

SP2

## Analytical Chemistry

### Gas Chromatography

It is the technique used to separate different samples to analyze components.

OR

It is the technique used to separate the mixture between stationary phase and mobile phase.

The mobile phase is "gas", so this is also known as "gas chromatography." And the stationary phase may be liquid or solid.

Gas chromatography is also known as "Vapour Phase Chromatography" and "Gas-Liquid Partition Chromatography."

#### Instrumentation :-

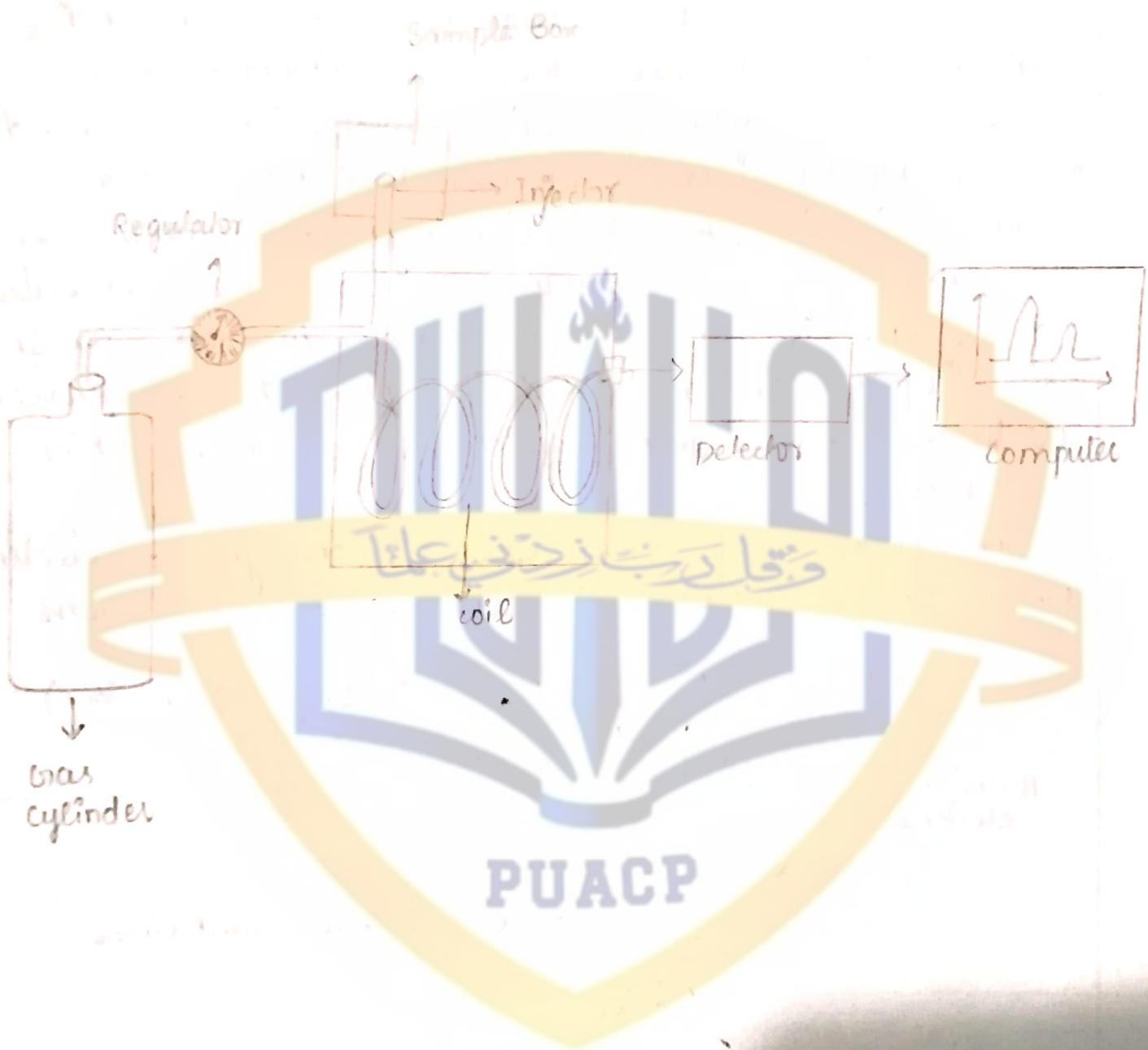
There are 4 components of gas

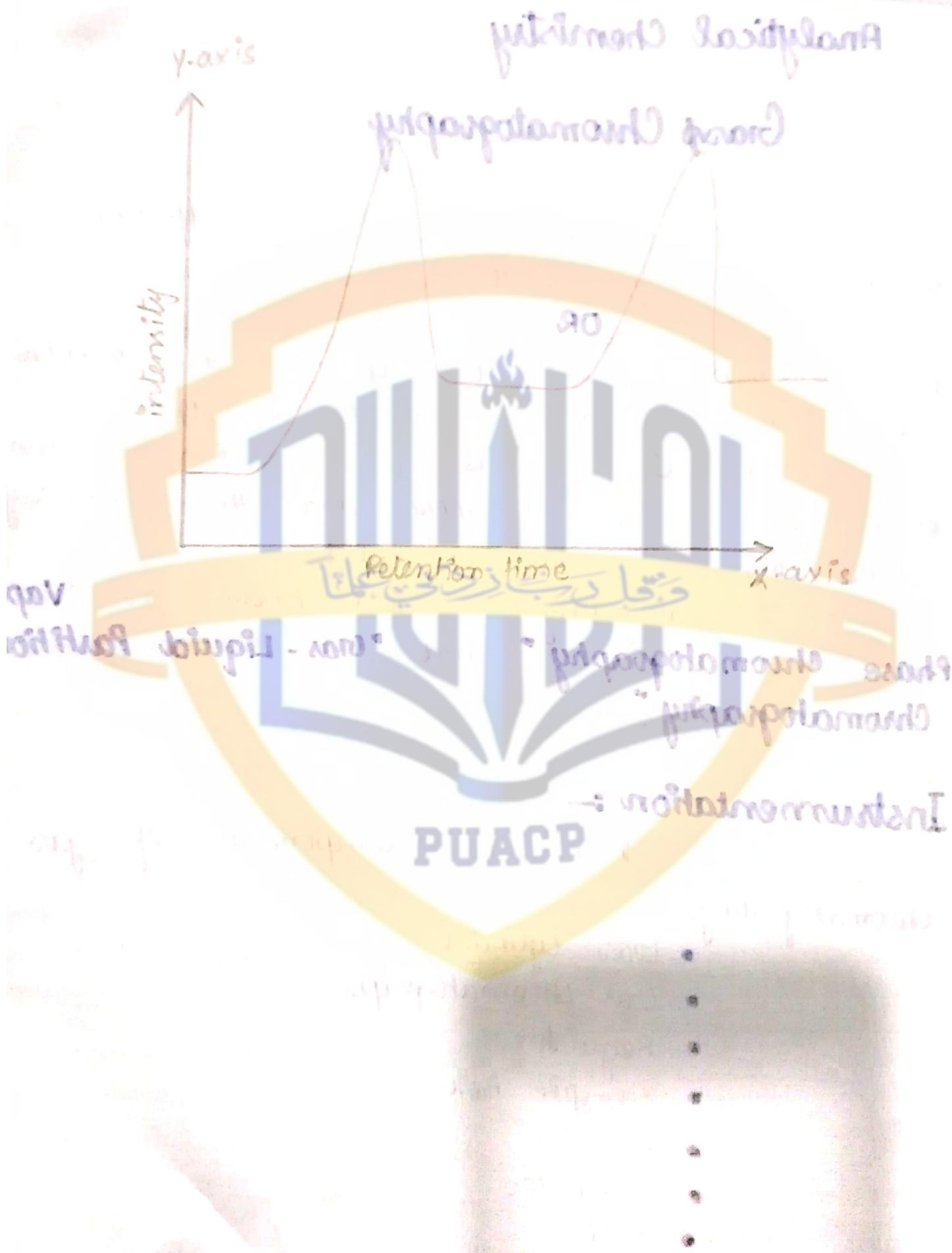
chromatography -

- Gas cylinder
- Gas chromatograph
- Regulator
- Sample Box
- Detector
- computer
- coil
- Injector

petroleum gas cylinder

Detector :-





The gas cylinder is fitted with regulator which is connected with gas chromatograph. A sample is injected before gas chromatograph. The coil present in the gas chromatograph is directly linked with detector, which detect the signals and show the result on the computer.

### Working :-

The gas present in the sample cylinder uses as mobile phase and use that gas which do not react with sample.

The 'Helium' gas is mostly used here because of its inert nature, it does not react with other species or substances.

The sample is used in the form of gas. If it is the sample of liquid, it should be converted into gas and its activity remain same. As the gas is passed and regulator control the flow rate of gas. The sample is introduced through injector. Its temperature must be high as if liquid sample injected in it due to temperature it converts into gas sample and inert gas all mix with another and passed through column which is coil shape and made up of stainless steel or glass. Its length is about (15 - 30m). The stationary

phase inside the column can either be liquid or solid.

If the stationary phase is liquid than this chromatography is known as "gas-Liquid chromatography". If the stationary phase is solid then it is known as "gas-solid chromatography".

A liquid should be used which have High Boiling Point because the high temperature stabilize the stationary phase which have high rate of Boiling point. Silicon grease is in liquid form and use in Labs as stationary phase. As the mixture moves through the oil in which silicon gel present. The molecules of mixture moves fast which have low boiling point and when move towards the detector or elute high boiling molecules through over. The detector detects the signals and send them to computer and the first peak show on computer will be choose boiling point is low. The high boiling molecules move slowly, they will reach the detector later. The second peak is probably of those molecules whose B.P. is high. The purification happening due to increase B.P. molecules. The temperature of oven increases Max.  $300^{\circ}\text{C}$  for the solution of molecules fast.

Sample

Vapour  
Head

Ionization  
chamber

Electron  
gun

Detector

PUACP

which is known as • Temperature Programming  
Small size molecules move first and large size  
molecules later.

[mass spectrometer detector]

**Detector:** Mass Spectrometry is used as detector so it is known as mass spectrometry or gas chromatography. A sample is injected into vapour box in which sample vaporizes and uses electron gun and then passes through ionization chamber which then converted into magnet which have North and South pole. The molecules fall onto the detector and detect the sample shows the result on the computer.

# Ch 1 Analytical Chemistry

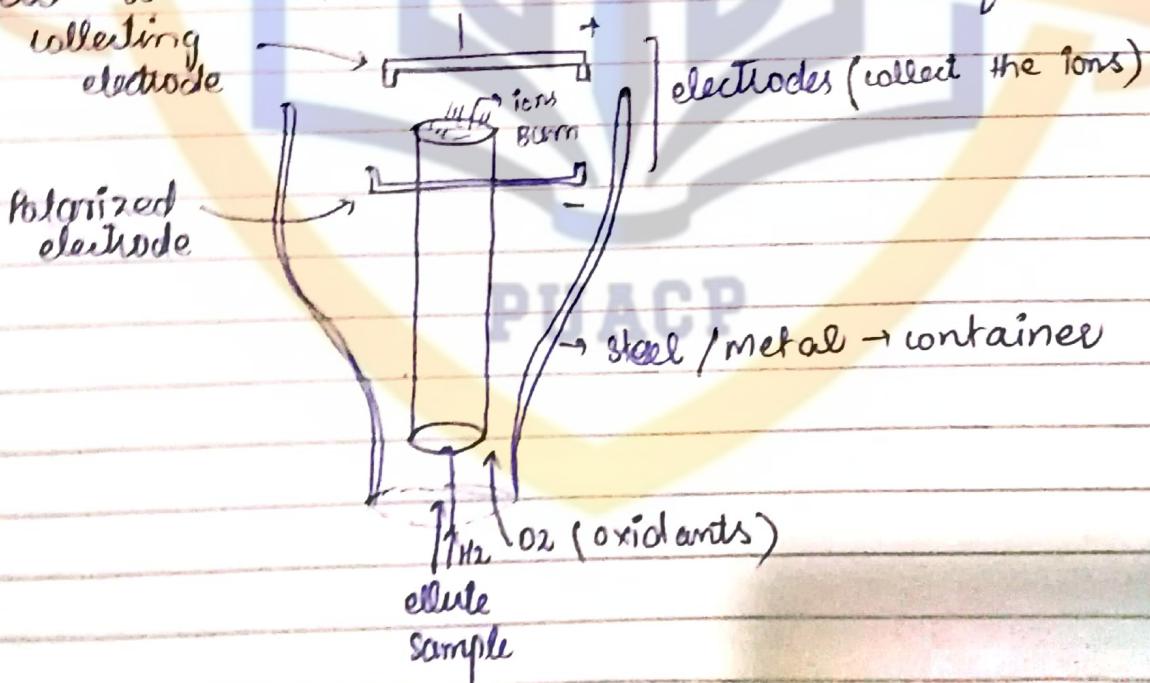
## Detectors:-

(by detect ions & burn jib.)

### (1) Flame ionization Detector (FID):-

This detector is only used for organic compounds when they are obtained from GCS in the form of elute. combustion is carried out by hydrogen gas which gives blue flame with oxidants (like  $O_2$ , Air) the burning of organic elute gives ions  $Q$  that compound so the concentration of sample is directly proportional to ions. as shown in diagram electric field is provided in between electrodes and specific field is obtained which is known.

The presence of ions creates a change of electrical field which shows the concentration of ions

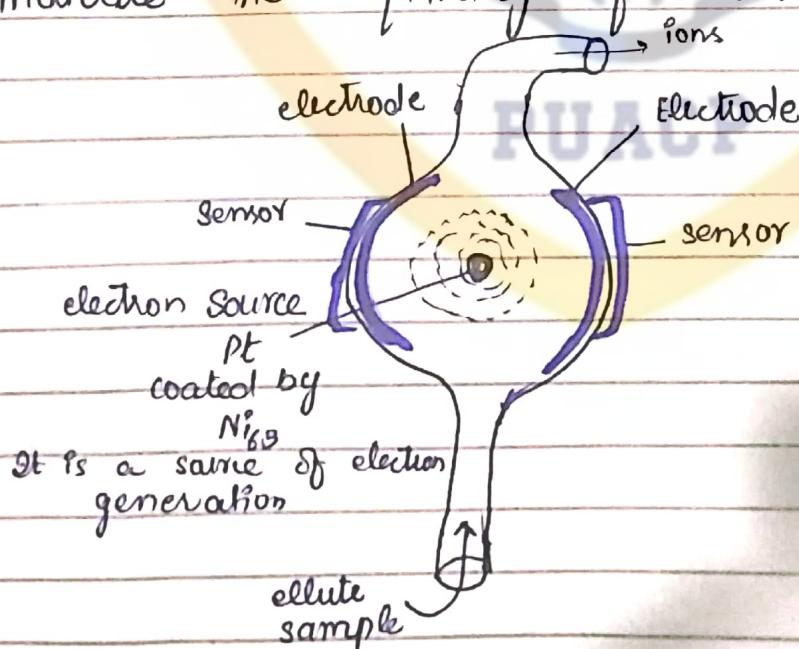


Sp?

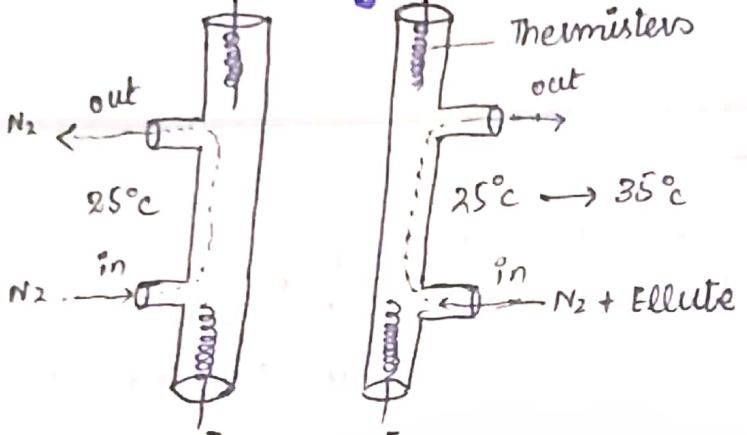
## Analytical Chemistry :-

### Electron Captured Detector, - [ECD]

This device is used for the detection of molecules and atoms especially halogens. In this detector molecules and atoms are converted into ions and this process carried out by generating electrons. In the middle of this detector, an electron generator is made by platinum wire which is coated by  $Ni_{63}$ . A particular number of electrons are present in this portion. When elute sample is entered in this regions these electrons are captured by atoms, molecules of elute sample and get the shape of ions. They are collecting on electrodes. Difference of electron in begining and end of this process indicate the quantity of atoms and molecules.



## Thermal Conductivity detector :- [TCD]



⇒ when  $N_2$  is only present in tube, there is the same current

⇒ whenever, you add elute, there is variance in temperature and thermal conducting.

⇒ Structure is resemble with wheat stone bridge.

In this detector, change in thermal conductivity of carrier gas is measured by thermistor, whereas thermistors is a small lid prepared by fused oxides of metals (such as  $FeO$ ,  $CuO$ ).

Carrier gas is  $He$ ,  $H_2$ ,  $N_2$ . Helium is costly, Hydrogen is dangerous so nitrogen is preferred but the sensitivity reduces as compared to  $H_2$ ,  $He$ . In this detector, two pairs of matched thermistors from the wheat stone bridge circuit are arranged.

carrier gas is passed in one pair reference while a mixture of carrier gas and <sup>column</sup> elute is passed in other reference. When pure gas passes in both pair bridge, there will be no change of thermal conductivity. When mixture of carrier gas and elute is passed in one pair and other is pure then bridge is unbalanced because of unequal cooling (temperature) of the two thermistors. This unbalanced extent of temperature is recorded.

## Derivatization:-

During Gas Chromatography, when sample is heated and convert into vapours and we know these components must be thermally stable.

There are some functional groups which create problems in G.C process due to their Hydrogen Bonding. e.g.  $-\text{NH}_2$ ,  $-\text{NH}$ ,  $-\text{HS}$ ,  $-\overset{\text{R}}{\text{C}}-\text{O}$ ,  $-\text{OH}$ .

So, they need to be derivatized which can be defined as "It is a such process in which a compound is chemically modified so Hydrogen is replaced by other groups but there are some conditions:

- 1- No change in structure
- 2- Must be effective for G.C
- 3- Only the modification in functional groups

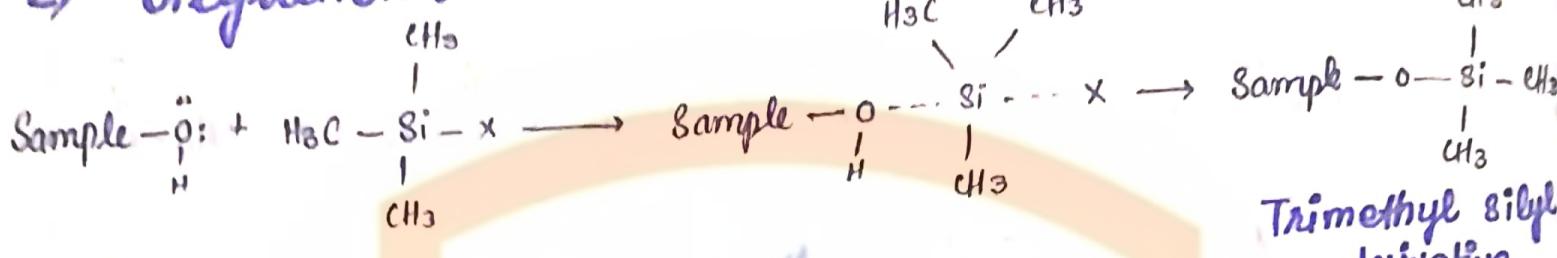
- This technique is also used in HPLC, UV-visible spectroscopy so basic principle is to increase volatility of above mention polar groups by removing them.
- To increase the stability
- To decrease the absorption in stationary phase.

# Types of Derivitization-

- 1- Silylation
- 2- Alkylation
- 3- Acylation
- 4- Chiral

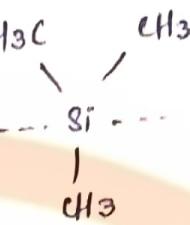
*(Si molecule is used)*

⇒ **Silylation :-**



*(intermediate state)*

$\text{H}_3\text{C}$        $\text{CH}_3$



*Acid*

+ HX

$\text{CH}_3$

|

$\text{CH}_3$

|

$\text{CH}_3$

Trimethyl silyl derivative

This derivative become more volatile, more stable after the replacement of Hydrogen. Its reactivity with different functional groups is different and order can be represented as:

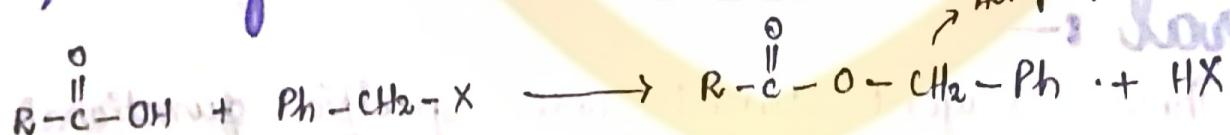
Alcohol > Phenol > carbonyl > Amine > Amide/Hydroxyl

**Disadvantage of Silylation :-**

1- They have ability to absorb moisture which is not for our experiment. It is only used (only those solvents) which are "apatic" means which have less Hydrogen atom.

⇒ **Alkylation :-**

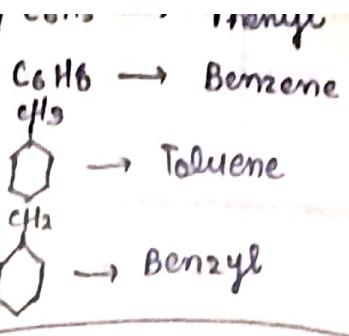
PUACP



*Alkyl group*

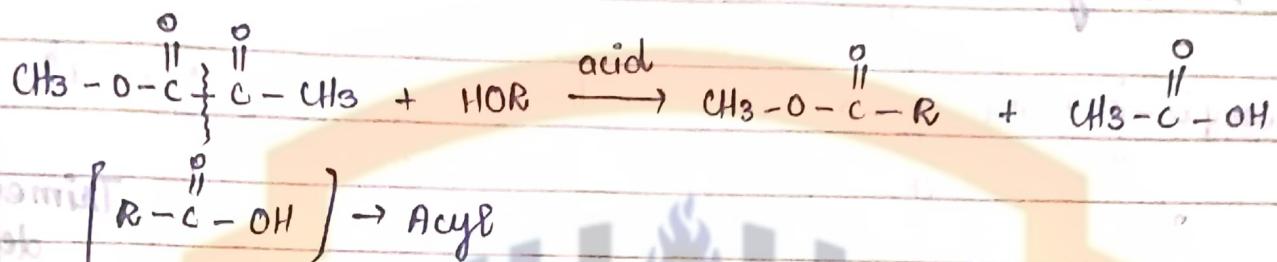
Alkylation means replacement of hydrogen present in a sample by alkyl group.

It reduces molecular polarity as in a reaction. Hydrogen of carboxylic group which is active hydrogen is replaced by



a benzyl group.

⇒ **Acylation** :— Substitution of Acetyl group ( $\text{CH}_3-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{CH}_3$ )



It Reduces the polarity of amine, hydroxyl and thiol (HS). Its reagent targeted to highly polar functional compounds such as carbohydrates, amines, for example, in following reaction in which hydroxyl group is targeted.

#### Advantages:-

- Addition of Halogenated carbon increases.
- Durability (strength) and derivative becomes hydrolytically stable

⇒ **Chiral** :-

These reagent target once specific functional group and produce individual stereoisomers of each enantiomers.

These enantiomers can be separated by an optically active stationary phase

For example:- Reagents which are used like

M- N-trifluoro acetyl (TFA)

L- Propyl chloride (TPC)

Methyl chloroformate

- Stationary Phase is optically active in column
- Additional compound react with the one component of enantiomer and then easily separate the substances.

## Column Of G.C.

According to  
Diameter

There are three types of columns of G.C.

U-shaped



W-shaped



coil shaped



• Packed column

• Capillary Tube

The shapes of the columns are classified into three types.

→ Material with which this column is prepared basically, the material which is used for the preparation of column must be inert for sample and gas. that may be copper, Aluminium, Glass, Stainless Steel(alloy).

### Classification on the basis of their Diameter :-

① Packed column

② Capillary column

## Formation of Packed column:-

The diameter of this tube which is used in column have  $2 - 10 \text{ mm}^{\text{m}}$  and length is  $1\text{m} - 4\text{m}$ .

Stationary Phase is mixed with supporting material like gel after heating this material is packed.

Packed

column  $\rightarrow$



stationary Phase

supporting  
material

## Advantages:-

Sample Holding capacity is best but the resolution are not so good.

## Capillary Column:-

The diameter of this capillary column is  $0.2 - 0.5 \text{ mm}$  and length is normally  $20\text{m} - 80\text{m}$  and can be extended up to  $1\text{km}$ . The material which is packed in this capillary tube is entered at higher temperature that is  $150 - 300^\circ\text{C}$ .

The efficiency of this column is good as compared to packed column.

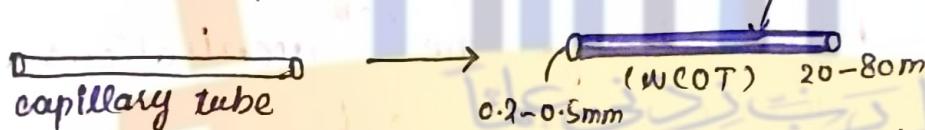
capillary  
column

# Classification of capillary column:-

- 1- Wall coated open Tubular column (WCOT)
- 2- Support coated open Tubular column (SCOT)
- 3- Porous Layer Open Tubular column (PLOT)

## 1- WCOT :-

This column is used for only G.L.C. In this case stationary phase is a liquid in capillary tube and it sticks with the walls of capillary tube and a small hole is left for entering gas and sample mixture as a mobile phase and its shape is just like-



## 2- SCOT :-

It is also used for G.L.C. In this case Liquid is also stationary phase but that liquid is supported by a solid material means a solid material is dipped in liquid and then that material is packed in this capillary tube.

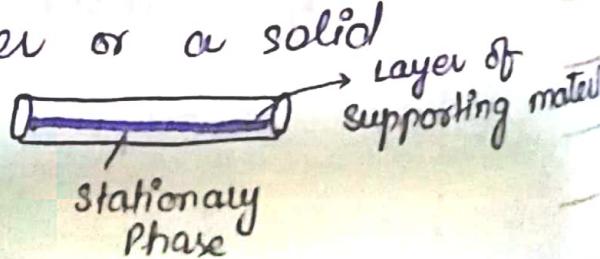


## 3- PLOT :-

This type of capillary tube is used for G.C. In this case, stationary phase is a solid which is again mixed with another solid which is basically support but produce a solid layer or a solid e.g. CHALK + TALCUM POWDER

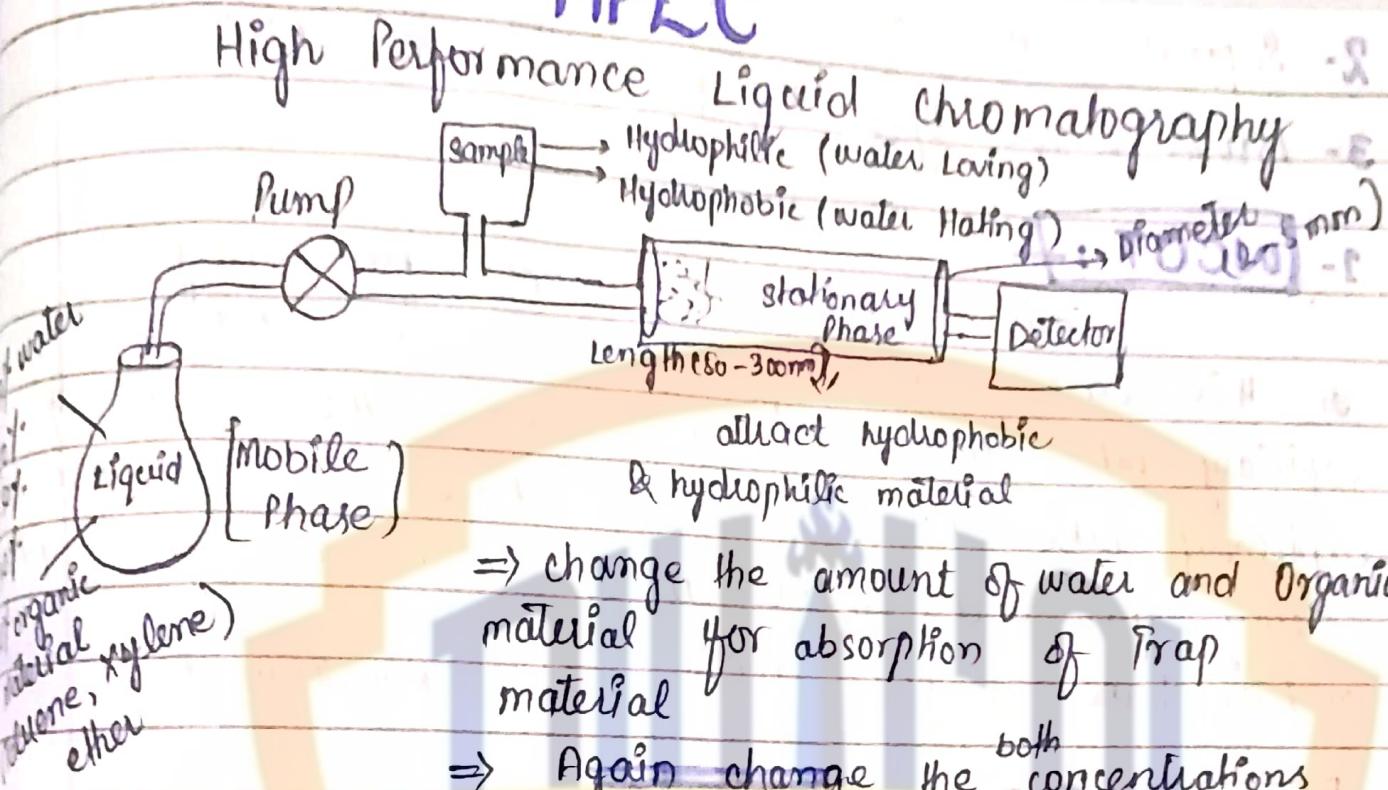
↓  
stationary  
Phase

↓  
supporting  
material



## Chapter No. 02

### HPLC



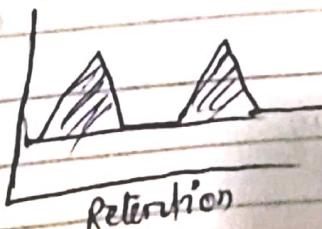
⇒ Separation is done due to dependence on a hydrophobic and Hydrophilic nature of substance.

• Buffer → Neutral

⇒ Equalizing system → straight line graph



⇒ By changing concentrations → different peaks of substances present in sample



## HPLC :-

This instrument is used to separate the components or to purify the components and give the proper quantity of components. Resolution is very good and the separation of the components is due to the polarity tendency to like or dislike water. As we know, **Hydrophilic** (if molecule is polar, it's like water) this property is hydrophilic.

**Hydrophobic** (if molecule is non-polar it's dislike water)

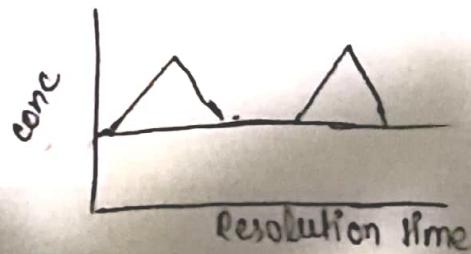
### Components :-

(1) **Stationary Phase** :- Stationary Phase is filled in a steel tube, length is (50-300 mm) and diameter is (2-5 mm). Solid adsorbent material is packed like silica gel. If it is coated by water, then it shows hydrophilic properties and can be modified by adding carbon-18.

(2) **Sample** :- Sample may contain hydrophilic and hydrophobic substances for example : Blood sample or bacterial components

(3) **Mobile Phase** :- It is a liquid solution having different percentage of water and organic solvents e.g. mixture contain 80% water and 20% organic solvent then Mobile phase is hydrophilic. By changing the concentration means concentration gradient different components present in sample can be separated through stationary phase.

- if sample contain hydrophobic & hydrophilic, then only hydrophilic will mixed with mobile phase.
- if it contains excess water, hydrophilic will stay in stationary phase due to the liking of water and only hydrophobic substances come out and get a peak of resolution time and concentration graph.



e.g., first peak shows hydrophobic concentration and after some period, the new peak shows the hydrophilic concentration.

Before, these peaks, first a straight line graph is obtained which is called "Equilibrate" the system when only buffer is passed as with no sample

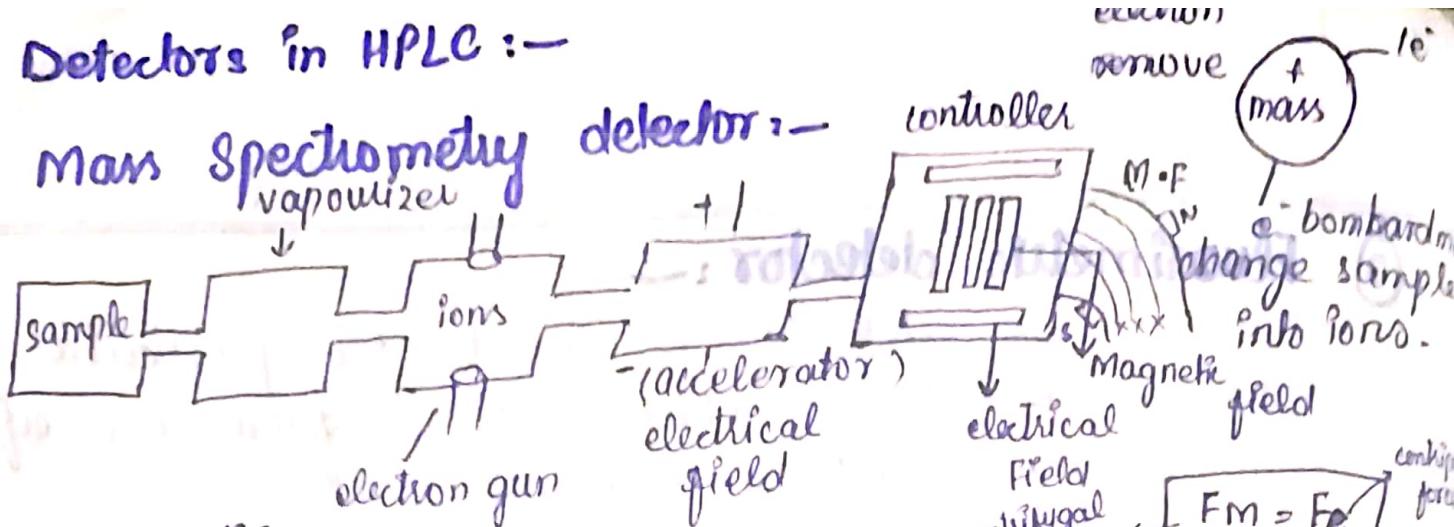
## Types of HPLC :-

There are four types of HPLC

- (1) General HPLC (In this case, stationary phase is a polar silica gel by absorbing moisture)
- (2) Reverse Phase HPLC (In this case stationary phase is non-polar having silica gel modified by C<sub>18</sub> and becomes hydrophobic.)
- (3) Filter<sup>ation</sup> HPLC (In this case, stationary phase is porous having pores and different size of molecules moved and trapped in pores and show different affinity.)
- (4) Affinity HPLC (In this case, stationary phase contains positive charged particles and mobile phase move in these charges).

## Detectors in HPLC :-

### ① Mass Spectrometry detector:-



• speed of particles must be same when passing through M·F

$$F_c = q \cdot E$$

- $q$  = charge
- $E$  = electrical field

$$F_m = F_c$$

$$q \cdot v \cdot B = \frac{mv^2}{r}$$

$$q \cdot B = \frac{mv}{r}$$

$$r = \frac{mv}{qB}$$



$$\text{Refractive index} = \frac{i}{n}$$

### ② Refractive Index Detector:-

With As you know, Refractive index is a ration between  $\sin i$  and  $\sin r$ . If we determine the refractive index of different substance. Each and every substances has its own value. and when different substances are obtained from outlet of stationary phase of HPLC they will show different values of refractive index of sample substances which can be compared with standards.

-: 0.59V at electrode

-: whole polarization min ①

### ③ Fluorimetric detector:-

This detector is used for particular those substances which shows fluorescence after absorbing light or radiation.

The nature of emitting fluorescence from a sample determine the nature of compound

### ④ Electrical Conductivity Detector:-

The base of this detector is the flow of electricity is directly proportional to the concentration of ions. It is used when cations and anions are present in sample.

### ⑤ Amperometric Detector:-

It works on the basis of reducing and oxidizing properties of the sample and the potential is applied as the concentration of sample increases and diffusion current also increase. For example : If you determine the concentration of  $\text{Fe}^{+2}$ , we can determine it because it will change into  $\text{Fe}^{+3}$ .

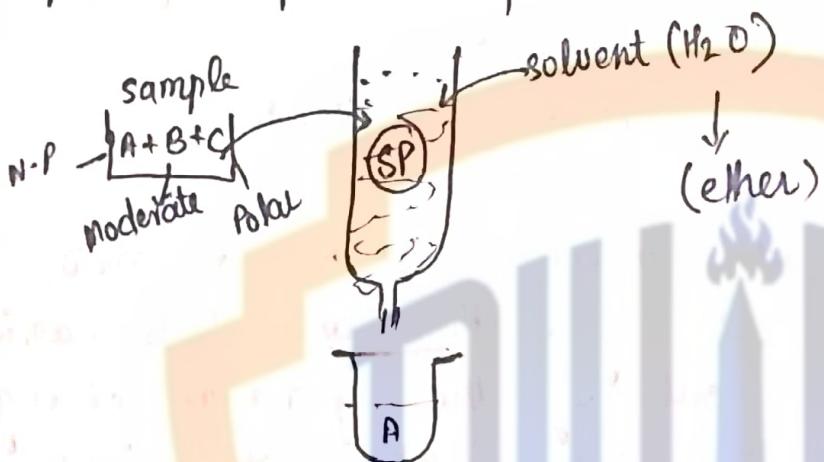


due to this, potential will also change.

## Gradierd Elution in HPLC :-

### Isocratic Elution

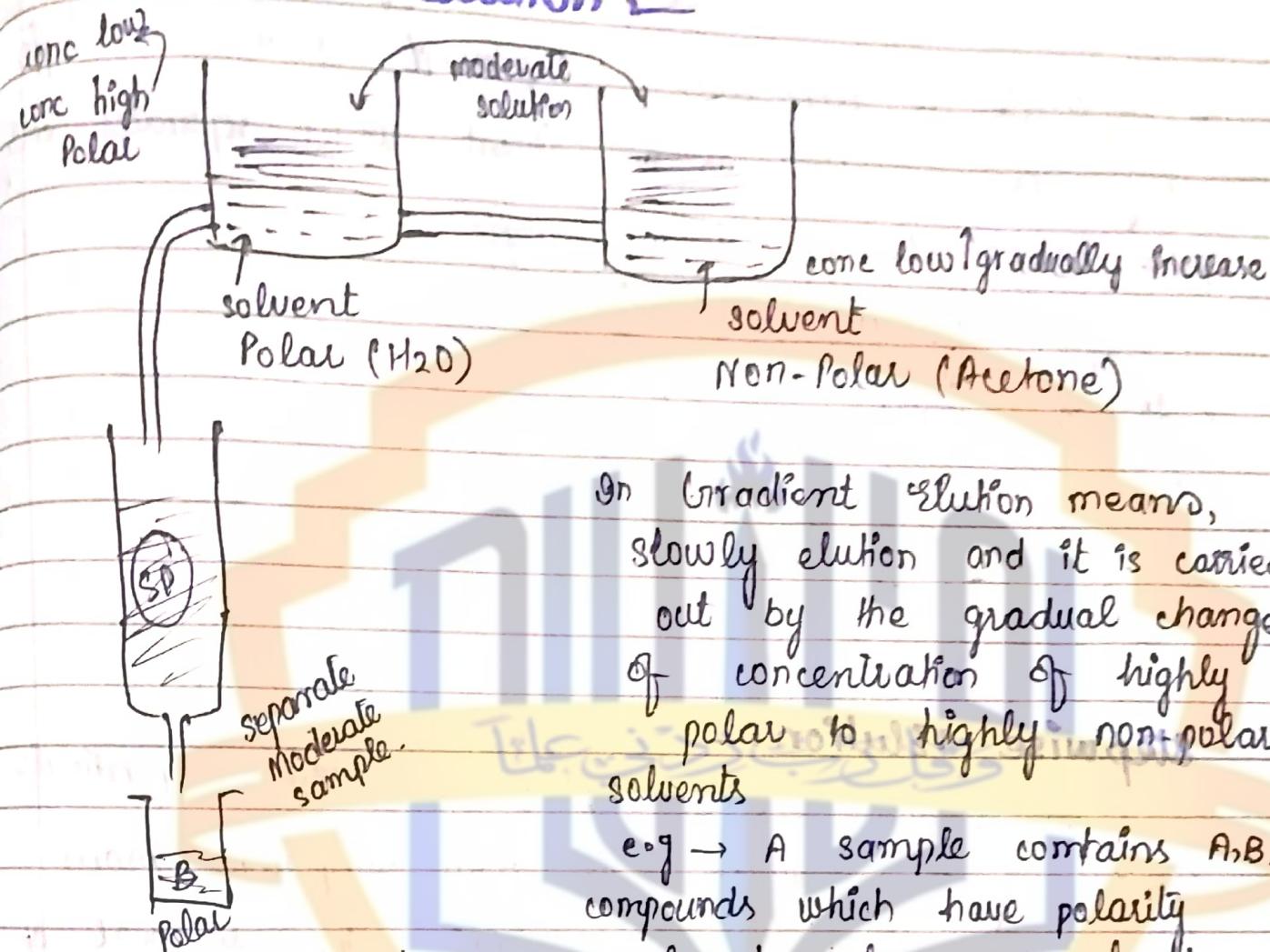
In Isocratic elution, we use a single type of solvent to separate a particular component from a sample e.g. → use  $\text{H}_2\text{O}$  as a solvent which separates only polar components present in sample.



### Stepwise Elution :-

In Stepwise elution, first we used a particular solvent say ( $\text{H}_2\text{O}$ ) which elute polar component from sample through stationary phase. After the removal of a compound, then we take another solvent like ether which is non-polar which will separate non-polar components present in sample through stationary phase. similarly, we use another solvent to separate other compounds which is called stepwise elution.

## Gradient Elution



In Gradient elution means, slowly elution and it is carried out by the gradual change of concentration of highly polar to highly non-polar solvents.

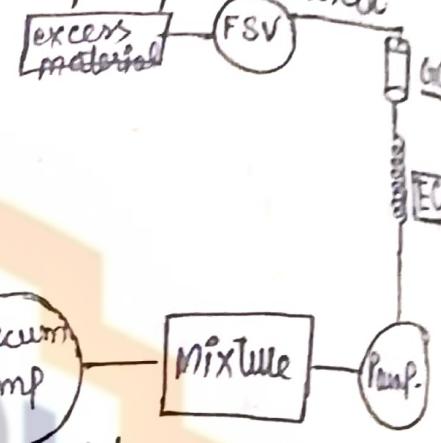
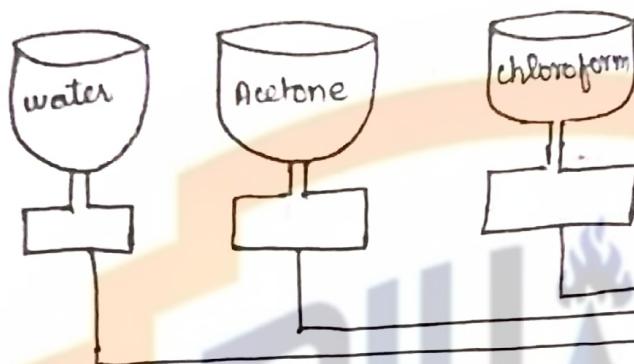
e.g. → A sample contains A, B, C compounds which have polarity from non-polar to polar. A solvent

which is highly polar and other solvent which is highly non-polar like acetone are connected through a small whole tube and then this solvent is entered in HPLC column. Slowly, the concentration of solvents change which separates all the components gradually through stationary phase

# Mobile Phase Delivery System :-

In Mobile Phase delivery system, different solvents like water, acetone, chloroform are taken in separate containers.

From each container, gases [dissolve gases] are removed by degasser in which vacuum pump is used.

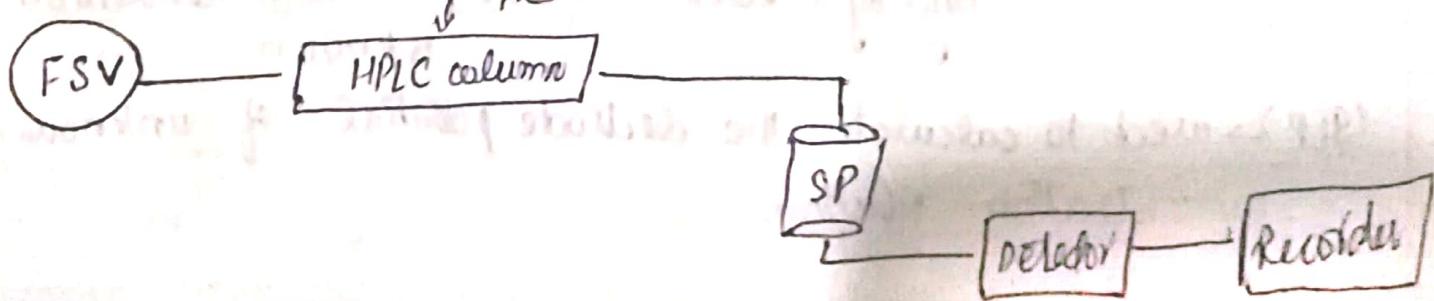


Then these <sup>almost</sup> pure gases are entered in a mixture.

After getting a mixture, this mixture is introduced in equilibrium column. This equilibrium column provides a chance to get equal and uniform concentration of all the solvents.

In Guard column, if any impurity is present that is removed like  $N_2$ ,  $O_2$ , and vapours. Then this solution is introduced in <sup>flow</sup> splitting value.

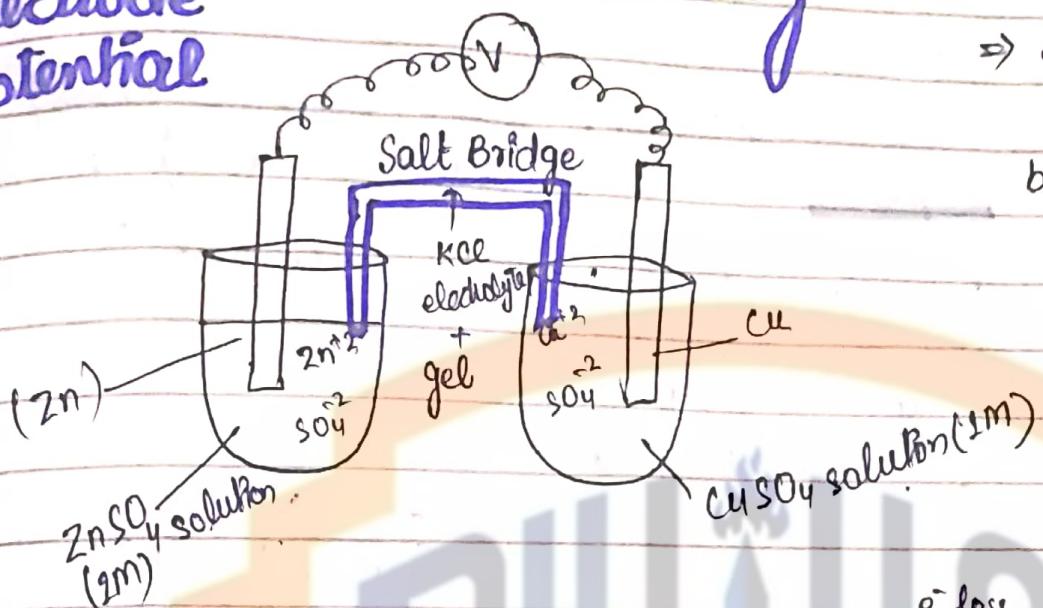
Flow splitting value is actually split or separate <sup>excess</sup> solvent which is not in our use during HPLC chromatography. Now this solvent is entered in a such compartment which contains sample.



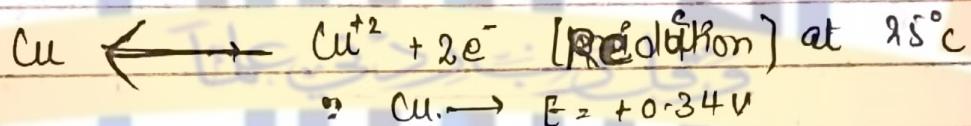
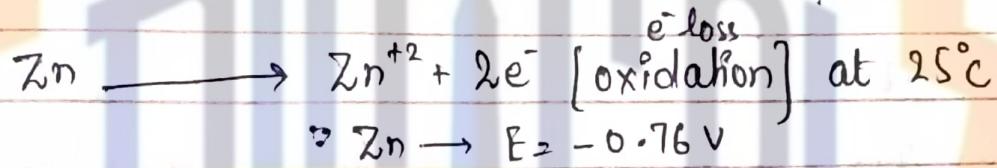
Ch # 3

# Potentiometry

## Electrode Potential

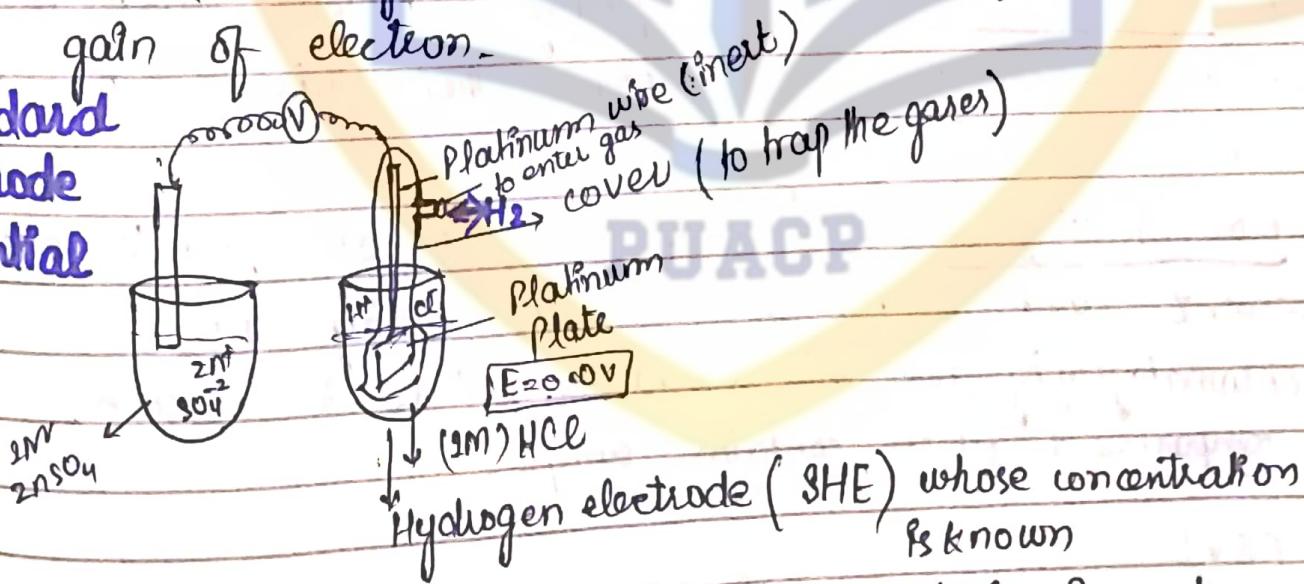


⇒ Salt Bridge  
is used to  
balance the  
solution

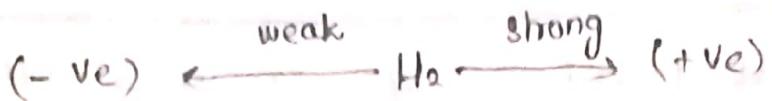
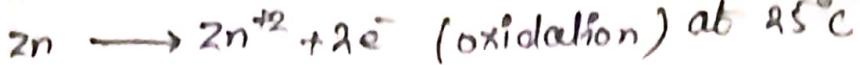


Here (-ve) sign shows the direction of loss or gain of electron.

## Standard Electrode Potential



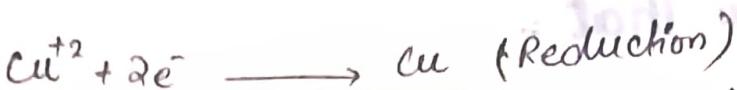
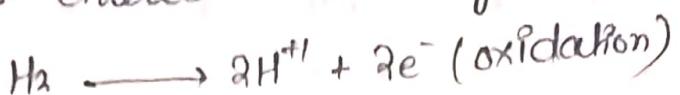
(SEEP) → used to calculate the electrode potential of unknown concentration solution.



$$E = 0.46V$$

$$E_{red} = 0.0V$$

when  $H_2$  is entered in the system, cell is working start



is used to calculate cell potential of any type  
of cell having different electrodes.

The conc of all the  
solids are always  
 $(+\text{ve}) \rightarrow 1$   
solids are always  
constant

### Nernst Equation :-

$$E_{cell} = E^\circ - \frac{RT}{nF} \ln Q$$
$$= - \frac{8.313 \times 298}{n \times 96500} (2.303) \log Q$$

$$E_{cell} = E^\circ = \frac{0.0591}{n} \log Q$$

$$E^\circ = 1.10V$$

$$E_{cell} = E_{oxi} + E_{red}$$

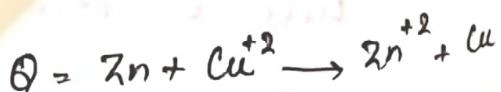
$$E_{cell} = 1.10 - \frac{8.31 \times 298}{2 \times 96500} \ln \frac{[Zn^{+2}][Cu]}{[Zn][Cu^{+2}]}$$

$$= 1.10 - \frac{8.31 \times 298}{2 \times 96500} \ln \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

$$= 1.10 - \frac{8.31 \times 298}{2 \times 96500} \times 2.303 \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

$$E_{cell} = 1.10$$

$$Q = K_c = \frac{P}{R}$$



$$Q = \frac{[Zn^{+2}][Cu]}{[Zn][Cu^{+2}]}$$

example:-

calculate the cell potential of Zn and Cu and the concentration of  $Zn^{+2}$  is 0.5M and the concentration of  $Cu^{+2}$  is 0.05M at 1 atm and 298K whereas standard potential is 1.10V.

As we know that :-

$$E_{cell} = E^{\circ} - \frac{0.0591}{n} \log Q$$

Q is  $K_c$  of Zn, Cu reaction



$$Q = \frac{[Zn^{+2}][Cu]}{[Zn][Cu^{+2}]} \Rightarrow \log 10 = 1$$

∴ Zn, Cu are constant = 1

$$Q = \frac{[Zn^{+2}]}{[Cu^{+2}]} , Q = \frac{0.5}{0.05} = 10$$

$$E_{cell} = 1.10 - \frac{0.0591}{2} \times \log 10$$

$$E_{cell} = 1.10 = -0.02955 \times 1$$

$$E_{cell} = 1.07045 V$$

It means when the solution of  $ZnSO_4$  has conc 0.5M  $[Zn^{+2}]$  and conc of  $CuSO_4$  is 0.05M  $[Cu^{+2}]$  and cell is constructed then the voltage which will appear in voltmeter is 1.07045V.

If we use standard conditions and standard equation having standard concentration of solution then the whole value of  $\left[ \frac{RT}{nF} \ln Q = 0 \right]$  and appear  $E_{\text{cell}} = \text{standard cell}$ .



$$E_{cell} = E^\circ - \frac{RT}{nF} \ln Q$$

$$E_{cell} = 1.10 - \frac{8.313 \times 298}{2 \times 96500} (a \cdot 308) \log Q$$

$$E_{cell} = E^\circ - \frac{0.0591 \log Q}{n}$$

$$E_{cell} = E_{oxi} + E_{red}$$

$$E_{cell} = 1.10 - \frac{8.313 \times 298}{2 \times 96500} \frac{\ln [2n^{+2}] [Cu^{+2}]}{[2n] [Cu^{+2}]}$$

$$E_{cell} = 1.10 - \frac{0.0591}{2} \frac{\ln [2n^{+2}]}{[Cu^{+2}]}$$

$$E_{cell} = 1.10 - 0.0295 \times \log 10$$

$$E_{cell} = 1.10 - 0.0295 \times 1$$

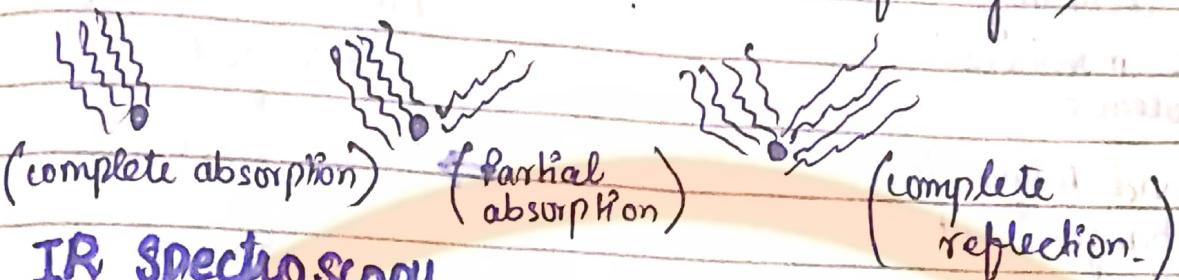
$$E_{cell} = 1.07045 V$$

change their bond length and bond angle

## Analytical Chemistry Sp Theory - II

### Spectroscopy :-

interaction of matter with electromagnetic rays. (detection of light)



### IR Spectroscopy :-

- wavelength  $\rightarrow 2.5\mu\text{m} - 15\mu\text{m}$
- wave number  $\bar{v} \rightarrow 4000 - 400\text{ cm}^{-1}$

We study IR spectroscopy normally for detection of functional groups.

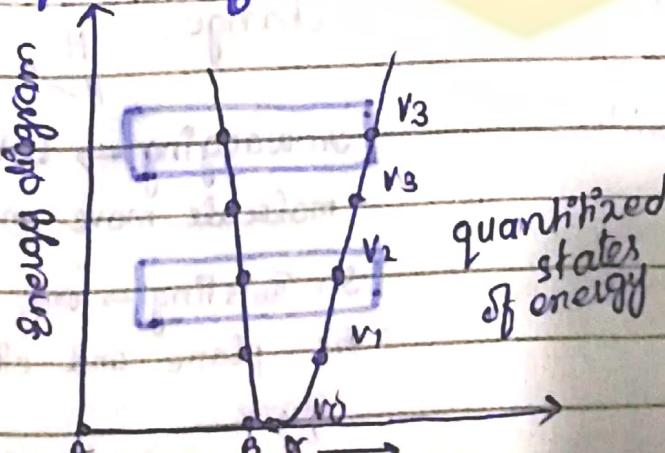
→ IR spectroscopy is also called

- functional group spectroscopy
- vibrational spectroscopy
- vibrational / Rotational spectroscopy
- Finger print spectroscopy

Bending/  
stretching  
spectroscopy

because every molecule has different spectra for identification.

### Absorption of IR Radiations:-



$A - B$   
↓  
(r)  
interatomic  
distance

$A - B$   
compromised  
energy  
state  
stable energy

## Vibrations

stretching vibration

gv

## Bending vibration

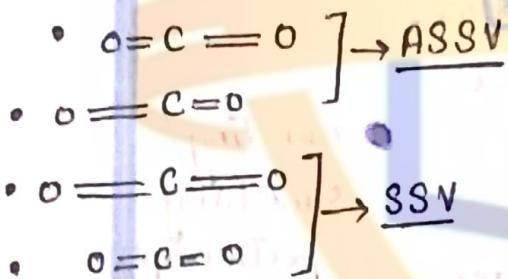
(BV)

calculate energy according to the movement of molecule.

→ Bond Angle is  
not changed but  
Bond Length is  
changed.

Atoms move along the directions of bonds

$$\Rightarrow 0 = c = 0$$



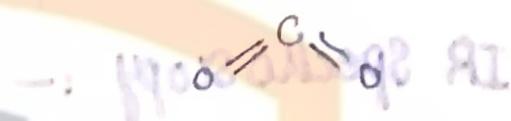
## Types:-

- Symmetric SV
  - Asymmetric SV

$\Rightarrow$  They have high energy spectra absorption

$$\Rightarrow \bar{v} \rightarrow 4000 \text{ cm}^{-1} - 1500 \text{ cm}^{-1}$$

→ Bond angle is changed  
but Bond Length is not  
changed.



→ They have low energy absorption.

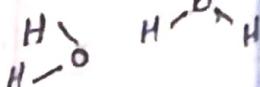
$$v = 1600 \text{ cm}^{-1} - 650 \text{ cm}^{-1}$$

## Types :-

- Inplane → Scissoring, Rocking
  - Outplane → wagging, Twisting

In scissoring → Two atoms move towards each other and bond angle reduces

In Rocking → Two atoms move in same directions bond angle b/w those atoms will not change.  $\text{H}_2\text{O}$



In wagging → Both the atoms of molecule move one side of the plane.

**In Twisting** → one molecule is above the plane and other is below the plane.

## Rules of Spectroscopy :-

1. There must be change in dipole moment for absorption of IR waves.
- Homoatomic molecules**  $\rightarrow$  Homatomic Diatomic molecules are IR inactive because their dipole moment is not changed.  
i.e.,  $H_2$ ,  $N_2$ ,  $O_2$
2. The molecules that have centre of symmetry are IR inactive.
3. The molecules that have not centre of symmetry are IR active.
- e.g.  $\begin{array}{c} H \\ | \\ C=C \\ | \\ Cl \\ | \\ H \end{array}$  }  $\rightarrow$  IR inactive molecules

## Fundamental Vibration :-

↳ depending upon the number of bending and stretching.

In diatomic molecules only 1 fundamental vibration (stretching vibration)

In Polyatomic molecules, it have two types

Linear

Non-Linear

Firstly, we calculate the degree of freedom.

## Linear

$$DOF = 3N - 5$$

$$= 3(3) - 5$$

$$= 9 - 5$$

$$DOF = 4 (CO_2)$$

$$S.V = n - 1$$

$$= 3 - 1$$

$$\boxed{S.V = 2}$$

$$B.V = 4 - 2$$

$$\boxed{B.V = 2}$$

## Non-Linear

$$DOF = 3N - 6$$

$$= 3(3) - 6$$

$$= 9 - 6$$

$$= 3 (H_2O)$$

$$S.V = 3$$

$$\boxed{S.V = 2}$$

$$B.V = 3$$

$$\boxed{B.V = 1}$$

→ Total Number of Motion of Molecules =  $3N$  (Translational, Rotational vibration)

→ Degree of Freedom is also called ~~Motion~~ Fundamental vibration.

**Total vibration** = Stretching vibration + Bending vibration

⇒ **Stretching vibration** =  $n - 1$   $\approx (n = \text{No of atoms})$

⇒ **Bending vibration** = Total vibration - Stretching vibration

## Dependence of Fundamental vibration :-

Fundamental vibrations depends upon the <sup>pp</sup> Hook's Law

According to Hook's Law:-

The Frequency of IR absorb by the matter is directly proportional to the bond strength

For Frequency:-  $\downarrow \uparrow \text{IR Absorption} \propto \text{Bond Strength} \uparrow \downarrow$

$$V = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

Here  $K \rightarrow$  Proportionality constant  $\Rightarrow$  Bond Strength

$\mu =$  Reduced Mass

$$\text{Reduced Mass } (\mu) = \frac{m_1 \times m_2}{m_1 + m_2}$$

$$C-C \\ K = 5 \times 10^5 \text{ dyne cm}^{-1}$$

$$C=C \\ K = 10 \times 10^5 \text{ dyne cm}^{-1}$$

$$C \equiv C \\ K = 15 \times 10^5 \text{ dyne cm}^{-1}$$

for wave number:-

$$\bar{v} = \frac{1}{2\pi c} \frac{K}{\mu}$$

Bond length

↑ Bond strength or Fundamental vibration ↑  
fundamental vibrations have equal space.

## Factors Affecting the Fundamental vibration

① Bond Order / Bond Strength  $\propto \bar{v} \propto K$

e.g C-C

700, 1100 cm<sup>-1</sup>

C=C

1650 cm<sup>-1</sup>

C≡C

2150 cm<sup>-1</sup>, 22000 cm<sup>-1</sup>

C≡N > C=N → F.V increase

② Inductive effect / Mesomeric effect

② Electronic Effect :- effect of neighbouring group on FV

(a) Electron withdrawing group

X-C=O, C=O 1700 cm<sup>-1</sup>  
1800 cm<sup>-1</sup>, (Increase  $\bar{v}$ )

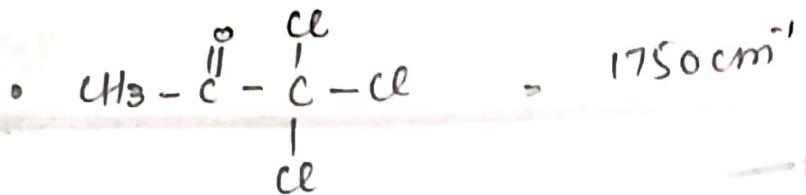
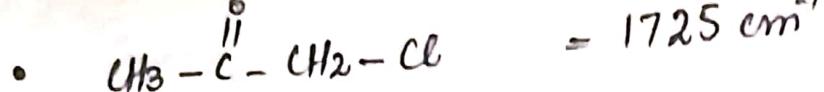
(b) Electron donating group

R-C=O (decrease  $\bar{v}$ )

(Halogen effect)

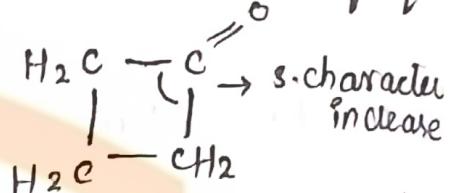
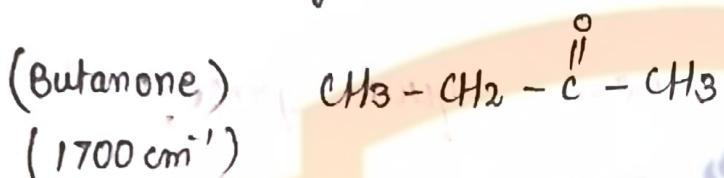
whenever, Electron withdrawing electron density is less, electronic repulsion is decrease and Bond strength is increase.  
and FV increase.

whenever, Electron donating, electron density is increase,  
electronic repulsion is increase and bond is weak, FV  
is decrease.



### ③ ↑ Bond Angle :- $\propto \frac{1}{\text{s-character}} \uparrow \downarrow$

In any Molecule, when more s-character, more bond strength and there will be more vibration frequency.

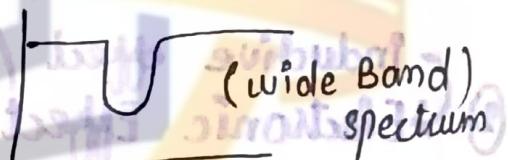


(cyclo butanone)  $(1720 \text{ cm}^{-1})$   
 $\overset{\text{O}}{\underset{\text{C}}{\text{C}}} \rightarrow \text{high frequency, high absorption than simple Butanone -}$

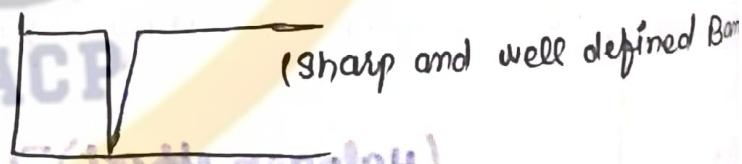
### ④ Hydrogen Bonding :-

H-B decrease the vibrational frequency.

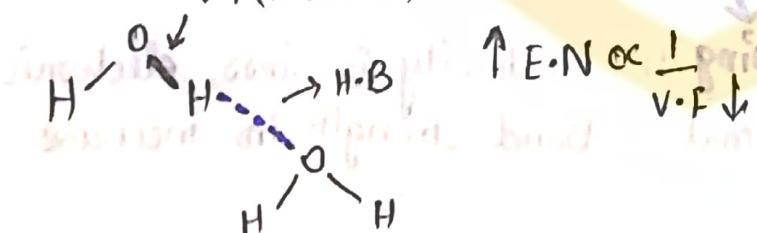
- intramolecular Hydrogen Bonding :-  
 $\hookrightarrow$  effect for long time



- Intermolecular Hydrogen Bonding :-



v.F (decrease)

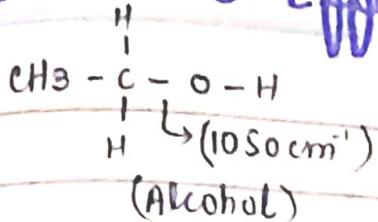


Electronegativity of alcohol is higher than amines so they have high less v.F.

For resonance to be necessary for resonance that electrons are in one plane.

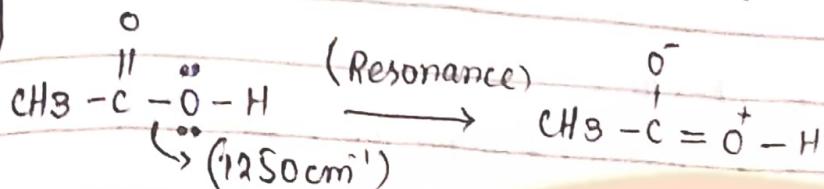
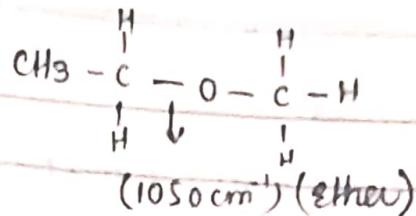
## Resonance Effect :-

Conditions  
- =  
- ≡  
- (+)  
- (-)



$\text{C} - \text{O} (1050 \text{ cm}^{-1})$

$\pi$ -electrons only move along their axis (x,y,z)

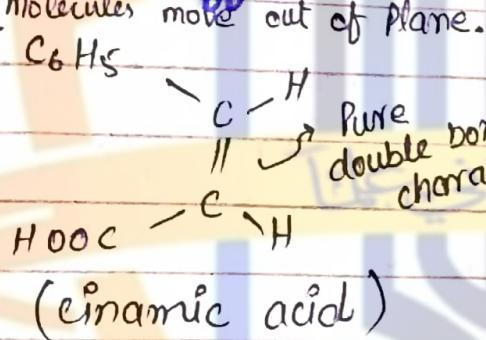


when double bond character increases, Resonance increases  
so vibrational frequency increases.

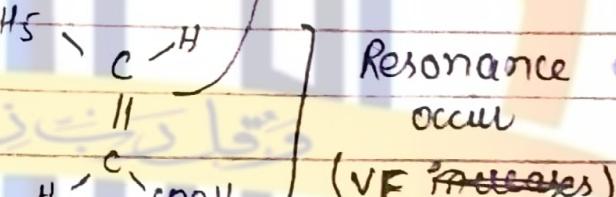
## ⑤ Cis-Trans Effect :-

2 Bulky groups at one side  
steric Hindrance

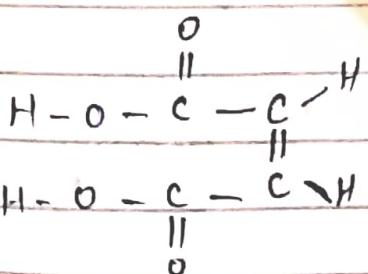
Molecules move out of Plane.  
Resonance can't occur.  
(VF decreases) increases



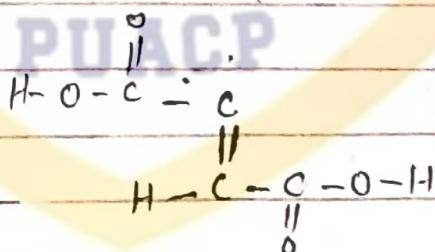
cis-isomer



Trans-isomer

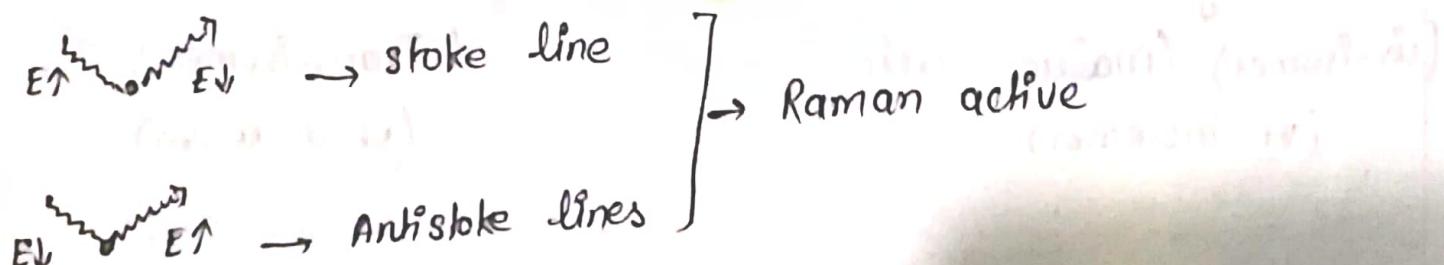


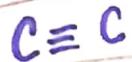
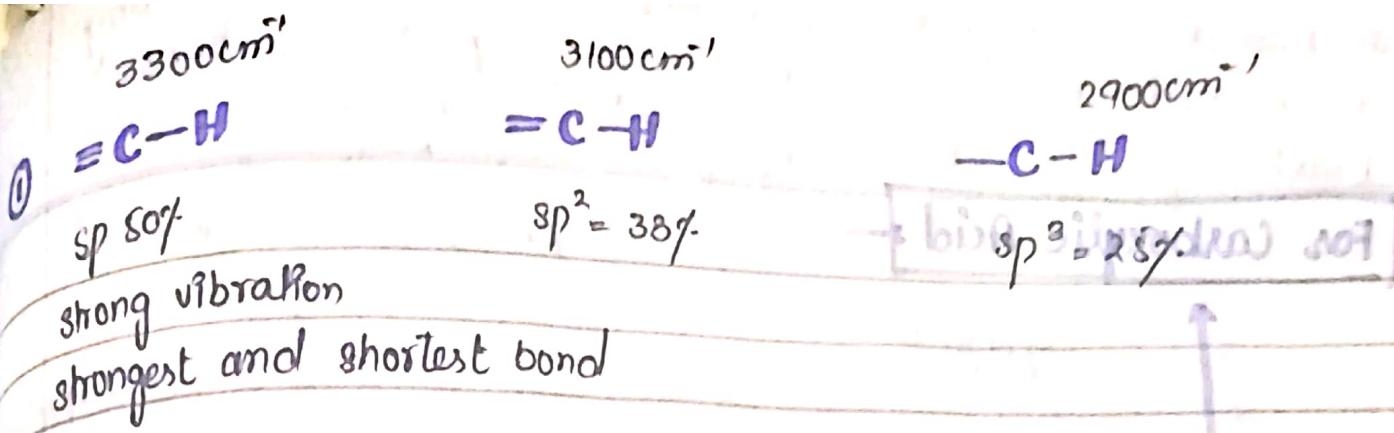
(cis-isomer) (Maleic acid)  
(VF increases)



(Trans-isomer)  
(VF decreases)

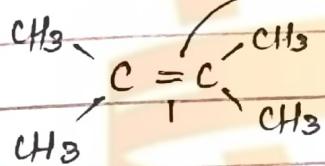
- In IR spectroscopy and Raman spectroscopy, in both we used infrared radiations.
  - IR spectroscopy absorb radiation  
Raman spectroscopy reflect/scattered radiation
  - IR molecules must be Polar.  
Raman spectroscopy can't should be polar. If they are non-polar, you can create polarizability.  
IR inactive molecules polarized by Raman spectroscopy.
  - In both spectrosopies, spectra is visible & molecules are identified due to bending + stretching vibrations.
  - Frequency of incident light is equal to the frequency of reflected light is known as "Rayleigh scattering"  
 $v_i = v_r$        $E_i = E_r$       → (Bond excitation)
  - Frequency of incident light is higher than reflected light is known as "Stoke scattering"
  - Frequency of incident light is lower than reflected light is known as "Anti-Stoke scattering"
- Raman inactive
- $E_i \rightarrow E_r$       → Rayleigh scattering → Raman spectroscopy



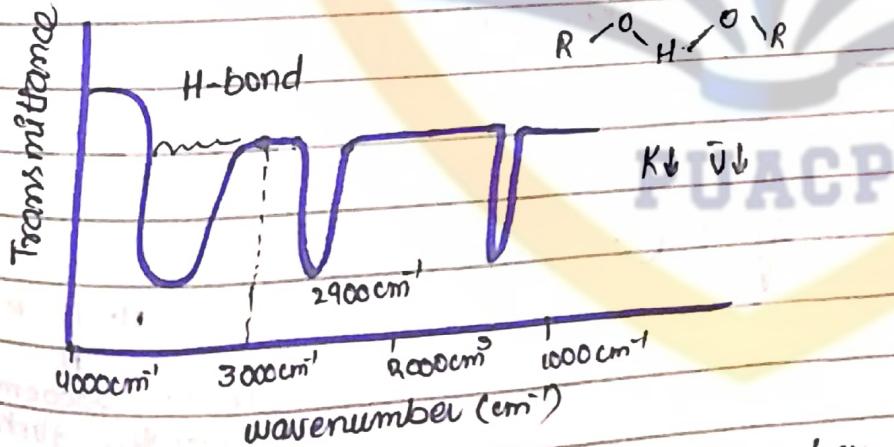
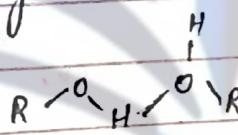

 $2100\text{cm}^{-1}$ 

 $1650\text{cm}^{-1}$ 

 $, 730\text{cm}^{-1}$ 
 $\text{C}=\text{C} \quad 1600 - 1450\text{cm}^{-1}$ 

 $\text{C}=\text{O} \quad 1715\text{cm}^{-1}$ 


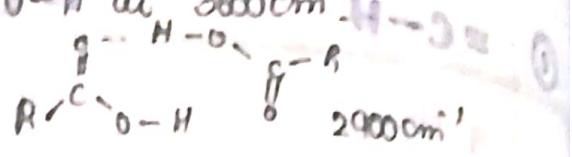
No signal for IR spectrum due to symmetrical alkene, there is no dipole moment election  
donating cancelled.



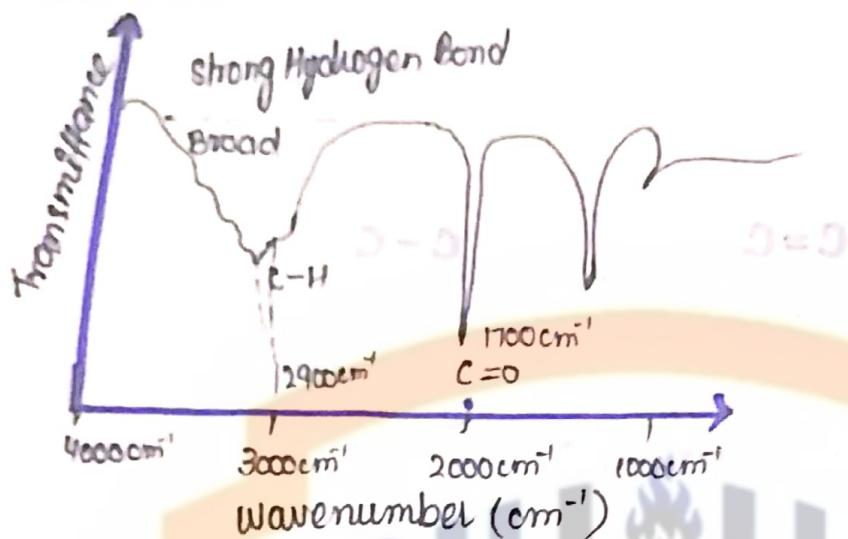
$\text{C}-\text{O} = 1100\text{cm}^{-1}$ 
 $\text{O}-\text{H} = 3600\text{cm}^{-1}$

Intermolecular Hydrogen decreases wave number and different molecule has different intensity of H-bond, so we get a broad spectrum ( $3200 - 3600\text{cm}^{-1}$ ).

In Aromatic and Aliphatic alcohol where there is no H-bonding due to steric hindrance of large alkyl group so there is no broad signal we obtained sharp signal - O-H at  $3600\text{cm}^{-1}$ .



### For Carboxylic Acid +

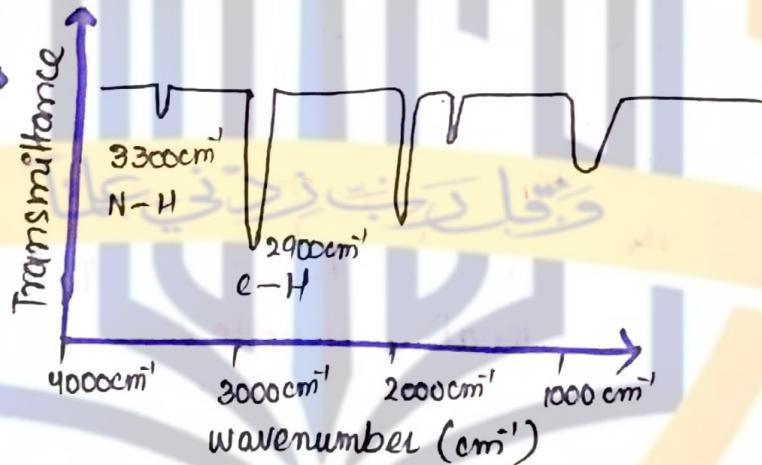
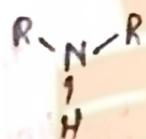


$C=O \quad 1700\text{cm}^{-1}$

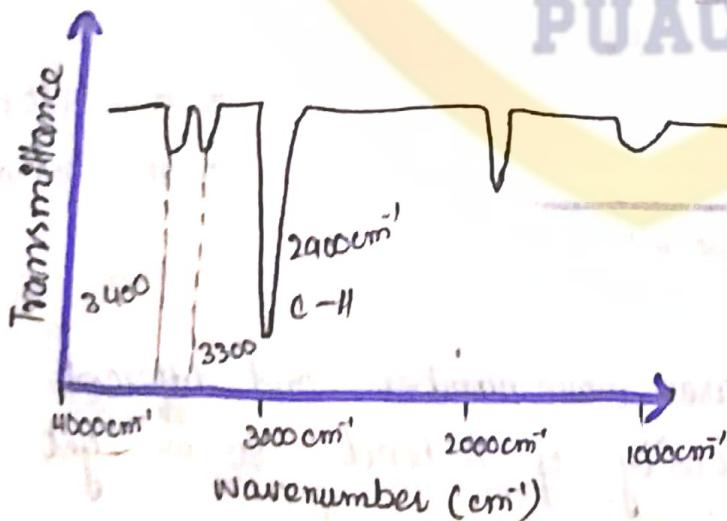
O-H Broad spectrum  
b/w  $2500\text{cm}^{-1}$  -  $3600\text{cm}^{-1}$

### For Amines

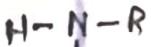
#### Secondary Amines



#### Primary Amines:-



PUACH



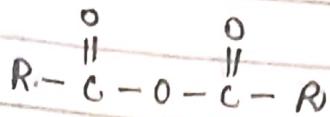
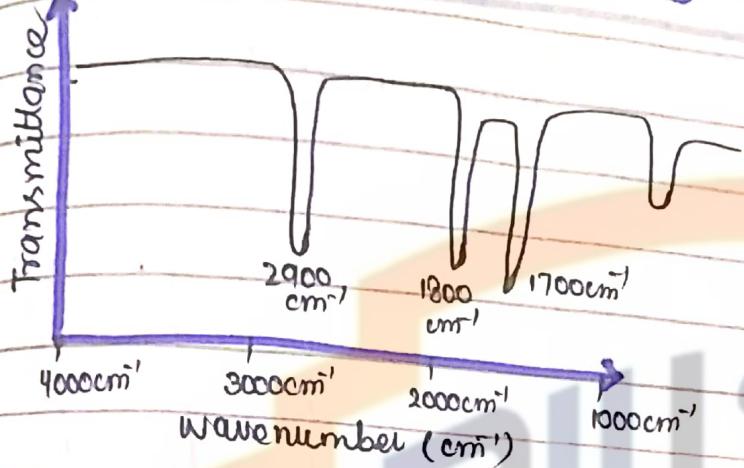
$N-H = 3300\text{cm}^{-1}$   
symmetric stretching

$N-H = 3400\text{cm}^{-1}$   
Asymmetric stretching

explain IR Spectroscopy:-

IR spectro

## For Acid Anhydride



C-H = 2900  $\text{cm}^{-1}$

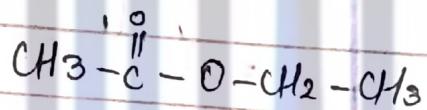
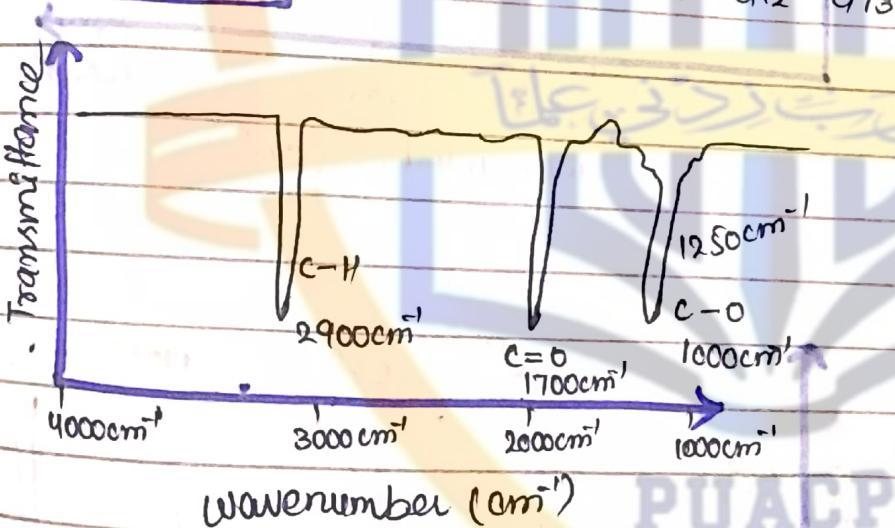
C=O = 1700  $\text{cm}^{-1}$

Symmetric Stretching

C=O, 1800  $\text{cm}^{-1}$

Asymmetric Stretching

## For Ester

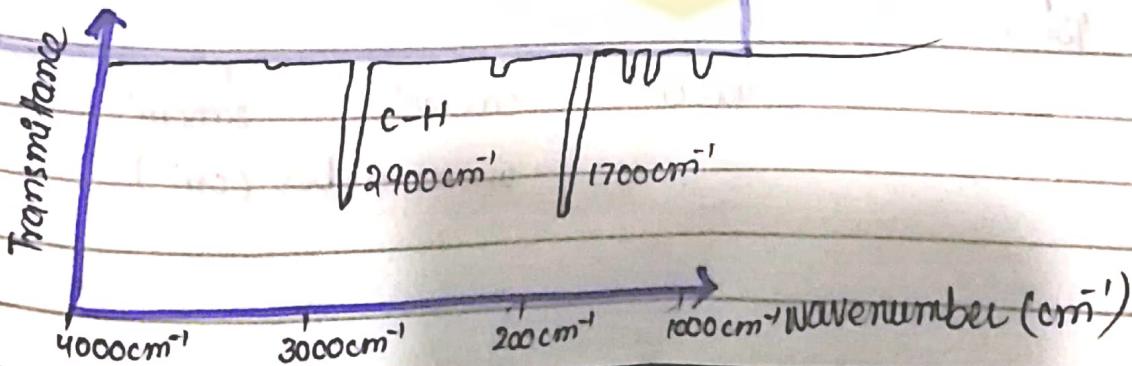


C-H = 2900  $\text{cm}^{-1}$

C=O = 1700  $\text{cm}^{-1}$

C-O = 1000  $\text{cm}^{-1}$

## For Ketone Propanone

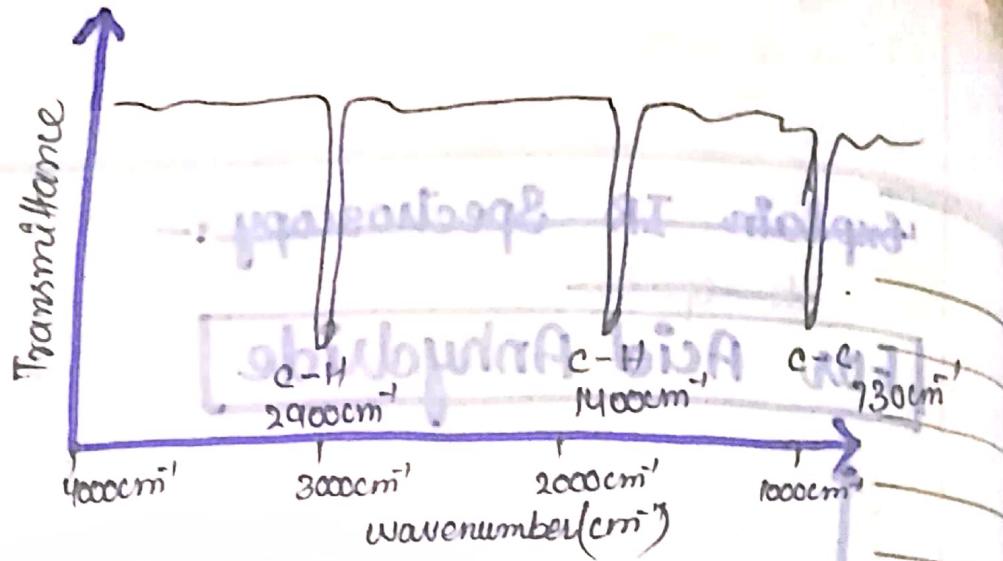


## Alkane

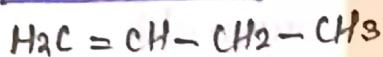
- C-H stretching =  $2900\text{cm}^{-1}$

- C-H bending =  $1400\text{cm}^{-1}$

C-C stretching =  $730\text{cm}^{-1}$



## Alkene



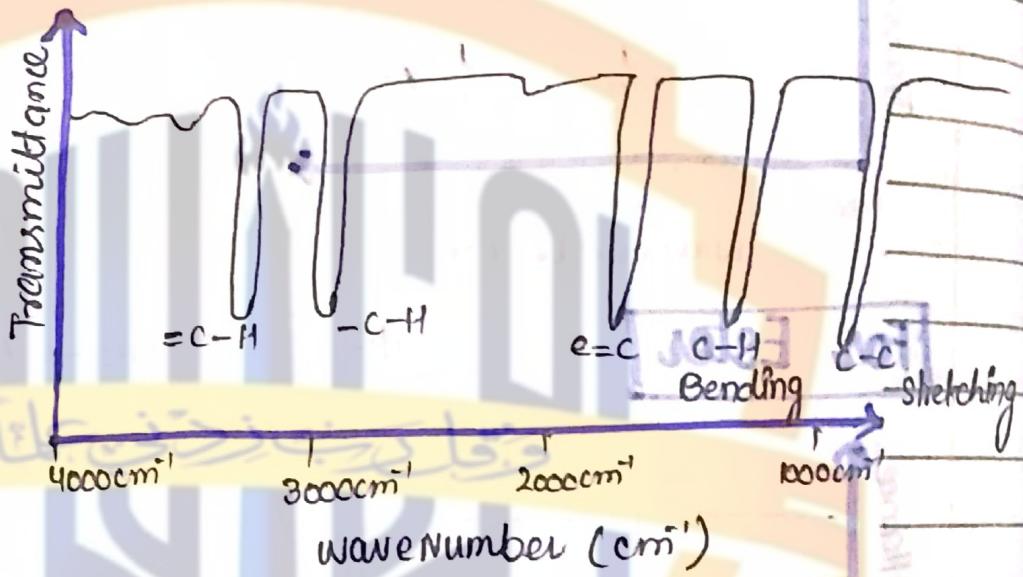
= C-H =  $3100\text{cm}^{-1}$

- C-H =  $2900\text{cm}^{-1}$

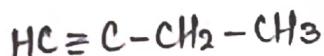
C=C =  $1600-1700\text{cm}^{-1}$

C-H bending =  $1400\text{cm}^{-1}$

C-C stretching =  $730\text{cm}^{-1}$



## Alkyne



= C-H =  $3300\text{cm}^{-1}$

- C-H =  $2900\text{cm}^{-1}$

C≡C =  $2200\text{cm}^{-1}$

C-H bending =  $1400\text{cm}^{-1}$

C-C =  $730\text{cm}^{-1}$

