# UNIT: V
# Chemical Analysis & Instrumentation

- Terms involved in Chromatography
- Classification of chromatographic methods
- Theory & Principle of chromatography

# CHROMATOGRAPHY

- Chromatography was first invented by Mikhail Tswett.
- He used this method to separate plant pigments into colored components & named this separation techniques as Chromatography
- in Greek ‘Chroma’ means color & graphic means writing, thus chromatography means color writing.

❑ **Def$^{n}$:**

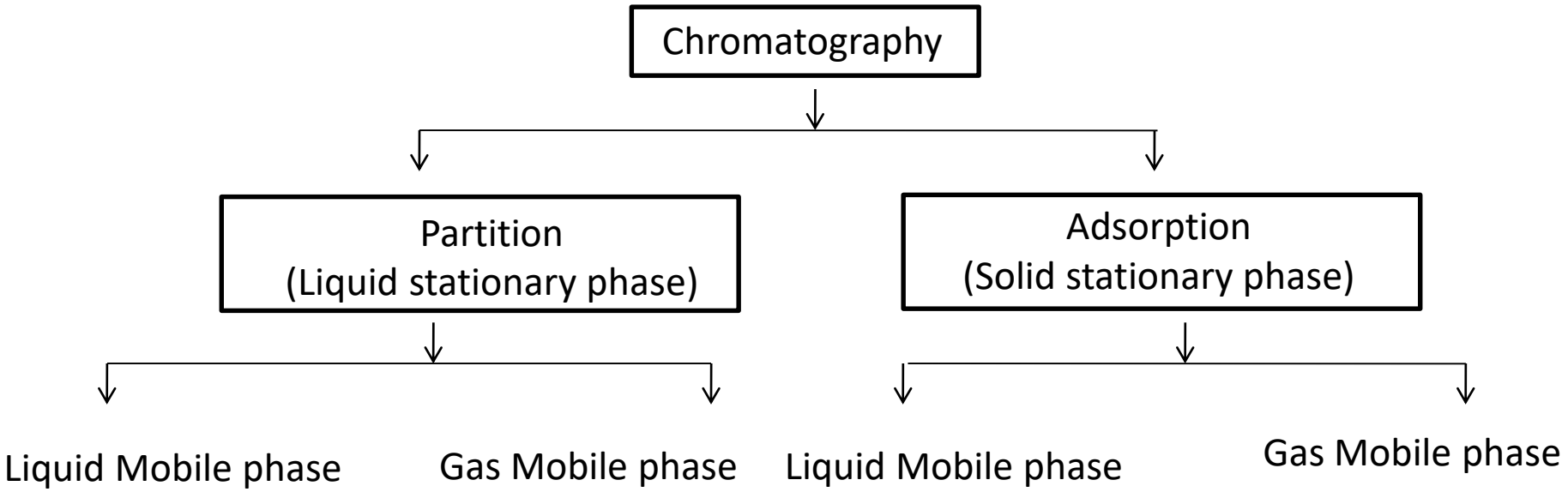
Chromatography can be defined as a ‘separation technique of a mixture of components & identification of individual components.’’

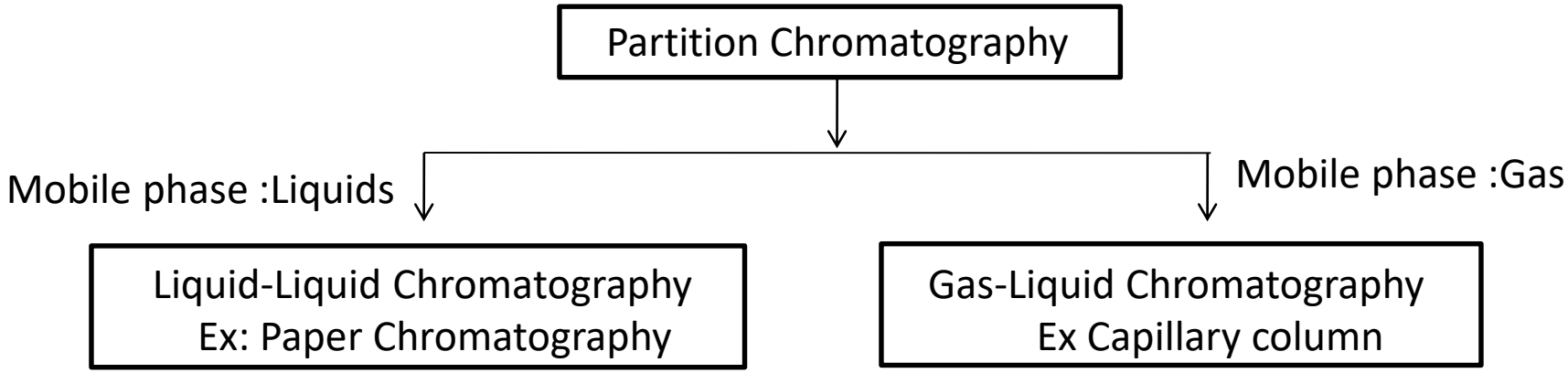
❑ **Principle:**

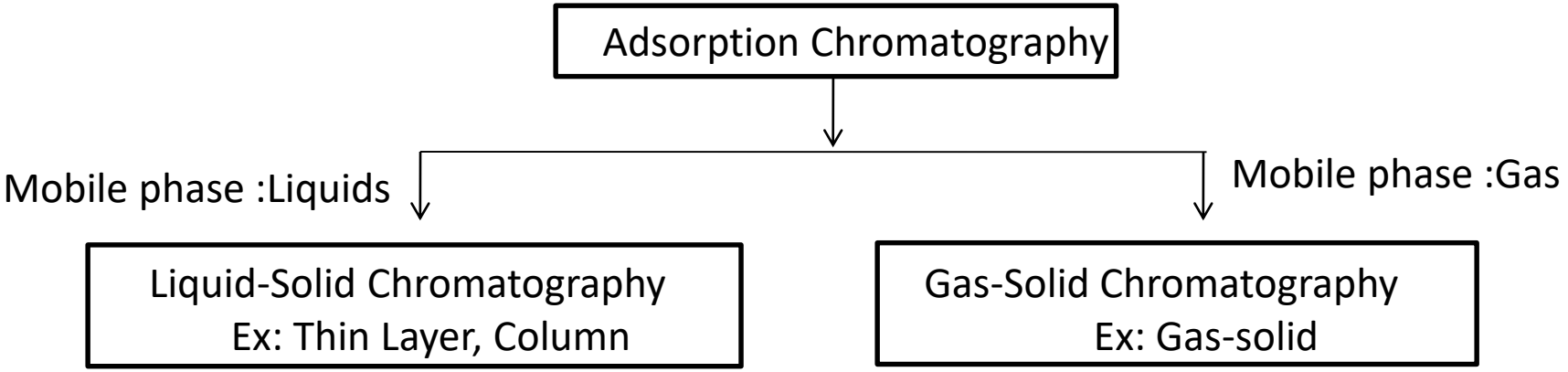
The principle involved in the separation is that ‘the difference in the rate at which the components of a mixture move through a porous medium (called stationary phase) under the influence of same solvent or gas (called moving phase).’

# Classification:

- Chromatography classification is based on the nature of stationary phase i.e. either solid or liquid & based on mobile phase i.e. either liquid or gas.
- In the stationary phase i.e. solid, the method is known as ''adsorption chromatography''.
- If the stationary phase is liquid, then the method is known as partition chromatography.




Partition Chromatography
Mobile phase :Liquids
Mobile phase :Gas
Liquid-Liquid Chromatography
Ex: Paper Chromatography
Gas-Liquid Chromatography
Ex Capillary column


Adsorption Chromatography
Mobile phase :Liquids
Mobile phase :Gas
Liquid-Solid Chromatography
Ex: Thin Layer, Column
Gas-Solid Chromatography
Ex: Gas-solid

# Terms used in chromatography:

:

## 1. Distribution ratio: (D)

- It is the ratio of concentration of solute in stationary phase to that in mobile phase ,"
- It decides the rate of flow of solute.
- The smaller is the D value , the faster will be the flow of solute through the mobile phase

$$D = \frac{[Solute]_{Stationary\ phase}}{[Solute]_{Mobole\ phase}}$$

# 2. Retention Volume ($V_R$):

- It is the volume of the mobile phase passing through the column required to move the solute from one end to other.
- It is expressed as

- $V_R = V_M + kV_M$
- Where, $V_{M-}$ volume of mobile phase in the column
- k- retention factor
- If k=0, then
- $V_R = V_M$
- i.e. solute is eluted without retention in stationary phase.
- If'k' is large, then retention volume is large.

# 3. Retention time ($t_R$):

- It is the time taken by the solute to reach the detector from the point of injection.
- $t_R = \frac{\text{Length of the column (l)}}{\text{Length of flow rate of solute (V)}}$

## 4. Retention factor($R_f$):

- It is the ratio of the distance travelled by a solute to that travelled by the mobile phase.

$$R_f = \frac{Distance\ travelled\ by\ solute}{Distance\ travelled\ by\ solvent}$$

It depends up on

a. Solvent used
b. Medium used for separation i.e. the quality of filter paper
c. The nature of mixture
d. Temperature
e. Size of vessel in which operation is carried out

# Paper Chromatography:

- It is a type of partition chromatography.
- It belongs to liquid-liquid chromatography.
- **Principle:**

- **Stationary phase:**

  Liquid (usually water) which is held in the fibers of a paper.

- **Mobile Phase:**

  Development liquid (solvent such as acetone, ethyl acetate, or a mixture of solvents)

- In this technique the substance are distributed between two liquids i.e. Stationary phase & mobile phase.
- The mobile phase by capillary action moves in upward direction.
- Whereas the stationary phase get sorbed.
- The components of the mixture also move in upward direction at different rates depending upon their solubility & their degree of retention by the paper.
- The components of the mixture appear as spots at different points on the paper.

- In this technique a drop of the test solution is applied as a small spot on a filter paper & spot is dried.
- This is kept in a close chamber & the edge of the filter paper is dipped into a solvent called developing solvent.
- As soon as the filter paper gets the liquid through its capillary axis & when it is reaches the spot of the test solution (a mixture of two or more substance) the various substances are moved by solvent system at various speeds.
- When the solvent has moved to a suitable height, the paper is dried & the various spots are visualized by suitable reagent called visualizing reagent.
- The movement of the substances depends on the $R_f$ values.

# Applications:

- Used for separation of very small amounts of a substances generally by biochemist's.
- Used for separating amino acids.
- 2-D chromatography is used for separating complex mixture such as protein hydrolyzes.
- Used for separating organic as well as inorganic substances.
- Used in analysis of mixture of sugars

# Thin Layer Chromatography (TLC):

- It is a type of Adsorption chromatography & belongs to liquid-solid chromatography.
- **Stationary phase:** Solid Ex: Silica gel, alumina etc.
- **Mobile phase:** Liquid Ex: Single or mixture of solvent
- **Principle:**

- In this technique substance of a mixture are distributed between a solid stationary phase & a liquid mobile phase.
- The mobile phase moves in upward direction & carries different components of the mixture along with it in upward direction.
- The movement of components depends on their solubility (or their polarity) & their degree of retention by the adsorbent.
- The components of the mixture appear as spots at different points on TLC plate.

# Experimental Techniques:

## ❑ Adsorbent (coating material):

- A large number of adsorbent materials are used. Ex: Silica gel, alumina, cellulose powder etc.
- A drop of the test solution is applied as a small spot on TLC plate & dried..
- It is kept in a development chamber at an angle of $45^{O}$.
- The bottom portion of the plate is dipped in solvent called as development solvent.
- The solvent moves in upward direction through pores by capillary action & various substance mixture also moves with solvent at different speed.
- When the solvent has moved to a suitable height, the TLC plate is dried & various spots are detected by using suitable reagents.
- Colored components can be detected under UV lamp.
- The separated components can be analyzed qualitatively & quantitatively.

# Applications:

- In organic chemistry

1. For checking the purity of sample
2. To obtain pure compounds
3. To check the completion of reaction
4. Identifying organic compounds.

- TLC is used for characterising & isolating of acids, alcohols, glycols, alkaloids, amines, amino acids etc.
- TLC is used in separation of inorganic ions.

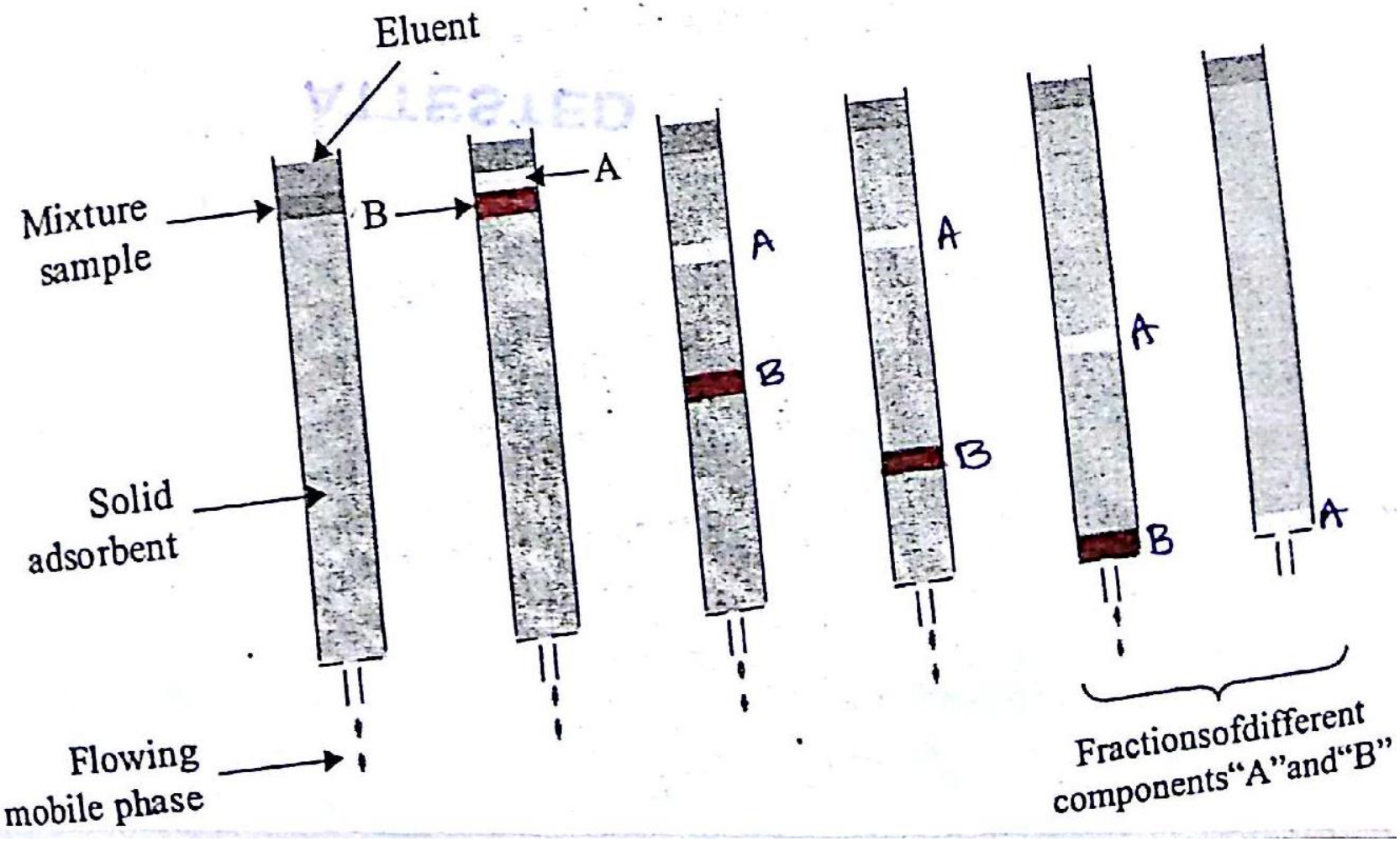
# Column Chromatography:

- It is a type of adsorption chromatography.
- **Stationary Phase:** Solid Ex. Silica gel or alumina
- **Mobile Phase:** Liquid. Ex. Suitable solvent such as ethyl acetate, hexane etc. & their mixtures.
- Liquid-Solid Chromatography.
- **Principle:** (Selective adsorption)

The mixture to be separated is dissolved in a suitable solvent & allowed to pass through a column containing the adsorbent.

- The component which has greater adsorbing power is adsorbed in the upper part of the column, & the component which has lesser adsorbing power is adsorbed in the lower portion of the column.

- As a result the materials are partially separated & adsorbed in the various parts of the column.
- By running or eluting suitable mobile phase (pure solvent or mixture of solvents) through column, individual components of the mixture can be separated & isolated from bottom part of the column.


Eluent
Mixture sample
Solid adsorbent
Flowing mobile phase
B
A
A
B
A
B
A
B
A
Fractionsofdifferent components"A"and"B"

# Gas Chromatography:

- It is a type of Adsorption/ Partition chromatography& belongs to Gas-solid chromatography or Gas-Liquid chromatography.
- **Stationary phase:** Solid/ Liquid
- **Mobile phase:** Gas
- Adsorption/ Partition Chromatography

# Advantages:

- The technique has strong separation power &even complex Mixture can be resolved into constituents.
- It requires only few mg of the sample for analysis.
- It gives good precision & accuracy.
- The analysis is completed in short time.

## ❑ Principle:

When a gas or vapor or mixture comes in contact with an adsorbent (solid or liquid), certain amount of it gets adsorbed on the solid surface or dissolved into liquid.

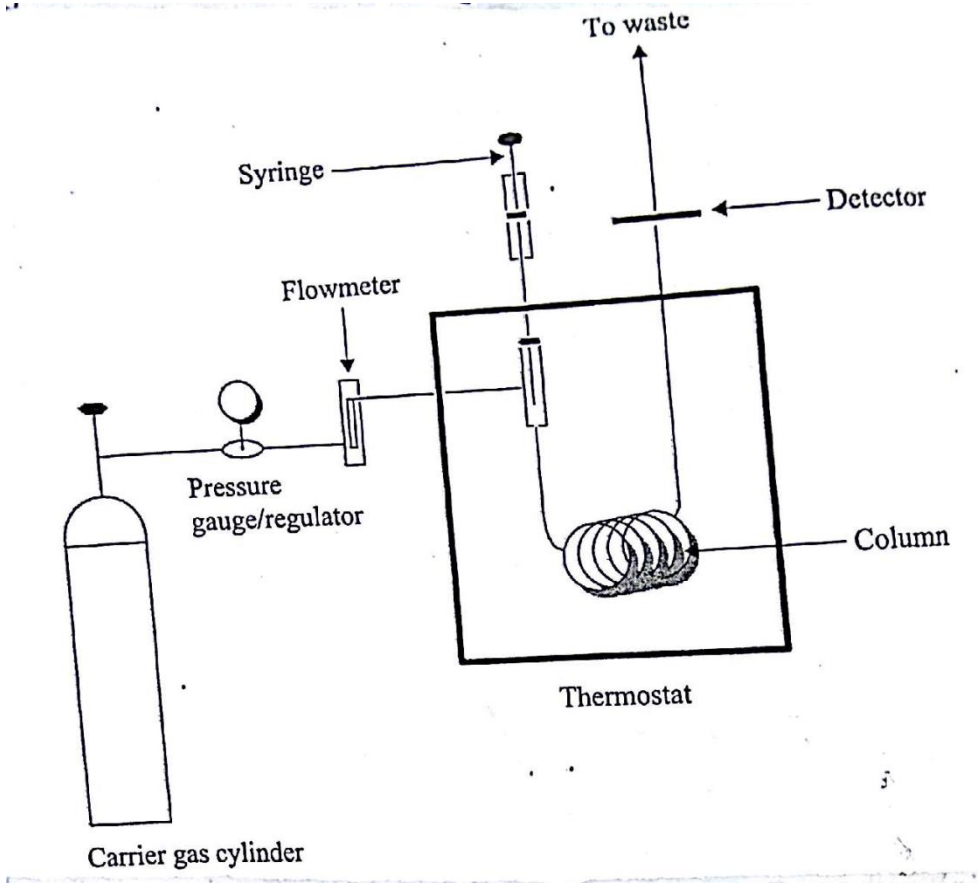
During the passage, different constituents migrate at different distribution ratios between mobile phase & stationary phases.

A continuous flow of gas elutes the components from the column in order of increasing distribution ratio.

## ❑ Instrumentation:

**Gas supply:** Mobile phases are generally inert gases such as helium, argon or nitrogen.

The gas is supplied from a high pressure cylinder having a pressure regulator & flow meter.



# Electrochemical cell:

It is a device which can interconvert chemical & electrical energy

chemical energy  Device  electrical energy

It is a device consisting of 2 electrodes, each in contact with a solution of its own ions, transforms the free energy change of the redox reaction at the electrode into electrical energy.

Electrochemical cells are classified into the following types as shown

Voltaic cell (Galvanic cell)

Electrolytic cell

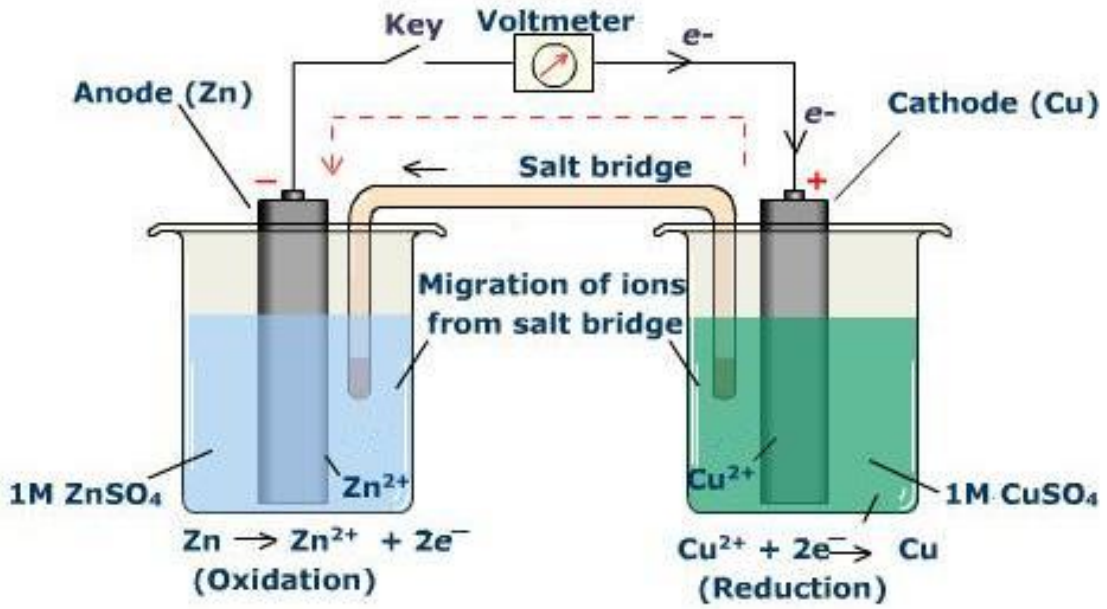
Concentration cell

Fuel cell

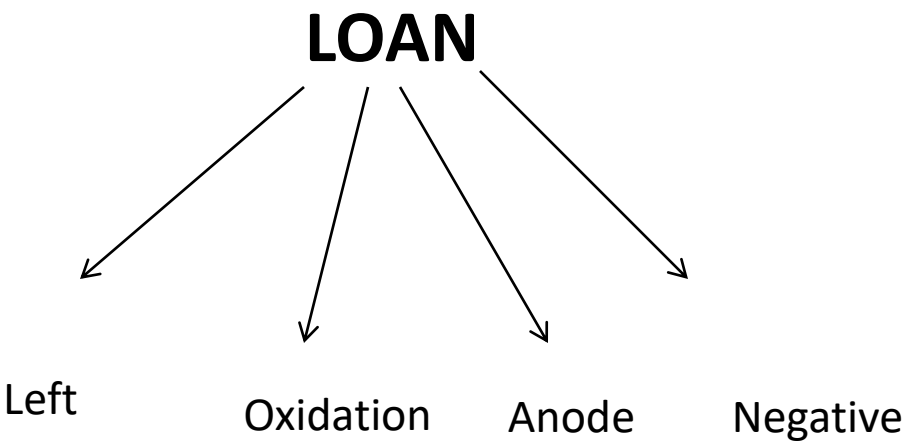
# 1. Voltaic cell (Galvanic cell)

It is a device to convert chemical energy into electrical energy.

Ex: Daniel cell



# Representation of Galvanic cell




IUPAC conversation

**Cathode:** where reduction take place
**Anode:** where oxidation take place
Reactivity series: Zn > Cu
Anode Cathode

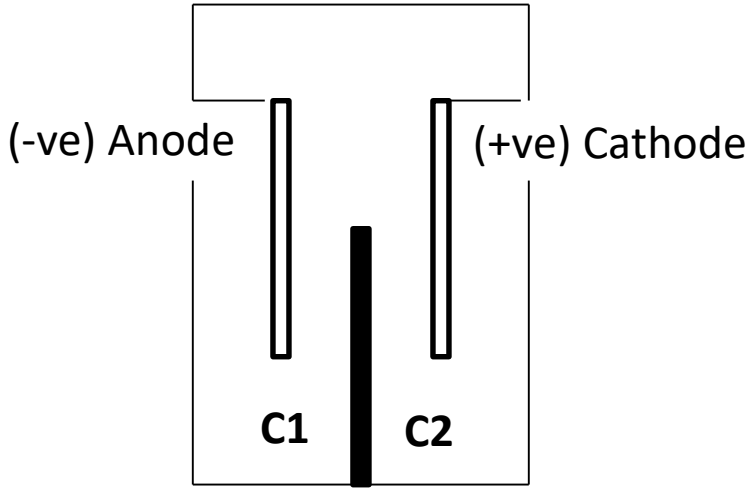
## 2. Electrolytic cell

It is a device to convert electrical energy into chemical energy.

| Electrolytic cell | Galvanic cell |
|---|---|
| 1. It converts electrical energy into chemical energy. | 1. It converts chemical energy into electrical energy. |
| Cathode: Negative<br>Anode: Positive | Cathode: Positive<br>Anode: Negative |
| A non spontaneous reaction is carried out using electrical energy. | The energy generated by a spontaneous rxn converted into electrical energy |
| | |

## 3. Concentration cell

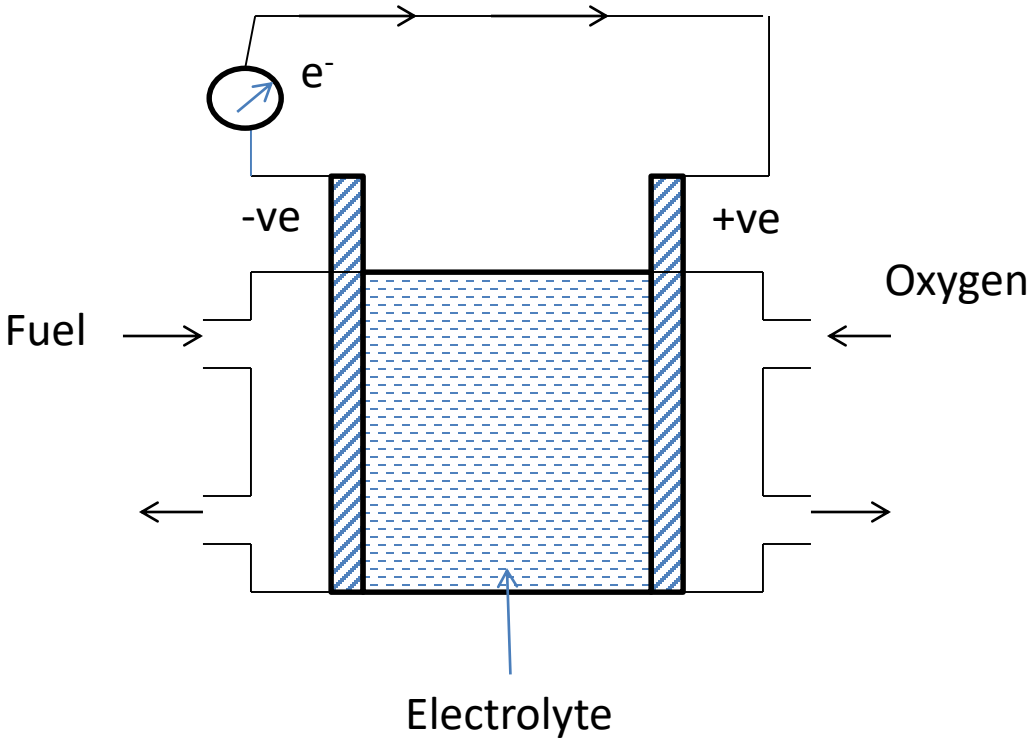
It is a device that generate electrical energy when two electrodes of the same metal are in contact with solutions of its ion at different concentrations.




**C2 > C1**

# 4. Fuel cell

A **fuel cell** is an electrochemical **cell** that converts the chemical energy from a **fuel** into electricity through an electrochemical reaction of hydrogen **fuel** with oxygen or another oxidizing agent.



# Electrode Potentials

## 1) Single electrode potential:

When two dissimilar metals are in contact with their own ion in a cell, the metal have a tendency to lose or gain electrons during their electrode processes.

- Therefore , the electrode potential of a metal electrode of a cell is dependant on the presence of the metal to lose or gain electrons, when it is in contact with a solution of its own ions.

- It is defined as the potential established at the interface between the metal (M) & the ionic solution ($M^{n+}$), when it is in contact with a solution of its own ions.

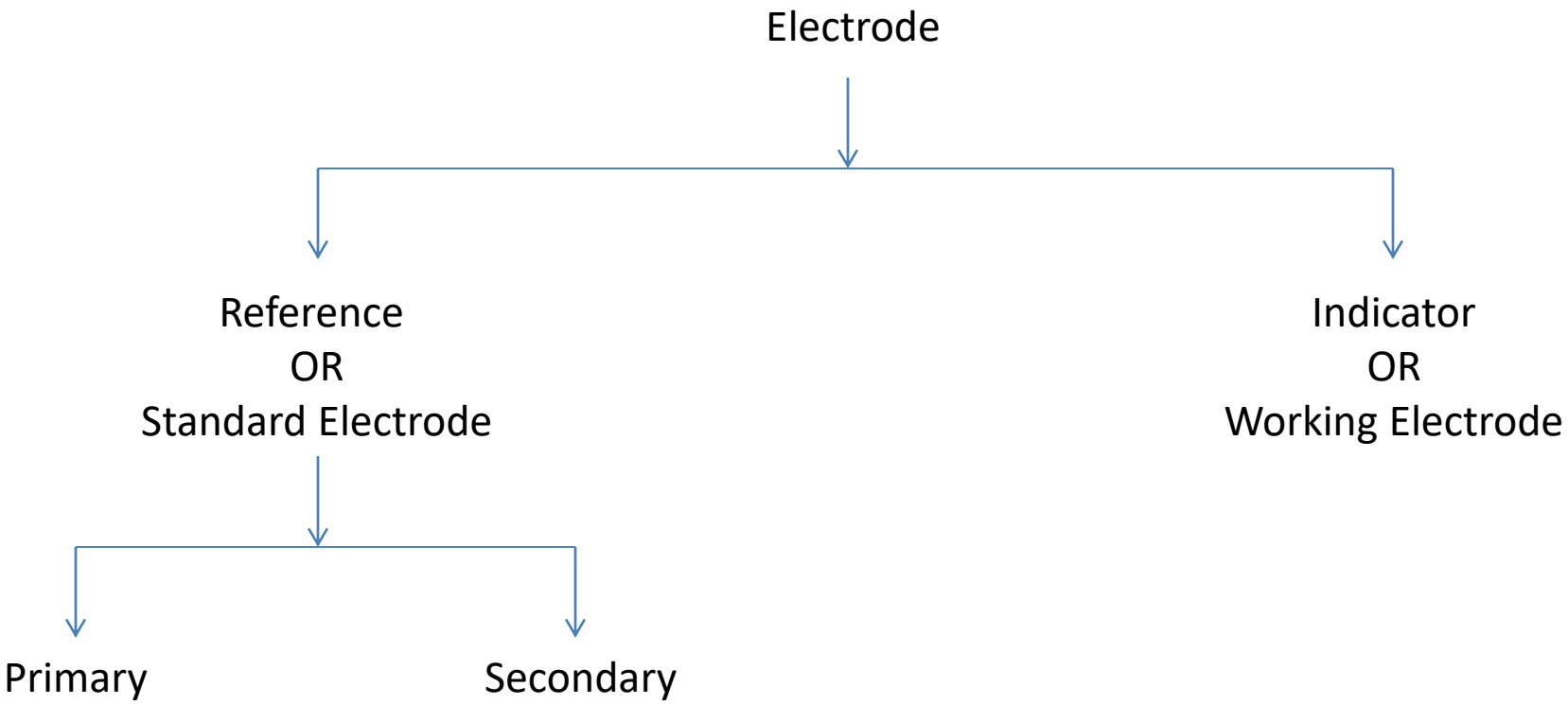
- It is denoted as $E^0_{Mn+/M}$

- When two electrodes are coupled to form a cell, the one with the lower reduction electrode potential (Higher oxidation potential) values act as anode due to oxidation & the electrode having the higher reduction electrode potential (lower oxidation potential) value act as cathode.

## **2) Standard Electrode Potentials**:- (Electrochemical Series)

The standard electrode potentials of a large number of half cells have been measured using SHE (Standard Hydrogen Electrode) as a reference electrode ($E^0=0$)

- It is defined as potential of an electrode measured at 298K & Unit (1M) ion concentration.


Electrode
Reference
OR
Standard Electrode
Indicator
OR
Working Electrode
Primary
Secondary

# A) Reference/Standard Electrode:-

Defined as the electrode which has stable & reproducible potential & complete the cell acting as half cell.

- It completes the cell
- Provides stable potential
- Helps in measuring the potential of any other electrode

Types:- 1) Primary: (SHE)
2) Secondary: Calomel electrode Ag, AgCl electrode

## B) Indicator / Working Electrode:-

It is the electrode whose potential changes upon change in the concentration of a particular ion / species.

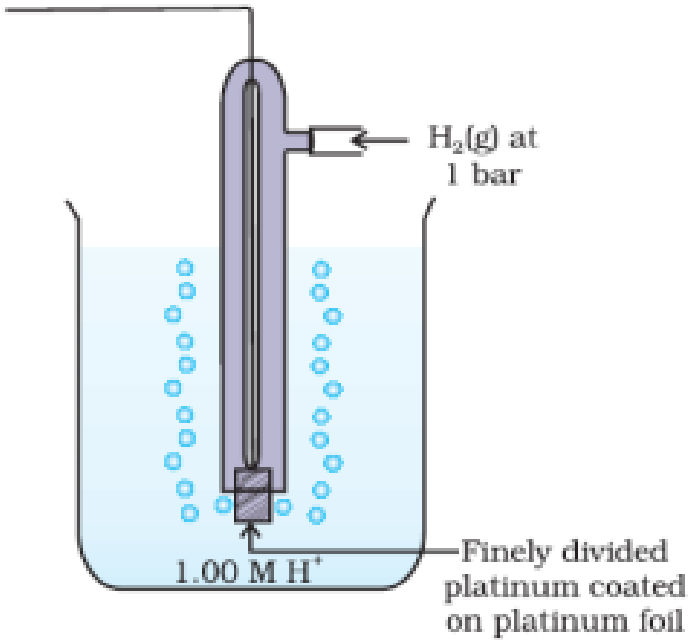
Ex: All ISE (Ion Selective electrodes) i.e. glass electrode, Calcium ISE etc.

Types of ISE

1) Glass Membrane Electrode
2) Polymer Membrane Electrode
3) Solid state Electrode
4) Gas Sensing Electrode

# 1) Primary Standard Hydrogen Electrode (SHE):

A common reference electrode used to measure the potential of the another electrode is the Standard Hydrogen Electrode (SHE) whose electrode potential at all temperatures is taken as zero i.e. $E^0 = 0$



# 2) Secondary Standard Electrodes:

## a] Calomel Electrode:

The most widely used reference electrode in a electrochemical cell is calomel electrode.

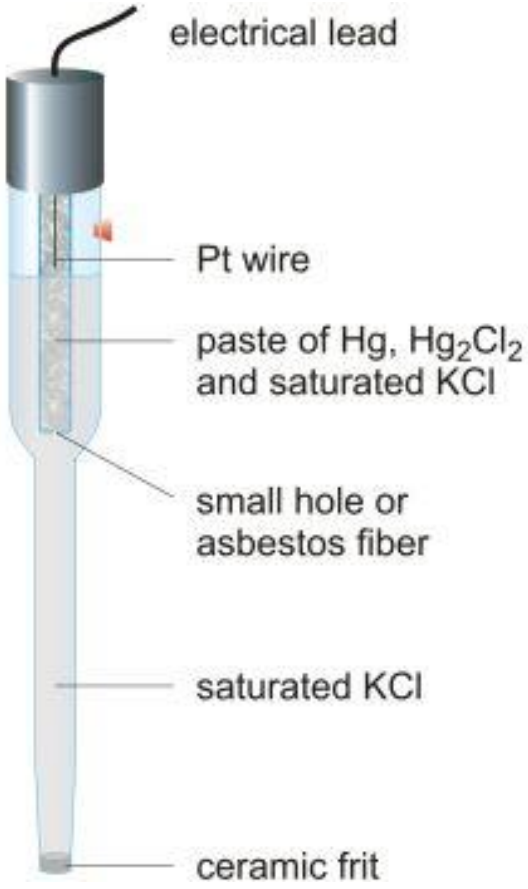
The potential of a calomel electrode is found to depend on the concentration of KCl solution used in the half cell.

| Conc. Of KCl | $E^0$ Calomel |
|---|---|
| 0.1 N | 0.3334 U |
| 1.0 N | 0.2810 U |
| Saturated | 0.2422 U |

Commonly used is saturated KCl.

## Construction:

- Consists of narrow glass tube.
- At its bottom a layer of Hg is present.
- A part of Hg2Cl2 & Hg is filled above it.
- Remaining portion of the glass tube is filled with saturated KCl solution
- A Pt wire is dipped into the Hg layer for electrical contact.
- This is placed inside an outer glass jacket with a temporary porous end & is filled with sat. KCl
- Representation Hg|Hg2Cl2|Cl- sat



Calomel as a cathode of cell the reaction is

$Hg_2Cl_2 + 2e^- = 2 Hg(s) + 2 Cl^-$

The reduction potential E is given as

$E_{cal} = E^0 - 0.0591 \log_{10} [Cl^-]$

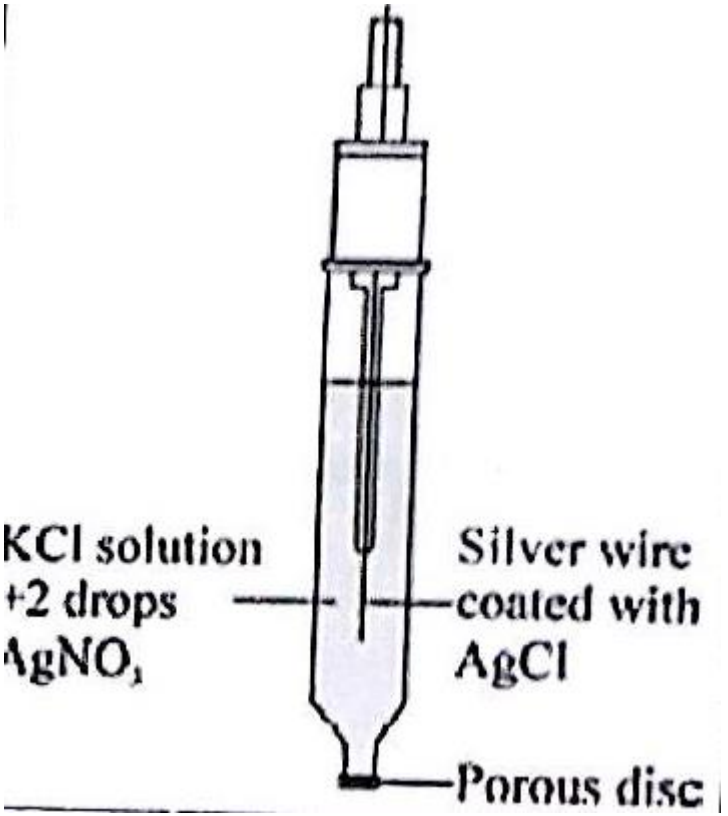
**Demerits:** 1) Above $50^0$C $Hg_2Cl_2$ decomposes.

2) Hg is poisons.

## b] Silver-Silver Chloride Electrode:

- This electrode is an example of a metal-metal salt ion reference electrode.
- It consist of a silver electrode coated with a sparingly soluble AgCl & is immersed in a solution containing $Cl^-$ ions (saturated KCl)
- Representation $Ag/ AgCl_{(s)} / Cl^-$
- The electrode potential E is given as

$$E_{Ag/AgCl} = E^0 - 0.0591 \log_{10} [Cl^-]$$



## Merits:

- Reduction pot. Of this electrode is dependent on the concentration of $Cl^-$ ions.
- Easy to manufacture
- Superior temperature range i.e. even above $130^0C$

## Application:

Used as a Reference electrode in pH meter

## B Indicator / Working Electrode:-

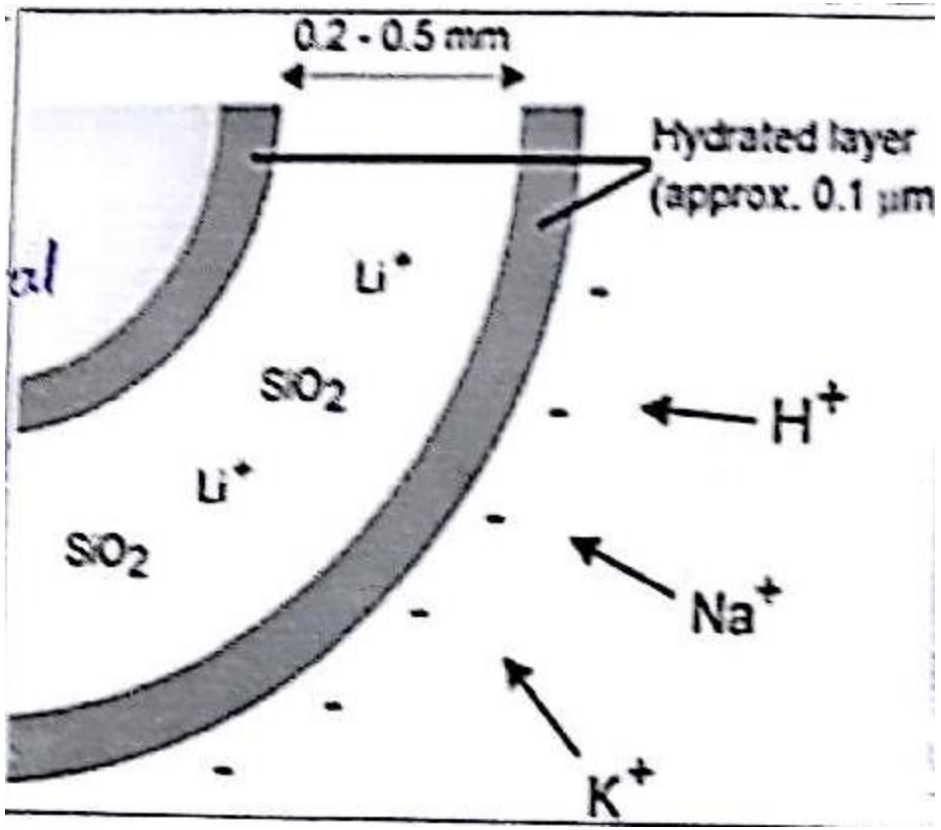
Ex: pH Electrode (Glass electrode)

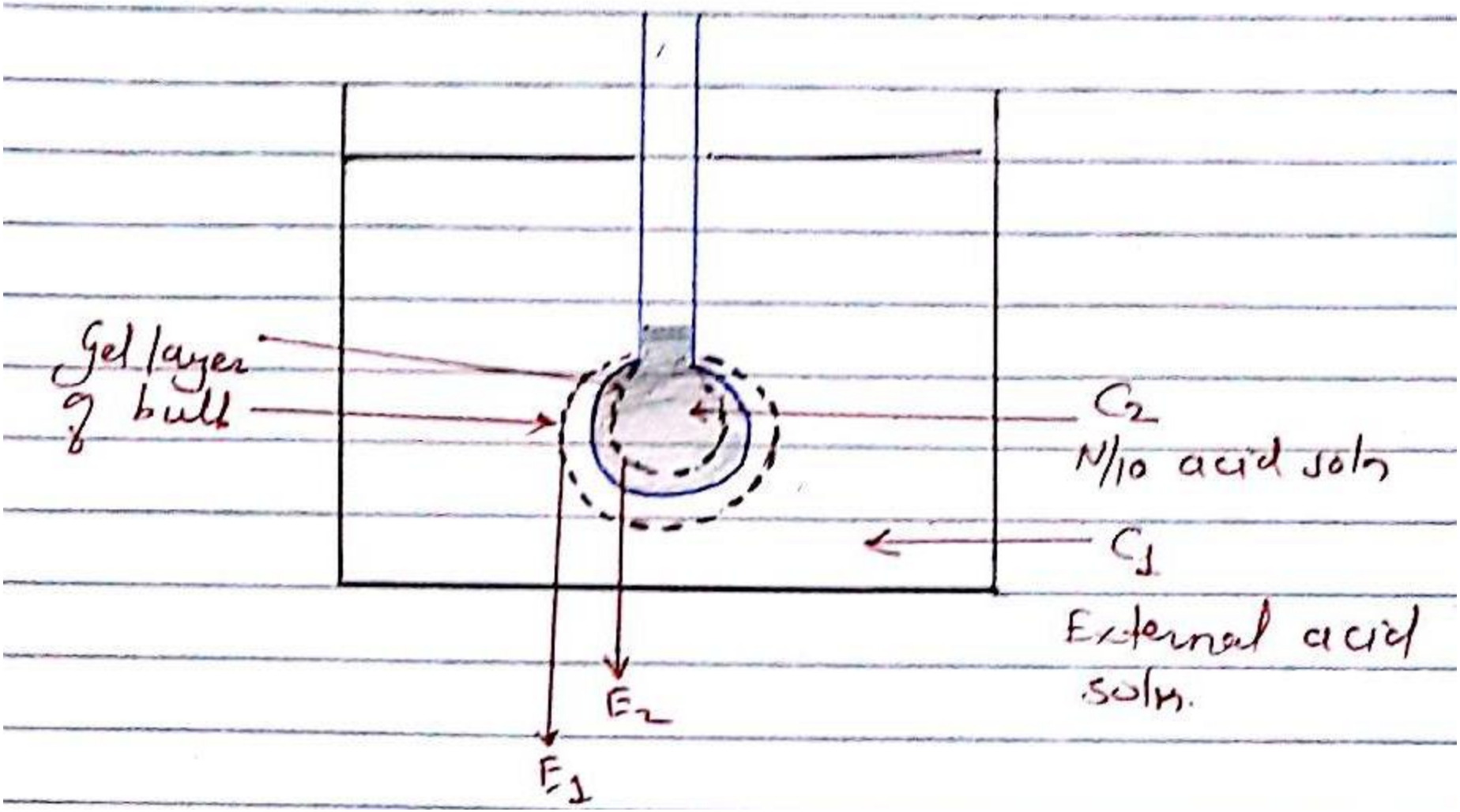
The most widely used ion- selective electrode is the glass pH electrode, which utilizes a thin glass membrane that is responsive to the changes in $H^+$ activity.

F. Haber, in 1901 was the first person to observe that the voltage of a glass membrane changed with the acidity of a solution

- The glass electrode i.e. pH sensitive glasses are manufactured primarily from $SiO_2$ (silicates)
- In addition, the glasses are made to contain varying amounts of other metal oxides like $Na_2O$, Cao etc.
- If these glasses are placed in an solution containing H+ , the glass surface in contact with solution becomes hydrated & causes it to swell.
- Hydrated layer is formed on the inner side surface of the bulb as well as due to presence of 0.1 N HCl solution inside the bulb

- Ions can penetrate through this thin layer & alter the electrochemical potential.
- The structure of the glass has been optimised so that virtually only H+ ions enter the gel layer.
- Thus the membrane undergoes ion exchange reaction, the Na+ ions or Li+ ions of glass are exchanged for H+ ions.
- [H+] + NaCl= $Na^+ + H^+ Cl^-$






Eb = E1 – E2

Potential Eb arises due to difference in the H+ ion concentration inside & outside the glass bulb

i.e. Eb = E1 – E2

Thus,

$$Eb = [E1 - E2] = \frac{2.303RT}{nF} \log\frac{C1}{C2}$$

## Principle of glass electrode:

When two solution of different [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 [H+] of the two solutions.

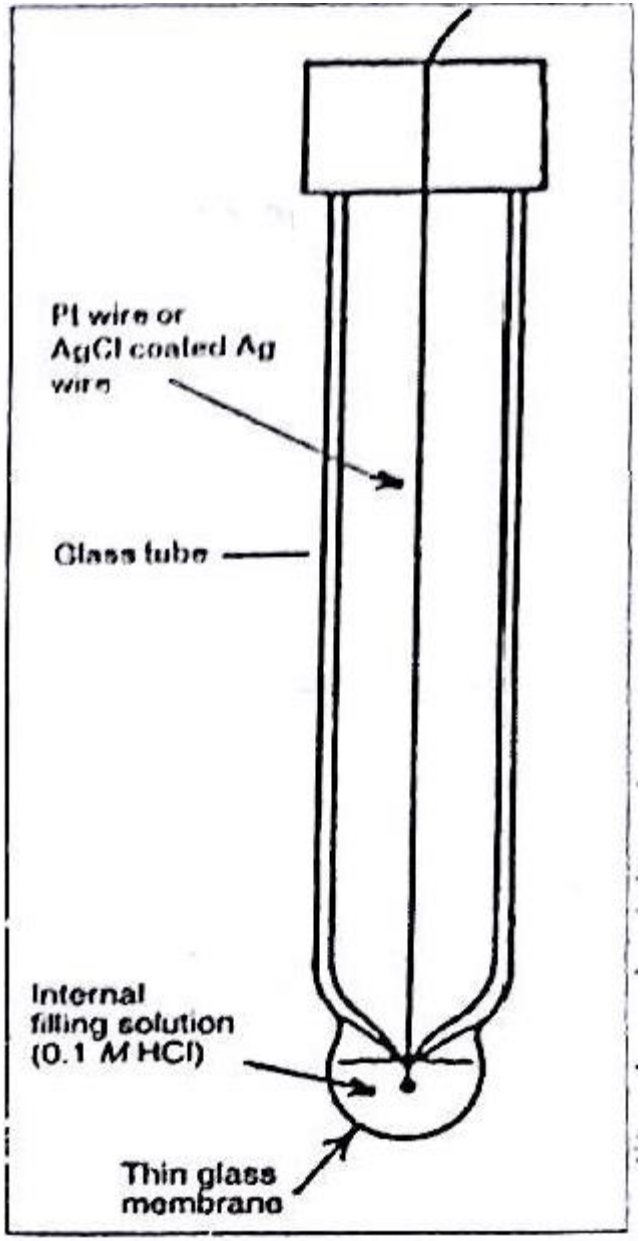
## Construction:

A glass electrode is made of a long glass tube with a thin walled glass membrane bulb at the bottom.
A Pt wire or AgCl coated Ag wire is dipped in the 0.1 M HCl, solution in the bulb

The glass electrode is represented as
Pt, 0.1M HCl / glass

Potential, $E_G = E_G^0 + 0.0591\ pH$

Where $E_G^0$ is potential of glass electrode in the solution of known pH.



# Determination of pH of solution

A glass electrode is coupled with Calomel electrode or Ag/ AgCl electrode, to determine the pH of a solution.
The electrode are dipped into the solution

The cell representation for glass coupled with calomel or Ag/AgCl electrode is as follows respectively.

1) Hg/ $Hg_2Cl_2/Cl^-$//unknown $H^+$ solution / glass electrode
2) Ag/ AgCl(s)/0.1N HCl//unknown $H^+$ solution / glass electrode

EMF of the cell is measured (considering sat calomel)

Ecell = Ecal – EG
= 0.2422-($E^0G$ + 0.0591 pH)

$$pH = \frac{0.2422-(Ecell-EoG)}{0.0591}$$

$E^0_G$ is the pot. of electrode when electrode is in contact of solution of known pH.

## Advantages:

1) Simple & easy to use.
2) Gives accurate & quick results.
3) It is stable electrode to use in strong oxidizing & reducing agent.
4) Can detect & determine H+ in the presence of other ions.
5) Portable & compact.

# pH Metry

## Buffer:

It is the solution which resists change in pH even if small amount of an acid or base is added in it. The solution containing a weak acid & its salt or weak base & its salt.

## Henderson equation: for buffer solution preparation

pH of acidic buffer= $pK_a$ +log$\frac{[Salt]}{[Weak\ acid]}$

pOHof basic buffer= $pK_b$ +log$\frac{[Salt]}{[Weak\ base]}$ .

pKa = -$\log_{10}$ Ka (Ka dissociation constant of weak acid)

pKb= -$\log_{10}$Kb (Ka dissociation constant of weak base)

# Types of Buffer

## 1) Acidic buffer

Ex: $CH_3COOH$ + $CH_3COONa$
Weak acid — salt of weak acid

## 2) Basic buffer

Ex: $NH_4OH$ + $NH_4Cl$
Weak base — salt of weak base

## pH Metric Titrations:

## 1) Strong Acid – strong base

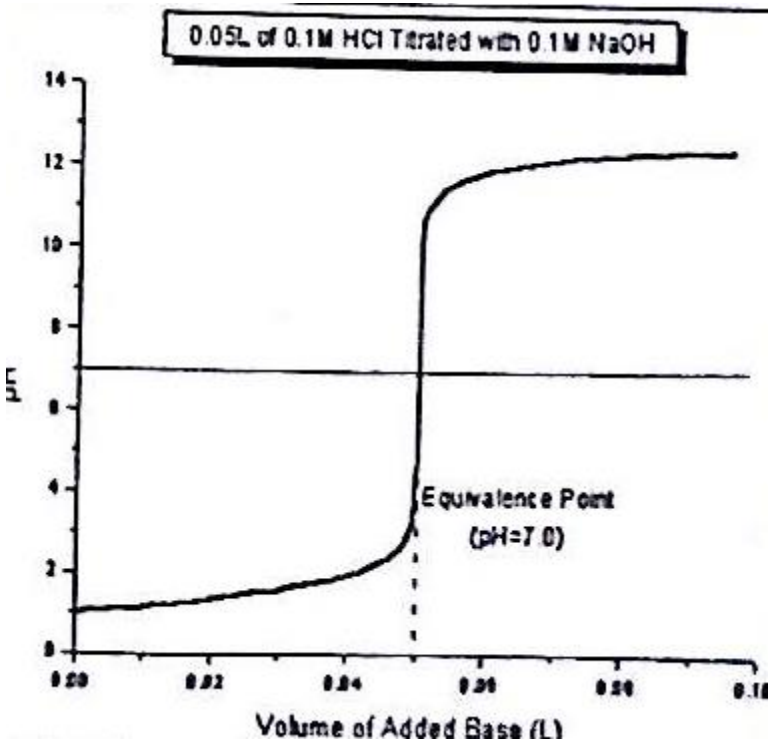
Ex: NaOH Vs HCl
Both these dissociates completely into ions.
Net reaction during titration is as

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

## Titration curves:

It is a plot of pH Vs ml of titrant added from burrete.

1) There is gradual change in pH during the initial stage of titration
2) pH is 7 at equivalence point of titration.
3) pH changes suddenly from 4 to 10, near equivalence point.
4) After eq. pt. pH change is again very slow.




Normality of either SA or SB is known & the normality of other can be calculated by formula

$N_1V_1 = N_2V_2$

Where, $V_1$ = Vol. of acid taken for titration ,

$V_2$ = Vol. of base added till end point

$N_1$ & $N_2$ are normality of acid & base respectively

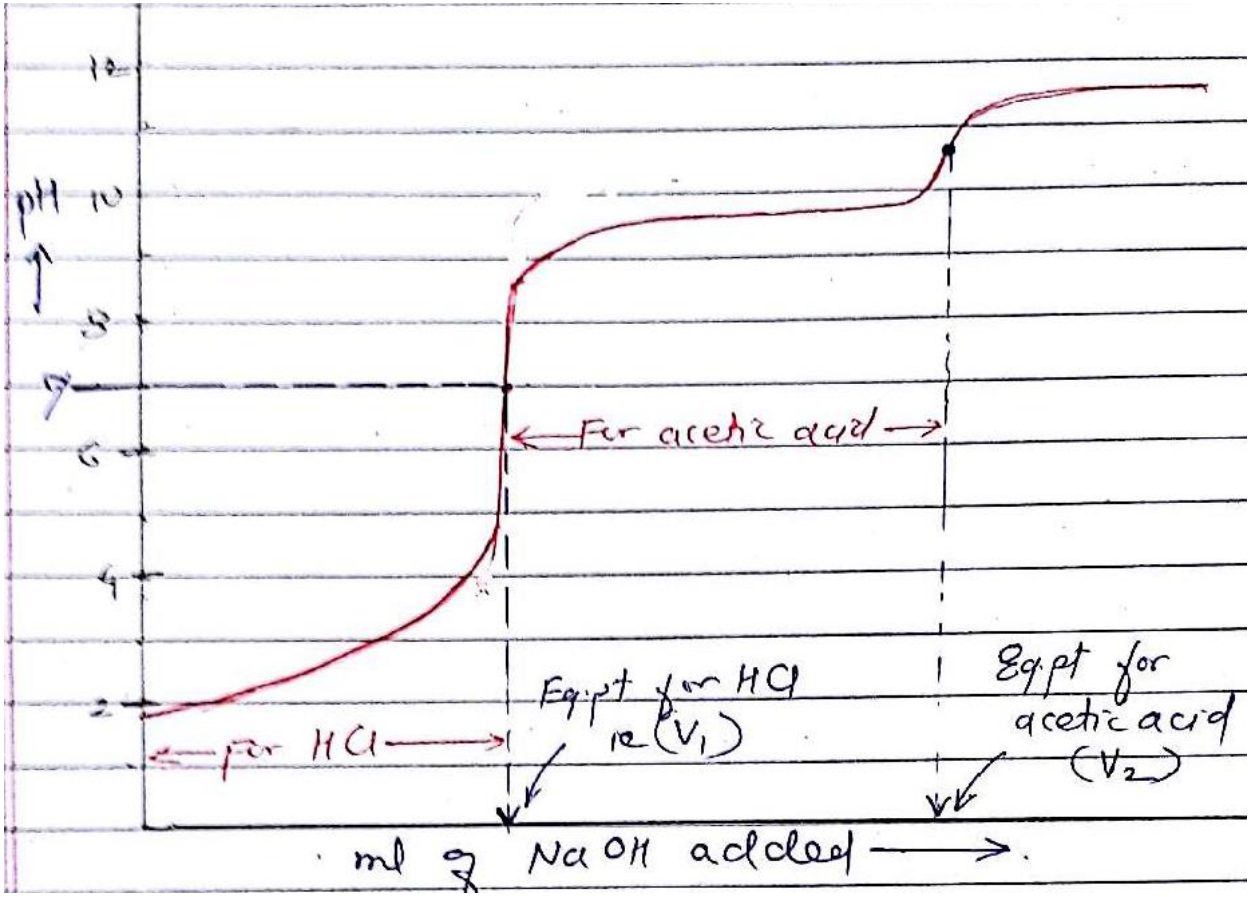
## Titration curve for the mixture of (SA & WA) acids verses strong base

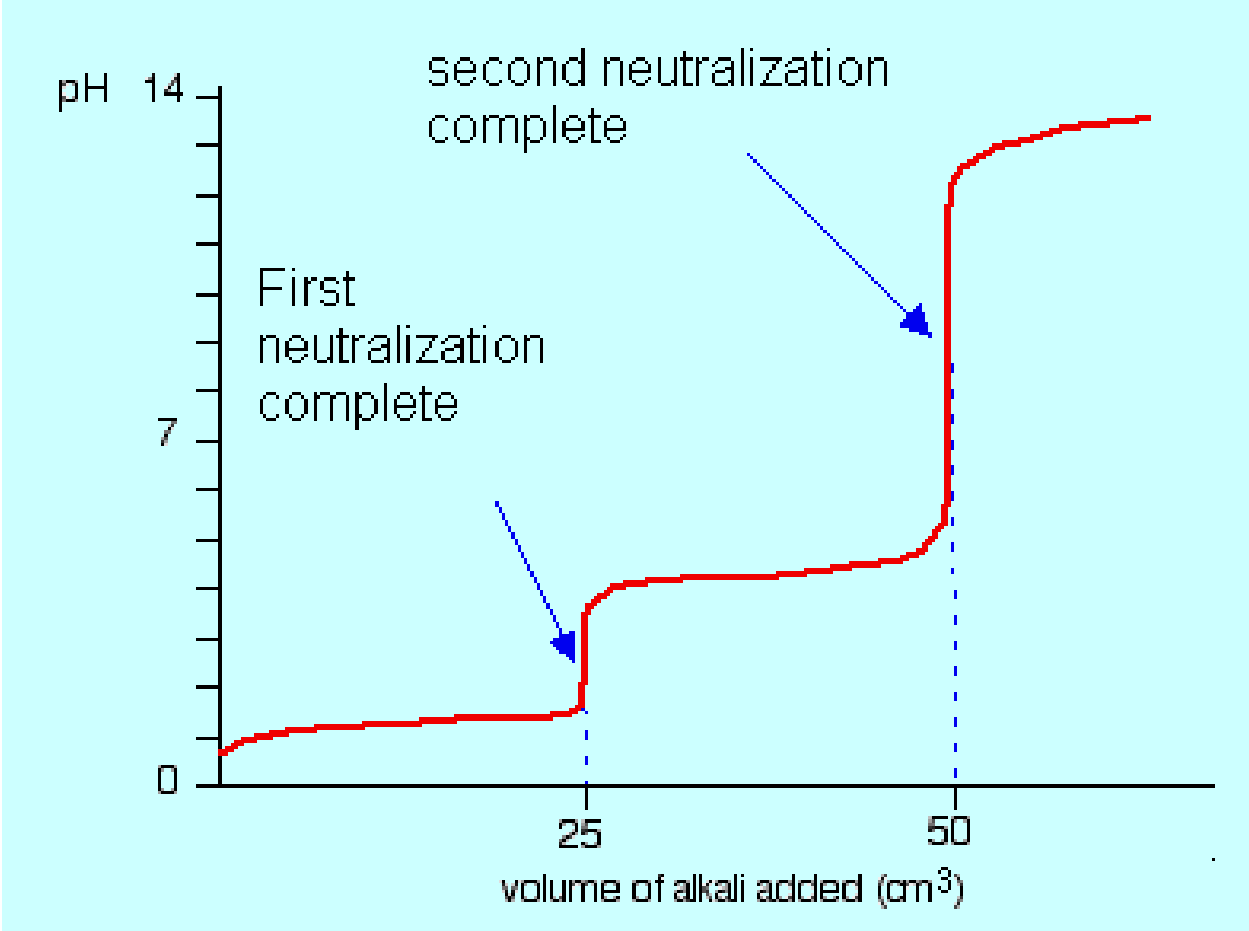
Ex: HCl + CH3COOH Vs NaOH

## Theory

- Strong acid (HCl) is completely ionized in water & weak acid is feebly in dissociated form.
- During titration, H+ from HCl gets first neutralized & pH increases slowly as
- H+ + Cl- + Na+ + OH- → Na+ + Cl- + H2O
- Near the end point there is sudden increase in pH, at pH about 3.7.
- On complete neutralization of HCl, neutralization of CH3COOH begins.
- There is formation of Na+ CH3COO- salt
- Thus upto the complete neutralization of CH3COOH, the flask contains CH3COOH + CH3COONa i.e. weak acid & its salt which acts as buffer solution.
- Therefore pH of titration mixture almost remains constant even though NaOH is added from burrete.
- CH3COOH + Na+ + OH- → Ch3COO- + Na+ + H2O

At the end point i.e. complete neutralization of CH3COOH, pH increases suddenly, at pH 8.3. After this point pH increases but slowly




pH
14
7
0
second neutralization complete
First neutralization complete
25
50
volume of alkali added (cm3)

## Procedure:

1) Wash the electrode with distilled water.
2) Pipette out V ml (25 ml) of acid mixture in a beaker & keep it on magnetic stirrer.
3) Fill the burrete with std. (0.1 N) NaOH solution.
4) Dip the electrode in the beaker.
5) Note the initial pH of the acid mixture.
6) Add 1 ml of NaOH solution from burrete & note down the pH of titration mixture after stirring the solution.
7) Repeat this procedure no. 6.
8) Note 4 to 5 readings after second sudden increase in pH.

# Calculations

1) HCl quantity from the acid mixture

∴HCl in 25 ml acid mixture ≡ V1 ml NaOH

∴HCl in 1000 ml acid mixture ≡ $\frac{1000 \times V1}{25}$ ml NaOH

= 40 V1 ml NaOH.

∴1 ml I N NaOH ≡ 36.5 mg HCl

∴40 ml Z N NaOH ≡ 40 x V1 x Z x 36.5 mg HCl/ lit

2) CH3COOH quantity from the acid mixture

∴CH3COOH in 25 ml acid mixture ≡ (V2-V1) ml NaOH

∴CH3COOH in 1000 ml acid mixture ≡ $\frac{1000 \times (V2 - V1)}{25}$ ml NaOH

= 40 (V2-V1) ml NaOH.

As, 1 ml I N NaOH ≡ 60 mg acetic acid

∴40(V2-V1) ml Z N NaOH ≡ 40 x (V2-V1) x Z x 60 mg CH3COOH/ lit

## Standardization of pH meter:-

- Switch on the instrument & allow it to warm up.
- Clean the electrode with distilled water.
- Immerse the electrode in standard buffer (pH 7) solution
- Adjust the temperature knob (if manual setting are possible for it)
- Select the pH mode
- Adjust the pH reading to 7 on the display, with the help of ‘standardize’ knob.
- Don’t disturb this knob after adjustment
- Then remove the electrode from the buffer solution of pH =7 & wash it with distilled water.
- Immerse the electrode in the another buffer solution of (pH = 4 or pH = 9)
- Adjust the pH reading on the display with slope knob to the pH of the solution.
- This is how calibration of pH meter is carried out.

# Conductometry

## Conduction by solutions of electrolytes:-

It is due to flow of electricity due to migration of ions, on application of potential difference between two electrodes.

- Positively charged cations move towards cathode & negatively charged anions move towards anode.
- Migration conducts electricity & transport of matter to the electrode
- Conduction increases with increase in temperature which is due to increased mobility of ions at higher temperature.

## Electrolytic Conductance:

Solution of electrolyte obey Ohms law

i.e. $I = \frac{E}{R}$

Where E = Voltage in volts

I = Current in ampere

R = Resistance in ohms

## Various Terms in Conductometry

## 1) Conductance:-

It is ease with which the current flows through a conductor/ solution & is reciprocal of resistance i.e. C = 1/R

**Unit: $Ohm^{-1}$ or mho**

# 2) Specific conductance (κ) :-

It is reciprocal of specific resistance (ϱ) & conductance of 1 c.c of solution.

**Unit of (κ)- ohm$^{-1}$ cm$^{-1}$**

SI Unit : Sm$^{-1}$

$$R = \rho \left(\frac{l}{A}\right)$$

$$K = \frac{1}{\rho} = \frac{1}{RA/l} = \left(\frac{l}{A}\right) \times \frac{1}{R}$$

$$K = \left(\frac{l}{A}\right) \times conductance\ of\ solution$$

$\frac{l}{A}$ = cell constant

## 3) Equivalent conductance (Λ) :-

1 gm equivalent of an electrolyte dissolved in V ml solution, then the conductivity of the solution by all the ions produced from 1 gm equivalent is known as equivalent conductance.

**Unit of (Λ)- ohm$^{-1}$ cm$^2$ per mole**

$\Lambda$ = kV = $\frac{k \times 1000}{C}$ Where C= conc. In normality

Eq conductance deals with equivalent weight of electrolyte.

## 4) Molar conductance (μ) :-

It is defined as conducting power of all the ions produced by one mole of an electrolyte in 1 dm3 of water.

**Unit of (μ)- ohm$^{-1}$ cm$^2$ per mole**

$\mu$ = kV = $\frac{k \times 1000}{M}$

# 5) Cell constant (l/A):

**Unit: $Cm^{-1}$ or $m^{-1}$**

(For a designed cell if l & A are constant)

K = $(\frac{1}{R}) \times cell\ constant$

= $conductance \times cell\ constant$

i.e. $Specific\ conductance = Conductance \times cell\ constant$

$$i.e. Cell\ Constant = \frac{specific\ conductance}{Conductance}$$

# Conductometric Titrations

Conductometric measurements are employed to find end points of acid-base titrations & precipitation titrations.

- There is no need to use any indicator to this titrations.
- The principle involved is that electrical conductance depends upon number & mobility of ions in the solution.

# Strong Acid verses Strong Base Titration

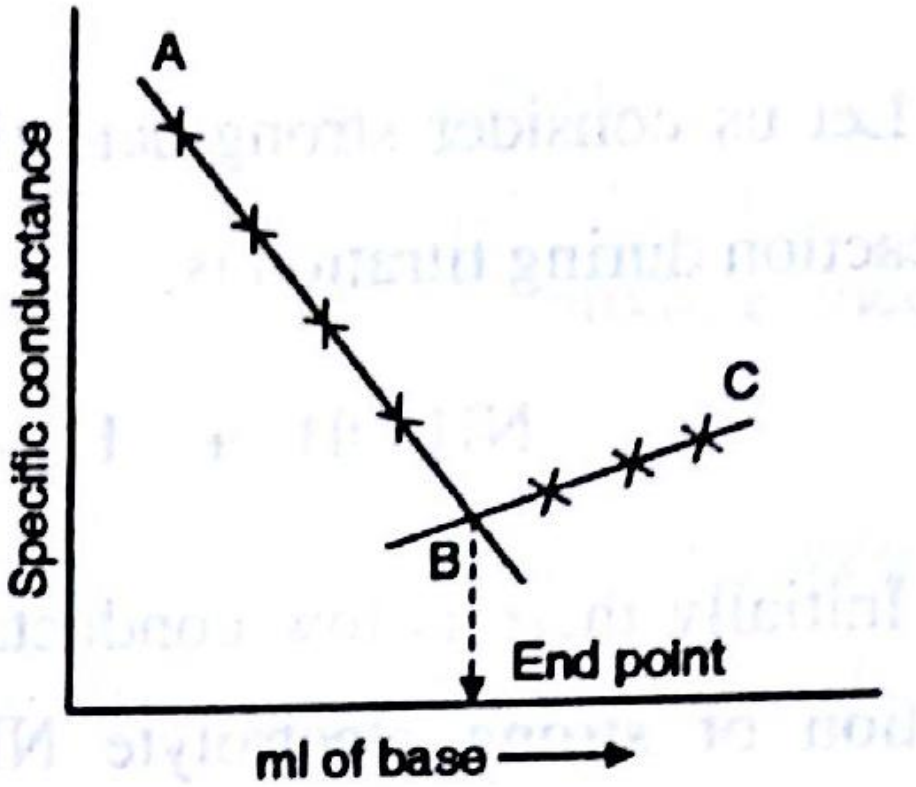



Figure : Strong Acid-Strong Base Titration

1 ml 1 N NaOH ≡ 36.5 mg of HCl

# Weak Acid verses Strong Base Titration

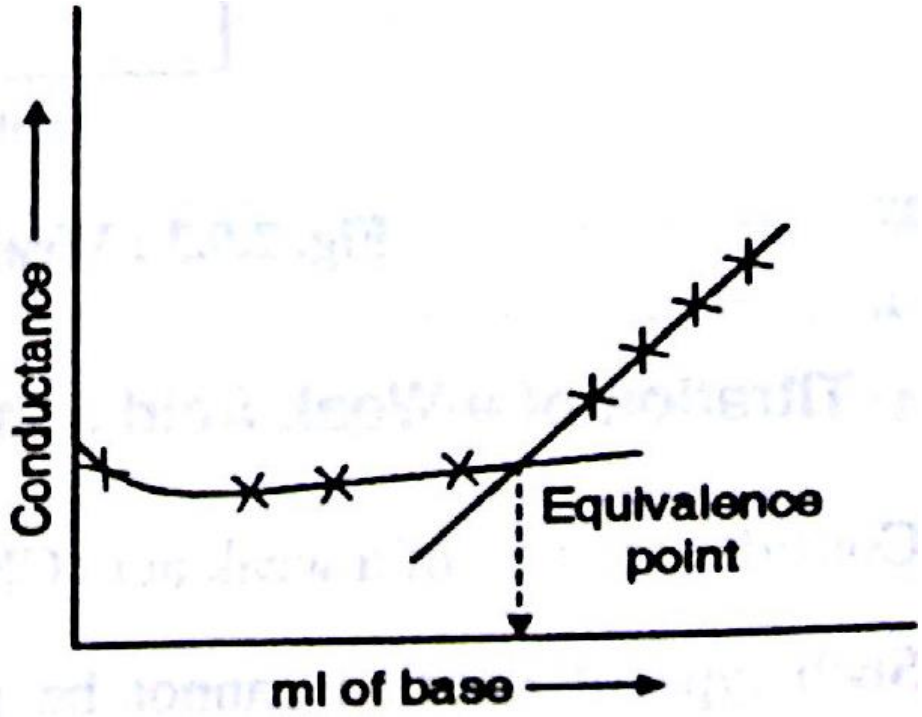



Figure : Weak Acid-Strong Base Titration

1 ml 1 N NaOH ≡ 60 mg of acetic acid

# Weak Base verses Strong Acid Titration

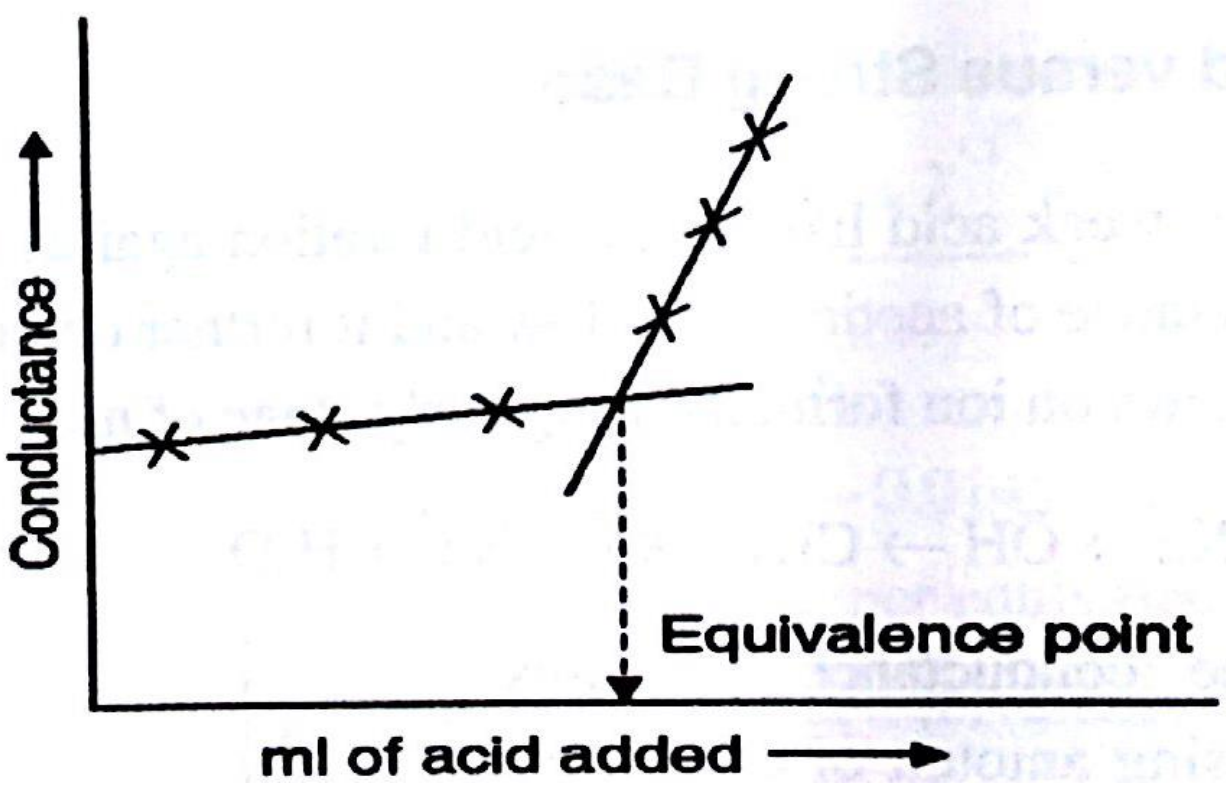



Figure : Weak Base -Strong Acid Titration

# Weak Acid verses Weak Base Titration

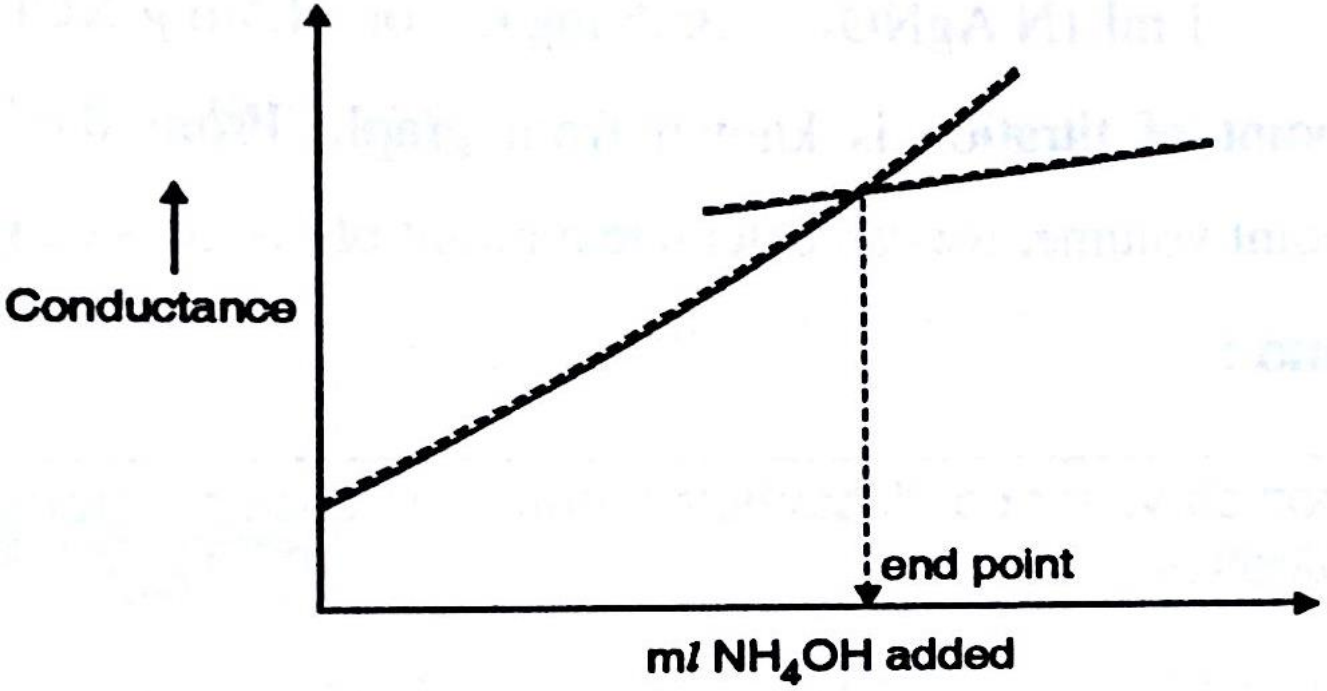



Figure : Weak Acid-Weak Base Titration

# Precipitation Titration

Precipitation Titrations can be carried out continently by conductivity measurements,
Example: KCl vs AgNO3 is added from burette & conductance of KCl solution observed at various occasions.

$$K^{+} + Cl^{-} + Ag^{+} NO3^{-} \rightarrow K^{+} + NO3^{-} + AgCl \downarrow$$

- The conductance of KCl decreases slowly upto equivalence point because grater mobility of $Cl^{-}$ are replaced by lower mobility $NO_3^{-}$ ions.

- Because conductance difference in them is not large therefore conductance decreases slowly upto equivalence point

- After that conductance increases rapidly, due to addition of $Ag^{+}$& $NO3^{-}$ ions from burette.

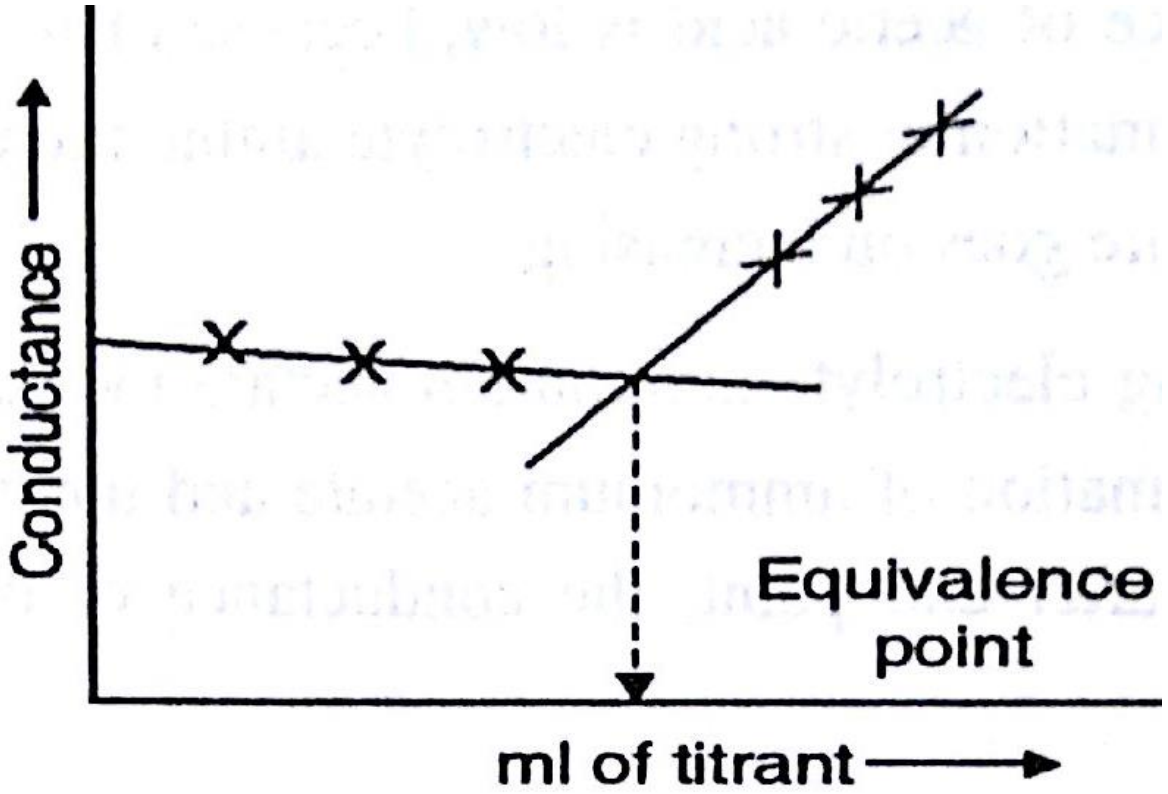
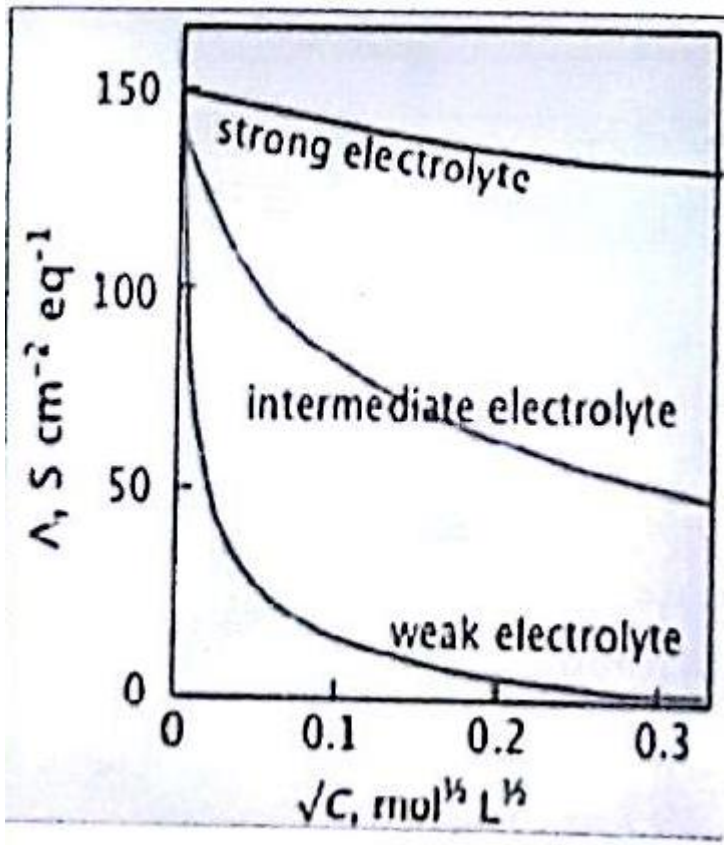



**Figure** : KCl verses AgNO3 titration

1 ml 1 N AgNO3 ≡ 35.5 mg of Cl- or 74.5 mg of KCl

# Variations in Eq. conductance on Dilution

1) Eq. conductance (Λ) increase with decreasing concentration for both weak & strong electrolytes.
2) Λ depends upon number of ions & their speed of the movement in solution.
3) At high concentration there are more interaction between the oppositely charged ions so less is Λ.
4) At infinite dilution interactions are almost nil, so more is 'Λ'



# Ionic mobility

- Although at infinite dilution, all electrolytes are completely dissociated, still the $\Lambda_0$ values differ from one another.
- This is attributed to differences in the speeds of ions
- e.g. $\Lambda_0$ for HCl is more than three times the $\Lambda_0$ for NaCl.
- As Cl- ion is common, it follows that speed of Na+ ions Very low compared to speed of H+ ions.

# Kohlrasch's law

Kohlrasch's law is regarding independent movement of ions, at infinite dilution.

- This law states that at infinite dilution, each ion migrates independently of its co-ion & contributes a definite share to the total equivalent conductance of the electrolyte.
- Thus

$$\Lambda_0 = \lambda_0^+ + \lambda_0^-$$

where $\lambda_0^+$ & $\lambda_0^-$ are the equivalent conductance of positive & negative ions respectively at infinite dilution

- Equivalent conductance of an electrolyte at infinite dilution is equal to the sum of equivalent conductance of positive & negative ions of the electrolyte

$$\lambda_0 = \lambda^+ + \lambda^-$$

| Electrolyte | $\Lambda_o$ ohm$^{-1}$ cm$^2$/equivalent | Difference |
|---|---|---|
| HCl | 426.6 | – |
| $HNO_3$ | 421.3 | 4.9 |
| KCl | 149.86 | – |
| $KNO_3$ | 144.96 | 4.9 |
| LiCl | 115 | – |
| $LiNO_3$ | 110.1 | 4.9 |
| $KNO_3$ | 144.96 | – |
| $LiNO_3$ | 110.1 | 34.86 |
| KOH | 271.5 | |
| LiOH | 236.7 | 34.8 |

## Applications of Kohlrasch's law

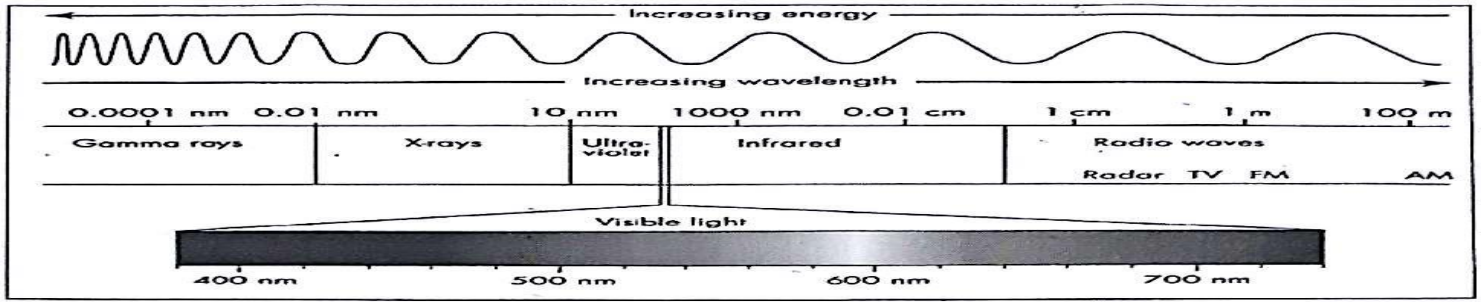
1. **Finding $\Lambda_0$ for weak electrolytes**
2. **Calculation of ionic conductance ($\lambda_0$)**

Ex. 1. Equivalent conductance at infinite dilution for KCl, $KNO_3$ and $AgNO_3$ at 25 $^0$C are 0.015, 0.0145 & 0.01334 ohm$^{-1}$ m$^2$ per equivalent respectively. What is $\Lambda_0$ for AgCl?

# Ultra- Violet (UV) Spectroscopy

- UV & Visible spectroscopy provide us information about the structure of the molecules that contains double bond or triple bond or conjugated bonds.
- It results from the interaction of EMR in the UV visible region with molecules, ions & or compounds.
- This spectroscopy can distinguish between conjugated & isolated dienes, between dienes and trienes, between carbonyl compounds and α:β unsaturated carbonyl compounds.
- It also put light on the stereochemistry or geometrical isomers and enables us to distinguish between cis & trans isomers.
- The spectrum is obtained within 3-5 minutes and requires 0.1 g of the sample.
- UV absorption spectra arises from the transition of electron within a molecule or ions from a lower to higher energy level of the molecule or ion.
- **Both UV and visible spectra are caused by electronic excitation.**

- When a molecules absorb UV radiation of frequency (v), the electrons in that molecule may undergo transition from a lower to higher energy level, the energy difference between the two states is given by
- Delta E = hv
- $E_1$-$E_o$= h$\vartheta$ Etotal=Eelectronic+Evibrotional+Erotational The energies decreases in the following order: Electronic ⩾Vibrational ⩾ Rotational
- Thus the energy of the radiation in the visible range is generally: 36 to 72 kcal/mole while that in the ultraviolet range goes as high as 143 kcal/mole



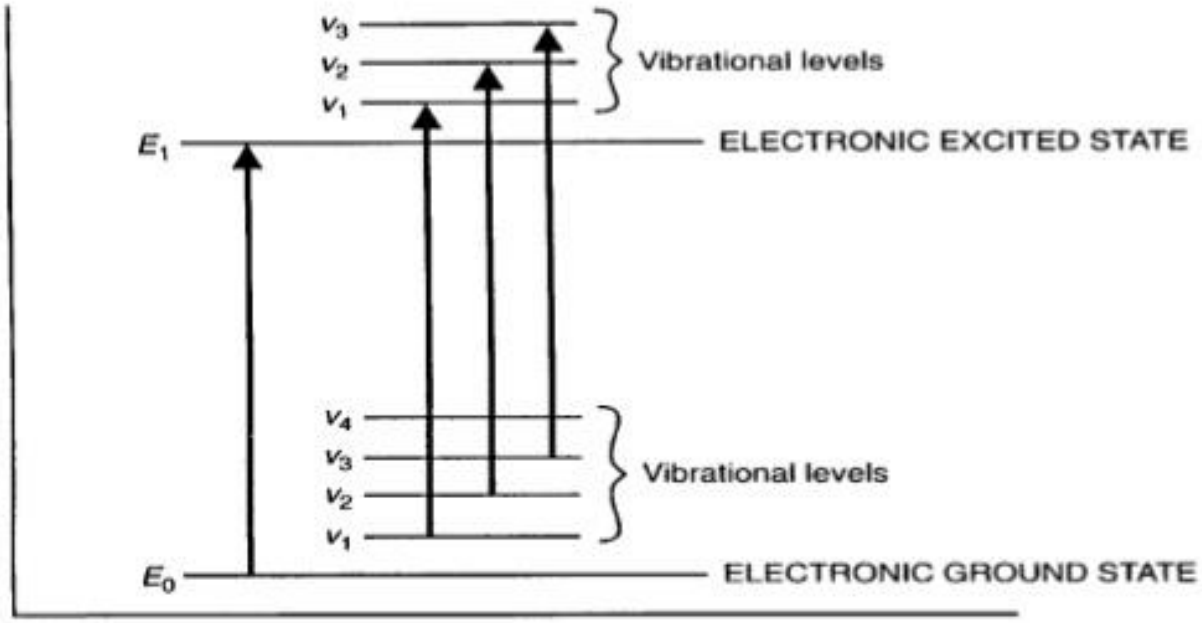

**Web Resource:** http://psychedelic-information-theory.com/em_spectrum

Portion below visible region is called as UV region. It has shorter wavelength than visible region. Portion above visible region is called as IR region has longer wavelength than visible region.

Absorption spectra :- During absorption some molecules (which are in path of light) get collided with photons of radiant energy. " Many photon molecules collisions take place but only in those where the energy of the photon exactly equals the difference ($\Delta E$) in energy between the ground state & excited state, then only molecule absorbs the energy $\Delta E = hc/\lambda$

Principle : By providing the sufficient energy in U.V. region e's get excited from ground state to excited state. The transmitted energy is passed through a device capable of resolving the beam into its constituent wavelengths & absorption gets recorded. The recorded graph is known as U.V. spectrum. The intensity of absorption is recorded by Beer - Lambert Law.

# CONTINUED




Thus the energy of the radiation in the visible range is generally: 36 to 72 kcal/mole while that in the ultraviolet range goes as high as 143 kcal/mole

# THE ABSORPTION SPECTRUM

When a sample is exposed to light energy that matches the energy difference between a possible electronic transition within the molecule, a fraction of the light energy would be absorbed by the molecule and the electrons would be promoted to the higher energy state orbital. A spectrometer records the degree of absorption by a sample at different wavelengths and the resulting plot of absorbance (A) versus wavelength (λ) is known as a spectrum.

The significant features:

- λmax (wavelength at which there is a maximum absorption)
- ϵmax (The intensity of maximum absorption)

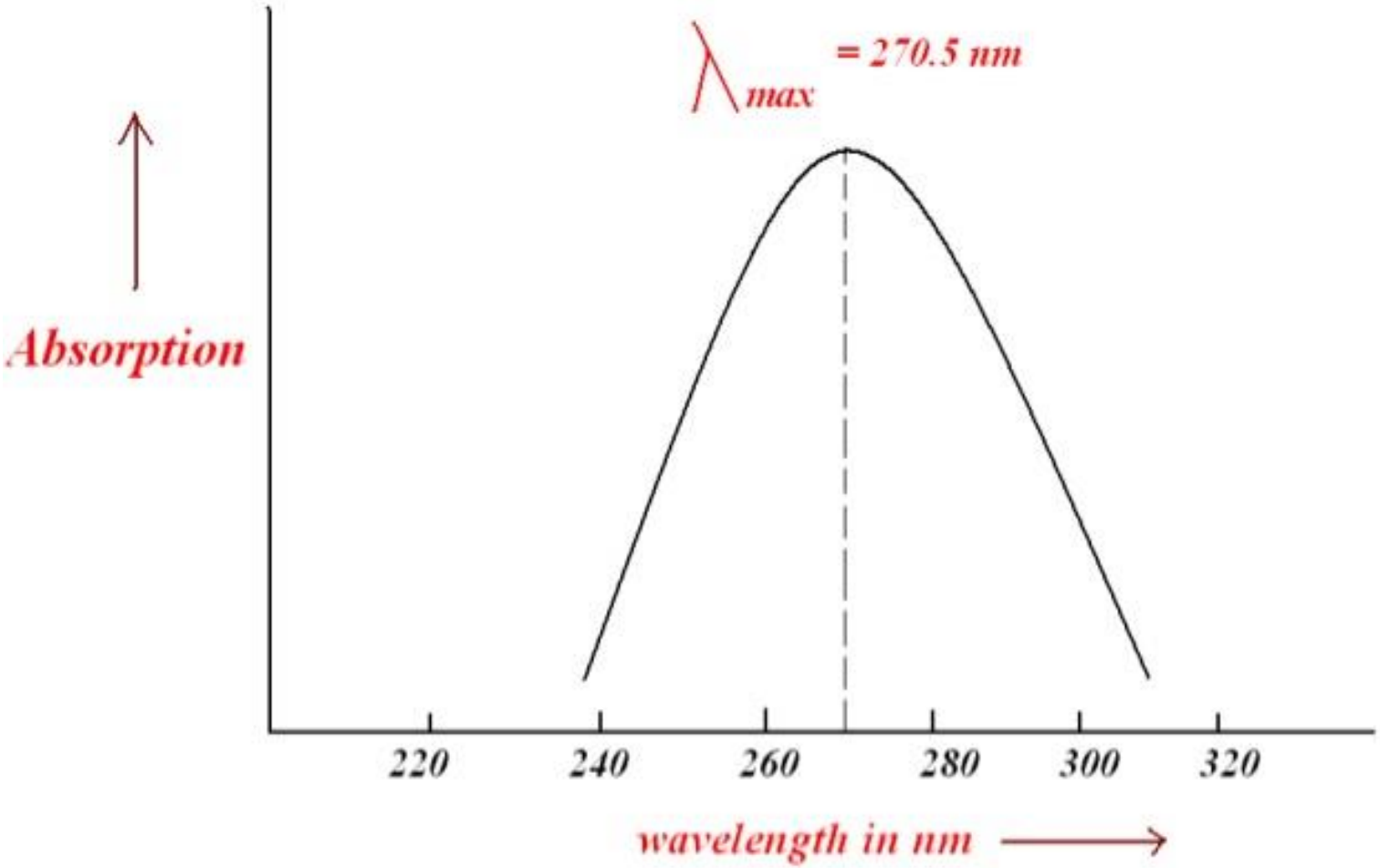



*fig:- UV spectrum of acetone*

# TYPES OF TRANSITIONS:

In U.V spectroscopy molecule undergo electronic transition involving σ, π and n electrons.

- Four types of electronic transition are possible.

i. $\sigma \rightarrow \sigma^*$ transition
ii. $n \rightarrow \sigma^*$ transition
iii. $n \rightarrow \pi^*$ transition
iv. $\pi \rightarrow \pi^*$ transition

# i. $\sigma \rightarrow \sigma^*$ Transition :

- An electron in a bonding $\sigma$ orbital of a molecule is excited to the corresponding anti-bonding orbital by the absorption of radiation.
- To induce a $\sigma \rightarrow \sigma^*$ transition it required LARGE ENERGY.
- Ex: Methane
- Methane contain only single C-H bonds it undergo only $\sigma \rightarrow \sigma^*$ transition only, it gives absorption maximum at 125nm.

# ii. n→ σ* transition :

In this type saturated compounds containing atoms with unshared electron pairs are undergo n → σ* transition.

It require less energy than the σ → σ* type.

Most of the absorption peaks appearing below 200nm.

In the presence of polar solvents the absorption maximum tend to shift shorter wavelength

Ex: Water , ethanol.

- In this the peaks in U.V region relatively small.

Ex: Methlychloried , Oxygen, Nitrogen.

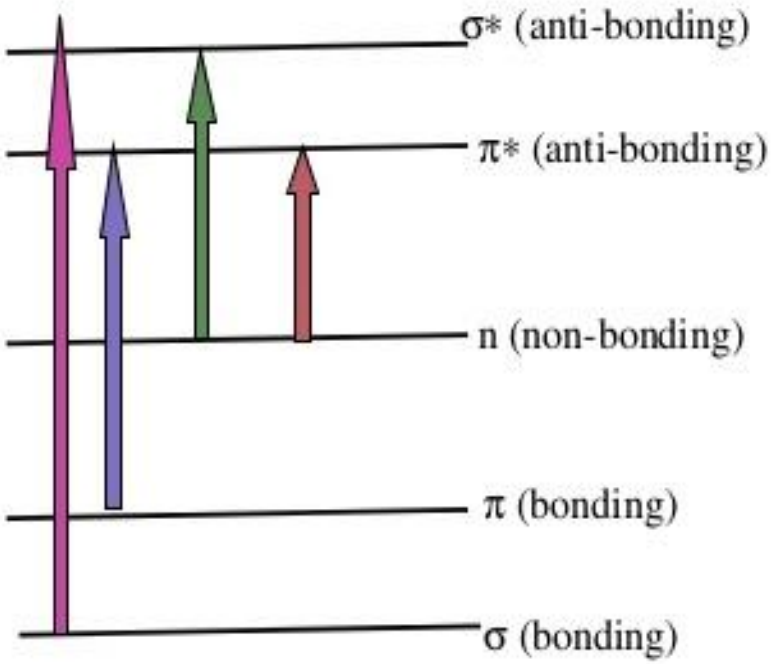
# iii n → π* & π → π* transitions

Most organic compounds are undergo transitions for n → π* and π → π* transition.

- Because energies required for processes bring the absorption peaks into spectral region.
- Both transition require the presence of an unsaturated functional group to the ´∏´ orbitals.

- Ex: For π → π* ⊩> Alkenes, carbonyl compounds, alkynes

- For n → π* ⊩> carbonyl compounds.




Four types of transitions

$\sigma \rightarrow \sigma^*$

$\pi \rightarrow \pi^*$

$n \rightarrow \sigma^*$

$n \rightarrow \pi^*$

# ABSORBANCE LAWS

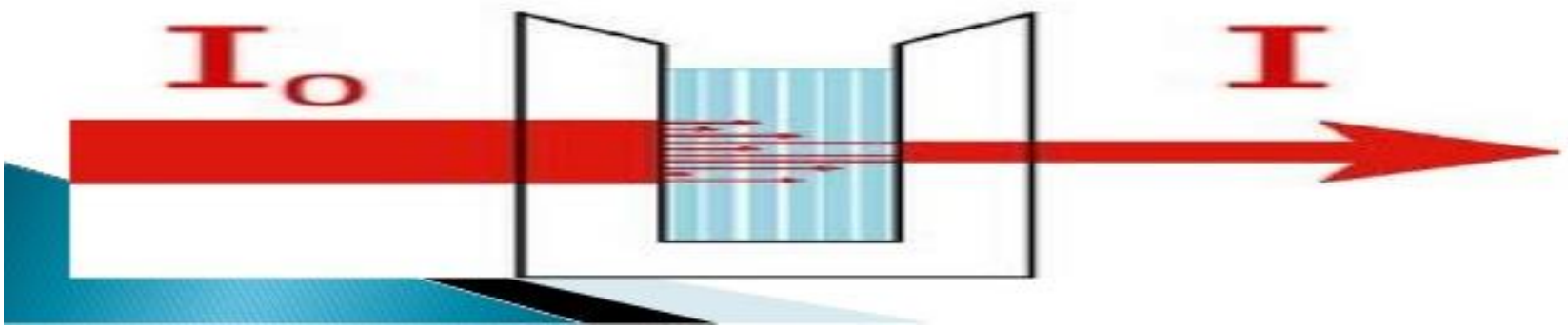
## BEER'S LAW

" The intensity of a beam of monochromatic light decrease exponentially with the increase in concentration of the absorbing substance" .

Arithmetically;

$$-dI/dc \propto I$$

$$I = I_o . e^{-kc} \text{ ----------eq (1)}$$



## LAMBERT'S LAW

" When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of the light"

mathematically;

$$-dI/dt \propto I$$

$$-\ln . I = kt+b \text{ ----------eq(2)}$$

the combination of eq 1 & 2 we will get

$$A = Kct$$

$$A = \varepsilon ct \qquad (K=\varepsilon)$$

# INSTRUMENTATION

Components of spectrophotometer

- Source
- Monochromator
- Sample compartment
- Detector
- Recorder

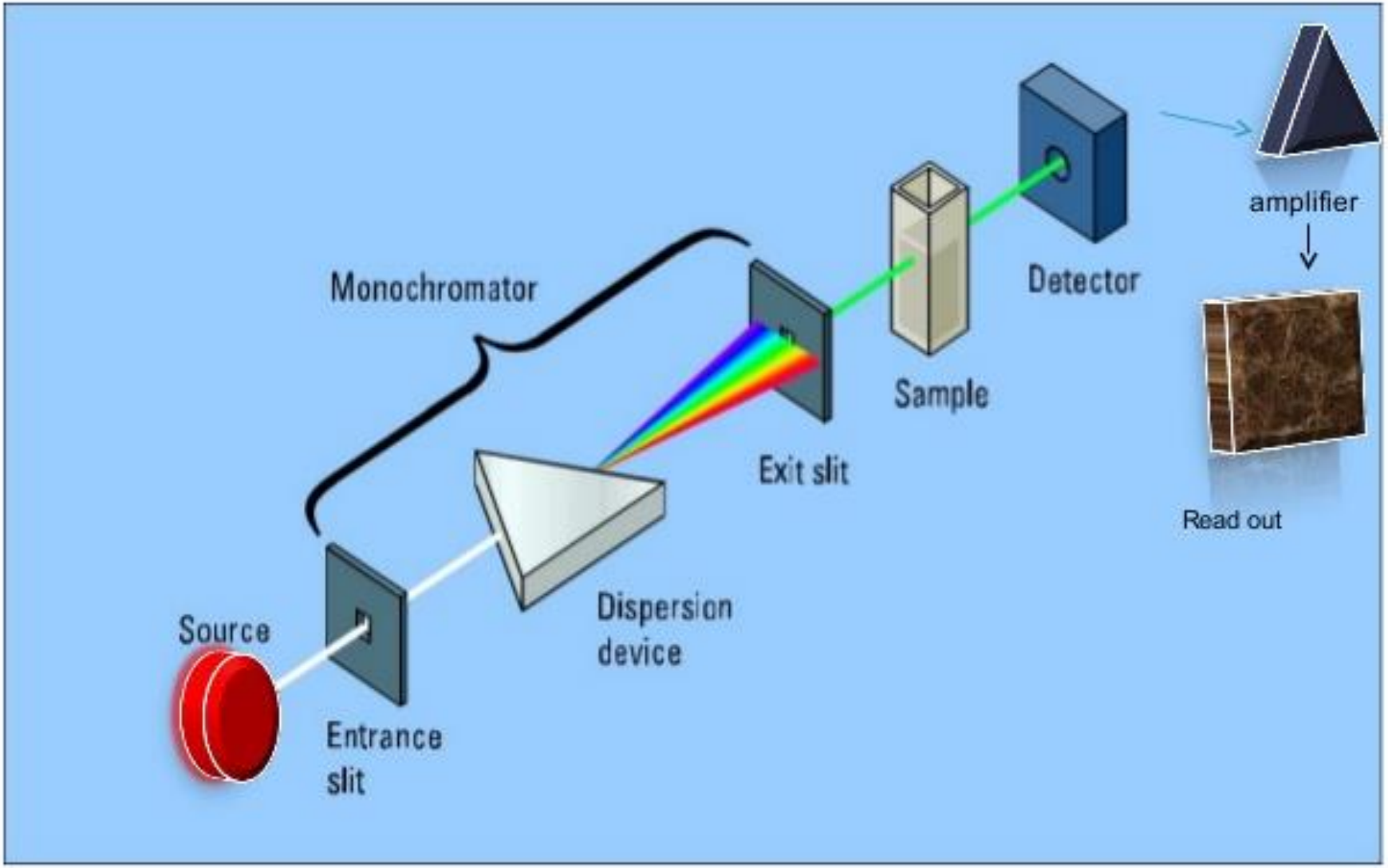



Fig: **block diagrammatic representation of UV-spectrophotometer**

# Terms Used in Ultra- Violet (UV) Spectroscopy

## CHROMOPHORE

- Any Functional group which is responsible for impairing colour to the compound is called as chromophore.

  Ex: $NO_2$

- Covalently unsaturated groups responsible for the impairing of the colures.

  Ex: C=C, C=O

- Two types of chromophore

  a) Independent chromophore

  b) dependent chromophore

# AUXOCHROME

It is the group which itself does not act as a chromophore but when attached to chromophore it shifts the absorption maximum towards longer wavelength along with an increase in intensity of adsorption.

Ex: -OH, -NH2, -OR groups

For example when the auxochrome –NH2 is attached to the benzene ring, it absorption changes from λmax 255 to 280nm.

TYPES

Two types

a. Bathochromic groups
b. Hypsochromic group

## BATHOCHROMIC GROUPS

Those groups which deepen the colour of chromogen are called bathochromic groups.

Deepening of colour means displacement to longer wavelength.

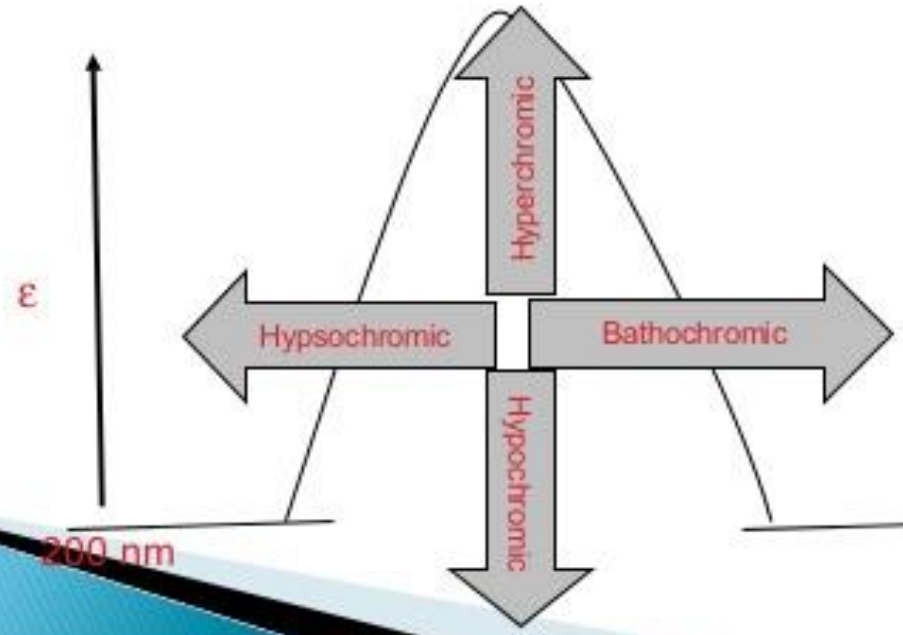
yellow→ orange → red → purple → violet→ blue → green

# HYPSOCHROMIC GROUPS

Those groups which diminish or lighten the colour of the chromogen are called hypsochromic groups.

- They cause displacement to shorter wavelength.

  Ex:- acetylation of –OH or –NH2 groups, -OCOCH3 and –NHCOCH3



# WOODWARD–FEISER RULE

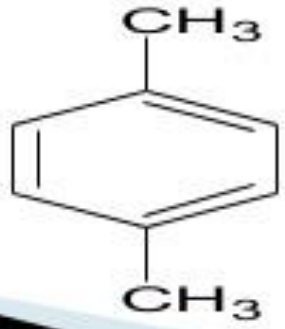
- It is used for calculating the absorption maxima
- Woodward (1941) gives certain rule for correlating λmax with the molecular structure

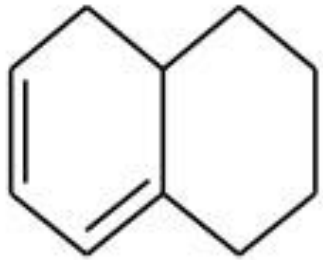
This rule for calculating λmax in conjugated dienes, trienes, polyenes.

- Homoannular dienes:-

  cyclic dienes having conjugated double bonds in the same ring.

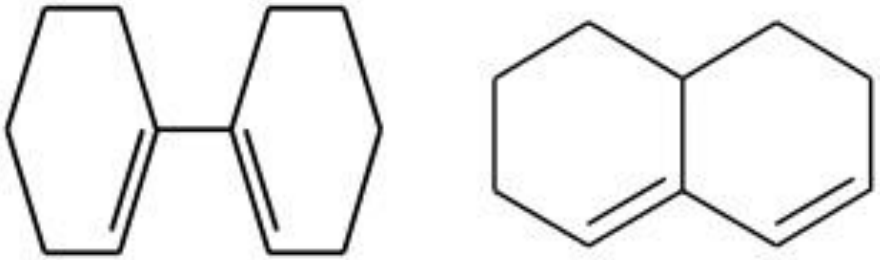
  e.g.



# CONTINUED

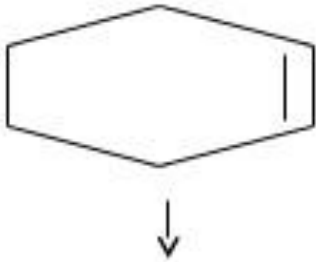
- Hateroannuler dienes



e.g. Heteroannuler dienes

- Endocyclic double bonds

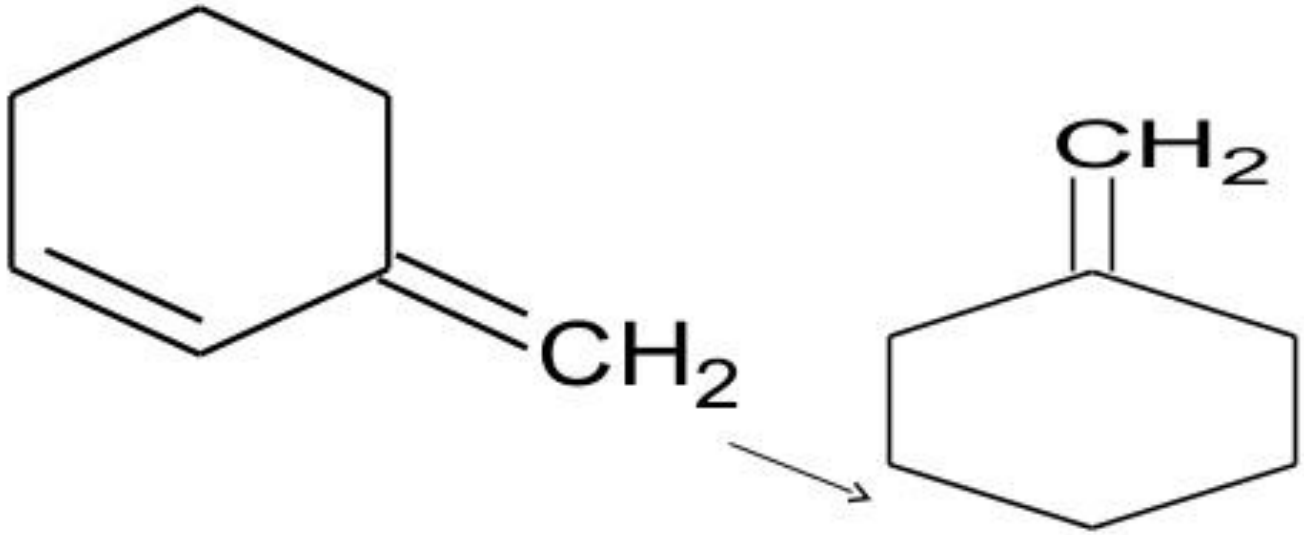
  it is the double bond present in ring as shown.



Endocyclic double bond

## Exocyclic double bonds

double bond in which one of the double bonded atom is the part of ring system.




Exocyclic double bond

# WOODWARD'S–FIESER RULE FOR CONJUGATED DIENES

- a)Parent values-

| | |
|---|---|
| 1. acyclic & Hateroannuler conjugated dienes | 215 nm |
| 2.Homoannular conjugated dienes | 253 nm |
| 3.Acyclic trienes | 245 nm |

- b)Increments-

| | |
|---|---|
| 1.Each alkyl substituent or ring residue | 5 nm |
| 2.Exocyclic double bond | 5 nm |
| 3.Double bond extending conjugation | 30 nm |
| 4.auxochromes- | |
| -OR | 6 nm |
| -SR | 30 nm |
| -Cl , Br | 5 nm |
| -NR2 | 60 nm |
| -OCOCH3 | 0 nm |

1,4- dimethyl cyclohex-1,3,-diene


Parent value for Homoannular dienes = 253 nm

| | | |
|---|---|---|
| Two alkyl substituent's | 2 × 5 | = 10 nm |
| Two ring residues | 2× 5 | = 10 nm |
| Calculated value | | = 273 nm |

Reference: https://www.slideshare.net/mariomS7/uvvis-spectroscopy#:~:text=Ultraviolet%20and%20visible%20(UV%2DVis,over%20an%20extended%20spectral%20range.