

16/8/16
Tuesday

Electrochemistry

LOAN → Loss of e. → Anode, Oxidation, A node
→ Gain of e. → Cathode, Reduction, C node
Negative

Electrochemistry is the branch of science which deals with the relationship between chemical reaction and electrical energy.

Electrochemical cell (Galvanic, Voltaic)

- chemical reaction is converted to electrical energy
- Redox Reaction will take place

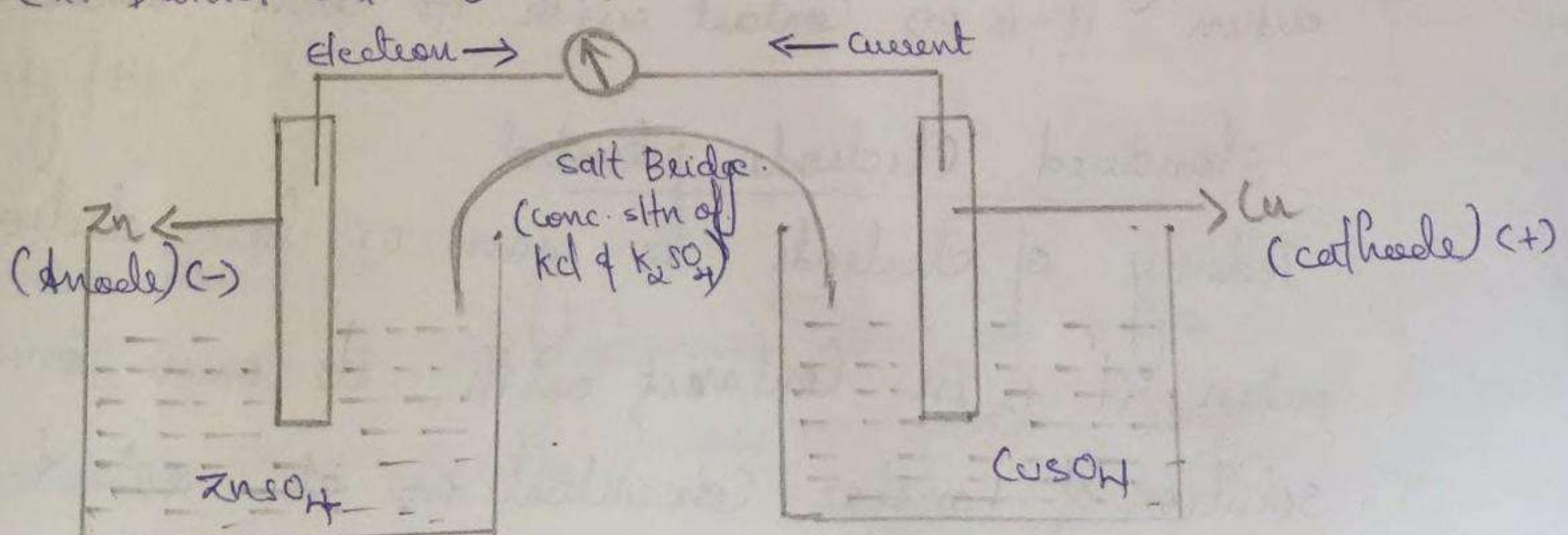
LEO - loss of electrons in Oxidation (Anode)

GCR - Gain of electrons in Reduction (Cathode)

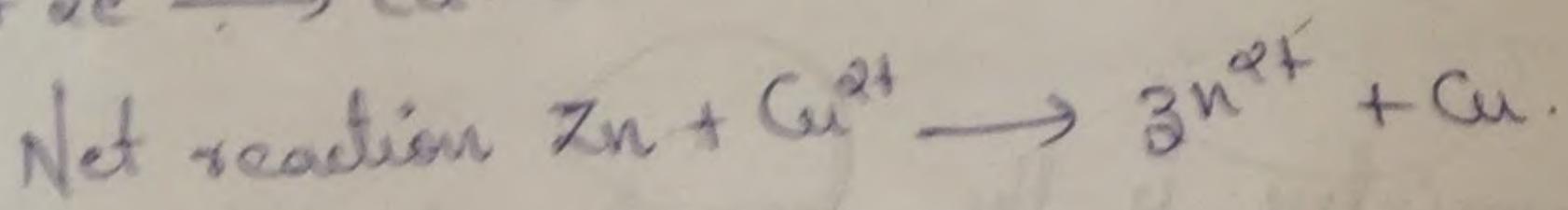
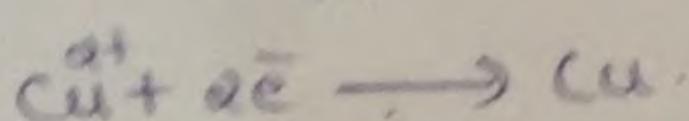
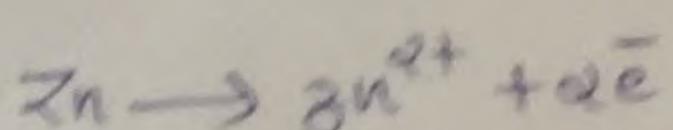
Anode: Oxidation $\rightarrow -Ve$

Cathode: Reduction $\rightarrow +Ve$

ex: Daniel Cell (Zn & Cu)

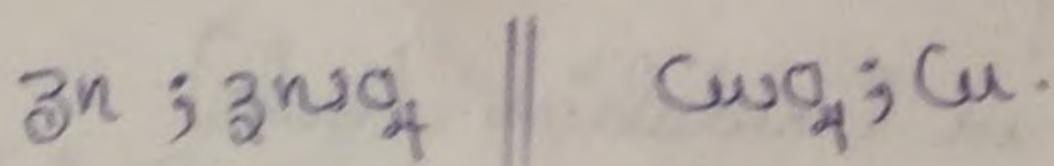
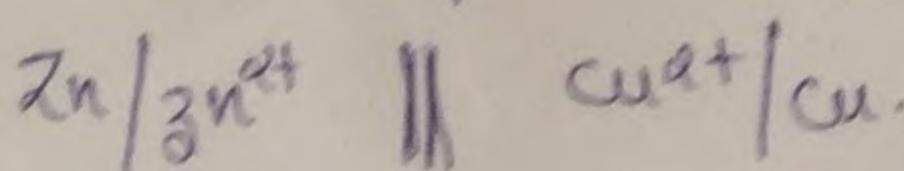
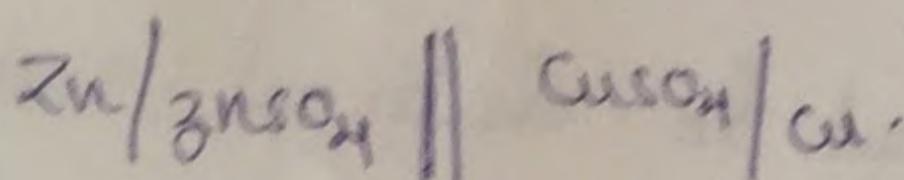


Salt bridge which allows the movements of ions and make them neutral.



Representation of a cell

Anode || cathode



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Electrode potential

Tendency of electrode to gain or lose electron when it is in contact with its own ionic solution.

Standard electrode potential

Tendency of electrode to gain or lose electron when it is in contact with its own ionic

solution of 1 molar concentration at $25^\circ C$ & 1 atm

Oxidation potential

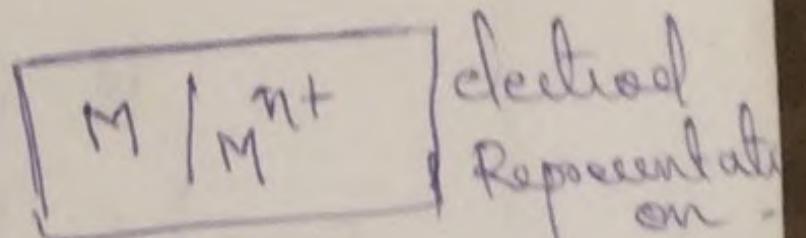
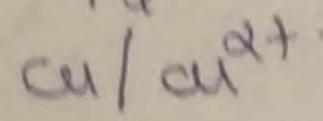
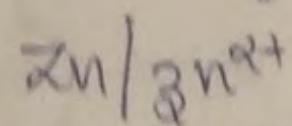
Tendency of electron to lose electron

Types of electrodes

1) Metal - Metal ion electrode

consist of pure metal

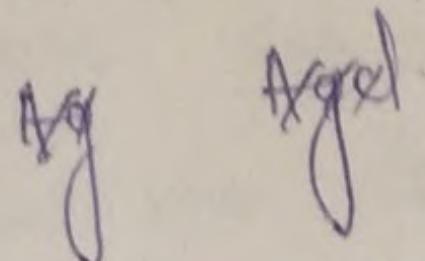
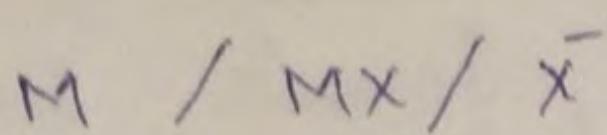
Ex: Zn, Cu.



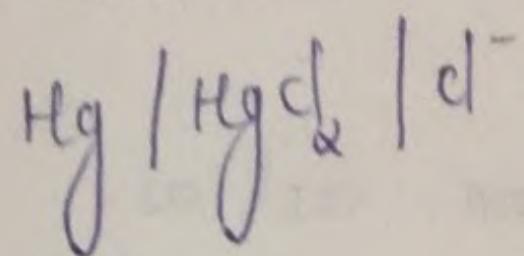
electrode
Representation

2) Metal - Metal Insoluble salt electrode

A Metal is Coated with Insoluble salt which is in contact with anionic solution.



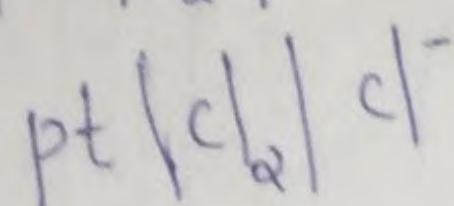
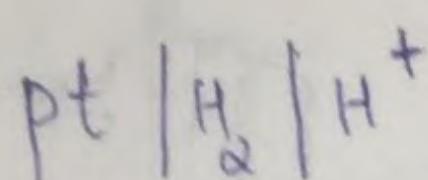
Ex: Calomel



3) Gas electrode

it consist of inert platinum electrode which is a contact with a gas & dipped in gaseous ionic solution.

Ex: SHE



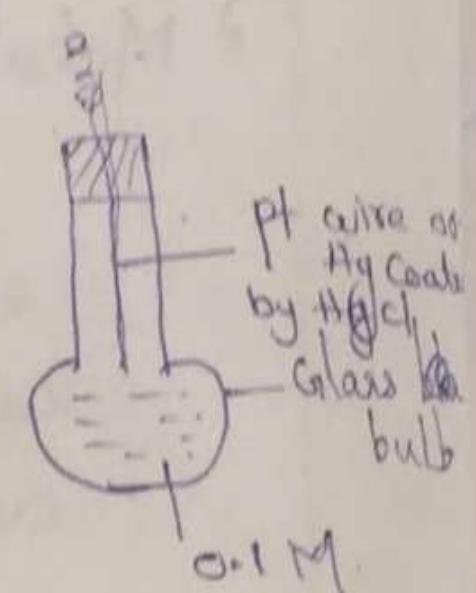
4) Ion Selective Electrode

it consist of thin glass membrane & it is sensitive to certain ions.

Ex: Glass electrode

Glass electrode is used to measure.

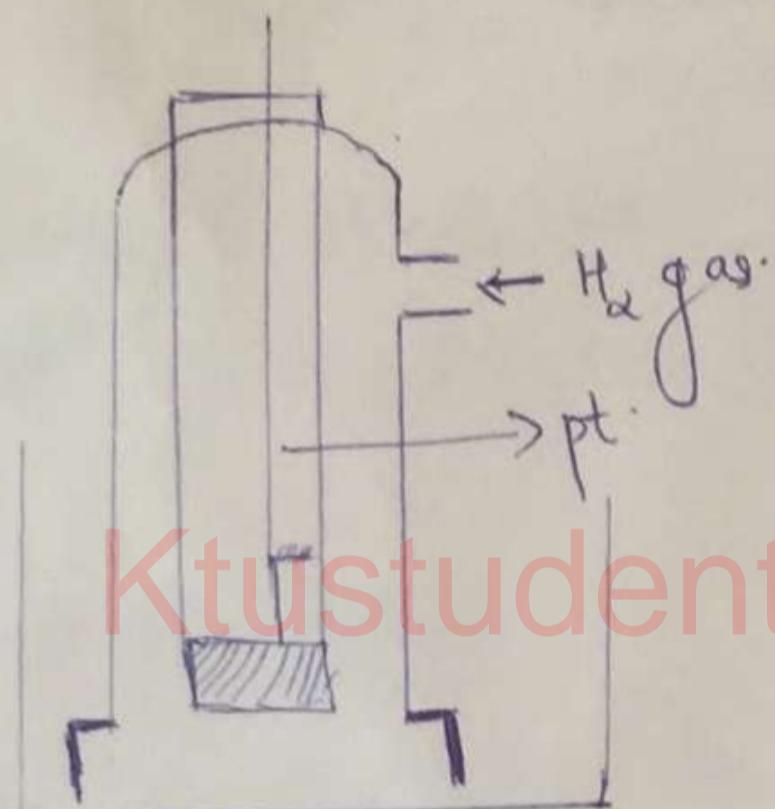
pH.



$$pH = -\log [H^+]$$

SHE

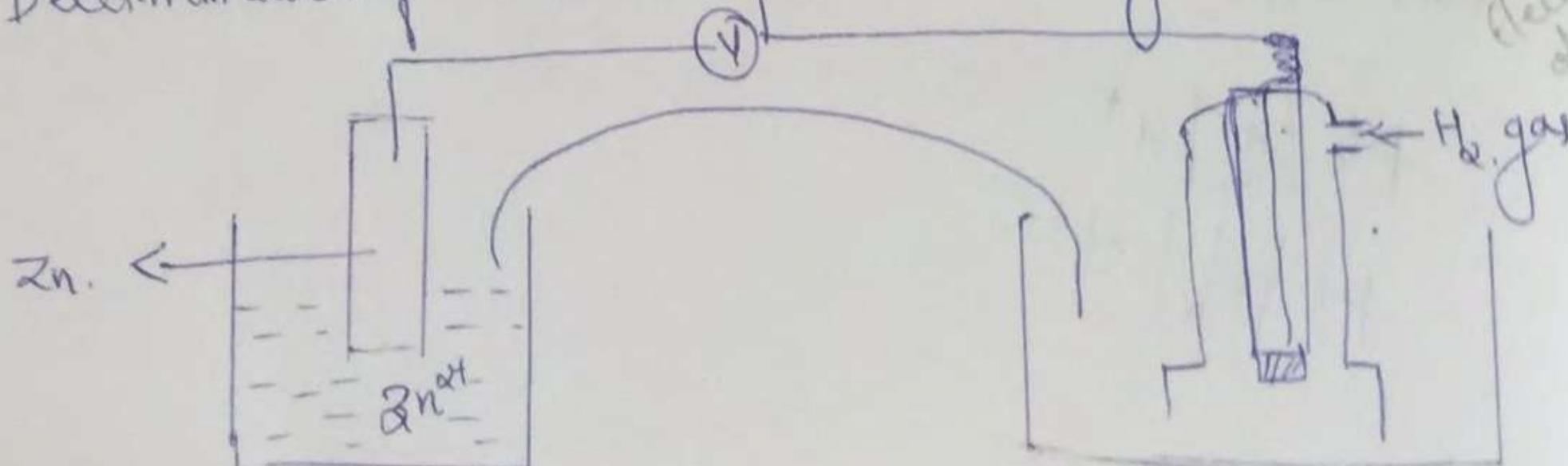
Imp



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- electrode potential SHE is zero
- reversible electrode (bcz the SHE can act as both Anode & Cathode depending upon other electrode which is connected. ex: if Cu is connected here SHE will be cathode)

Determination of electrode potential using SHE



Measuring
electrode
potential
of Zn using
SHE

$$\epsilon_{\text{cell}} = \epsilon_{\text{cathode}} - \epsilon_{\text{anode}}$$

$$0.76 = \epsilon_{\text{SHE}} - \epsilon_{\text{Zn/Zn}^{2+}}$$

$$0.76 = 0 - \epsilon_{\text{Zn/Zn}^{2+}}$$

$$\epsilon_{\text{Zn/Zn}^{2+}} = 0.76$$

- if Copper is connected instead to zinc Cu will act as cathode and SHE act as anode.

$$\epsilon_{\text{cell}} = \epsilon_{\text{C}} - \epsilon_{\text{H}}$$

$$0.34 = \epsilon_{\text{Cu/Cu}^{2+}} - 0$$

$$= 0.34$$

Calomel Electrode

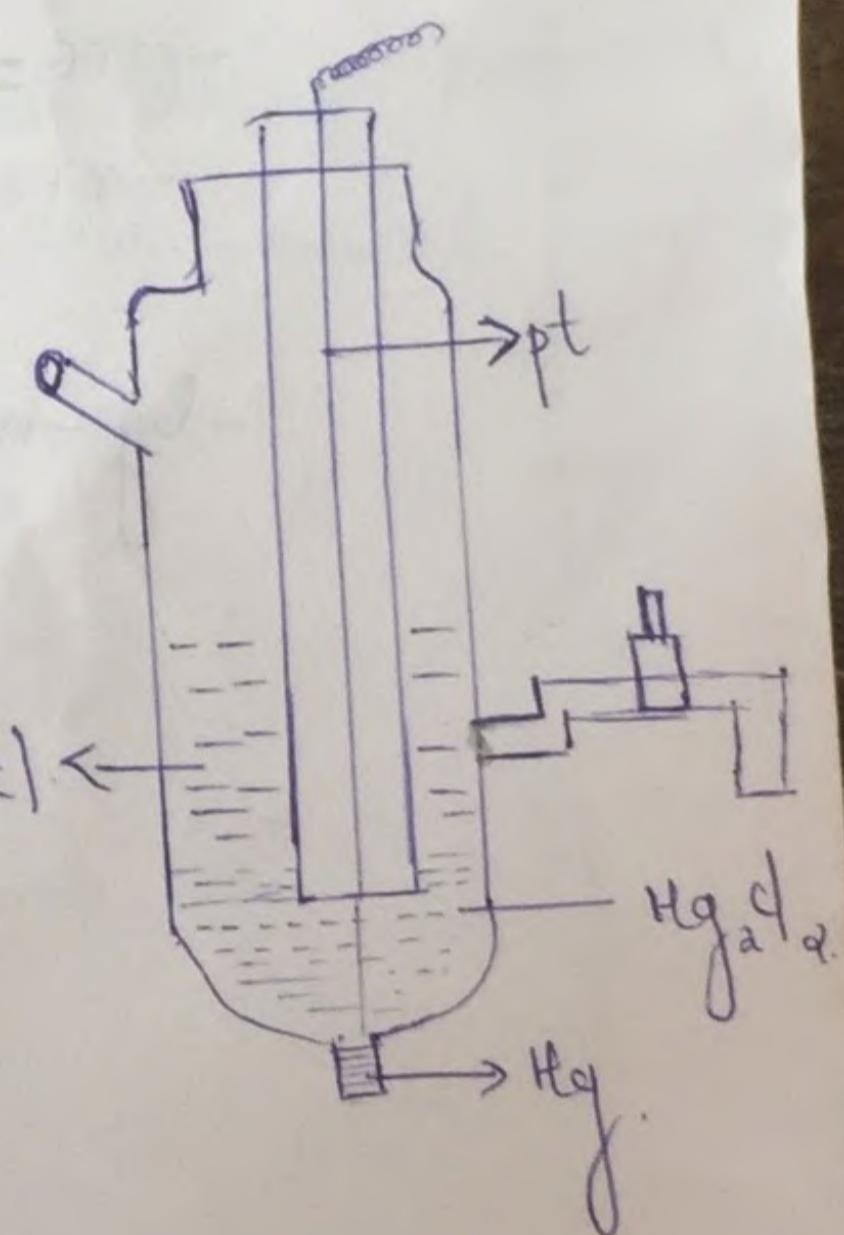
0.1 N decinormal (0.3335)

1 N Normal (0.2810)

>1 N Saturated (0.2422)

if we use saturated electrode
KCl electrode potential of Calomel electrode is 0.2422.

Used as an Reference electrode



Emf of cell is 1 Volt (case of Zn)

$$\epsilon_{\text{cell}} = \epsilon_{\text{C}} - \epsilon_{\text{H}}$$

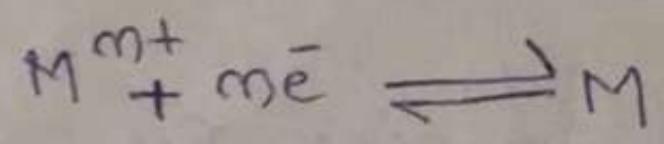
$$1 = \epsilon_{\text{Calomel}} - \epsilon_{\text{Zn/Zn}^{2+}}$$

$$1 = 0.2422 - \epsilon_{\text{Zn/Zn}^{2+}}$$

$$0.2422 - 1 = -0.76$$

Nernst Equation

gives the relationship b/w electrode potential & Conc. of electrode.



$$\Delta G = \Delta G^\circ + RT \ln k \quad \text{--- (Nernst equation)}$$

$$\Delta G = -nFE$$

$$\Delta G^\circ = -nFE^\circ$$

$$-nFE = -nFE^\circ + RT \ln k$$

$$-nFE = -nFE^\circ + RT \frac{\ln [M]}{[M^{n+}]}$$

$$\therefore \log -nF$$

$$= E = E^\circ - \frac{RT}{nF} \frac{\ln [M]}{[M^{n+}]}$$

$$E = E^\circ - \frac{0.303}{nF} \frac{RT \log [M]}{[M^{n+}]}$$

$$E = E^\circ - \frac{0.303}{nF} \frac{RT \log \left[\frac{1}{M^{n+}} \right]}{[M^{n+}]}$$

$$E = E^\circ + \frac{0.303}{nF} \frac{RT \log [M^{n+}]}{[M^{n+}]}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, T = 298 \text{ K}, F = 96500 \text{ C}$$

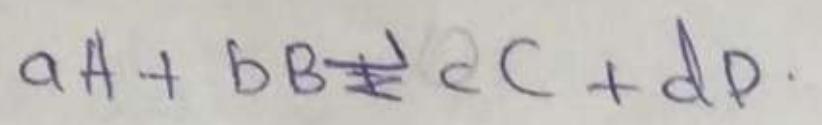
Substituting the values of R, T, F

$$E = E^\circ + \frac{0.303}{96500} \times 8.314 \times 298 \log [M^{n+}]$$

$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}]$$

Application of Nernst Equation

- gives the relationship b/w electrode potential & Conc. of electrode



$$\epsilon = \epsilon^\circ - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

out of
four.

$$\log \frac{(3n^{2+}) [Cu]}{(2n^2) [Cu^{2+}]}$$

- for calculating pH of a solution
- calculate the known unknown electrolyte
- Valency of electrode or no. of electrons transferred in a reaction

1. calculate the EMF of a Daniell cell when the $[Zn^{2+}] = 0.01 M$ & $[Cu^{2+}] = 0.1 M$. given that $\epsilon^\circ_{Zn/Zn^{2+}} = -0.76 V$.

$$\epsilon^\circ_{Cu/Cu^{2+}} = +0.34 V$$

$$= \frac{0.1 - 0.01}{0.01}$$

$$\epsilon = \epsilon^\circ - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

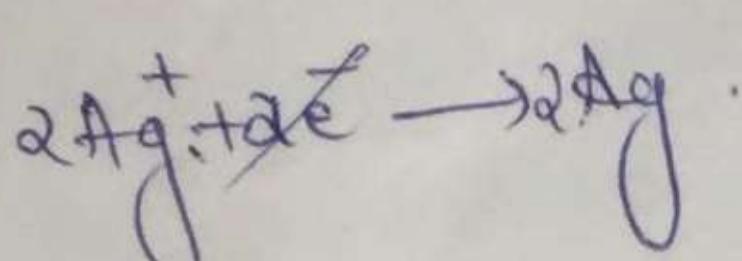
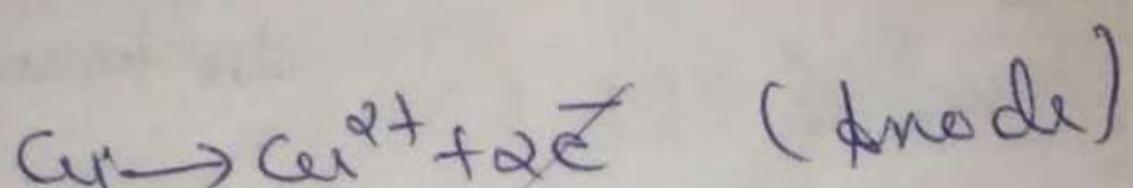
$$\epsilon = \epsilon^\circ - \frac{0.0591}{2} \log \left(\frac{0.01}{0.1} \right)$$

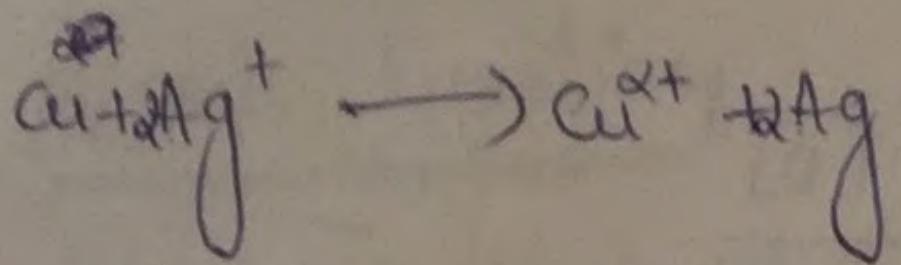
$$= \frac{\frac{1}{2} (0.34 + 0.76)}{1.10}$$

$$\epsilon = 1.1 - \frac{0.0591}{2} \log \left(\frac{0.01}{0.1} \right)$$

$$\underline{\underline{1.12955 V}}$$

- write the cell reaction & cell representation of Cu-Ag cell. at $25^\circ C$. given that $Ag/Ag^+ = +0.80 V$ $Cu/Cu^{2+} = +0.34 V$
- calculate the Emf of the cell. when the conc. of Ag^+ is $0.1 M$ molar & conc. $Cu^{2+} = 0.01 M$.





$$\epsilon = \epsilon^\circ - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}][\text{Ag}]}{[\text{Cu}][\text{Ag}^+]}$$

$$\begin{aligned}\epsilon^\circ &= \epsilon_c^\circ - \epsilon_A^\circ \\ &= 0.80 - 0.34 \\ &= 0.46.\end{aligned}$$

$$\epsilon = 0.46 - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$\begin{aligned}\epsilon &= 0.46 - \frac{0.0591}{2} \log \left(\frac{0.01}{(0.1)^2} \right) \\ &= 0.48985 \\ &= 0.49 V.\end{aligned}$$

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Effect of Temperature & Concentration on electrode potential.

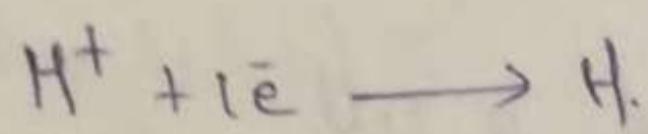
$$\epsilon - \epsilon^\circ = \frac{2.303RT}{nF} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

i) $[\text{Zn}^{2+}] = [\text{Cu}^{2+}] \quad \epsilon = \epsilon^\circ_{\text{cell}}$

ii) $[\text{Zn}^{2+}] > [\text{Cu}^{2+}] \quad \epsilon < \epsilon^\circ_{\text{cell}} \quad (\text{Temp} \uparrow, \epsilon \downarrow)$ (Independent)

iii) $[\text{Zn}^{2+}] < [\text{Cu}^{2+}] \quad \epsilon > \epsilon^\circ_{\text{cell}} \quad (\text{Temp} \uparrow, \text{Electrode potential also increases})$

Variation of emf of hydrogen electrode with pH.



$$\epsilon = \epsilon^\circ - \frac{0.0591}{n} \log \frac{1}{[H^+]}$$

$$\boxed{\epsilon = \epsilon^\circ - 0.0591 \text{ pH.}}$$

$$\boxed{\epsilon = -0.0591 \text{ pH}}$$

|| log (1/a) = -log a.

$$\epsilon^\circ = 0 \text{ (SHE)}$$

we

In acidic medium

$$\epsilon = \epsilon^\circ - 0.0591 \times 0.$$

$$\epsilon = \epsilon^\circ$$

Basic - +ve
acidic - 0
Neutral - 7.

Neutral.

$$\epsilon = -0.0591 \times 7.
-0.41 \text{ Volt}$$

Basic Medium

$$\epsilon = -0.0591 \times 14
-0.82 \text{ Volt}$$

Electrochemical Series. (based on Red) increasing order
of Red. ptl.

it is series in which it is arranged based on
the increasing order of Reduction potential.

Application of EC. To know Oxidn & Red tendency
if Red potential value is -ve the electrode will
go for oxidation easily.

- To know reactivity of a metal electrode which have low reduction it has high reactivity
- To find standard emf of a cell.
- To know displacement reaction the metal which have less reduction potential will reduce the high reduction potential
Ex: Zn in CuSO_4

Reactivity
↑ ↓
 $\text{H} \uparrow$

Cell.

Primary cell. (chemical \rightarrow electrical)

• not Reversible.

Ex: Dry cell, Mangan Cell.

• Secondary cell.

Reversible and Reusable.

Ni - cd.

lead - storage battery

• Fuel cell

long

Lithium - ion Cell (α°)

- Li ion act as both electrolyte & electrochemical cell.
- +ve electrode is made of LiCoO_2 .
- -ve electrode is made of Graphite (C_6) / C₆₀
- Li - ion is transferred b/w anode & cathode
- Electrolyte is the solution of Li salt dissolved in organic solvent ether.

Ex: LiPF_6 , LiClO_4 ,

LiBF_4 Lithium tetraborate

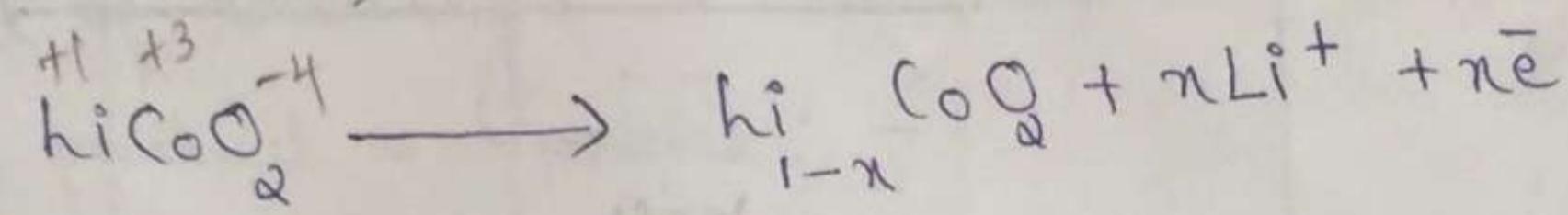
charging (electrical \rightarrow chemical) electrolytic cell.

Anode (+)

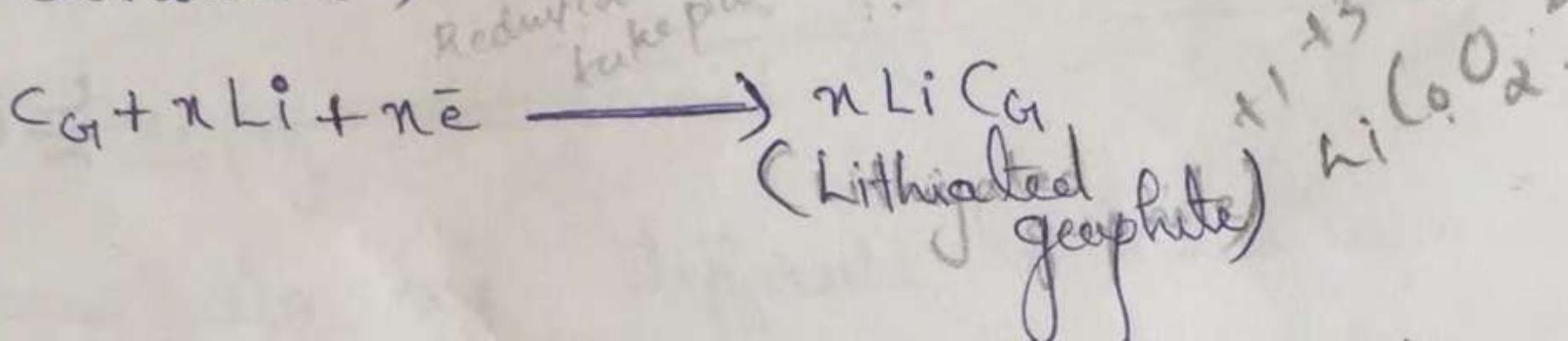
Anode (+)

Cathode (-)

Cathode (-)



Cathode (-)



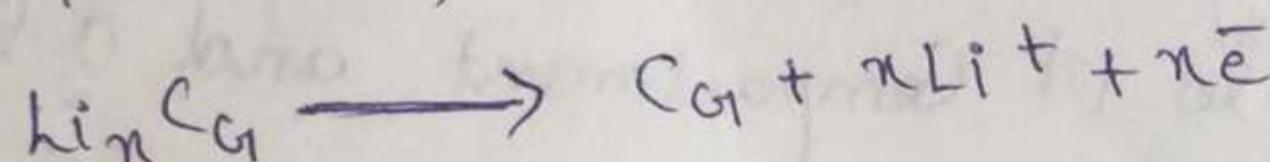
Discharging (chemical \rightarrow electrical) electro chemical cell.

Oxidant

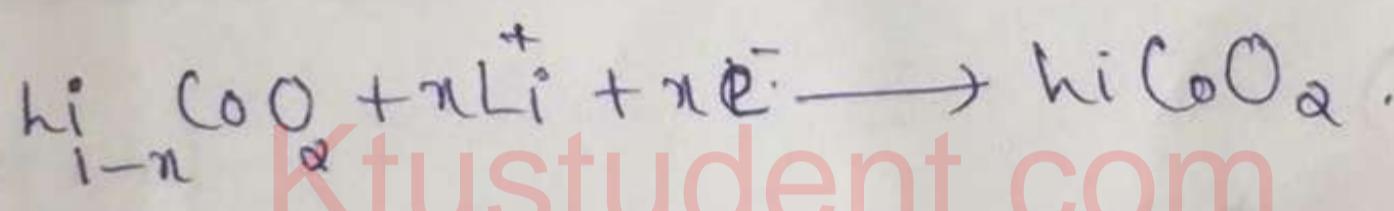
Anode (-)

Anode (-)

Cathode (+)



Cathode (+)



Li-ion produce a current of 3.7 Volt.

Ex: Mobile, laptop, digital, Camera.

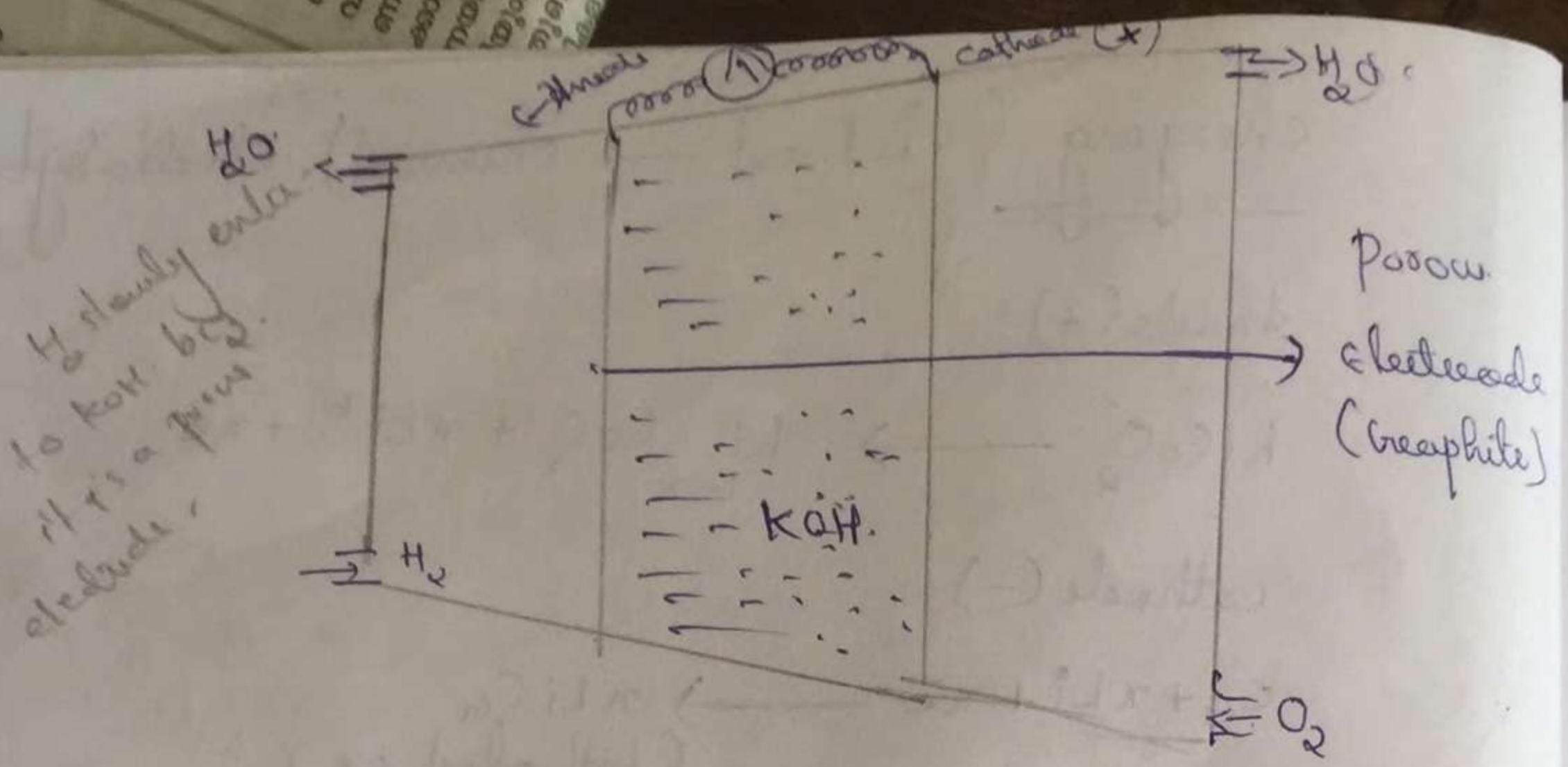
Fuel Cell (Electro chemical cell)

Fuel + Oxidant $\xrightarrow{\text{presence of catalyst}}$ Electrical Energy.

Fuel are applied external.

Fuel cell is diffent from other electro chemical cell.

Ex: $\text{H}_2 - \text{O}_2$ fuel cell.

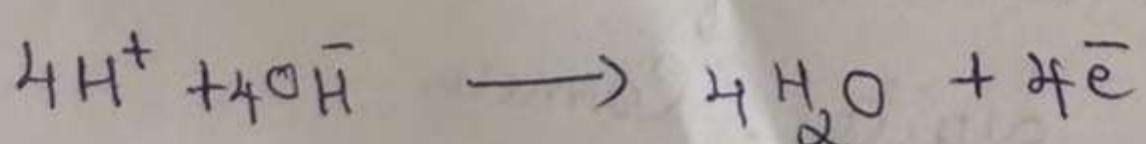
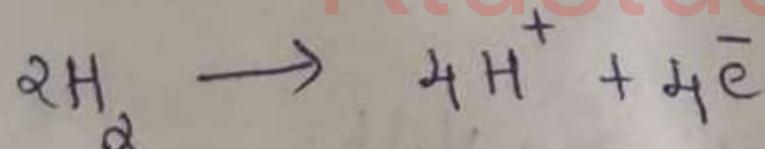


Middle Compartment will act as electrolyte. (KOH)

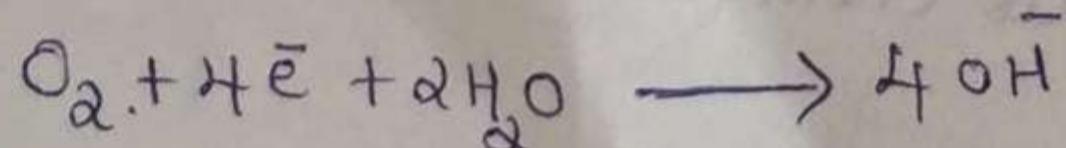
$H_2 \rightarrow$ Anode, $O_2 \rightarrow$ Cathode.

H_2 is passed to 1st Compartment and O_2 to 3rd Compartment.

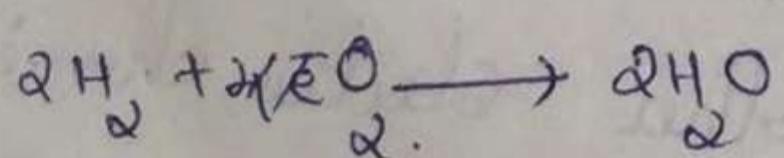
Anode (-)



Cathode (+)



Net Rxn,



- H_2 is got as byproduct.

- Fuels are kept in the presence of electrolyte.

- highly efficient.
- pollution free.
- Concⁿ of electrolyte is Constant or maintain
- by product is water
- it produce Electrical Energy Continues as long as fuel supply maintained.
- Gasous fuels are difficult to maintain
- electrolyte is highly Corrosive.
- Used in space Vehicles, military Vehicles

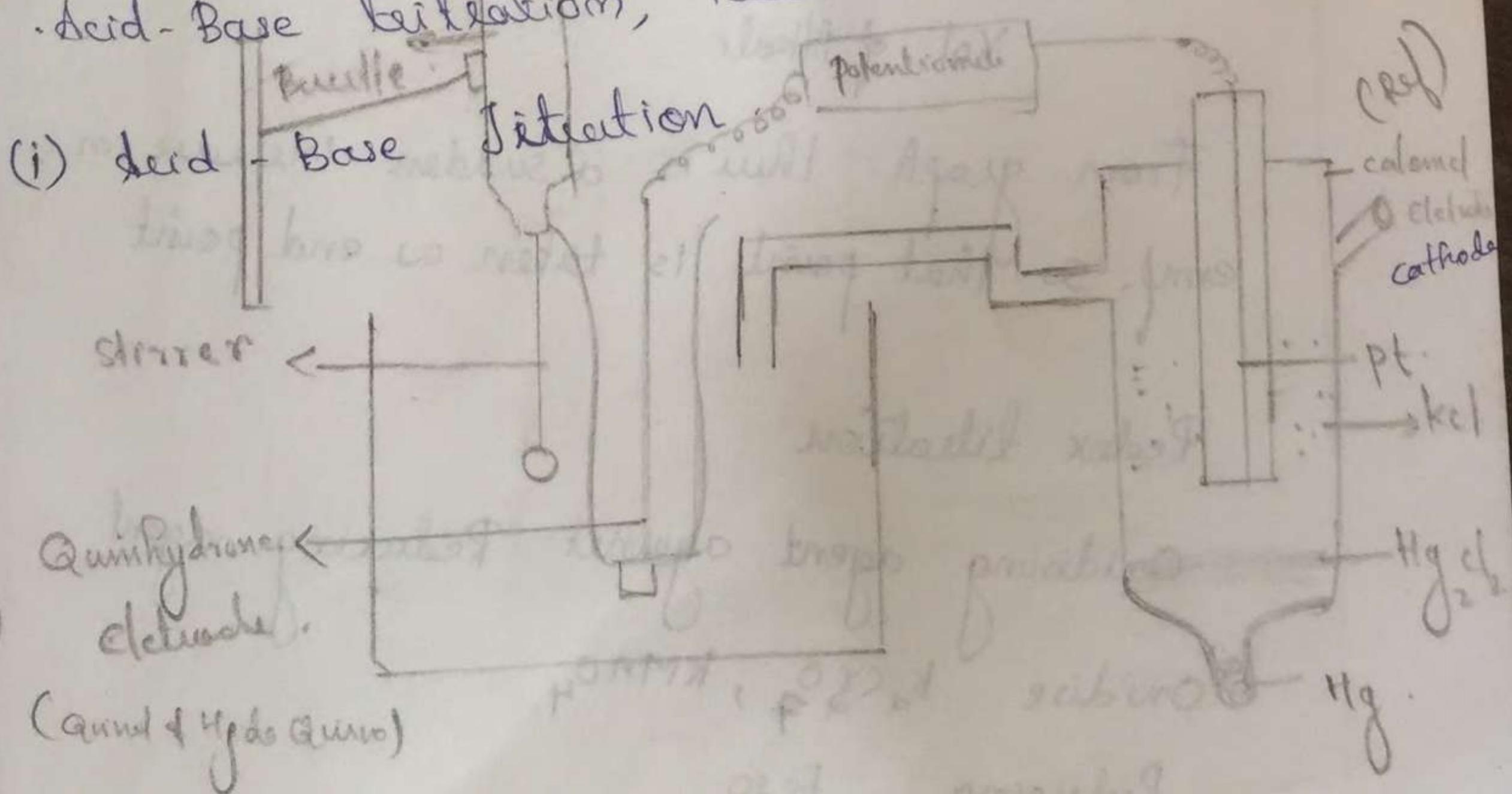
Potentiometer Titration

Applⁿ of emf : Ktustudent.com

$$\epsilon = \epsilon^{\circ} + \frac{0.059}{n} \log [M^{n+}]$$

principle. Neerut Sawn.

Acid-Base titration, Redox titration



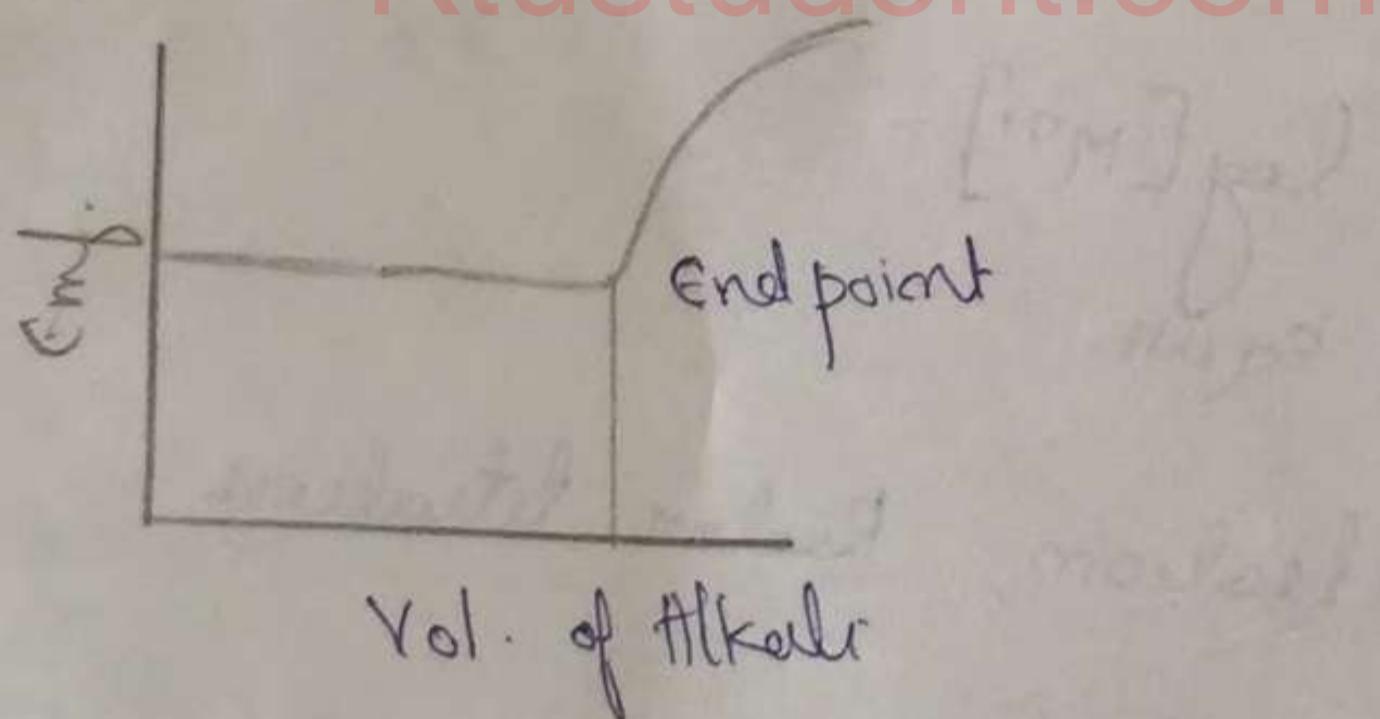
In acid-base titration calomel electrode is used as reference electrode & quinhydrone electrode as indicator electrode. The a electrometer is connected through a potentiometer & known.

Volume of acid is taken in the beaker. A quinhydrone electrode is dipped in it. A stirrer is also provided. In burette, we take alkali.

- Emf of the cell is measured after the each addition of alkali from the burette
- Here emf of cell gradually increases & at the end point there is a sudden increase in emf.

A graph is plotted Volume of alkali Vs Emf.

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From graph, there is a sudden increase in emf. so that point is taken as end point.

Redox titration

Oxidising agent against Reducing agent

Oxidise $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 .

Reducing - FeSO_4 .

Beaker - Reducing agent
Burette - Oxidising agent

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23/8/16
Tuesday

Spectroscopy

Spectroscopy is used to find out bond angle, bond length, bond strength, atomic strength, molecular strength.

The instrument used to study spectroscopy is spectrometer.

Types of spectra

Based on the nature of interaction they are classified in two:

(i) Absorption spectra.

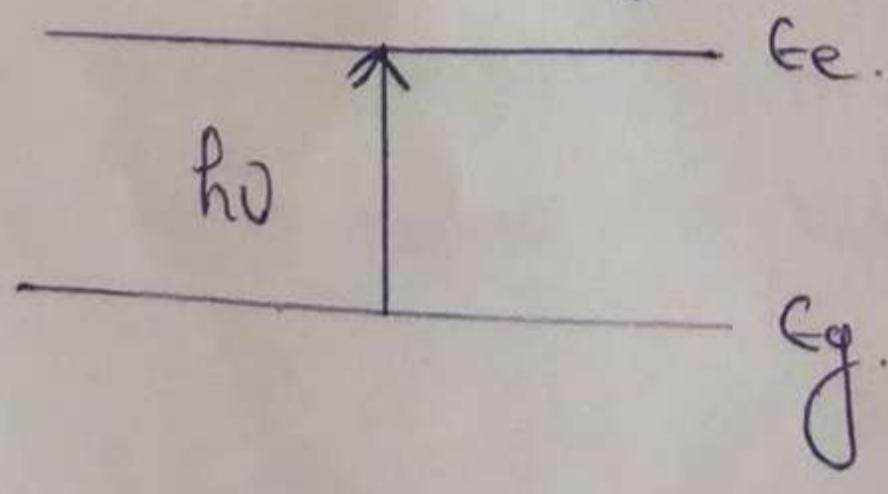
(ii) Emission spectra.

Absorption spectra

When an atom or molecule absorbs the photon of energy $h\nu$ they undergo transition from ground level to higher level.

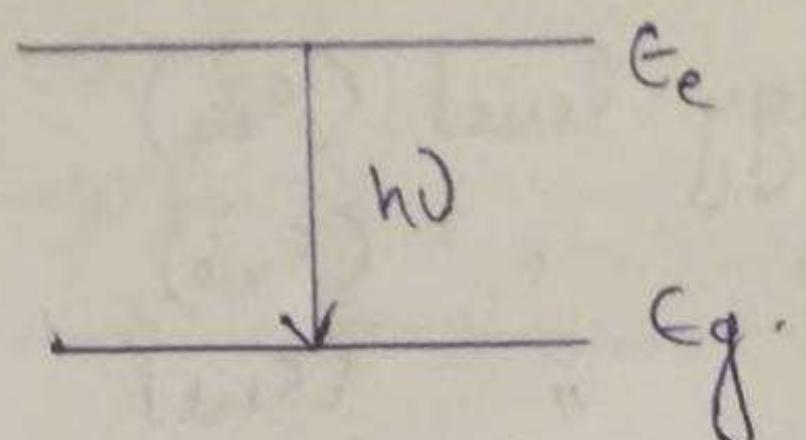
U.V, I.R, MICRO, NMR belongs to the

G.L. stat ↑



Emission spectra

A atom or molecule undergoes transition from higher level to lower level by emitting a photon of energy $h\nu$.



Hydrogen Spectra
fluorescent ..
atomic emission spectra.

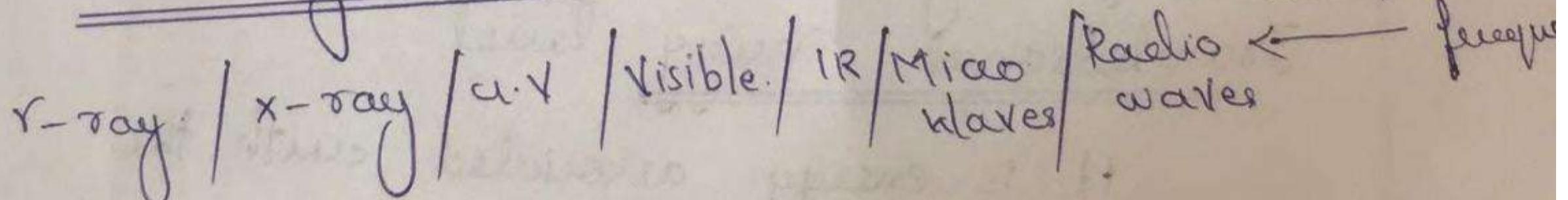
a) Based on the nature of interacting species.

- (i) Atomic spectra
- (ii) Molecular spectra

Atomic spectra
Transmissions occur at atomic & energy level.
atoms give rise to atomic spectra.

Molecular spectra
Molecules give rise to molecular spectra.
Emissions of \bar{e} occur at molecular energy level.

Electromagnetic Spectrum



$$\begin{matrix} R \rightarrow F \\ M \\ I \\ V \\ U \\ X \\ \checkmark \\ F \end{matrix} \quad c = \frac{hc}{\lambda}, \quad c = h\nu$$

$$\text{high } h = 6.623 \times 10^{-34} \text{ Js.}$$

it posses both particle nature and wave nature

Imp

Molecular Energy Level.

A single molecule posses 4 types of energy

- (i) Electronic Energy level (E_{ele})
- (ii) Vibrational. " " (E_{vib})
- (iii) Rotational " " (E_{rot})
- (iv) Translational " " (E_{trans})

Electronic Energy Level

- it is associated with the distribution of electrons in various energy levels.

Vibrational Energy Level

it is associated with the vibration of the molecule.

Rotational Energy Level

it is the energy associated with the spinning of the molecule about the axis of gravity.

Translational Energy Level

it is energy associated with the overall movement of molecule on 3 axis

$$E_{total} = E_{ele} + E_{vib} + E_{rot} + E_{trans}$$

$$E_{total} = E_{ele} + E_{vib} + E_{rot}$$

$$E_{ele} > E_{vib} > E_{rot} > E_{trans}$$

(lowest Energy)
 E_{trans}

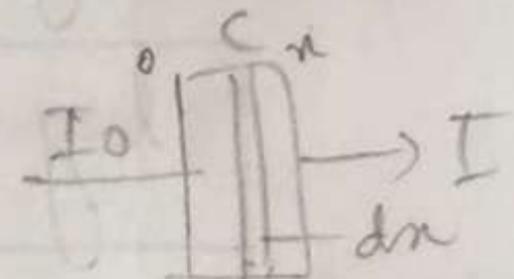
UV & Visible. using electronic energy level.

$E_{vib} \rightarrow I.R.$

$E_{rot} \rightarrow Far\ I.R.$

$E_{trans} \rightarrow Radio\ Waves.$

U.V spectrum appears broad. bcz when U.V is. spectrum is passed. E_{ele} , E_{vib} , E_{rot} , E_{trans} take place. the electronic energy is combined by



Beers - hamber's law

it states that when a parallel beam of monochromatic electromagnetic radiation is passed through an absorbing solution of concentration C . the rate of decrease in ~~is~~ the intensity ($-dI$) with respect to thickness of sltn (dn). is proportional to the intensity of incident light & Concentration of the solution.

$$-\frac{dI}{dn} \propto IC.$$

$$-\frac{dI}{dn} = KIC \dots$$

$$-\frac{dI}{I} = KC dn.$$

$$-\int \frac{dI}{I} = KC \int dn.$$

$$\left[-\log I \right]_I^I = KCn:$$

$$-\log I - \log I_0 = KCn$$

$$\log I_0 - \log I = kcn$$

$$\ln I_0 - \ln I = kcn$$

$$\ln \left(\frac{I_0}{I} \right) = kcn$$

$$2.303 \log \left(\frac{I_0}{I} \right) = kcn$$

$$\log \left(\frac{I_0}{I} \right) = \frac{kcn}{2.303}$$

$$\boxed{\log \left(\frac{I_0}{I} \right) = \epsilon cn}$$

$$\epsilon = \frac{k}{2.303}$$

$\epsilon \rightarrow$ Molar absorption coefficient / Molar extinction coefficient.

$$A = \log \left(\frac{I_0}{I} \right)$$

Absorbance.

$$A = \log \left(\frac{I_0}{I} \right)$$

Absorbance is defined as the logarithm of ratio of

Intensity of incident light to transmitted light.

$$\boxed{A = \epsilon cn}$$

Transmitted

$$T = \frac{I}{I_0}, \text{ defined as the ratio of}$$

intensity of transmitted light to the intensity of incident light.

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U.V - Visible Spectroscopy (electronic spectroscopy)

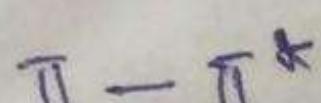
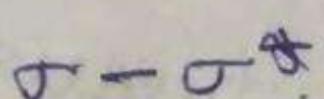
When the e of a molecule are existed from lower energy state to higher energy state or vice versa. electronic spectrum is obtained since the energy involved in this process is large. electronic spectra usually occurs in U.V - Visible reaction.

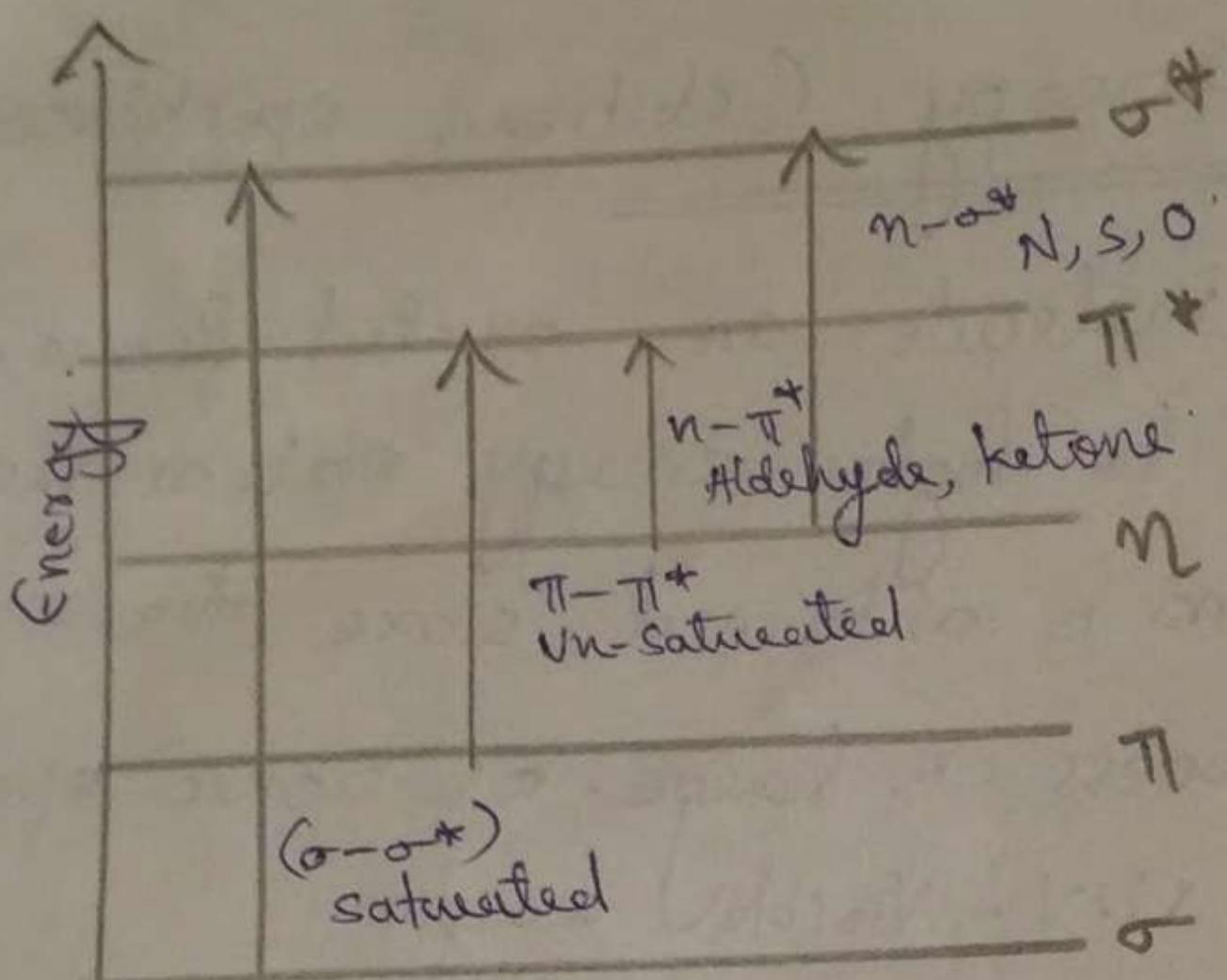
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+ discrete light is not obtained in the case of electronic transmission. bcz electronic transmission is accompanied by vibration & rotational energies so. a group of various band is occurs. U.V spectroscopy is used to detect multiple bond conjugated system. aromatic nucleus.

Types of Electronic Transmission.

When a molecule absorb energy in U.V visible reaction its electron are promoted from bonding M.O to Anti molecular M.O. 3 types of es are involved in this process. they are σ , π , n (non-bonded e) for σ & π es. if have both. both bonding & Anti bonding molecular orbitals.

The electronic transmission are of 4 types





Electronic Transmission.

$\sigma-\sigma^*$ transmission.

Saturated hydrocarbons give $\sigma-\sigma^*$ transmission.
this transmission occurs below 150 nm. but
ordinary UV spectra occurs at 200-300 nm
so, saturated hydrocarbon cannot produce UV spectra.

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$\pi-\pi^*$

Unsaturated hydrocarbon having $=\sigma\equiv$ show
this type of transmission. In the case of molecule
containing double bond transmission due
 $n-\pi^*$ from HOMO to LUMO
The compounds which contains both π es &
non bonded e⁻ shows

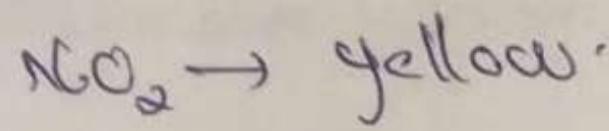
Ex: Aldehydes, ketones etc.

$n-\sigma^*$

Compounds containing N, S, O which contain
non bonded e⁻ shows this type of transmission

Chromophores

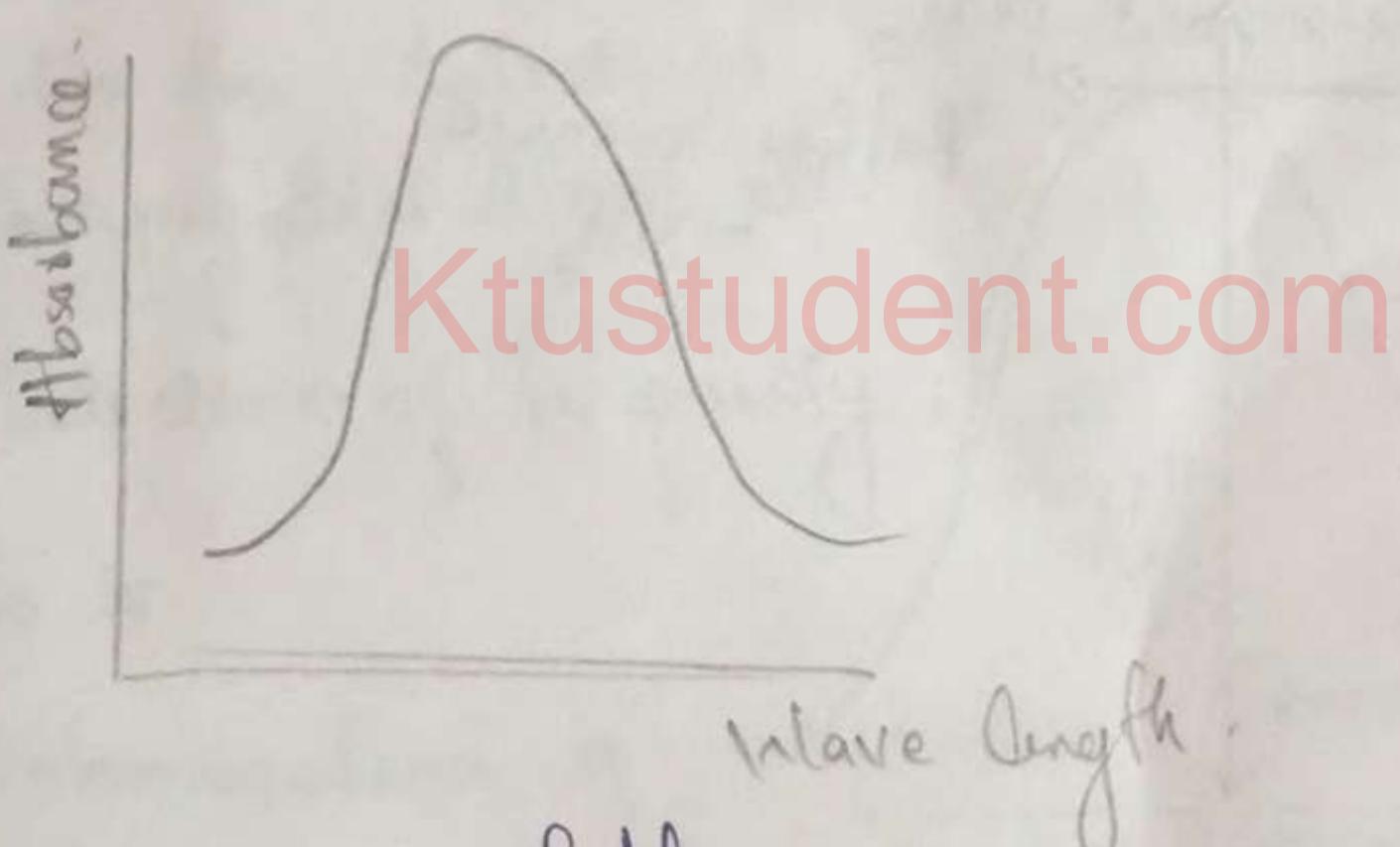
This are the group which gives colour to the compound.



Auxochromes

This group doesn't give colour to the compounds. Ex: -OH, -SH, -OR. But others.

Auxochromes is attach to chromophores if it enhance the colour of a compound.



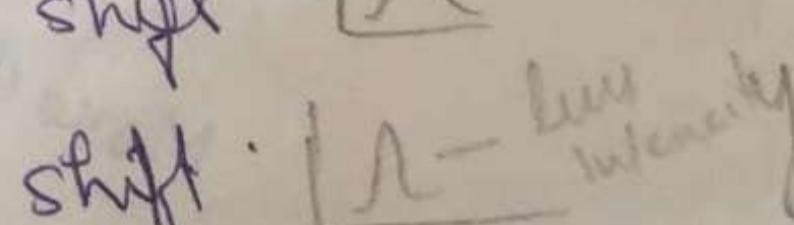
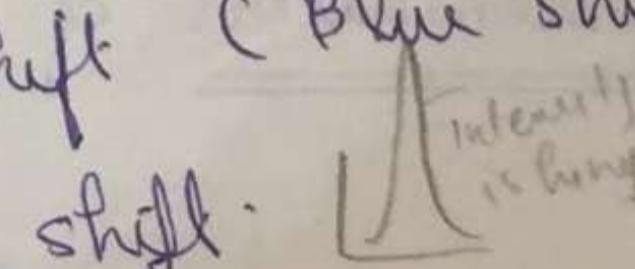
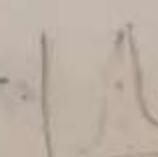
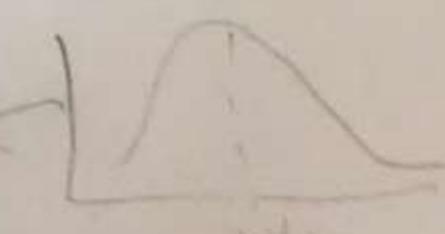
4 types of shift

(1) Bathochromic shift (Red shift)

(2) Hypsochromic shift (Blue shift)

(3) Hyperchromic shift

(4) Hypochromic shift



Bathochromic shift

A shift of absorption towards longer wavelength is more.

A shift of absorption towards longer wavelength is called Batho chro. -NH₂.

Hypsochromic shift

shift is toward the shorter wavelength.

If carbonyl group is attached to the molecule.

Hyperchromic shift

If the peak intensity increases that shift is.

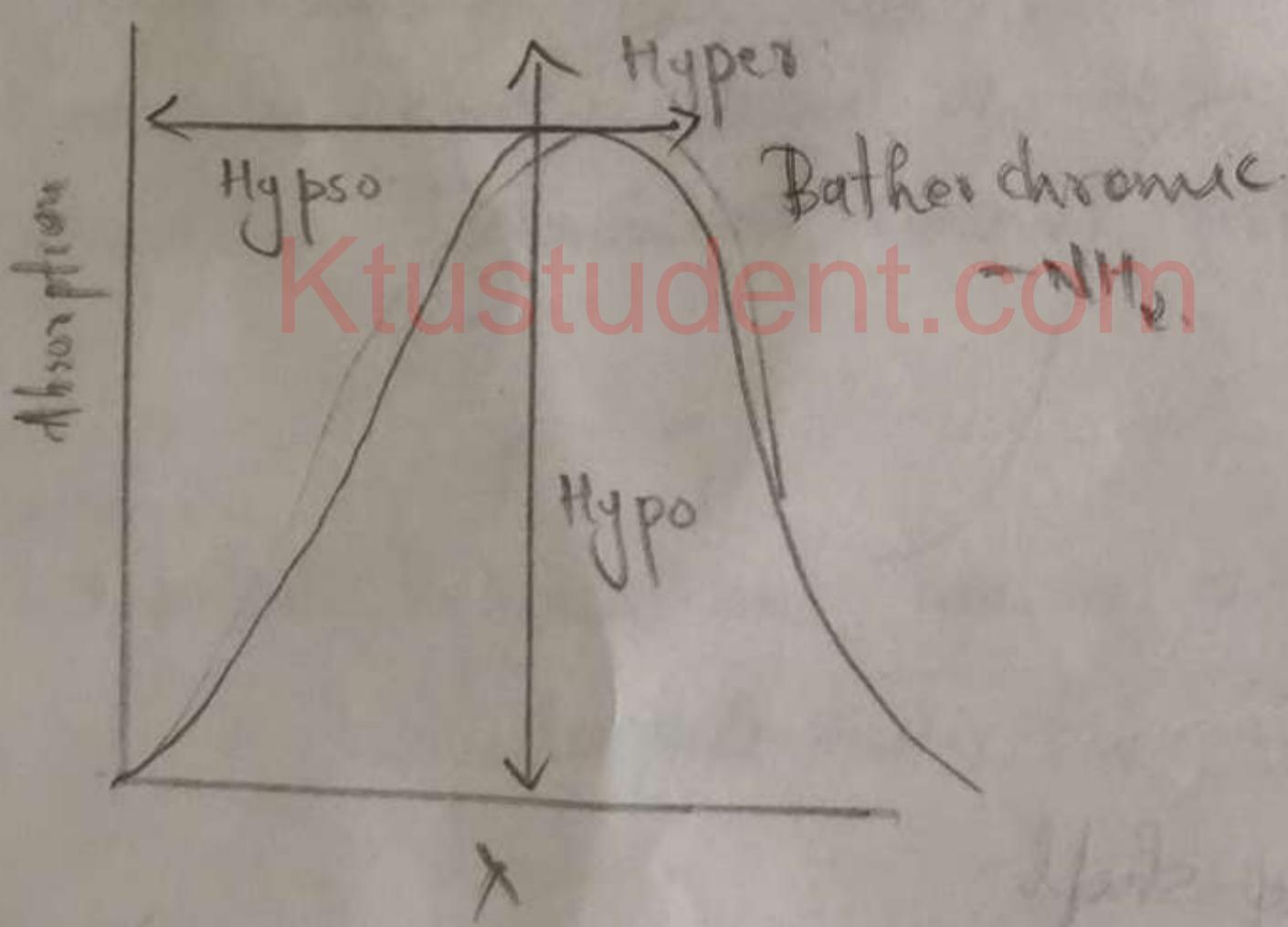
Hyperchromic shift

→

Hypochromic shift

The peak intensity decreases that shift is.

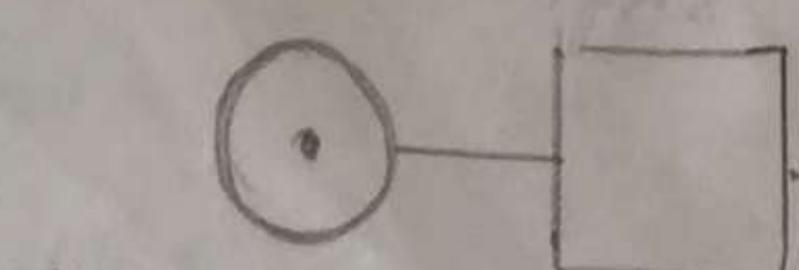
Hypochromic shift



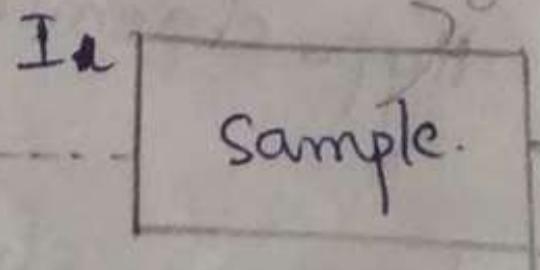
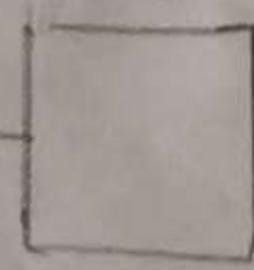
Instrumentation of U.V Visible spectroscopy

Principle
Components

Monochromator



Light Source

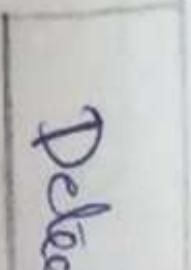


I_a

Sample

I_o

Reference



Detector

Rec.

U.V. Absorption
e. Name descent gile
other short, scattered

light source can be. Tungsten filament lamp,
 H_2 - discharge lamp, Xenon - Kerosene flash lamp.

Monochromator (prism, grating)

Most of the instruments are (double-beam light) Apparatus

Solvent can be water, ethanol, cyclohexane.

Reference cuvette we take pure solvent.

If Sample is absorbed $I < I_0$.

If Sample is not absorbed $I = I_0$.

iii Application of U.V. Spectroscopy

- for the detection of aromatic compounds,
- Conjugated diene etc.
- Detection of Impurity.

to to

- Determination of unknown Concentration
- Determination of molecular weight of a compound for the study of chemical rxn.

IR (vibrational spectroscopy)

it occurs due to the change in dipole moment.

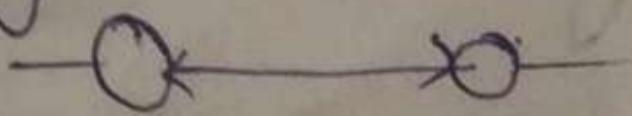
vibrations are 2 types.

(i) stretching vib

(ii) bending "

Stretching

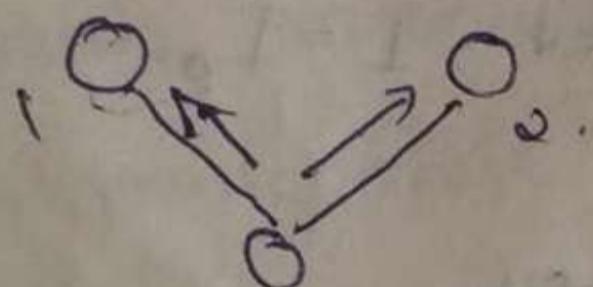
The distance b/w 2 atoms increases or decrease along the same axis. bond angle doesn't change.



stretching are classified into two.

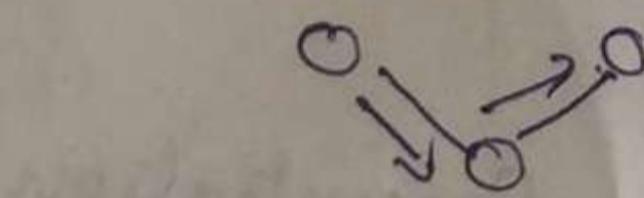
(i) symmetric stretching vibration

here the motion of 2 atoms with respect to the central atom is in same direction.



(ii) Asymmetric stretching

One atom approaches the central atom & other move away from the central atom.



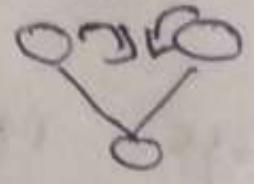
(iii) bending vibration

The bond angle changes due to the motion of atoms. There are 4 types of bending.

- Scissoring
- Rocking
- Wagging
- Twisting

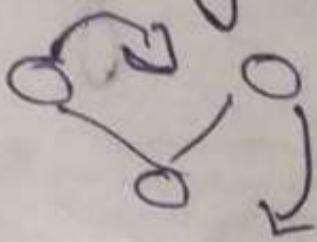
a) scissoring.

In the case of scissoring, 2 atoms approaches each other.



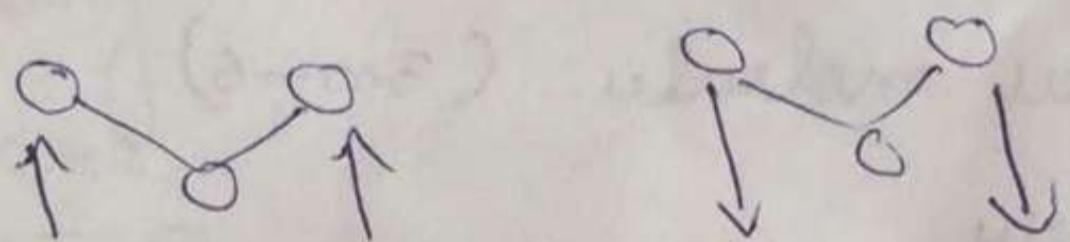
b) Rocking.

In rocking the 2 atoms move in same direction i.e., in clockwise direction.



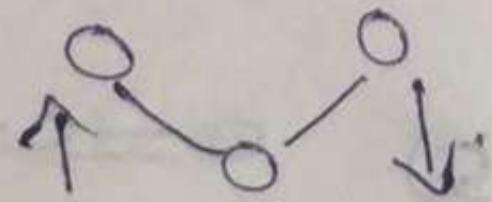
c) wagging

In case of wagging, 2 atoms moves apudal. or downwards simultaneously with respect to central atom.



d) Twisting.

In case of Twisting one atom moves apudal of other moves down wards with respect to central atom.



- stretching requires more energy than that of bending vibration.

Homonuclear diatomic - IR inactive.

they have no dipole moment. & so they all.

IR inactive ex: H_2, N_2, O_2 .

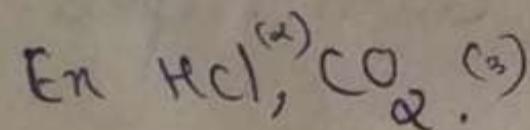
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Heavy Nuclear diatomic.

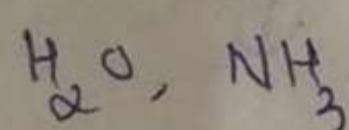
they have dipole moment in case of HCl.
 & hence one has more negative charge i.e. H will
 have δ^+ & Cl will have δ^- . due to IR radiation
 dipole moment changes. Hence they are
 IR active.

No. of Vibrational modes in a molecule.

($3n - 5$) degrees of freedom
 for linear molecule ($3n - 5$)



Non linear molecule. ($3n - 6$)



$n \rightarrow$ no. of atoms

HCl ($3n - 5$)

$$3 \times 2 - 5 = \underline{\underline{1}} \quad n=2$$

1 stretching vibration

$$\text{CO}_2 \quad (3n - 5) \quad \text{O}=\text{C}=\text{O}$$

$$3 \times 3 - 5 = \underline{\underline{4}} \quad 3 \times 3 - 6 = \underline{\underline{3}}$$

symmetric.

Asymmetric.

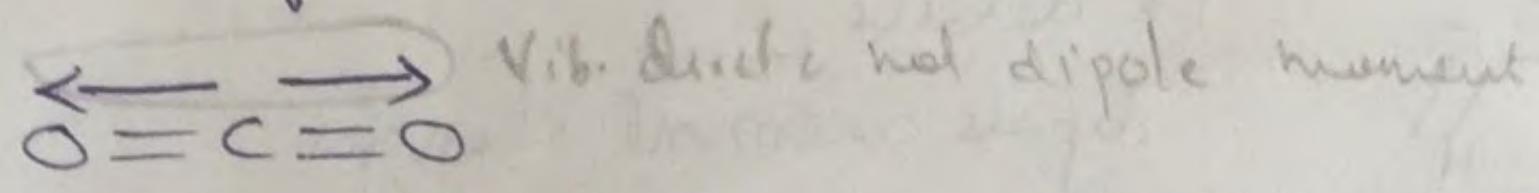
$$= \underline{\underline{2}}$$

i.e., 2 for stretching & 2 for bending

for stretching it should be symmetric, Asymmetric.

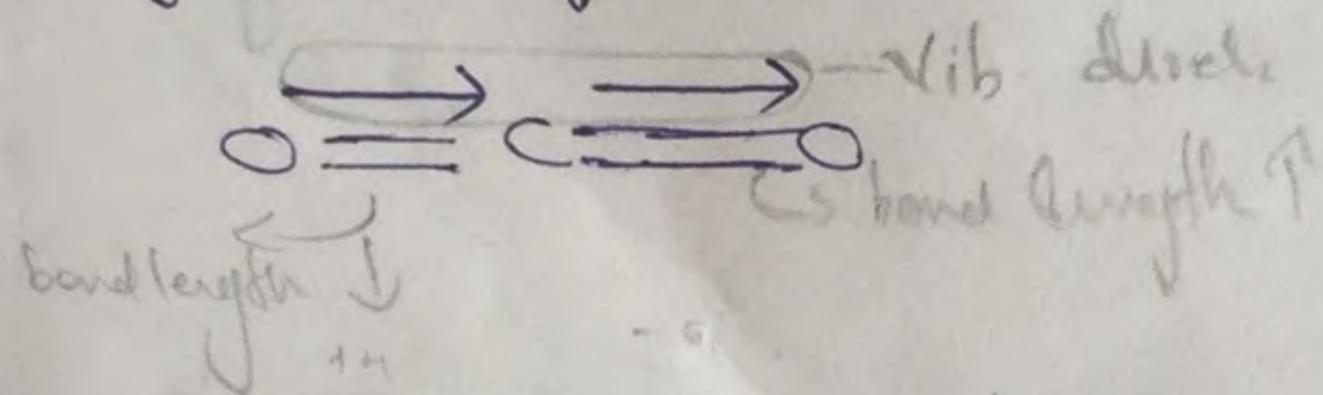
bending \rightarrow in plane, Out plane.

• Symmetric of CO_2 .



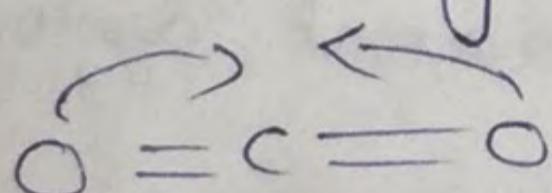
In the case of symmetric vibrations. CO_2 is inactive.
ie, IR. inactive (they cancel each other)

• Asymmetric of CO_2 .



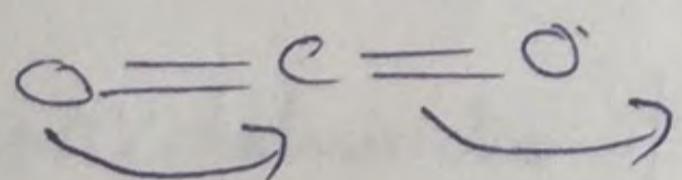
These is change in dipole moment. \therefore it is IR active.

• In plane bending.



change in dipole moment
IR active.

• Out plane bending.



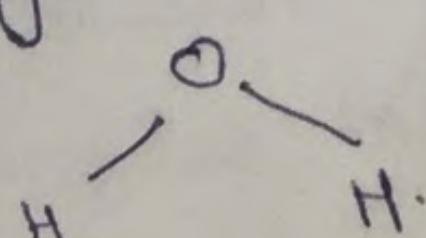
IR active. change in bond angle \Rightarrow dipole moment.

• H_2O

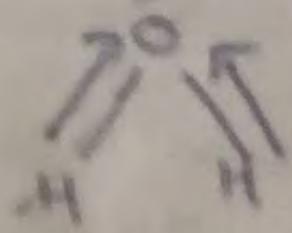
$3m - 6$

$$3 \times 3 - 6 = \underline{\underline{3}}$$

2 stretching, 1 bending.



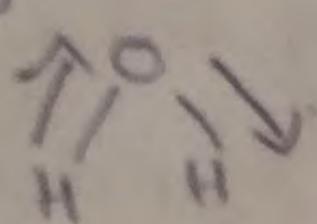
Symmetric



I-R active

dipole moment changes.

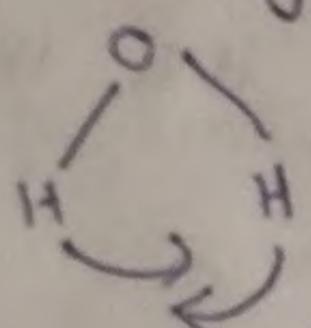
Symmetric



I-R active

dipole moment changes.

Bending



I-R active

dipole moment changes.

Vibrational Energy of Dipole moment diatomic molecule

for diatomic molecule.

k = Constant force

$$\omega = \frac{1}{2\pi} \sqrt{k/M} \quad M = \text{Reduced Mass}$$

$$\omega_0 = \frac{1}{2\pi} \sqrt{k/M} \quad \text{if } \omega = \omega_0$$

$$\boxed{\omega = \frac{1}{2\pi c} \sqrt{\frac{k}{M}}}$$

fundamental vibrational
wavenumber $\nu_0 = \bar{\omega}$

$$M = \frac{m_1 m_2}{m_1 + m_2}$$

Application of I-R

Determination of Molecular structure

to study bond length, bond angle etc

Detecting Impurities In the Sample.

To distinguish b/w the isomers & India molecules.

Hydrogen bonding-

Study of Coordination Compounds

Identify Unknowns

Identify functional groups In Organic molecule

King

H¹NMR (Nuclear Magnetic Resonance)

NMR spectroscopy involves the transition of a nucleus from one spin state to another with the absorption of electromagnetic radiation by a spin active nuclei when it is placed in a external magnetic field.

Ans
of
see
for
ex
(c)

• NMR spectrum is produced by the interactions of radio frequency waves.

• Spin active nuclear means the spin quantum number value > 0 .

• NMR deals with the nuclei having spin no (I)

$$I = \frac{1}{2}$$

• the I value = $\frac{1}{2}$ is for nucleus for mass number.

odd

For a Nucleus to be magnetic it must possess spin angular momentum $\geq \frac{\hbar}{2\pi} \int I(I+1)$

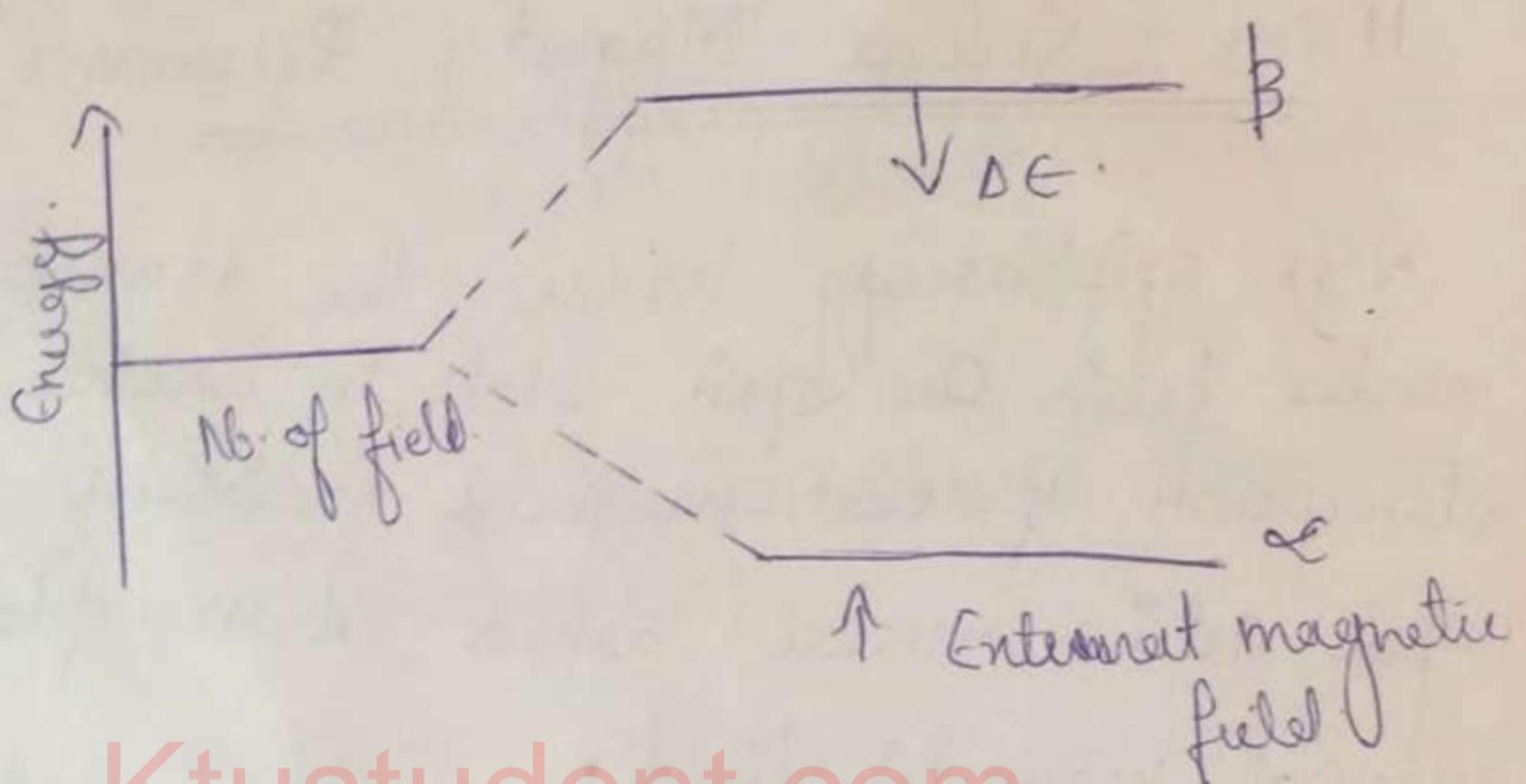
h = Planck's Constant

I = Spin number.

for a nucleus of spin I it have $2I+1$ orientation

Ex: if $I = \frac{1}{2}$, 1H , ${}^{13}C$ the orientation is 2.

In the absence of external magnetic field this 2. orientation has same energy. when a magnetic field is applied. the energy level split



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without an external magnetic field. the nuclear spins are random in all direction but when a external magnetic field is applied the nuclei align themselves either with or against the direction of external magnetic field. & form 2 energy level α & β . here an energy term for $ΔE$ is possible b/w ground state & excited state.

When the spins returns to its ground

state level. the energy of absorbed

radio waves is emitted. The emitted radio

frequency signal gives the NMR spectrum

of the nucleus:

The emitted radio frequency is proportional to the applied magnetic field.

$$\nu \propto B_0$$

$$\nu = \frac{r}{2\pi} B_0, \text{ this frequency is called.}$$

Larmor frequency.

The paramagnetic nuclei from 1 spin.

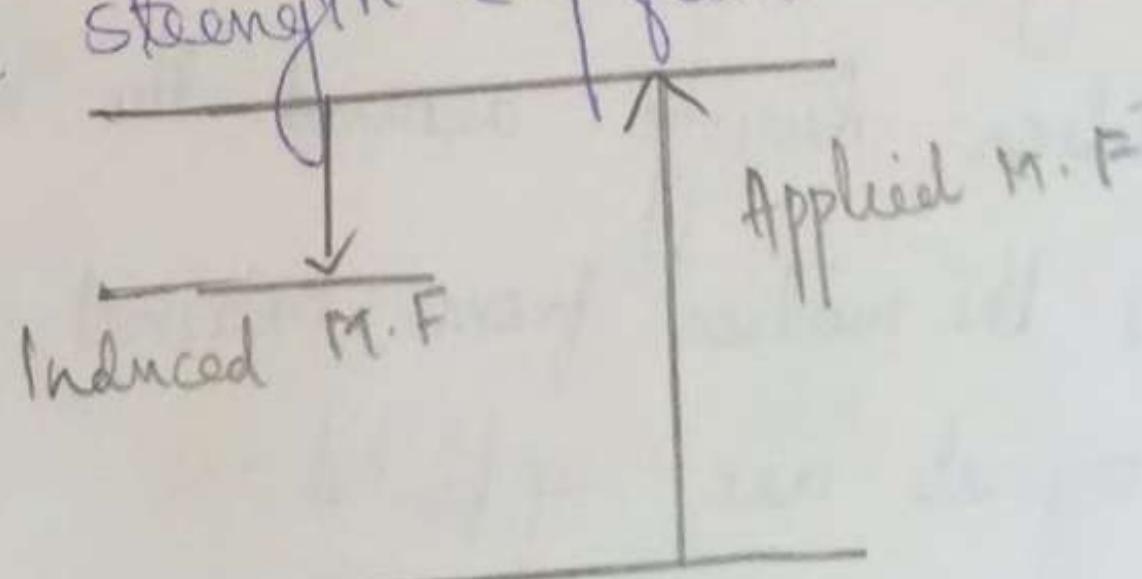
state to another is called flipping. Here the nuclear becomes excited & unexcited & it is said to be in the state of resonance.

chemical shift

When a molecule is placed in a external magnetic field its electrons are forced to circulate & produce secondary magnetic field or induced magnetic field. This induced m.f may oppose or reinforce the applied magnetic field.

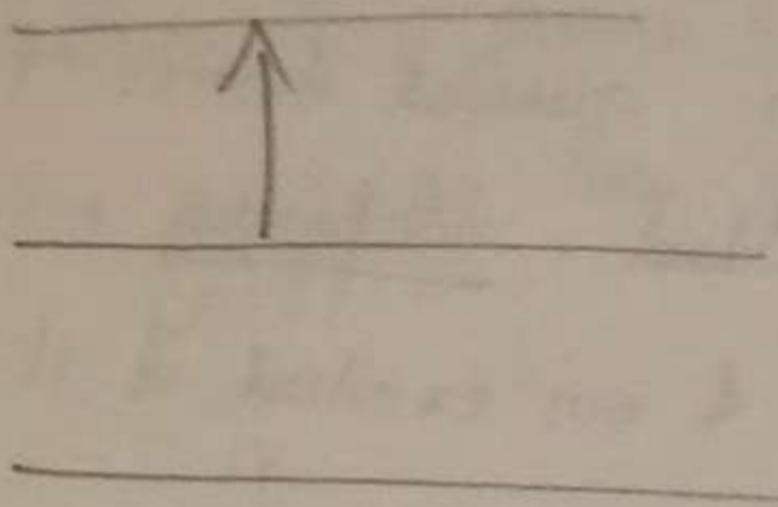
shielding

If the induced m.f opposes the of applied field the net field felt by a proton will be less than the applied field & here the proton is said to be shielded proton. A shielded proton absorb R.F radiation at higher field strength (up field)



Deshielding

If the induced M.F reinforces the applied M.F then the net field felt by proton will be greater than the applied M.F & the proton is said to be deshielded. Deshielded proton absorb R.F radiation at lower field strength.

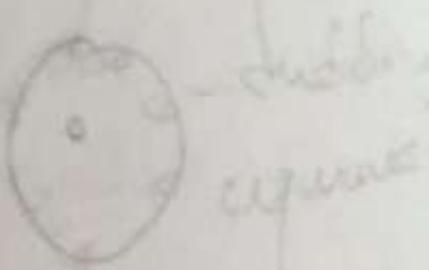


The shift in frequency which depends upon the chemical environment of proton is called shift. The chemical shift is defined as resonance frequency different from frequency of Sample peak or of tetra methyl silane $[(CH_3)_4 Si]$.

TMS.

Is a Reference Compound bcz the protons of TMS are more shielded than all other Organic Compounds so all the signals of the sample appear at lower field than that of TMS.

- Deshielding \uparrow chemical shift \uparrow
- if the electron density around the nucleus \uparrow it shields the nucleus from external M.F
if the signals are upfield.



- If the ϵ density around nucleus \downarrow H shields the nucleus from external M.F. \downarrow . signals are downfield

Factors Effecting Down chemical shift

- presence of electro negative group. \rightarrow ^{afford} molecule \downarrow take.
 - the chemical shift \downarrow is also \uparrow CH ^{plan} \downarrow if electropo-ve group is attached to. \downarrow ^{dist} \uparrow if group the electro density around proton (H) \downarrow & here deshielding \downarrow & chemical shift \uparrow
- $\text{F} > \text{Cl} > \text{Br} > \text{I}$
- CH-Cl close
 (H) density
 \downarrow \downarrow

(ii) Magnetic Anisotropy of π -es.

If there is π -es in a molecule it interact with the M.F. & create a magnetic anisotropy so the shielding & deshielding take place.

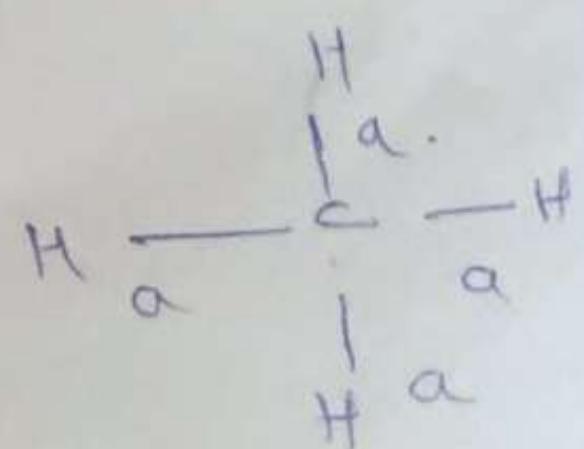
(iii) Hydrogen Bonding

If hydrogen bond is present in a molecule the protons are deshielded \downarrow so the chemical shift is also high.

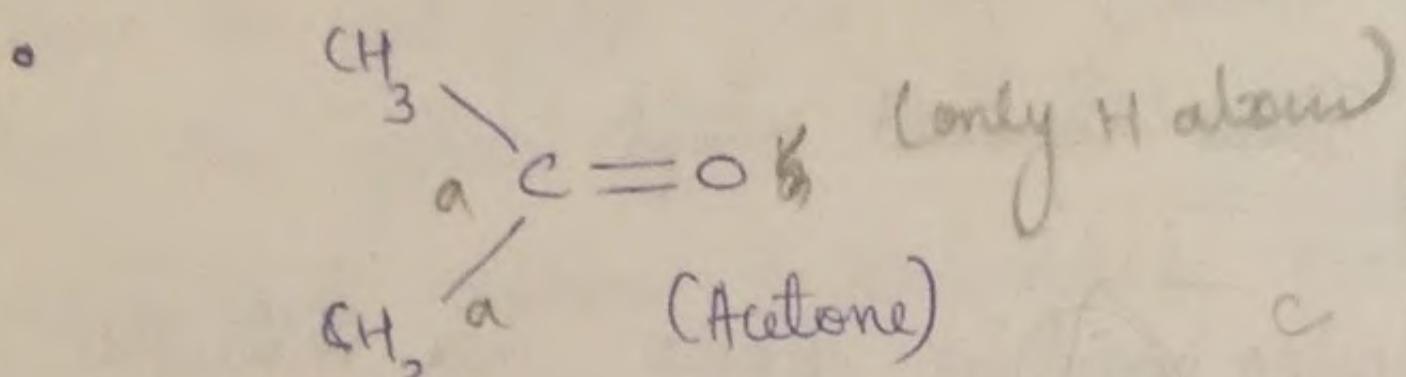
No. of Signals

The No. of Signals will give how many different types of protons in a molecule.

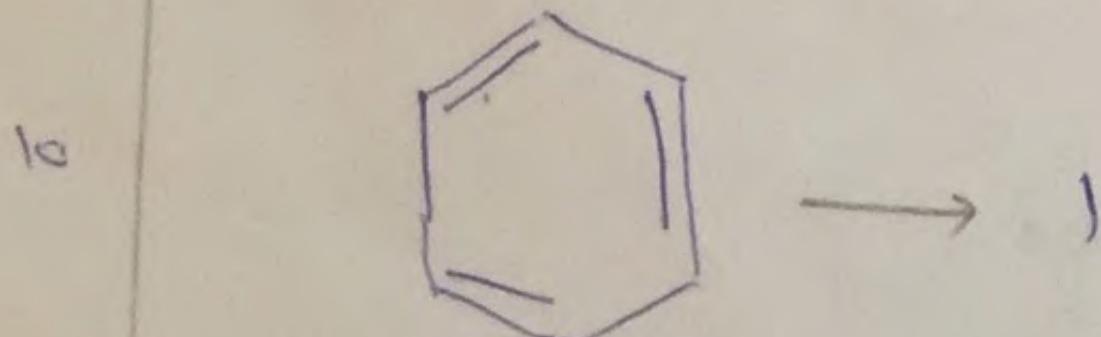
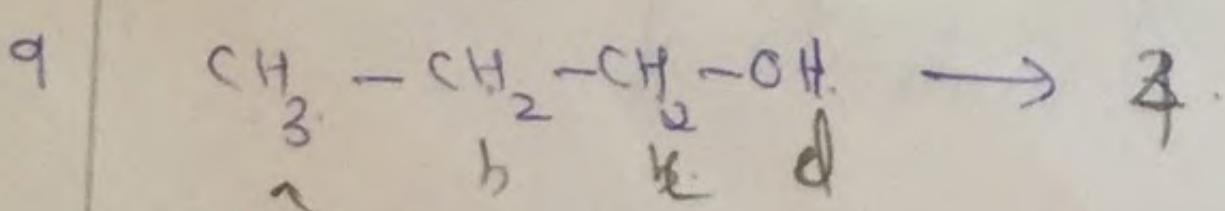
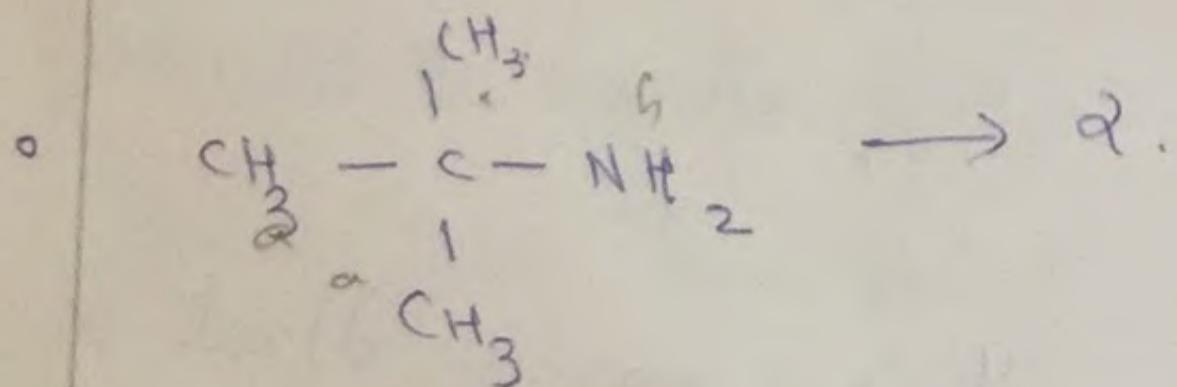
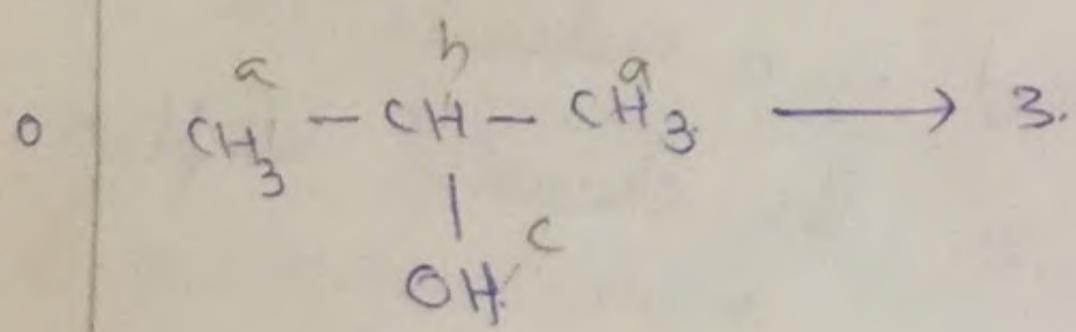
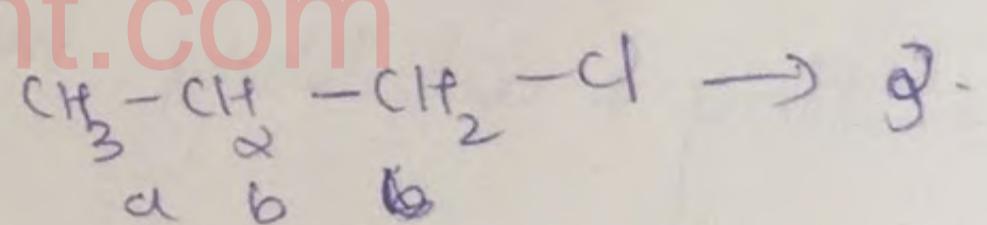
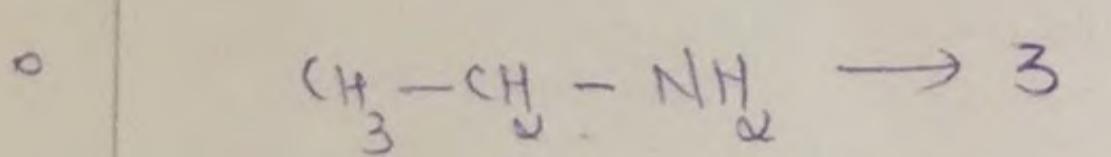
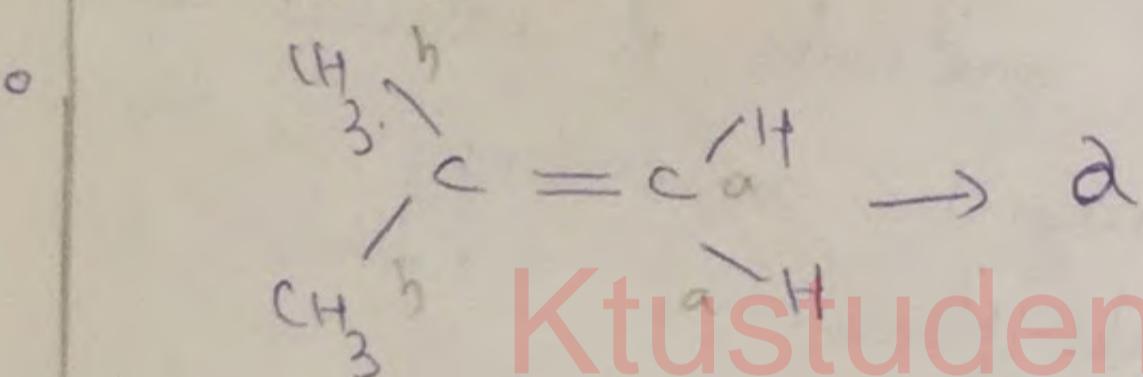
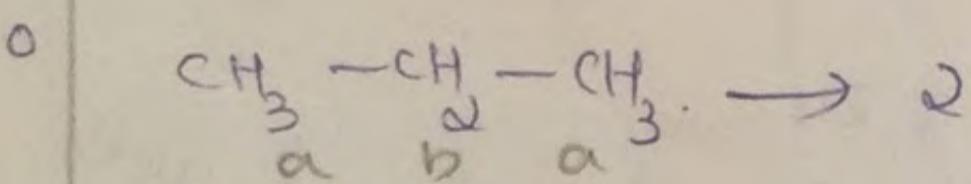
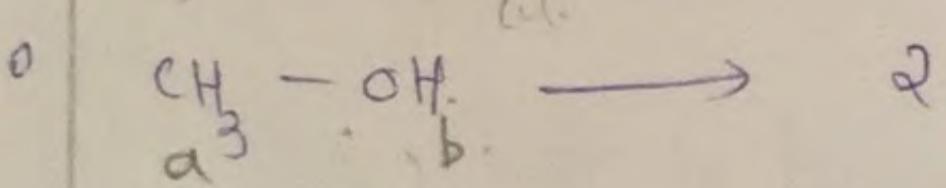
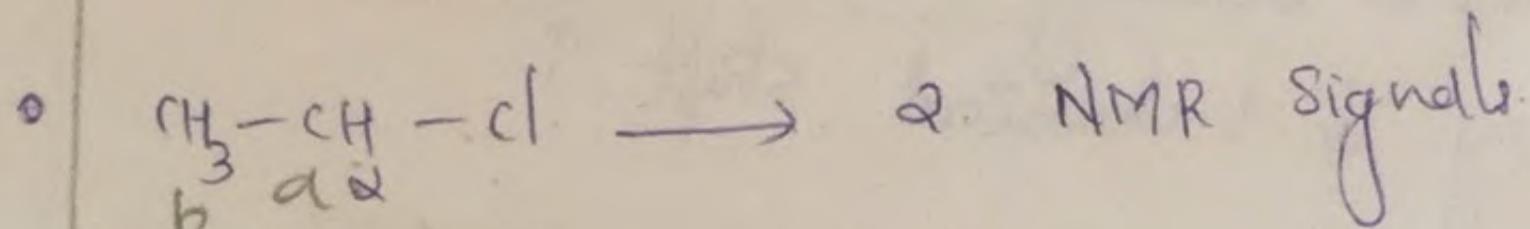
Ex: CH_4



In methane all H atom have only 1 NMR signal

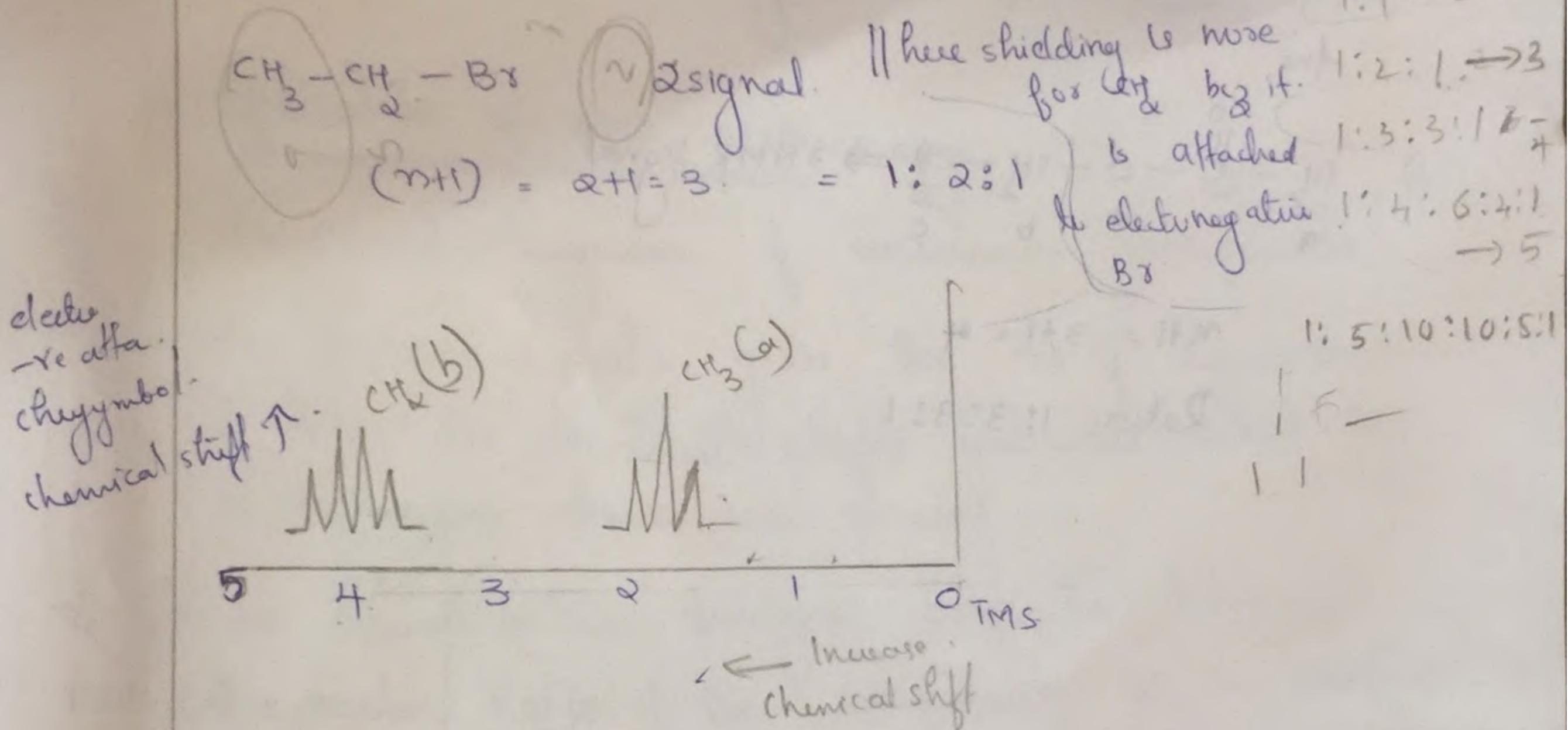


Only 1 NMR signal

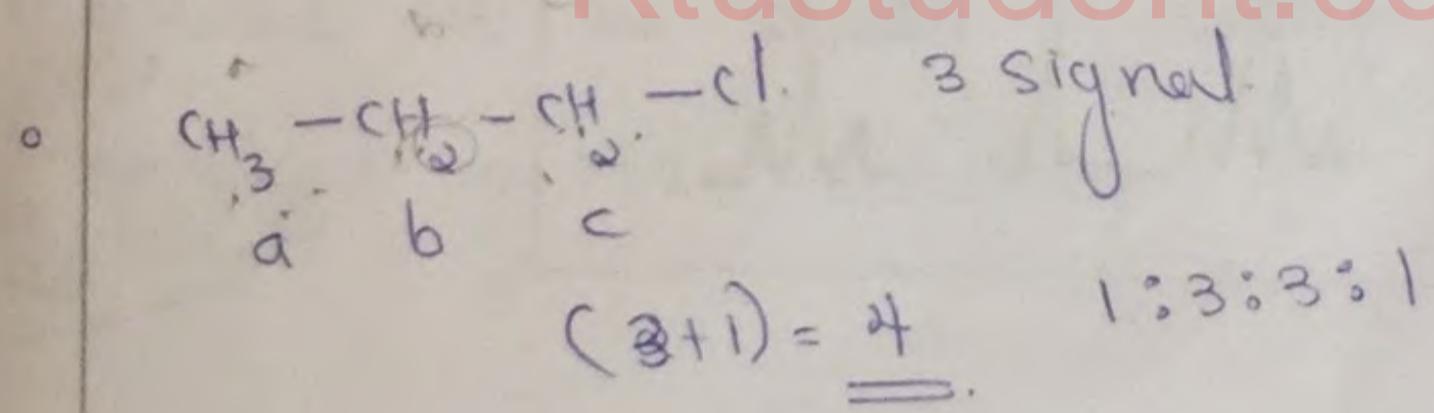


Splitting of NMR

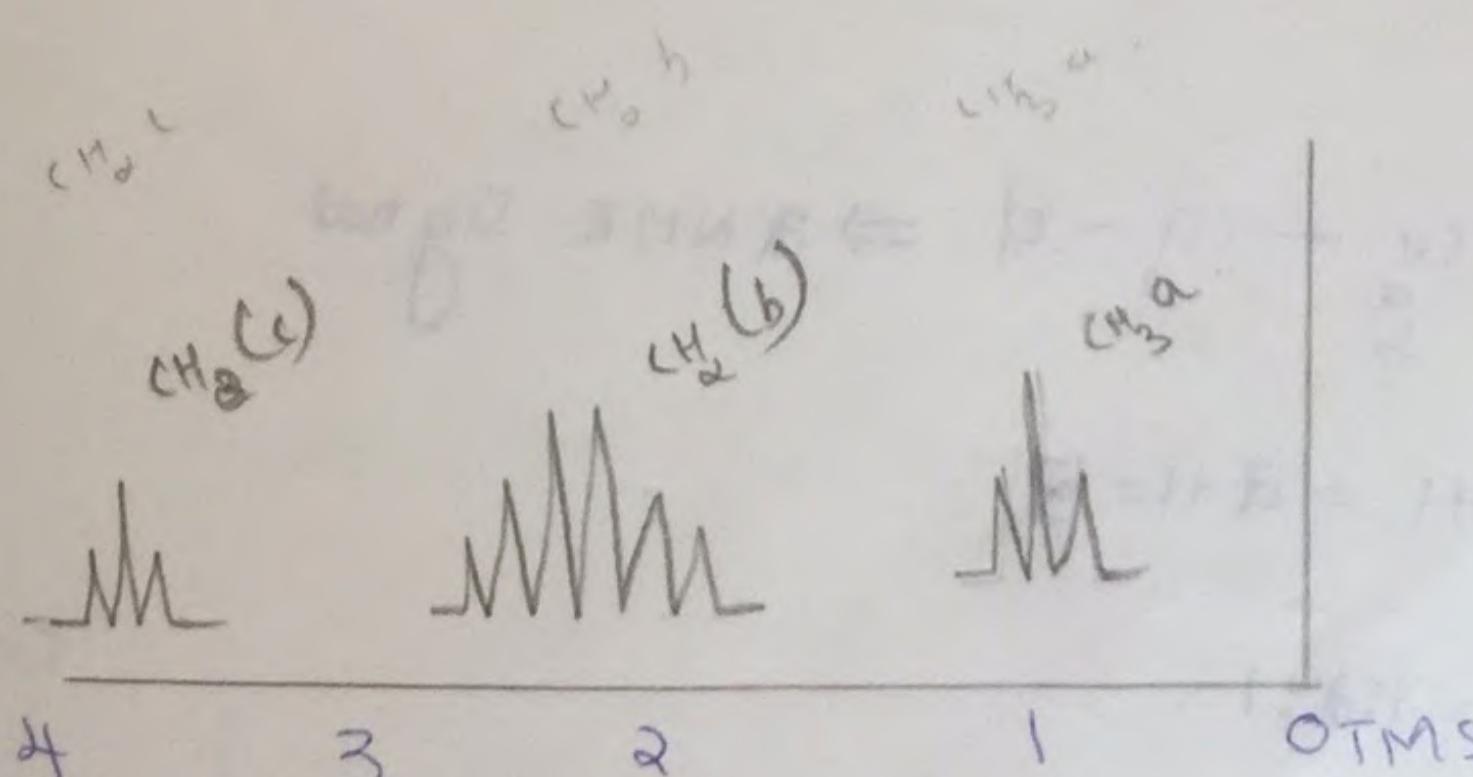
spin - spin splitting (spin - spin splitting)



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$\text{CH}_3 \rightarrow$ Neighbour proton



Height

$\text{CH}_3(\text{a}) \rightarrow 2\text{proton}$

$(\text{CH}_2(\text{b})) \quad \alpha+\beta=3$

$(\text{CH}_2(\text{c}))$

thus ratio $1:2:1$

$\text{CH}_2(\text{b}) \rightarrow n\text{ proton}$

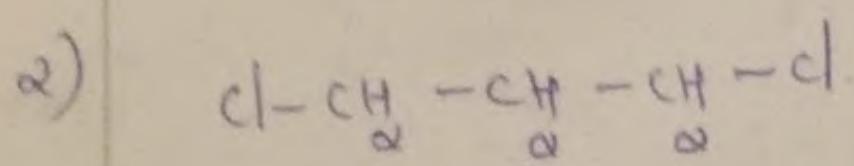
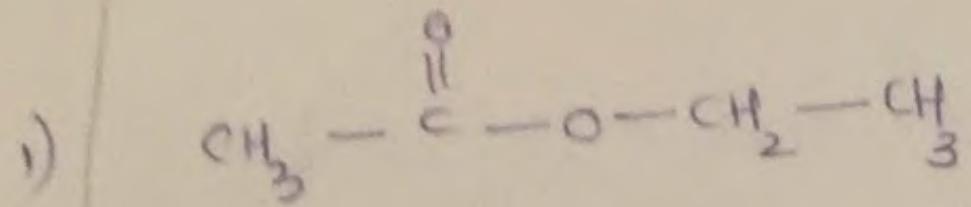
$= \alpha+\beta = 3\text{ signals}$

$1:5:10:10:5:1$

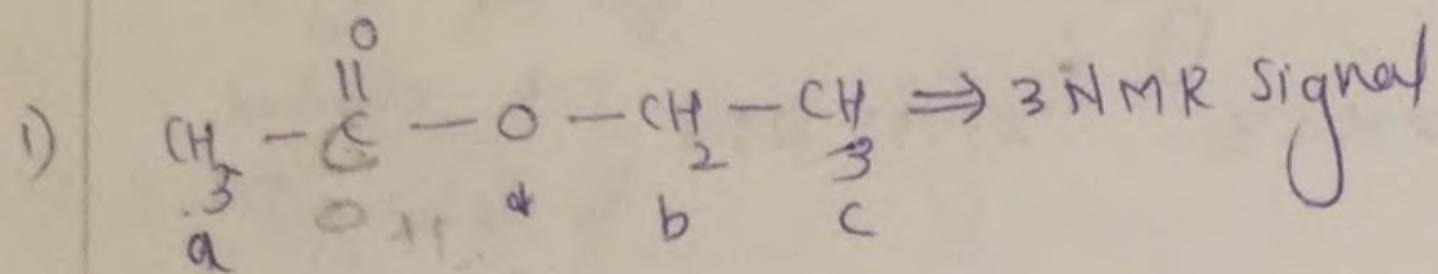
$\text{CH}_2(\text{a}) \rightarrow 2\text{ proton}$

$\alpha+\beta=3\text{ signals}$

$1:2:1$



Ans

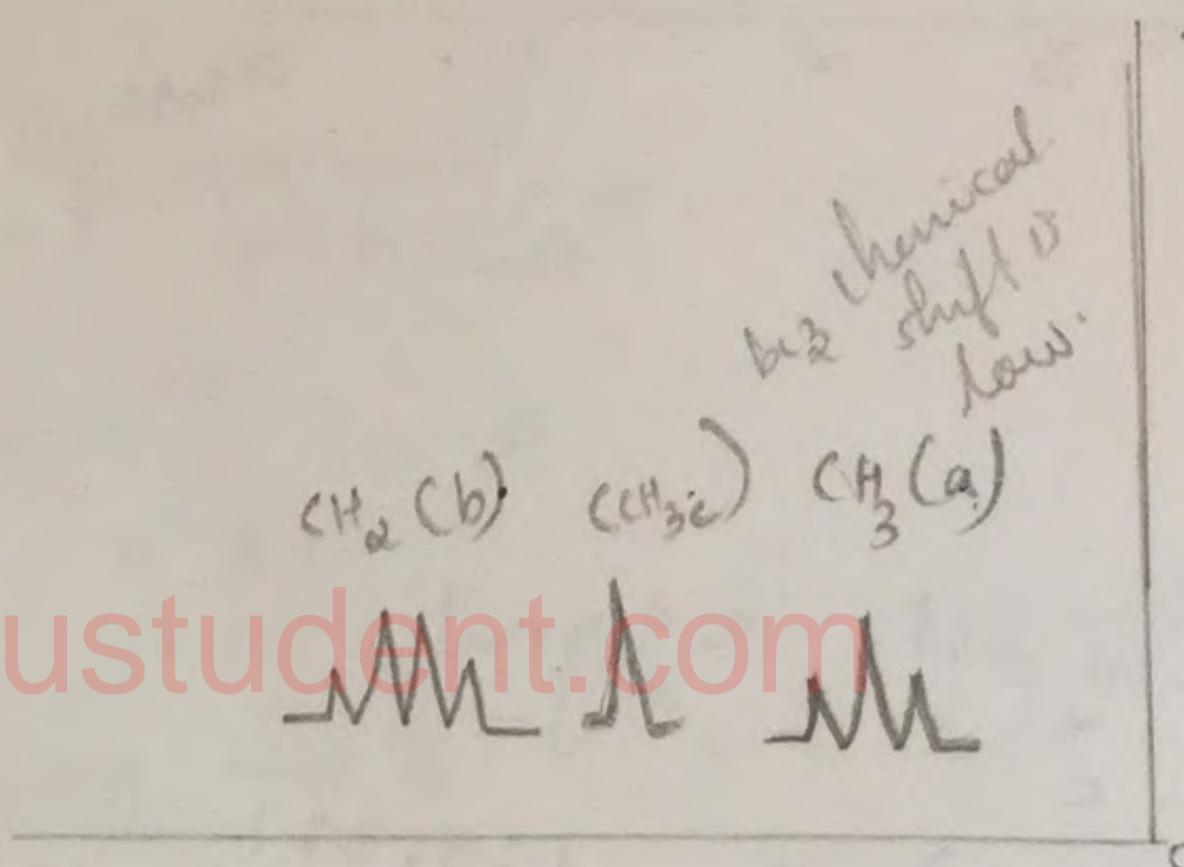


$$n+1 = 3+1 = 4$$

Ratio 1:3:3:1

Oxygen
singlet
bent shape

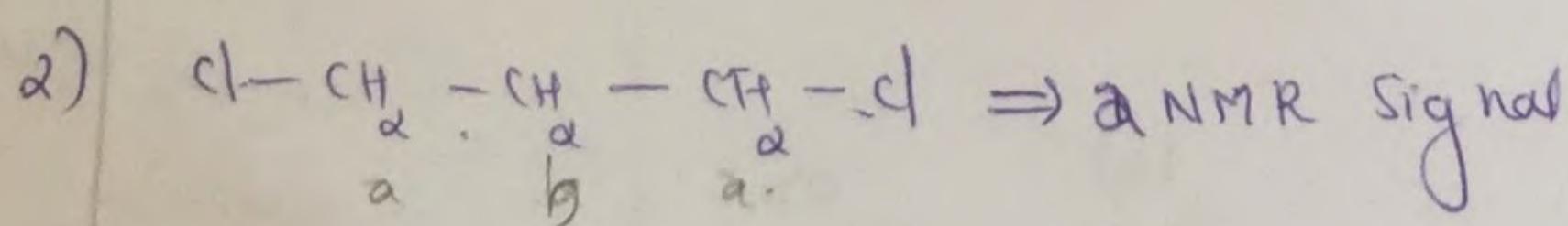
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TMU

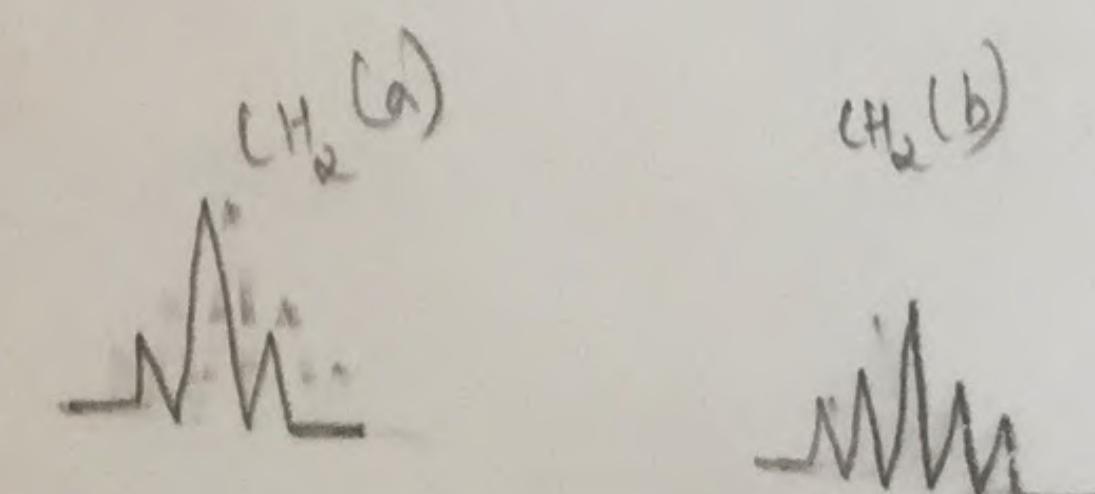
$$\begin{aligned} & \text{CH}_3(\text{a}) - 1:2 \\ & \text{CH}_2(\text{b}) \quad 3\text{H} = 4 \\ & \text{CH}_2(\text{c}) = 2\text{H} \\ & \text{Total} = 7\text{H} \end{aligned}$$

1:3:3:1



$$n+1 = 2+1 = 3.$$

Ratio = 1:2:1



$$\begin{aligned} & \text{CH}_2(\text{a}) \\ & = 2+1=3 \end{aligned}$$

$$\begin{aligned} & \text{CH}_2(\text{b}) \\ & = 2+2 = 4 \\ & = 5 \end{aligned}$$

Coupling Constant (J)

The distance between 2 peaks in a multiplet denoted by letter (J). Unit is Hertz.

Application of NMR Spectroscopy

- Structural diagnosis of unknown Compounds
- No. of NMR signals gives the no. of equivalent Protons. The chemical shifts indicate what type of hydrogen atoms are present
- In Quantitative analysis, helps to determine the molar ratio of the components in a mixture
- Used in the study of hydrogen bond.
- Used in the study of isotopes
- Used in MRI Scanning

Minuvalar S.
R.A.

MODULE III

INSTRUMENTAL METHODS

1. THERMAL ANALYSIS

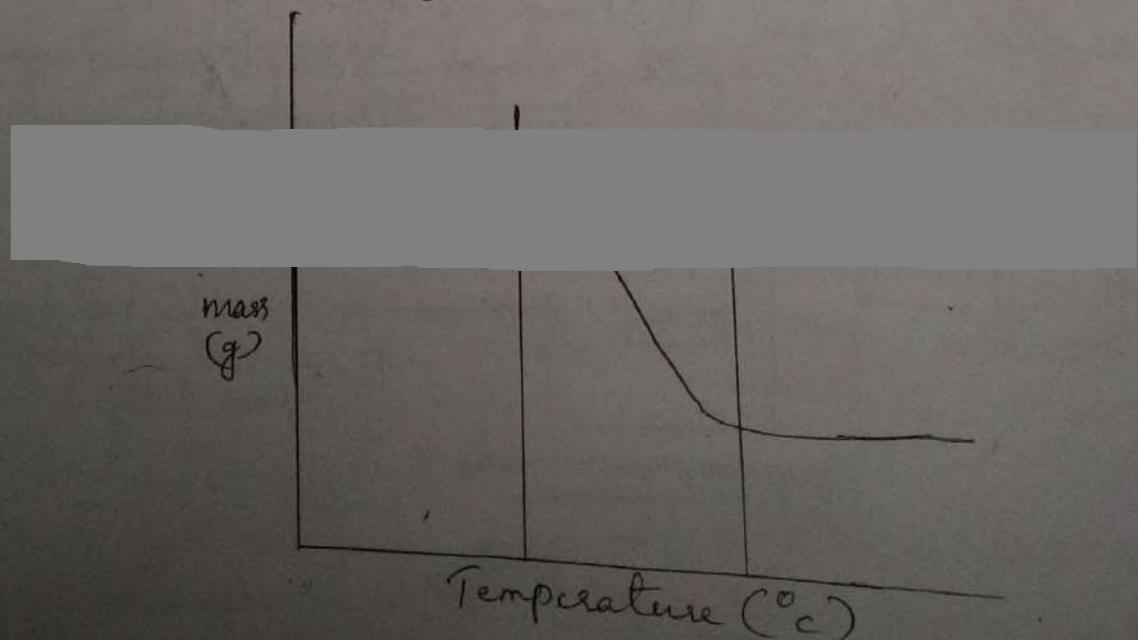
These methods are based on the measurement of dynamic relationship between temperature and any one of the property such as mass change or heat change etc.

1.1. THERMOGRAVIMETRIC ANALYSIS

It is a technique in which the mass of a substance is monitored as a function of temperature, as the sample is heated from room temperature to temperature as high as 1200°C in a controlled atmosphere. The graph obtained is known as thermogram (TG) which is a plot of mass Vs temperature. As the temperature increases the sample may undergo physical or chemical change which will be accompanied by mass loss. The measurement is normally carried out in air or in an inert atmosphere (N_2 , Helium, Argon) and weight is recorded as a function of increasing temperature.

THEMOGRAM :

It is a plot of mass Vs temperature.

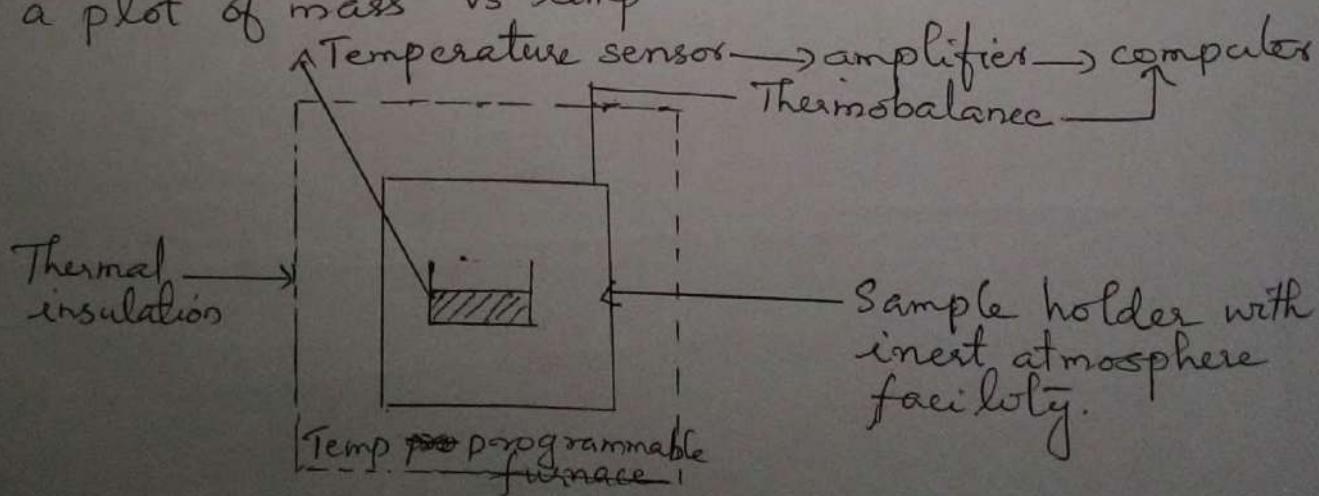


INSTRUMENTATION

The main components of TGA apparatus are the following:-

1. Sample holder
2. Furnace with temperature programming facility.
3. Thermo balance
4. Temperature sensor
5. Environment control equipment
6. Detector and recorder.

The sample to be analyzed is taken in the sample holder. The sample holder is surrounded by a furnace with temperature programming facility, i.e. the heating rate can be adjusted according to the requirement of the experiment, in $5^{\circ}\text{C}/\text{minute}$ or $10^{\circ}\text{C}/\text{minute}$ etc. The environment control equipment provides suitable atmosphere for analysis such as air, N_2 , He etc. The sample holder is attached to a thermo balance which is highly temperature sensitive, i.e. whenever temperature changes it automatically measures the mass of the sample. The temperature sensor records the sample temperature. The signals are amplified and recorded. The graph obtained is a plot of mass Vs temp.

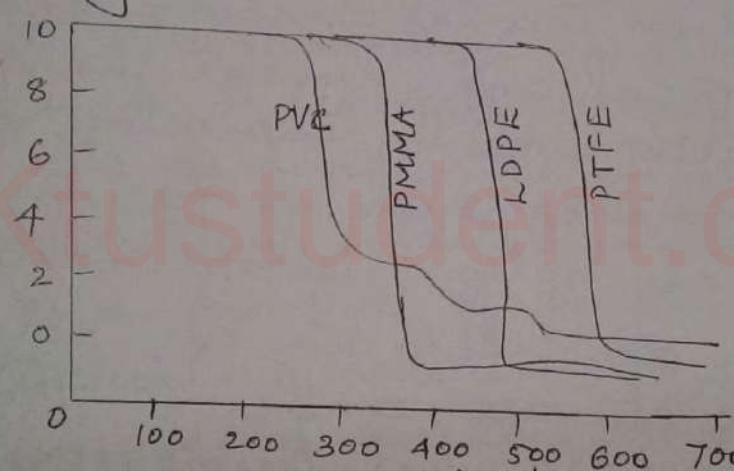


TGA apparatus

Applications of Thermogravimetry

1. Determines temperature and weight change of decomposition reactions, which often allows quantitative composition analysis.
2. Allows analysis of reactions with air, oxygen or other reactive gases.
3. Used to determine evaporation rates of liquid mixtures.
4. Can measure the fill materials added to some foods.
5. Can determine the purity of a mineral, inorganic compound or organic material.

TGA of Polymers



It is seen that PVC starts decomposing at low temperature compared to low density polyethylene (LDPE). This is due to the fact that elimination of HCl takes place in PVC. Also it is seen that PTFE (poly tetra fluoro ethane) is having high thermal stability, owing to strong C—F bond than C—H bond.

Limitation of TGA

TGA will not give any information regarding phase change such as transition from crystalline

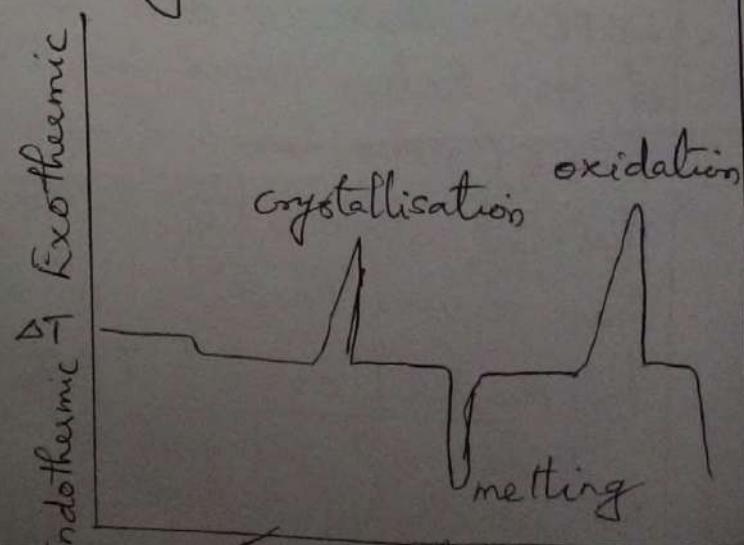
form into another and melting of a solid into liquid. These transitions does not involve weight change but involve heat change.

Differential Thermal Analysis (DTA)

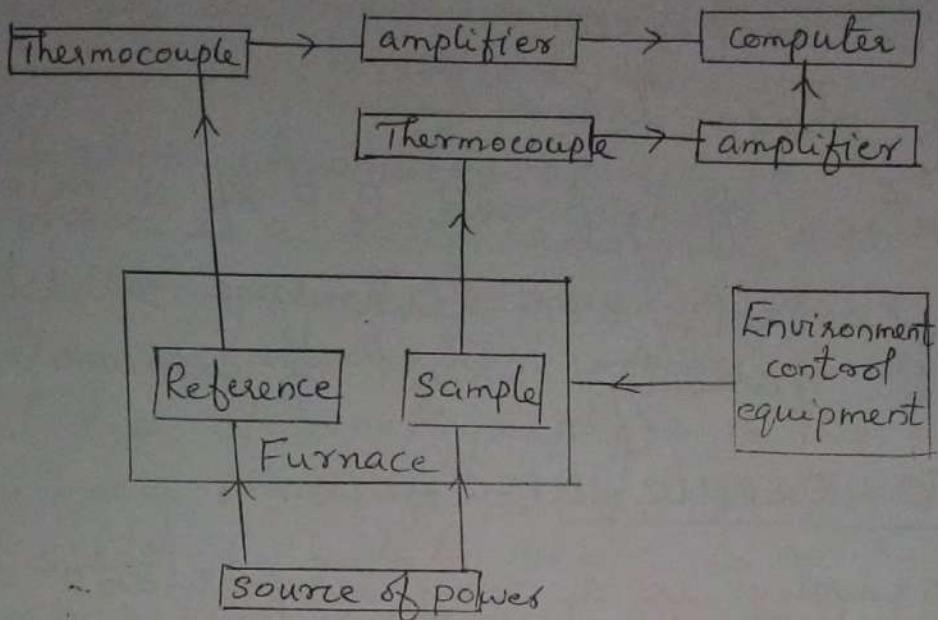
Differential thermal analysis is a technique in which the difference in temperature between the sample and an inert reference compound (alumina) is measured as a function of temp. as both are heated uniformly at a const rate. The difference in temp(ΔT) between the sample and the reference compound is monitored continuously and plotted against sample temp to obtain a differential thermogram.

Differential thermal analysis peaks can result both from physical and chemical changes undergone by the substance due to temperature changes. Physical processes such as fusion, vapourisation, sublimation, absorption, desorption etc are endothermic while oxidation in air, polymerisation, decomposition etc are exothermic. The upward peaks in the differential thermogram stand for exothermic changes while the downward peaks stand for endothermic changes.

The area under a DTA peak gives the enthalpy change of the process.



INSTRUMENTATION



Block diagram of DTA apparatus

The sample is placed in one chamber and a thermally inert reference material, such as Al_2O_3 , is placed in other chamber. The temperature of the furnace is linearly increased at a rate of 5°C to 12°C per minute. The difference in temp between sample and reference is continuously measured as a function of sample temperature. For the temperature measurements, thermocouple is directly placed in the sample and reference so we get the highest accuracy. The sample undergoes transitions with liberation or absorption of energy hence the deviation of sample temp from that of reference tells whether the transition was exothermic or endothermic and the temperature of transition.

Applications of DTA

1. In the characterization of polymer mixture by analyzing the characteristic m.p of each polymer.

2. To study the thermal stability of inorganic compounds or complexes.
3. Study of phase transitions
4. Determination of m.p and B.P of substances.
5. Quality control - DTA technique is widely used for the quality control of cement.

CHROMATOGRAPHIC METHODS

Chromatography is a very important analytical technique used widely and frequently for the separation, purification and identification of chemical components in complex mixtures.

Chromatography involves two mutually immiscible phases - mobile phase and stationary phase.

Mobile Phase - It is a moving phase which can be a liquid or gas. The components to be analyzed are carried by this mobile phase through the stationary phase.

Stationary phase - It is a fixed phase. Eg: a column of adsorbent, paper, a thin film of liquid supported on inert solid, a thin layer of adsorbent coated over a glass plate etc.

A sample to be analyzed is introduced into the mobile phase. It can be carried along through a stationary phase. The components of the mixture are separated depending upon the rates at which they are carried by the mobile phase through the stationary phase, which in turn depends on the relative affinity of the components towards the stationary phase & mobile phase.

Classification

Based on the mechanism of separation, chromatography can be classified as,

- a) Adsorption chromatography - In this the stationary phase is a solid and the mobile phase is a liquid or gas. The separation occurs due to difference in adsorption coefficient of the components.
- b) Partition chromatography - In this type the stationary phase is a ~~by~~ liquid supported on inert solid. The mobile phase is a liquid or gas. The separation is caused by partitioning of the component between stationary phase and mobile phase.
- c) Ion-Exchange chromatography - The stationary phase is an ion-exchanger and the distribution of the components of the mixture is based on the ion-exchange principle. This type of chromatography is applicable to ionic species.

Based on the mobile phase, chromatography can be classified as:-

- 1) Liquid chromatography - The mobile phase is a liquid and stationary phase can be a solid or liquid supported on inert solid.

Eg: HPLC

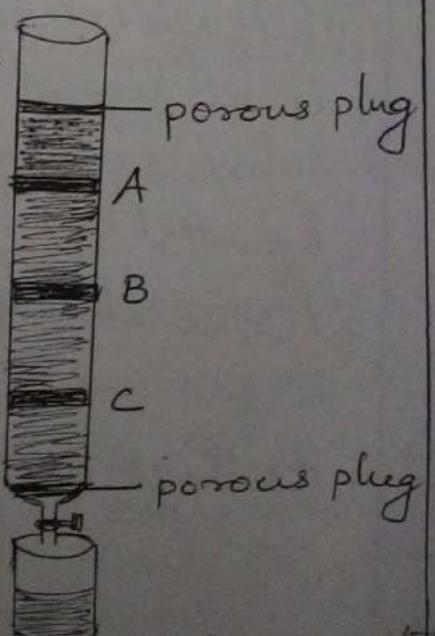
- 2) Gas chromatography - The mobile phase is a gas and stationary phase can be a solid or liquid supported on inert solid.

COLUMN CHROMATOGRAPHY or LIQUID-SOLID ADSORPTION CHROMATOGRAPHY

One of the most useful method for the separation and purification of both solids and liquids. This is a solid-liquid technique in which the stationary phase is a solid and mobile phase is a liquid. The principle of column chromatography is based on differential adsorption of substance by the adsorbent.

The common adsorbents employed in column chromatography are silica, alumina, calcium carbonate etc. The rate at which the components of a mixture are separated depends on the activity of the adsorbent and polarity of the solvent.

The adsorbent is packed in a cylindrical tube and is plugged at the bottom by a piece of glass wool. The mixture to be separated is dissolved in a suitable solvent and introduced at the top of the column and is allowed to pass through the column. As the mixture moves down through the column, the components are adsorbed at different regions depending on their ability for adsorption. The components with greater adsorption power will be adsorbed at the top and the other will be adsorbed at the bottom. The different components can be desorbed and collected separately.



Components A, B & C separated by a column chromatography

by adding more solvent at the top and this process is known as elution. i.e. the process of dissolving out of the components from the adsorbent is called elution and the solvent is called eluent. The weakly adsorbed component will be eluted more rapidly than the other. The different fractions are collected separately.

Distillation or evaporation of the solvent from the different fractions give the pure components.

Applications

1. Column chromatography is best suited to separate organic compounds from plant materials.
2. In separation of compounds after organic synthesis to obtain desired molecules.
3. To separate or purify natural compound mixtures like alkaloids, glycosides etc.
4. It is extensively used for the purification of organic substances from their contamination.

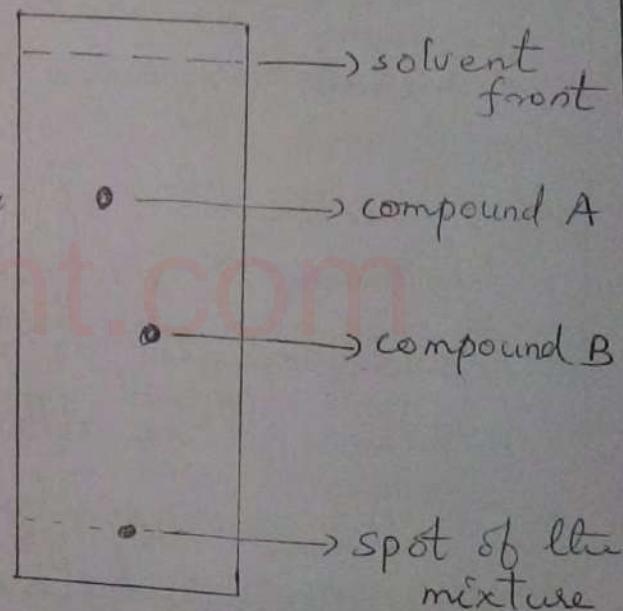
THIN LAYER CHROMATOGRAPHY (TLC)

TLC can be used to determine the number of components in a mixture, identify the components and the purity of a compound. TLC is a sensitive technique i.e. microgram quantities can be analyzed by TLC and it takes little time for analysis (about 5–10 minutes).

Commercially available TLC plate is a sheet of glass, metal or plastic which is coated with a thin layer of a solid adsorbent usually silica or alumina. A small amount of the mixture

to be analyzed is spotted near the bottom end of this plate using a capillary tube. The TLC plate is then placed in a developing chamber containing a shallow pool of a solvent such that the sample spot is just above the solvent level. The lid of the developing chamber is closed. The solvent very slowly rises up the TLC plate by capillary action. As the solvent passes the spot, it carries the components at different rate, resulting in separation of the components.

When the solvent has reached near the top of the plate, the plate is removed from the developing chamber, dried and the separated components of the mixture are visualized. If the components are not coloured, uv lamp, iodine vapours and specific colour reagents can be used for TLC plate. the visualization.



After a separation is complete, individual compounds appear as spots separated vertically. Each spot has a retention factor (R_f), which is the ratio of distance travelled by the sample spot to the distance travelled by the solvent front.

$$; R_f = \frac{\text{distance travelled by the sample spot}}{\text{distance travelled by the solvent front}}$$

The R_f value can be used to identify compds due to the uniqueness of each compound in a particular solvent. When comparing two different compounds under the same conditions, the compd with the larger R_f value is less polar because it does not stick to the stationary phase as long as the polar compound, which would have a lower R_f value.

Applications

1. TLC can be used for the rapid separation, purification and identification of even those components which are present in very minute quantities.
2. TLC can be used for the analysis of complex organic mixtures.
3. To check the purity of a sample.
4. Used for the identification and separation of drugs and plant extracts such as alkaloids.
5. Used for the detection of contaminants or adulterants in chemical samples in the laboratory as well as in industry.

Gas Chromatography

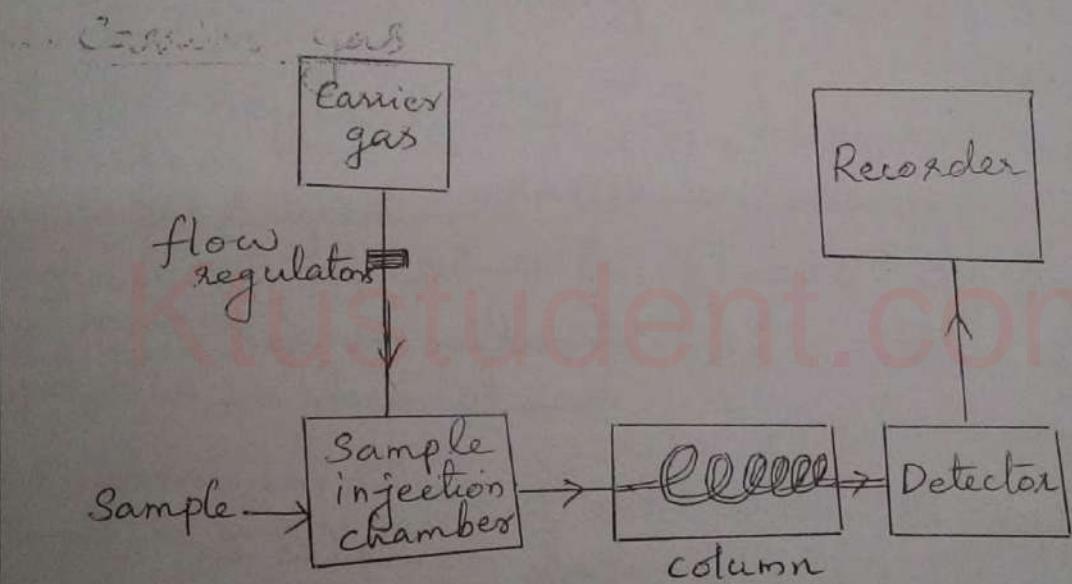
Chemical analysis of mixtures of volatile organic compounds is generally done using GC. The principle of GC is the differential distribution of the components between stationary and mobile phase. The mobile phase is a gas (carrier gas) usually nitrogen. The stationary phase may be solid or liquid. If the stationary phase consists

silica, alumina or carbon, the chromatography is termed as gas solid chromatography (GSC) and if the stationary phase is a non volatile liquid held as a thin layer on a solid support, then the technique is known as gas liquid chromatography (GLC).

Instrumentation

Basically all gas chromatographic instruments consist of four basic components.

- (1). Carrier gas (2) Sample injection system
- (3). The column (4) Detectors.



1. Carrier gas - The carrier gas is allowed to flow through the system, carrying the sample in the vapour state through the column.
The carrier gas (a) should be chemically inert
(b) should be suitable for the detectors and the type of sample analyzed (c) it should give best column performance consistent with required speed of the analysis.

2.) Sample Injection System - The carrier gas is connected from the gas reservoir to the sample port injector. The sample must be converted to vapour state. The injection port is heated to a temperature which will ensure rapid vapourisation but not thermal degradation of the solute. The sample is injected by a syringe into the sample injection port. It is easily vapourises and mixes with the flowing carrier gas and is swept into the column.

3.) Columns - Two types of columns are commonly employed in GLC, the capillary column and packed column which are made of stainless steel, copper, nickel or glass. Inner diameters may range from 1.6 to 9.5 mm. and length is often 3m.

Capillary column is fabricated from capillary tube, the inner surface of which is coated with a very thin film of the liquid phase. The packed columns are packed with either a solid powder substrate (GSC) or a liquid coating on an inert solid support (GLC).

Usually a temperature which gives the elution in a reasonable time of 2 to 30 minutes and is equal to or slightly above the average boiling point of the sample is selected as column temperature.

4.) Detectors - Any physical property, which varies widely from one gas to another and which can be monitored form the basis of the detectors.

Based on these physical properties, detectors are of two kinds:-

a) Thermal conductivity Detectors (TCD)

It is based on the rate of heat loss from a heated wire placed in a gas stream, which depends on the thermal conductivity of the gas, so the temperature of the wire changes, consequently the resistance.

b) Flame ionisation detector (FID) —

The flame ionisation detectors are based on the electrical conductivity of the gas. With a burner (H_2 -air flame), the effluent from the column is mixed with H_2 and air and then ignited electrically. Most organic compounds, on ignition produce ions and electrons that can conduct electricity through the flame. The resulting current is then directed into an amplifier for measurement.

Procedure

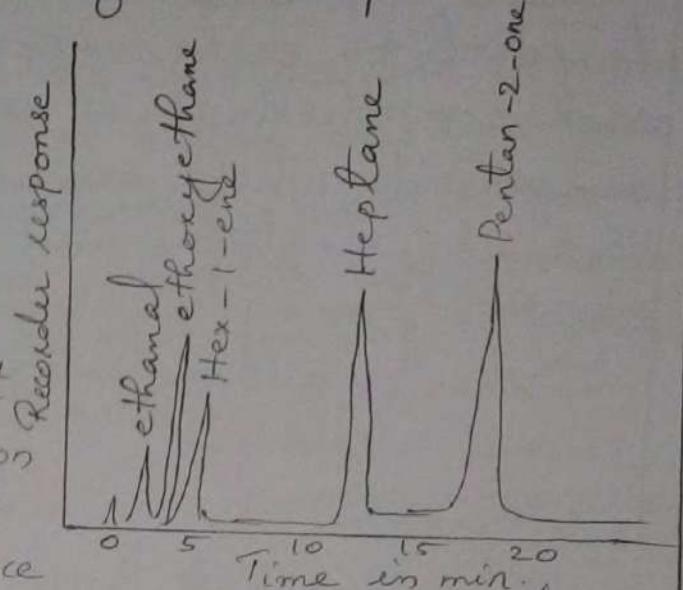
The sample mixture is injected into the injection port where it gets vapourised and carried by the carrier gas into the heated chromatographic column. During the passage of mixture through the column, the components of the mixture get distributed between the two phases. Some components are adsorbed by the stationary phase better than others, and hence, they are retained for longer time in the column. Thus each component of the mixture is carried along the column at different rates and finally emerges from the column at different time. The time taken by each component to pass through the

column is a characteristic property which helps for its identification. They are then detected by the detector, in which the recorder gives a peak for each component. The size and location of the peak is an identification of the nature of the component.

Retention time (t_R)

It is the time taken by the solute to pass between the sample injection port and the detector.

Identification of the component is carried out by the comparison of the GC retention time against those of the reference standards.



Applications

1. To test the purity of organic compounds. The presence of impurities are revealed by the presence of additional peaks.
2. Gas chromatography coupled with mass spectrometry (GC-MS) is widely used for the analysis of hydrocarbon fuels, perfumes, flavours etc.
3. GC is widely used to study the extent of air pollution
4. By using GC, the ethyl alcohol content in blood can be determined with high accuracy.
5. Banned drugs used by athletes can be detected by taking GC of blood or urine sample.

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

It is a technique in analytical chemistry used to separate the components in a mixture, to identify each component, and to quantify each component. It is especially suitable for compounds which are not easily volatilized, thermally unstable and have high molecular weights. For eg: cholesterol, terpenoids, polypeptides etc which contain large numbers of atoms ie 30 and above.

Principle

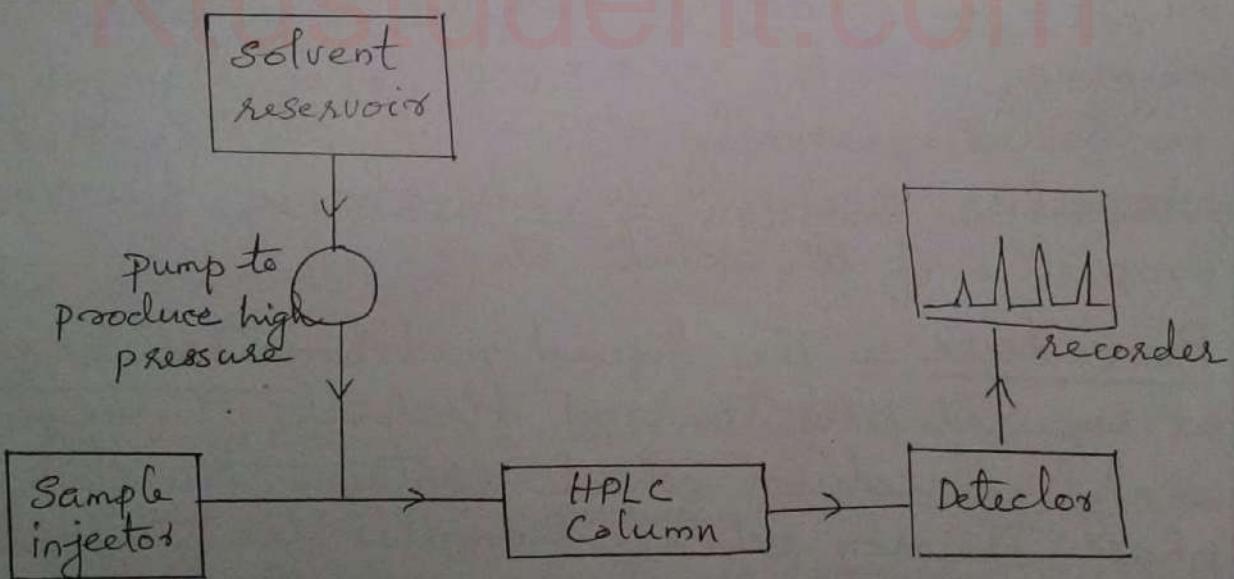
Microgram to gram quantities of mixtures can be separated by passage of sample by means of a pressurized flow of a liquid mobile phase through a column containing a stationary solid phase. When a mixture of components are introduced to a HPLC column, they travel according to their relative affinities towards the stationary phase. The component which has more affinity towards adsorbent travel slowly and the component which has less affinity towards adsorbent travels faster. ie each component in the sample interacts slightly differently with the adsorbent material, causing different flow rates for the different components and leading to the separation of the components as they flow out of the column.

Instrumentation

1 HPLC Mobile Phase - Mobile phase serves to transport the sample to the system. Essential

Criteria of mobile phase are inertness to the sample components. Pure solvent or combinations are commonly used. The mobile phase should be free of particulate impurities and degassed before use.

2. Mobile Phase reservoirs — They are inert containers for mobile phase storage and transport. Generally transparent glass bottles are used so as to facilitate visual inspection of mobile phase level inside the container. stainless steel particulate filters are provided inside for removal of particulate impurities in the mobile phase.
3. HPLC pumps — To produce an appropriate pressure to push solvent into sample. A pump capable of pumping solvent up to a pressure of 5000 psi (pounds per square inch) and at a flow rate of 1-10ml/min.



- 4). HPLC Injectors — Injectors are used to provide constant volume injection of sample into the mobile phase stream.

5) HPLC column — A column is a stainless steel tube 10-30cm long packed with stationary phase. These columns have an inner diameter of 4 to 10mm.

and common particle size of packing are 3, 5 and 10 μm . A column oven maintains constant column temperature using air circulation.

Guard Column — A short guard column is kept before the analytical column. This helps to remove particulate matter present in the solvent and thereby increases the life of analytical column.

Detector — Detectors used in HPLC are of two types - Bulk property detectors and solute property detectors. Bulk property detectors respond to bulk properties like refractive index, dielectric constant, density etc. When a particular molecular species are eluted out, these properties will change and detector gives the signal and the component is collected in the sampling tube along with solvent. The solvent is distilled out and the pure component can be recovered.

Solute property detectors respond to solute properties such as uv-absorbance, fluorescence properties of the solute etc.

Procedure — The liquid mobile phase is pumped at required pressure and flow rate through the analytical column which contains the stationary phase. The non-volatile samples are injected to the analytical column with the help of a microsyringe. The components are carried along the column at different rates due to the differential distribution between stationary phase and mobile phase. The elution can be done in two ways.

- a) Isocratic elution - a single solvent of constant composition is used.
- b) Gradient elution - Two or more solvents that differ very much in polarity is used.

The gradient elution is found to be more effective. During elution the ratio of the solvent is varied in a programmed manner. The gradient elution gives better separation in less time. The common organic solvents used are n-hexane, benzene, acetone, methanol etc. The components that emerge out of the column are detected and recorded.

HPLC is distinguished from low pressure liquid chromatography because operational pressures are significantly higher. HPLC columns are made with smaller adsorbent particles 2-10 μ m in particle size. This gives HPLC superior resolving power when separating mixtures. So HPLC is considered as a popular chromatographic technique.

Applications

1. Pharmaceutical industry - To control the drug stability, quantity of drug determinations from pharmaceutical dosage forms, quantity of drug determinations from biological fluids. eg: blood glucose level
2. Analysis of natural contamination - In the analysis of phenol and mercury from sea water.
3. Forensic test - Determination of steroid in blood, urine, sweat

[That distance between electrodes]

4. Food and essence manufacture — sweetener analysis in the fruit juice, preservative analysis in sausage.

5. Enables the determination of fat soluble vitamins, synthetic colours etc.

Advantages

1. It takes less time.
2. It enables determination of compounds present even in trace concentrations as low as parts per trillion (PPT).
3. Precise and accurate results

Disadvantage

1. High cost
2. Only trained technicians can operate the equipment.

Advantages of Chromatographic Method

1. It enables analysis of mixtures containing any number of components in a single process.
2. It enables detection and effective separation of components present even in trace amounts.
3. It is useful for the purification of substances.

CONDUCTIVITY (K) or Specific Conductance

Electrical resistance measures the obstruction to the flow of current. Resistance of a conductor is proportional to length (l) and inversely proportional to area of cross-section (a) of the conductor.

$$\text{ie } R \propto \frac{l}{a} \quad \text{or } R = \frac{\rho \times l}{a}$$

The proportionality constant ' ρ ' is called specific resistance or resistivity of the material. The unit of resistivity is ohm.cm.

The reciprocal of specific resistance is called specific conductance. It is defined as the conductance of one cm³ of a conductor held between two electrodes of 1cm² area placed on the opposite pairs of faces of cube of 1cm length.

$$\text{ie } K = \frac{R a}{l}$$

$$K = \frac{1}{\rho} = \frac{1}{R} \frac{l}{a} = C \times \frac{l}{a}$$

The unit of conductivity is ohm⁻¹ cm²/a
In a conductivity cell, the distance between two electrodes (l) and the area of electrodes are fixed. This constant is called cell constant K .

$$\text{ie } K = \frac{l}{a}$$

Conductivity cell

A conductivity cell consists of two electrode plates coated with finely divided platinum black. These two are welded with the ends of platinum wires that are sealed through such glass tubes. The tubes are strongly fixed so that distance between electrodes remains unaltered.

Determination of cell constant

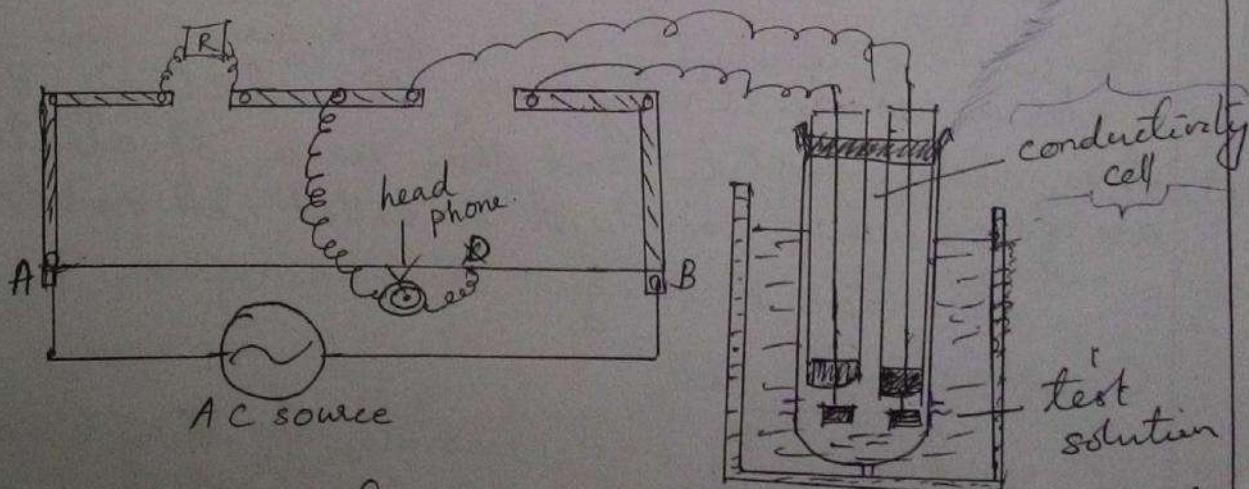
Cell constant may be obtained by measuring 'l' and 'a'. But it is very difficult to measure the actual area precisely in this type of small cells. In actual practice cell constant is measured by filling the conductivity cell with a known conductivity like 0.1M KCl solution. The conductivity of 0.1M KCl solution is $0.01288 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 298 K.

Sp. conductance of KCl solution = conductance \times cell const.

By measuring the conductance, the cell constant can be determined.

Method of Conductance Measurement

A modified form of Wheatstone bridge is used for conductance measurement. One arm of the bridge is connected to conductivity cell containing the test solution. A known resistance R is introduced in the circuit. An alternating current source of frequency 1000–4000 Hz is connected between A and B as shown in fig.



Here an alternating current is used since it can prevent electrolysis. Here the null point detector is a head phone which produces a sound corresponds to AC frequency. The bridge can be balanced by moving the sliding jockey.

Module 4

Polymers

Polymers are large molecules that are built up of a no. of repeating units called monomers. It is also known as macromolecules. The name of the polymer is often based on their repeating units.

Polymerisation is the process of combination of 2 or more monomer units of the same type or different types with or without elimination of smaller units like water (H_2O), HCl etc... to form a high molecular weight compound.

Homo polymers

Homopolymers consist of one kind of repeating unit

throughout the whole backbone structure
(C-C bond)

copolymer

It consists of more than one type of repeating monomer units. The freedom of design depends on structure of repeating units, its ratio and position in the backbone sequence.

4 types

1) Block copolymer: It consists of 2 or more segments of pure homo sequence.



2) Alternating copolymer: It is having strictly alternating repeating units.



3) Random copolymer: It possess an arbitrary heterogeneous sequence.



4) Graft copolymer: In this the polymeric structures of one repeating units are grafted to a strand of another repeating unit.

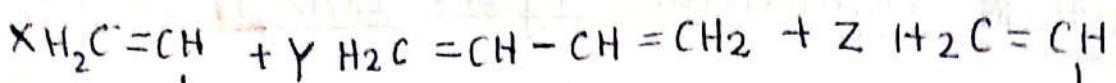


Acrylonitrile Butadiene Styrene [ABS]

ABS is a terpolymer of acrylonitrile butadiene and styrene. The composition is half ~~so~~ styrene and the balance is devided b/w Acrylonitrile and butadiene. Acrylonitrile have chemical resistance, heat resistance and high strength. Butadiene have toughness, impact strength and low temperature property of tension and styrene is having rigidity, glossiness, and process ability. different ways of grades of ABS with wide range of features and applications can be produced by varying their composition. ABS is used in the temperature range [20-80°C].

Preparation

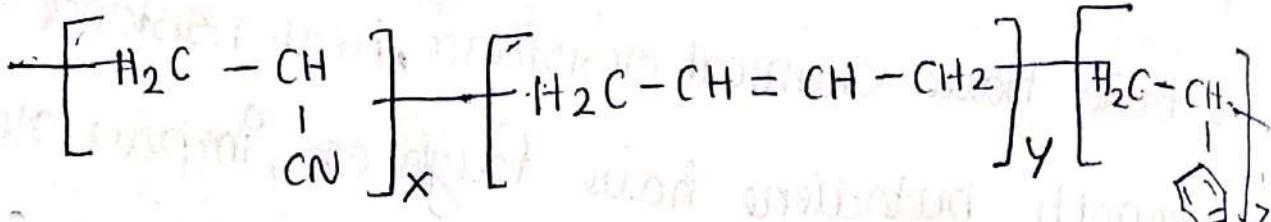
- 1) Blending: In this the 2 copolymers [styrene acrylonitrile and acrylonitrile butadiene] are mixed and coagulated.
- 2) Copolymerisation:



X acrylonitrile Y butadiene
 Y styrene



Styrene



Properties

- * high heat resistance
- * flame resistance.
- * good process ability.
- * very high impact resistance.
- * high glossiness.
- * good chemical resistance.

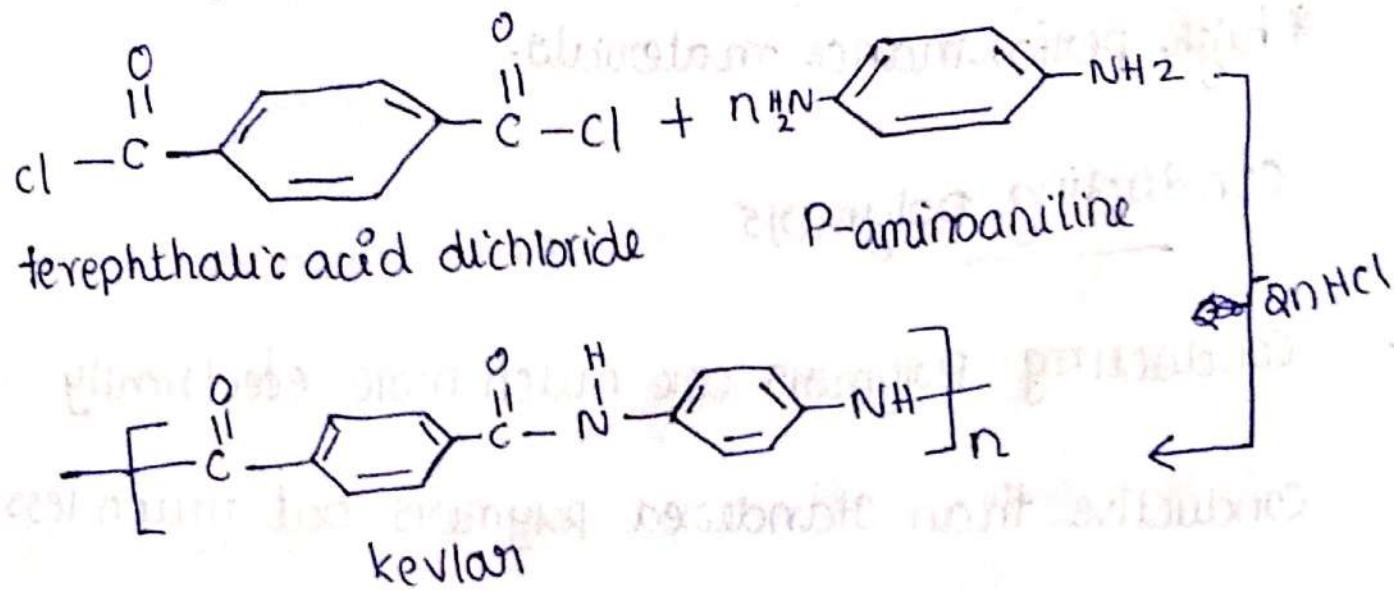
Applications

used in

- * Automobile Industry.
- * Molded articles.
- * Electrical and electronic applications.
- * household goods.
- * Sports goods.

* KEVLAR

fibrous aromatic polyamide formed by Polymerisation of terephthalic acid dichloride and paraaminoaniline. It is an advanced polymer resembling nylons with wide ranging appli practical applications.



Properties

- * It is an aromatic polyamide (aramid polymer)
- * high mechanical properties including strength.
- * light weight
- * flexibility with heat stability.
- * more rigid than nylons.

Applications

- 1) Aerospace and aircraft industries.
- 2) bullet proof vests.

- * Motorcycle helmets.
- * Tires, breaks, clutch lining and other car parts.
- * Protective clothing
- * Rock-ropes and cables.
- * high performance materials.

conducting polymers

conducting Polymers are much more electrically conductive than Standard polymers but much less than metals such as Cu.

conductivity of these materials are characterized by low charge carrier mobility - a measure of how easily the electric charge moves. A polymer which can conduct electricity is termed as conducting polymers.

conducting Polymers

Intrinsically CP

CP

a) Doped CP

b) conjugated CP

Extrinsically CP

a) blended CP

b) element filled.

Doped conducting Polymers (DCP)

Polymers with conjugated π electron can be easily oxidised or reduced as they have low ionisation potential and high electron affinity. The conductivity can be increased by creating +ve or -ve charge on Polymer backbone by oxidation or reduction. The polymer is exposed to a charge transfer agent in either gas or solution phase. Doping increases the surface conductivity of the polymer.

Classification of Doped CP

- 1) +ve doping (oxidation)
- 2) -ve doping (reduction).

Positive doping

Treating an intrinsically conducting Polymer with a Lewis acid [Electron deficient eg: $\text{BF}_3, \text{FeCl}_3$] thereby oxidation process takes place by the formation of charges on polymeric backbone. The delocalised ~~radicals~~ ions [polaron] which can move around the polymer chain by rearrangement of double and single bonds.

-ve doping [Reduction]

Treating an intrinsically conducting polymer with a Lewis base [Electron rich] thereby ~~o~~ reduction process takes place by the formation of -ve charges on polymeric backbone. The delocalised ~~radicals~~ ions which can move around the polymer chain by rearrangement of double and single bonds.

Int

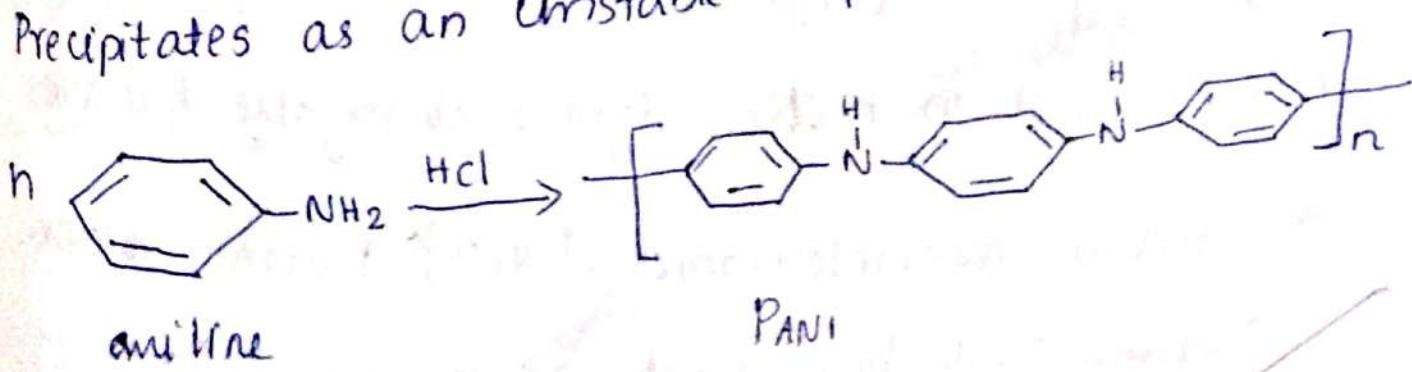
Polyaniline (PANI)

It is the oldest conductive polymer emeraldine (oxidative form of PANI) is ~~the~~ a synthetic metal and conductivity like metals, metallic sound and lusture.

Preparation

oxidative polymerisation of aniline under acidic conditions gives polyaniline. The oxidant is ammonium persulphate. The 2 components are dissolved in HCl and slowly combined by exothermic reaction. The polymer

precipitates as an unstable dispersion.



Properties

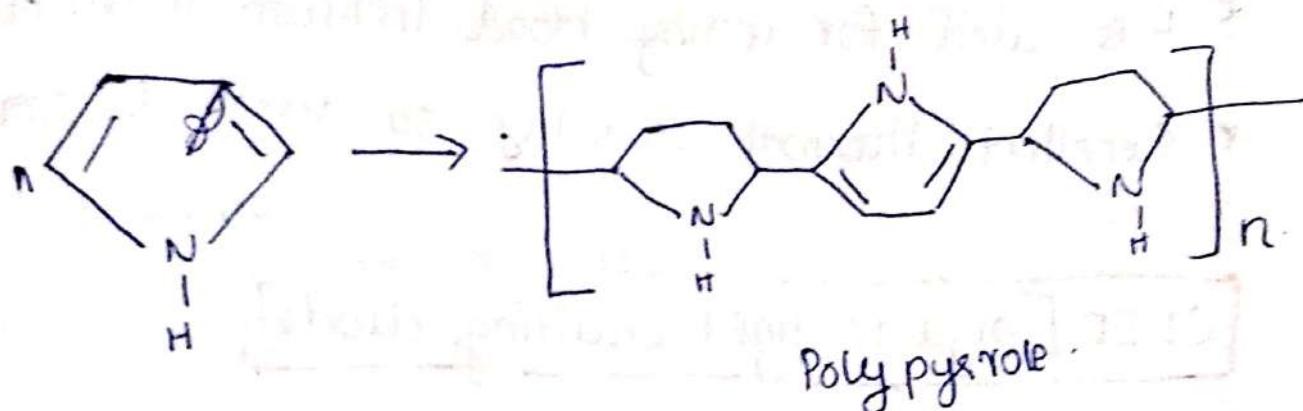
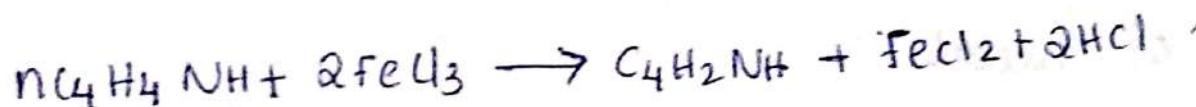
- * It is a synthetic metal having conductivity like metals, metallic lusture.
- * Light weight and mechanical flexibility
- * Doped for increasing the conductivity.
- * PANI have 3 oxidation states.
- * Shows different colours.
- * Environmentally friendly with no heavy metals.

Applications

- * It is used in chemical vapour sensors, super capacitor, and biosensors.
- * It is used for corrosion protection.
- * It is used in active electronic components such as non-volatile memory.
- * It is used in the manufacture of electrostatic dispersing coatings and blends.
- * It is used in button type rechargeable batteries.
- * Used in microelectronic devices, telecommunication systems and biomedical equipments.

a) Poly pyrrole

It is prepared by chemically or electrochemically through the oxidative polymerisation of pyrrole monomer is done by using ferric chloride in methanol.



Pyrrole

Poly pyrrole

Properties

- * Polypyrrole films are yellow but darken in air due to oxidation doped films are blue or black.
- * Undoped and doped films are insoluble in solvents but swellable.
- * It have high chemical resistance.
- * It is an insulator but its oxidative derivatives are electric conductors.

Applications

- 1) It is used in biosensors, gas sensors and electrostatic

coatings, smart windows and displays, light weight rechargeable batteries and in electronic devises.

- * It is a potential vehicle for drug delivery system
- * Poly pyrrole based polymers used to protect corrosion of metals
- * It is used for testing blood lithium levels of patient
- * Excellent thermal stability so used in carbon composites.

OLED [organic light emitting diode]

Light emitting diodes [LED's] are optoelectronic devices which generate light when they are electrically biased in the forward direction.

Light emitting devices made with organic materials are called organic light emitting diodes [OLED].

The new OLED devices are based on multilayer structure and they consist of a transparent anode, a hole transporting layer, an electron emitting layer and a cathode during operation electron and holes are injected from a cathode.

and anode respectively. And recombination of electron and holes leads to efficient light generation.

There are 2 main families of OLED

① based on small organic molecule.

eg: organometallic chelates.

② based on organic polymers

eg: Polyfluorene.

OLED Structure

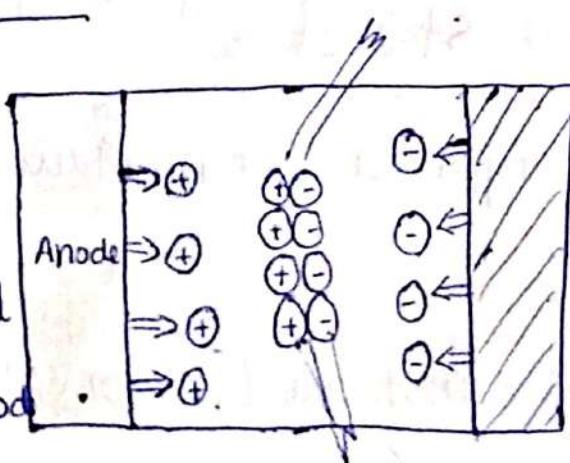
A typical OLED structure consists of the following 5 parts:

- 1) substrate [clear plastic, glass] supporting OLED
- 2) Anode - adds electron holes when a current flows through the device. [eg: ~~LiF~~ ITO, Gold]
- 3) A hole transport layer [HTL] - This is the "conducting" polymer layer that transports holes from anode eg: Polyaniiline.

- 4) An electron Transport layer $\xrightarrow{\text{ETL}}$ ~~This~~ It is emissive layer made of ^{an} organic molecule or polymer where light is made eg: Polyfluorine.
- 5) A metallic cathode injects electrons when a current flows through the device.
eg: Ag, Ca.. etc.

Working Principle of OLED

A typical OLED is composed of a layer of organic materials situated between an anode and cathode.



deposited on a substrate. The organic ~~light~~ ^{emission} molecules are electrically conductive due to delocalization of conjugated π electrons.

When a current is applied electrons flow from cathode to anode when these electrons go through the OLED layer photons are released. The cathode pushes electrons to the emissive layer while the

anode removes electrons from the conductive layer [which leads to hole in conductive layer]. The new electrons in emissive layer combine with the hole in conductive layer releasing photons and light is created. Depending on the nature of emissive material the colour can vary and light is controlled by amount of current applied, and intensity of light is controlled by amount of current applied.

OLED Advantages

- * Light weight and flexible plastic substrates.
- * Better power efficiency and thickness.
- * Low cost.
- * They have greater energy efficiency than halogen and incandescent light.
- * Considered as cold lighting source and do not generate extensive heat.

Disadvantage

- * low lifespan
- * water damage → water can instantly damage the system.

Applications

- * It is used in commercial application eg. displays for mobile, portable digital media player, old cameras, smart watch with OLED screen.
- * Smart phone
- * OLED T.V

Module 5 - Water Technology

waste water treatment

water which has high dissolved minerals is known as hard water. It has poor soap and detergent performance. Water that does not produce easy and readily lather with soap solution a white scum is called hard water.

Hardness of water

mg/L as CaCO3

0-17

→ soft

17-60

→ slightly hard

60-120

→ moderately hard

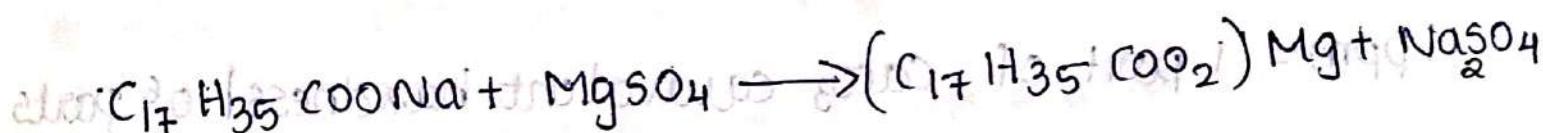
120-180 \rightarrow hard

more than 180° - very hard



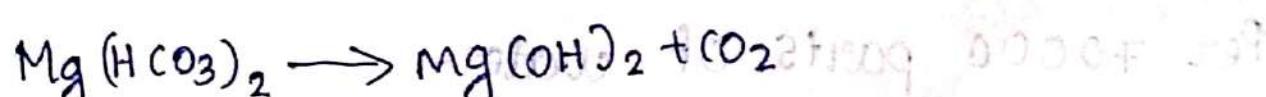
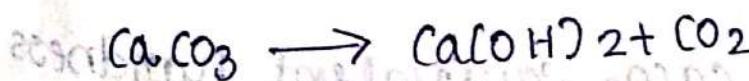
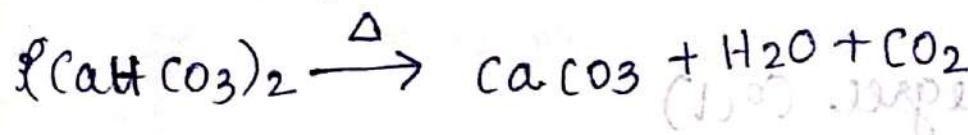
Na soap

Sodium stearate



Types of hardness (carbonate hardness).

* Temporary hardness: It is due to the presence of dissolved bicarbonates of Ca, Mg other heavy metals etc. It can be removed by boiling. Soluble bicarbonates on boiling gives insoluble carbonates on hydrolysis.



Permanent hardness (Non-carbonate hardness).

It is due to the presence of Sulphides and chlorides.

des of Ca, Mg, Fe and other heavy metal. It cannot be removed by boiling.

Units of hardness

1) Parts per million (ppm): The no. of parts of CaCO_3 equivalent hardness present in 10^6 parts of water.

$1 \text{ ppm} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness} / 10^6 \text{ parts}$ of water

2) milligram per litre (mg/L): $1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3$ equivalent hardness per 1 litre of water.

$= 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness} / 10^6 \text{ mg of water}$
ie $1 \text{ mg/L} = 1 \text{ part per million}$

3) Clarkes degree (${}^\circ\text{Cl}$)

$1 {}^\circ\text{Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness}$

Per 70000 parts of water.

4) Degree French (${}^\circ\text{Fr}$): $1 {}^\circ\text{Fr} = 1 \text{ part of } \text{CaCO}_3$ equivalent hardness per 10^5 parts of water.

5) milliequivalence per litre (meq/L) \rightarrow 1 milliequivalent of CaCO_3 equivalent hardness per 1 litre of water = 50 parts per million.

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1^{\circ}\text{FGR} = 0.07^{\circ}\text{CH}$$

Degree of hardness

* CaCO_3 is used for expressing hardness because it is the most insoluble salt and can be precipitated during water treatment.

* The molecular weight of CaCO_3 is 100.

$$\text{Equivalent weight} = 50 = 100/2 = 50/1$$

Equivalent hardness of CaCO_3 is $\frac{\text{mass of hardness}}{\text{produced in g}}$

= mass of hardness produced using

Substance \times 2 \times equivalent weight of CaCO_3

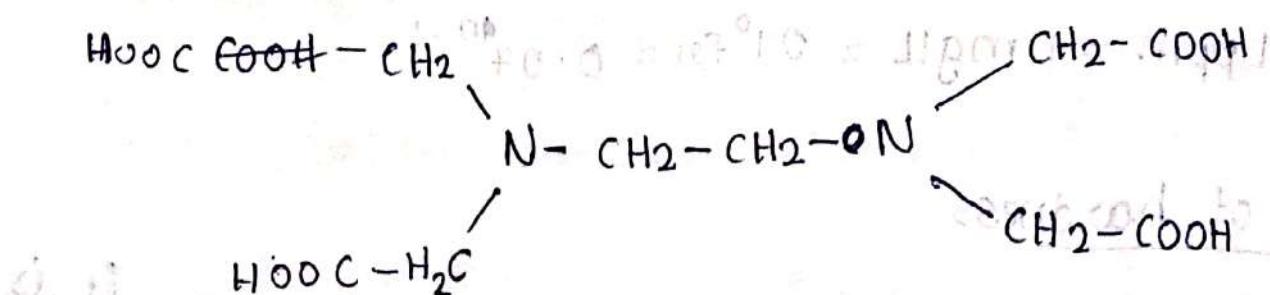
$\alpha \times \text{eq. weight of hardness producing substance}$

substance.

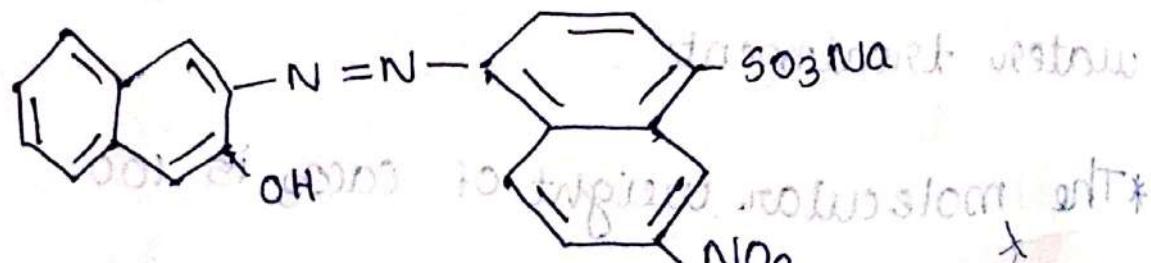
= mass of hardness producing substance \times multiplication factor.

Estimation of hardness

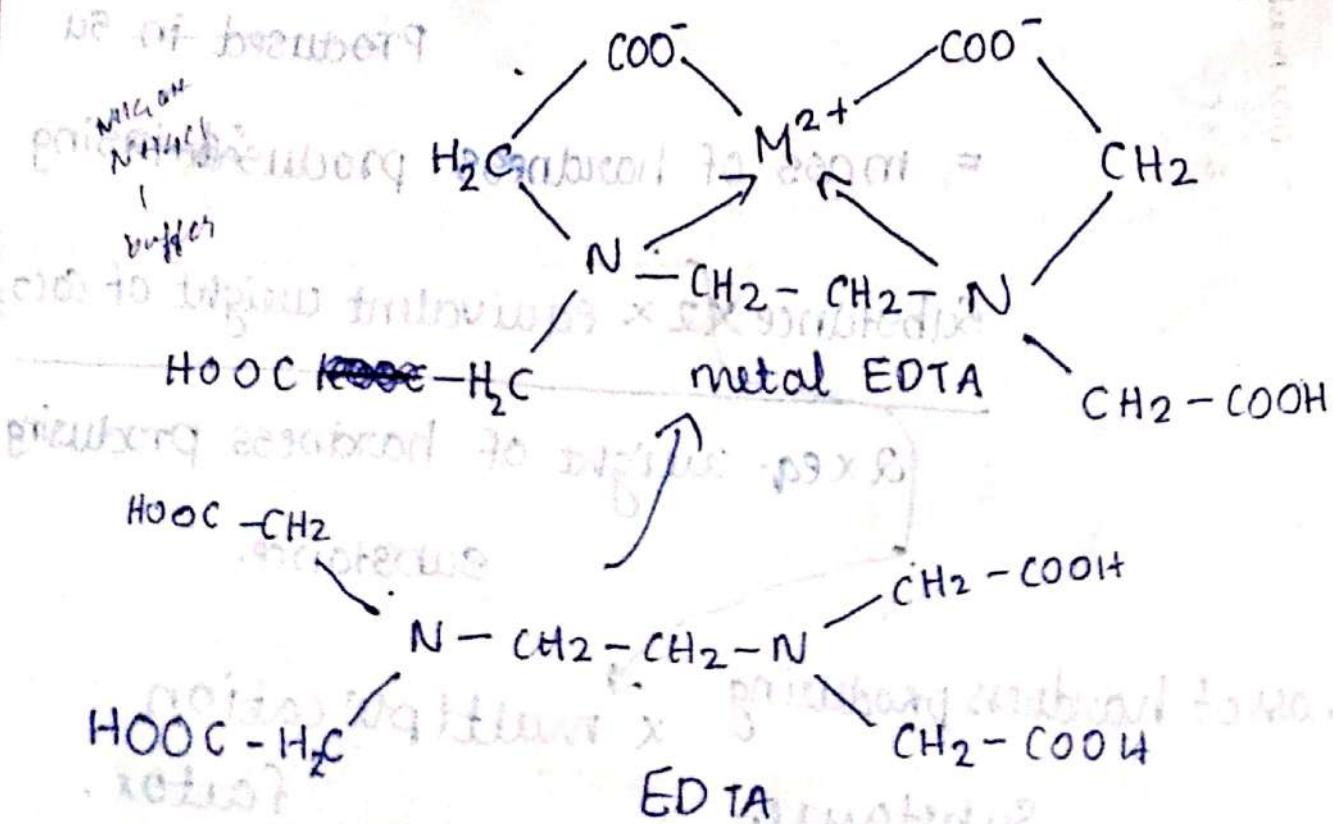
EDTA method (Ethylene diamine tetra acetic acid)



Eriochrome black T → Indicator



The structure of metal EDTA complex



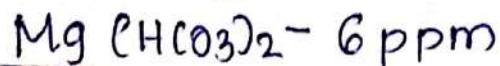
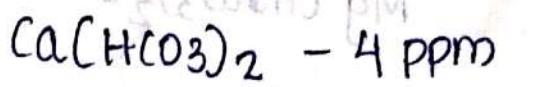
Hard water or sample water is pipetted and the buffer solution ($\text{NH}_4\text{OH-NH}_4\text{Cl}$) is added to maintain the pH around 10. Then indicator (Eriochrome black T) is added to the solution and it becomes wine red colour due to the formation of metal-EBT complex. Then the solution is titrated against EDTA. EDTA form complexes with metal ions present in water.

Near the end point there is no free metal ions on EDTA making complex so EDTA break the metal EBT complex and take the metal ions from there.

Therefore, the free indicator is regenerated and the solution becomes dark blue in colour.

* The stability of metal-EBT complex is less than metal EDTA complex.

? calculate the temporary, permanent and total hardness of water (in ~~the~~ ppm) having following composition:



CaSO_4 - 8 ppm and MgSO_4 - 10 ppm.

Temporary hardness is due to the bicarbonates of Ca and Mg.

$$\text{Temporary hardness} = \frac{4 \times 100}{81 \times 2} = \underline{\underline{400}} \quad \frac{400}{81 \times 2}$$

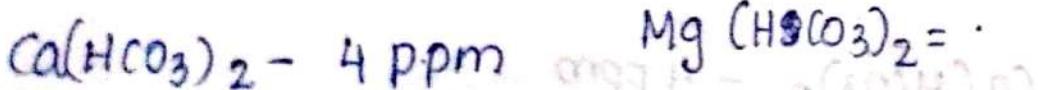
$$\frac{4 \times 100}{81 \times 2} + \frac{6 \times 100}{73 \times 2} = \frac{400}{162} + \frac{600}{146} = \underline{\underline{6.58 \text{ ppm}}}$$

Permanent hardness is due to CaSO_4 and MgSO_4 .

$$\text{Permanent hardness} = \frac{8 \times 100}{136} + \frac{10 \times 100}{120} = \underline{\underline{14.21 \text{ ppm}}}$$

$$\text{Total hardness} = \underline{\underline{6.58 + 14.21 = 20.79 \text{ ppm}}}$$

? calculate the temporary, permanent and total hardness of water having following composition.



$\text{CaSO}_4 = 8 \text{ ppm}$ $\text{MgSO}_4 = 10 \text{ ppm}$ $\text{NaHCO}_3 = 3 \text{ ppm}$ 8

When NaHCO_3 is present in water the temporary hardness increases at the expense of permanent hardness. But the total hardness remains the same.

? calculate the temporary and permanent hardness of water which contain $\text{Ca}^{2+} = 800 \text{ ppm}$.

$\text{Mg}^{2+} = 96 \text{ ppm}$, $\text{HCO}_3^- = 976 \text{ ppm}$, $\text{Cl}^- = 146 \text{ ppm}$

$\text{SO}_4^{2-} = 96 \text{ ppm}$ $\text{Na}^+ = 112 \text{ ppm}$

Estimation of hardness - volume calculation

Standardization of EDTA

D) Step 1

EDTA [burette] \times 50 ml • Std. Hard water

+ Buffer solution (10-15 ml)

+ Indicator [EBT] - (3-4 drops)

Endpoint \rightarrow wine red \rightarrow blue.

Volume of EDTA = V_1 ml

Step 2

Titration of unknown hardwater.

Burette \rightarrow EDTA, Pipette \rightarrow 50 ml unknown hard water
Burette add indicator + buffer solution (10^{-5} M)
and titration to

End point \rightarrow wine red to blue.
Volume of EDTA = V_2 ml

Step 3

Titration for permanent hardness.

50 ml boiling water - pipetted out
Burette [EDTA]

Volume of EDTA = V_3 ml

1) Calculation
50 ml of Standardized hard water $\Rightarrow V_1$ ml of EDTA.

$$= 50 \times \frac{1 \text{ g of Ca}}{\text{1 ml of EDTA}}$$

$$= 50 \times 1 \text{ mg of } \text{CaCO}_3 = V_1 \text{ ml of EDTA}$$

$$1 \text{ ml of EDTA} = \frac{V_1 \times 1 \text{ ml of EDTA}}{50 \text{ mg of CaCO}_3}$$

2) Total hardness

50 ml of unknown hard water = pipetted out
 $\times \frac{V_2}{V_1} \text{ ml of } 60$

$$1 \text{ ml of EDTA} = \frac{50 \text{ ml}}{V_2} = \frac{V_2 \times 50 \text{ mg of CaCO}_3}{V_1}$$

\checkmark 50 ml of unknown hard water = $V_2 \times \frac{50}{V_1}$ mg of CaCO_3^{10}

1 L of unknown hard water = $\frac{V_2 \times 1000}{V_1}$ mg of CaCO_3 .

Total hardness of water = $\frac{V_2 \times 1000}{V_1}$ mg/L or ppm

3) Permanent hardness

50 ml boiled water = V_3 ml of EDTA.

$$= V_3 \times 1 \text{ ml}$$

$$= V_3 \times \frac{50}{V_1} \text{ mg of } \text{CaCO}_3.$$

Permanent hardness of water = $\frac{V_3 \times 1000}{V_1}$ mg/L or ppm.

Temporary hardness = Total hardness - Permanent hardness.

$$= \frac{V_2 \times 1000}{V_1} - \frac{V_3 \times 1000}{V_1}$$

$$\frac{1000}{V_1} [V_2 - V_3] \text{ mg/L or ppm.}$$



Water softening methods

1. Lime Soda process
2. Ion exchange process.

Water Softening methods

hardness level $< 2 \text{ ppm}$ is required for ~~old~~ boiler. Softening of water is the removal of hardness.

Producing substance for ions from water by various method.

Lime Soda process

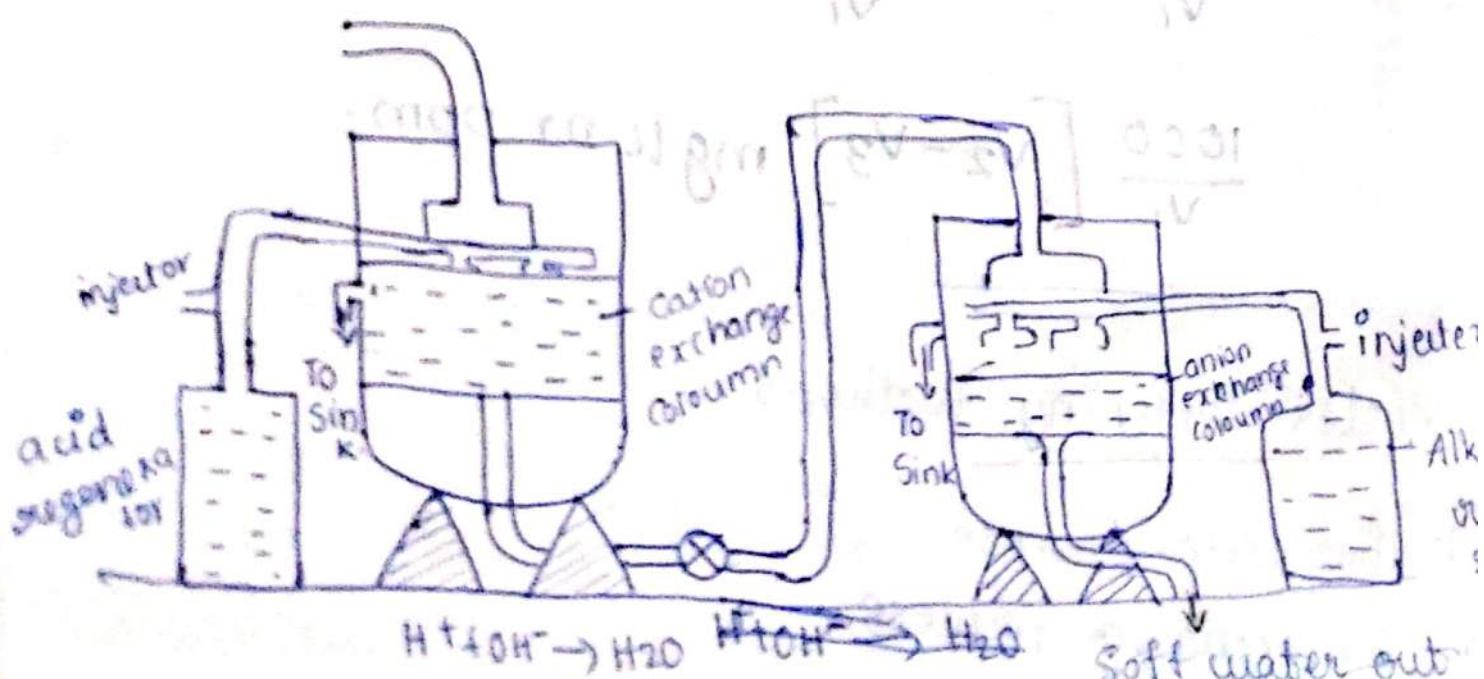
and ion exchange process.

Ion exchange process \rightarrow It is a reversible chemical reaction in which ions from solution exchanged for a similarly charged ion attached to an immobile solid particles.

The solid ion exchange particle may be naturally occur-

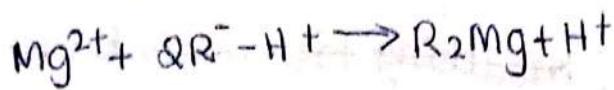
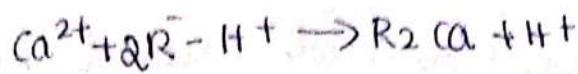
ing inorganic zeolites or synthetically produced organic resins.

Cation exchange resin



At cation exchange column

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At anion exchange column



Regeneration of Exchange column

At cation exchange column

in the case of $R_2 Ca + 2HCl \rightarrow 2R^- H^+ + CaCl_2$.

in the case of $MgCl_2$. $R_2 - Mg + H_2SO_4 \rightarrow 2R^- H^+ + MgSO_4$.

At anion exchange column (regeneration of anion exchange column)



Advantages

* To soften even acidic or alkaline waters.

* Treated water has residual hardness of 0 ppm

only and hence it is desirable for using high pressure boilers.

- * NO sludge formation.
- * Resins can be regenerated and reused hence it can be applied for ~~breathing~~ for ~~air to be used~~ treating to be used in high pressure boilers.

Disadvantages

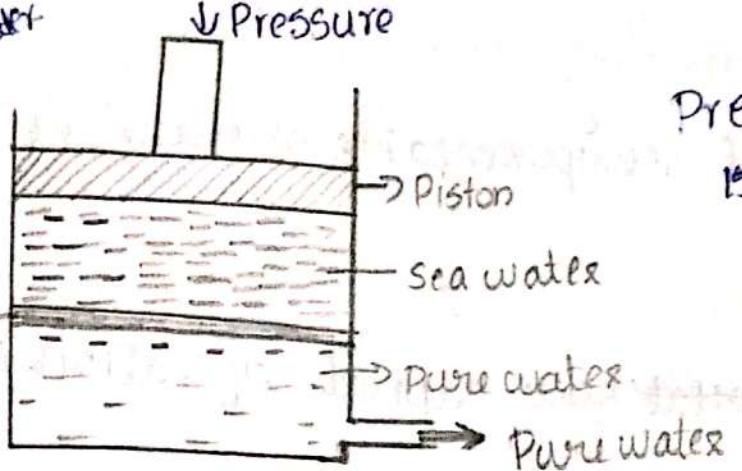
- * Highly cost.
- * It cannot be used for the purification of pathogens.
- * Water above 100 ppm cannot be purified.

Osmosis

It is the flow of solvent from ~~to lower concentration~~ to higher concentration through a semipermeable membrane. or [flow of solute from higher concentration to lower concentration].

If the external applied voltage is more than osmotic pressure solvant flow from higher concentration to lower concentration. It is known as reverse osmosis.

Purification
of seawater
by reverse
osmosis



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Pressure

15-40 kg/m²

Osmosis is the flow of solvent molecules from a region of small conc. to a region of higher conc. through a semipermeable membrane [which allows only the movement of solvent molecules].

Films of cellulose acetate, polyamide, polymers

etc are used as
Polymethacrylate etc

Semipermeable membrane. When a pressure \uparrow than osmotic pressure [$15-40 \text{ kg/m}^2$] is applied externally the osmosis takes place in the oppo. reverse direction which is known as reverse osmosis. i.e. pure solvent is separated from its contaminants.

Advantages

- * In this ionic, non ionic, colloidal and high molecular weight organic impurities can be

removed

- * The life of semipermeable membrane is very high.
- * ~~No capital~~ Low capital operation and maintenance cost.
- * It removes colloidal silica which is not removed by demineralisation.
- * Simple and reliable process.
- * The membrane can be replaced ~~by~~ within few minutes thereby ensuring unlimited water supply.

Domestic water or manipulated water treatment

Removal of suspended impurities

- 1) Screening
- 2) Sedimentation - if colloidal particles are present coagulants will be used like alum ($\text{K}_2\text{SO}_4 \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$) for sedimentation.
- 3) Filtration → filter paper or sand filters will be used for filtration.

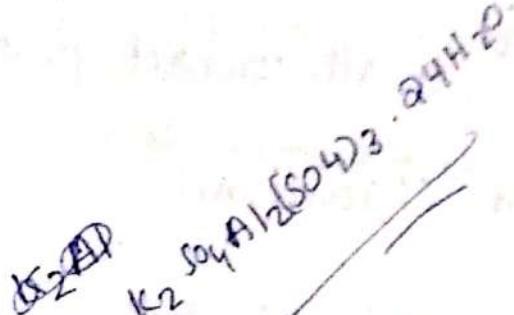
Q) Removal of micro organisms (Disinfection Method)

i) ~~Chlorination~~ chlorination

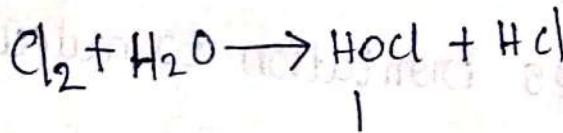
2) by using ozone

3) U-V disinfection.

Chlorination



The process of removing or killing the pathogenic bacteria and other microorganisms from water to make it safe for use is called disinfection. The chemicals added to water for this process are called disinfectants.



hypochlorous acid. (it acts as disinfectant) deactivate the pathogen.

Factors affecting efficiency of chlorine

Time of contact

The rate of killing of microorganisms is maximum at the beginning and decreases with time.

Temperature of water

When temperature increases the death rate also

increases.

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pH of water

At lower pH small contact period require to kill major % of organisms.

Advantages of chlorine

- * It is economical and effective.
- * Storage is easy.
- * It can be used at low and high temperature.
- * Salty impurities are not introduced to water.

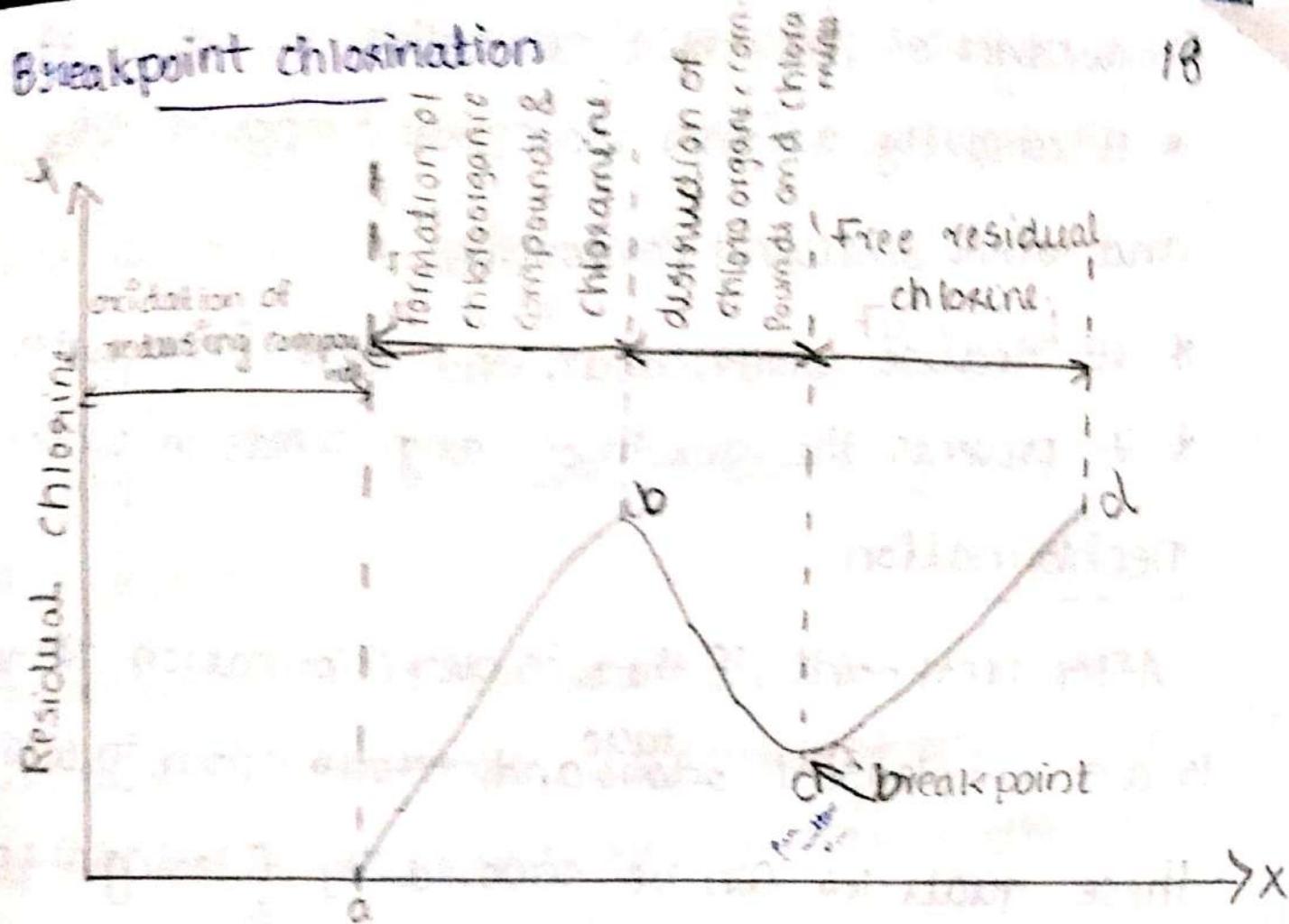
Disadvantages

- * Cl when added excess produce an unpleasant taste and odour and causes irritation to mucus membrane.
- * It is more effective below $\text{pH} = 6.5$ and less effective at higher pH values.

Breakpoint chlorination

Breakpoint chlorination

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Applied chlorine dose

The addition of Cl at the dip or break is called breakpoint chlorination.

Addition of Cl to water in insufficient amounts to kill all microorganisms and destroy it completely by oxidation. Water leaves behind some free chlorine (0.1 - 0.2 ppm).

To continue the disinfection action against further contamination by disease causing bacteria during storage and transport.

Advantages of breakpoint chlorination

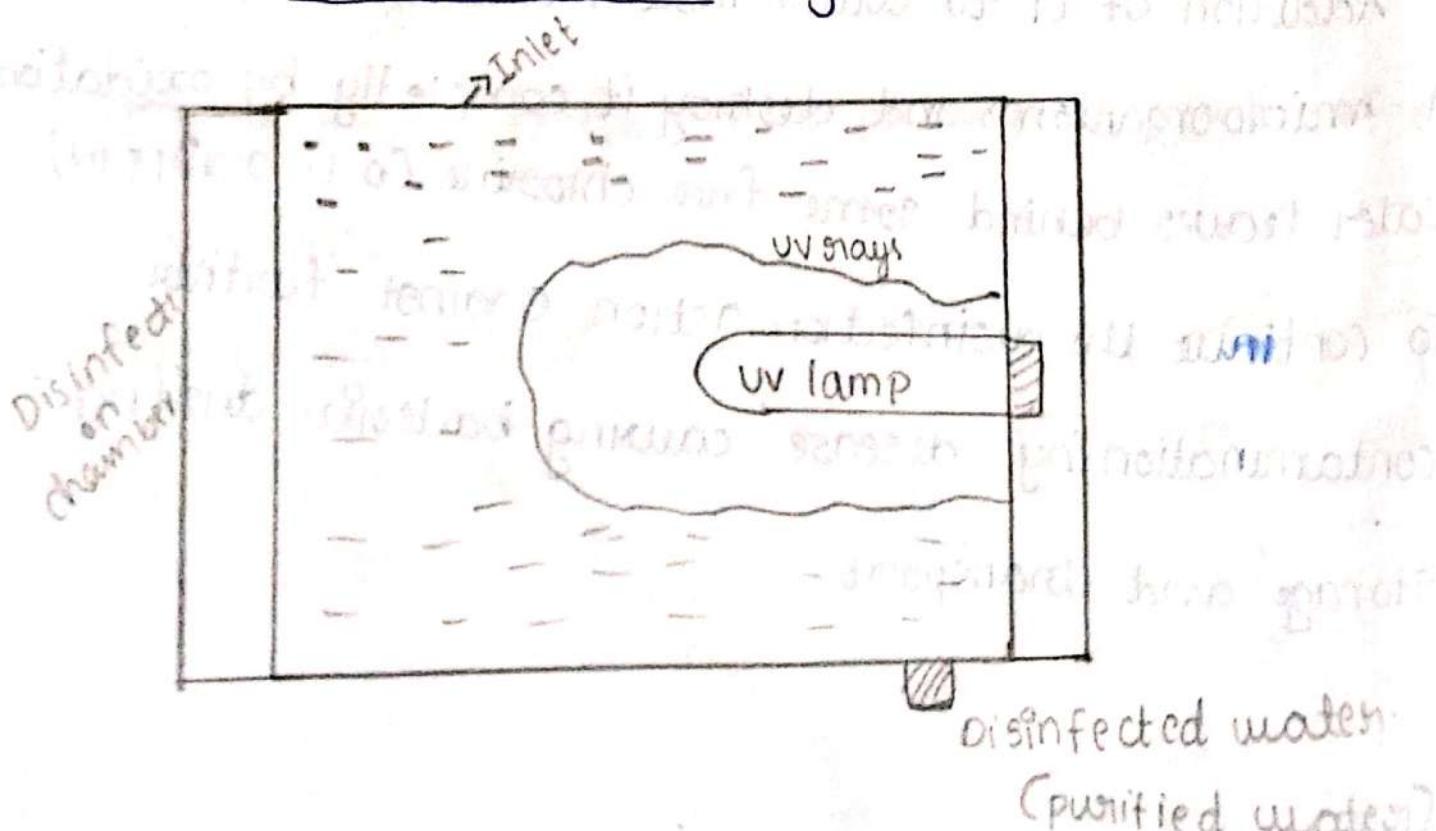
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- * It completely oxidises the organic compound NH_3 and other reducing compounds.
- * It reduces colour, odour, and taste from water.
- * It prevents the growth of any weeds in water.

Dechlorination

After breakpoint, if there is over chlorination there is an unpleasant ~~odour~~^{taste} and ~~toxic~~ odour in water, these qualities can be removed by filtering the over chlorinated water through a bed of molecular carbon.

② Disinfection by U-V light



UV light in the range of 200-400 nm is used for disinfection process. It is a very good disinfecting agent and kills all disease causing bacteria.

Advantages

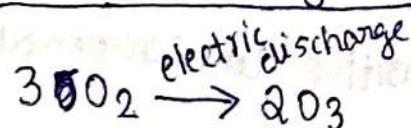
- * UV effectiveness is relatively insensitive to temperature and pH differences.
- * It requires very little contact time.
- * UV treatment is rapid in terms of energy use it is approximately 20000 times effective than boiling.
- * It requires minimum space for equipment and contact chamber.
- * It does not affect minerals in water.
- * No impact on the environment except for disposing of used lamps.

Disadvantages

- * UV is not suitable for water with high levels of suspended solids, turbidity, colour, or organic matter.
- * It leaves no residual disinfectant in water.
- * No technical database exist on how well the equipment works.
- * No standardised mechanism to measure.

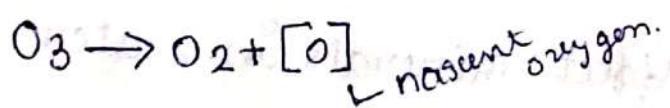
* If the flow rate is high without sufficient UV exposure heat will build up in the chamber and damage the UV lamp.

Disinfection by ozone / ozonation.



Ozone is an excellent disinfectant which is produced by passing silent electrical discharge through cold and dry oxygen.

O_3 is highly unstable and breaks down liberating nascent oxygen



Nascent oxygen is a powerful oxidising agent and kills almost all bacteria as well as oxidises the organic matter present in water. For carrying out the disinfectant by ozone is released ^{to water} it is injected to water and they are allowed to come in contact in a sterilisation tank. The disinfectant water is removed from the top. The contact period is 10-15 min and the usual dose strength is 0.2-3 ppm.

Advantages

- * The process is not harmful, since it is unstable and decomposes to oxygen.
- * The taste of water is improved with ozone.
- * It removes colour, odour etc without any residue.
- * O₃ sterilisation is an expensive process.

Dissolved oxygen [DO]

The free non compound oxygen present in water is known as dissolved oxygen. It is an important parameter in assessing water quality, because of its influence on the organisms living within a body of water. The bonded oxygen molecule in water cannot be counted towards dissolved O₂ levels. Pure water at 30°C can ~~hold~~ hold 7.8 ppm DO, but in 20°C it can hold 9.2 ppm.

Henry's law: Dissolution of a gas in liquid is \propto pressure and inversely proportional to ~~absolute~~ Temperature.

BOD and COD

BOD → biological oxygen demand.

COD → chemical oxygen demand or biochemical oxygen demand

BOD

It can be defined as the amount of oxygen required by aerobic microorganism for oxidation of biologically oxidisable matter present in 1L of sewage water for a period of 5 days at 20°C.

Significance of BOD

- * DO is an important factor that determines the quality of water.

- * The presence of ~~BOD~~ Biologically oxidisable substances like carbohydrates, proteins etc increase the BOD of water.

- * By knowing the value of BOD extent of pollution can be determined.

$$\text{BOD}_5 = \frac{D_1 - D_2 \times \text{vol of sample after dilution}}{\text{vol of sample before dilution}}$$

D_1 - initial DO content

D_2 - final DO content after 5 days

COD

COD is the amount of O_2 required for the complete oxidation of biologically active and inert materials present in 1L of sewage water using chemical oxidising agent such as $K_2Cr_2O_7$ (potassium dichromate).

COD measurements takes only 3 hours for the result.

Procedure

* Known volume of sewage water + chemical $K_2Cr_2O_7$ soln + dil. H_2SO_4 (1N)

* Reflected, for 2 hours in presence of Ag_2SO_4 catalyst

- Solution cooled and titrated with standardised ferrous ammonium sulphate soln.

$$COD = \frac{(V_1 - V_2) \times N \times 8 \times 1000}{X}$$

V_1 and V_2 are volume

of ferrous ammonium sulphate soln used for blank and test sample.

$N \rightarrow$ Normality of FAS solution (in mol/l)

$X \rightarrow$ Sample volume.

BOD

- * It is defined as the amount of O_2 required by aerobic microorganisms for oxidation of biologically oxidisable matter present in 1L of sewage water for a period of 5 days at $20^\circ C$.

- * It takes days for the result.

$$\text{BOD} = \frac{(D_1 - D_2) \times \text{Vol of sample}}{\text{Vol of sample before dilution}}$$

~~Sewage tank~~

- * Less efficient than COD

COD

- * It is the amount of O_2 required for the complete oxidation of biologically active and inert materials present in 1L of sewage water using chemical oxidising agents such as $K_2Cr_2O_7$.

- * It takes only 3 hrs for the result.

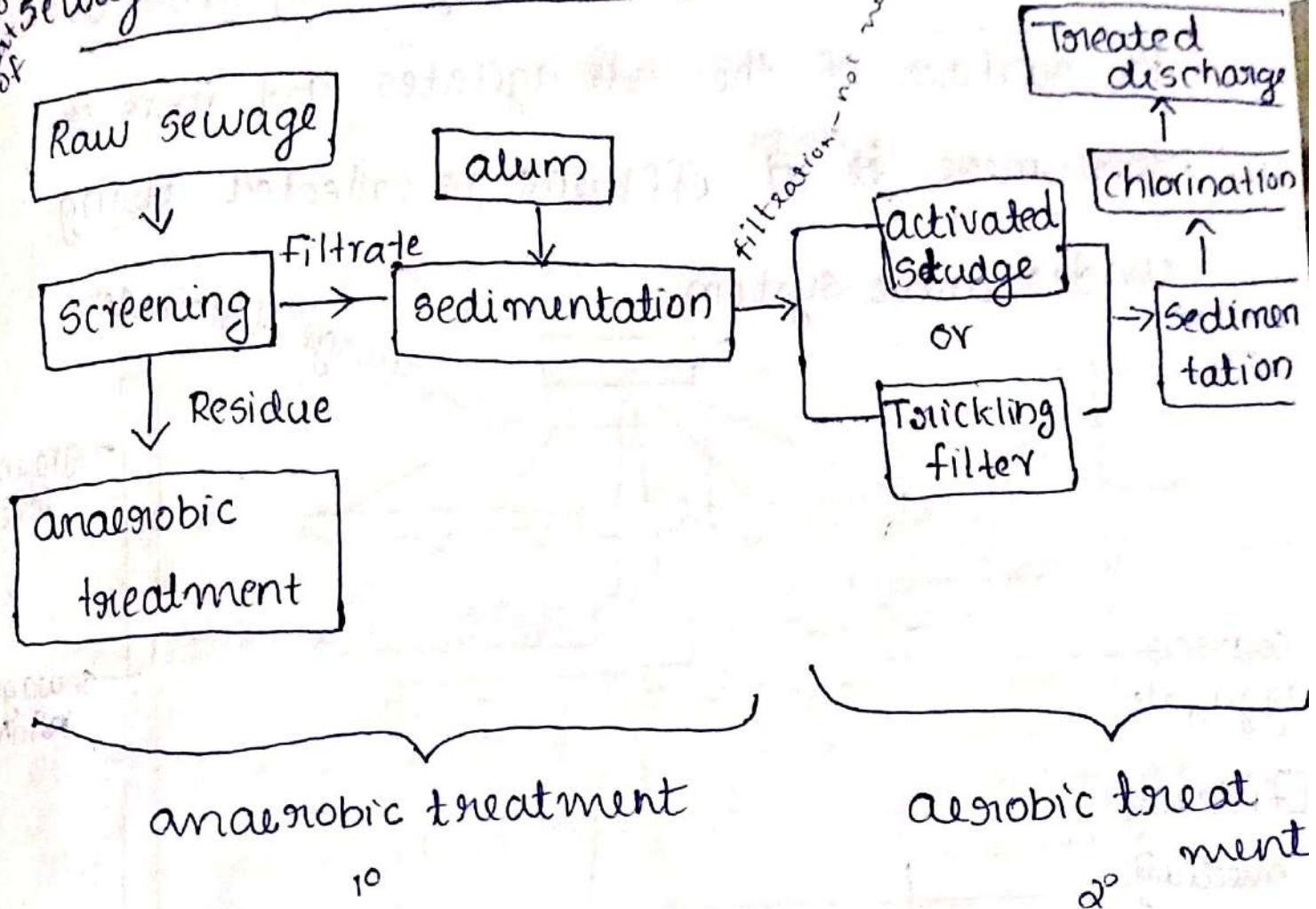
$$\text{COD} = \frac{(V_1 - V_2) \times N \times 8 \times 1000}{DC}$$

- * Efficient.

Sewage treatment

The sewage water is treated before sending it into running streams. The presence of biologically oxidisable matter increases BOD of water. The artificial sewage treatment process is known as sewage.

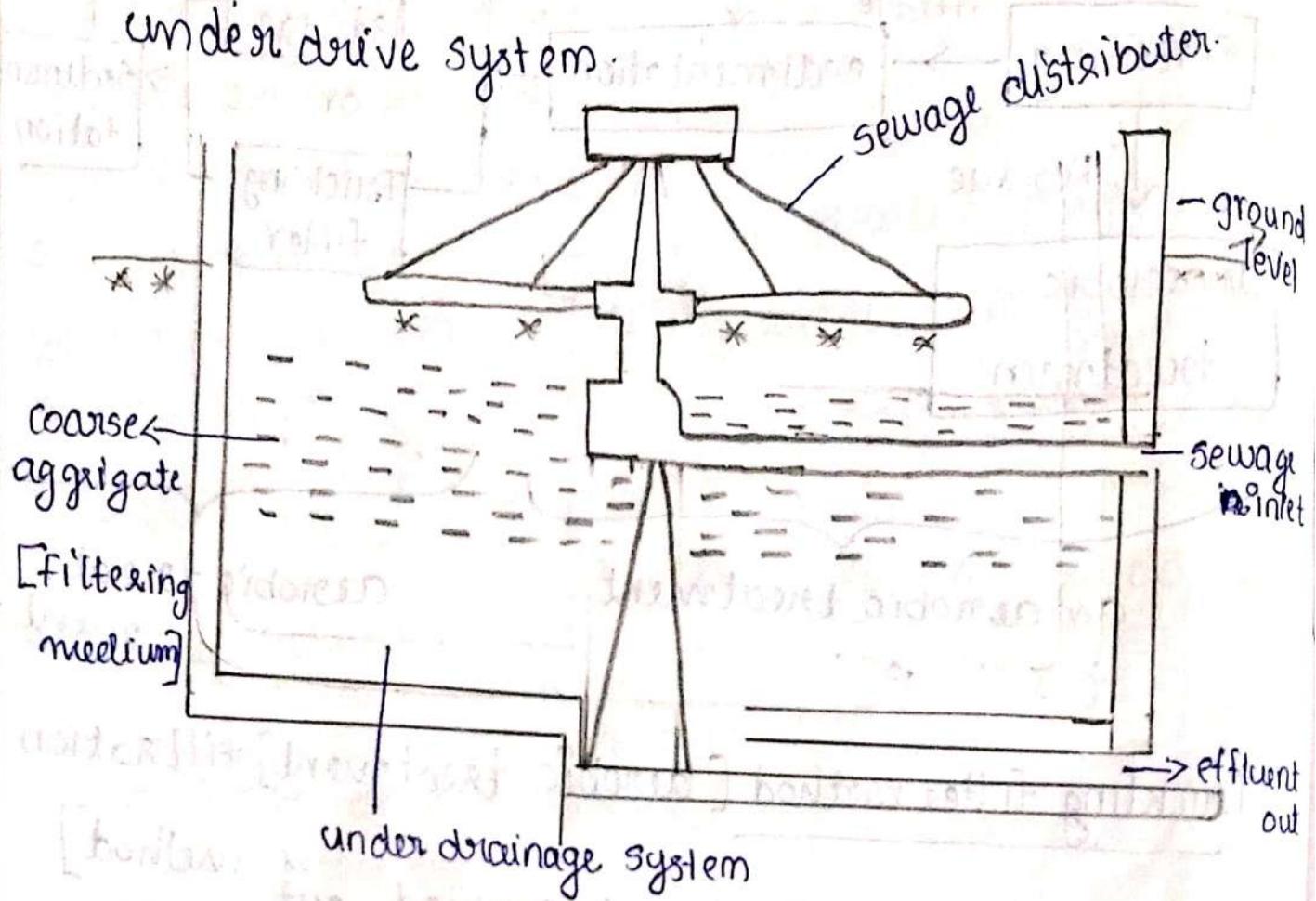
Flow chart of sewage treatment (sewage)



Trickling filter method [aerobic treatment] filtration

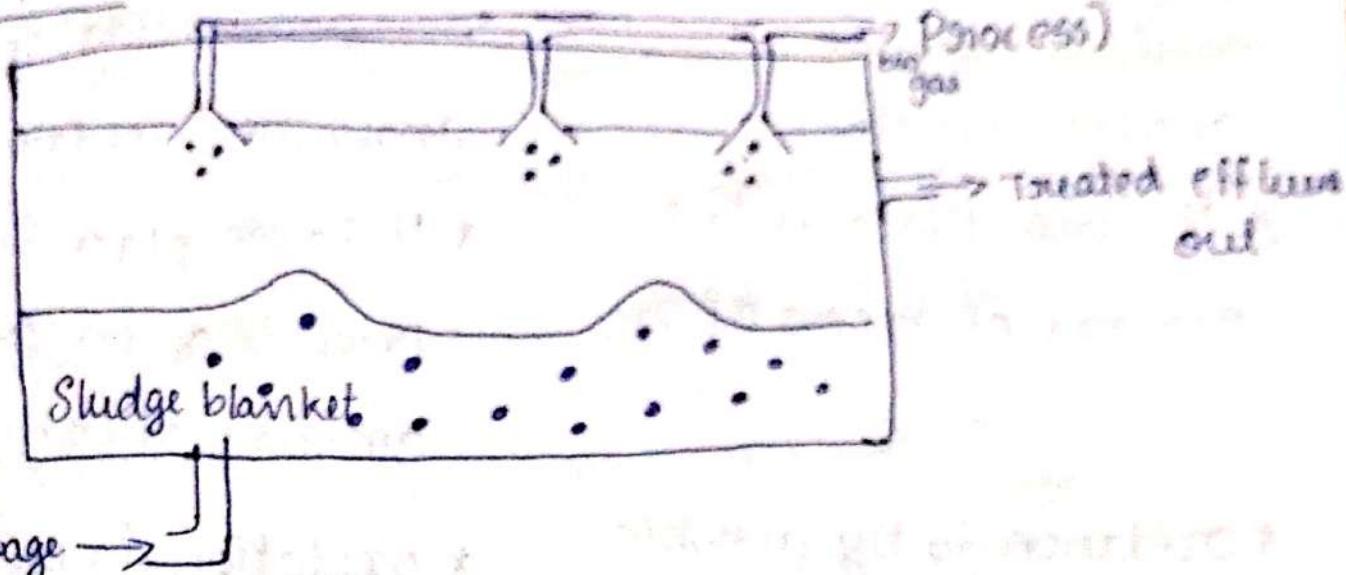
It's a biological treatment carried out with trickling filters. The filter is a rectangular shaped tank with about .8m depth and its is filled with broken bricks, crushed stock etc. And it is fitted with a rotating distributor. The sewage trickles over the filter with the help of rotating distributor. Then it moves down through the filtering medium and the microorganism starts consuming

organic matter in the sewage. They grow over the surface of the site agitates and more or less mere ~~it~~^{clean} effluent is collected using under drive system.



The another biological treatment is activated sludge process. aerobic processing of the sewage is carried out in the presence of a part of sludge taken from the previous oxidation process. It is a fast process and known as activated sludge process.

USAB process [Upflow anaerobic Sludge bed reactor] 26



The effluent or sewage water is fed from the bottom of reactor. It moves upward through the sludge blanket.

The sludge blanket is made of biologically formed granule of diameter 1-5 mm. The waste comes in contact with granule which contain aggregation of bacteria.

The gases like methane are formed under anaerobic condition which make internal circulation easy and help the formation and maintenance of granules. The gases are set to free and associate particles rises to the top. Degassed granules drop back to sludge blanket. Gases are collected through the upflow gas collector done at top of the reactor. The upflow

Velocity is $0.6 \text{ to } 0.9 \text{ ml/h}$.

Differentiate b/w aerobic oxidation and anaerobic oxidation

aerobic oxidation

anaerobic oxidation

* It takes place in the presence of excess of O_2 .

* It takes place in the presence of insufficient amount of O_2 .

* Oxidation is by aerobic bacteria.

* Oxidation is by anaerobic bacteria.

* The products of oxidation are CO_2 , nitrates, phosphates, sulphates etc.

* The products of oxidation are CH_3COO^+ , H_2S , NH_3 , CH_4 , phosphene etc.

* Products are non offensive smelling.

* Products are offensive smelling.

* Energy released is more and decomposition is slow.

* Less energy is released and decomposition is fast.

* No biogas fuel is produced.

* Biogas fuel (CH_4) is produced.