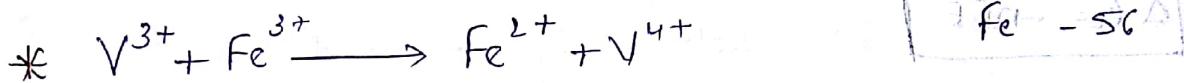


Current \propto rate of chemical reaction

Voltage \propto Change in free energy

$$1 \text{ mole of } e^- \text{ charge} = 1.6 \times 10^{-19} \text{ C} \times 6.023 \times 10^{23} / \text{mole}$$
$$= 96500 \text{ C} = 1 \text{ Faraday}$$

$$\text{Current (I)} = \frac{q}{t} = \frac{\text{charge}}{\text{time (in sec)}}$$



5.6 gm

e⁻ transfer = 1

$$\frac{5.6}{56} \times 1 = 0.1 \text{ mole.} = n$$

$$\text{Quantity of charge transferred } q = n \times F$$
$$= 0.1 \times 96500 = 9650 \text{ C}$$

* 5 millimoles of Sn⁴⁺ is converted into

Sn²⁺ in 1 hr



$$q = n \times F$$

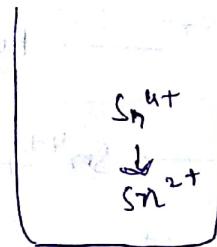
$$= 10^{-2} \times 96500$$

$$n = 5 \times 10^{-3} \text{ moles} \times 2 \rightarrow \text{no. of } e^- \text{ transfer}$$

$$= 10^{-2}$$

$$q = 965 \text{ C}$$

$$I = \frac{965}{3600} \text{ C/sec}$$



$$V_1 - \textcircled{9}$$

$$E = V_1 - V_2 \text{ (Volt)}$$

$$\text{Work} = E \times q \xrightarrow{\text{volt}} \text{coulomb}$$

$$\text{volt-coulomb} = \text{Joule}$$

$$\text{Work to be done} = -\Delta G$$

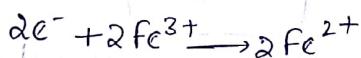
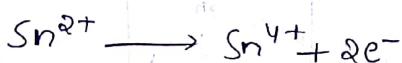
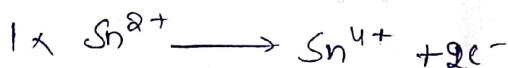
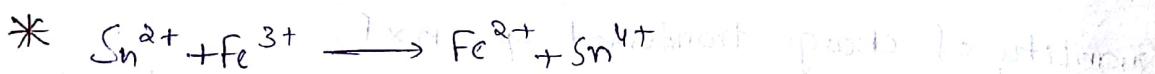
$$W = -\Delta G = Eq$$

$$= E(nF)$$

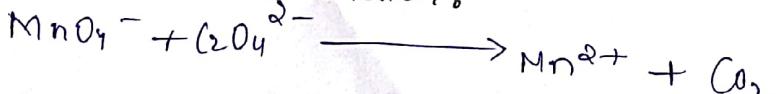
$$-\Delta G = nFE$$

$$\boxed{\Delta G = -nFE}$$

$$\text{Power} = \frac{\text{Work}}{\text{time(sec)}} = \frac{nFE}{S}$$



* Method of half reaction:

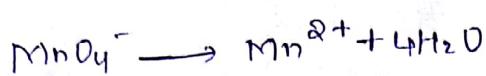


Balance elements other than oxygen & hydrogen & split





Balance oxygen by adding water



similar to no. of oxygen atoms on other side



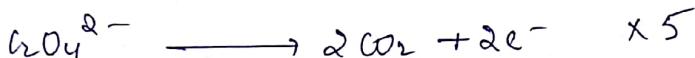
Balance hydrogen by adding



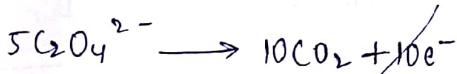
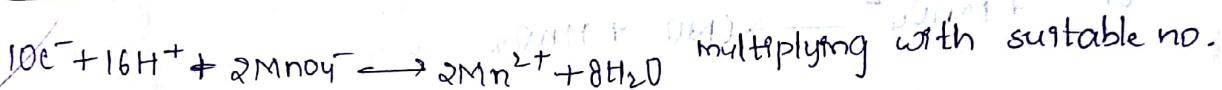
no. of protons on other side



Balance charge by adding e⁻

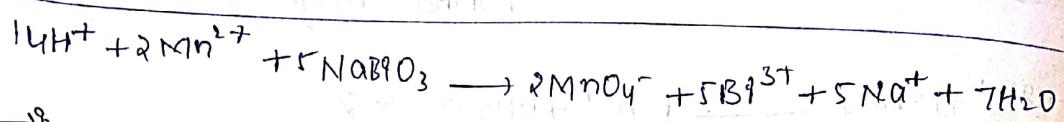
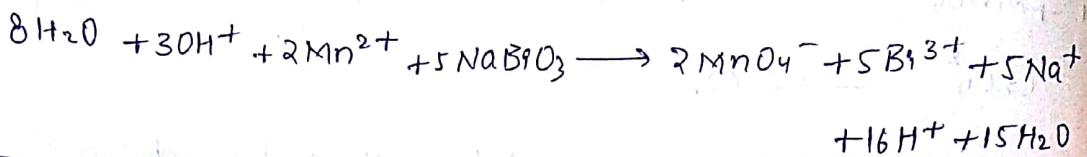
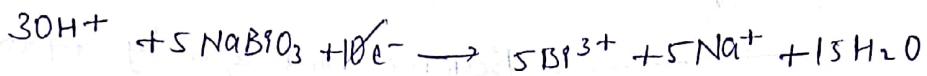
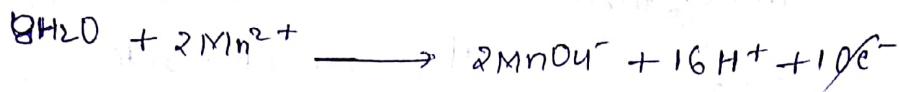
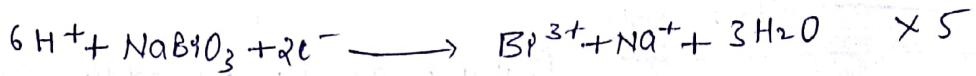
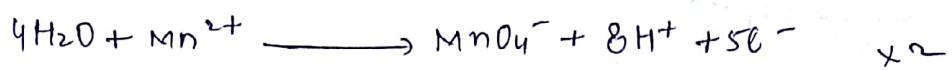


Match the no. of e⁻ by

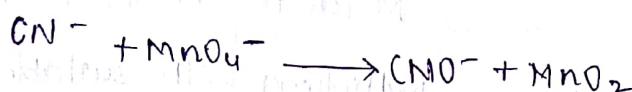


Add Na ion





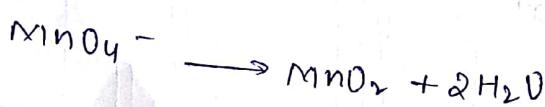
Basic Medium:



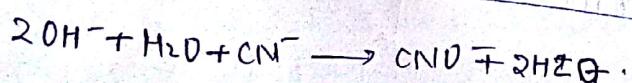
Balance elements other than O & H



Balance 'O' by adding water

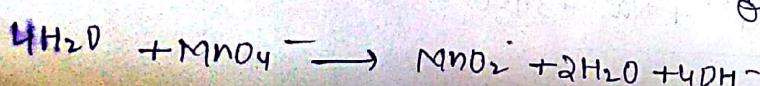


Balance 'H' by adding protons

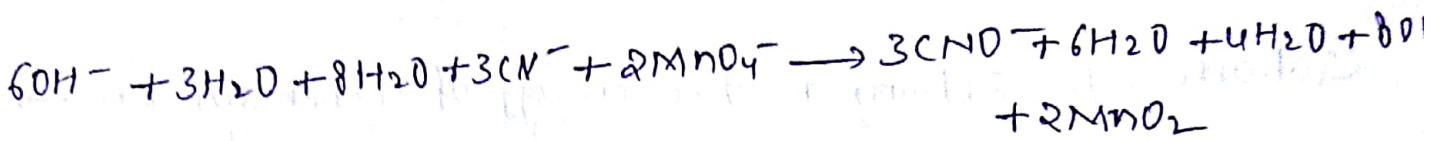
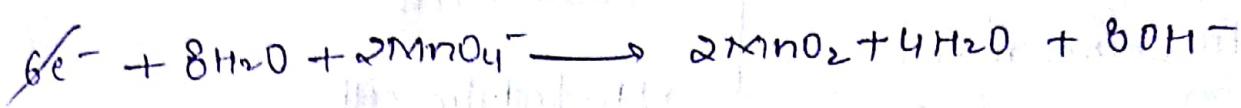
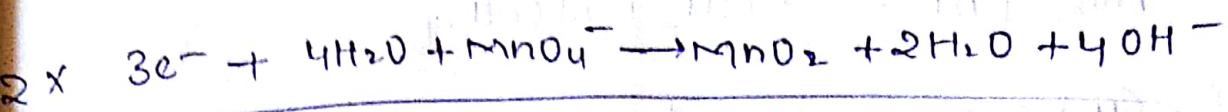


Add OH^- to neutralise H^+ to H_2O

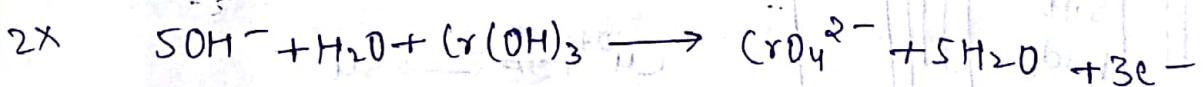
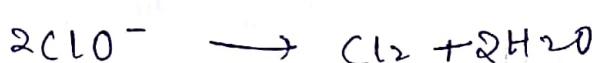
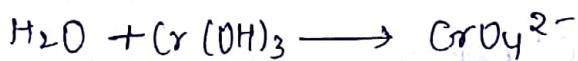
On both sides



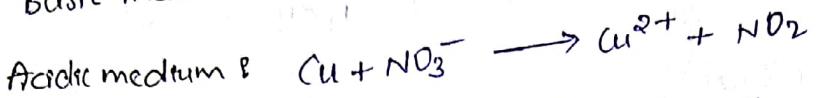
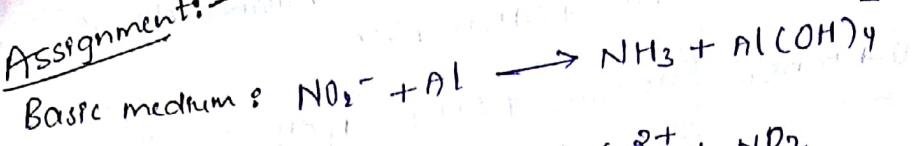
Balance charge



Cancel terms



Note

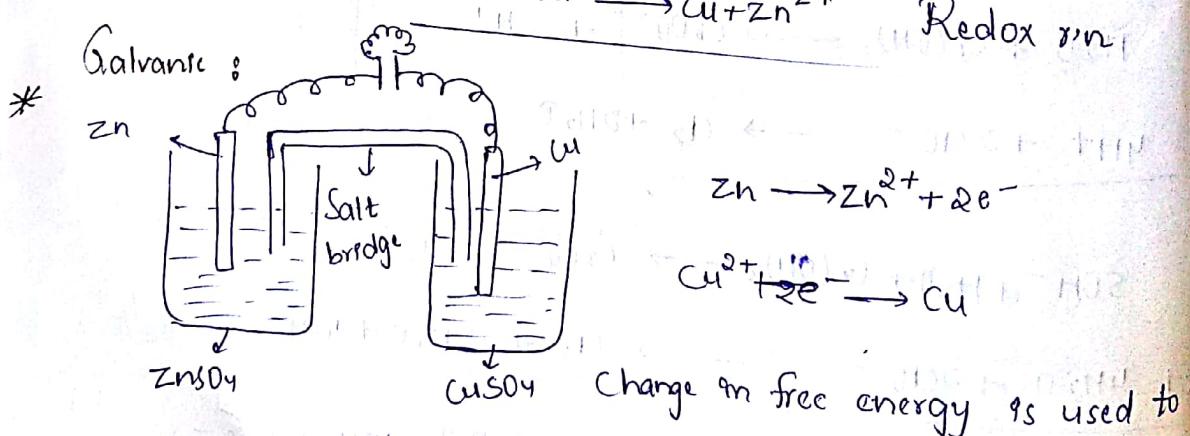
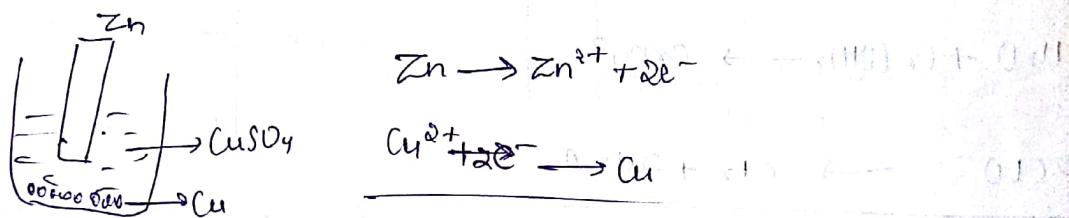
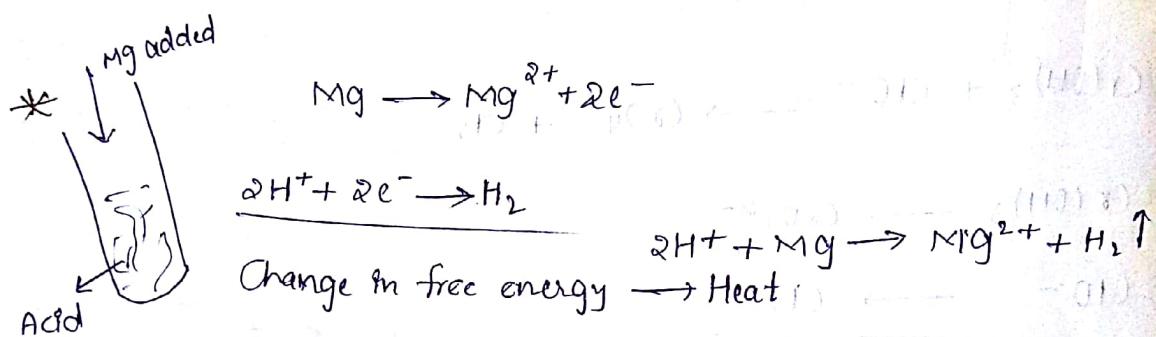


* Electrochemical cell →

- Galvanic cell
- Electrolytic cell

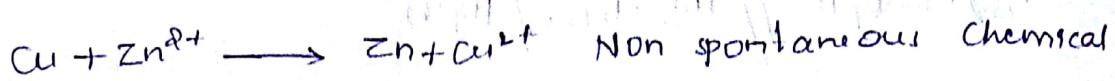
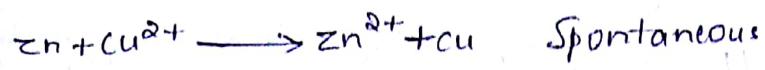
Galvanic cell: change in free energy of a chemical rxn → electrical energy

Electrolytic cell: electrical energy →



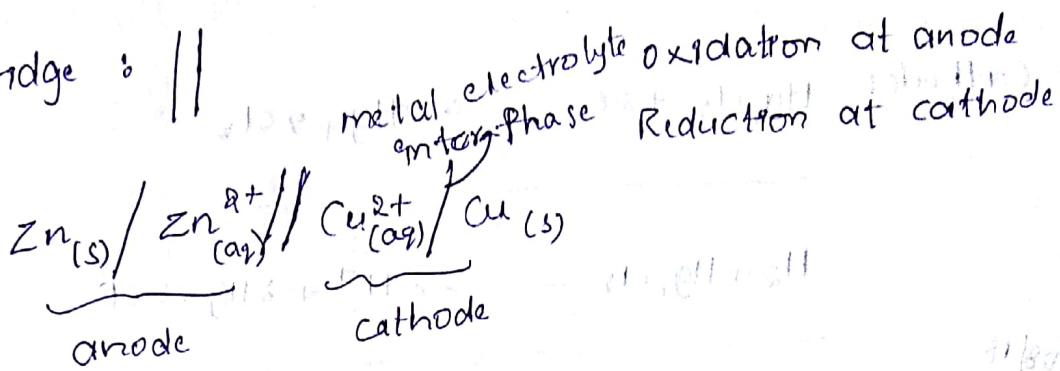
do some work by the flow of e- through an external circuit

$\Delta G^\circ = \text{spontaneous chemical rxn}$

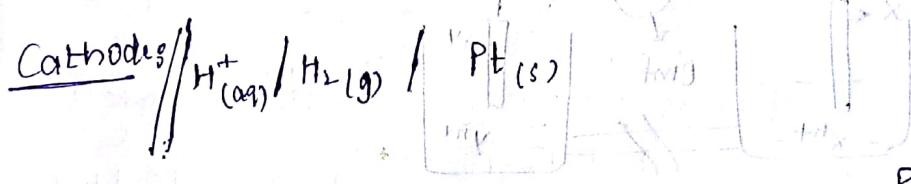
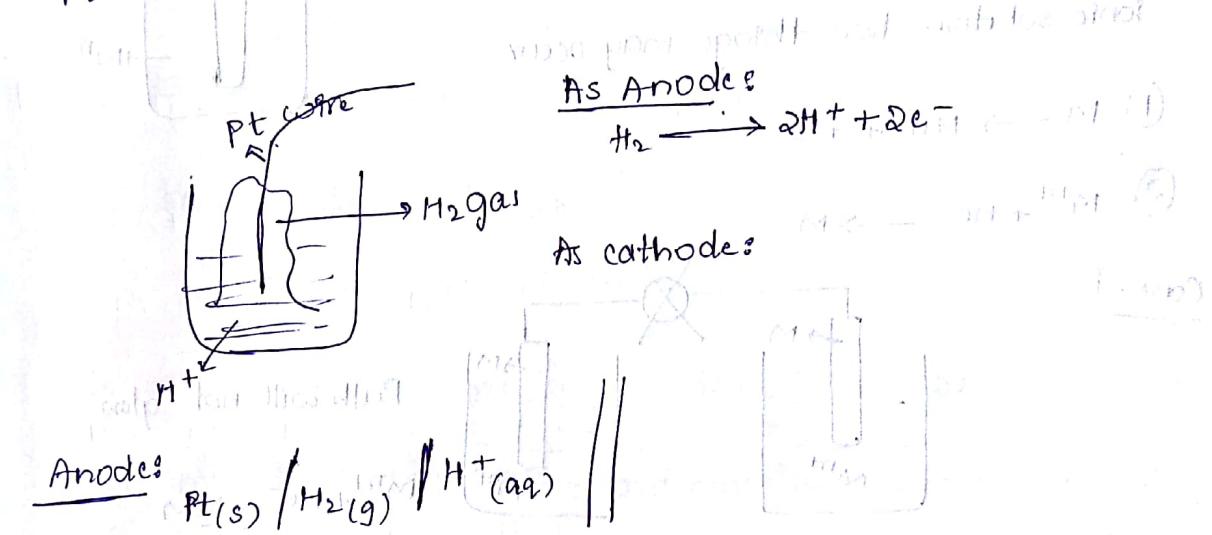


∴ can be run at expense of electricity in electrolytic cell.

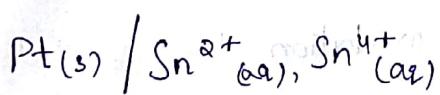
Salt Bridge : //



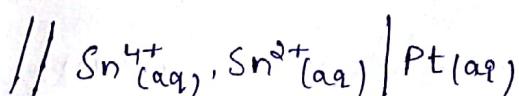
* Pt wire will not involve any chemical ∵ it is inert to all chemicals

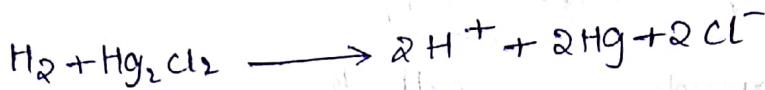
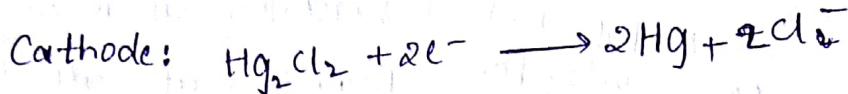
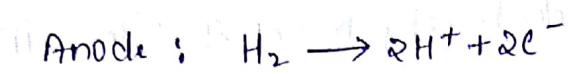
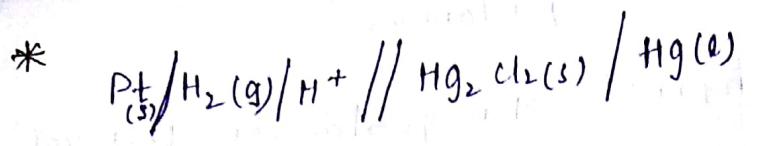


* Anodes: $Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$ to form



Cathode: $Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$

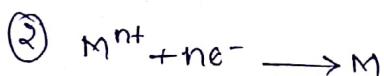
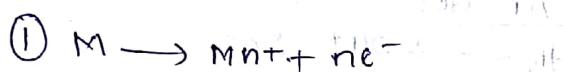




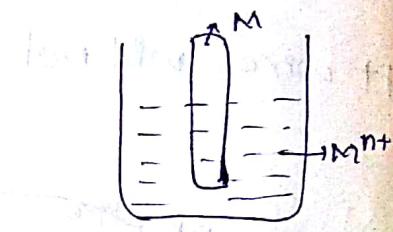
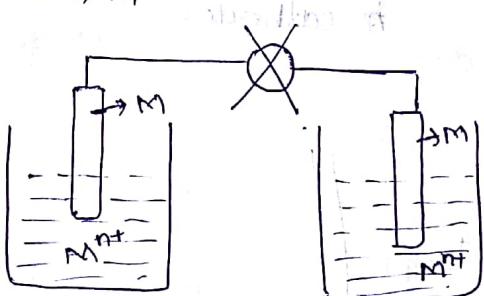
21/08/18

When we immerse a metal rod in its

Ionic solution two things may occur

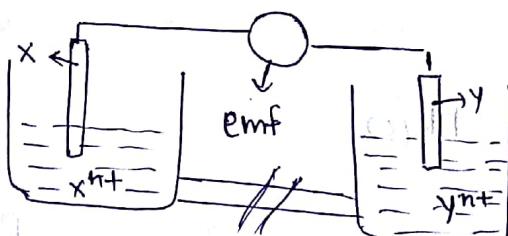


Case-i



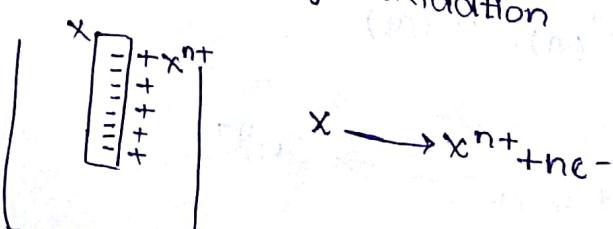
Bulb will not glow

Case-ii

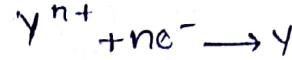
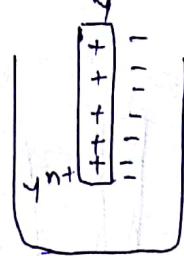


If reduction potential of $y > x$ i.e., $E_{x^{n+}/x} < E_{y^{n+}/y}$
then Y will force X to undergo oxidation

At anode: (Oxid.)

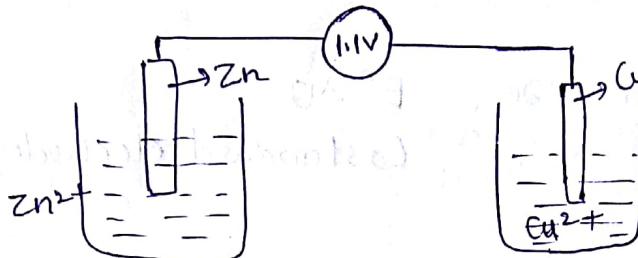


At cathode : (red.)



When we connect these two we can measure the potential

difference of the potentials developed at anode & cathode.



$$E_{Cu^{2+}/Cu} = 0.34 \text{ V}$$

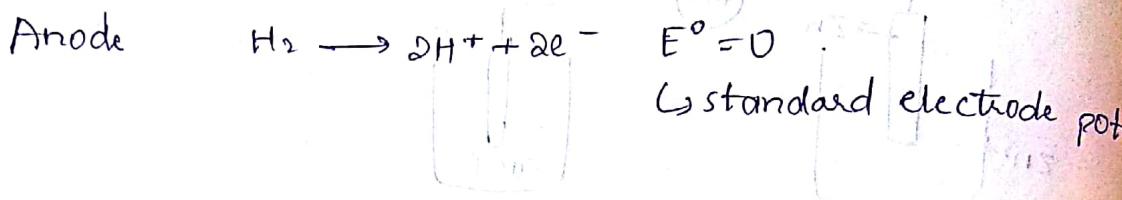
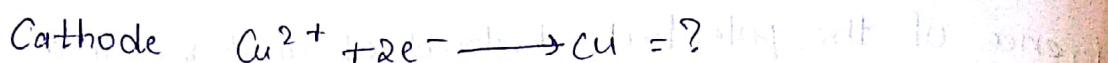
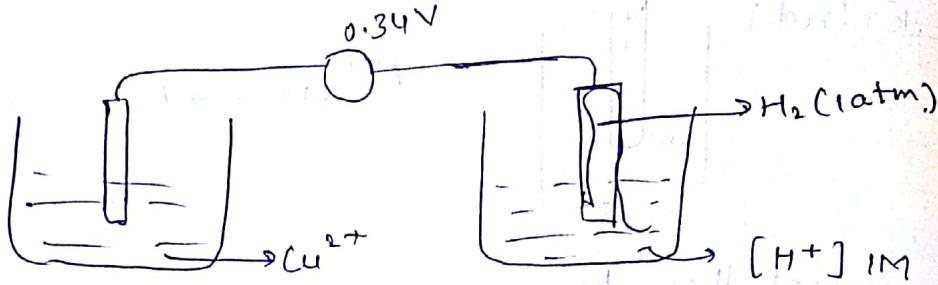
$$E_{Zn^{2+}/Zn} = -0.76 \text{ V}$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= 0.34 - (-0.76) \approx 1.1 \text{ V} \end{aligned}$$

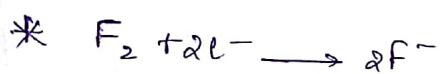
We fix metal ion conc. as 1M, temp. 25°C (298K), if gas used maintain 1 atm (standard conditions) so that we get

- same potential everywhere.

To measure standard potential of metals we use standard hydrogen electrode assuming its reduction potential to be '0V'.

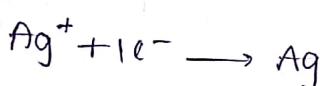


$$E_{\text{cell}} = 0.34 \quad E_{\text{all}} = E_{\text{cathode}} - E_{\text{anode}} \Rightarrow E_{\text{cathode}} = 0.34 + 0 = 0.34$$



$$+ 2.87 \text{ V}$$

} Large reduction potential

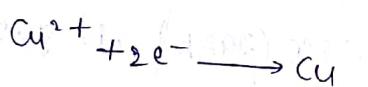


$$+ 0.8 \text{ V}$$

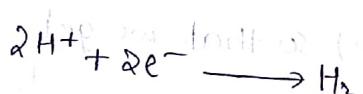
} more easy to reduce



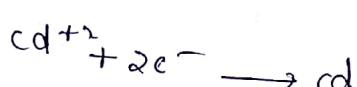
$$0.77 \text{ V}$$



$$0.34 \text{ V}$$

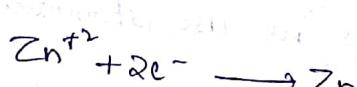


$$0$$

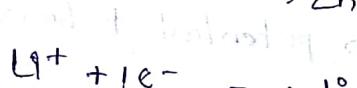


$$-0.4 \text{ V}$$

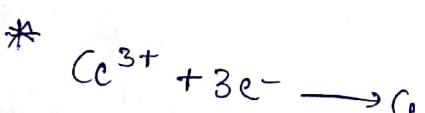
} More easily oxidised



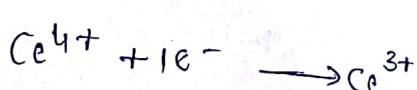
$$-0.76 \text{ V}$$



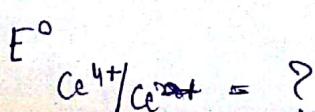
$$-3.0 \text{ V}$$



$$E^\circ \text{ Ce}^{3+}/\text{Ce} = -2.48 \text{ V} \rightarrow ①$$



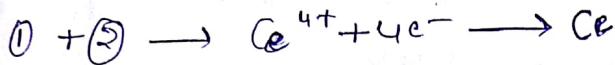
$$E^\circ \text{ Ce}^{4+}/\text{Ce}^{3+} = 1.61 \text{ V} \rightarrow ②$$



$$\Delta G_{\text{cell}}^{\circ} = \Delta G_{\text{cathode}}^{\circ} - \Delta G_{\text{anode}}^{\circ}$$

$$-nFE_{\text{cell}}^{\circ} = (-nFE_{\text{cathode}}^{\circ}) - (-nFE_{\text{anode}}^{\circ})$$

$$\Rightarrow E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$



$$\therefore \Delta G_{\text{Ce}^{4+}/\text{Ce}}^{\circ} = \Delta G_{\text{Ce}^{3+}/\text{Ce}}^{\circ} + \Delta G_{\text{Ce}^{4+}/\text{Ce}^{3+}}$$

$$\Rightarrow nFE_{\text{Ce}^{4+}/\text{Ce}}^{\circ} = -nFE_{\text{Ce}^{3+}/\text{Ce}}^{\circ} - nFE_{\text{Ce}^{4+}/\text{Ce}^{3+}}$$

$$-4 \times E_{\text{Ce}^{4+}/\text{Ce}}^{\circ} = -3(-2.48) - 1(1.61)$$

$$-E_{\text{Ce}^{4+}/\text{Ce}}^{\circ} = \frac{7.5 - 1.6}{4} = 1.45 \text{ V}$$

$$E_{\text{Ce}^{4+}/\text{Ce}}^{\circ} = -1.45 \text{ V}$$

* $E > 0$ spontaneous

< 0 non spontaneous

0 equilibrium

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$\text{We know } \Delta G = -nFE$$

$$-nFE = -nFE^{\circ} + RT \ln Q$$

Q - reaction quotient

ΔG - Change in free energy

$$Q = \frac{a_M}{a_{M^{nt}}}$$

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

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_M}{a_{M^{nt}}}$$

Activity of pure metal & saturated solution = 1

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{a_{M^{n+}}}$$

$$E = E^\circ + \frac{RT}{nF} \ln a_{M^{n+}}$$

At very low concentration activity = conc.

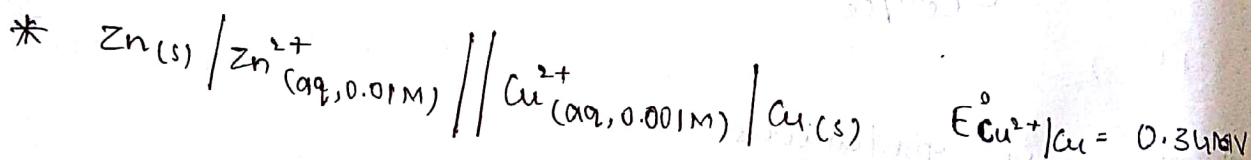
$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

$$T = 298$$

$$E = E^\circ + \frac{8.314 \times 298}{96500 \times n} \times 2.303 \log [M^{n+}]$$

$$** E = E^\circ + \frac{0.0592}{n} \log [M^{n+}] \quad \text{NERNST EQ.}$$

At const. temp. 'E' of cell increases with concentration



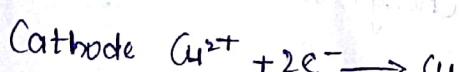
$$E^\circ_{Cu^{2+}/Cu} = 0.34 \text{ V}$$

$$E_{cell}^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= 0.34 - (-0.76)$$

$$= 1.1 \text{ V}$$

Anode



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

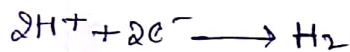
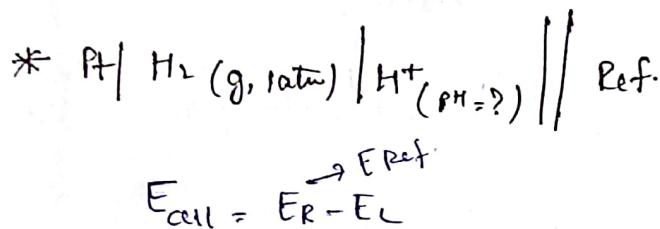
$$\alpha_{Zn} = 1$$

$$E = E^\circ - \frac{0.0592}{n} \log \left[\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right]$$

$$= 1.1 - \frac{0.0592}{2} \log \left[\frac{0.01}{0.001} \right]$$

$$= 1.1 - \frac{0.0592}{2} \times 1$$

$$= 1.1 - 0.0296$$



$$E_L = E^\circ - \frac{0.0592}{n} \log Q$$

$$E_L = -\frac{0.0592}{n} \log \left[\frac{P_{\text{H}_2} = 1}{[\text{H}^+]^2} \right]$$

$$E_L = -\frac{0.0592}{n} \log \left(\frac{1}{[\text{H}^+]^2} \right)$$

$$E_L = \frac{0.0592}{2} \log [\text{H}^+]^2$$

$$= \frac{0.0592}{2} \times 2 \log [\text{H}^+]$$

$$E_L = 0.0592 \log [\text{H}^+]$$

$$E_{\text{cell}} = E_{\text{Ref}} - E_L$$

$$= E_{\text{Ref}} - (0.0592 \log [\text{H}^+])$$

$$= E_{\text{Ref}} + 0.0592 (-\log [\text{H}^+])$$

$$E_{\text{cell}} = E_{\text{Ref}} + 0.0592 P^{\text{H}}$$

$$P^{\text{H}} = \frac{E_{\text{cell}} - E_{\text{Ref}}}{0.0592}$$

When H is used as anode

$$\frac{E_{\text{cell}} + E_{\text{ref}}}{0.0592} = \text{pH} \quad \text{When H electrode is used as cathode}$$



$$E = E^\circ - \frac{RT}{nF} \ln \vartheta$$

at equilibrium $E = 0, \vartheta = K$

$$0 = E^\circ - \frac{RT}{nF} \ln K$$

$$E^\circ = \frac{RT}{nF} \ln K$$

$$\ln K = \frac{E^\circ nF}{RT}$$

$$K = e^{\left[\frac{E^\circ nF}{RT} \right]}$$

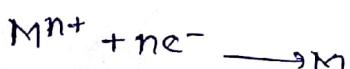
Classification of Electrodes:

- Metal-Metal ion electrode
- Metal-Metal insoluble salt electrode
- Metal-amalgam electrode
- Gas-ion electrode
-

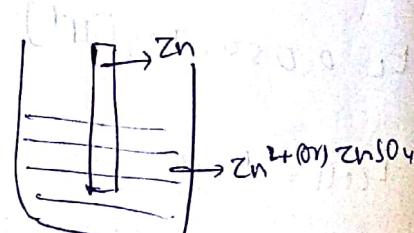
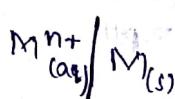
Metal-Metal ion electrode:

Zn in ZnSO_4 solution

Cu in CuSO_4 solution



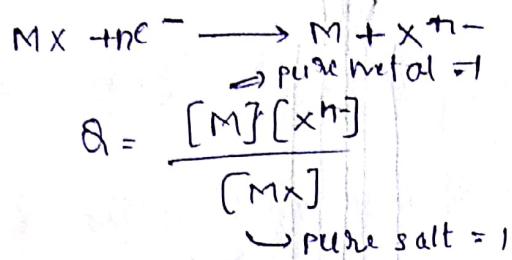
Electrode representation



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

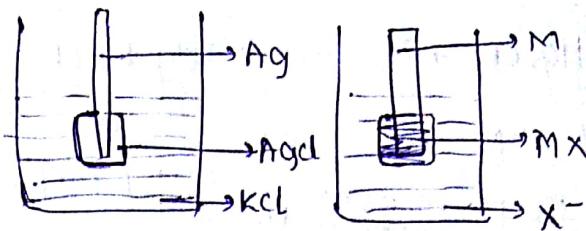
$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

Metal-Metal Insoluble salt electrode:

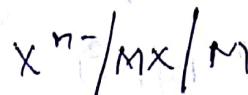


$$Q = [x^{n-}]$$

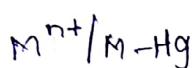
$$E = E^\circ - \frac{RT}{nF} \ln [x^{n-}]$$



representations:



Metal amalgam electrodes:

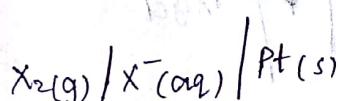


at 298K

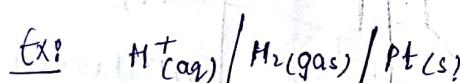
$$E = E^\circ - \frac{0.0592}{n} \log \frac{[M-Hg]}{[M^{n+}]}$$

$$= E^\circ - \frac{0.0592}{n} \log \frac{(c_2)}{(c_1)}$$

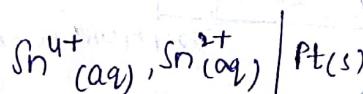
Gas ion electrodes:



$$E = E^\circ - \frac{0.0592}{2n} \log \frac{[X^{n-}]}{P_{X_2}}$$

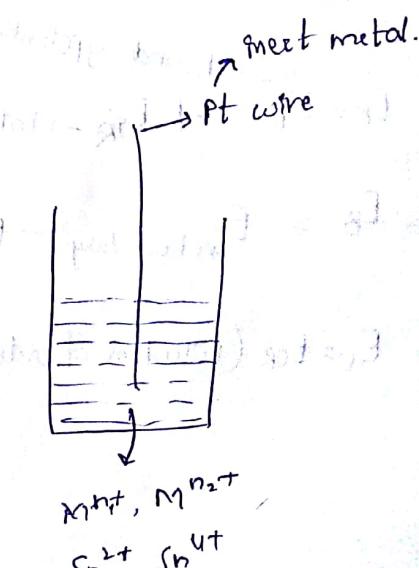
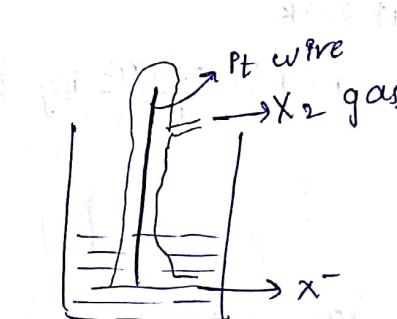


Redox electrode:



at 298K

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[M^{n+}]}{[M^{n+}]}$$



Calomel electrode:



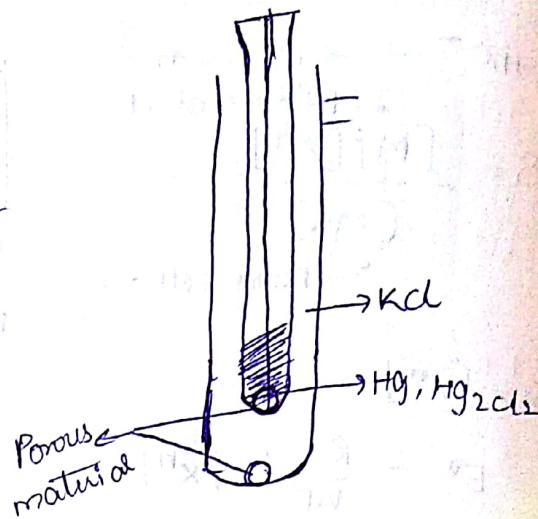
at 298K

$$E = E^\circ - \frac{0.0592}{2} \log \frac{[\text{Hg}]^2 [\text{Cl}^-]^2}{[\text{Hg}_2\text{Cl}_2]}$$

$$E = E^\circ - \frac{0.0592}{2} \log [\text{Cl}^-]^2$$

$$= E^\circ - \frac{0.0592}{2} \log [\text{Cl}^-]$$

$$E = E^\circ - 0.0592 \log [\text{Cl}^-]$$

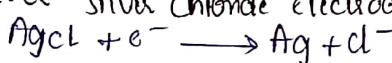


Saturated KCl = 0.24V

1M KCl = 0.23V

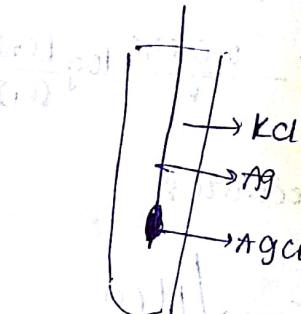
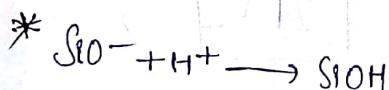
∴ 0.1M KCl = 0.334 V

* Silver-Silver chloride electrode:



at 298K

$$E = E^\circ - \frac{0.0592}{1} \log \frac{[\text{Ag}][\text{Cl}^-]}{[\text{AgCl}]}$$



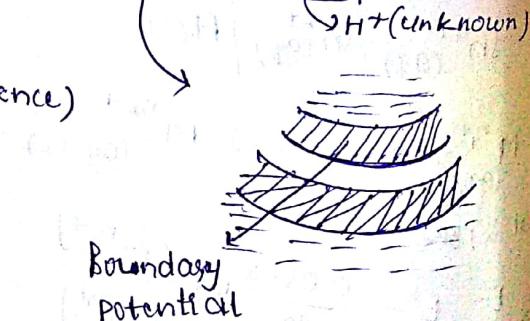
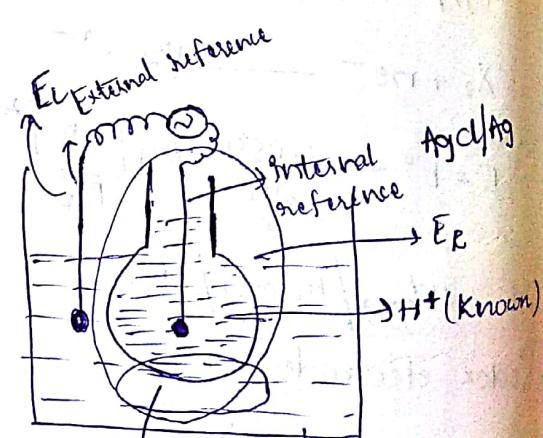
$$E_{\text{cell}} = E_R - E_L$$

$$E_R = E_B \rightarrow \text{Boundary potential}$$

$$+ E_{IR} \rightarrow \text{internal reference Potential}$$

$$E_B = E_{\text{in. boundary}} - E_{\text{out. boundary}}$$

$$E_L = E_{OR} \text{ (potential of outer/external reference)}$$



$$E_B = E^\circ - 0.0592 \log \frac{1}{[H^{+m}]} - \left(E^\circ - 0.0592 \log \frac{1}{[H^{+out}]} \right)$$

$$= E^\circ - 0.0592 \log \frac{1}{[H^{+m}]} - E^\circ + 0.0592 \log \frac{1}{[H^{+out}]} \quad \text{[cancel]} \quad \text{[cancel]}$$

$[H^{+m}]$ is constant

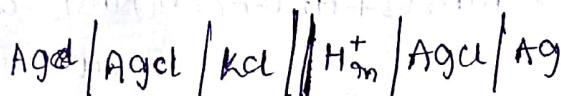
$$= \text{constant} + 0.0592 (-\log [H^{+out}])$$

$$= \text{constant} + 0.0592 P^H$$

$$E_{cell} = \text{constant} + 0.0592 P^H + E_{IR} - E_{OR}$$

$$E_{cell} = \text{constant} + 0.0592 P^H + \text{constant} - \text{constant}$$

$$E_{cell} = \text{constant} + 0.0592 P^H$$

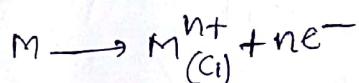


Concentration Cell:

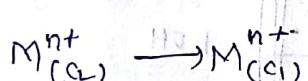
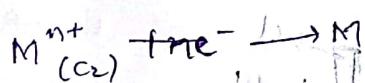
1) Electrolyte concentration cell

2) Electrode concentration cell

Anode

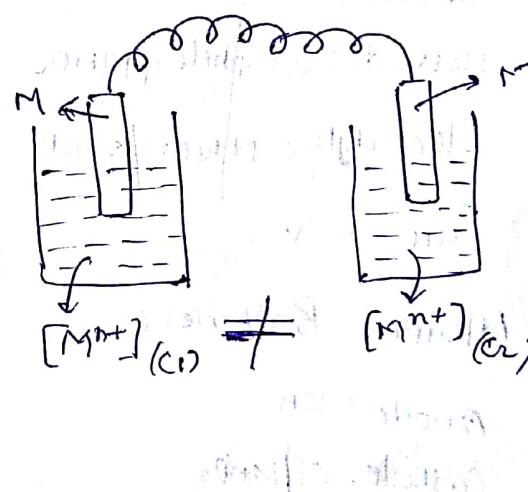


Cathode



$$\text{at } 298 \text{ K, } E = E^\circ - \frac{0.0592}{n} \log \frac{[C_1]}{[C_2]}$$

$$E = \frac{0.0592}{n} \log \frac{[C_2]}{[C_1]}$$

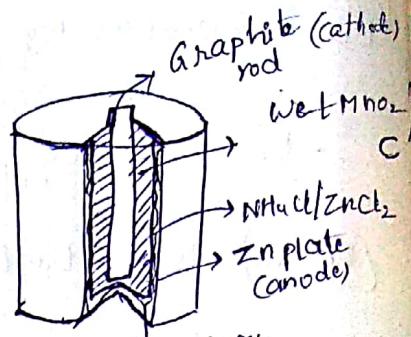
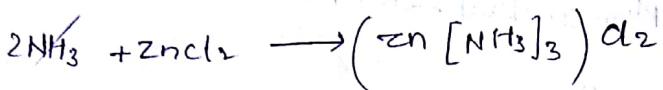
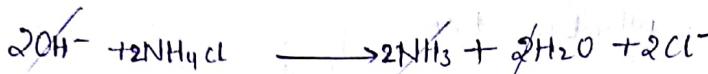
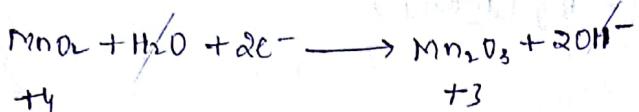


Lagrange cell / Dry cell:

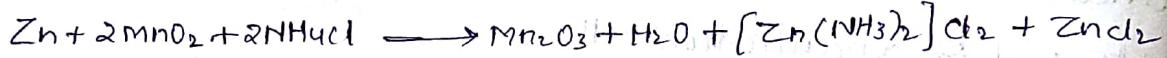
Anode



Cathode



Overall reaction:



Anode: Zn

Cathode: Graphite / MnO₂

Electrolyte: NH₄Cl / ZnCl₂

$$E_{\text{cell}} = 1.5V$$

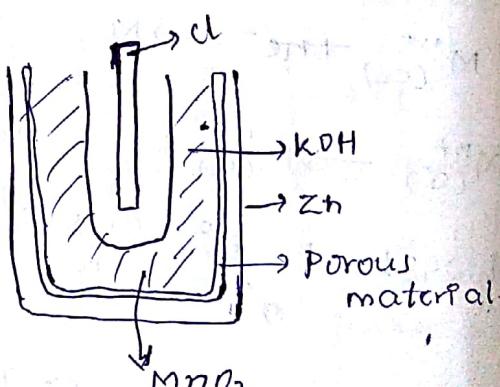
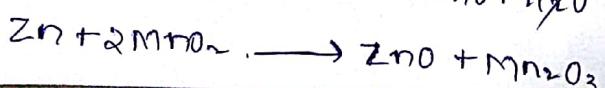
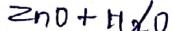
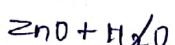
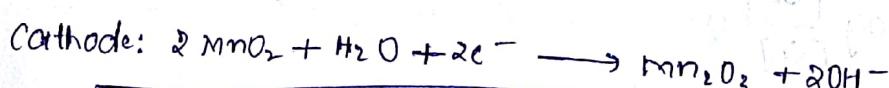
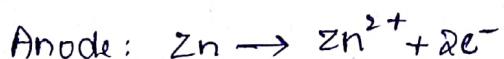
Alkaline Batteries:

Anode: Zn

Cathode: C / MnO₂

Electrolyte: KOH

Max. Voltage: 1.5V



Zn-Ag₂O Cell:

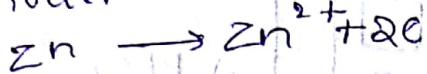
Anode: Zn

Cathode: Metal / Ag₂O

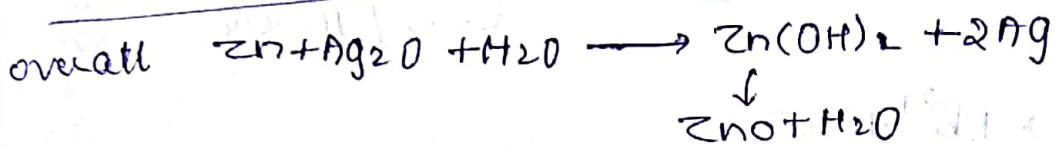
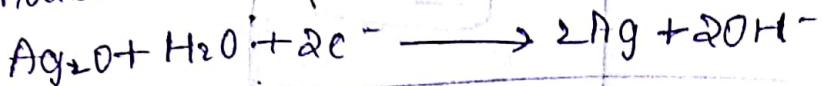
Electrolyte: Sat. KOH

Max. Volt.: 1.8V

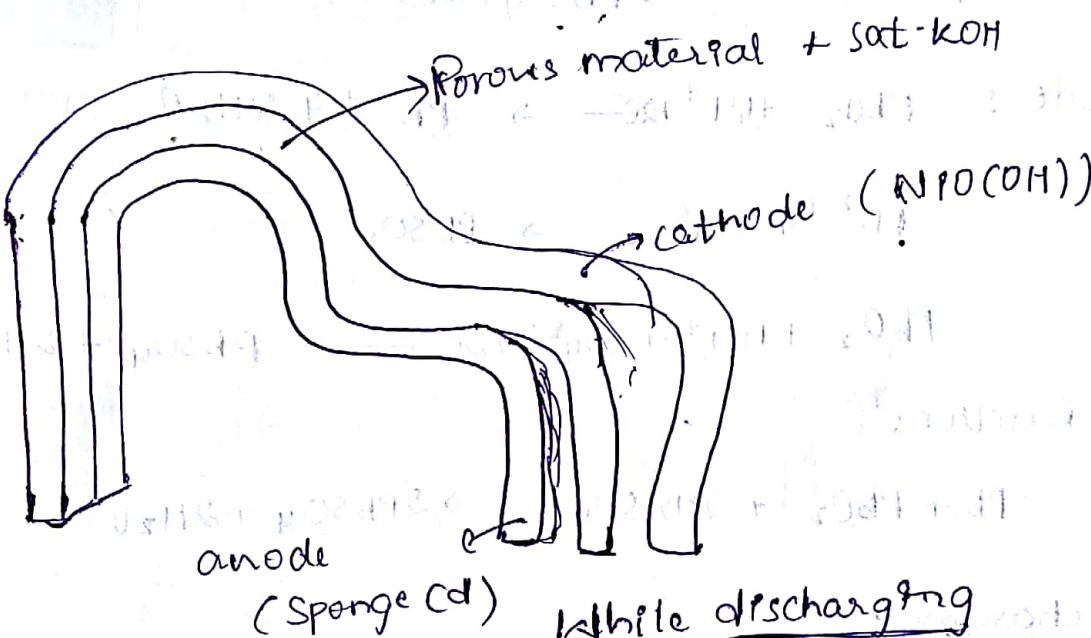
Anode:



Cathode:



Secondary Cell:

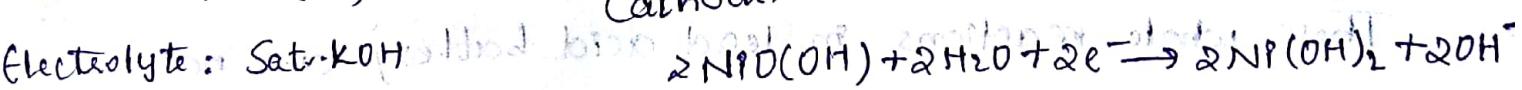


Anode: Spongy

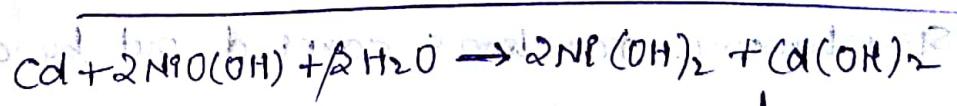


Cathode: NiO(OH)

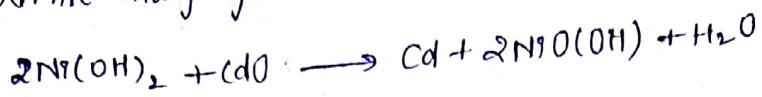
Cathode:



Max. Volt.: 1.2V



While charging:



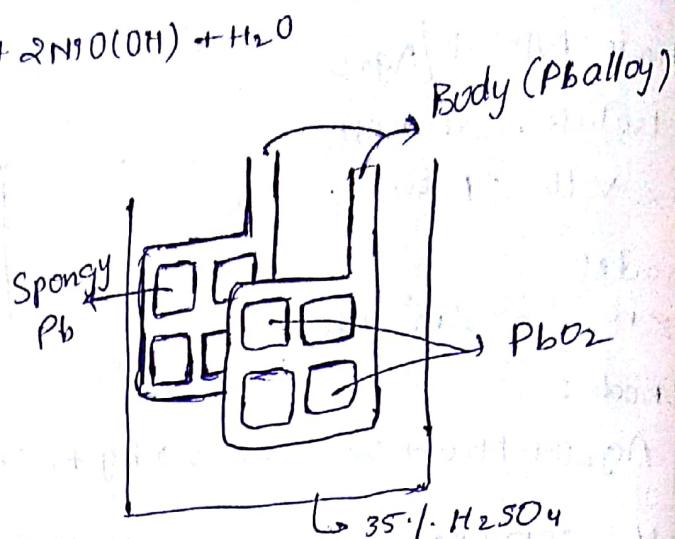
lead-acid battery:

Anode: Pb

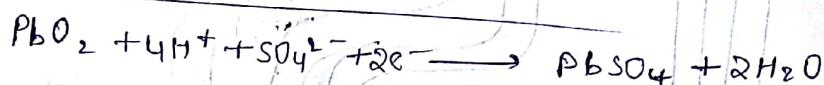
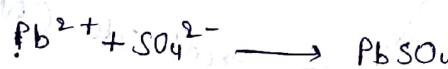
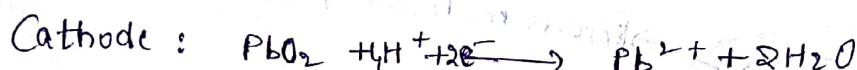
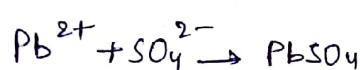
Cathode: PbO₂

Electrolyte: 35% H₂SO₄

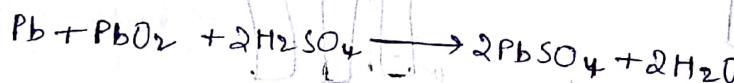
Max. Volt: 2V



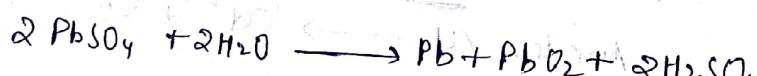
While discharging



Overall reaction:



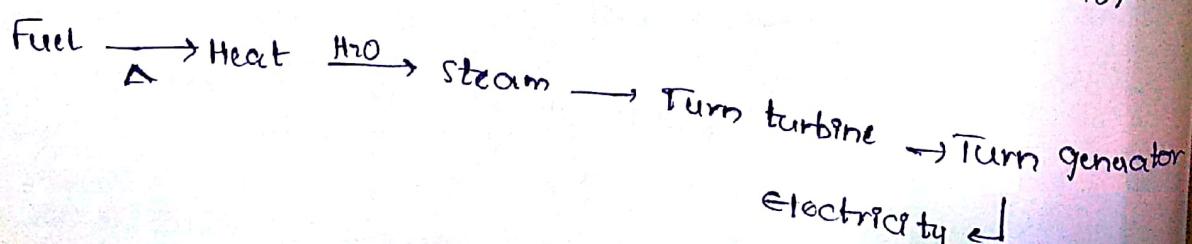
While charging:



These whole reactions in lead acid battery are non-spontaneous reactions carried out by applying external voltage.

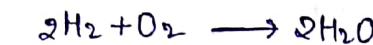
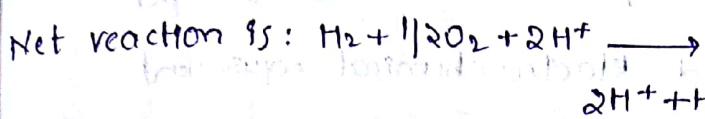
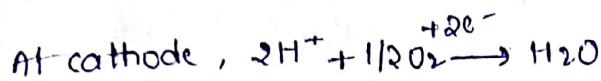
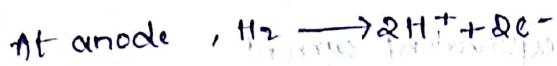
Fuel cell:

It is 80% efficient than the normal cell which is 40% efficient.

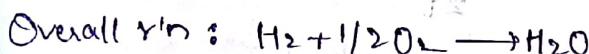
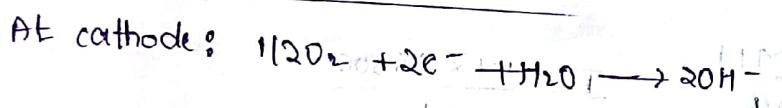
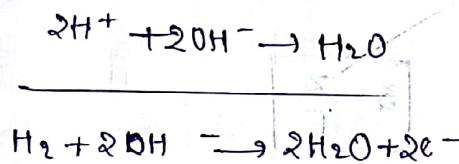
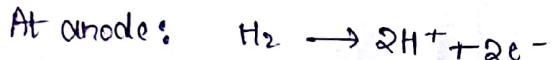


PEM Fuel cell

Max. voltage $\approx 1.23V$



Alkali Fuel cell:

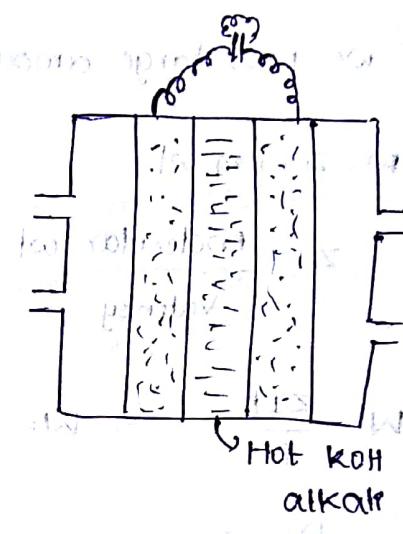


Electro plating:

Cathode (Object to be plated)

Electrolyte: Ion of the metal to be plated

Anode: Metal of the metal ion



1) Current passed through electrolyte

2) Time duration of current

3) charge on metal ion

Faraday's first law of electrolysis:

The quantity of cathode deposited is directly proportional to the amount of charge passed through it.

$W \propto I$

$W = ZIT$ Electrochemical equivalent current

The amount of substance deposited on the cathode per one ampere per sec is called electrochemical equivalent.

$$I = 1, t = 1, W = Z$$

If we pass large amount of current say 1 Farad, then

$$W = Z \rightarrow \text{eq. wt}$$

$$Z = \frac{\text{molecular wt}}{\text{Valency}} = \frac{M}{V}$$

$$\bar{Z} = \frac{Z}{F}$$

$$= W = \frac{ZIT}{F} \rightarrow W = \frac{MIT}{VF} \quad I = \frac{W \times 96500}{zt}$$

Faraday's Second law:

When same quantity of current in same time is passed through the different masses of different solutions connected in series with the cell, then the masses of each substance deposited at each electrode is proportional to the equivalent weights of the respective metal in each solution.

Ex:

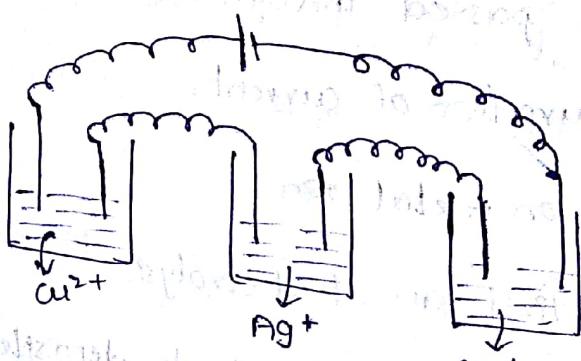
$$W \propto \text{Eq.}$$

$$\frac{m_{Cu^{2+}}}{\frac{63.5}{2}} = \frac{m_{Ag}}{\frac{108}{1}} = \frac{m_{Al^{3+}}}{\frac{27}{3}}$$

$$\text{Density} = \frac{\text{mass}}{\text{surface area} \times \text{thickness}}$$

$$D = \frac{W}{S \times t}$$

$$W = DST$$



$$\frac{ZIT}{F} = DST \Rightarrow t = \frac{ZIT}{DS}$$

Efficiency of Fuel cell :

$$\text{Efficiency} = \frac{\text{Quantity of metal plating}}{\text{Theoretical value}} \times 100$$

Theory of Electroplating:

1) Concentration polarization

2) Decomposition potential

3) Over potential

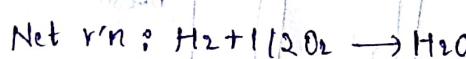
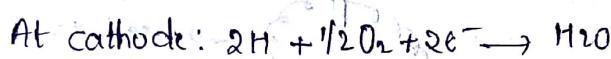
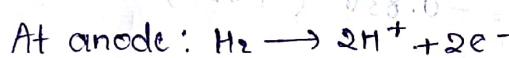
1) Concentration polarization:

It arises due to rate of diffusion and rate of deposition - inequality this can't be overcome in two ways:

1) Stirring and 2) increasing temp.

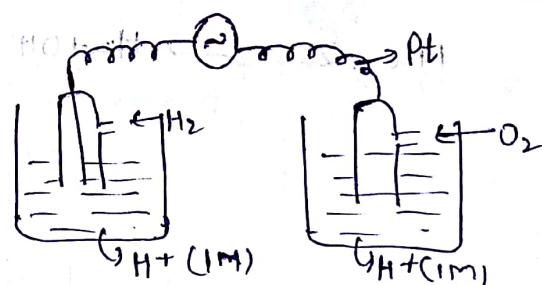
2) Decomposition potential:

The minimum potential required for the working of continuous cell is called decomposition potential.

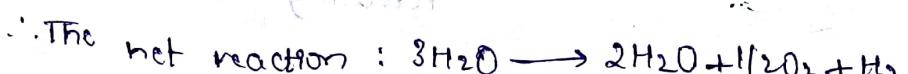
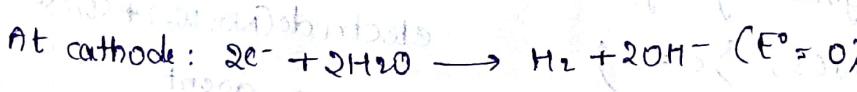
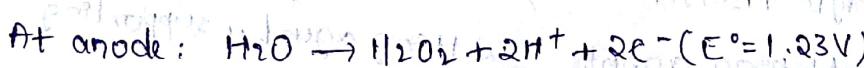


$$E_{\text{cell}} = 1.23\text{V}$$

$$E_{\text{cell}} = 1.23\text{V} - 0 = 1.23\text{V} \quad E^\circ = 0$$



$$E^\circ = 1.23\text{V}$$



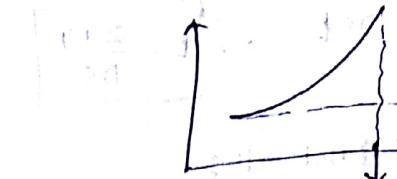
\downarrow Back emf

Theoretical value of this cell = 1.23 V

Current vs Voltage Graph:

Graphically or practically

Cell for this cell is 1.7V



Decomp:
- Poten.

Over potential:

- Over potential = practical value of potential - Theoretical value of potential.

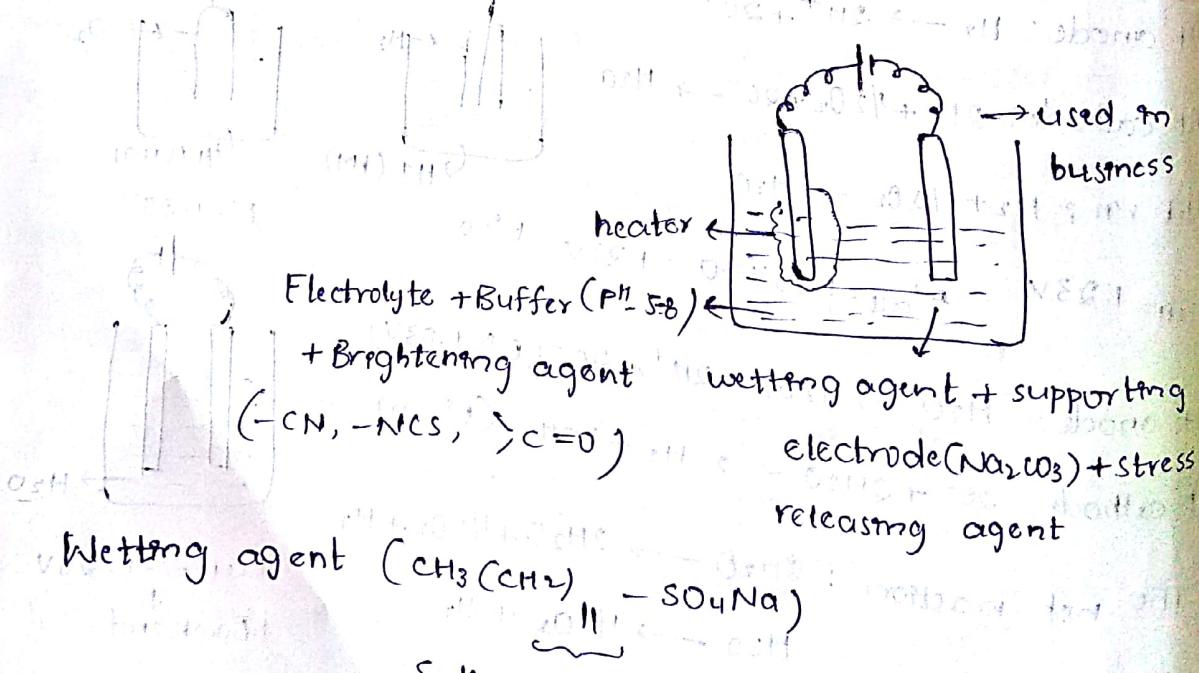
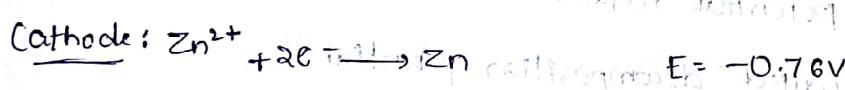
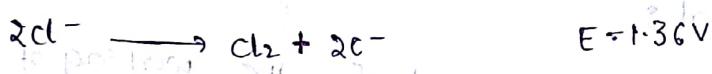
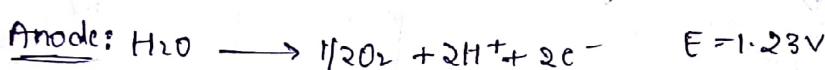
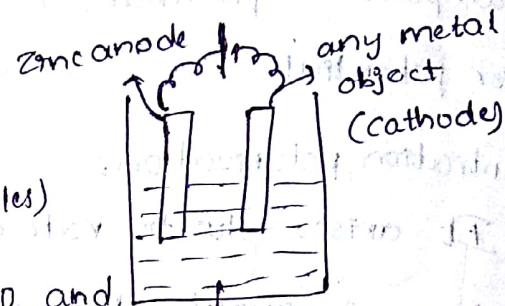
$$\text{Over potential of the cell} = 1.7 - 1.23 = 1.47 \text{ V}$$

Applications of over-potential:

Electrolyte: ZnCl₂ solution

(which has water molecules)

There was a competition between H₂O and ZnCl₂ to undergo electrolysis in this cell.

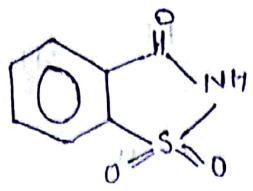


Wetting agent ($\text{CH}_3(\text{CH}_2)_\text{x}-\text{SO}_4\text{Na}$)

Sodium lauryl sulphate

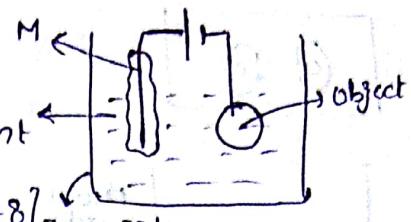
Stress releasing agent is succharin

Sachharin:



Electroplating:

Electrolyte + supporting electrolyte or Activator (Na_2CO_3) + Brightening agent (e.g.: $-\text{CN}^-$, $-\text{O}^-$, $-\text{NCS}$) + Buffer [pH: 5-8] + wetting agent (sodium lauryl sulphate) + Sachharin



These are all additives required for electroplating.

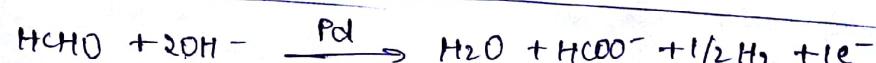
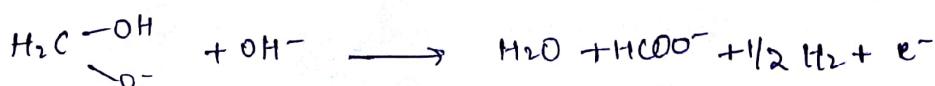
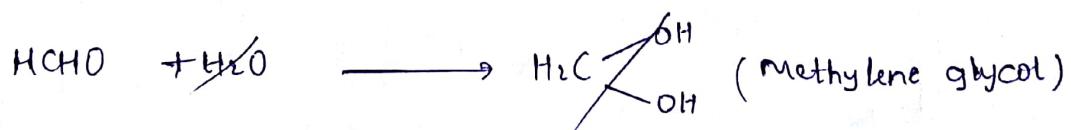
→ Dichloro methane (CH_2Cl_2) or Trichloro ethane ($\text{Cl}_3\text{C}_2\text{OH}$) are used to wash the electrolyte and use as organic solvents.

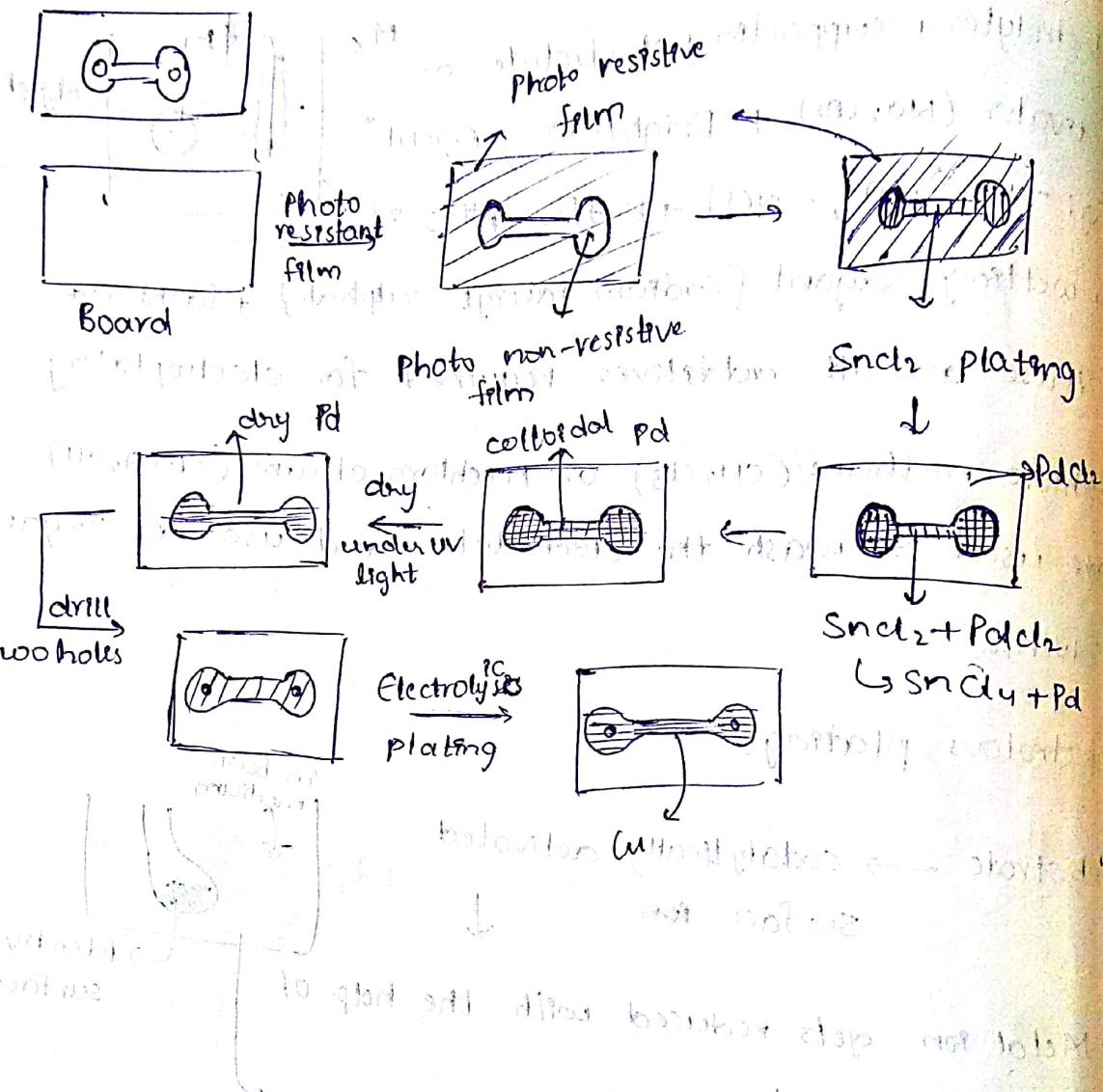
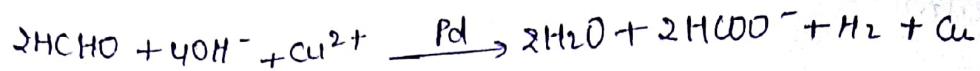
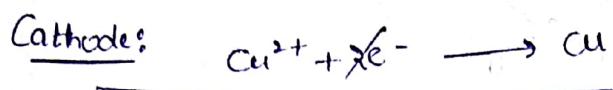
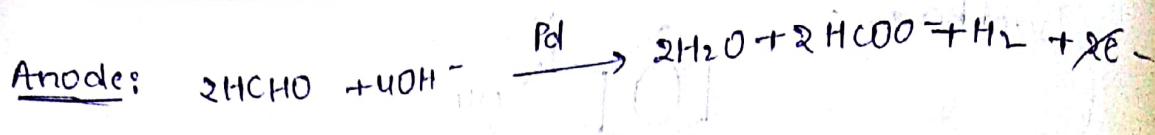
Electroless plating:

Substrate → catalytically activated surface

Metal ion gets reduced with the help of chemical reagent

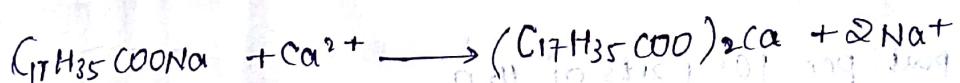
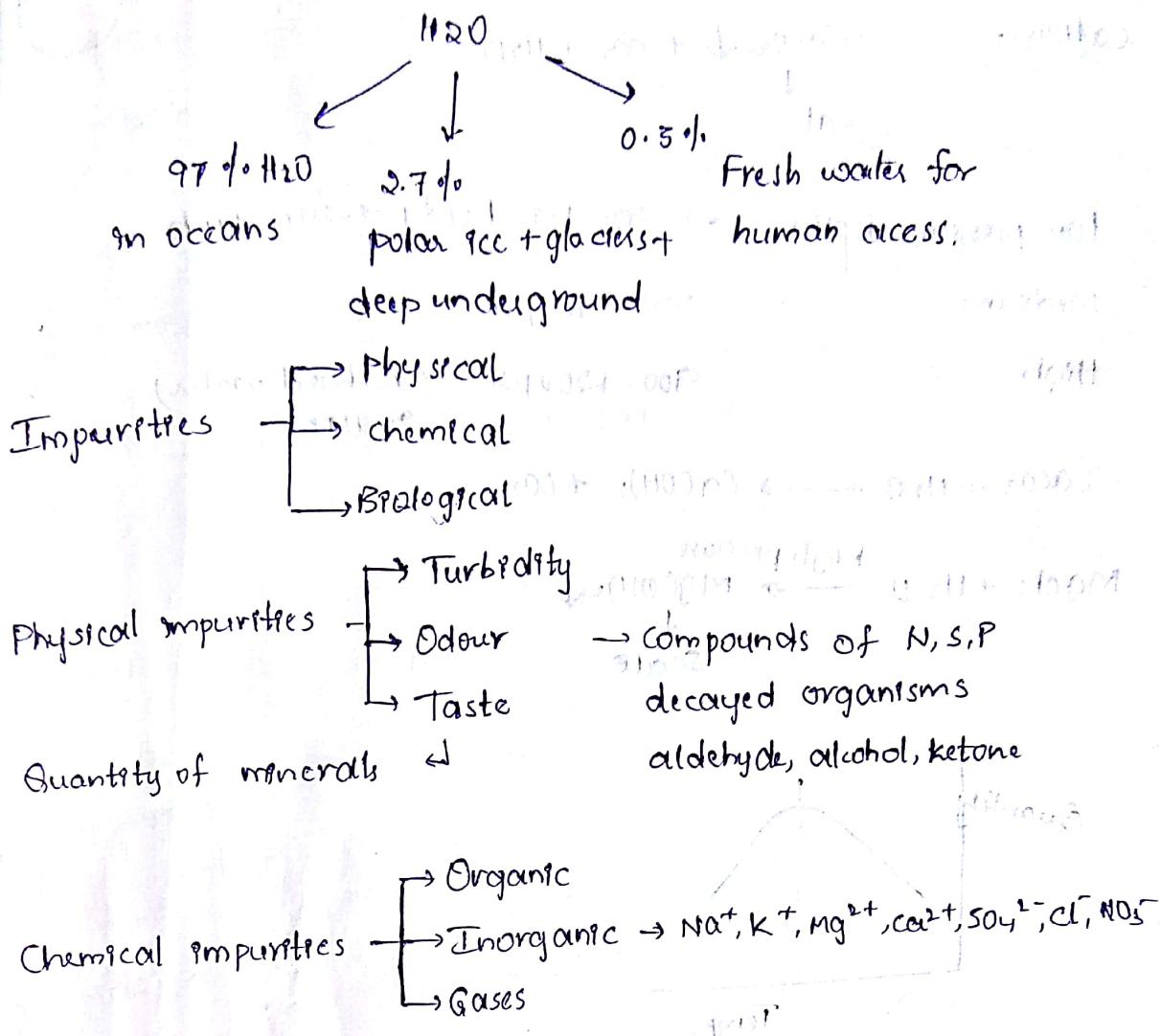
Electrolyte + Reducing agent + Buffer (pH=8)
containing metal ion (HCHO) (caustic soda + Tartaric acid) + EDTA
(chelating ligand)
(To prevent reduction of Cu^{2+} to Cu(OH)_2)





Water technology

Process of improving quality of H_2O .



Hard water don't give foam/lather on the soap like soft water

Hardness of water → permanent - chlorides, sulphides
 temporary - carbonates.

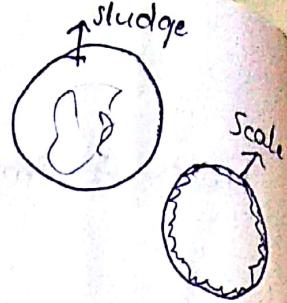


Industrial use of water → Cooling → Steam generation

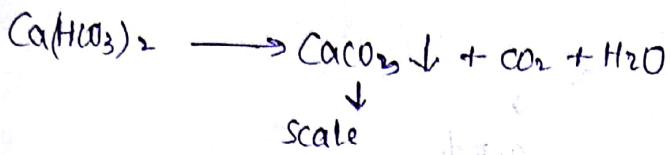
When hard water is used for steam generation we find settlement of salt. and it may lead to → scales & sludge

Boiler corrosion

Precipitate floats in the water loosely - sludge



Precipitate settles hardly - scale



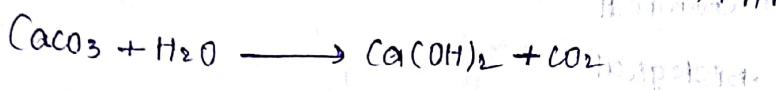
Low pressure boiler \rightarrow 300 PSF hold pressure \leq 100

Medium

300 - 900 PSF

High

900 - 1200 PSF (no hard water)
Hence HRB



Scale

Quantity

Temp.

PPm = 1 part per 10^6 parts of H_2O

Mg/l $\times 10^6$ ppm of H_2O in salted water \rightarrow Parts per million

Clark's degree = 1 part per 70000 parts of H_2O
(°cl)

degree France = 1 part per 10^5 parts of H_2O
(°fr)

Quantity of $FeSO_4$ required to attain 200 PPM of hardness in H_2O .

* Hardness in term of $CaCO_3$ = $\frac{\text{wt. of hardness causing part}}{\text{eq. wt. of } CaCO_3}$

$$1 \text{ ppm} = \frac{1}{106}$$

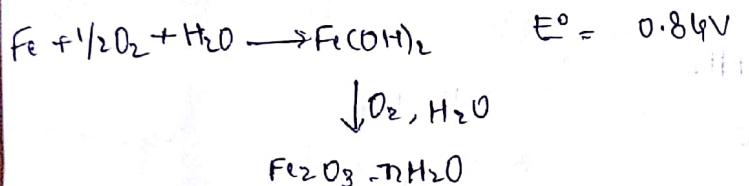
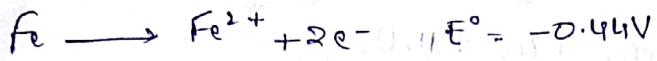
$$\frac{200}{106}$$

Boiler Corrosion:

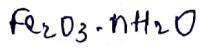
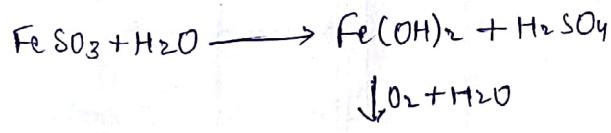
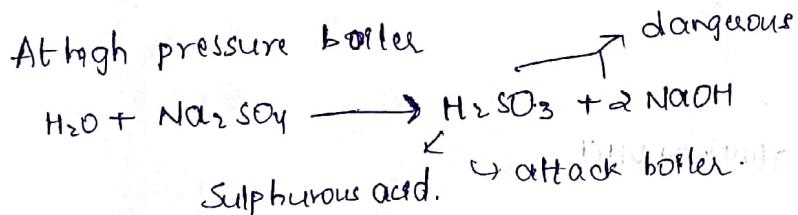
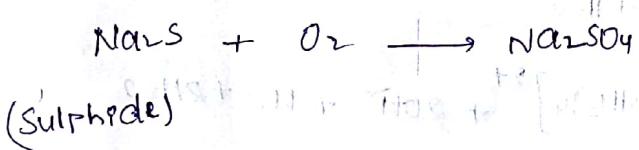
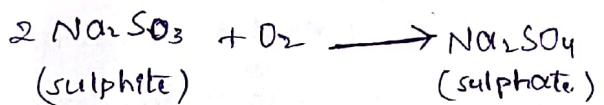
1) Corrosion due to O₂

2) Corrosion due to CO₂

3) Corrosion due to Acid.

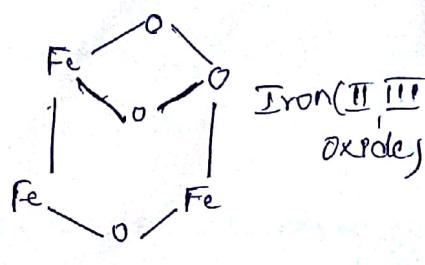
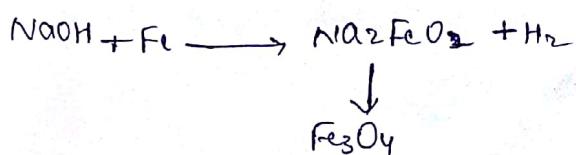


Removal of O₂



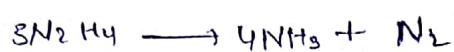
Corrosion due to NaOH → Caustic embrittlement

Rivet / conc. / dil. / NaOH / Boiler.

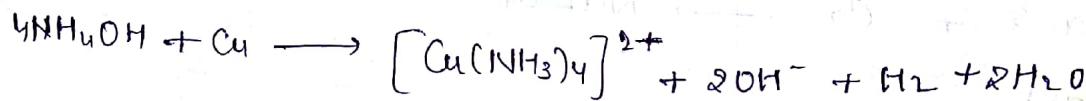
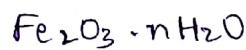
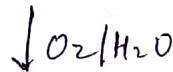
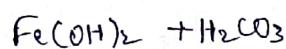
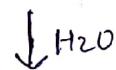
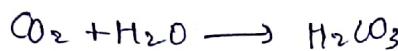
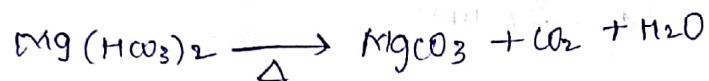




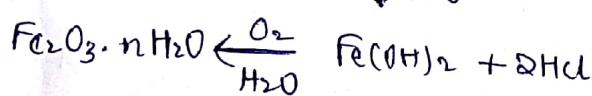
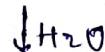
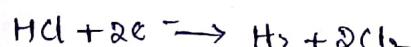
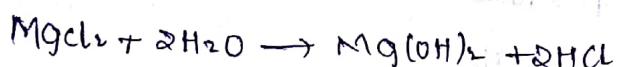
40% hydrazine



Corrosion due to O_2 :



Corrosion due to acids:



H₂O treatment

Internal treatment

• H₂O treated inside the boiler

External treatment

• H₂O treated outside the boiler

2. Called corrective method 2. Preventive method

3. Low pressure boiler 3. Used in high pressure boilers.

Sequestration → reduce the activity of an ion by converting it from one form to another.

Internal treatment

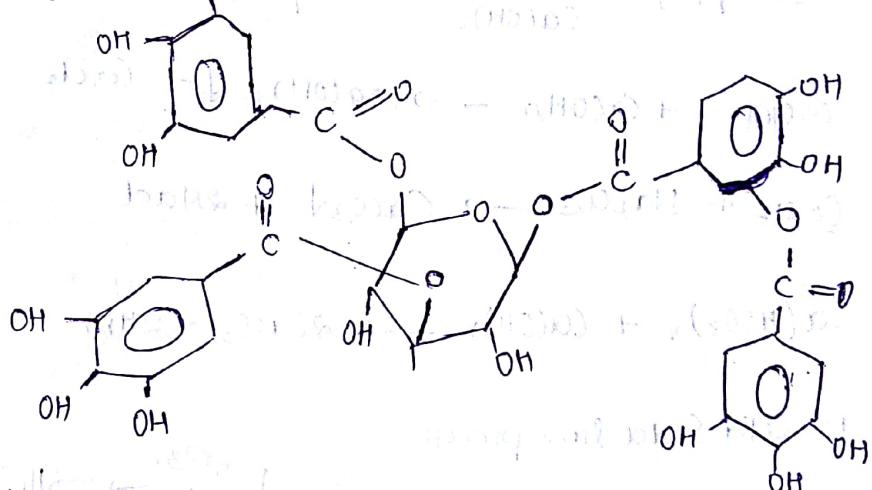
1. Colloidal conditioning

2. Carbonate conditioning

3. Phosphate conditioning

4. Calgon conditioning

Tannin



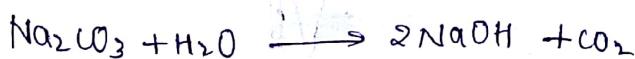
→ Precipitate 100%.

Carbonate conditioning:

Convert water soluble sulphate → water insoluble carbonate

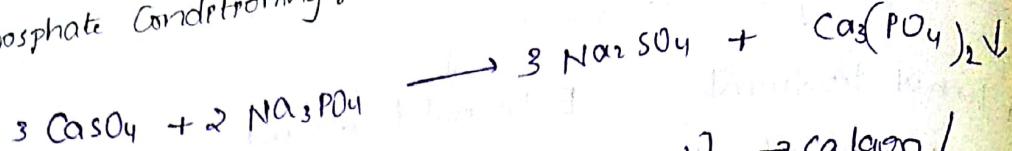


If excess Na₂CO₃ is added in water it decomposes.

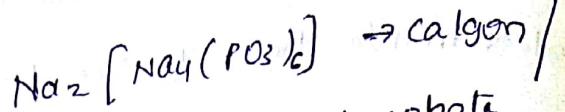


Corrosion inhibitor /缓蚀剂

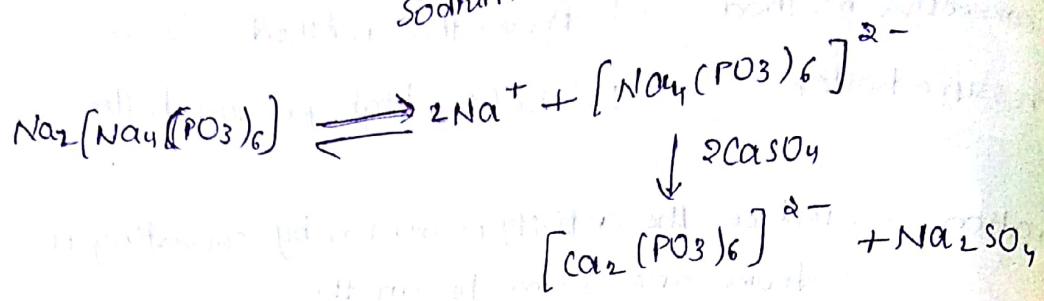
Phosphate Conditioning



Calgon conditioning:



Sodium hexa meta phosphate



External : → 1. Soda lime process

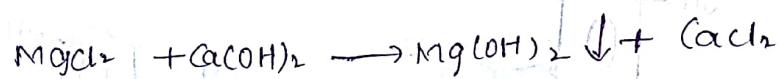
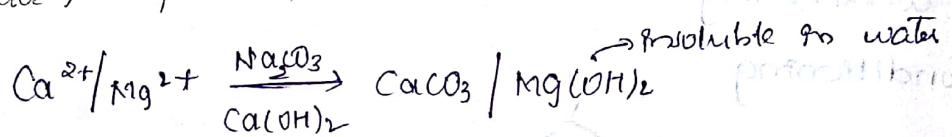
Lime - CaOH

2. Zeolite process

Soda - Na_2CO_3

3. Demineralization / ion exchange process.

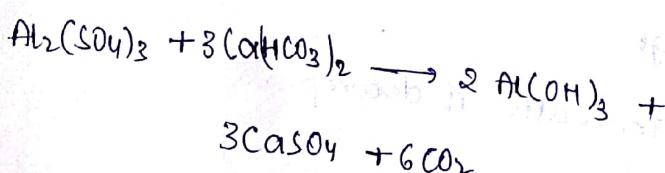
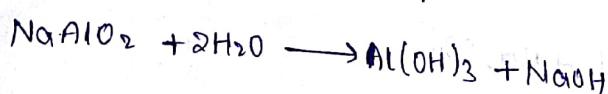
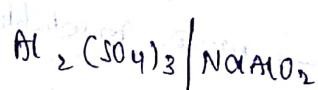
Soda lime process:



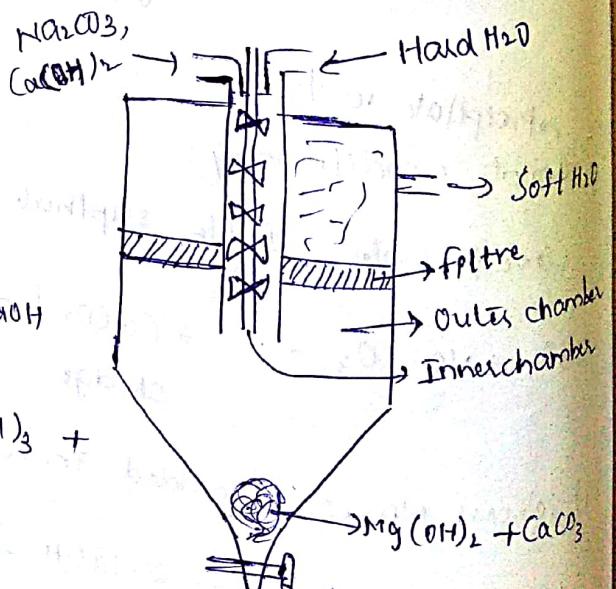
1) Cold Soda lime process

2) Hot soda lime process

1) Coagulant



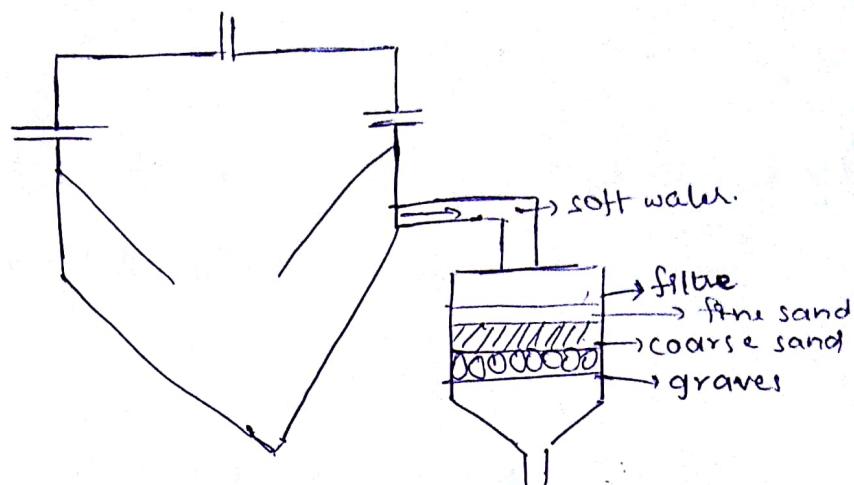
Hardness of water in the form



2) $80 - 150^{\circ}\text{C}$.

no coagulant

15 - 30 ppm

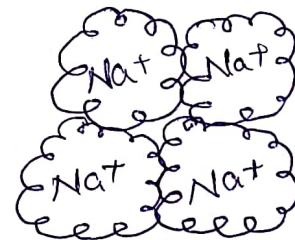


Zeolite process:

Zeolite: $\text{Na}_2\text{Al}_x\text{O}_3 \cdot n\text{Si}_y\text{O}_4 \cdot y\text{H}_2\text{O}$

$$x = 2 - 10 \quad y = 2 - 6$$

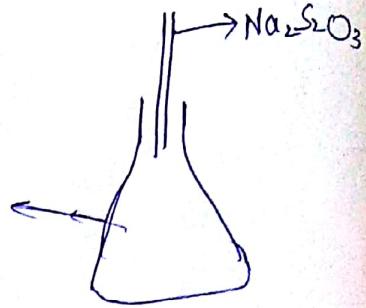
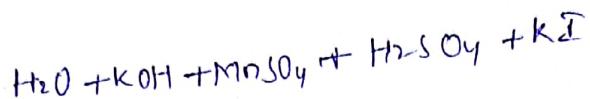
natural synthetic
 $x=4, y=2$ $\text{Na}_2\text{Si}_4\text{O}_7$
 NaAlO_2
 $\text{Al}_2(\text{SO}_4)_3$



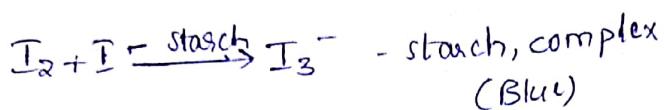
Dissolved Oxygen (DO)

DO → ppm (or) mg/l

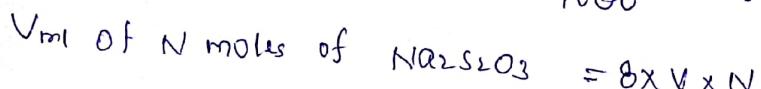
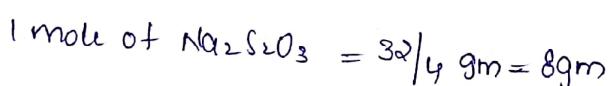
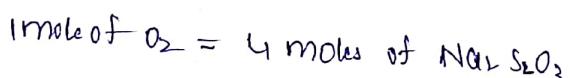
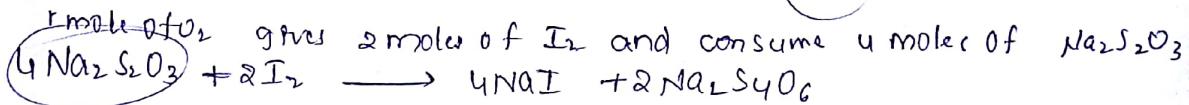
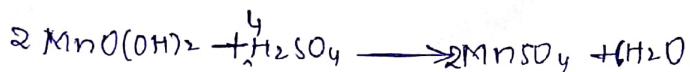
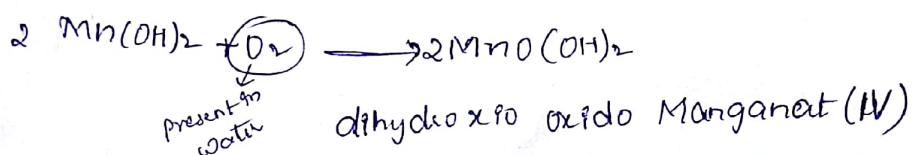
Winkler's method: to estimate DO



Indicator: starch



End point: disappearance of blue colour



for V_{ml} of H_2O

$$DO = \frac{8 \times V \times N}{V_1} \times 1000$$

per 1 ml

Per 1 litre of water

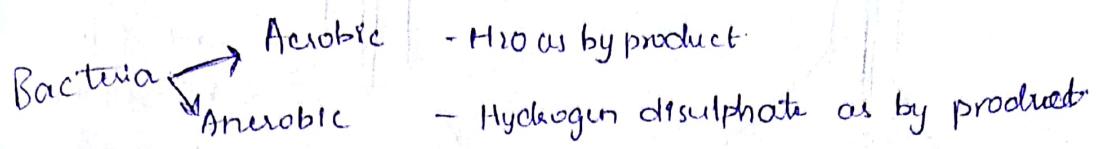
V - volume of $Na_2S_2O_3$

consumed during titration

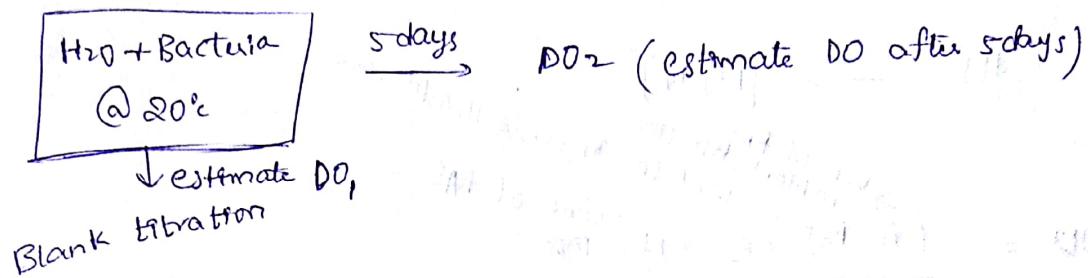
N - concentration of $Na_2S_2O_3$

V_1 - volume of H_2O taken for

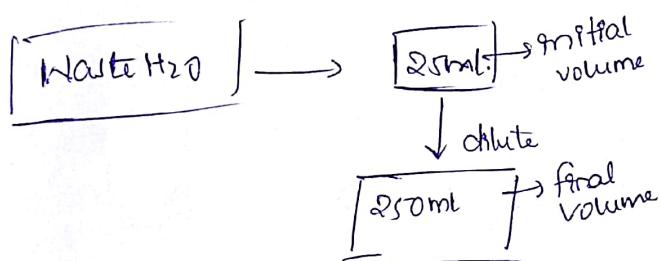
BOD : Biological Oxygen Demand.



Amount of O₂ required by bacteria to breakdown oxidisable impurities per 1 litre of water in 5 days. at 20°C



$$* \quad \text{BOD} = \frac{\text{DO}_1 - \text{DO}_2}{P} \quad P \rightarrow \text{dilution ratio}$$



$$P = \frac{\text{initial volume (V}_2\text{)}}{\text{final volume (V}_3\text{)}}$$

$$\text{BOD} = \frac{\frac{A \times 8 \times 1000 \times N}{V_1} - \frac{B \times 8 \times 1000 \times N}{V_1}}{\frac{V_2}{V_3}}$$

A - Vol. of Na₂S₂O₃ consumed in blank titration

$$* \quad \text{BOD} = \frac{(A-B) 8 \times 1000 \times N}{V_1} \times \frac{V_3}{V_2}$$

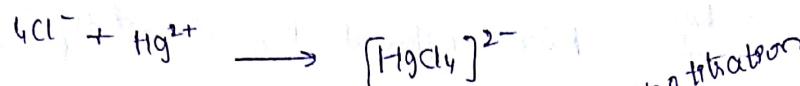
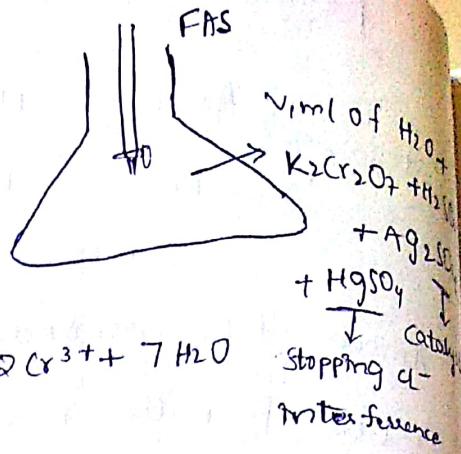
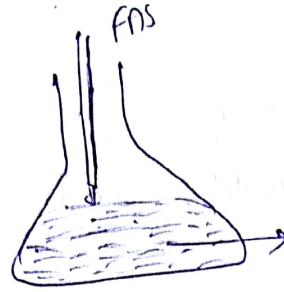
B - Vol. of Na₂S₂O₃ in titration after 5 days.

N - conc of Na₂S₂O₃

V₁ - vol. of H₂O taken for titration

V₂ - final vol. of H₂O

V₃ - initial vol. of H₂O.

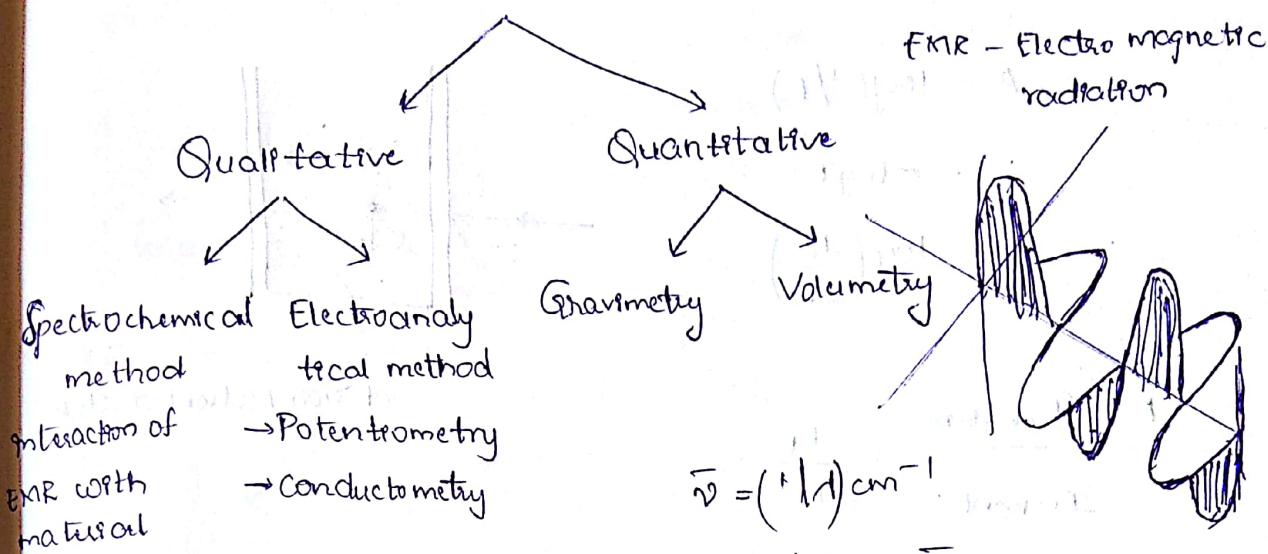


$$COD = \frac{(A - B) \times E \times N \times 1000}{\text{vol. of FAS in blank titration} \times \text{vol. of FAS in waste } H_2O \text{ titration}}$$

$V_1 \rightarrow$ vol. of water.

Instrumental Method of Chemical Analyses

- a collective of analytical technique

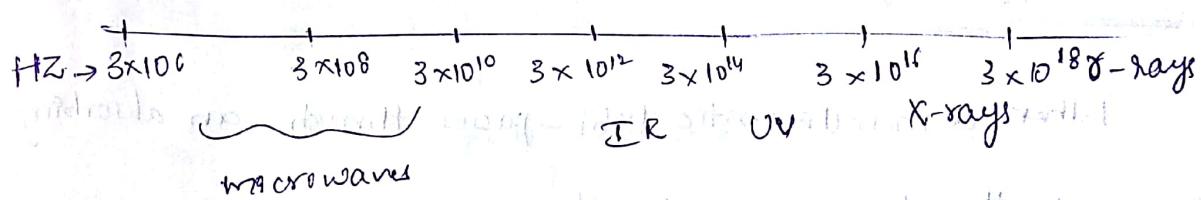


$$\text{Momentum } P = \frac{\epsilon}{c} = \frac{hc\nu}{c} = h\nu$$

$$\nu = (\text{?}) \text{ cm}^{-1}$$

$$v = c/d = c\nu$$

$$E = h\nu = \frac{hc}{\lambda} = hc\nu$$



Calorimetry:

To planck's law of black body theory of radiation

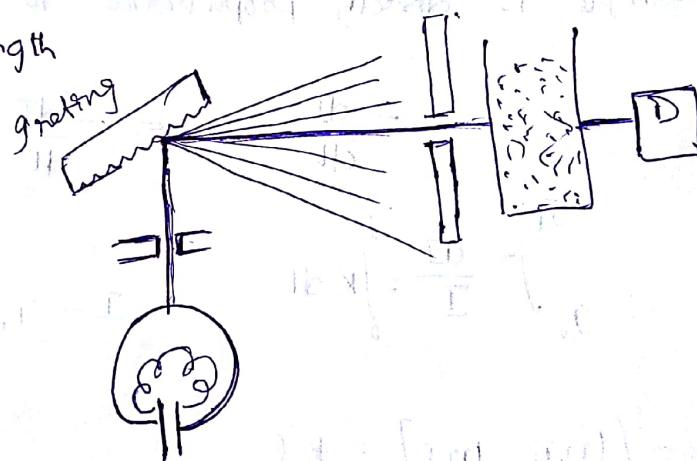
Monochromatic - Single wavelength

$$M \xrightarrow{h\nu} M^*$$

ES

\downarrow

M + heat



Transmittance

A fraction of specific wavelength of electromagnetic material radiation that passes through absorbing material

$$T = \frac{I_t}{I_0} \quad (\text{transmittance})$$

Absorbance (A) :

A fraction of specific wavelength of light that is absorbed by the absorbing material.

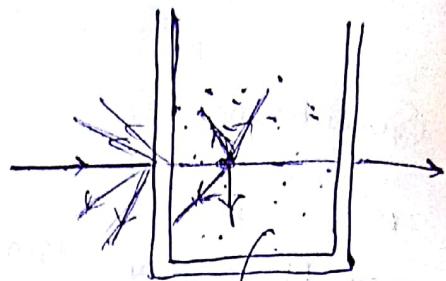
$$A = \log(1/T)$$

$$= -\log T$$

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

$$T = \frac{I_{\text{solution}}}{I_{\text{solvent}}} = \frac{I_t}{I_0}$$

$$A = \log \left(\frac{I_{\text{solvent}}}{I_{\text{solution}}} \right)$$



Solution + solvent + solute

Path length

Lambert's law:

When a monochromatic light passes through an absorbing material, the decrease in intensity of light wrt thickness of sample is directly proportional to the intensity of incident light.

$$-\frac{dI}{dl} \propto I \Rightarrow -\frac{dI}{dl} = kI$$

$$\int_{I_0}^{I_t} -\frac{dI}{I} = \int_0^l k dl$$



$I \rightarrow I_0 \text{ to } I_t, 0 \rightarrow l : l$

$$-\ln \left(\frac{I_t}{I_0} \right) = kl$$

$$\ln \left(\frac{I_0}{I_t} \right) = kl$$

$$2.303 \times \log \left(\frac{I_0}{I_t} \right) = kl$$

$$\log \left(\frac{I_0}{I_t} \right) = \frac{k}{2.303} l$$

$$A = \epsilon l$$

ϵ - molar absorptivity

Beer's Law

$$-\frac{dI}{dt} \propto Ic$$

I - Intensity

c - concentration of solution

l - length of the sample

A - Absorbance

$$A = \epsilon cl$$

→ Beer's Lambert's law

c = moles/litre

l = cm

$$\epsilon = \frac{\text{litre mol}^{-1} \text{cm}^{-1}}{\text{M}^{-1} \text{cm}^{-1}}$$

valid for monochromatic light

for lower conc.



$$c = 8 \times 10^{-6}$$

$$l = 2.3 \text{ cm}$$

$$\frac{441}{100} \times 523 = 230.12$$

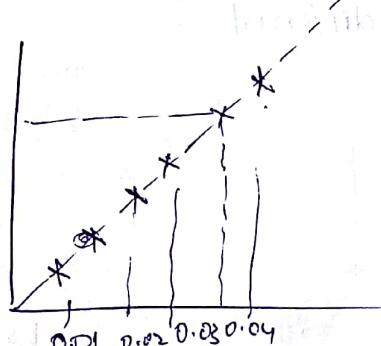
$$A = \log \left(\frac{230.12}{523 - 230.12} \right)$$

$$\log \left(\frac{523}{230.12} \right) = 8 \times 10^{-6} \times 2.3 \times \epsilon$$

$$\epsilon = 19 \times 10^3$$

$$* \quad \epsilon = ad$$

$$A = \epsilon dl$$



λ_1 & λ_2

$$\text{for } \lambda_1, A_1 = \epsilon_1' cl$$

$$= \log \left(\frac{I_0'}{I_t'} \right)$$

$$\text{for } \lambda_2, A_2'' = \epsilon_2'' cl$$

$$= \log \left(\frac{I_0''}{I_t''} \right)$$

for λ_1 and λ_2

$$A = \log \left(\frac{I_0' + I_0''}{I_t' + I_t''} \right)$$

$$\log \left(\frac{I_o'}{I_t'} \right) = \varepsilon' c l$$

$$\frac{I_o'}{I_t'} = 10^{\varepsilon' c l}$$

for λ_1 , $I_o' = I_t' \times 10^{\varepsilon' c l}$

for λ_2 , $I_o'' = I_t'' \times 10^{\varepsilon'' c l}$

$$A = \log \left(\frac{I_t' \times 10^{\varepsilon' c l} + I_t'' \times 10^{\varepsilon'' c l}}{I_t' + I_t''} \right)$$

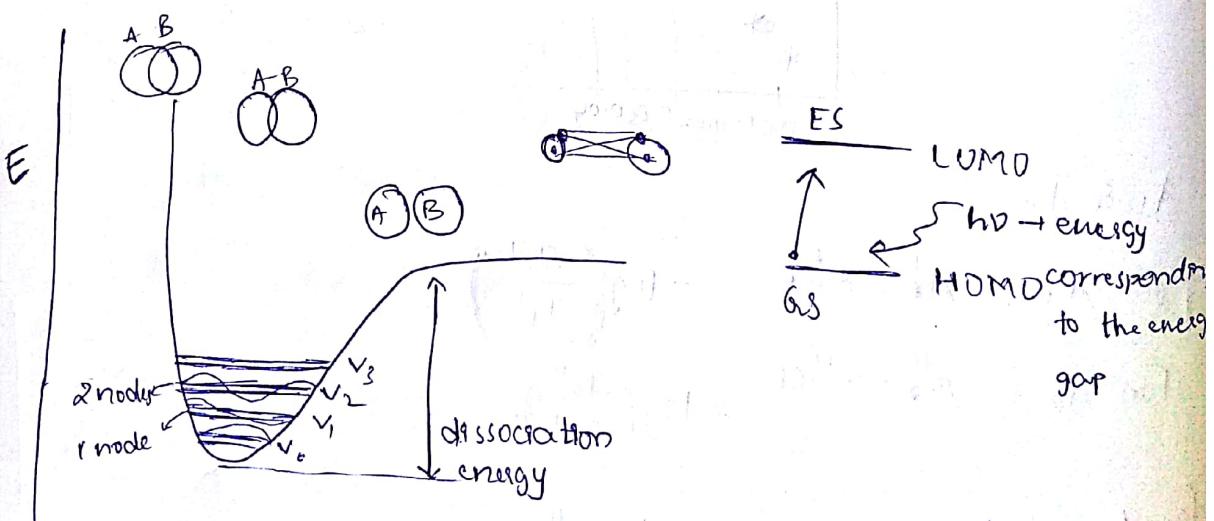
Say $\varepsilon' = \varepsilon''$ (almost)

$$A = \log \left[\frac{I_t' + I_t''}{I_t' + I_t''} (10^{\varepsilon c l}) \right]$$

$$= \log (10^{\varepsilon c l}) \Rightarrow A = \varepsilon c l$$

\therefore If ε are same almost then we can retain the linearity when wavelengths are different.

U-V Visible Spectroscopy:



Mohr's potential energy curve



γ - rotational transition

$$\Delta E_c \gg \Delta E_v \gg \Delta E_r$$

Frank Condor Principle

When there is electronic transition there is no change in equilibrium distance of the molecule.

equilibrium state of E_1 is larger than E_0 because of anti bonding character of sigma bond. the more the sigma bond is strong the bond depth of P.E curve is more

slope shallow - flexible bond
slope is sharp - rigid bond

If the electro magnetic radiation given is same as it is enough to transfer the electron then only the transition happen. This is

Frank Condor Principle



\downarrow \rightarrow spin is not changed during

transition



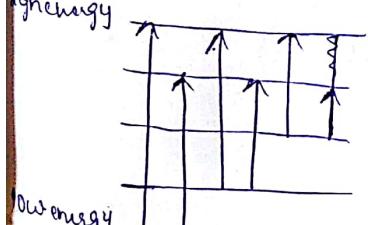
Transition \rightarrow forbidden \rightarrow less ϵ values

\rightarrow allowed $\rightarrow \epsilon > 10^4$

If e^- is in p' then it should go to d (or) s in transition

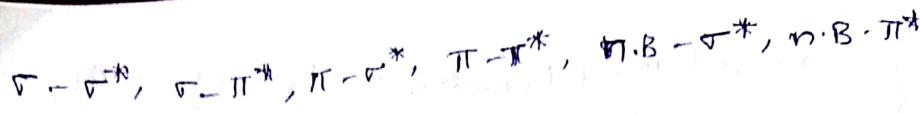
i.e., it can change by γ .

Molecular orbitals : $\sigma, \sigma^*, \pi, \pi^*, \text{Nonbonding}$



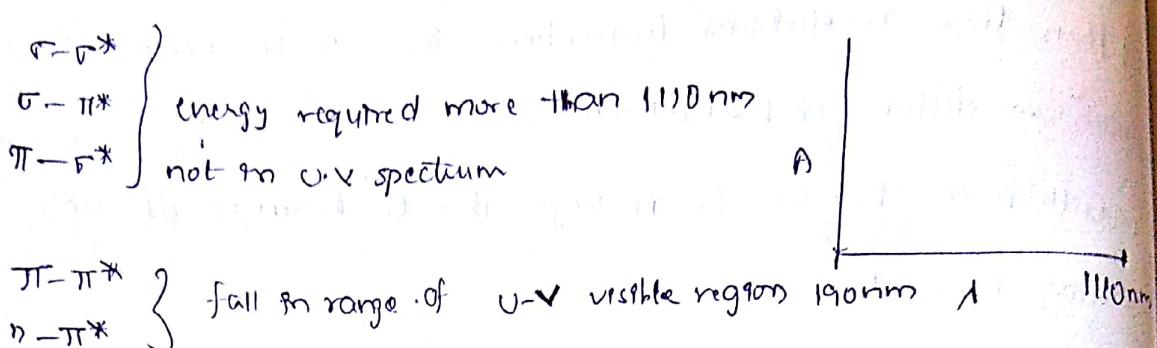
σ^* } empty
 π^* } empty
Nonbonding } filled mostly
 π

e^- from filled goes to empty
6 possible transitions



$\sigma - \sigma^*, \sigma - \pi^*, \pi - \sigma^*$ very high energy relative to U.V spectrum

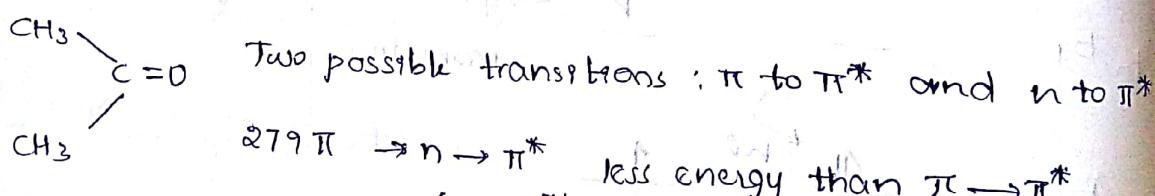
Transition with energy less than 190 nm is not visible in UV spec.



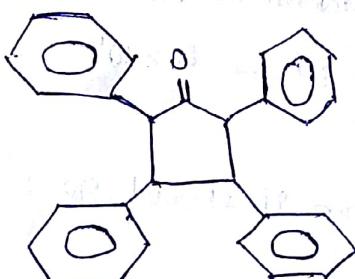
Chromophore - functional group that exhibits colour / that absorb electromagnetic radiation in U.V visible region.

Alkyne, alkane, ketone, alke, amine, halides, always in visible region.

$\text{CH}_3 - \text{CH}_2 - \text{CH}_3 \rightarrow$ it has $\sigma \leftrightarrow \sigma^*$ MO: It requires energy more than UV radiation.

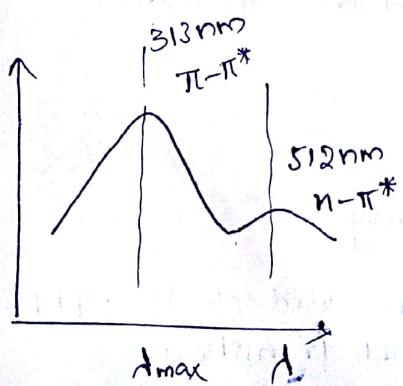


Cyclopentadienone

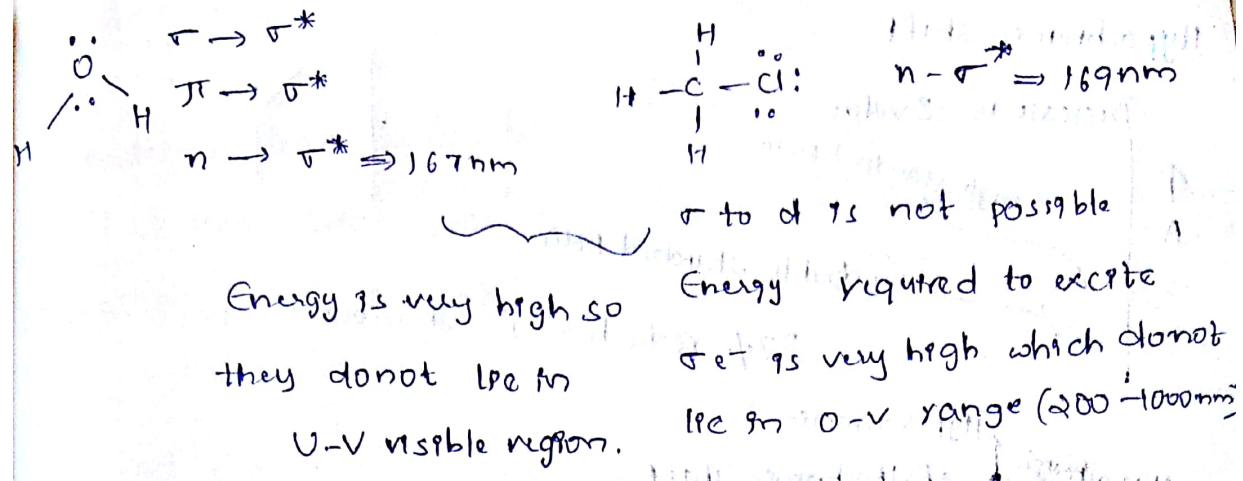


Tetraphenyl cyclopentadienone

energy gap h/w



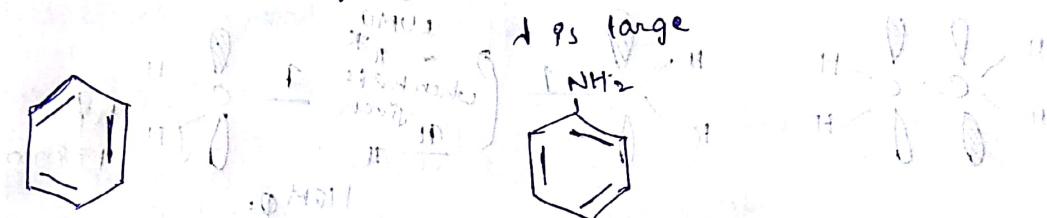
$\pi \leftrightarrow \pi^*$ decreases



Aurochromes: -OH, -NH₂, -OR, -X

They do not absorb the radiation under U-V region but after chromophore might change value of ϵ_max & λ_max .

→ Bathochromic shift or Red shift



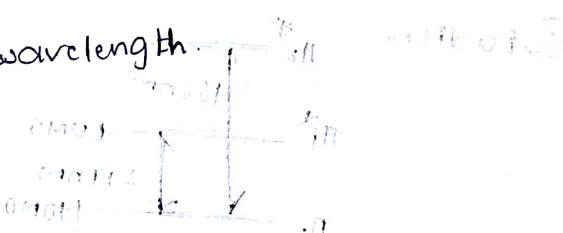
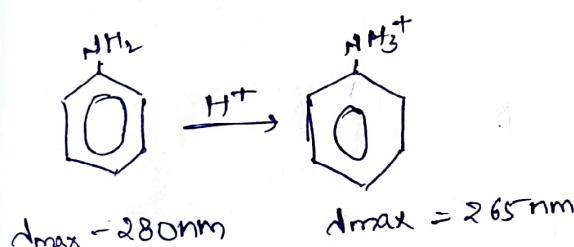
transition

$\pi \rightarrow \pi^* 255 \text{ nm}$

$\pi \text{ max}$

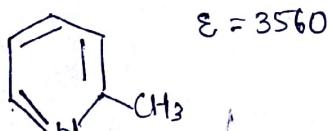
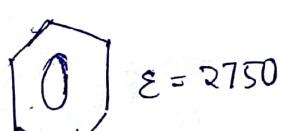
$\lambda_\text{max} = 280 \text{ nm}$
 $n \rightarrow \pi^*$

λ_max shifts to longer wavelength.



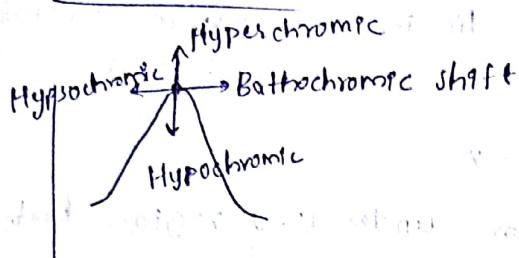
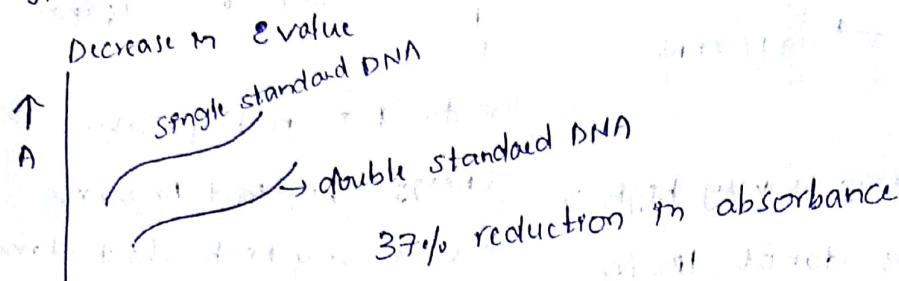
Hypochromic shift (Blue shift)

Hypochromic shift

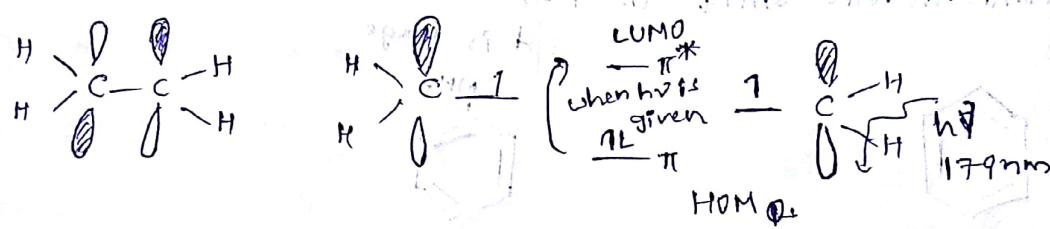


As ϵ increases absorbance increases

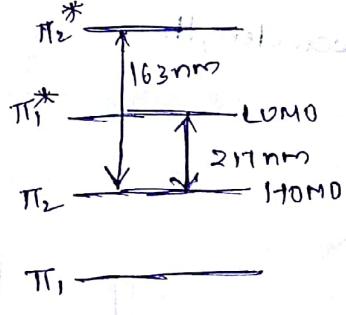
Hypochromic shift



When there are multiple bonds first b/w π & π^* will decrease

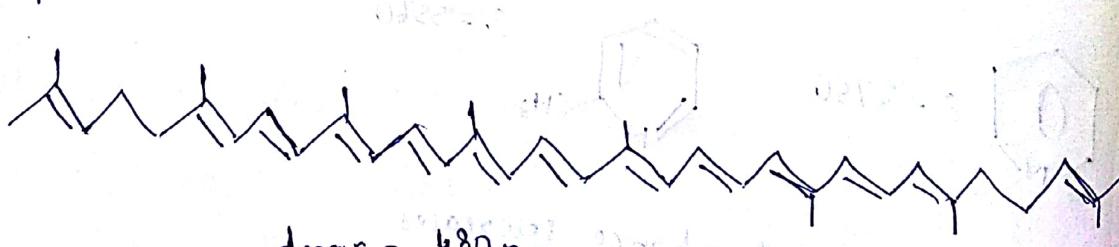


Butadiene



As conjugation increases energy gap b/w π & π^* orbitals increases.

Lycopene



Woodward-Fischer's rule

Butadiene (trans) = 217 nm

If butadiene is in cyclic form then we need to add 3 nm.
→ Butadiene with the ring = $217 + 36 = 253 \text{ nm}$



for each extra double bond add 30 nm.

→ Extended double bond = +30 nm.

Exocyclic double bond exocyclic



exocyclic double bond = +5 nm

including in conjugation,

→ Metal group is substitute included in = +5 nm conjugation

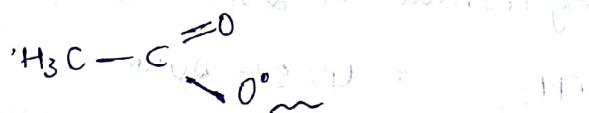
→ Ring residue part having conjugated part = +5 nm.

→ Ring residue part having conjugated part = +5 nm.



→ Auxochrome

O - Aryle = 0 nm

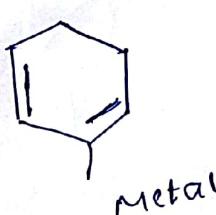


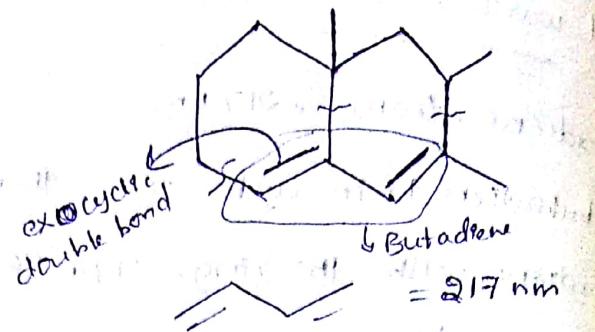
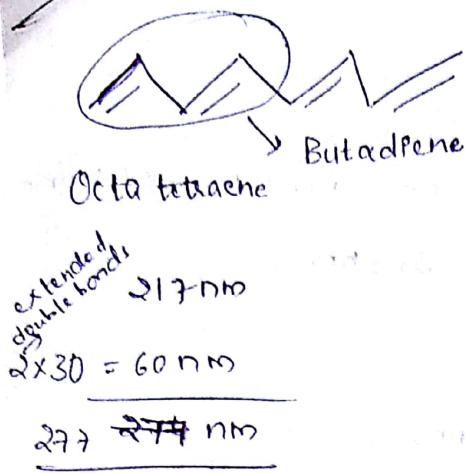
O - Alkyl = 6 nm S Alkyl = 30 nm

N - Alkyl = 60 nm Cl, Br = 5 nm



Eg:



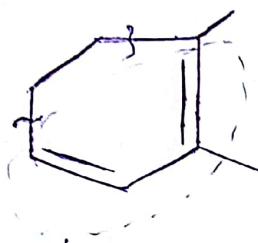


$$\text{CH}_3 \times 1 = 5 \times 1 = 5$$

$$3 \text{ ring residues} = 5 \times 3 = 15$$

$$\text{exocyclic double bond} = 5 \times 1 = 5$$

$$\underline{242 \text{ nm}}$$



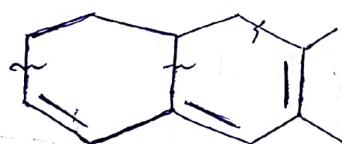
$$\text{Butadiene} = 217 \text{ nm}$$

$$\text{CH}_3 \times 2 = 5 \times 2 = 10$$

$$2 \text{ ring residue} = 5 \times 2 = 10$$

With in the

$$\text{ring(1)} = \frac{36}{273 \text{ nm}}$$



$$\text{Butadiene} = 217 \text{ nm}$$

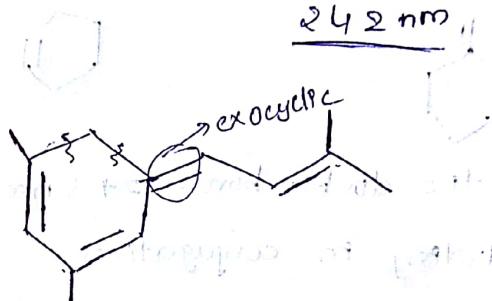
$$\text{ring residue 3} = 3 \times 5 = 15 \text{ nm}$$

$$\text{CH}_3 (2) = 2 \times 5 = 10 \text{ nm}$$

$$1 \text{ exocyclic bond} = 5 \text{ nm}$$

$$\text{With in the ring} = 36 \text{ nm}$$

$$\text{Extended double bond} = \frac{30 \text{ nm}}{343 \text{ nm}}$$



$$\text{Butadiene} = 217 \text{ nm}$$

$$\text{With in the ring} = 36 \text{ nm}$$

$$2 \text{ extended double bonds} = 2 \times 30 = 60 \text{ nm}$$

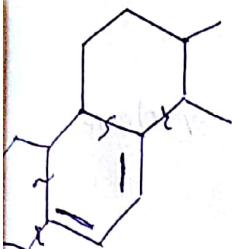
$$1 \text{ exocyclic bond} = 5 \text{ nm}$$

$$1 \text{ ring residue} = 2 \times 5 = 10 \text{ nm}$$

$$\text{CH}_3 = 4 \times 5 = 20 \text{ nm}$$

$$\underline{343 \text{ nm}}$$



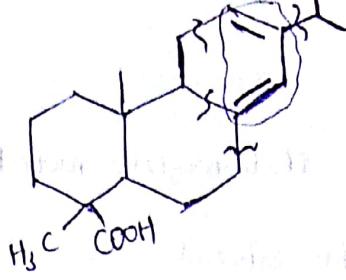


Butadiene = 217 nm

ring residue (4) = $4 \times 5 = 20$ nm

width to the ring
cis form = 36 nm

2 exocyclic
double bond
 $= 2 \times 5 = 10$ nm
 $\underline{\underline{283 \text{ nm}}}$



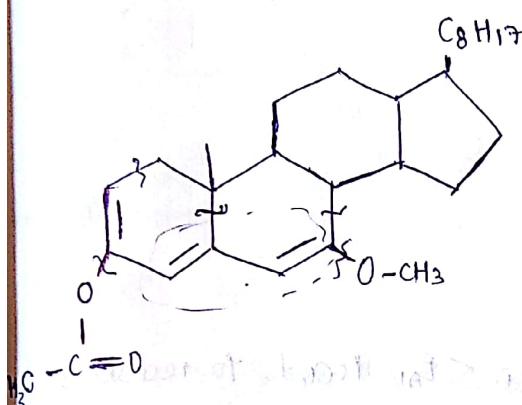
Butadiene = 217 nm

ring residue = $3 \times 5 = 15$ nm

exocyclic bond = $1 \times 5 = 5$ nm

width to the ring
cis form = 36 nm

$\underline{\underline{278 \text{ nm}}}$



Butadiene = 217 nm

1 extended (=) bond = 30 nm

ring residue = $3 \times 5 = 15$ nm

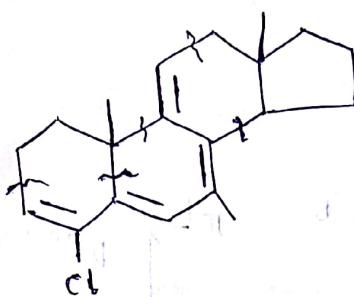
exocyclic
bond = $1 \times 5 = 5$ nm

Butadiene width
in ring = 36 nm

O-alkyl group = 1×6

1 acyl group = 1×0

$\underline{\underline{309 \text{ nm}}}$



Butadiene = 217 nm

ring residue = $5 \times 5 = 25$ nm

exocyclic ring bonds = $3 \times 5 = 15$ nm

Extended double
bond = $2 \times 30 = 60$ nm

Butadiene width
in ring = 36 nm

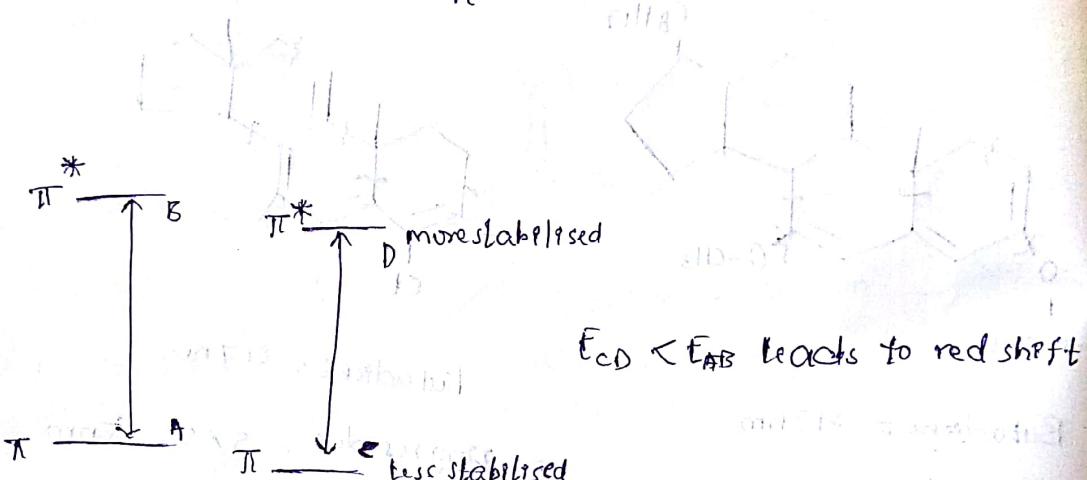
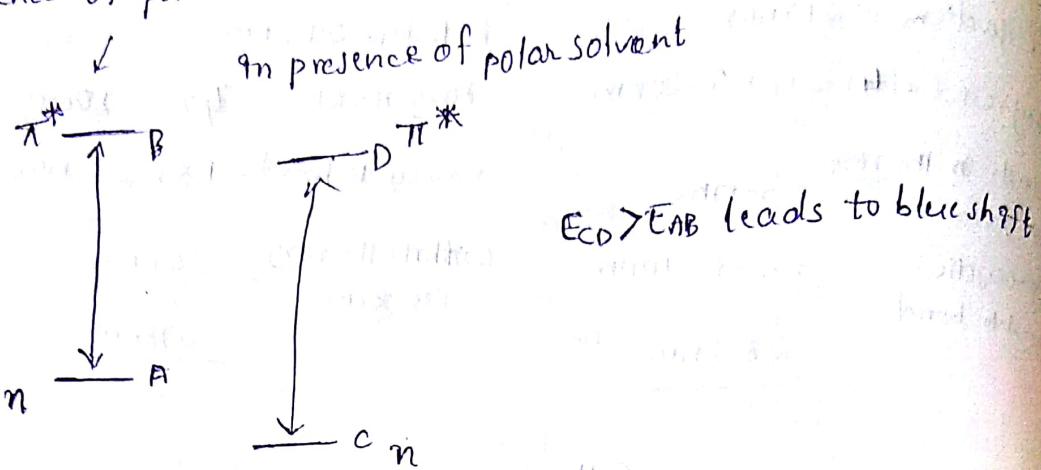
$\text{CH}_3 + \text{CH}_3 + \text{CH}_3 + \text{CH}_3 = 1 \times 5 = 5$ nm

+ Cl⁻ = 5

$\underline{\underline{363 \text{ nm}}}$

Solvent
Shouldn't absorb electromagnetic radiation for U.V visible spectrum.

absence of polar solvent



$A = \epsilon c l$ ϵ is const. for a given sample at a given wavelength.

Mixture of 3 compounds

$$A^I = \epsilon^a c_a l + \epsilon^b c_b l + \epsilon^c c_c l$$

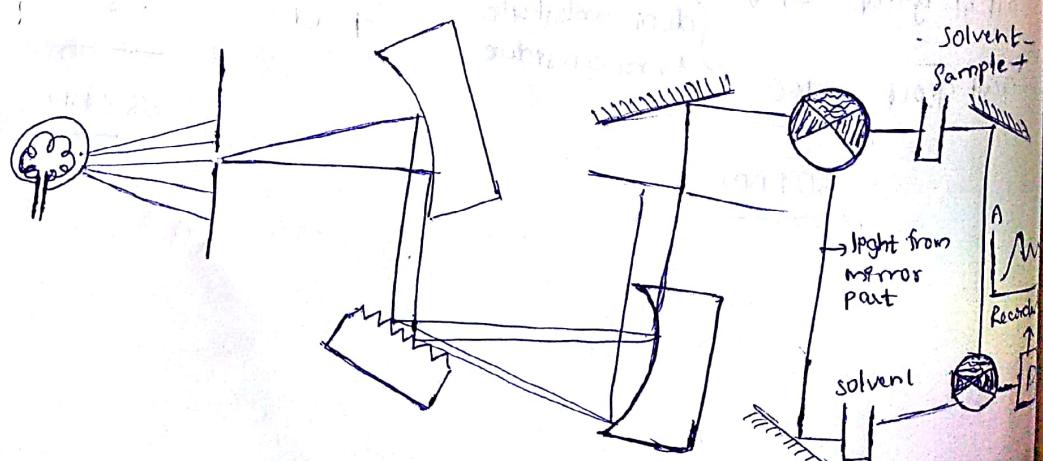
$$A^{II} = \epsilon^a c_a l + \epsilon^b c_b l + \epsilon^c c_c l$$

base parts

Black - absorb

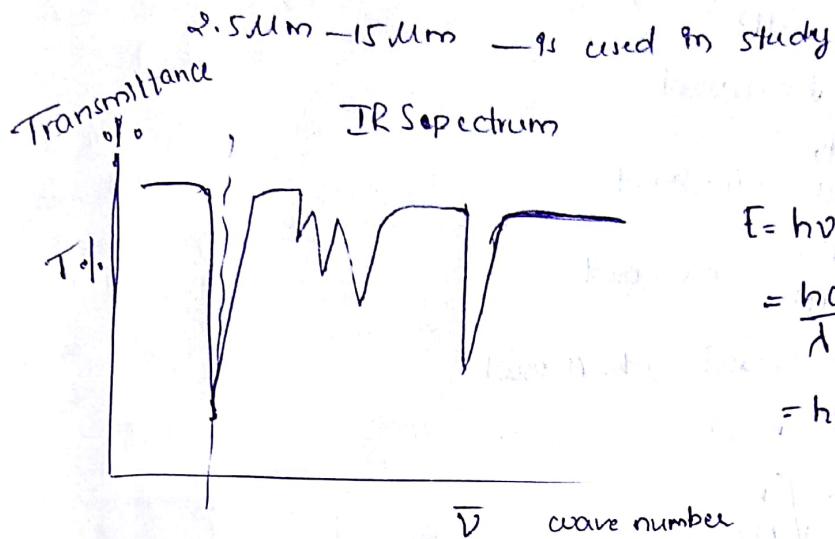
Mirror - reflect light

transparent - allow



IR Spectroscopy :

IR	Near IR Middle IR Far IR	0.78 μm - 2.5 μm 2.5 μm - 50 μm 50 μm - 1000 μm
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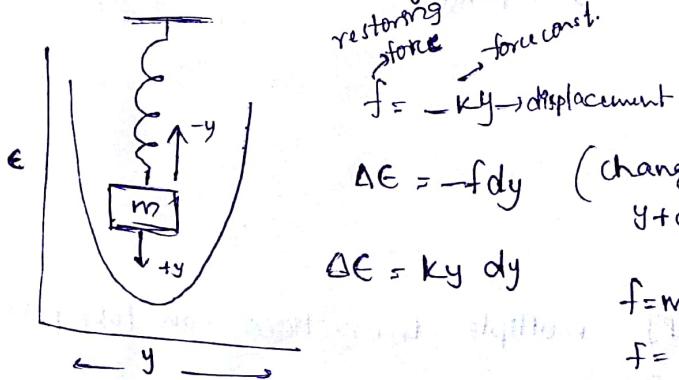


$$\begin{aligned} E &= h\nu \\ &= \frac{hc}{\lambda} \\ &= hc\nu \end{aligned}$$

→ All molecules have certain vibration frequencies! If radiation suitable to these frequencies is passed through them they vibrate that vibration increases the amplitude. It should change the dipole moment of molecule so that the molecule can be studied. This is the principle behind IR spectroscopy.

→ For a molecule to absorb electromagnetic radiation, the dipole moment of the molecule must change. Because when dipole is changing, charges move which makes electric field oscillate.

→ Vibration occurs by disturbing other molecules so it generally occurs at higher energy.



$$\Delta E = -f dy \quad (\text{change in energy when it changes from } y \text{ to } y+dy)$$

$$\Delta E = ky dy$$

$$\begin{aligned} f &= ma \\ f &= m \frac{d^2y}{dt^2} \end{aligned}$$

$$\int_0^t \Delta E = k \int_0^y dy$$

$$\epsilon = \frac{1}{2} ky^2$$

$$f = -ky \Rightarrow m \frac{d^2y}{dt^2} = -ky$$

$$y = A \cos \omega t$$

$$\frac{dy}{dt} = -A\omega \sin \omega t$$

$$\frac{d^2y}{dt^2} = -A\omega^2 \cos \omega t$$

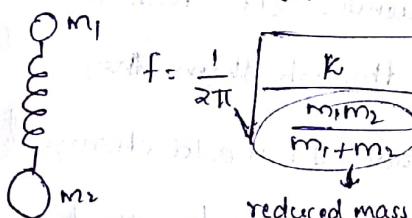
$$+mA\omega^2 \cos \omega t = fK A \cos \omega t$$

$$k = m\omega^2$$

$$\omega = \sqrt{\frac{k}{M}}$$

$$\omega = 2\pi f$$

$$f = \frac{\omega}{2\pi} \quad f = \frac{1}{2\pi} \sqrt{\frac{k}{M}}$$



$$\epsilon = \left(v + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

vibrational quantum number (0 to v)

$$v=0, \quad \epsilon_0 = \frac{1}{2} \frac{h}{2\pi} \sqrt{\frac{k}{M}}$$

$$v=1, \quad \epsilon_1 = \frac{3}{2} \frac{h}{2\pi} \sqrt{\frac{k}{M}}$$

$$v=2, \quad \epsilon_2 = \frac{5}{2} \frac{h}{2\pi} \sqrt{\frac{k}{M}}$$

$$hcv = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

at this wave number stretching frequency of vibration is seen

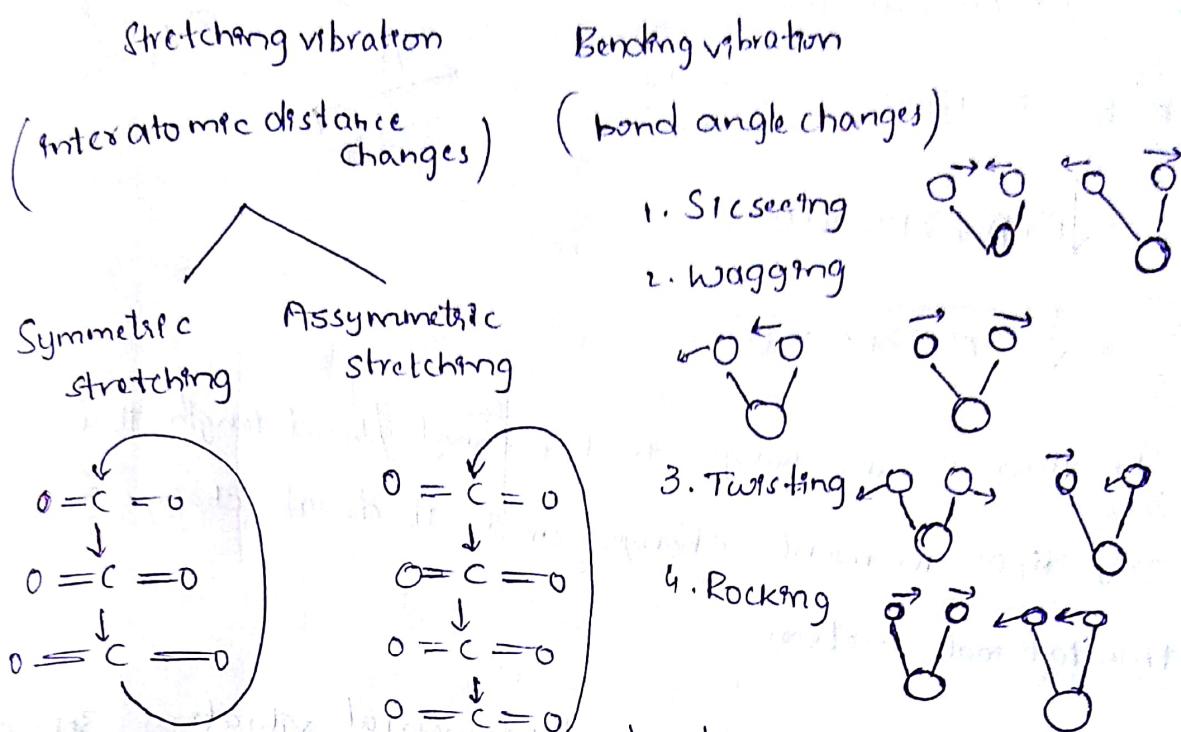
$$\Delta v = \pm 1$$

$$\Delta v = \pm 2 \rightarrow 1^{\text{st}} \text{ overtone}$$

$$\Delta v = \pm 3 \rightarrow 2^{\text{nd}} \text{ overtone}$$

During this spectroscopy, multiple transactions can take place hence these are called overtones

Molecular Vibration



Stretching frequency of $\text{C}=\text{O}$

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k \text{ cm}^{-1} \text{ nm}^2}{m_1 m_2}}$$

$$M_1 = \frac{12 \text{ g/mol}}{6.023 \times 10^{23} / \text{mol}} = 1.99 \times 10^{-23} \text{ g} = 1.99 \times 10^{-26} \text{ kg}$$

$$M = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.99 \times 10^{-26})(2.656 \times 10^{-26})}{(1.99 + 2.656) \times 10^{-26}} = 5.2854 \times 10^{-26} \text{ kg}$$

$$= \frac{16 \text{ g/mol}}{6.023 \times 10^{23} / \text{mol}} = 2.656 \times 10^{-26} \text{ kg}$$

$$= 2.656 \times 10^{-26} \text{ kg} \times 3 \times 10^8 \text{ m/s} = 7.968 \times 10^{-18} \text{ Hz}$$

$K = 0.5 \times 10^{-3} \text{ N/m}$ — single bond

$K = 1.0 \times 10^{-3} \text{ N/m}$ — double bond

$K = 1.5 \times 10^{-3} \text{ N/m}$ — triple bond

$$\bar{v} = \frac{1}{2\pi \times 3 \times 10^8} \sqrt{\frac{1 \times 10^{-3}}{1.13 \times 10^{-26}}} \text{ Hz}$$

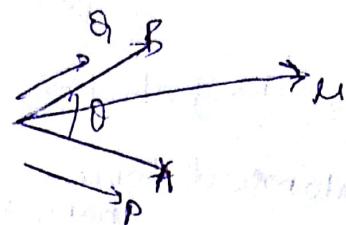
Whole molecular motion doesn't bring any change in dipole moment

$$\mu = \sqrt{P^2 + Q^2 + 2PQ\cos\theta}$$

$$P = Q \quad \theta = 180^\circ$$

$$= \sqrt{P^2 + P^2 + 2P^2\cos(180^\circ)}$$

$$= \sqrt{2P^2 - 2P^2} = 0$$



If there is any change in bond angle / bond length then only dipole moment changes and it doesn't change in translational motion.

for non-linear molecule no. of fundamental vibrations = $3N - 6$

where N = no. of atoms in the molecule.

H_2O : 3 atoms

$$3N - 6 = 3 \times 3 - 6 = 9 - 6 = 3$$

So there are 3 interatomic motions which brings change in bond length and bond angle.

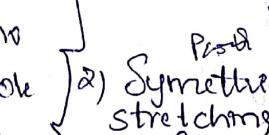
Wagging
Twisting
Rocking

these are IR inactive

Whole molecular motion so no change in dipole movement so

$P = Q$
change in θ

1) Scissoring inter atomic motion



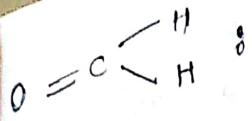
2) Symmetric stretching



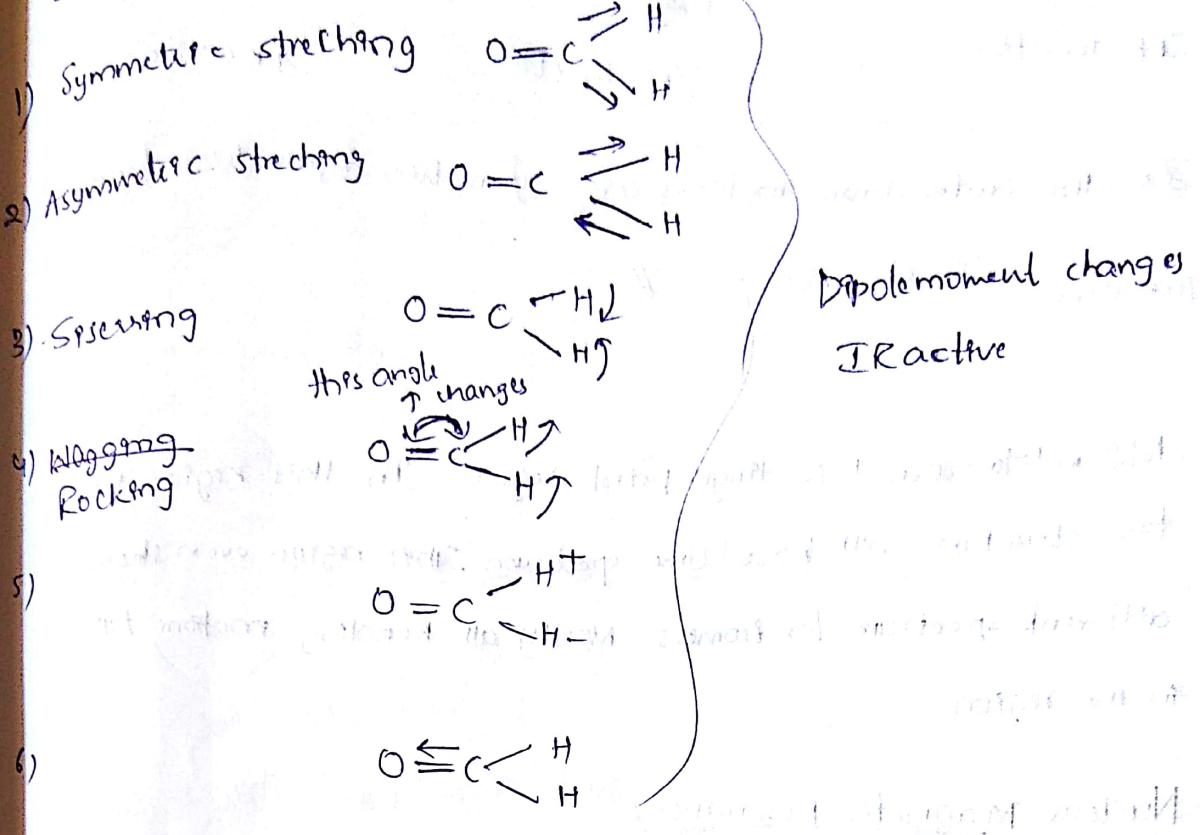
3) Asymmetric stretching

bring change in dipole movement (IR active)

So water molecule has 3 IR bands.



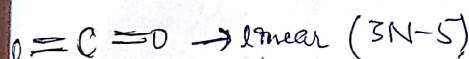
$3N-6 = 3 \times 4 - 6 = 6$ interatomic motions.



If a molecule (linear) is rotated along interatomic axis it is not
considered to change its configuration so it is not considered
as change in position.

Total interatomic motions for linear molecule = 5

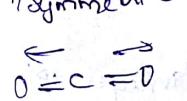
No. of vibrational mode possible for linear molecule = $3N-5$



$$3 \times 3 - 5 = 4$$

whole molecular motions

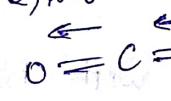
1) Symmetric



IR inactive

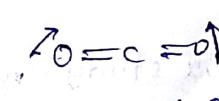
X not absorb

2) Asymmetric C

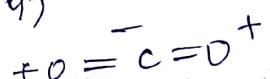


IR active
 2730 cm^{-1}

3) Splaying

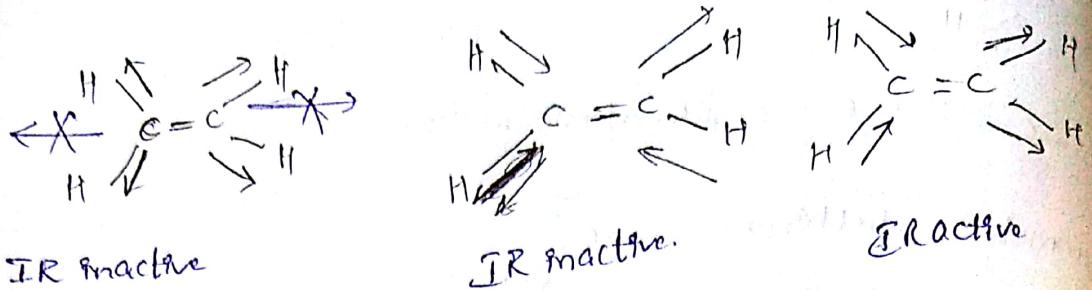


O is changing



700 cm^{-1} absorbs ϵ_{MR}

∴ Only 2 absorption signals are found.



For H₂O interatomic motions are symmetric, Asymmetric, bending

non linear - $3N-G = 3 \times 3 - 6 = 3$

1500 cm⁻¹ to 500 cm⁻¹ is finger print region. In this region no two structures will have same spectrum. This region even shows different spectrum for isomers. Mostly all bending motions fall in this region.

Nuclear Magnetic Resonance:

We detect nuclei of atoms in a molecule.

Nuclei act as a tiny magnet in presence of magnetic field.

Nuclear spin flips up & down on absorbing EMR

A Z Odd mass no. → half integer spin, $B = \frac{1}{2}$, H = $\frac{1}{2}$, $^{13}\text{C} = \frac{1}{2}$, $^{15}\text{N} = \frac{1}{2}$

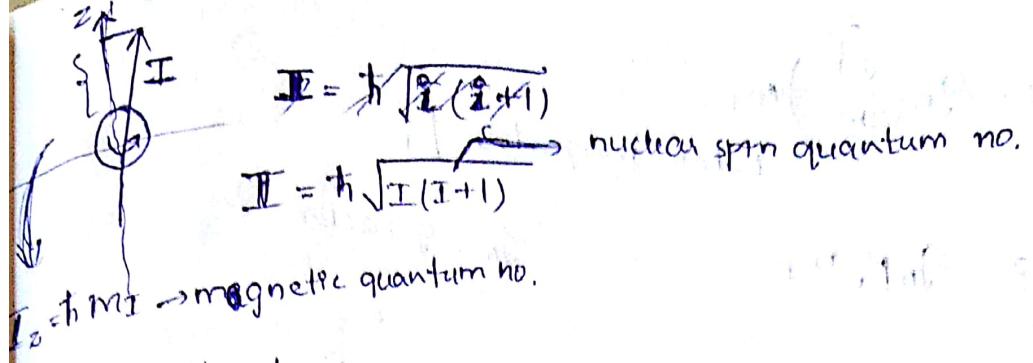
Even mass no. & atomic no. - zero nuclear spin $^{12}\text{C}_6$

Even mass no. & odd atomic no. - integer spin $^{14}\text{N}_7$

→ We can study nuclei that have $I \neq 0$ → nuclear spin $\neq 0$

In NMR spectroscopy we study nuclei with half integer spin like ^1H , ^{13}C , ^{31}P , ^{19}F

→ The direction of spin angular momentum (I) is given by right hand thumb rule when fingers are curled in the direction of the spin of the nucleus



$$m_I = (2I+1) \text{ values}$$

$$-I, -I+1, -I+2, \dots, +I$$

I_H : spin quantum no. = $I = 1/2$

$$m_I \text{ multiplicity} : 2I+1 = 1/2+1=2$$

$$m_I = \begin{cases} (-I) \\ -1/2, -1/2+1=1/2 \\ (+I) \end{cases}$$

$\rightarrow M$ - magnetic moment

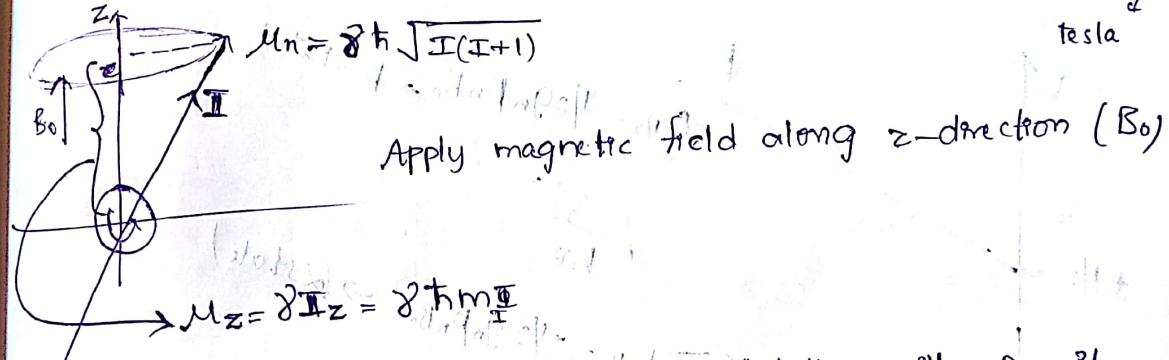
$$\mu_n = \text{Nuclear magnetic moment} = \gamma I \rightarrow$$

nuclear spin angular momentum

gyromagnetic ratio

$$\mu_n \text{ & } I \text{ are in same direction if } \gamma \text{ is +ve}$$

$$\gamma = 2.6 \times 10^8 \text{ rad s}^{-1} T^{-1}$$



\rightarrow Magnetic moment instead of aligning totally with B_0 it spins around B_0 with frequency ω_0 - Larmors frequency

$$\omega = \gamma B_0$$

\rightarrow The mag. of angular moment will not change if the nuclei have same I value. but M_n changes as γ is different for different nuclei.

$$M_z = \gamma I_z = \gamma h m_I \quad \gamma = g_n \frac{e}{2m}$$

Boltzmann constant of nuclear magneton

m - mass of nucleus

$$M_z = g_n \left(\frac{e\hbar}{2m} \right) m_I$$

Bohr magneton β_n

$$M_z = g_n \beta_n m_I$$

g_n - g factor

Energy of interaction b/w M_z & B_0 , $E = -M_z B_0$

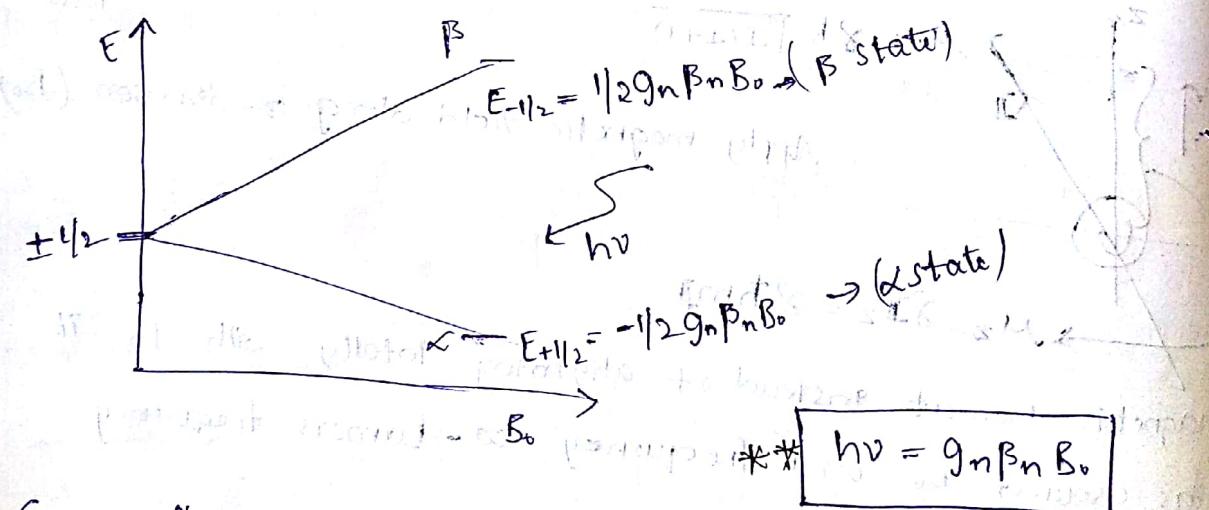
$$E = -g_n \beta_n B_0 m_I$$

Base proton, $I = 1/2$

$$m_I \text{ value} = 2I + 1 = \underline{2}$$

$$m_I = -1/2, +1/2$$

$$\begin{aligned} E_{+1/2} &= -1/2 g_n \beta_n B_0 \\ E_{-1/2} &= +1/2 g_n \beta_n B_0 \end{aligned} \quad \left. \begin{array}{l} \text{if we apply } B_0 \text{ energy of } E_{+1/2} \text{ is increasing} \\ \text{& other is decreasing } (E_{-1/2}) \end{array} \right.$$



$$\text{Energy difference} = \Delta E = E_{-1/2} - E_{+1/2} = g_n \beta_n B_0$$

Resonance condition

If we supply EMR ($h\nu$) equal to $g_n \beta_n B_0$

$+1/2$ state goes to $-1/2$ state. This is NMR.

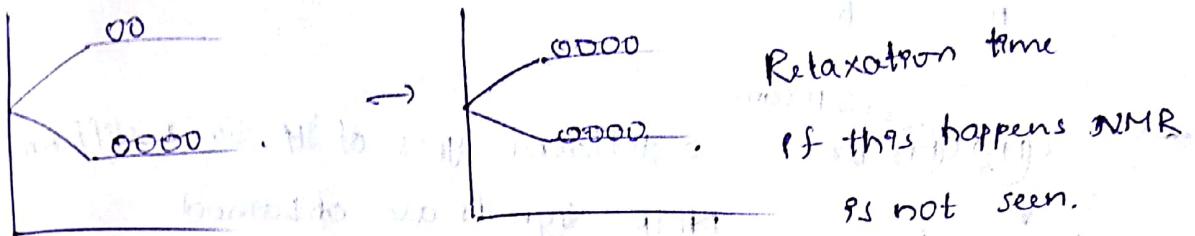
Splitting of energy level in presence of magnetic field is called zeeman effect.

Intensity $e^{-\Delta E/kT}$ is proportional to population ratio of β and α

$$\frac{N_B}{N_\alpha} = e^{-\Delta E/kT}$$

at 0K - no spin in higher state all population is in lower state.

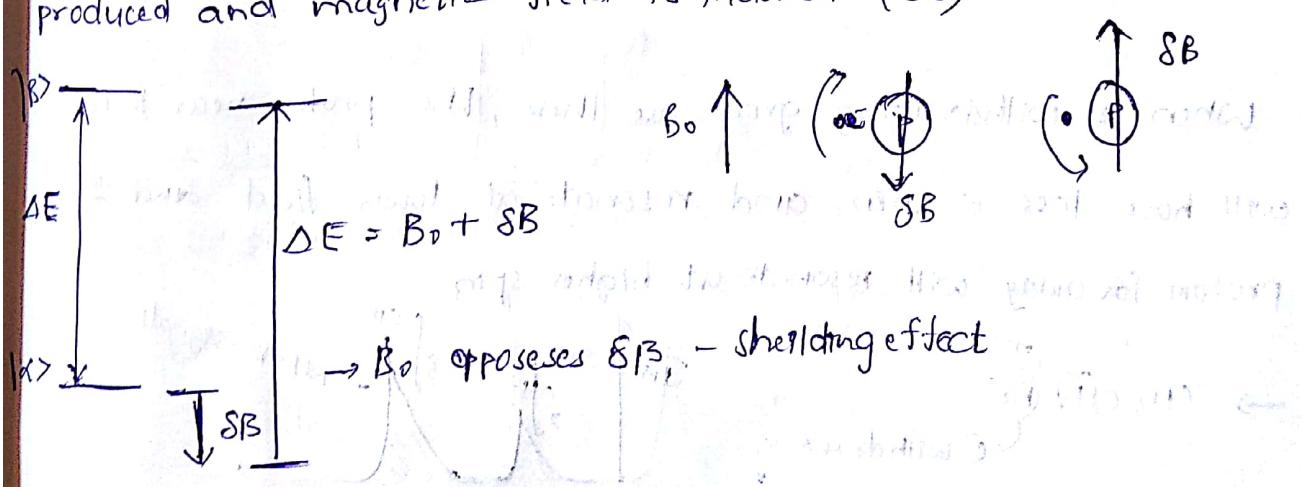
At 300K $\frac{N_B}{N_\alpha} = 0.999$ meaning the



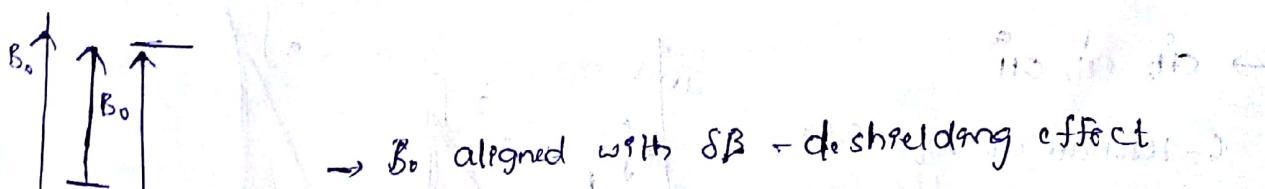
But this doesn't happen as the excited spins come back in spin lattice relaxation time

If the energy of excitation is used by surrounding or lattice spin lattice and if it is used by another spin it is spin spin relaxation time

When a charged particle e^- is spinning due to applied magnetic field around proton EMF is produced and magnetic field is induced (δB)



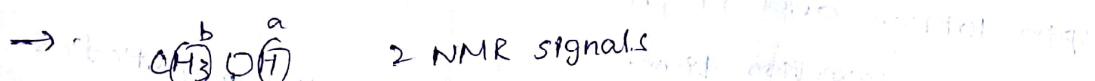
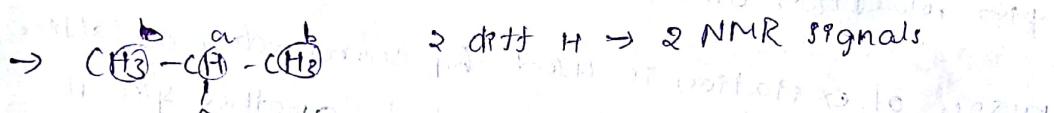
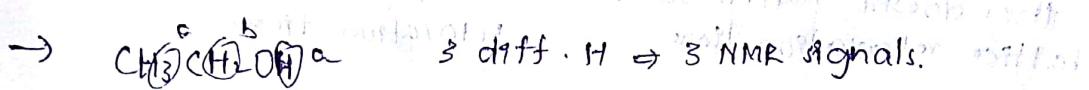
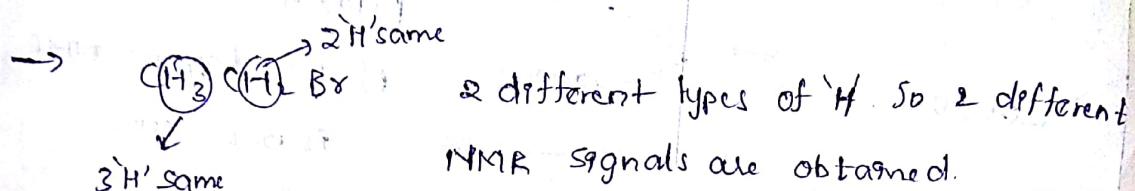
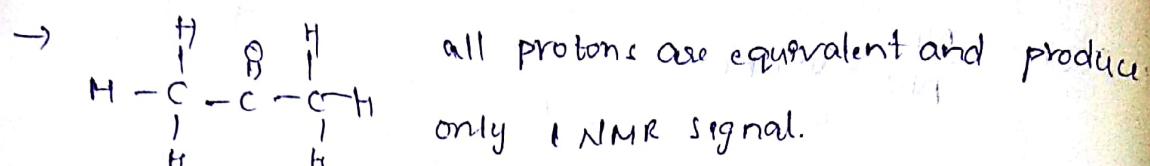
When induced δB is aligned with B_0 - no effect



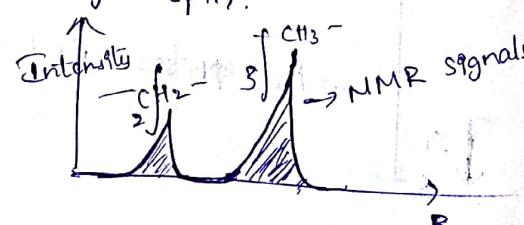
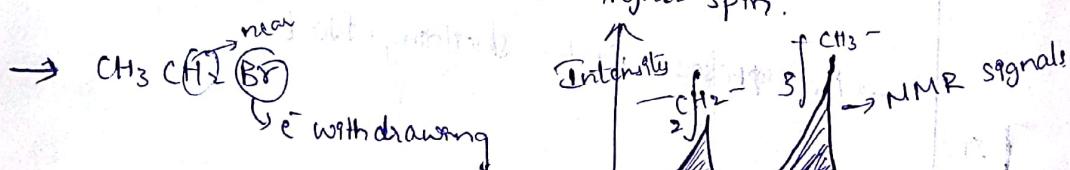
Equivalent protons share similar environment.

No. of NMR signals depend on equivalent proton.

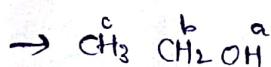
All equivalent protons will resonate at same frequency and gives only 1 NMR signal.



When e^- -withdrawing groups are there the proton near to it will have less e^- spin and resonate at lower field and the proton far away will resonate at higher spin.



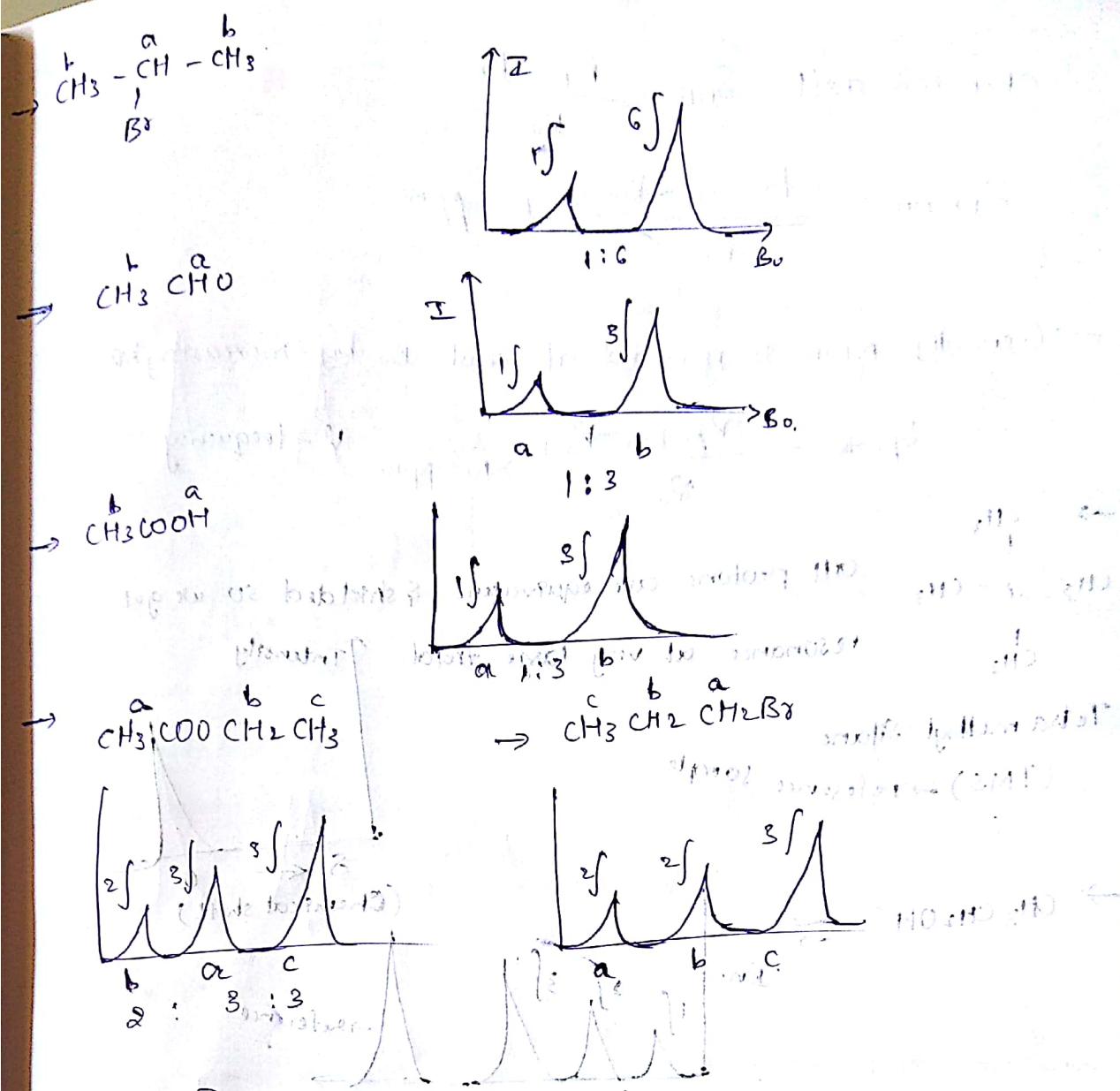
Ratio of areas gives no. of protons.



c - resonate at high field

a - resonate at low field





$$\rightarrow SB \propto B_0$$

σ - shielding constant

$$SB = -\sigma B_0$$

opposing the applied mag. field

$$B_{\text{local}} = B_0 + SB = B_0 - \sigma B_0 = B_0 (1 - \sigma)$$

total field experienced by proton

$$B_A = B_0 (1 - \sigma_A)$$

$$B_B = B_0 (1 - \sigma_B)$$

Shield of B wrt. A

$$B_A - B_B = B_0 (1 - \sigma_A) - B_0 (1 - \sigma_B)$$

$$= B_0 (\sigma_B - \sigma_A) \rightarrow \text{chemical shift } (\delta_{AB})$$

$$= B_0 S_{AB}$$

$$\text{Chemical shift } \delta_{AB} = \frac{B_A - B_B}{B_0}$$

$$\delta_{\text{proton}} = \frac{\nu_{\text{proton}} - \nu_{\text{ref.}}}{B_0} \times 10^6 \text{ ppm}$$

→ Generally, NMR is recorded at const. B_0 by increasing ν .

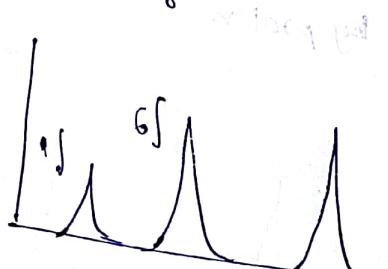
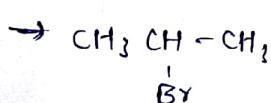
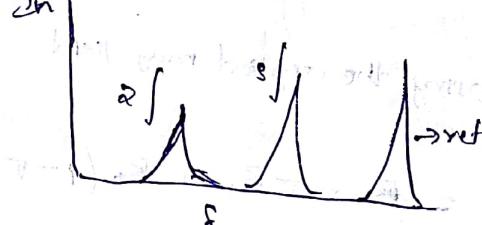
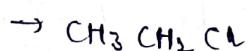
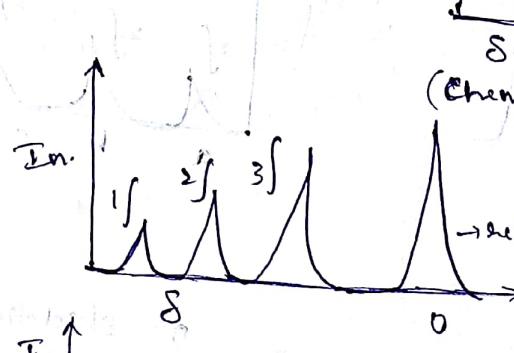
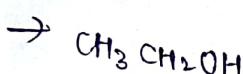
$$\delta_{\text{proton}} = \frac{\nu_{\text{proton}} - \nu_{\text{ref.}}}{\nu_0} \times 10^6 \text{ ppm} \quad \nu - \text{frequency}$$



All protons are equivalent & shielded so we get resonance at very large field. ↑ Intensity

Tetra methyl Silane

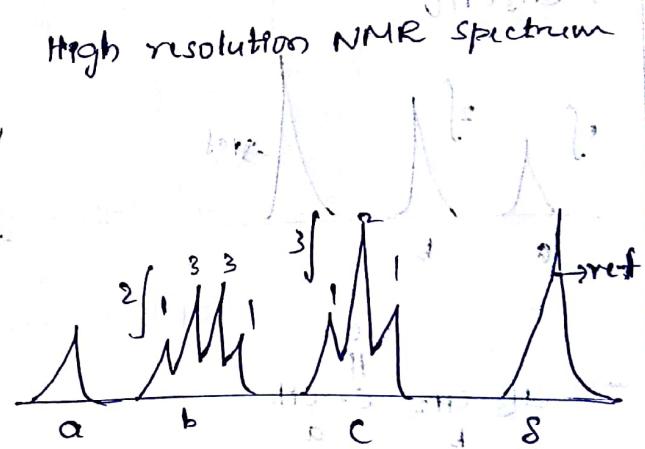
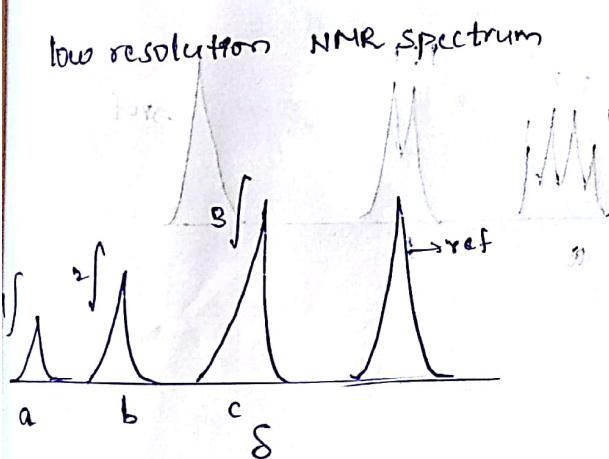
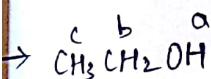
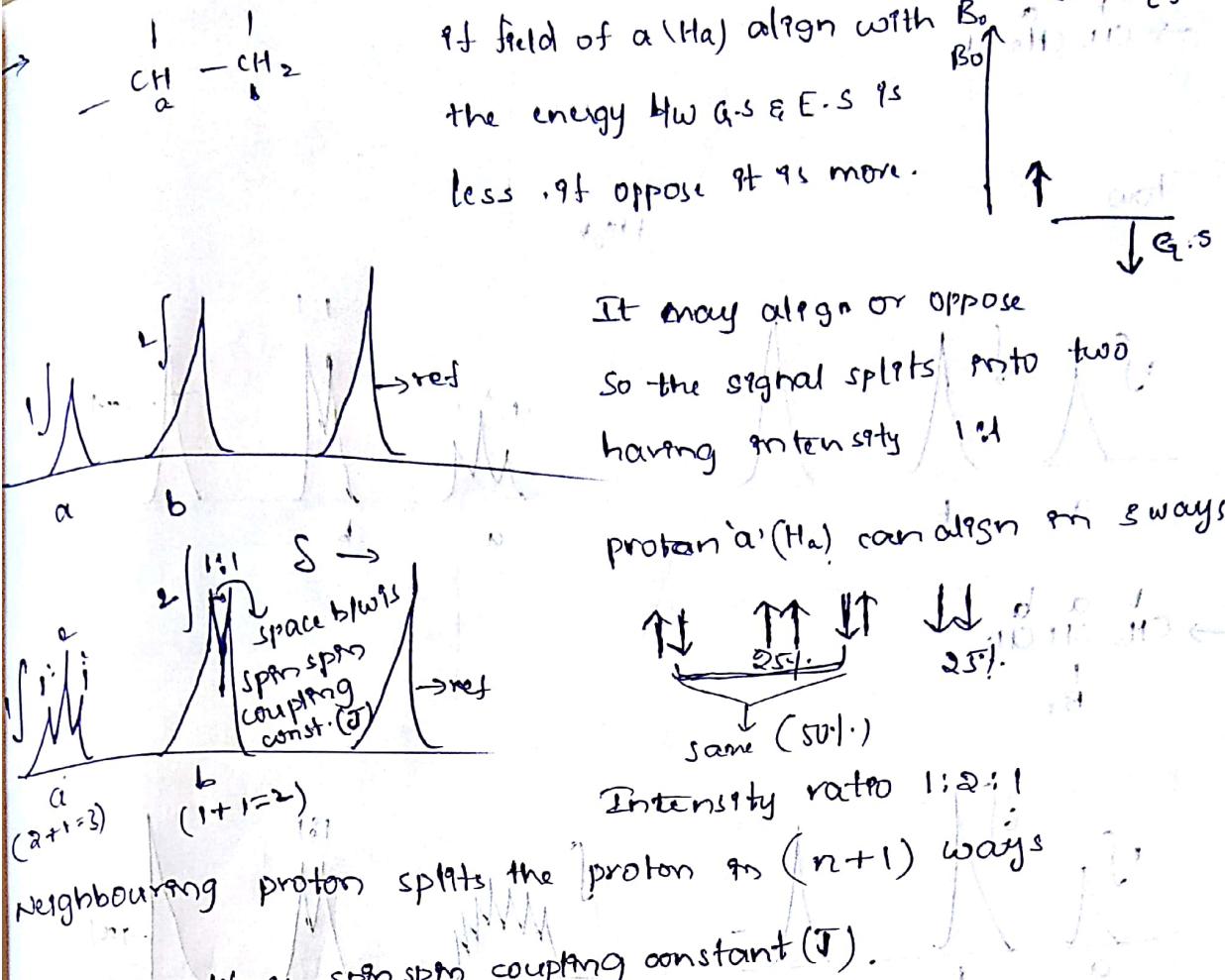
(TMS) → reference sample



In NMR we change frequency keeping the constant field.

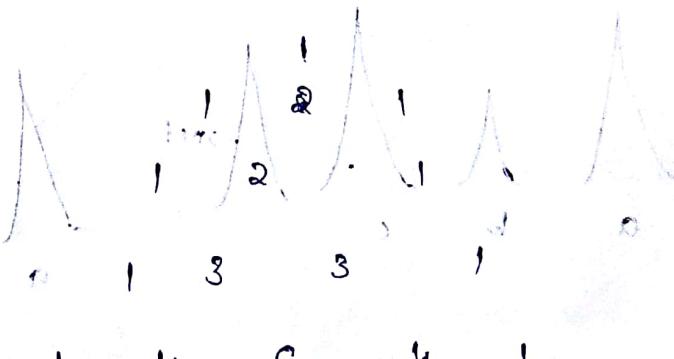


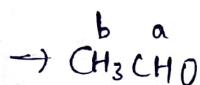
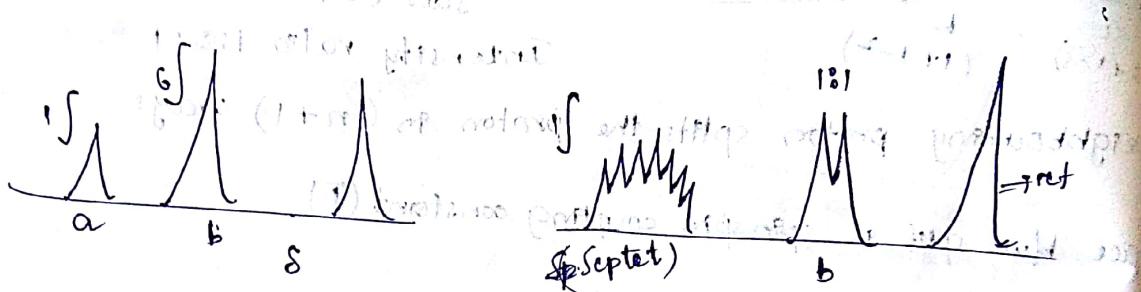
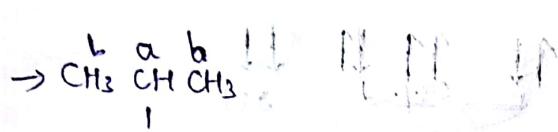
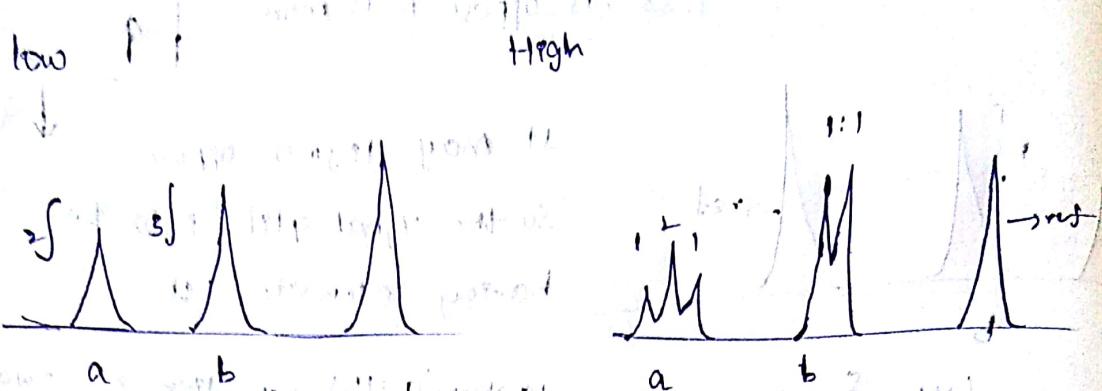
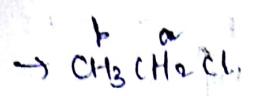
→ Spin spin coupling



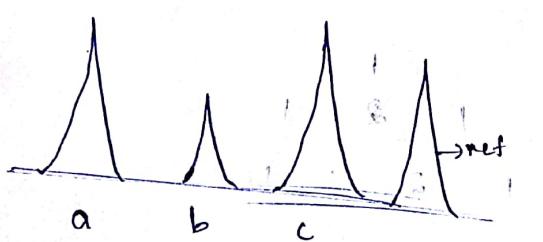
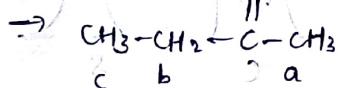
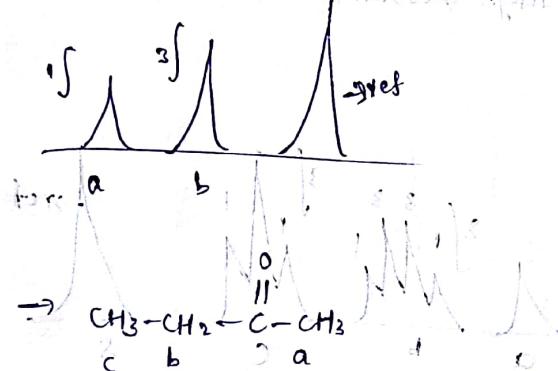
Intensity ratio is given
 by binomial triangle

by knowing the no. of
 splits.

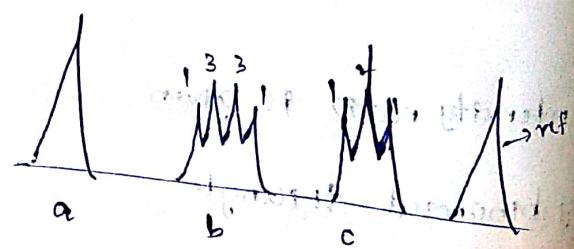


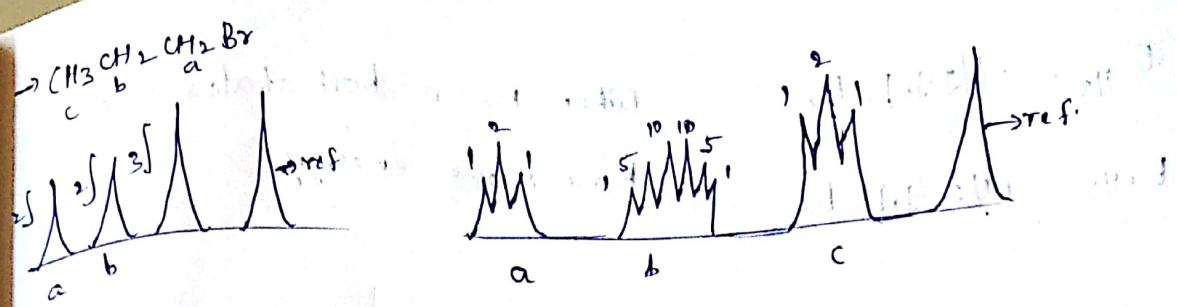


Integration: 2.00, 1.00, 0.99



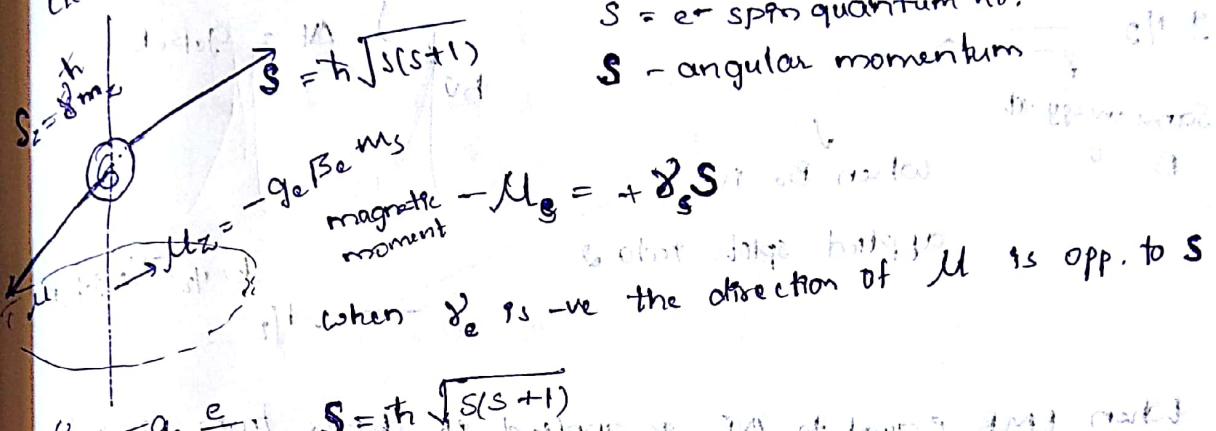
Integration: 2.00, 1.00, 0.99





Electron Magnetic Resonance (EMR)

Electron spin paramagnetic resonance (ESR) or (EPR)



$$S = \text{electron spin quantum no.}$$

S - angular momentum

$$g = -g_e \frac{e}{2m} \quad S = \hbar \sqrt{\frac{S(S+1)}{2}}$$

$$\mu_s = -g_e \frac{e}{2m} \beta_e \quad m - \text{mass of } e^- \quad e - \text{charge of } e^-$$

$$\beta_e = \frac{e}{2m} \hbar \quad \text{condition of resonance} \rightarrow \boxed{\omega = g_e \beta_e B_0}$$

$$\mu_s = -g_e \frac{e}{2m} \beta_e \sqrt{S(S+1)}$$

When B_0 is applied μ will rotate with frequency

$$\omega = g_e \beta_e B_0$$

$2S+1$ multiplicity

$$\mu_s = -g_e \beta_e m_s \quad m_s = +s, +s-1, \dots -s, \dots$$

$$E = -\mu_s B_0$$

$$E = -(-g_e \beta_e m_s) B_0$$

$$= g_e \beta_e m_s B_0$$

for single e^- $s = 1/2$ $m_s \pm 2(1/2) + 1 = 2$ m_s values

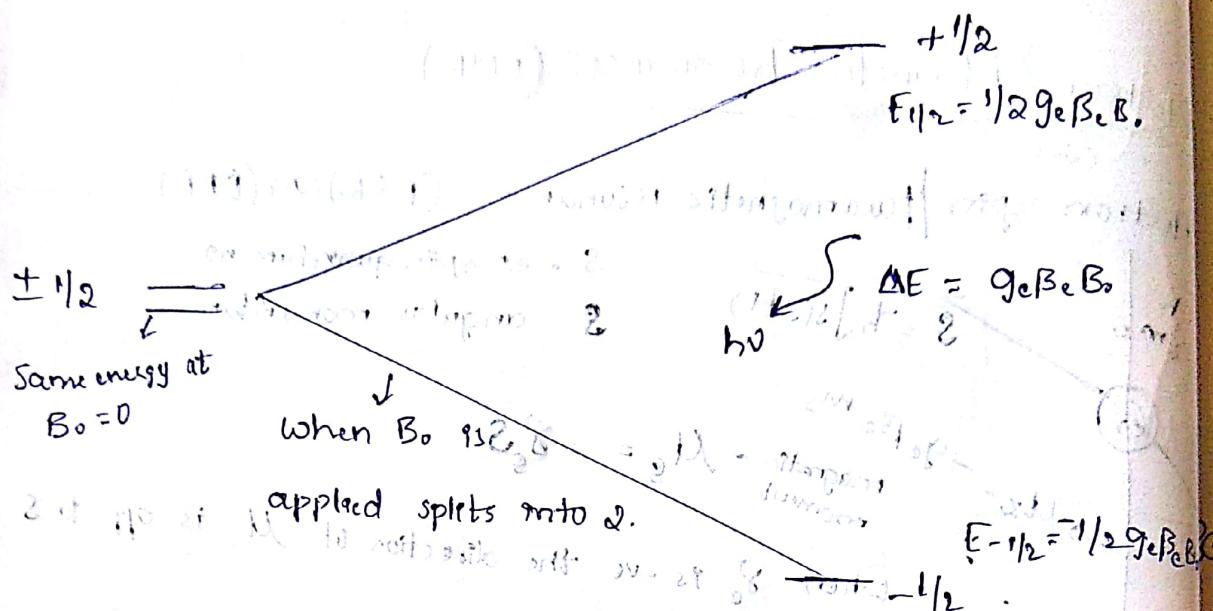
No. of m_s values = 2

$$-1/2, +1/2$$

$$E_{-1/2} = -1/2 g_e \beta_e B_0$$

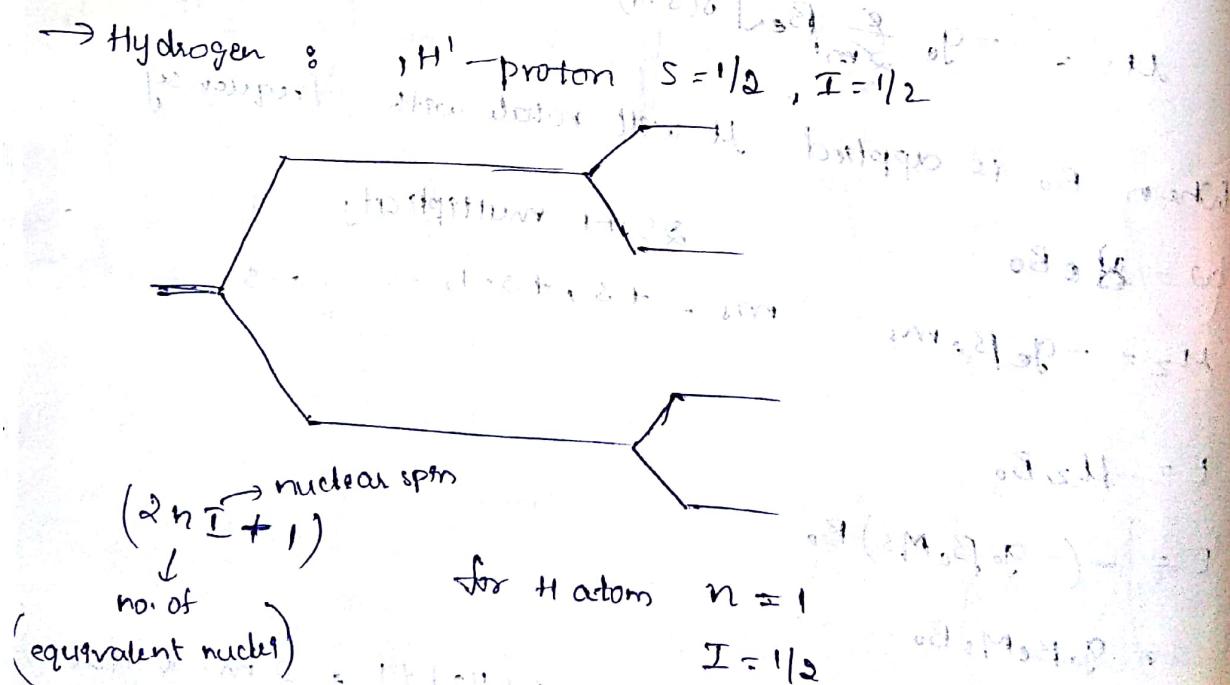
When $B_0 = 0$ both states will have same energy.

$$E_{+1/2} = +1/2 g_e \beta_e B_0$$



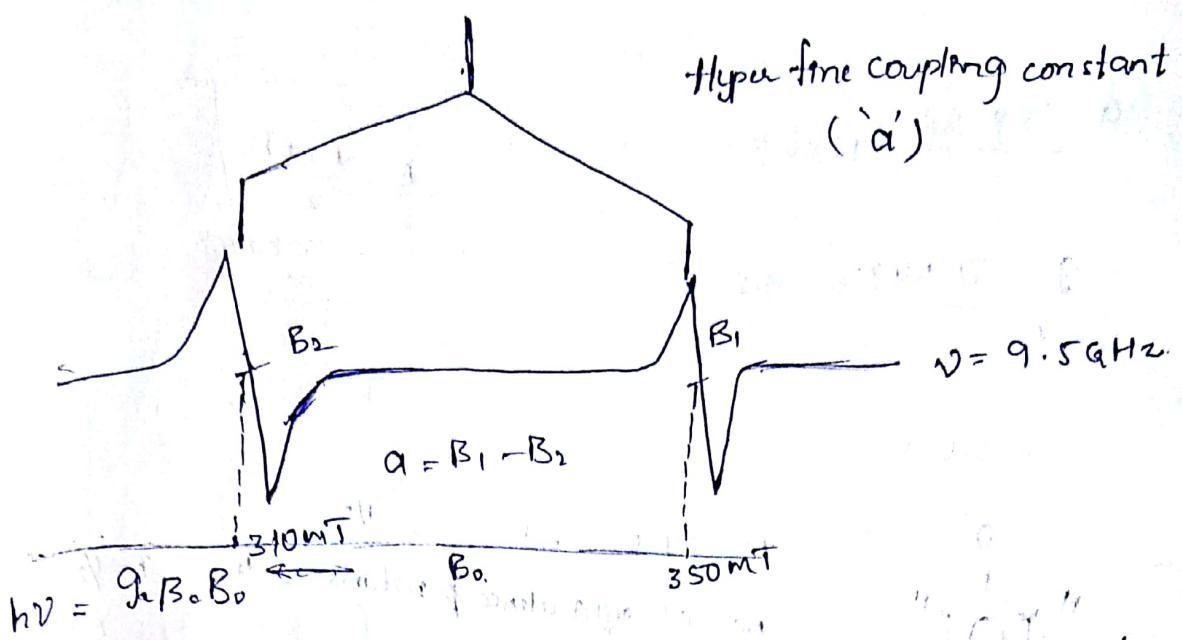
When EMR equal to ΔE is applied it shifts from ground state to excited state.

$$h\nu = g_e B_e B_0 \rightarrow \text{resonance condition}$$



$$\text{No. of splittings} = 2 \times 1 \times 1/2 + 1 = 2$$

Hyperfine coupling constant
('a')



$$g = \frac{h\nu}{B_e B_0} \quad \nu - \text{frequency at which spectrometer is working.}$$

h - plank's constant.

$$\frac{B_0 + B_1}{2} = \frac{B_1 + B_2}{2}$$

$$g = \frac{71.44836 \times \nu (\text{GHz})}{B(\text{mT})}$$

$$a = B_1 - B_2 = 350 - 310 = 40.$$

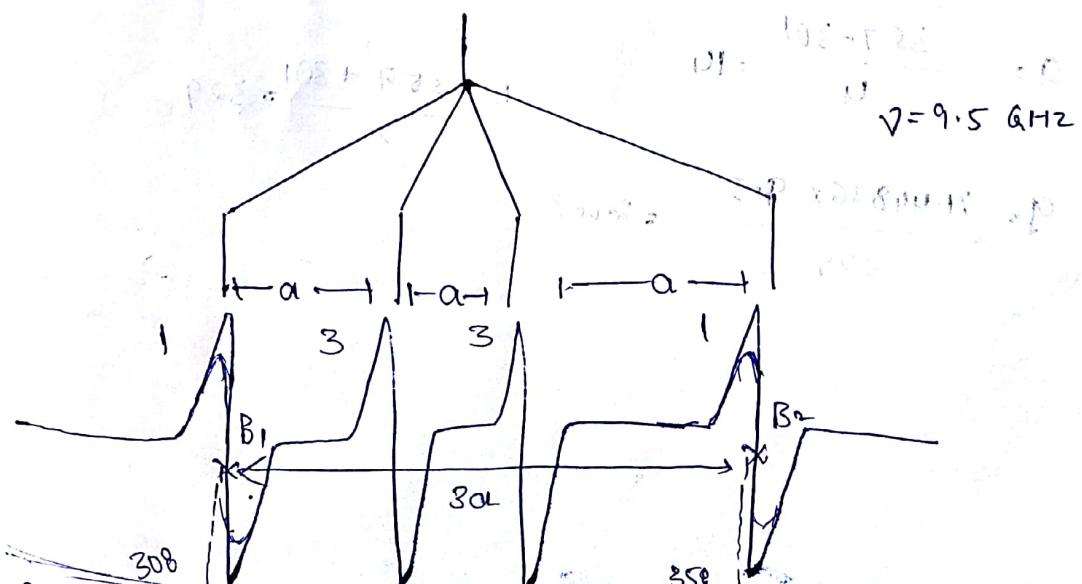
$$B = \frac{350 + 310}{2} = 330$$

$$g = \frac{71.44836 \times 9.5}{330} = 2.0568$$

→ ${}^{\circ}\text{CH}_3$ - methyl radical

$$1e^- \Rightarrow S = 1/2$$

3 equivalent proton $I = 1/2$ $2nI+1 = 2 \times 3 \times 1/2 + 1 = 4$ splits



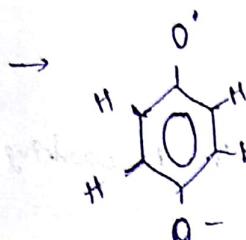
$$\alpha = \frac{358 - 308}{3} = 16.66$$

$$B = \frac{B_1 + B_2}{2}$$

$$= \frac{358 + 308}{2} = 333$$

$$g = \frac{71.44836 \times 9.5}{333}$$

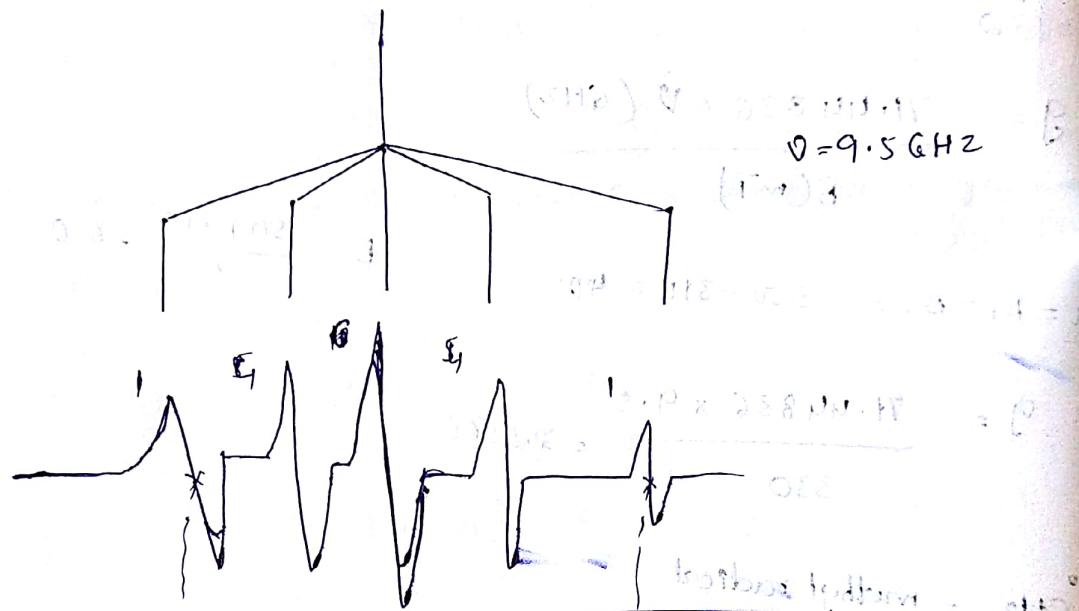
$$= 2.038$$



$$\text{no. of } e^- = 1 \quad S = 1/2$$

no. of equivalence p-rotations = 4 $I = 1/2$ for proton

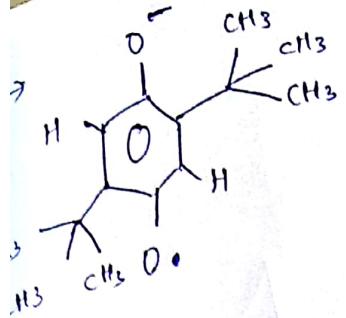
$$2mI + 1 = 2 \times 4 \times 1/2 + 1 = 5 \text{ transitions}$$



$$\alpha = \frac{357 - 301}{4} = 14$$

$$g = \frac{71.44836 \times 9.5}{329} = 2.063$$

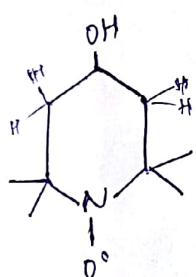
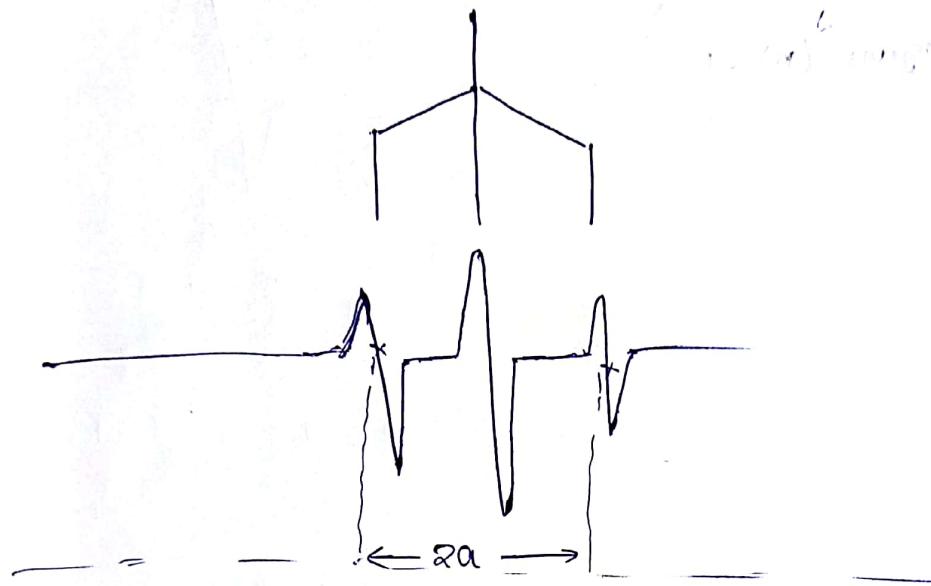
$$B = \frac{357 + 301}{2} = 329$$



$$\text{no. of } e^- = 10 \quad S = 1/2$$

no. of equivalent protons = 18 $I = 1/2$

$$2nI + 1 = 2 \times 18^2 \times 1/2 + 1 = 193$$

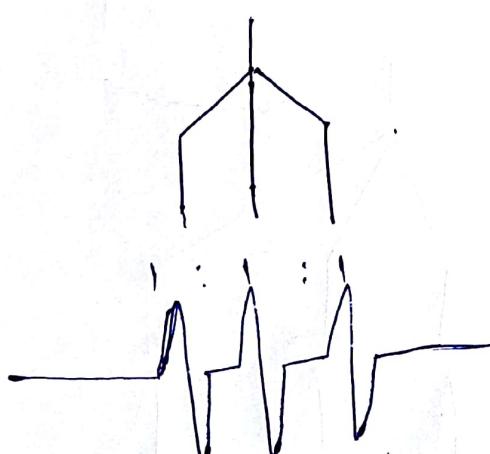
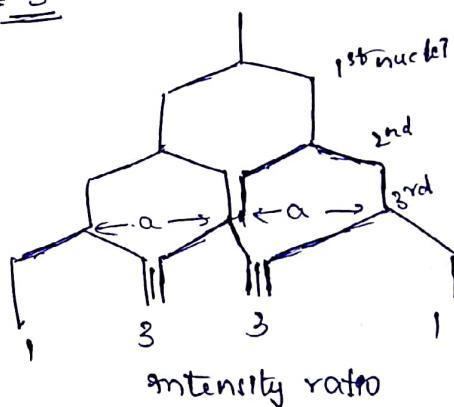


$$I = 1 \text{ for nitrogen} \quad \text{no. of } e^- = n_e = 1$$

no. of equivalent protons = 1 I

$$2nI + 1 = 2 \times 1 \times 1 + 1 = 3$$

it has only one equivalent proton so
we don't need to see for intensity ratio
it is 1:1:1 as there are 3 splits.



$L.P - L.P > L.P - B.P > B.P - B.P$ - repulsion
 $\Sigma > = > -$

$A \times n^m$

A - central atom

X - atom/molecule bound to the central atom.

E - lone-pair electrons attached to central atom.

Struct. numbers / Spin density

It is sum of atoms attached and lone pairs on central atom.

$$\text{Struct. no.} = n + m$$

Struct. no.

2

Angle

Not 180°



shape

linear

3



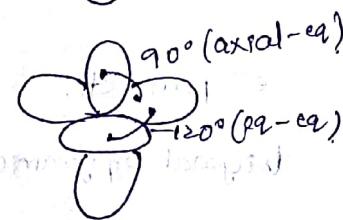
trigonal planar

4



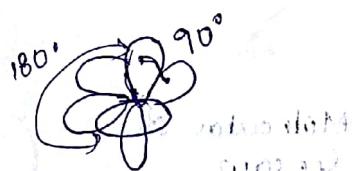
tetrahedral

5



trigonal bipyramidal

6



Octahedral

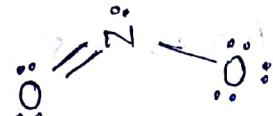
$\rightarrow N_3^-$

$$1 \times N = 5$$

$$2 \times O = 12$$

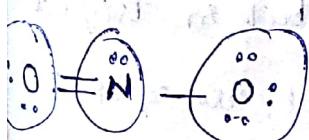
$$1 \times -ve = +1$$

trigonal planar
e-pair structure

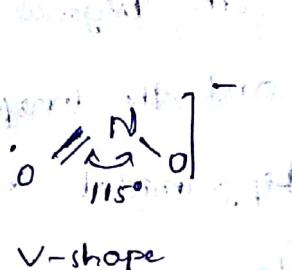


18

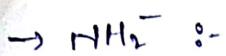
Molecular structure



3 spin densities.



V-shape

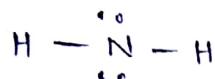


$1 - \text{N} = 5$

$2 - \text{H} = 2$

$1 - \text{ve} = 1$
 $\frac{1}{8}$

$8 - 4 = 4$ \Rightarrow Molecular structure

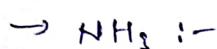
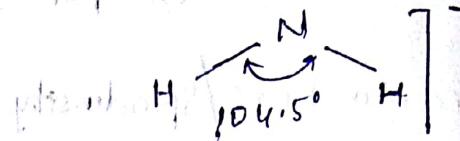
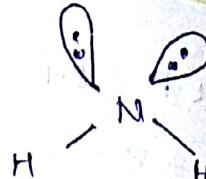


Steric no. = 4

e-pair structure

-trigonal

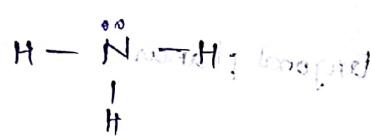
tetrahedral



$1 - \text{N} = 5$

$3 - \text{H} = 3$

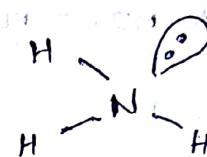
$8 - 6 = 2$



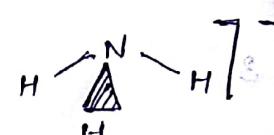
Steric no. = 4

e-pair structure

tetrahedral



Molecular structure

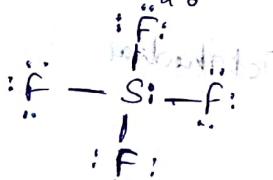


$1 - \text{S} = 6$

$4 - \text{F} = 4 \times 7 = 28$

$\underline{34}$

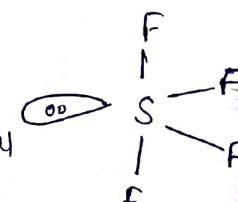
$34 - 8 = 26$



Steric no. = 5

e-pair str.

trigonal bipyramidal



Molecular str.
Seesaw



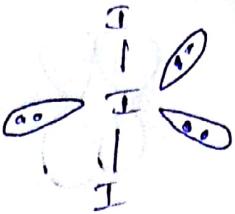
In trigonal planar & tetrahedral all positions are equal
and the lone pair can be placed anywhere but in trigonal bipyramidal axial are equal and 2 equatorial are equal & lone pair should be in equatorial position

$$\rightarrow I_3^- : -3I = 7 \times 3 = 21$$

$$e^- ve = \frac{1}{\underline{22}}$$

e-pair str.

trigonal bipyramidal

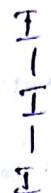


$$22 - 4 = 18$$



Molecular str.

linear



$$\text{sterc no.} = 5$$

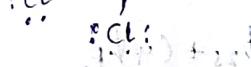
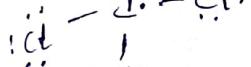
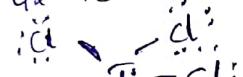
$$\rightarrow ICl_5^+ :$$

$$1I = 7$$

$$5Cl = 7 \times 5 = 35$$

$$\underline{42}$$

$$42 - 10 = 32$$



e-pair str.

Octahedral

Molecular str.

square planar

$$\text{sterc no.} = 6$$

$$\rightarrow \text{One } e^- \text{ wave fn } \Psi = \phi(1)$$

$2 e^-$ s wave fn

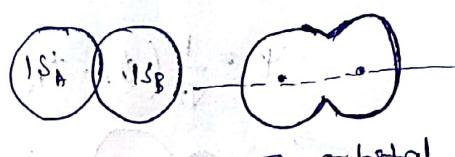
$$\Psi = \phi_A^{(1)} \phi_B^{(2)}$$

constructive coherence

$$\phi_A^{(2)} \phi_B^{(1)}$$

probability of finding e^-

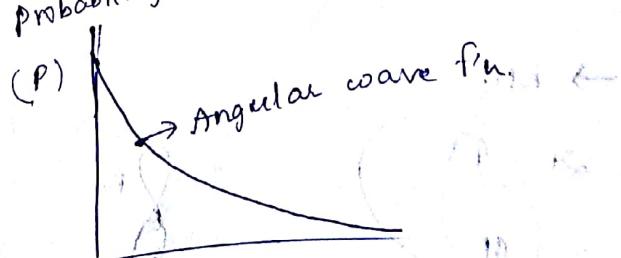
H_A H_B

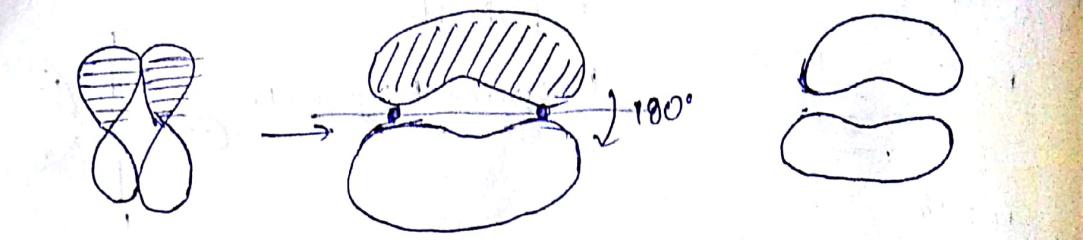


When we rotate along interatomic axis

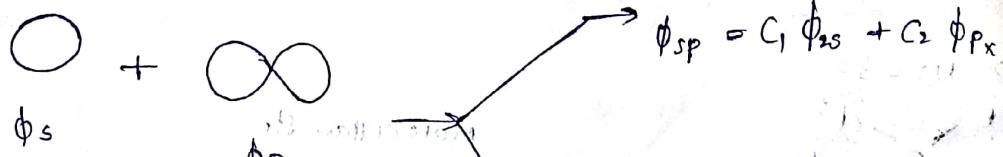
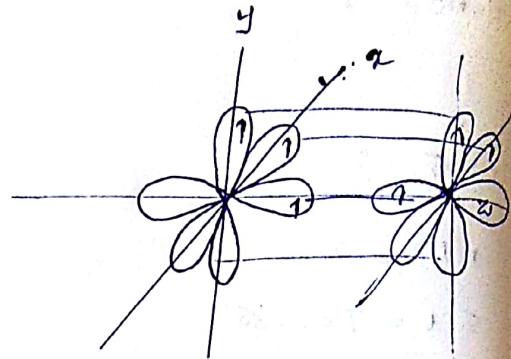
If we don't see any change in position of atoms it is cylindrical symmetry.

Orbital must have a cylindrical symmetry along interatomic axis.



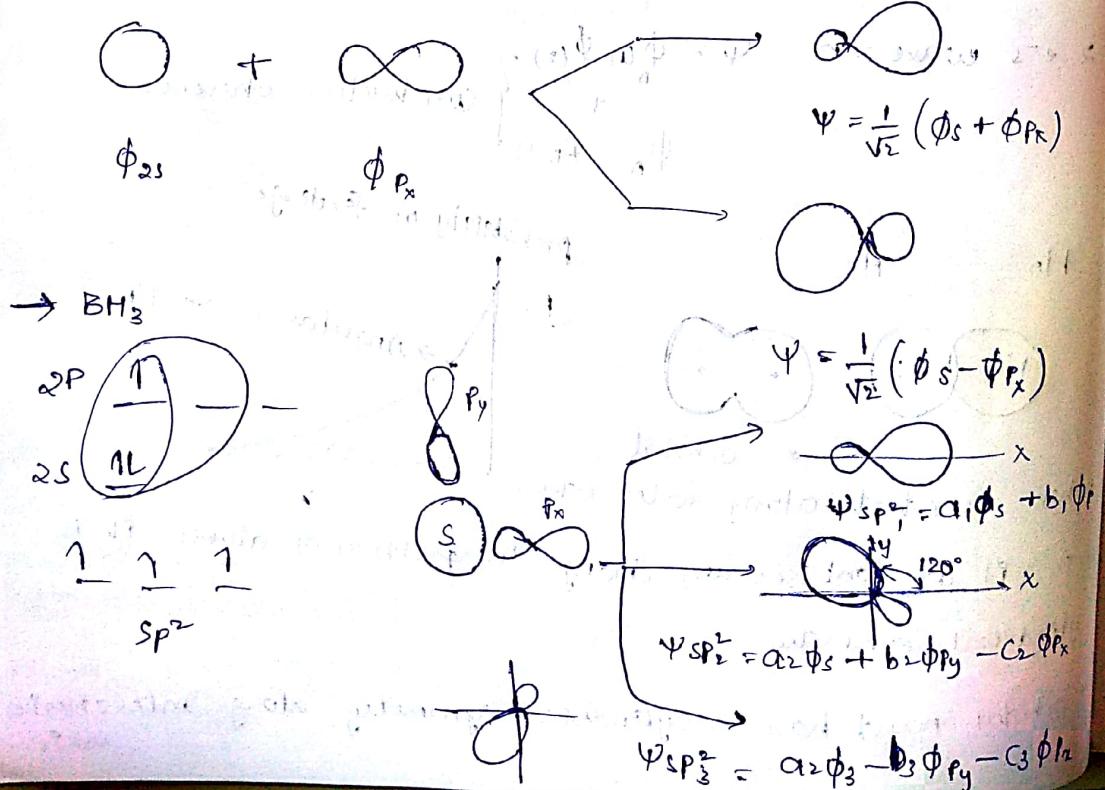


When we rotate 180° along internuclear axis if sign changes
it is π orbital.

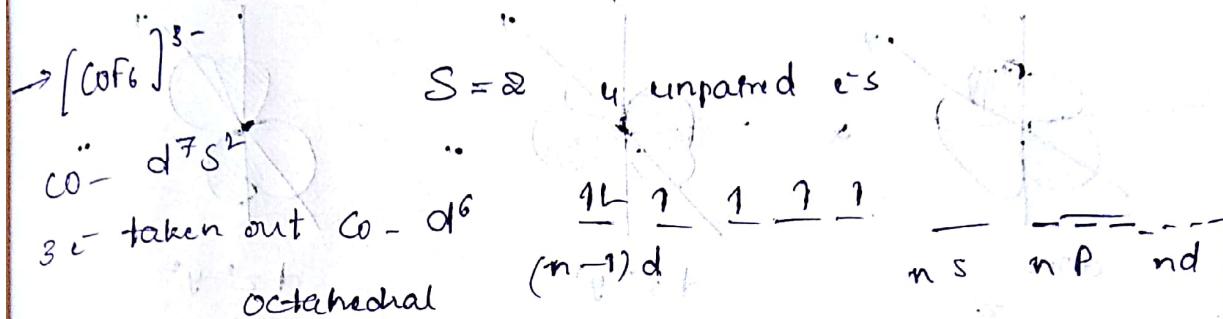


$$C_1^2 + C_2^2 = 1 \quad (\text{normalised wave function})$$

$$C_1 C_3 + C_2 C_4 = 0 \quad (\text{orthonormal wave function})$$



- sp - linear
- sp^2 - trigonal planar
- sp^3 - tetrahedral
- dsp^2 - square planar
- sp^3d - trigonal bipyramidal
- sp^3d^2/d^2sp^3 - octahedral



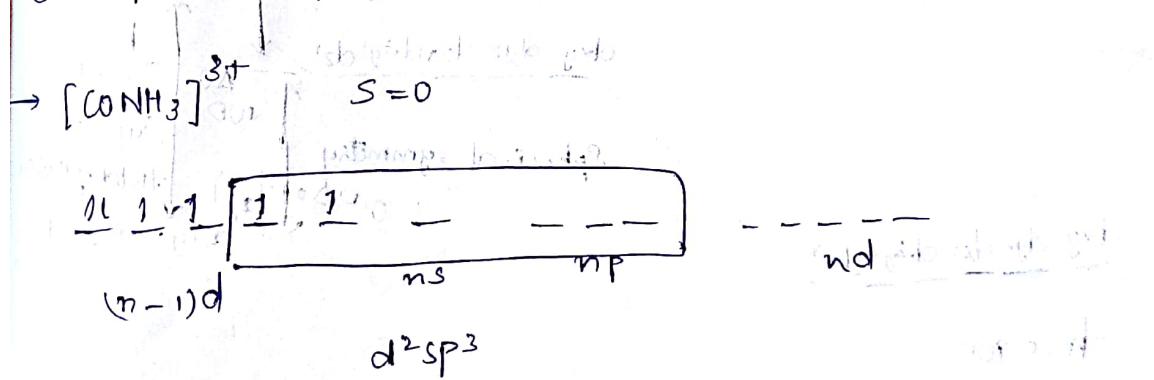
Outer sphere complex - d orbital from 'nd' 'sp³d²'

Inner sphere complex - d orbital from '(n-1)d' 'd²sp³'

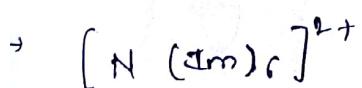


6 F⁻ gives $\approx 1^-$ each

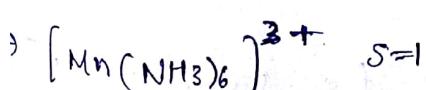
Outer sphere complex - more reactive



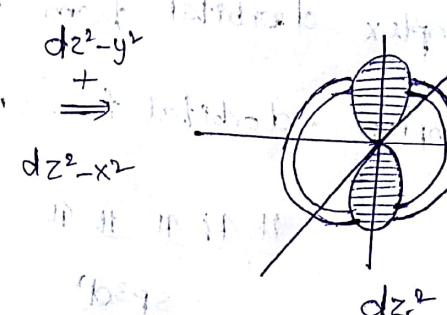
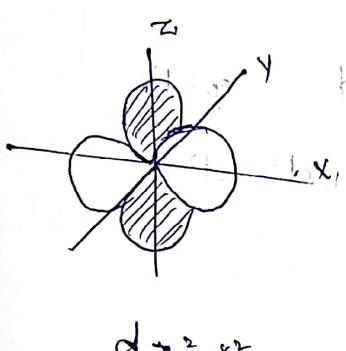
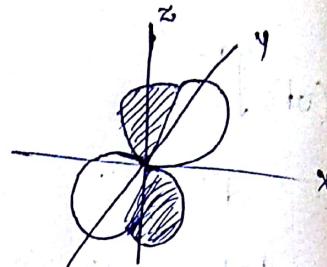
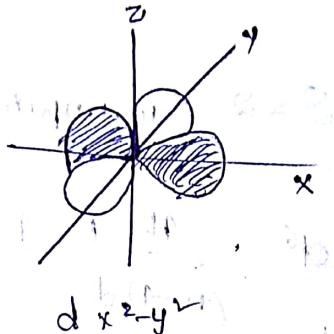
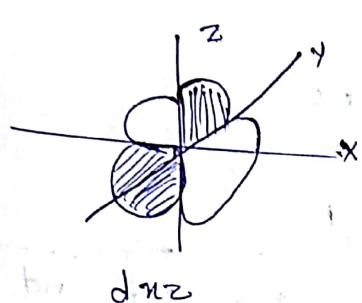
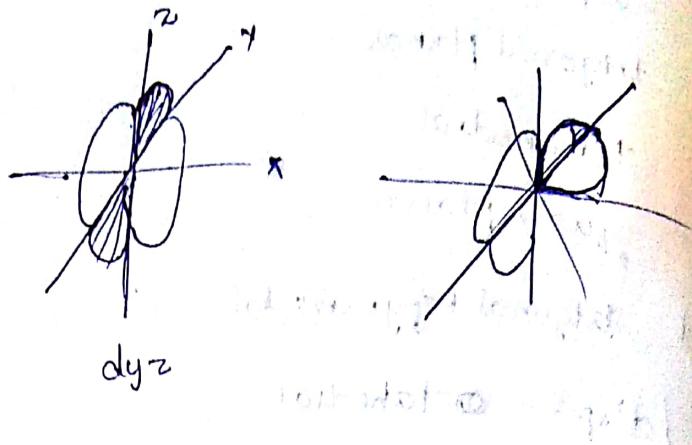
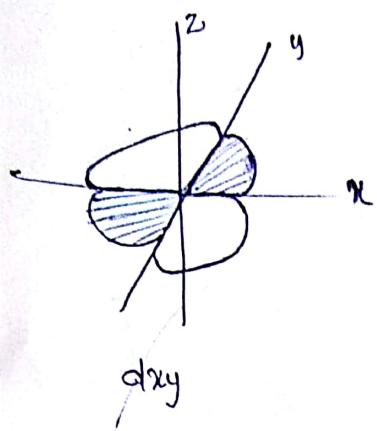
Im - Imidazole neutral ligand.



sp³d²



S=1



→ Octahedral geometry: $t_{2g}^3 e_g^2$

9 - general (even)

$d_{xy} \quad d_{yz} \quad d_{zx}$
 $d_{x^2-y^2} \quad d_{z^2}$

free ion

Δ_0 → O represent octahedral

Crystal field

energy (CFSE)

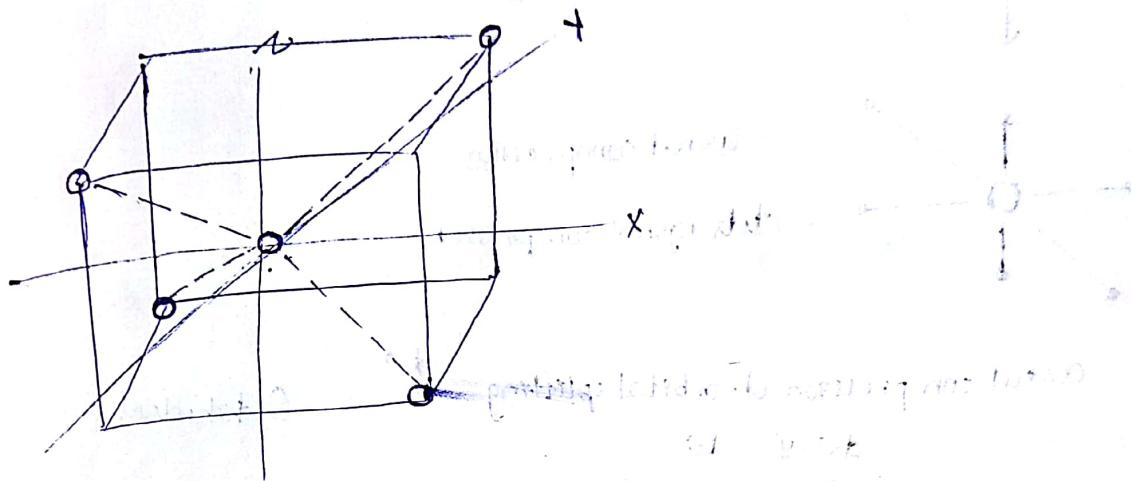
$$CFSE = \text{no. of } e^- \text{ in } t_{2g} \times 0.4\Delta_0 - \text{no. of } e^- \text{ in } e_g \times 0.6\Delta_0$$

Pairing energy

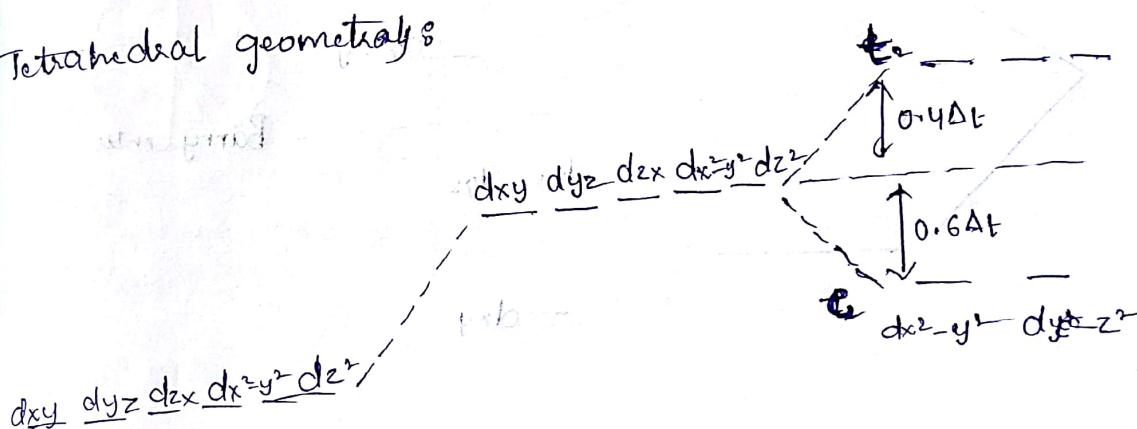
When $\Delta_o \gg \text{pairing energy}$ - low spin complex is favourable
 $\Delta_o \ll \text{pairing energy}$ - high spin complex is favourable

$\frac{1}{2} \quad \frac{1}{2}$	$\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2}$
Low spin	High spin

$\Delta_o \gg \text{P.E}$



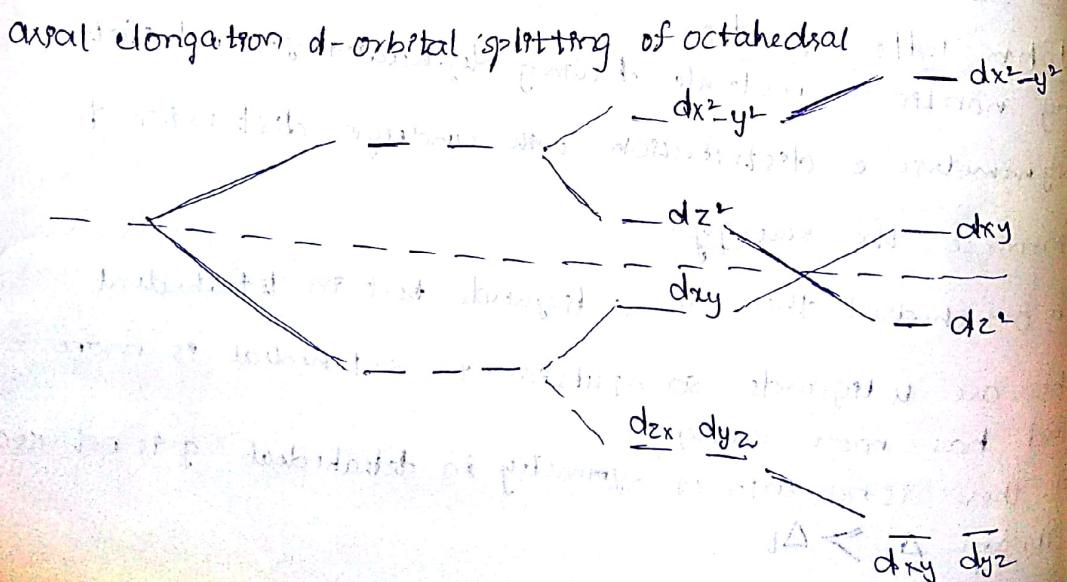
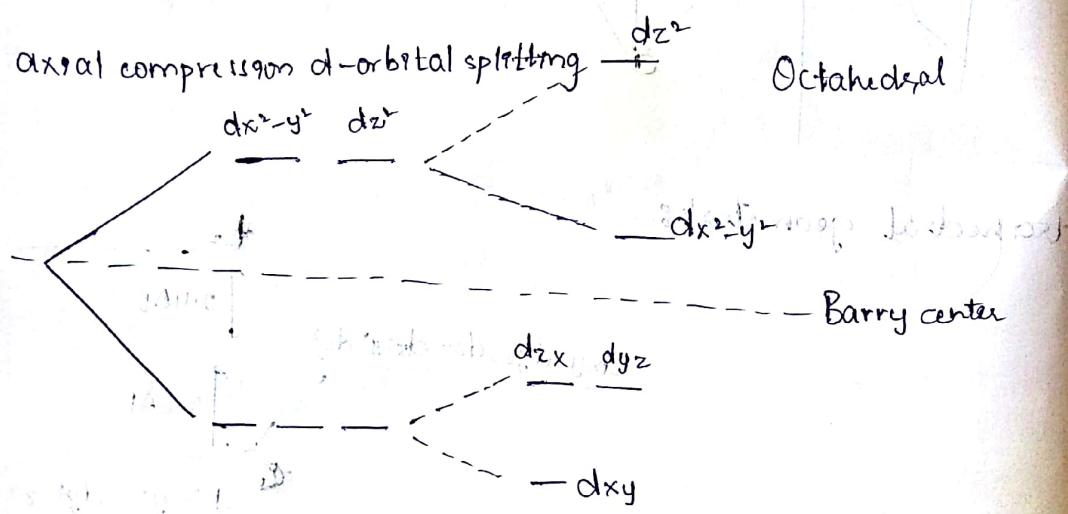
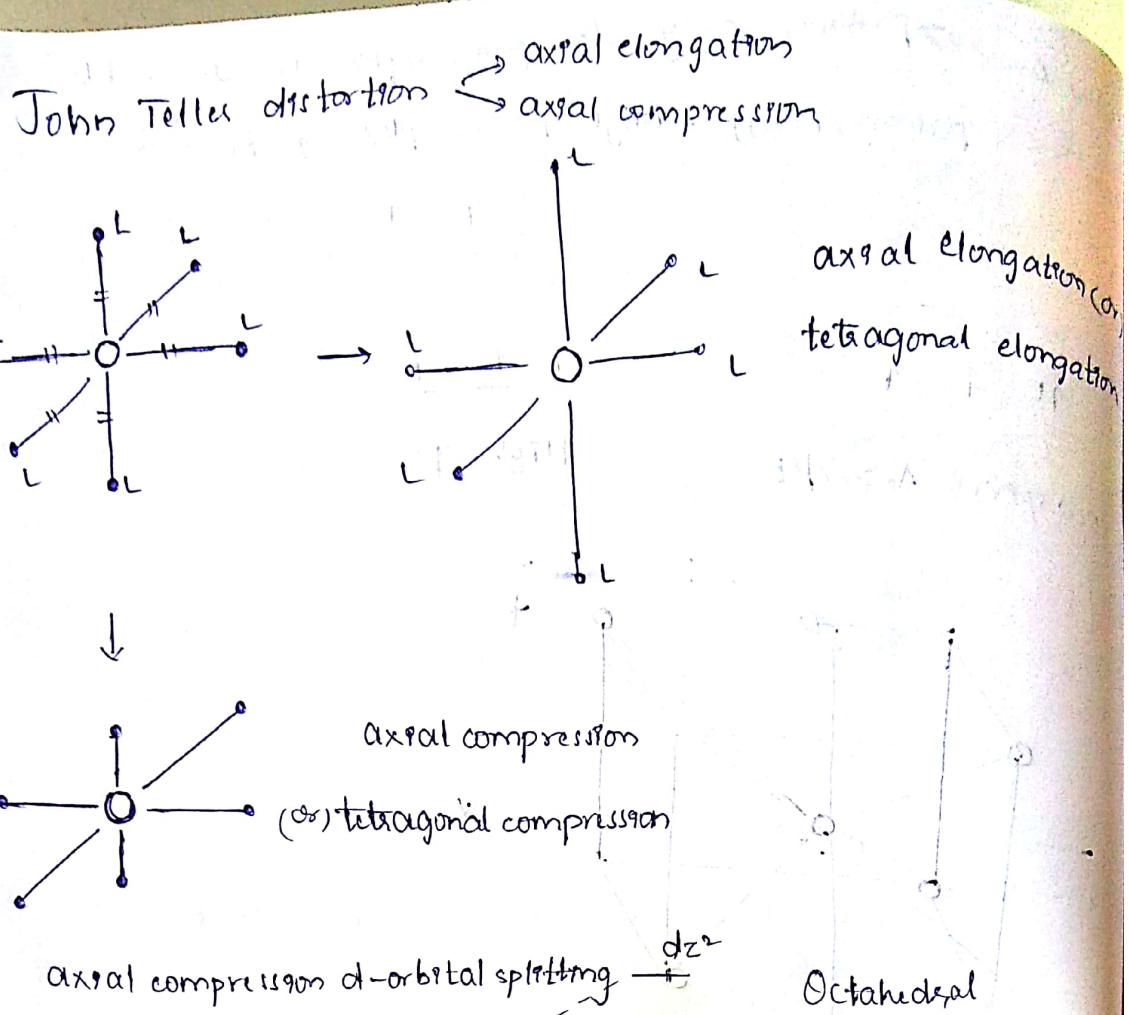
Tetrahedral geometry:



Johnson-Teller effect: Any non-linear molecule having degenerated ground state will undergo distortion to minimise the energy.

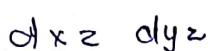
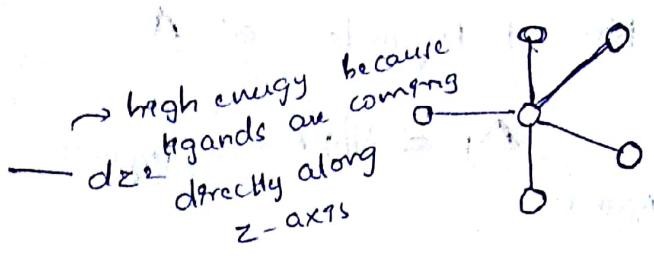
- In octahedral there are 6 ligands but in tetrahedral there are 4 ligands so repulsion in octahedral is more and has more energy.
- As there is no centre of symmetry in tetrahedral g is not used. Always $\Delta_o > \Delta_t$

$$\Delta_t = \frac{4}{9} \Delta_o$$

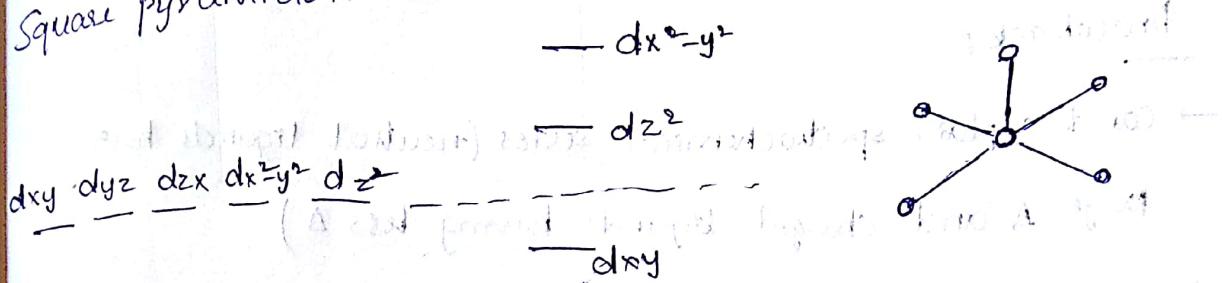


Square planar

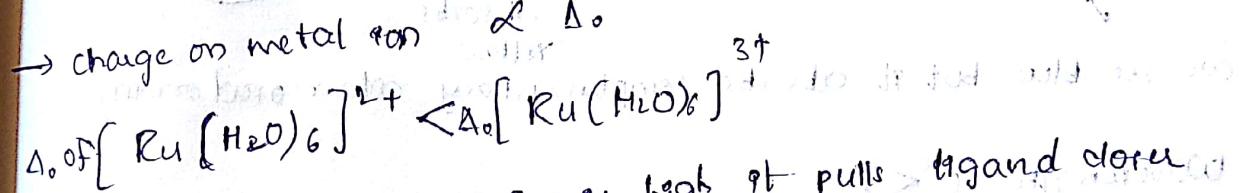
Trigonal bipyramidal :-



Square pyramidal :-

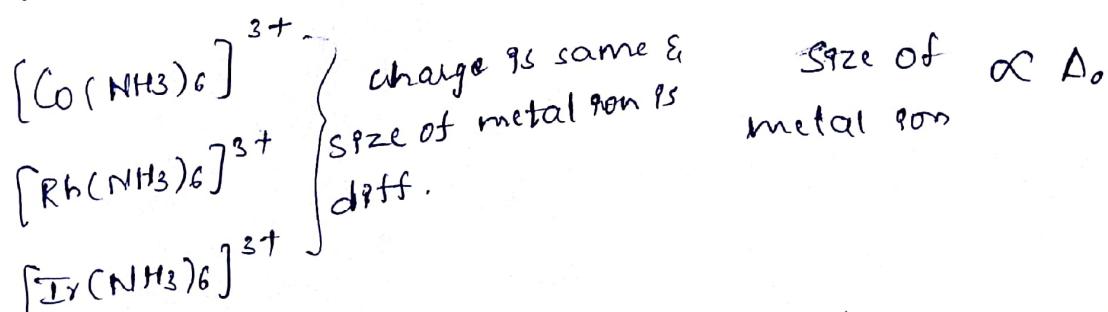


Factors affecting crystal field splitting Δ_o



When charge on metal ion is high it pulls ligand closer and repulsion is more.

→ Nature of metal ion

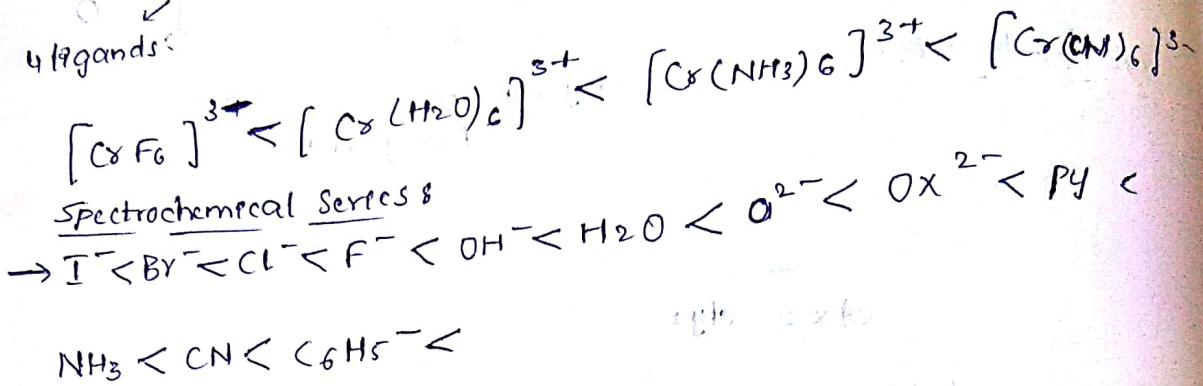


When size of metal ion increases the ligands are close to the metal ion & repulsion is more.

\rightarrow No. of ligands $\propto \Delta$

$\Delta_t = 4/9 \Delta_0 \rightarrow 6$ ligands

4 ligands: $\Delta_t < \Delta_0$

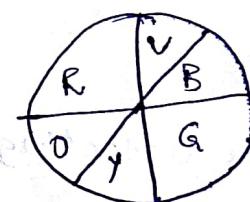
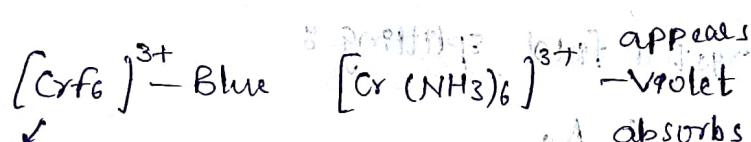


Drawback:

\rightarrow Can't explain spectrochemical series (neutral ligands having large Δ and charged ligands having less Δ)

Application 8

\rightarrow We can find colour of complexes



We see blue but it absorbs complementary colour red or orange

wavelength $\lambda_{\text{abs}} < \lambda_{\text{em}}$

A to be seen

Colour of ligands

and their position

in the series

and its effect on

the colour of complex

and its effect on

the colour of complex

and its effect on

the colour of complex

and its effect on

the colour of complex