters are used in the medical field to monitor the pH levels of blood, urine and other body fluids to help to monitor various health conditions.

## C) UV-Visible Spectroscopy:

### \* Statement of Lambert's Law:

- When a beam of monochromatic light is passed through a transparent solution, decrease in intensity of incident radiation is directly proportional to path length at constant concentration.
- Mathematically;

$$\frac{-dI}{I_0} \propto dx$$

Where,  $I_0$  = Intensity of the incident radiation.

$dx$  = small thickness of solution or path length

$dI$  = small decrease in intensity of light =  $I_0 - I_t$

### \* Statement of Beer's Law:

- When a beam of monochromatic light is passed through a transparent solution, decrease in intensity of incident radiation is directly proportional to concentration at constant path length.
- Mathematically;

$$\frac{-dI}{I_0} \propto dc$$

### \* Combined Beer-Lambert's Law:

It states that, Absorbance (A) is directly proportional to path length (x) and concentration (C).

$$A \propto x \cdot C$$

$$\therefore A = \alpha \cdot x \cdot C$$

where, 'α' is proportionality constant called as absorptivity coefficient. If path length 'x' is given in cm and concentration 'C' is given in mol/litre, then proportionality constant is called as molar absorptivity coefficient or molar extinction coefficient indicated by 'E'.

- Thus, Beer-Lambert's law can be represented as;

$$A = E \cdot x \cdot C$$

## \* Electronic transitions :-

### • Theory :-

- i) When the molecule absorbs UV or visible light, its electron gets promoted from the ground state to the higher energy state.
- ii) In the ground state, the spins of the electrons in each molecular orbital are essentially paired.
- iii) In the higher energy state, if the spins of the electrons are opposite & unpaired, then it is called as an excited singlet state.
- iv) On the other hand, if spins of the electrons in the excited state are parallel and unpaired, it is called as an excited triplet state. The triplet state is always lower in energy than the corresponding excited singlet state. Therefore, triplet state is more stable as compared to the excited singlet state.
- v) In the triplet excited state, electrons are further apart in space & thus, electron-electron repulsion is minimized.
- vi) Normally the absorption of UV or visible light results in singlet ground state to excited singlet state transition, i.e. excitation proceeds with the retention of spins.
- vii) An excited singlet state is converted to excited triplet state with the emission of energy as light. The transition from the singlet ground state to excited triplet state is symmetry forbidden.

- VIII) The higher energy states are designated as high energy molecular orbitals & also called as anti-bonding orbitals
- IX) The higher probable transition due to absorption of quantized energy involves the promotion of one electron from the highest occupied molecular orbital (HOMO) to the lowest available unfilled molecular orbital (LUMO)
- \* The higher is the energy gap, the lower is the wavelength of the light absorbed.

#### \* Types of Electronic Transitions :-

According to the molecular orbital theory, when a molecule is excited by the absorption of energy (UV or visible light), its electrons are promoted from a bonding orbital to an anti-bonding orbital.

There are several types of electronic transition available to a molecule including:

- The anti-bonding orbital which is associated with the excitation of  $\sigma$ -electron is called  $\sigma^*$  anti-bonding Orbital.  $\sigma \rightarrow \sigma^*$  transition takes place when  $\sigma$ -electron promoted to anti-bonding ( $\sigma^*$ ) orbital.
- When a non-bonding electron ( $\eta$ ) gets promoted to an anti-bonding sigma orbital ( $\sigma^*$ ), then it represents  $\eta \rightarrow \sigma^*$  transition.

- Similarly,  $\pi \rightarrow \pi^*$  transition represents the promotion of  $\pi$ -electrons to an anti-bonding  $\pi$ -orbital ( $\pi^*$  orbital).
- Similarly, when a  $\eta$ -electron (non-bonding) is promoted to an anti-bonding  $\pi$ -orbital, it represents  $\eta \rightarrow \pi^*$  transition.
- When molecule absorbs the UV-Visible radiation, then electrons are excited from lower energy orbital (bonding orbital) to higher energy orbital's ( antibonding orbital).

The energy required for various transitions obey the following order:

$$6 \rightarrow 6^* > \eta \rightarrow 6^* > \pi \rightarrow \pi^* > \eta \rightarrow \pi^*$$

Energy Level diagram :-

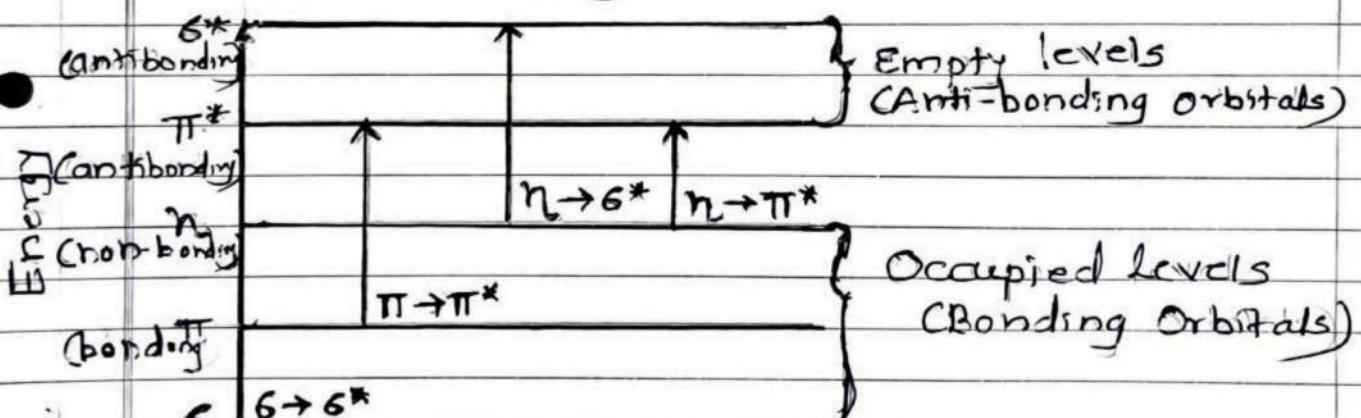


Fig. Types of electronic transitions.

### \* Types of Transitions :-

#### a) $\sigma - \sigma^*$ transition :-

- This transition is only observed in compound containing  $\sigma$  bond / electron and not lone pair electrons on any atoms.
- In this transition, the electrons of  $\sigma$  bond in bonding  $\sigma$  orbital (lower energy) excited to antibonding  $\sigma^*$  orbital (higher energy). This transition requires higher energy.
- e.g. Transition is saturated compounds like  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  etc.
- The absorption band occurs in the far ultraviolet region in the range of 100 to 135 nm wavelength.

#### b) $\pi - \pi^*$ transition :-

- This transition is only observed in double bonded compounds containing  $\pi$  electrons.
- In this transition, the  $\pi$  electrons in bonding orbital's (lower energy) are excited to antibonding orbital (higher energy).
- The compound containing isolated double bond shows large absorption in the range of (160 - 175 nm). This band is called as E-band.
- The compound containing conjugated double bond shows very large absorption in the range of 210 nm - 280 nm. This band is called as K band.
- The aromatic & heteroaromatic compounds absorbed at 220 - 270 nm wavelength. This band is called as B-band.

c)  $n-\pi^*$  transition :-

- This transition is observed in unsaturated compound containing double bond and lone pair of electrons on one atom.  
eg.  $C=O$ ,  $C=N$ ,  $C=S$  etc.
- In this transition non bonding or lone pair of electrons are excited from non-bonding orbital to  $\pi^*$  antibonding orbital.
- The absorption band occurs in region of 270 - 320 nm. This band is called as R band.
- eg. Aldehyde, ketone shows absorption in the range of 270 - 320 nm but unsaturated Aldehyde and Ketone are absorbs at 300 - 350 nm wavelength.

d)  $n-\sigma^*$  transition :-

- This transition is only observed in compound containing  $\sigma$  bond and lone pair electrons on at least one atom. eg.  $C-O$ ,  $C-N$ ,  $C-S$ .
- In this transition non. bonding or lone pair of electrons are excited from non-bonding orbital to  $\sigma^*$  antibonding orbital.
- This band is observed in near UV region (180 - 225) nm.

e)  $\sigma-\pi^*$  and  $\pi-\sigma^*$  transition :-

- These transitions are Forbidden transitions & are only theoretically possible.

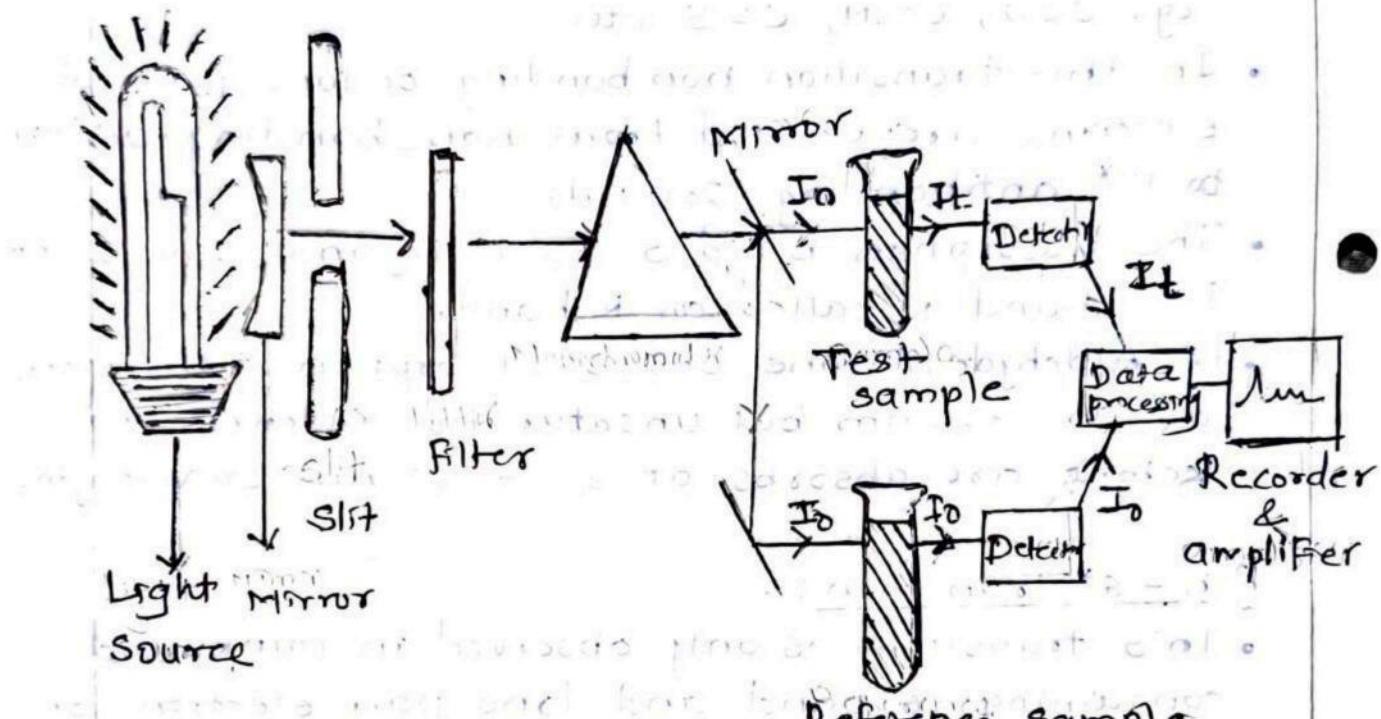


Fig. Double beam UV-Visible spectrophotometer

It has two beam paths. In one path, the sample is placed.

In the other path, reference sample is placed.

Both the paths are equal.

→ Double beam spectrophotometers are used for rapid analysis of samples.

## \* Instrumentation (double beam spectrophotometer) :-

The instrument that is used to measure the amount of electromagnetic radiation absorbed by the substance is called spectrophotometer or Spectrometer.

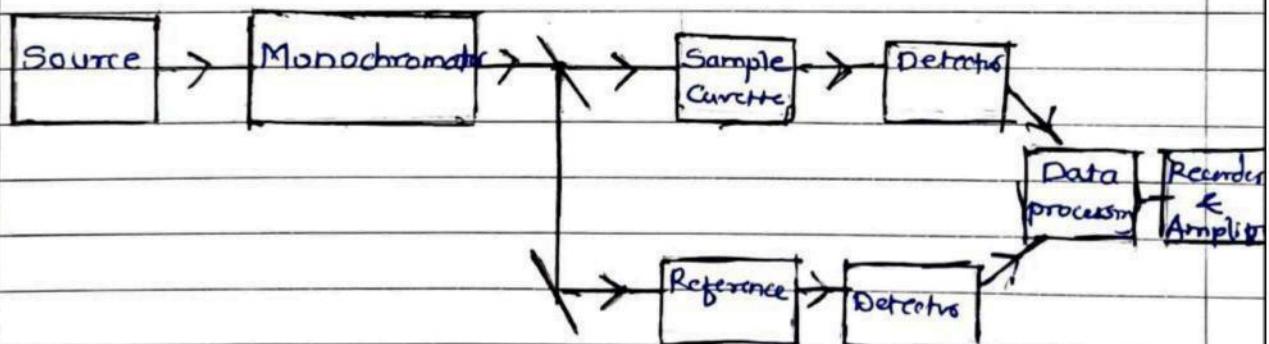
Various component of UV-visible spectrophotometer & their functions are as follows -

### • Principle :-

The spectrophotometer is an instrument which measures an amount of light that a sample absorbs. The spectrophotometer works by passing a light beam through a sample to measure the light intensity of a sample.

### • Instrumentation :-

Various components of UV-visible spectrophotometer & their function are as follows :-



1) Light Source (Source of radiation) :-

- The radiation source must be stable and produce sufficient intensity of radiation.
- In visible region (400-800 nm) a tungsten filament lamp is widely used.
- In UV region hydrogen lamps, deuterium lamps, xenon discharge lamp & mercury lamps are used.

2) Mirror :-

The light emitted by source falls on the mirror and a single ray gets reflected and enters a monochromator.

3) Filters :-

A slit or window is used to select a small portion of light to pass through.

4) Monochromator :-

- Radiation source provides polychromatic light which is passed through monochromator through entrance slit. Monochromator disperses radiations according to wavelength. By moving the dispersing element or the exit slit, radiation of only particular wavelength leaves the monochromator through exit slit.
- Monochromator used are quartz prism, colour filters.

5) Sample holder / cuvette :-

- Sample holders or cuvettes are used to hold sample or reference solution. They are constructed

of transparent material which does not absorb radiation in UV or visible range.

- e.g. quartz cuvettes (UV), glass cuvette (Visible spectroscopy)

#### 5) Detector :-

It converts transmitted light energy directly into electrical energy. The output current of photo detector is directly proportional to the intensity of light falling on it.

e.g. photoelectric tube, photomultiplier tube, photovoltaic cell.

#### 6) Amplifiers and recorders :-

- It is a display device which automatically draws the spectrum.
- Signal received from detector is amplified & read on recorder.
- The result can be manually noted, directly printed or plotted.

#### 7) Applications :-

The use of spectrophotometers spans various scientific fields, such as physics, materials science, chemistry, biochemistry & molecular biology.

## \* Terms Involved in UV-Visible Spectroscopy:-

### 1) Chromophore :-

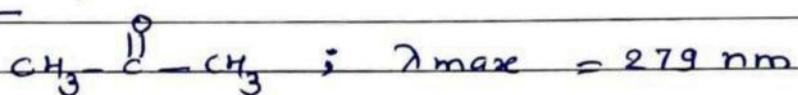
chromophore is a functional group containing multiple bond capable of absorbing radiations above 200 nm due to  $\pi \rightarrow \pi^*$  transitions and  $n \rightarrow \pi^*$  transitions. is called as chromophore.

eg.  $\text{NO}_2$ ,  $\text{N}=\text{O}$ ,  $\text{C}=\text{O}$ ,  $\text{C}\equiv\text{N}$ ,  $\text{C}=\text{C}$ ,  $\text{C}=\text{S}$  etc.

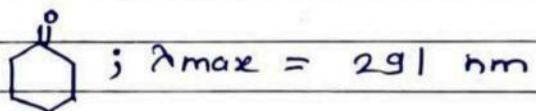
• While interpreting UV-visible spectrum following points are kept in mind.

1. Non-conjugated carbonyl group of compound give a weak absorption band in the 200-300 nm region.

eg. Acetone -



cyclohexanone :-



2. When double bonds are conjugated in a compound  $\lambda_{\text{max}}$  is shifted to longer wavelength.

eg. 1,5-Hexadiene :  $\lambda_{\text{max}} = 178 \text{ nm}$  (non-conjugated)

3. Conjugation of  $\text{C}=\text{C}$  & Carbonyl group shifts the  $\lambda_{\text{max}}$  of both groups to longer wavelengths.

eg. Ethylene :-  $\text{CH}_2=\text{CH}_2 ; \lambda_{\text{max}} = 171 \text{ nm}$

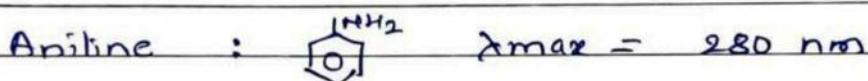
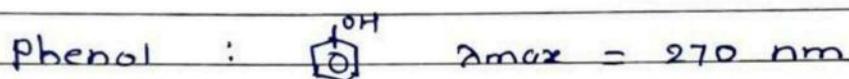
Acetone :-  $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3 ; \lambda_{\text{max}} = 279 \text{ nm}$

Propanaldehyde :-  $\text{CH}_3-\text{CH}=\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H} ; \lambda_{\text{max}} = 290 \text{ nm}$

## 2) Auxochrome :-

Auxochrome is a functional (saturated) group with non-bonding electrons that does not absorb radiation in near UV regions but when attached to a chromophore alters the wavelength & intensity of absorption.

- It causes shift in absorption to longer wavelength. It is a group, which extends the conjugation of a chromophore by sharing of non-bonding electrons.
- e.g.

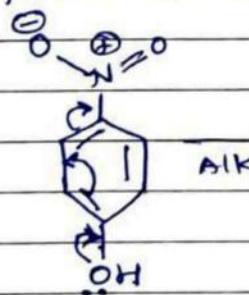


## 3) Bathochromic shift (Red shift) :-

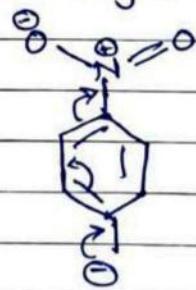
When absorption maxima ( $\lambda_{\text{max}}$ ) of a compound shifts to longer wavelength it is known as bathochromic shift or red shift.

This effect is due to the presence of an auxochrome or by the change of solvent.

e.g. a) An auxochromic group like  $-\text{OH}$ ,  $-\text{OCH}_3$  cause absorption of compound at longer wavelength.



$\lambda_{\text{max}} = 255 \text{ nm}$   
p-nitrophenol



$\lambda_{\text{max}} = 265 \text{ nm}$

#### 4) Hypsochromic Shift (Blue shift):-

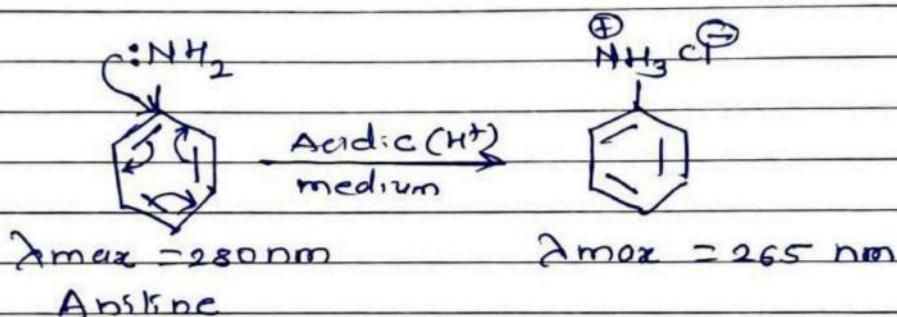
When absorption maxima ( $\lambda_{max}$ ) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.

This shift is caused due to,

a) Removal of conjugation

b) changing the polarity of the solvent.

e.g. Aniline shows blue shift in acidic medium as in acidic medium it loses conjugation.

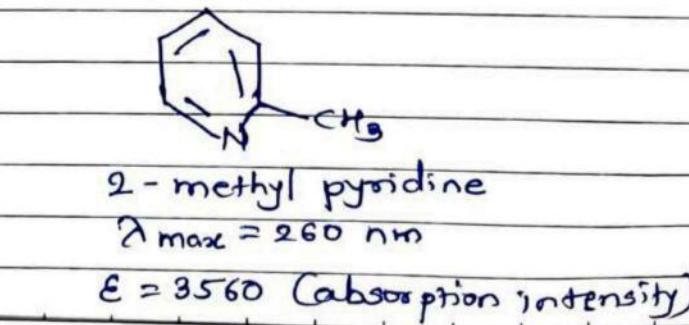
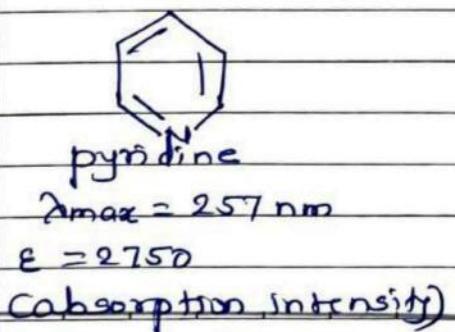


#### 5) Hyperchromic shift :-

An increase in intensity of absorption maxima is called hyperchromic shift.

Introduction of auxochrome usually increase the intensity of absorption.

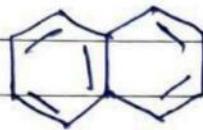
e.g.



### 6) Hypochromic shift :-

Decrease in intensity of absorption maxima is called hypochromic shift.

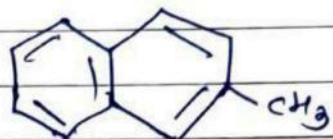
It occurs due introduction of groups that distorts the original geometry of the molecule.



Naphthalene

$$\epsilon = 19000$$

Cabsorption intensity

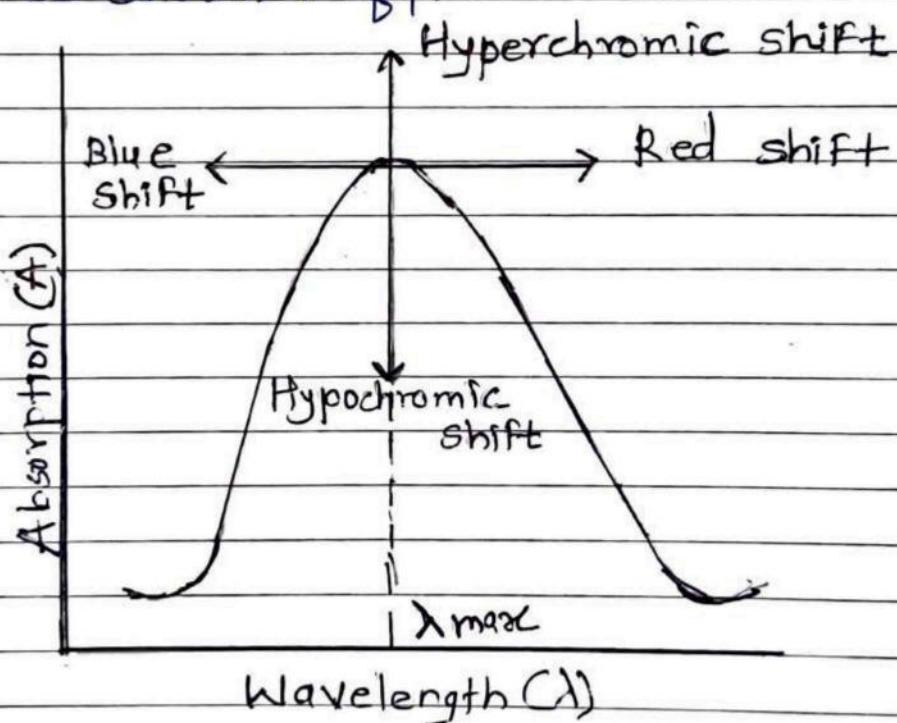


2 - Methyl naphthalene

$$\epsilon = 10250$$

Cabsorption intensity.

These shifts on absorption and intensity can be shown in fig.



## \* Application of UV-Visible Spectroscopy :-

### i) Qualitative analysis :-

#### ii) Detection of functional groups :-

The technique is used to determine presence or absence of chromophore. If spectrum is transparent above 200 nm, it indicates absence of conjugation, carbonyl group, aromatic compounds.

#### iii) Extent of conjugation :-

Extent of conjugation  $R-C(H=CH)_n-R$  can be detected by UV-visible spectroscopy. Increasing number of double bonds in conjugation shifts absorption band to longer wavelength.

#### iv) Distinguishing conjugated & non-conjugated double bonds :-

The technique is used for distinguishing conjugated & non-conjugated compounds. Conjugated system shows absorption at longer wavelength than the one with non-conjugated system.

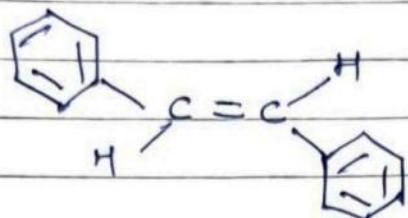
#### v) Identification of Unknown compounds :-

An unknown compound is identified by comparing spectrum of given compound with that of spectrum of known compound.

### vi) Detection of Cis & trans isomers :-

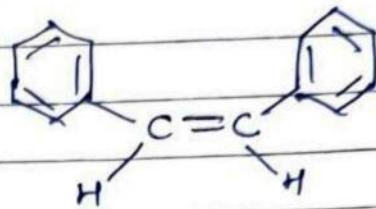
This technique is useful to distinguish geometrical isomers (Cis & trans isomer). Thus

distinction is possible when one of the isomers is forced to be non-coplanar by steric hindrance.



Trans-stilbene

$$\lambda_{\text{max}} = 295 \text{ nm}$$



Cis-stilbene

$$\lambda_{\text{max}} = 280 \text{ nm}$$

#### 3) Determination of molecular weight :-

- Molecular weight of the compound can be determined by recording absorbance using Beer-Lambert's law,  $A = \epsilon \times c$ , molecular weight of compound can be determined by determining concentration.

#### 4) Detection of impurities :-

- UV-visible spectroscopy is one of the best methods for determination of impurities in organic compounds. Additional peaks can be observed due to impurities in the sample & it can be compared with that of standard raw material. By measuring absorbance at particular wavelengths, impurities can be detected.

#### 5) Quantitative Analysis :-

- UV-visible absorption spectroscopy can be used for quantitative determination of compound by using Beer-Lambert's law,  $A = \epsilon \times c$ .

### \* Determination of Molar Absorptivity & Concentration

Using a spectrophotometer one can find out i) Verification of Beer-Lambert law practically if one keeps the path length constant & study variation of absorbance as a function of concentration at the  $\lambda_{max}$  of the sample solution under study.

$$A = \epsilon bc$$

where,

$A$  = Absorbance of the solution.

$\epsilon$  = molar extinction coefficient

$b$  = path length

$c$  = concentration of the solution.

using the above equations one can calculate.

ii) Molar extinction coefficient if concentration and absorbance is known.

iii) If absorbance values are given at different concentrations one can find out unknown concentration.

\* Numerical :-

- 1) In a spectroscopy experiment the absorbance of 0.0035 N KMNO<sub>4</sub> solution at  $\lambda_{max}$  was found to be 0.75 find out molar absorption coefficient.  
 → Solution,

$$A = \epsilon bc$$

$$0.75 = \epsilon \times 1 \times 0.0035$$

$$\epsilon = \frac{0.75}{0.0035}$$

$$\boxed{\epsilon = 214.28 \text{ mole/cm}}$$

- 2) Experimental values of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution are given below. Find out molar extinction coefficient of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.



concentration	Absorbance
0.001	0.15
0.002	0.30
0.003	0.46
0.004	0.60
0.005	0.75

$$\epsilon = \frac{A_2 - A_1}{c_2 - c_1}$$

$$\epsilon = \frac{0.60 - 0.45}{0.004 - 0.003}$$

$$\boxed{\epsilon = 150 \text{ mole/cm}}$$

- 3) A solution shows a transmittance of 20%, when taken in a cell of 2.5 cm thickness. calculate its concentration, if the molar absorption coefficient is  $12000 \text{ dm}^3/\text{mol/cm}$ .

→ Given,

$$\begin{aligned} A &= 2 - \log_{10} \% T \\ &= 2 - \log_{10} 20 \\ &= 2 - 1.301 \\ &= 0.698 \end{aligned}$$

$$A = \epsilon \cdot l \cdot c$$

$$\therefore l = 2.5 \text{ cm}$$

$$\epsilon = 12000 \text{ dm}^3/\text{mol/cm}$$

$$A = 0.698$$

$$c = ?$$

so,

$$\therefore c = \frac{A}{\epsilon l} = \frac{0.698}{12000 \times 2.5}$$

$$\therefore c = 2.33 \times 10^{-5} \text{ mol/l dm}^3$$

