

# Water

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\* Types of water

- (i) Soft water (ii) Hard water

\* What is Soft water?

Ans  $\Rightarrow$  Water that easily produce lather with soap is called soft water

Ex  $\Rightarrow$  rain water, river water

\* What is Hard water?

Ans  $\Rightarrow$  Water that not easily produce lather with soap is called Hard water

Ex  $\Rightarrow$  Sea water

\* What is the difference between Soft and Hard water

Ans  $\Rightarrow$ 

Soft water	Hard water
water that easily produce lather with soap is called soft water	water that not easily produce lather with soap is called hard water

(i) water that easily produce lather with soap is called soft water

water that not easily produce lather with soap is called hard water

(ii) Soft water does not have dissolved salts of Ca, Mg

Hard water has dissolved salts of Ca and Mg

(iii) It consumes less soap for washing and bathing

It consumes lot of soap for washing and bathing

\* What is hardness of water? Why it is due to?

Ans  $\Rightarrow$  Hardness of water is the character of water which prevents the lathering of Soap is called hardness of water, hardness of water due to presence of Ca, Mg and any heavy metals.

\* What is the cause of hardness of water?

Ans  $\Rightarrow$  Hardness of water due to presence of many salts of Ca and Mg and other Heavy metals in water

Ex  $\Rightarrow$  bicarbonate, chloride, sulphate salts of Ca, Mg and Fe.

1.2 \* Types of hardness of water

i) Temporary hardness or carbonate hardness

ii) Permanent hardness or non carbonate hardness

1.2 # What is Temporary hardness?

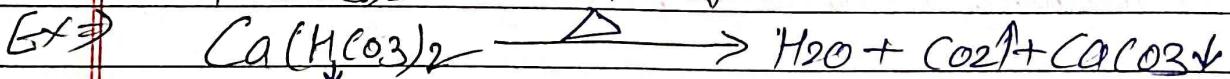
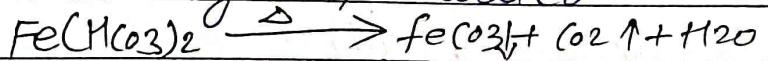
Ans  $\Rightarrow$  Temporary hardness of water due to presence of bicarbonate salts of Ca, Mg, Fe is called temporary hardness. Ex =  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$

1.2 # What is permanent hardness?

Ans  $\Rightarrow$  Permanent hardness of water due to presence of chloride and sulphate salts of Ca, Mg, Fe is called permanent hardness. Ex =  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{MgCl}_2$

\* Removal of temporary hardness?

Ans  $\Rightarrow$  Temporary hardness of water can be removed by boiling of water.



1.3 \* Why temporary hardness of water is removed by heating?

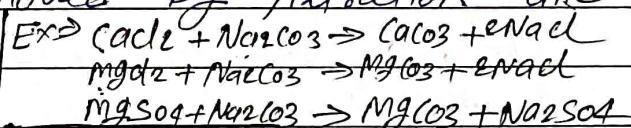
because calcium and magnesium bicarbonate are soluble in water and when we heat this water than Ca and Mg bicarbonate both decompose and convert into  $\text{CaCO}_3$  and magnesium hydroxide and we know that  $\text{CaCO}_3$  is insoluble in water then we filter it and we get soft water.

1.1 \* Total Hardness of water = total hardness of water is the combination of temporary and permanent hardness of water is called total hardness of water.

Washing soda process

1.4 \* How is permanent hardness removed?

2.0 Any  $\Rightarrow$  Permanent hardness is removed by adding Sodium Carbonate ( $\text{Na}_2\text{CO}_3$ ) which reacts with chloride and sulphate of Ca and Mg and produce insoluble carbonate and this insoluble carbonate can be removed by filtration and water becomes soft.



1.5 \* What is unit of hardness?  $\text{CaCO}_3 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$   
 Any  $\Rightarrow$  (ppm)  $\rightarrow$  Part per million in this process  $\text{Ca}^+$ ,  $\text{Mg}^{2+}$   
 (mg/L)  $\rightarrow$  milligram per million ions are removed and water become soft  
 (°fr)  $\rightarrow$  degree french  
 (°d)  $\rightarrow$  Degree clark

1.6 \* What is EDTA?

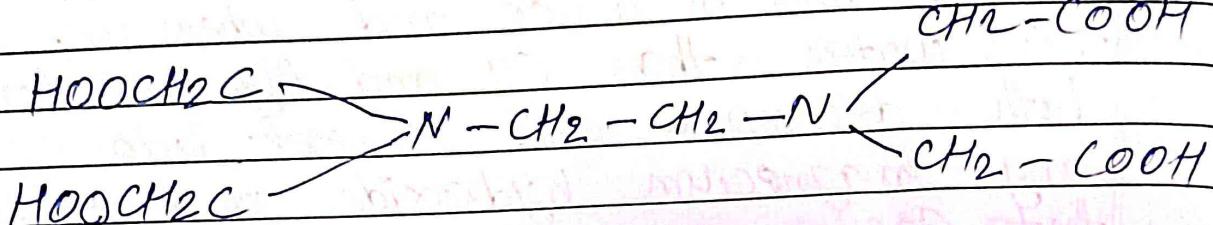
Any  $\Rightarrow$  Ethylene diamine tetraacetic acid  
 formula of EDTA:  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$

Note: Ppm and (mg/L) are generally used to measure the hardness of water.

1.6 \*

What is the structure of EDTA?

Ans →



\* Methods for Removal of hardness of water

Permanent Hardness

Washing soda process

Total hardness of water

Lime-Soda process

Permutite process / Zeolite process

Calgon process

Ion-Exchange process

# Softening of water

\* Zeolite process or Permutite process.

→ It is the best and widely used method to remove hardness of water. In this method zeolite is used.

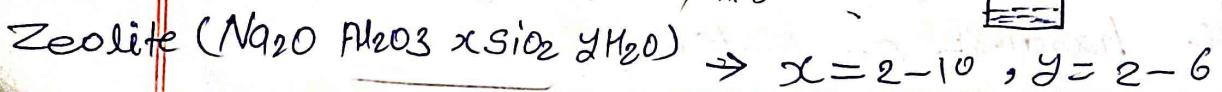
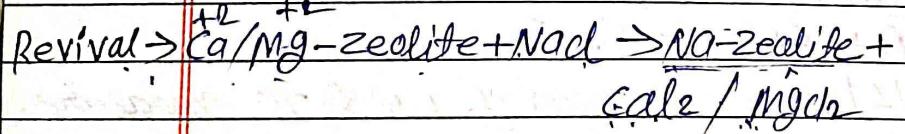
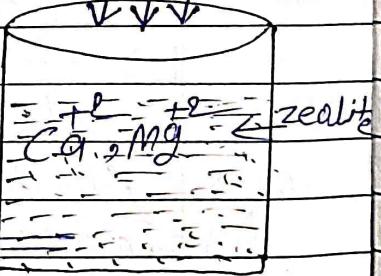
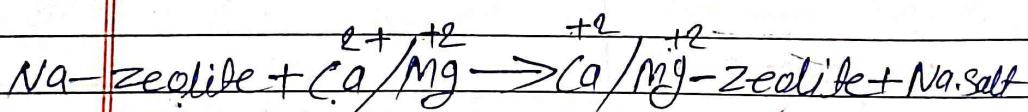
→ It is inorganic in nature & it is capable of exchanging its cations with water.

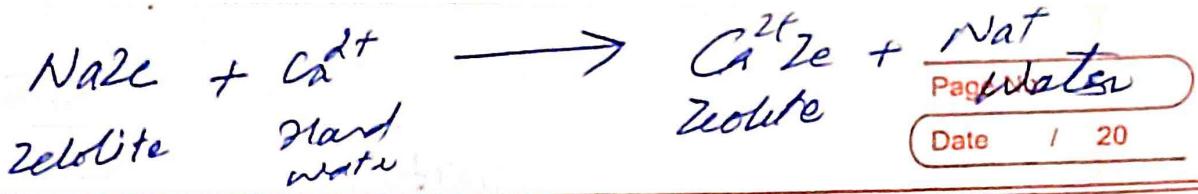
→ Zeolite : Zeolite is naturally mineral

Zeolite like sand

Hard water

Zeolite ( $\text{Na}_2\text{O Al}_2\text{O}_3 4\text{SiO}_2 2\text{H}_2\text{O}$ )  
(Sodium alumino silicate)



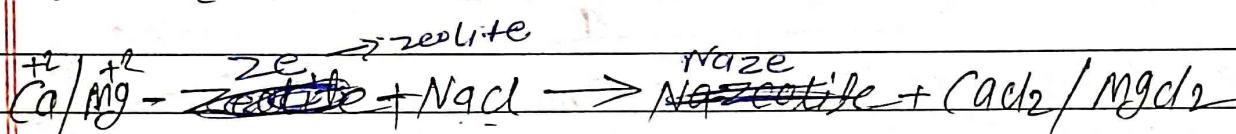


JMP

Zeolite process  $\rightarrow$  In this process we take a pot first and we take zeolite in this pot and when we passing hard water or total hardness of water than zeolite caught the  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions and zeolite release  $\text{Na}^+$  then we get soft water.

Regeneration:

Revival: Due to continuous running of zeolite process there is lack of  $\text{Na}^+$  in zeolite. So that we add  $\text{NaCl}$  in zeolite then again  $\text{Na}^+$  revival in zeolite.

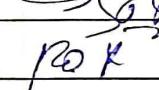
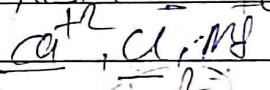


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Ion Exchange process:

i) Cation Exch Resin

ii) Anion Exch Resin



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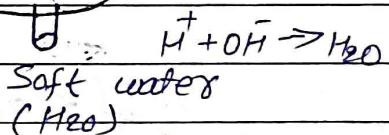
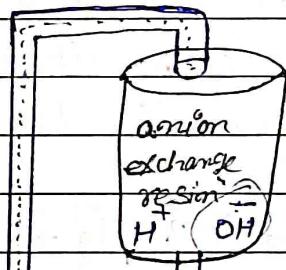
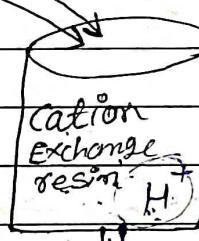
Cation exchange resin

$\rightarrow$  such resin have  $\text{H}^+$   
 $\text{--SO}_3\text{H}_2$ ,  $\text{--COOH}$

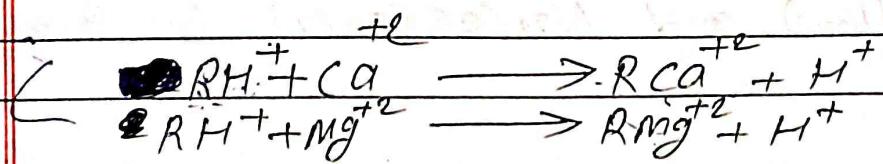
Anion exchange resin

such resin have  $\text{OH}^-$   
 $\text{--NH}_2$ ,  $\text{--NHCH}_3$ ,  $\text{--OH}$ ,  $\text{--N(CH}_3)_2$   
 $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$

Hard water



process: In this process we take two pot and first we take one pot and we take cation exchange resin in the first pot and when we hard water is passed through cation exchange resin which replace  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  with  $\text{H}^+$  from hard water and produce  $\text{H}^+$  ion.

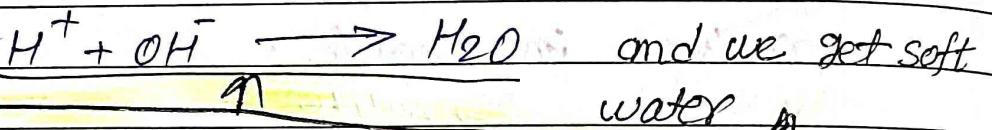


water

After this process, water is passed through second pot in this pot we take anion exchange resin which replace anions from water and produce  $\text{OH}^-$  ion



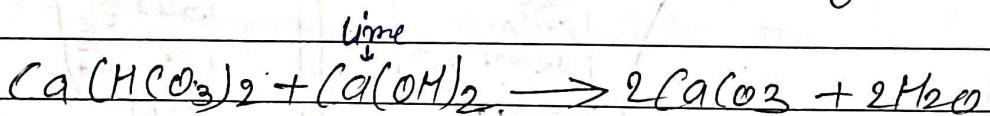
after this  $\text{H}^+$  ion and  $\text{OH}^-$  ion combined into water



\* Note: lime ( $\text{Ca(OH)}_2$ ), calcium hydroxide

~~Lime soda process:~~

\* Clark's process: Temporary hardness of water is reacted with calculated amount of lime ( $\text{Ca(OH)}_2$ ) then  $\text{Ca(HCO}_3)_2$  and  $\text{Mg(HCO}_3)_2$  is converted in to  $\text{CaCO}_3$  and  $\text{Mg(OH)}_2$



\* Lime Soda process: Lime soda process is the combination of boiling and Clark's process through this process temporary hardness and permanent hardness can be removed. In this process we add calculated amount of ( $\text{Ca(OH)}_2$  → lime) and  $\text{Na}_2\text{CO}_3$  (soda) in hard water.

\* Regeneration of cation exchange resin :-

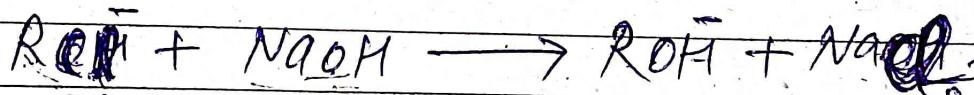
by adding (dilute) HCl to cation ex. region

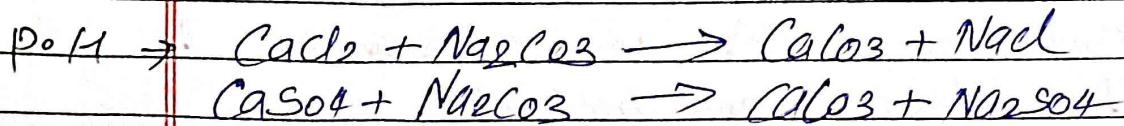
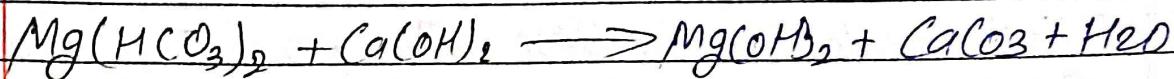
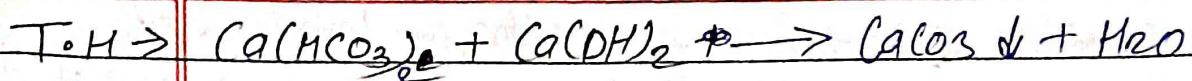


→ Re-generated cation ex. region

\* Regeneration of anion ex. - Resin :-

by adding (dilute) NaOH to anion ex. region





### \* Drinking water :

- ① Screening / screening  $\doteq$  impurity suspended and Removing large size of particles
- ② (i) Sedimentation  $\doteq$  in this process we take a tank which is 5m deep and we add water in this tank for 2-6 hours then suspended particles settle down, that called sedimentation on the surface of the tank
- (ii) Coagulation  $\doteq$  Coagulants are chemicals which are added to water before sedimentation, coagulants react with bicarbonates of water and produce  
 $\text{Al}^{+3}, \text{Fe}^{+3} \rightarrow \text{Al}_2(\text{SO}_4)_3 + \text{Ca}(\text{HCO}_3)_2 \rightarrow 2\text{Al}(\text{OH})_3 + \text{CaSO}_4 + 6\text{CO}_2$   
 Coagulants  $\doteq$  (i) Alum  $\rightarrow \text{Al}_2(\text{SO}_4)_3 \rightarrow \text{Al}^{+3}$   
 (ii) ferric sulphate  $\rightarrow \text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O} \rightarrow \text{Fe}^{+3} + \text{SO}_4^{2-} + 7\text{H}_2\text{O}$   
 $\text{Fe}_2(\text{SO}_4)_3 + \text{Mg}(\text{HCO}_3)_2 \rightarrow \text{Fe}(\text{OH})_3 + \text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{Fe}(\text{OH})_3$
- ③ Filtration  $\doteq$  When sedimented water is passed through sand and then colloidal particles, micro-organisms are removed is called filtration.



(4) ~~Chlorination of bacteria~~  $\rightarrow$  Nitrogen bacteria  $\rightarrow$   $NH_3$   
 $\rightarrow$  Sulphur bacteria  $\rightarrow$   $H_2S$

(4) Disinfection of water  $\therefore$  The process of killing these bacteria is called disinfection.

i) By boiling water  $\therefore$  for 10 - 15 minutes. This kills all the disease and bacteria.

ii) By adding bleaching powder  $\therefore$  ( $CaOCl_2$ ) 1 kg of  $CaOCl_2$  bleaching powder / 1000 kiloliter of water is added and water is allowed to stand for several hours. During which  $CaOCl_2$  release  $Cl_2$ .



$\hookrightarrow$  Hypochlorous acid  $\rightarrow$  kills the microbes

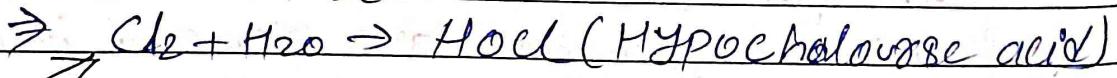
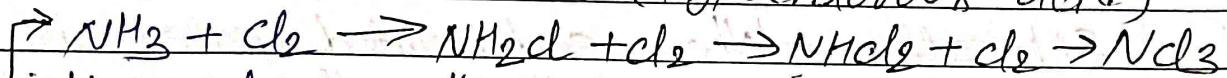
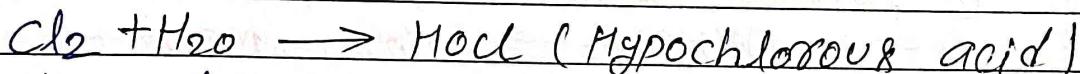
$\therefore$  disinfection  
and bacteria

$ClNH_2$  - Monochloramine

$Cl_2NH$  - dichloramine

$Cl_3N$  - Trichloramine

(\*) Chlorination  $\therefore$  Chlorination is the process of adding chlorine. This method is used to kill bacteria, viruses and microbes in water.



Break  
point  
chlorination

## \* Break point chlorination :-

Ans In this process chlorine is added to water until  $\text{NH}_3$  is converted to  $\text{NH}_4^+$  and  $\text{H}_2\text{S}$  to  $\text{HCl}$ , a process called break point chlorination.

Ques A point of time when  $\text{NH}_3$  is completely converted into  $\text{NH}_4^+$  and  $\text{H}_2\text{S}$  is completely converted into  $\text{HCl}$  is called break point chlorination.

$$\begin{aligned}\text{NH}_3 + \text{Cl}_2 &\rightarrow \text{NH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{NH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{NH}_4^+ \\ \text{H}_2\text{S} + \text{Cl}_2 &\rightarrow \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}_2 \rightarrow \text{HCl}\end{aligned}$$

## \* Disadvantages of Hard water in industries

- Scale and sludge formation
- Caustic Embrittlement
- Boiler corrosion
- Priming and foaming.

## \* Scale and sludge formation:-

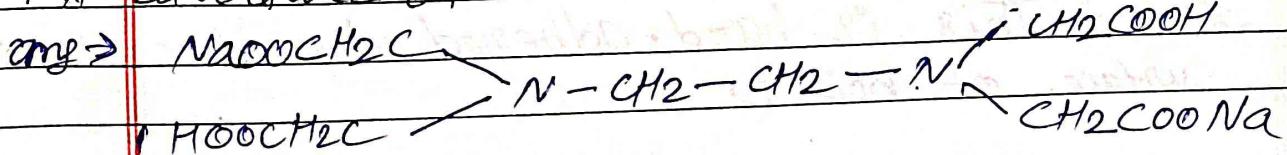
### \* What is scale?

Ans If the precipitated matter forms a hard coating on the inner walls of the boiler, it is called Scale.

### \* What is sludge?

Ans If the precipitation takes place in the form of loose and slimy precipitate, it is called sludge.

### Ques Structure of Di Sodium salt of EDTA.



## \* Scale and Sludge formation in Boilers

⇒ Boilers are used for the production of steam. When the hard water is directly fed into boiler ~~water~~, it leads to formation of scales and sludge.

In the boilers, water evaporates continuously and concentration of salts dissolved in water increases. It reaches a saturation point, forming precipitates on the inner walls of the boiler.

Sludge ⇒ If the precipitates are in the loose and slimy form, is called sludge,

Scale ⇒ If the precipitates are in the hard and adhering coat form, is called scale.

\* Removal of sludge : Sludge can be removed from the boiler by using 'wire brush'.

\* Disadvantages of sludge :

- i) It is a poor conductor of heat and hence lot of time and fuel is needed.
- ii) It disturbs the functioning of the boiler.

\* Prevention of sludge formation :-

- i) By using soft water.
- ii) By using blow down pipe operation.

\* Scale : This is hard, adhered deposit on inner surface of boiler.

\* formation of scale :

- i) Decomposition of  $\text{Ca}(\text{HCO}_3)_2$  present in water  
 $\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 + \text{CO}_2 \uparrow + \text{H}_2\text{O}$

ii)

Deposition of calcium sulphate ( $\text{CaSO}_4$ ) : This is soluble in water. As temperature increases, solubility of  $\text{CaSO}_4$  decreases in water. Hence  $\text{CaSO}_4$  gets ppt.

iii)

Hydrolysis of Magnesium salts :



iv)

presence of silica ( $\text{SiO}_2$ ) : Silica reacts with Ca and Mg present in hard water to form  $\text{Ca}(\text{SiO}_3)_2$  and  $\text{MgSiO}_4$ . These silicates stick to the inner wall of the boiler.

\* Disadvantage of scale formation :

- i) Fuel wastage : Scales are bad conductors of heat so that a lot of fuel and time is wasted to heat water.

ii)

Lowering of Boiler Safety

iii)

Decreased efficiency

iv)

Danger of explosion

\* Removal of scale :

i)

using wire brush

ii)

chemicals

iii)

Blow down operation

## \* Prevention of scale formation :

(i) External treatment : By using soft water in the boiler, scale formation can be removed.

## (ii) Internal treatment / Conditioning / sequestration :

In this method, a ion is prohibited to show its original character by adding appropriate reagent, which :

- (a) May convert scale to sludge which can be blown out.
- (b) May convert the scale to salt which are soluble in water.

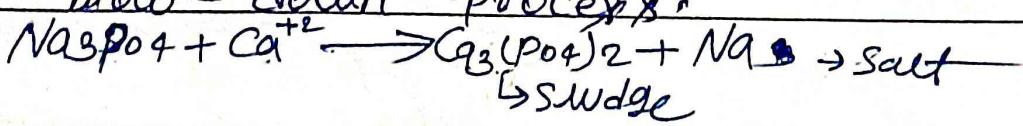
These salts remain in water and cause no harm.

## \* Sequestration or Conditioning

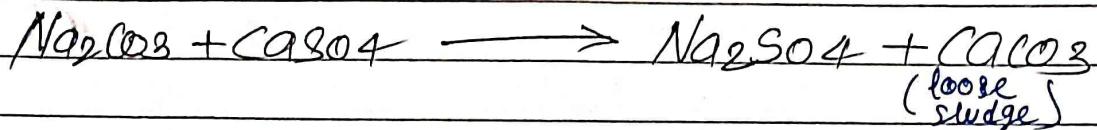
(a) Colloidal Conditioning : In this process we add some organic substances like agar - agar in water this organic substance creat a coating over scale forming and this is converted in to non-sticky and convert into sludge is call colloidal condition which can be removed by blow down process.

In this process ~~we~~

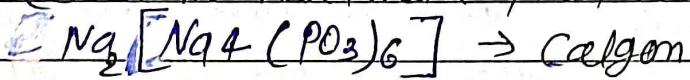
(b) Phosphate conditioning : In high pressure ~~tanks~~ we add sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) to hard water then sodium phosphate react with  $\text{Ca}$  and  $\text{Mg}$  salts and produce calcium phosphate and salts and Calcium phosphate is sludge which can be removed by blow - down process.



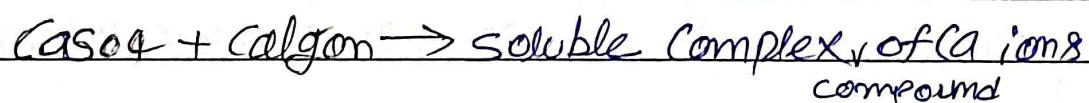
(C) Carbonate Conditioning : In this process we add  $\text{Na}_2\text{CO}_3$  sodium carbonate to hard water then  $\text{Na}_2\text{CO}_3$  reacts with  $\text{CaSO}_4$  and converts into Calcium carbonate and this  $\text{CaCO}_3$  is loose sludge which can be removed by blow down operation.



(4) Calgon Conditioning : Calgon is the commercial name of - (sodium hexameta phosphate)

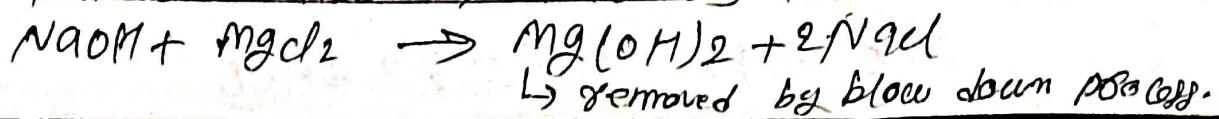
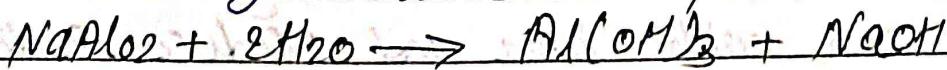


In this process we add calgon to hard water, calgon prevent the scale and sludge formation, calgon convert scale forming into highly soluble complex which are not produce easily.



(5) Treatment with sodium aluminate : In this process we add sodium aluminate ( $\text{NaAlO}_2$ ) to hard water then Sodium aluminate react with hard water and Sodium aluminate convert into Aluminium hydroxide and Sodium hydroxide ( $\text{Al(OH)}_3$ ) ( $\text{NaOH}$ )

and again  $\text{NaOH}$  react with Mgcl<sub>2</sub> and magnesium salt and convert into magnesium hydroxide ( $\text{Mg(OH)}_2$ ) and Nacl and  $\text{Mg(OH)}_2$  are removed by blow down operation.



⑥ Electrical conditioning : In this process we passed electric charge through water, which prevent scale formation.

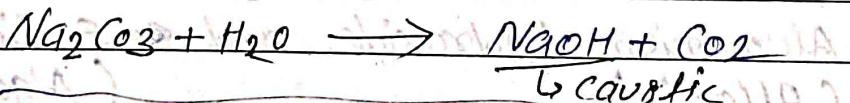
⑦ Radioactive conditioning : In this process we add the tablets of radioactive salts in hard water and these tablets emit radiation of energy and prevent scale formation.

\* Caustic Embrittlement :  $\text{Caustic} \rightarrow \text{NaOH}$

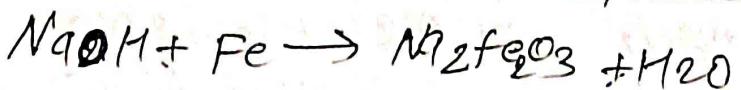
brittle  $\rightarrow$  जानें, यह क्या है तो यह एक रसायनिक प्रक्रिया है।

\* Caustic Embrittlement : Caustic Embrittlement is a type of boiler corrosion, in this process Caustic embrittlement is a process in which boiler material becomes brittle due to presence of caustic like  $\text{NaOH}$ ,  $\text{KOH}$ , etc.

When we were doing softening of water then for softening of water we add  $\text{Na}_2\text{CO}_3$  in hard water than some  $\text{Na}_2\text{CO}_3$  is present in water so that  $\text{Na}_2\text{CO}_3$  react with water



$\text{NaOH}$  in water makes alkline or caustic and as we know water evaporates continuously so that concentration of ~~water~~  $\text{NaOH}$  increases hence  $\text{NaOH}$  moves to the crack body of boiler and  $\text{NaOH}$  react with iron and produce sodium ferrate



and due to non availability of  $O_2$  in the crack Iron behaves as anode and Boiler behave as Cathode. Therefore iron gets corroded.

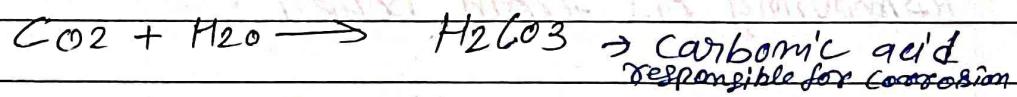
\* prevention of Caustic Embrittlement :-

- (i) By using sodium phosphate in place of  $Na_2CO_3$
  - (ii) By adding tannin  $^{O_2}$  lignin.
  - (iii) By adding sodium sulphate ( $Na_2SO_4$ )
  - (iv) By not using sodium carbonate  $Na_2CO_3$ .
- \* Boiler corrosion :- water has dissolved oxygen which attack the boiler body.

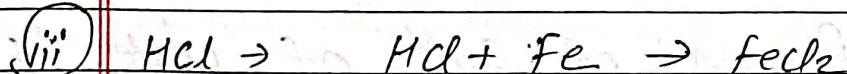


\* Removal of  $O_2$  :- By adding sodium sulphite ( $Na_2SO_3$ )

(ii)  $CO_2$  :- Dissolved  $CO_2$  in water reacts with water and produce carbonic acid which attack the boiler.



\* Removal of  $CO_2$  :- By adding ammonia because ammonia ~~absorbs~~ absorbs  $CO_2$ .



$HCl$  reacts with the boiler body and produce a chain reaction

## \* Priming and foaming

in the boiler continuously

\* priming : formation of wet steam is called priming.

\* Cause : i) presence of dissolved solids.

ii) High steam velocity.

iii) sudden boiling.

iv) sudden increase in steam production.

v) salts of water

\* Foaming : formation of bubbles in the boiler continuously is called foaming.

\* Cause : If oil is present, it decrease surface tension of water.

\* disadvantage of foaming : we can't find bubble of air in water in foaming; it is disadvantage due to foaming decrease the efficiency of the engine.

\* Prevention of foaming : using antifoaming agent Ex  $\rightarrow$  castor oil.

(ii) Removing oil from boiler.

\* disadvantage of priming : priming effect turbine blades and bursting.

\* Desalination : Removal of salts of water is called desalination.

\* Why Soaps are not effective in hardwater

ans  $\Rightarrow$  Soaps are not effective in hardwater because soap is salts of sodium or potassium of higher fatty acids so that when these salts of soap react with salts of Ca and Mg and forms scum or precipitate so that soaps are not effective in hardwater.

\* What is disinfection of water?

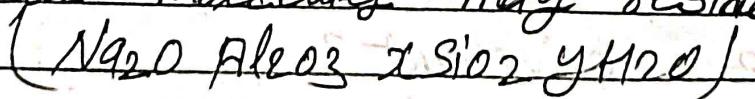
ans  $\Rightarrow$  Removing of disease producing bacteria this process called disinfection of water.

\* What are the main disinfectants used for purification of water?

ans  $\Rightarrow$  chlorine and chloramine are the main disinfectants used for purification of water.

\* What is Zeolite?

ans  $\Rightarrow$  Zeolite is crystalline solid structure made of silicon, aluminium and oxygen that form a structure with cavities and channel inside where cations, small molecules may reside.



\* Disadvantage and advantage of zeolite or merit or demerit of zeolite.

## advantage / merit

- i) it remove about 10 ppm of hardness.
- ii) it take less time for softening.
- iii) less skill require in this process

## disadvantage / demerit

- i) it leaves acidic ions ( $\text{HCO}_3^-$ )
- ii) Treated water has more  $\text{Na}^+$  ions.

\* what is ion-exchange resin? or process?

$\Rightarrow$  Ion exchange resin is insoluble organic polymers with micropores. The functional groups attached to the ion exchange resin which are responsible for ion exchange resin, or process.

\* Calgon conditioning is better than phosphate Conditioning how?

$\Rightarrow$  Calgon Conditioning is better than phosphate Conditioning because it forms soluble complex compound and not form scales. There itself phosphate conditioning forms sludge so that Calgon Conditioning is better than phosphate Conditioning.

\* Why hardness of water is expressed in terms of  $\text{CaCO}_3$  equivalent?

$\Rightarrow$  Hardness of water is expressed in terms of  $\text{CaCO}_3$  equivalent because

i)  $\text{CaCO}_3$  having molecular weight (100)

ii)  $\text{CaCO}_3$  is the most insoluble in water.

\* Calculate the hardness of a sample of water which contains 0.012 gрамм/L of  $MgSO_4$

⇒

$$\text{Hardness of water} = \frac{n \times 100}{\text{M. of salt}}$$

$MgSO_4$  Molecular weight  
 $CaCO_3$  weight

$$MgSO_4 \text{ present per liter in water} = 0.012$$

$$n = 0.012$$

$$\text{Molecular weight of } MgSO_4 = 24 + 32 + 64 \\ = 120 \text{ gram}$$

$$\text{So the hardness of water} = \frac{0.012 \times 100}{120}$$

$$= \frac{12 \times 10}{12 \times 10^3} = 0.01 \text{ g/L}$$

$$= 0.01 \times 10^3$$

$$\text{hardness of water} = 10 \text{ ppm}$$

\* A water sample has 19 mg/L of  $MgCl_2$  of water. Calculate the hardness of water in  $CaCO_3$  equivalent.

$$\Rightarrow MgCl_2 \text{ present in water per liter} = 19 \text{ mg/L}$$

$$\text{M. weight of } MgCl_2 = 24 + 35.5 \times 2 \\ = 95$$

∴

$$\text{hardness of water} = \frac{n \times 50}{\text{M. of salt}}$$

in terms of  
 $CaCO_3$  equivalent

$$= \frac{19 \times 50}{95} = \frac{19 \times 10^3}{95 \times 5} = 10 \times 10^3 \\ = 10000 \text{ mg/L (ppm)}$$

$$= 10000 \text{ ppm}$$

\* Calculate the hardness of water, one litre of which contain 0.001 mole of  $MgSO_4$

$\Rightarrow$  we that 1 mole  $MgSO_4$  = 120 gms  
 $\therefore$  then 0.001 mole of  $MgSO_4$  =  $120 \times 0.001$   
 $= 0.12$  gms  
 Mo of  $MgSO_4$  = 120

$\therefore$  hardness of water =  $\frac{0.12 \times 100}{120}$

$= 0.12$   
 $\Rightarrow 0.12 \times 10^3 = 120$  (mg/l) ppm

\* if 20 ml of a water sample consumes 5 ml of  $N/50$  HCl solution using only Methyl orange as indicator. what type of the alkalinity is this?

$\Rightarrow$  water Sample = 20 ml  
 HCl Solution = 5 ml  
 $N/50$

$$N_1 \times V_1 = N_2 \times V_2$$

$$N_1 \times 20 = \frac{1}{5} \times 5$$

$$N_1 = \frac{1}{5000} \quad N_1 = \frac{5}{5000}$$

$$N_1 = \frac{5}{1000}$$

Normality of water in terms of alkalinity of water  
 Strength of water in terms of alkalinity of water

$$-\frac{5}{1000} \times 50 = \frac{1}{200} = 0.25 \text{ ppm}$$

$$0.25 \times 10^3 = 250 \text{ ppm}$$

\* 10 ml. of a water sample was titrated against N/100  $\text{AgNO}_3$  solution  
 1.5 ml of  $\text{AgNO}_3$  was used for end point. Calculate the amount of chlorine in water.

Ans :-

water Sample = 10 ml

$N/100 \rightarrow 1.5 \text{ ml } (\text{AgNO}_3)$

$$N_1 \times V_1 = N_2 \times V_2$$

$$N_1 \times 10 = \frac{1}{100} \times 1.5$$

$$N_1 = \frac{1.5}{1000} \quad N_1 = 0.0015$$

Normality of water in terms of chloride content = 0.0015

Strength of water in terms of chloride content

$\Rightarrow N_1 \times \text{eq wt of Cl}$

$$\Rightarrow 0.0015 \times 35.5 \text{ gm/l}$$

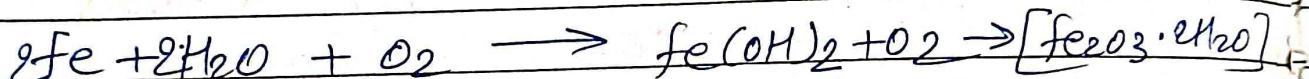
$$= 0.05325 \times 10^3$$

$$= 53.25 \text{ ppm}$$

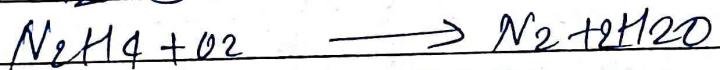
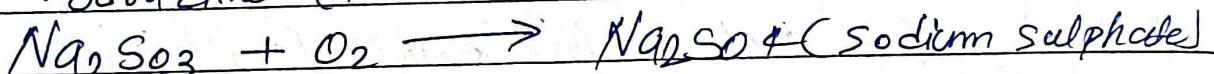
\* Boiler corrosion = Loss of boiler body material and it is useful property by chemical and electrochemical interaction with its environment is known as boiler corrosion.

### Boiler corrosion reasons

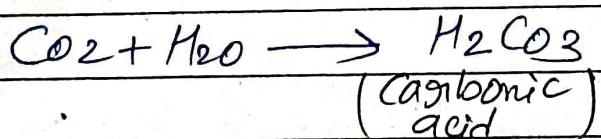
i) By dissolved  $O_2 \rightarrow$  Water has 8 ml/l dissolved oxygen which attack the boiler body.



Removal of  $O_2 \rightarrow$  by adding Sodium sulphite and hydrazine ( $N_2H_4$ )



ii) By dissolved  $CO_2 \rightarrow$  Dissolved  $CO_2$  in water reacts with water and produce carbonic acid which attack the boiler.



Removal of  $CO_2 \rightarrow$  by adding ammonium hydroxide



iii) By dissolved  $HCl \rightarrow HCl$  react with iron and produce ferrous chloride flocs

Removal of  $HCl \rightarrow$  By adding suitable alkali

## \* Advantages of Zeolite Process :-

- (i) Less time for softening.
- (ii) Less skill required for maintenance.

## \* Disadvantages

- (i) This method leaves acidic ion ( $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) cations in soft water.
- (ii) Soft water has more  $\text{Na}^+$  ions.

## \* Advantage of ion exchange process

- (i) This process kill both types of ions cation and anion.

- (ii) It produce very low hardness in water.

- or disadvantage  $\rightarrow$  (i) this equipment is costly.
- (ii) it take more time than ~~zeolite process~~.

## \* ion exchange process is better than zeolite process How?

any ion exchange process is better than zeolite process

- (i) because zeolite method replaces only  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions by  $\text{Na}^+$ , it does not replace anions or acidic ions. but ion exchange process removed not only cations impurity ( $\text{Ca}^{2+}, \text{Mg}^{2+}$ ) but also removes anions and acidic ions ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ).

- (ii) soft water produced by zeolite method has 10-15 ppm hardness which cannot be used in boiler.

but soft water produced by ion exchange process has as low as 2 ppm hardness in water which can be use in boiler so that ion exchange process is better than zeolite method.

\* Osmosis  $\hat{=}$  flow of solvent from high concentration to low concentration is called osmosis.

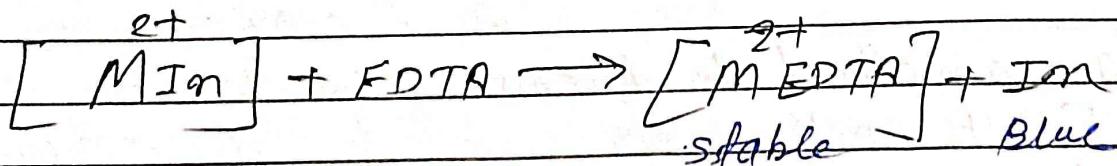
\* Reverse osmosis  $\hat{=}$  When two solutions of unequal concentration are separated from semipermeable membrane then flow of solvent from lower concentration to higher concentration is called reverse osmosis.

Q \* When indicator is added why wine red colour appreence.

$\Rightarrow$  When we added indicator in Buffer solution than wine red colour appreence because when we add indicator in buffer solution than indicator makes a coordinate complex compound with the presence salts of Ca and Mg so that wine red colour appreence.

3 \* When we add EDTA in water than why there is appreence of Blue colour.

$\Rightarrow$  When we add EDTA than Blue colour appreence because when we add EDTA than EDTA makes coordinate complex compound with salts of Ca and Mg and EDTA replace indicator so that Blue colour appreence.



gram

2.1 \* Normality  $\doteq$  Number of equivalents of solute which are present in per liter solution.

$$N = \frac{\text{no of gram equivalent}}{\text{volume of solution in (L)}}$$

2.2 \* Equivalent weight  $\doteq$  Number of molecular weight divide by n-factor  $\therefore$  called Equivalent weight.



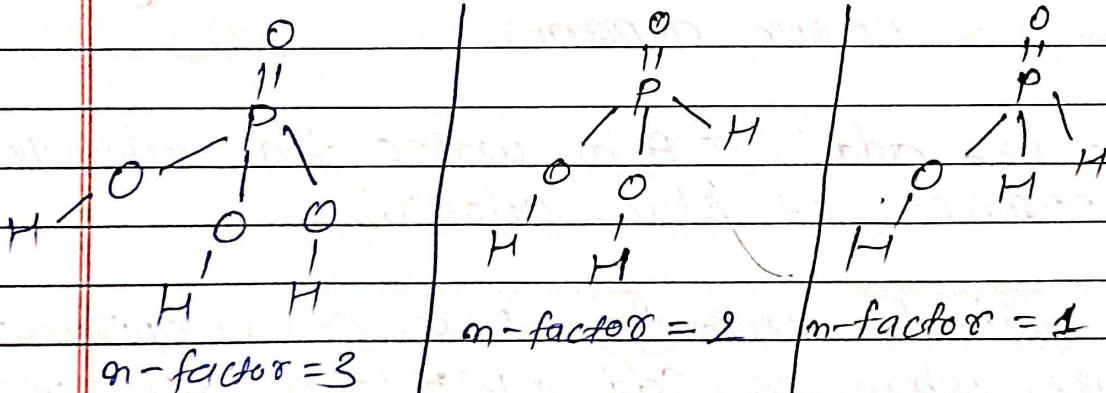
$$\text{Eqw} = \frac{M_o}{\text{n-factor}}$$

$$\text{Eqw} = \frac{106}{2}$$

$$\text{Eqw} = 53$$

2.4 \* n-factor  $\doteq$  Acid &  $\times$  = Basicity  
 Base  $\times$  = Acidity  
 Salt  $\times$  = Total +ve or -ve ions  
 acid and cation

Ex  $\Rightarrow$  i)  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{H}_2\text{PO}_4^-$



\* Ex  $\Rightarrow$  Base  $\rightarrow \text{Al(OH)}_3 \rightarrow n\text{-factor} = 3$

Ex  $\Rightarrow$  Salt  $\rightarrow \text{Na}_2\text{CO}_3 \Rightarrow 2\text{Na}^+ \text{CO}_3^-$   
 $n\text{-factor} = 2$

2.5 \* Name a method to determine hardness of water?

Ans  $\Rightarrow$  EDTA method is used to determine hardness of water.

viii) \*

Calculate the amount of lime and soda required for softening of 25000 liters of water having following impurities in ppm.

$$Ca(HCO_3)_2 = 4.086$$

$$Mg(HCO_3)_2 = 7.30$$

$$CaSO_4 = 6.8$$

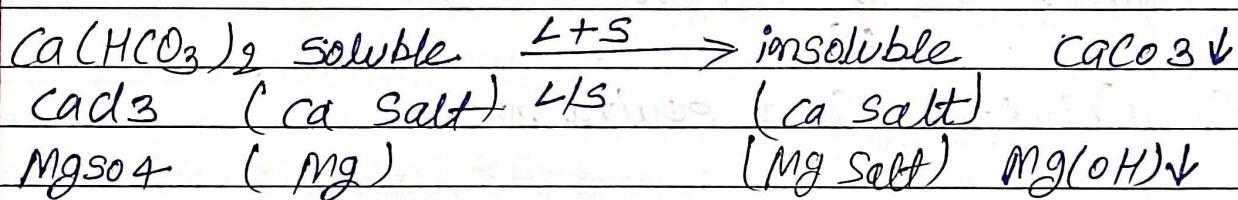
$$MgCl_2 = 5.7$$

$$MgSO_4 = 9$$

$\Rightarrow SiO_2 = 3 \rightarrow$  can not be removed by lime and

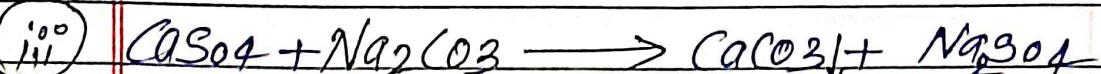
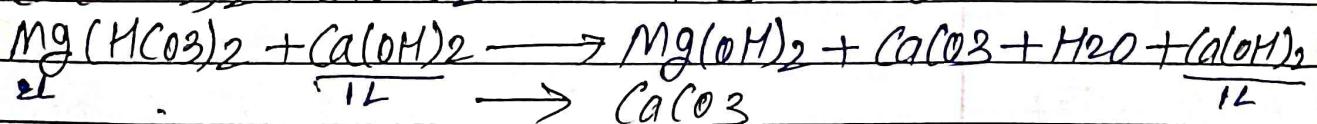
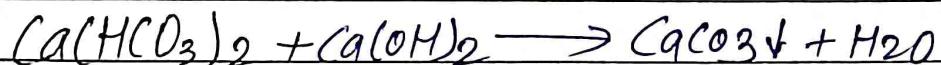
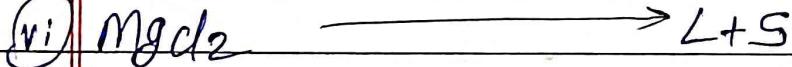
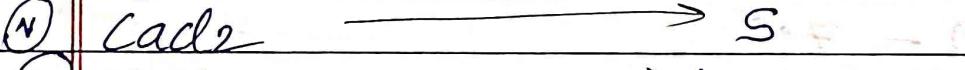
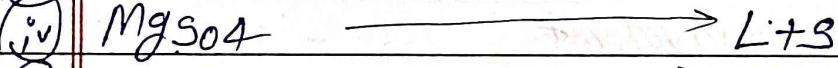
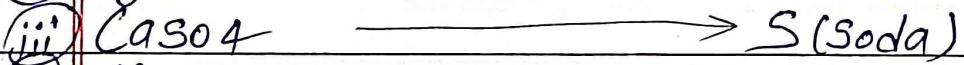
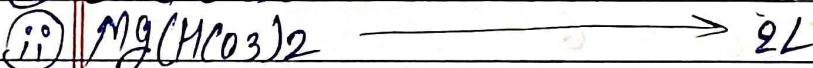
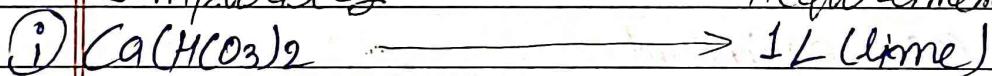
$\Rightarrow NaCl = 7 \rightarrow$  Soda process.

General principle is



### Impurities

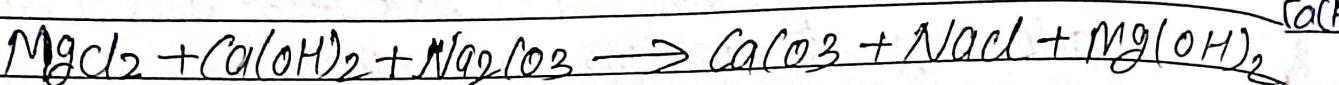
### Requirement



(V)



(vi)



\*

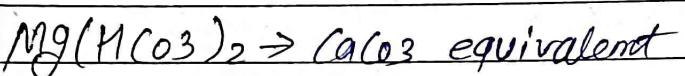
$$\text{CaCO}_3 \text{ equivalent} = \frac{\text{Mo of CaCO}_3 \times \text{amount of Impurity}}{\text{Mo of Impurity}}$$

(i)



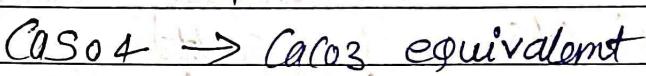
$$\text{CaCO}_3 \text{ equivalent} \rightarrow \frac{100}{164} \times 4.86 = 2.98 = 3$$

(ii)



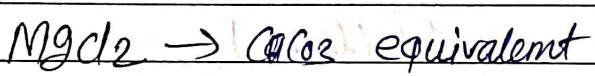
$$\text{CaCO}_3 \text{ equivalent} \rightarrow \frac{100}{148} \times 7.30 = 4.93 = 5$$

(iii)



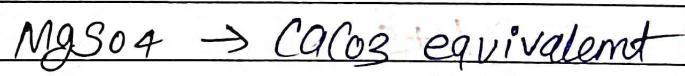
$$\rightarrow \frac{100}{136} \times 6.8 = 5$$

(iv)



$$\rightarrow \frac{100}{94} \times 5.7 = 6.06 = 6$$

(v)



$$\frac{100}{120} \times 9 = 7.5$$

$$\text{Ca}(\text{HCO}_3)_2 = 4.86$$

$$\text{Mg}(\text{HCO}_3)_2 = 7.30$$

$$\text{CaSO}_4 = 6.8$$

$$\text{MgCl}_2 = 5.7$$

$$\text{MgSO}_4 = 9$$

Impurity	$\text{CaCO}_3$ equivalent	Requirement (L/S)	Lime =	Soda =
$\text{Ca}(\text{HCO}_3)_2 = 4.86$	$\frac{100}{164} \times 4.86 = 3$	$1L + 0S$	$1 \times 3 = 3$	$1 \times 0 = 0$
$\text{Na}_2\text{HCO}_3 = 7.30$	$\frac{100}{146} \times 7.30 = 5$	$2L + 0S$	$2 \times 5 = 10$	$1 \times 0 = 0$
$\text{Ca}(\text{SO}_4) = 6.8$	$\frac{100}{136} \times 6.8 = 5$	$0L + S$	0	$1 \times 5 = 5$
$\text{MgCl}_2 = 5.7$	$\frac{100}{95} \times 5.7 = 6$	$0L + S$	$1 \times 6 = 6$	$1 \times 6 = 6$
$\text{MgSO}_4 = 9$	$\frac{100}{120} \times 9 = 7.5$	$L + S$	$1 \times 7.5 = 7.5$	$1 \times 7.5 = 7.5$
			$SL = 26.5$	$SS = 18.5$

$$\text{Lime required} = \frac{\text{Mo wt of lime} \times \text{water} \times 100\% \text{ purity of}}{\text{Mo wt of } \text{CaO}_3}$$

$$\text{Lime required} = \frac{\text{M}_0 \text{ wt of lime} \times \sum L \times \text{val. rate}}{\text{M}_0 \text{ wt of CaCO}_3} \times 100$$

$$\text{Soda required} = \frac{\text{Mol wt of Soda} \times \text{ES} \times \text{Vol. wt} \times 100}{\text{Mol wt of CaCO}_3} \quad 100$$

$$\therefore \text{lime required} = \frac{74 \times 26.5 \times 25000}{100} = 490250 \text{ lime (ppm)}$$

$$\text{Soda required} = \frac{106 \times 18.5 \times 25000 \times 100}{100} = 490250 \text{ Soda (ppm)}$$

\* Calculate the amount of lime 90% pure and Soda 95% Pure as in the previous statement question.

$$\text{Time requirement} = \frac{\text{Mount of line} \times \Sigma L \times V \cdot W}{\text{loop width}} \text{ time}$$

$$\text{Lime req} = \frac{74 \times 26.5 \times 85000 \times 100}{95}$$

$$\text{Lime req} = 4902500 \text{ (in ppm) L}$$

$$\text{Soda req} = \frac{106 \times 18.5 \times 85000 \times 100}{95} = 516052.632 \text{ (mg) s}$$

\* A Sample of water on analysis give the following result  $\rightarrow$  calculate first total hardness of water lime soda required for 1 liter of water sample.

$$(Ca, Mg) Ca = 30$$

$$\text{From } Mg^{2+} = 18$$

$$\text{Remaining hardness } CO_2 = 11$$

$$HCO_3^- = 122$$

$$\times K^+ = 20$$

$$\times Cl^- = 30$$

calculate: i) Total hardness of water

ii) Lime Soda required for 1 litre of water sample.

Impurity	CaCO <sub>3</sub> equivalent	Requirement	Lime	Soda
i) Ca = 30	$\frac{106 \times 30}{40} = 75$	L + S	$75 \times 0 = 0$	$75 \times 1 = 75$
ii) Mg <sup>2+</sup> = 18	$\frac{100}{4} \times 18 = 75$	L + S	$75 \times 1 = 75$	$75 \times 1 = 75$
iii) CO <sub>2</sub> = 11	$\frac{106}{4} \times 11 = 28$	L	$28 \times 1 = 28$	$28 \times 0 = 0$
iv) HCO <sub>3</sub> <sup>-</sup> = 122	$\frac{100}{61} \times 122 = 200$	$\frac{L - S}{2}$	$200 \times \frac{1}{2} = 100$	$200 \times \frac{1}{2} = 100$
v) $\sum L = 200$				
			$\sum S = 50$	

i) Total hardness of water  $\Rightarrow 75 + 75 = 150$   
CaCO<sub>3</sub> equivalent of Tens or per

$$\text{Lime requirement} = \frac{74}{100} \times \frac{200}{100} \times 1 \times 100 = 148$$

$$\text{Soda requirement} = \frac{106}{100} \times \frac{50}{2} \times 1 \times 1 = 53$$

Lime required for 1 litre of water sample  
= 148 mg/L

Soda required for 1 litre of water sample  
= 53 mg/L

A Sample of water on analysis has been found to contain following in ppm.

$$\text{Ca}(\text{HCO}_3)_2 = 4.86$$

$$\text{CaSO}_4 = 6.80$$

$$\text{MgSO}_4 = 8.40$$

Calculate the temporary and permanent hardness of the water.

Impurity

$$\text{Ca}(\text{HCO}_3)_2 = 4.86$$

CaCO<sub>3</sub> equivalent

$$\frac{100}{162} \times \frac{4.86}{100} = 3 \text{ ppm}$$

$$\text{CaSO}_4 = 6.80$$

$$\frac{100}{136} \times \frac{6.80}{100} = 5 \text{ ppm}$$

$$\text{MgSO}_4 = 8.40$$

$$\frac{100}{120} \times \frac{8.40}{100} = 7 \text{ ppm}$$

$$\text{Temporary hardness} = 3 \text{ ppm}$$

$$\text{Permanent hardness} = 5 + 7 = 12 \text{ ppm}$$

\* Calculate the amount of lime and soda required per litre for the chemical treatment of water containing  $\text{Ca}^{2+} = 80 \text{ ppm}$ ,  $\text{Mg}^{2+} = 36 \text{ ppm}$ ,  $\text{K}^+ = 39 \text{ ppm}$ ;  $\text{HCO}_3^- = 294 \text{ ppm}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  added as coagulant =  $69.5 \text{ ppm}$ .

Impurity ( $\text{CaCO}_3$ equivalent)	Requirement	Lime	Soda	M
$\text{Ca}^{2+}$ $\text{Ca} = 80$	$\frac{100}{40} \times 2 = 200$	5	0	200
$\text{Mg}^{2+}$ $\text{Mg} = 36$	$\frac{100}{62} \times 189.3 = 150$	$\text{L} + \text{S}$	150	150
$\text{HCO}_3^-$ $\text{HCO}_3^- = 294$	$\frac{100}{60} \times 294 = 490$	$\frac{1}{2}\text{L} - \frac{1}{2}\text{S}$	200	-200
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ $= 69.5$	$\frac{100}{278} \times 69.5 = 25$	$\text{L} + \text{S}$	$\frac{25}{2} = 12.5$	$\frac{25}{2} = 12.5$
			$5\text{L} = 375$	$\Leftrightarrow \text{S} = 175$

$$\text{Lime requirement} = \frac{74 \times 375 \times 1 \times 100}{100} = 277.5 \text{ mg/l}$$

$$\text{Soda requirement} = \frac{106 \times 175 \times 1 \times 1}{100} = 185.5 \text{ mg/l}$$

\* Calculate the amount of lime (91% pure) and soda (97.2% pure) required for softening one million litres of water containing  $\text{Ca}(\text{HCO}_3)_2 = 30.5 \text{ ppm}$ ;  $\text{Mg}(\text{HCO}_3)_2 = 35.5 \text{ ppm}$ ;  $\text{MgSO}_4 = 20.0 \text{ ppm}$ ;  $\text{CaSO}_4 = 24.0 \text{ ppm}$ ;  $\text{CaCl}_2 = 28.0 \text{ ppm}$  and  $\text{NaCl} = 10.0 \text{ ppm}$ .

Also calculate the temporary and permanent hardness of water sample.

Impurity	CaCO <sub>3</sub> equivalent	Requirement	L	S
Ca(HCO <sub>3</sub> ) <sub>2</sub> = 30.5 ppm	$\frac{100}{162} \times 30.5 = 18.8$	L	$18.8 \times 1 = 18.8$	0
Mg(HCO <sub>3</sub> ) <sub>2</sub> = 35.5 ppm	$\frac{100}{196} \times 35.5 = 18.3$	2L	48.6	0
MgSO <sub>4</sub> = 20.0 ppm	$\frac{100}{120} \times 20 = 16.7$	L + S	16.7	16.7
CaSO <sub>4</sub> = 24.0 ppm	$\frac{100}{136} \times 24 = 17.6$	S	0	17.6
NaCl = 28 ppm	$\frac{100}{111} \times 28 = 22.5$	S	0	22.5

$$\sum L = 84.1 \quad \sum S = 56.8$$

$$\text{Temporary hardness} = 18.8 + 24.3 = 43.1 \text{ ppm}$$

$$\text{Permanent hardness} = 20.5 + 17.6 + 16.7 = 54.8 \text{ ppm}$$

~~$$\text{lime requirement} = \frac{79 \times 84.1 \times 10^6 \times 100}{100 \times 91} = 68.38 \text{ kg}$$~~

~~$$\text{soda requirement} = \frac{106 \times 56.8 \times 10^6 \times 100}{100 \times 97.2} = 61.96 \text{ kg}$$~~

\* Calculate the amount of lime (84% pure) and soda (92% pure) required for treatment of 20,000 L of water whose analysis is as follows: Ca(HCO<sub>3</sub>)<sub>2</sub> = 40.5 ppm; Mg(HCO<sub>3</sub>)<sub>2</sub> = 36.5 ppm; MgSO<sub>4</sub> = 30.00 ppm; CaSO<sub>4</sub> = 34.0 ppm; CaCl<sub>2</sub> = 27.75 ppm and NaCl = 10.00 ppm. Also calculate the temporary and permanent hardness of water.

Impurity	$\text{CaCO}_3 \text{ eq.}$	Requirement	Lime	Soda
$\text{Ca}(\text{HCO}_3)_2 = 40.5$	$\frac{100}{162} \times 40.5 = 25$	L	25	0
$\text{Mg}(\text{HCO}_3)_2 = 36.5$	$\frac{100}{146} \times 36.5 = 25$	L + S	50	0
$\text{Mg}(\text{SO}_4) = 30$	$\frac{100}{120} \times 30 = 25$	L + S	25	25
$\text{CaSO}_4 = 34$	$\frac{100}{136} \times 34 = 25$	S	0	25
$\text{NaCl} = 27.75$	<del><math>\frac{100}{111} \times 27.75 = 25</math></del>	S	0	25
			$\sum L = 100$	$\sum S = 75$

Temporary hardness  $\therefore 25 + 25 = 50 \text{ mg/L (ppm)}$

Permanent hardness  $\therefore 25 + 25 + 25 = 75 \text{ ppm}$

Lime requirement  $= \frac{74 \times 100 \times 20,000 \times 100}{100} = 1.476 \text{ kg}$

Soda required  $= \frac{106 \times 75 \times 20,000 \times 100}{92} = 1.072 \text{ kg}$

\* Calculate the amount of lime (91% pure) and soda (97.2% pure) for softening one million litres of water containing:

H (free acidity) = 1.05 ppm;  $\text{HCO}_3^- = 896.5 \text{ ppm}$ ;  $\text{Mg}^{+2} = 40 \text{ ppm}$ ,  $\text{Ca}^{2+} = 90 \text{ ppm}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 14 \text{ ppm}$

[Given atomic masses of H = 1, Ca = 40, Mg = 24, O = 16, C = 12, S = 32, Fe = 56]

impurity

$$H^+ = 1.5$$

CaCO<sub>3</sub> eq.

Requirement

L

S

$$\frac{L}{2} + \frac{S}{2}$$

$$75$$

$$75$$

$$CO_3^- = 396.5$$

$$\frac{100}{61} \times 396.5 = 650$$

$$\frac{1}{2}L - \frac{1}{2}S$$

$$325$$

$$-325$$

$$Cl^- = 42 \text{ ppm}$$

$$\frac{100}{24} \times 42 = 175$$

$$L+S$$

$$175$$

$$175$$

$$SO_4^{2-} = 90$$

$$\frac{100}{40} \times 90 = 225$$

$$S$$

$$0$$

$$225$$

$$CaSO_4 \cdot 7H_2O = 14$$

$$\frac{100}{278} \times 14 = 5.03$$

$$L+S$$

$$5.03$$

$$5.03$$

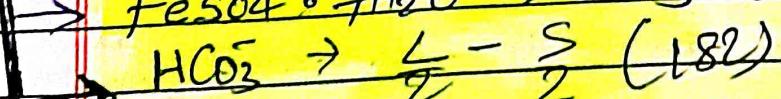
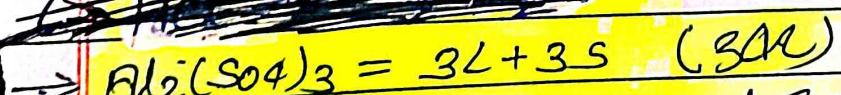
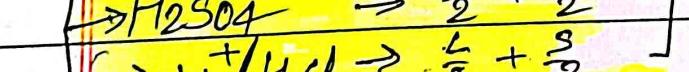
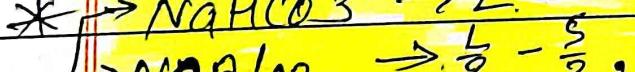
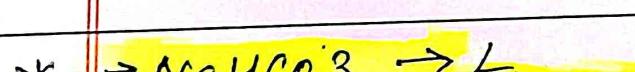
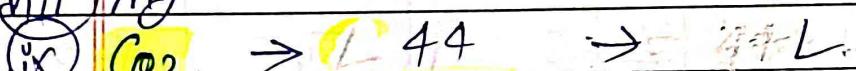
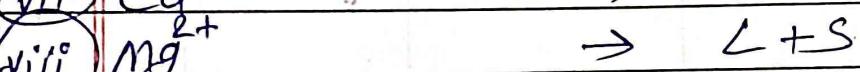
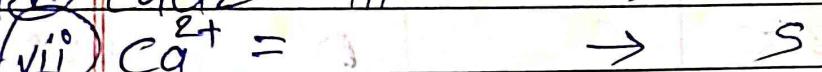
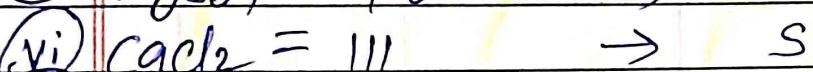
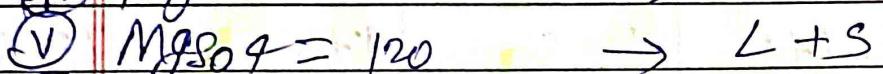
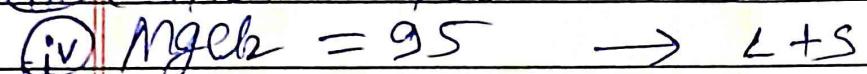
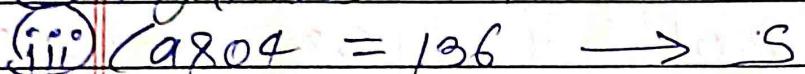
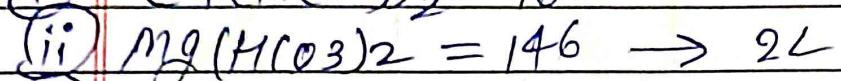
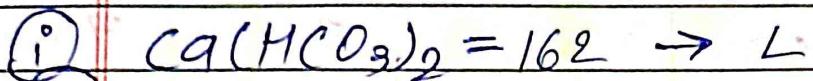
$$EL = 580.03$$

$$ES = 155.0$$

$$\text{Lime requirement} = \frac{74}{100} \times \frac{580.03}{91} \times \frac{10^6}{100} \times \frac{100}{97.2} = 471.67 \text{ kg}$$

$$\text{Sand requirement} = \frac{106}{100} \times \frac{155.03}{97.2} \times \frac{10^6}{100} \times \frac{100}{97.2} = 169.0 \text{ kg}$$

# Impurity of water in Total hardness of water



2.0  $\rightarrow$  Why it is called permanent hardness and how it removed by?

$\Rightarrow$  It is called permanent hardness because of presence of chloride and sulphate salts of Ca, Mg, Fe and it cannot be removed by heating of water so it is called permanent hardness.

There are some method to removal of PH

① washing Soda process

(2.6)

What is concordant reading?

$\Rightarrow$  If reading have been taken several times and readings are close to each other is called concordant reading.

\* A water sample on analysis give the following in ppm  $\text{Ca}^{+2} = 30$ ,  $\text{Mg}^{+2} = 24$ ,  $\text{CO}_2 = 24$ ,  $\text{HCl} = 50$  and  $\text{K}^+ = 10$  calculate the quantities of lime (purity 90%) and soda (purity 99%) required to soften one million litres of water.

Impurity	$\text{CaCO}_3 \text{ eq}$	Requirement	L	S
$\text{Ca}^{+2} = 30$	$\frac{100}{40} \times 30 = 75$	S	0	75
$\text{Mg}^{+2} = 24$	$\frac{100}{24} \times 24 = 100$	L + S	100	100
$\text{CO}_2 = 24$	$\frac{100}{44} \times 24 = 54.54$	L	54.54	0
$\text{HCl} = 50$	$\frac{100}{56.5} \times 50 = 87.5$	$\frac{L}{2} + \frac{S}{2}$	68.5	68.5
		$\Sigma L = 223.04 \text{ ES} = 243.5$		

$$\text{Lime req} = \frac{74 \times 223.04 \times 10 \times \frac{90}{100}}{100} \times \frac{100}{90}$$

Lime = 183.38 kg

Soda = 274.57 kg

## Chapter - 2

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### Spectroscopy technique and Application

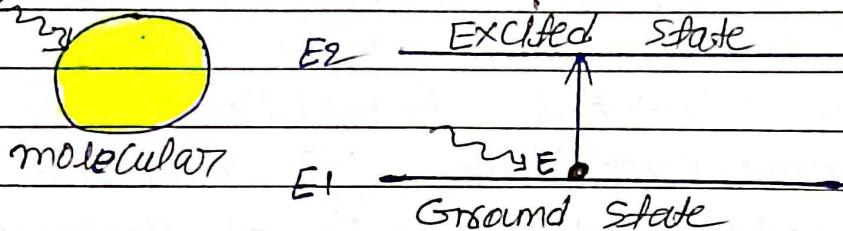
#### Molecular Spectroscopy

Molecular + Energy  $\rightarrow$  shift ground state from

high energy state

E- UV light

E- IR light  $\rightarrow$  Electromagnetic radiation



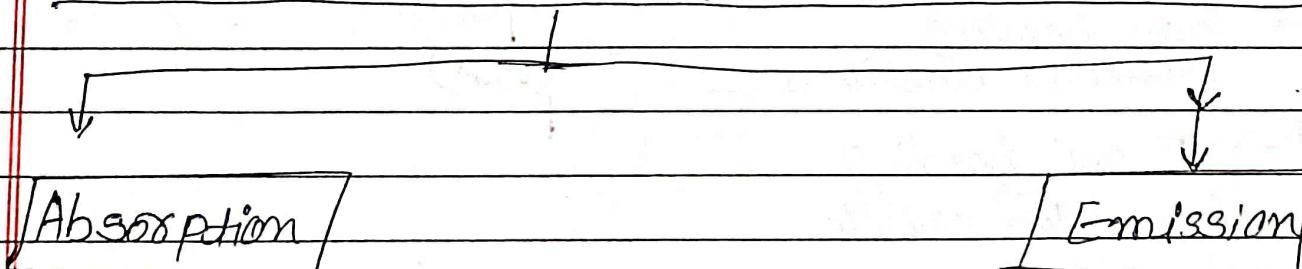
\* Spectroscopy : The branch of science dealing with the study of interaction of electromagnetic radiation with particle is known as spectroscopy.

Molecular + Energy  $\rightarrow$  Excitation

UV-visible - spectrophotometer

IR Spectrophotometer

\* Interaction of Electromagnetic wave and Molecular



Excited State

Excited state

by release one  
Photon

Ground state

Ground state



\* What is Spectrophotometer?

Q) The energy change or frequency of electromagnetic radiation emitted or absorbed can be recorded (Spectra) with the help of instrument, which is known as spectrophotometer.

\* Electronic transitions -

Ground state ( $E_0$ )  $\rightarrow$  Excited state

Electronic change + change in the position of electrons.

\* Types of electrons

- i)  $\sigma$  electrons (presence in all molecule)
- ii)  $\pi$  electrons ( $C = \equiv \pi$ ) ( $C_6H_6$ )
- iii) non bonding electrons ( $O, N, Cl, F$ )

\* Types of transitions

$\sigma \rightarrow \sigma^*$

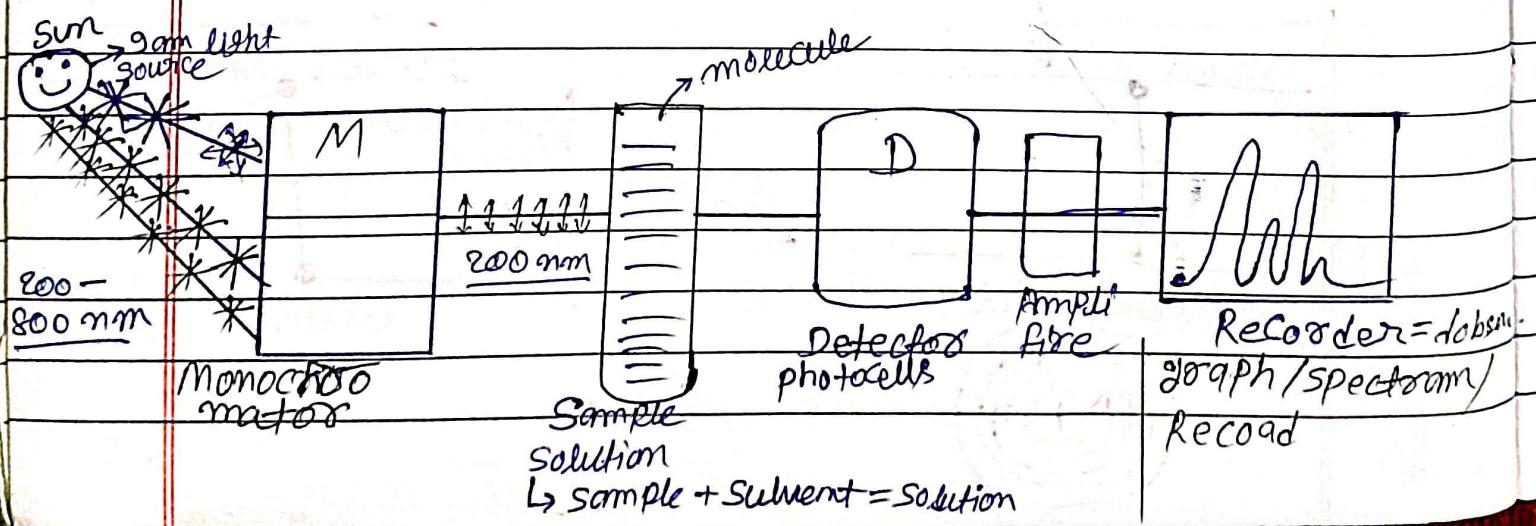
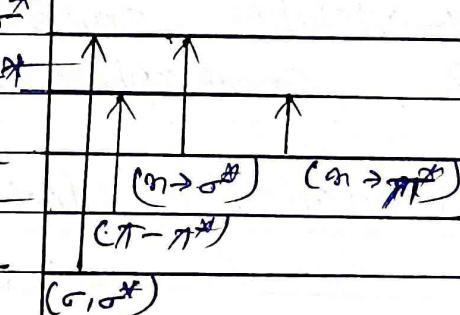
$\pi \rightarrow \pi^*$        $\sigma^*$

$n \rightarrow \sigma^*$

$n \rightarrow \pi^*$

$n \rightarrow$  non bonding molecular orbital

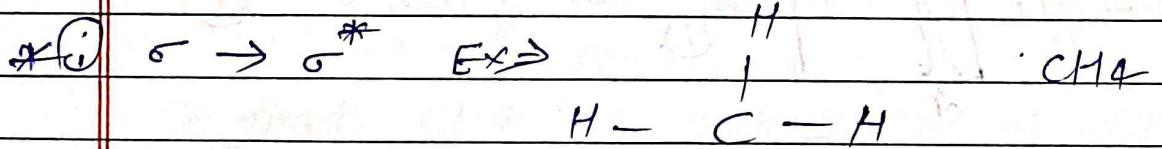
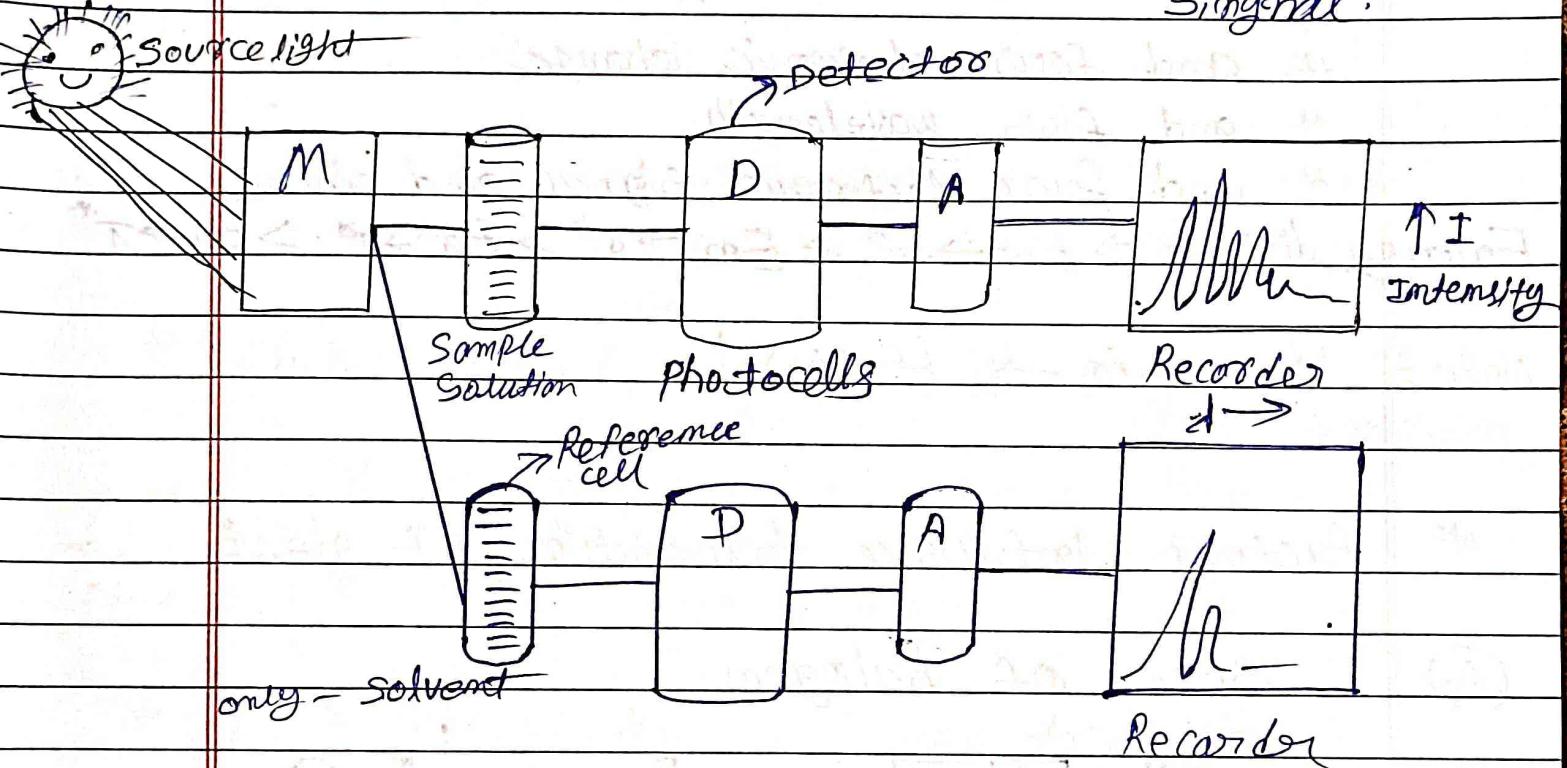
$\pi^* \rightarrow$   $\pi$  anti bonding molecular orbital



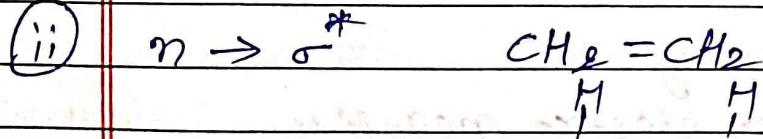
\* Detector → i) Detector detects the wavelength by the Sample

ii) Detector detects the missing wavelength (λ)

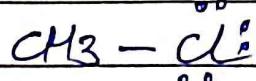
iii) Detector converts wavelength energy into electric signal.



$$\boxed{\frac{E=hc}{d}}$$



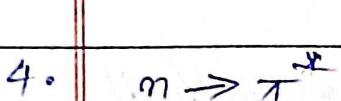
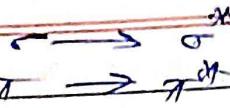
$\text{C}=\text{C}$  can't show  $n \rightarrow \sigma^*$   
because it hasn't form pair



# UV-VIS Spectroscopy = Electronic Spectroscopy

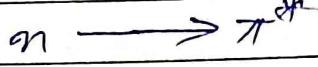
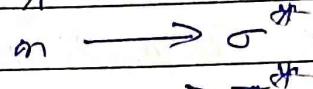
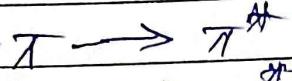
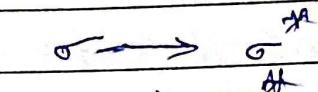
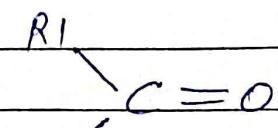
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R<sub>1</sub>

R<sub>2</sub>



\* and four electronic change

\* and four wavelength

\* and four electronic signal and energy

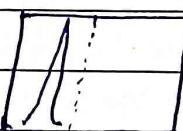
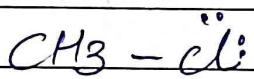
Energy difference  $\rightarrow E_{\sigma} \rightarrow \sigma^* > E_n \rightarrow \sigma^* > E_{\pi} \rightarrow \pi^* > E_n \rightarrow \pi^*$

Note: Lone pair  $\rightarrow (\text{S}, \text{O}, \text{N}, \text{X})$

\* factors influence transition of one o

(A) Size of halogen

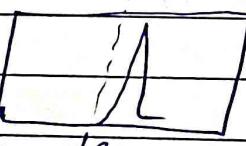
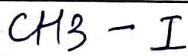
i)



$E_n \rightarrow \sigma^* > E_n \sigma^*$

① ②

ii)



$E_n \rightarrow \sigma^* < E_n \rightarrow e^*$

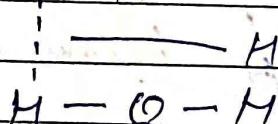
① ②

(B)

Hydrogen bonding

Sample: R-OH

electro negative



$\hookrightarrow$  electro positive

H bonding  $\rightarrow$  more energy to excitation

\* What is the effect of hydrogen bonding on transition of  $\pi$  electrons?

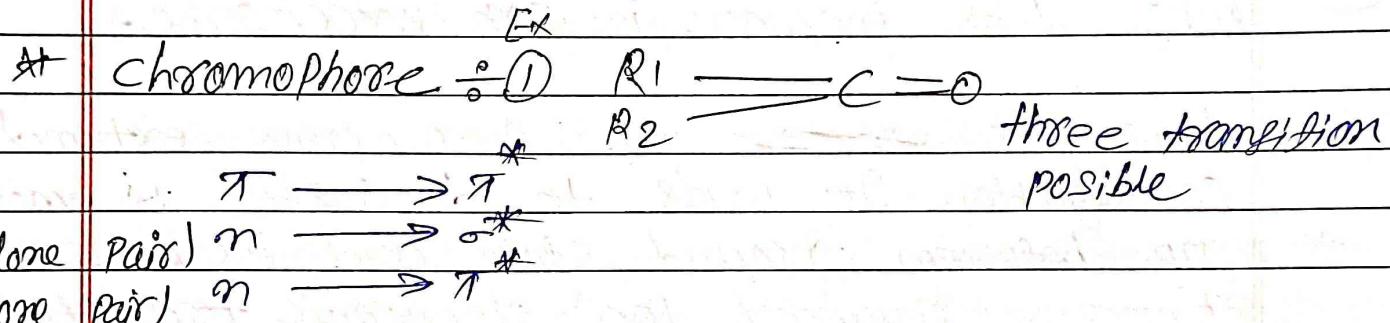
$\Rightarrow$   $\pi$  electrons have more energy to excitation

\* chromophore  $\therefore$  chromophore is a molecule which absorb energy and show excitation is called chromophore.



Note  $\therefore$  UV visible has no energy to show  $\sigma \rightarrow \sigma^*$

$\text{Ex} \Rightarrow \text{CH}_4 \rightarrow$  Not possible  $\sigma \rightarrow \sigma^*$  formation

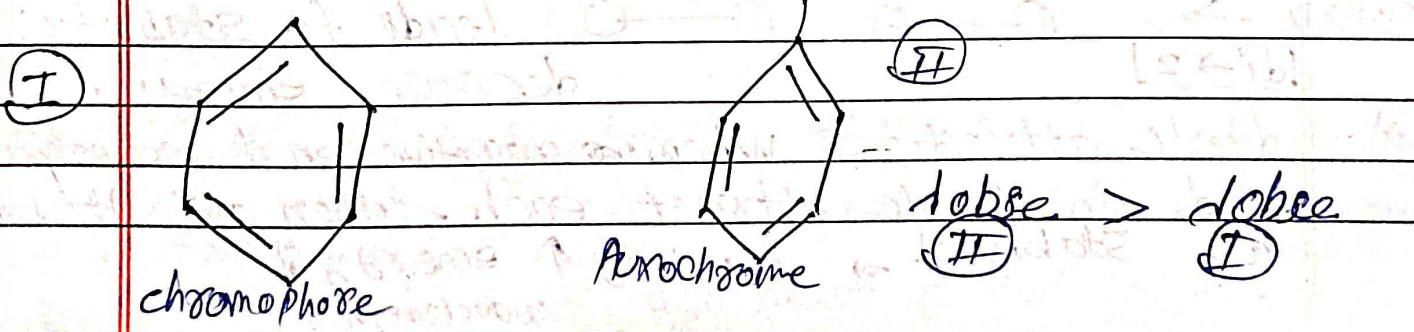


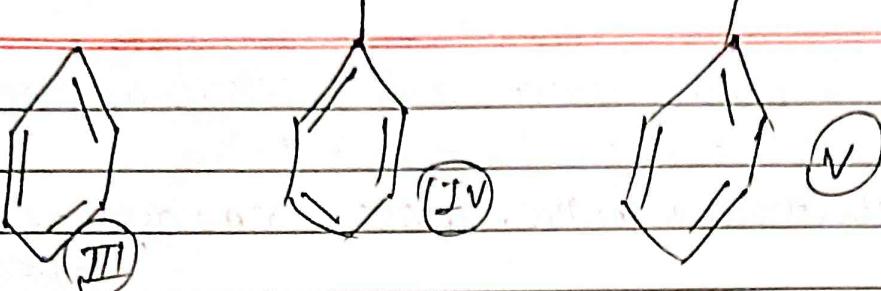
$\text{Ex} \Rightarrow \text{CH}_2 = \text{CH}_2$  only one transition  
 $\sigma \rightarrow \sigma^*$  not possible ( $\times$ ) (UV visible observation)  
 $\pi \rightarrow \pi^*$  possible ( $\checkmark$ )

So that  $\text{CH}_4$  is not a chromophore.

\* Auxochrome  $\therefore$  it is a group which has lone pairs is called Auxochrome, lone pairs increase wavelength observe.

\* Examples  $\therefore$





III dobs < IV dobs

(III) dobs < (V) dobs

\* Effect of Auxochrome  $\therefore$  dobs increase

\* what is the cause of effect of Auxochrome or why dobs increase in ~~Auxochrome~~ Auxochrome:

ans  $\Rightarrow$  lone pair ~~on auxochrome~~ on auxochrome extend the conjugation. It leads to decrease in energy gap between ground state and excited state. Energy required for electronic transition decreases. Hence dobs increase.

\* What is the effect of a Polar Solvent on  
 $\text{O}^\ddagger \text{n} \rightarrow \pi^*$  of Carbonyl compounds  
 $\text{ii}^\ddagger \pi \rightarrow \pi^*$

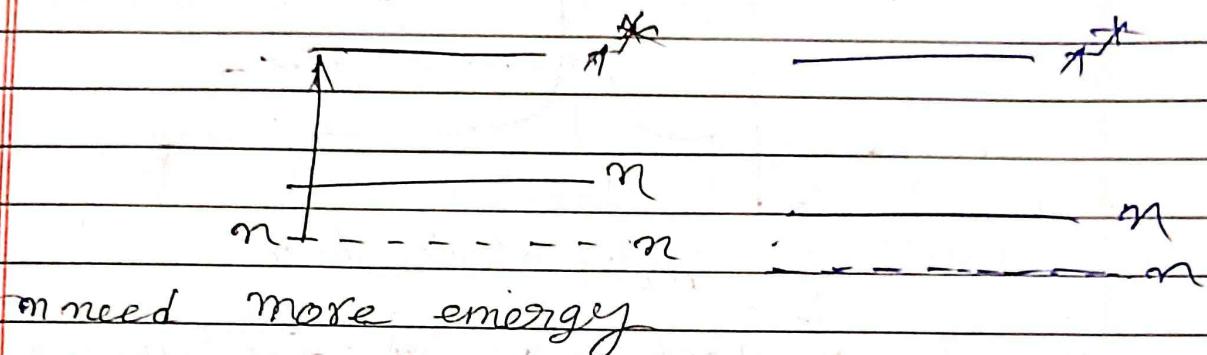
ans  $\Rightarrow$  carbonyl compound  $\rightarrow$  any molecule which have  $(=)$   
 $\text{C}=\text{O}$

Polar  $\rightarrow$   ${}^+\text{O} \text{---} {}^-\text{O} \text{---} {}^+\text{O} \text{---} {}^-\text{O}$  leads to stability to decrease energy.  
 $\boxed{\text{di} \rightarrow 2}$

\* dipole attraction: When ~~negative~~ negative end and positive end on dipole attract each other and it leads to stability  $\rightarrow$  stability  $\uparrow$  energy  $\downarrow$  wavelength  $\uparrow$

Solvent effect of  $n \rightarrow \pi^*$

Due to dipole-dipole interaction molecule will stabilize and due to stability of molecule energy of the molecule is decreased so that energy gap increased so  $n$  need more energy to show  $n \rightarrow \pi^*$  transition

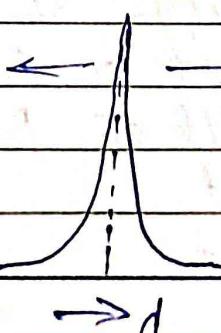


Solvent effect of  $\pi \rightarrow \pi^*$

When an electron goes for transition so that there becomes dipole-dipole interaction so that energy available  $\pi^*$  decreases, hence energy gap decrease so that  $\pi$  needs less energy and more wavelength to show  $\pi \rightarrow \pi^*$  transition it is solvent effect.

\* Absorption and Intensity shift

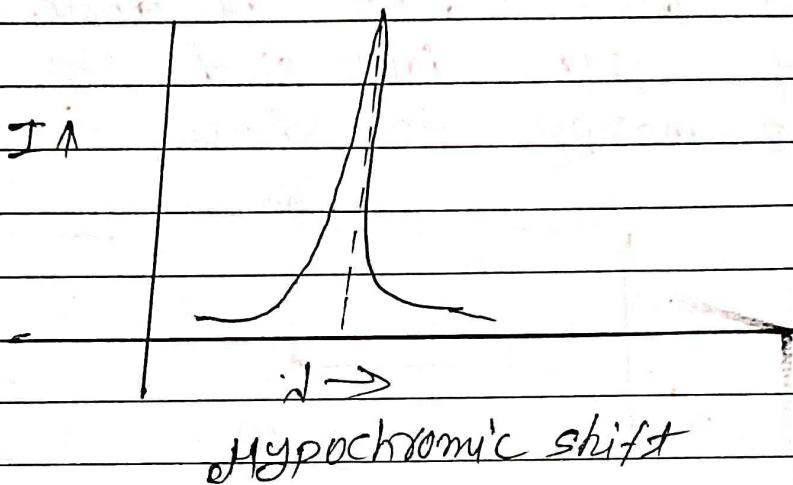
Hypsochromic shift  
or Blue shift  $\lambda \uparrow$



Bathochromic shift  
or Red shift

\* Cause of Bathochromic shift : when the wavelength of solution increase is called Bathochromic shift or Red shift.  
Bathochromic shift also known as Red shift.

- \* Cause of Hypsochromic shift : when the wavelength of solution decrease is called Hypsochromic shift. Hypsochromic shift is known as blue shift Hyperchromic shift



- \* Hyperchromic shift : when the intensity of the solution increase is called Hyperchromic shift.
- \* Hypochromic shift : when the intensity of solution or absorption decrease is called Hypochromic shift.
- \* What is Intensity shift : shift in the Intensity of the signal it can be increase, it can decrease is called Intensity shift.
- \* Types of Intensity shift :
  - Bathochromic shift or Red shift
  - Hypsochromic shift or Blue shift
  - Hyperchromic shift
  - Hypochromic shift

## # Infrared (IR) spectroscopy or vibrational - rotational spectroscopy

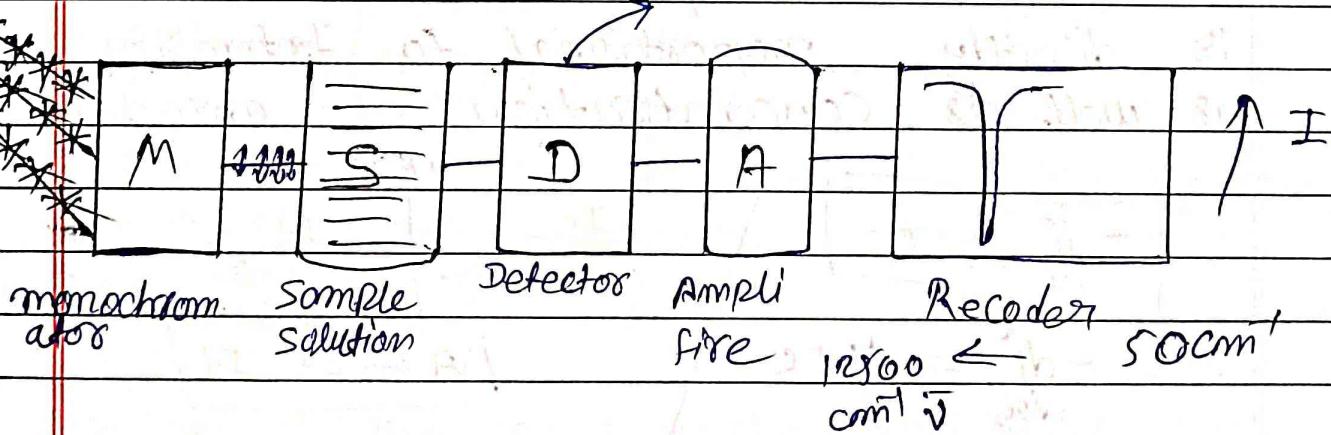
↓ →

0.8μ	2.5μ	15μ	200μ
near IR	IR Region	for IR Region	
12500 cm <sup>-1</sup>	4000 cm <sup>-1</sup>	677 cm <sup>-1</sup>	500 cm <sup>-1</sup>

$$\boxed{\bar{v} = \frac{1}{\lambda}} \text{ wave number} \quad \boxed{\bar{v} = \nu \text{ in cm}}$$

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

$$E = hc\nu$$



vibrational change

vibrational change in position

# Heteronuclear diatomic molecular



↓ ↓ different

· different

H<sub>2</sub> → Homo molecular

S.H.O

 $m_1$  $m_2$ 

O O O O O O O O O O

$$f = -kx$$

$$F = -kx$$

spring constant

$$\boxed{\omega = \frac{1}{2\pi c} \sqrt{\frac{k}{m}} \rightarrow \text{reduce mass}}$$

$$\downarrow \propto k$$

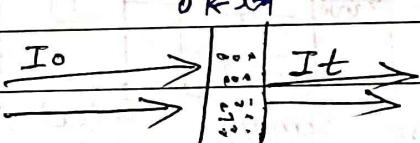
$$\downarrow \propto \frac{1}{m}$$

$$\boxed{m = \frac{m_1 m_2}{m_1 + m_2}}$$

when a beam of monochromatic radiation passes through a solution

\* Beer Lambert Law  $\therefore$  Decrease in intensity of light with respect to thickness of solution is directly proportional to Intensity of light as well as concentration of absorbing solution

$$\boxed{-\frac{di}{dx} \propto Ic}$$



$$\boxed{-\frac{di}{dx} = Kic}$$

$$\boxed{A = I_0 - I_t}$$

$$\boxed{-\frac{di}{I} = Kcdx}$$

A  $\propto$  C Beer lawA  $\propto$  x Lambert law

$$\int_{I_0}^{I_t} \frac{di}{I} = Kc \int_0^x dx$$

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

$$-\left[ \log \frac{I_t}{I_0} \right]_{x_0}^x = Kc [x]_{x_0}^x$$

$$-\left[ \log I_t - \log I_0 \right] = Kc [x - 0]$$

$$-\left[ \log \frac{I_t}{I_0} \right] = Kcx$$

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

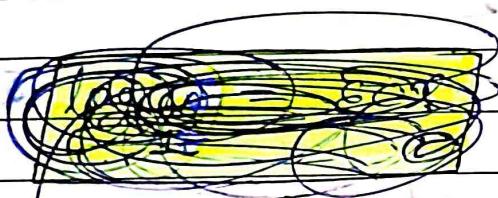
$$\log \frac{I_0}{I_t} = Kcx$$

$$2.303 \log \frac{I_0}{I_t} = Kcx$$

$$\log \frac{I_0}{I_t} = \frac{k}{2.303} \times c \times x$$

$$\therefore T = \frac{I_t}{I_0}$$

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



$$\left\{ \begin{array}{l} A = \log \frac{I_0}{I_t} \\ T = \frac{I_t}{I_0} \end{array} \right.$$

$$A = \epsilon cx \quad A = \log \frac{I_0}{I_t}$$

$$T = \frac{I_t}{I_0}$$

$$A = -\log T$$

$$A = \log \frac{I_0}{I_t}$$

$$\epsilon = L \text{ mol}^{-1} \text{ cm}^{-1}$$

$\epsilon \rightarrow$  molar extinction coefficient / molar Absorptivity

$A \rightarrow$  Absorption / Absorbance  $[L \text{ mol}^{-1} \text{ cm}^{-1}]$

$I \rightarrow$  Intensity of light

$K \rightarrow$  Constant

$x \rightarrow$  Thickness of solution / path length

$T \rightarrow$  Transmittions / Transmittance

$c \rightarrow$  Concentration

$I_0 \rightarrow$  incident Intensity

$I_t \rightarrow$  Transmitterd Intensity



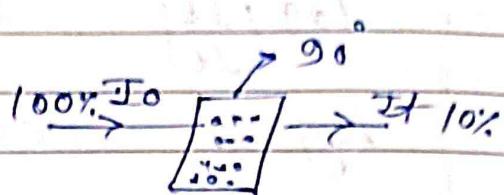
Calculate transmitties, absorption and molar extinction coefficient of a solution which absorbs 90% of an incident radiation passing through 1 cm cell containing 0.25 M Soln.

$$T = ? \quad A = ? \quad \epsilon = ?$$

Given  $C = 0.05 \text{ M}$

$x = 1 \text{ cm}$

$$\text{ab80b8} = 90^\circ$$



$$I_0 = 100\% \quad T = 10^\circ$$

$$T = \frac{I_t}{I_0}$$

$$T = \frac{10}{100} \quad \boxed{T = 0.1}$$

$$\boxed{A = \log \frac{1}{T}}$$

$$A = \log \frac{I_0}{I_t} \quad A = \log \frac{100}{10}$$

$$\boxed{A = 1}$$

$$\epsilon = ?$$

$$A = \epsilon C x$$

$$\epsilon = A \quad \epsilon = 1$$

$$C x = 0.05 \times 1$$

$$\epsilon = \frac{100}{28}$$

$$\boxed{\epsilon = 4 \text{ L mol}^{-1} \text{ cm}^{-1}}$$

\* A substance when dissolved in water at 10 molar concentration absorbs 10% of the incident light in a path of 1 cm length. What should be the concentration of the solution in order to absorb 90% of the same radiation?

Ans = with first statement  $C = 10^{-3}$

$$I_0 = 100$$

$$I_t = 100 - 10$$

$$x = 1 \text{ cm}$$

$$\boxed{I_t = 90/1}$$

$$\therefore A = \epsilon C x$$

$$\boxed{A = \log \frac{I_0}{I_t}}$$

$$A = \log \frac{100}{90}$$

$$\boxed{A = \log 1.11}$$

$$\boxed{A = 0.0457}$$

$$A = 0.045$$

$$\therefore A = \epsilon c x$$

$$\epsilon = \frac{A}{c x} \quad \epsilon = \frac{0.045}{10^3 \times 1}$$

$$\epsilon = 0.045 \times 10^3$$

$$\boxed{\epsilon = 45 \text{ L mol}^{-1} \text{ cm}^{-1}}$$

Now, with second statement.

$$C = ?$$

$$A = \log \frac{I_0}{I_t}$$

$$I_0 = 100$$

$$I_t = 100 - 90$$

$$I_t = 10$$

$$A = \log \frac{100}{10} \Rightarrow A = 1$$

$$\epsilon = 40$$

So that

$$C = \frac{A}{\epsilon x}$$

$$C = \frac{1}{40 \times 1}$$

$$\boxed{C = 0.025 \text{ mol L}^{-1}}$$

- \* A solution shows a transmittance of 20% when taken in a cell of 2.5 m thickness calculate concentration if molar absorption coefficient is  $12000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

$$C = ?$$

$$T = 20\%$$

$$x = 2.5 \text{ metre}$$

$$\epsilon = 12000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

$$T = \frac{I_t}{I_0} = \frac{20}{100}$$

$$A = \log \frac{I_0}{I_t}$$

$$A = 0.69$$

$$A = \log \frac{100}{20} \quad A = 1.39$$

$$x = 2.5 \times 100 \text{ cm}$$

$$x = 250 \text{ cm}$$

$$\boxed{A = 0.69}$$

$$C = \frac{0.69}{18000 \times 250}$$

~~$$C = \frac{69}{12 \times 25 \times 10^6} = 5.75$$~~

$$C = \frac{5.75}{25 \times 10^6} = 2.3 \times 10^{-8}$$

$$C = \frac{2.3}{10^8}$$

$$C = \frac{2.3}{10^7}$$

$$C = 2.3 \times 10^{-7} \text{ g mole}^{-1}$$

\* Calculate the wave number for the stretching vibration of a single bond between carbon  $^{12}\text{C}$  and hydrogen  $^1\text{H}$ . Given that  $K = 5 \times 10$  dyne  $\text{cm}^{-1}$  and Avogadro number ( $N_A = 6.022 \times 10^{23}$ )

$$\text{wave number} = \bar{\nu} = \frac{1}{2\pi C} \sqrt{\frac{K}{M}}$$

$$\text{Given } \therefore \text{Mass of } C = \frac{12}{N_A}$$

$$\text{Mass of H atom} = \frac{1}{N_A}$$

$$\text{C Mass} = \frac{12}{6.022 \times 10^{23}}$$

$$C = 1.99 \times 10^{-23}$$

$$\text{H Mass} = \frac{1}{6.022 \times 10^{23}}$$

$$H = 1.66 \times 10^{-23}$$

$$\left[ M = \frac{m_1 \cdot m_2}{m_1 + m_2} \right]$$

$$M = \frac{3.03034 \times 10^{-23}}{3.658 \times 10^{-23}}$$

$$\left[ M = 1.077 \times 10^{-23} \right]$$

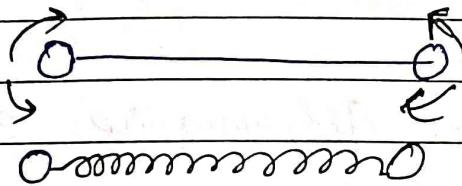
$$M = 0.9080$$

$$V = \frac{1}{2 \times 3.14 \times 3 \times 10^8} \left[ \frac{5 \times 10^5}{0.90} \right]$$

$$V = \frac{1}{2 \times 3.14 \times 3 \times 10^8} \times 745.3$$

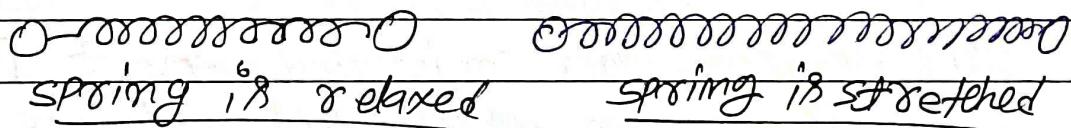
$$V = 39.55 \times 10^{-6} \text{ cm}^{-1}$$

### \* Molecular vibrations



Note : When any molecule absorb IR radiation than they show (vibration) and (rotational)

\* Vibration  $\rightarrow$  Stretching vibration  
 $\rightarrow$  Bending vibration



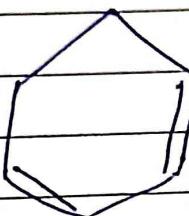
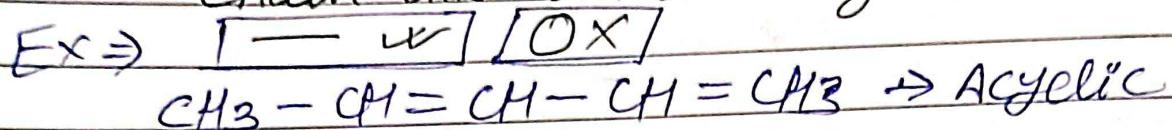
i) Stretching vibration : That vibration in which distance between two atoms increases or decreases but the atoms remain in the same bond axis are known as stretching vibration.

ii) Bending vibration : That vibration in which positions of atom change and angle of atom change is known as bending vibration.



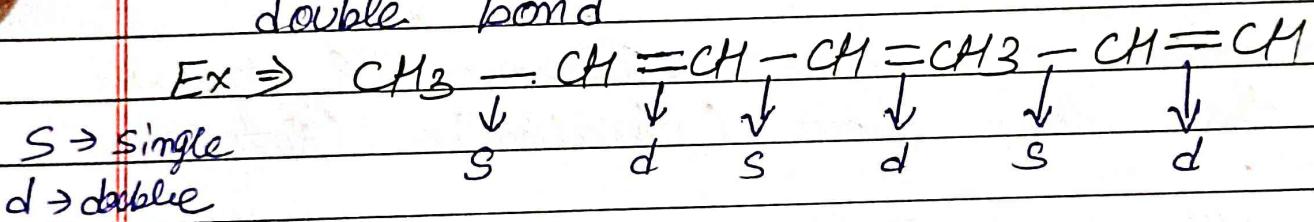
\* Woodward - Fieser Rules  $\therefore \Delta_{\text{max}}$

(i) Acyclic conjugated diene  $\therefore$  without any chain and without any cycle



$\rightarrow$  Not Acyclic

Conjugation  $\rightarrow$  Mean Alternative single or double bond

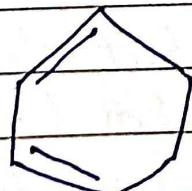


diene  $\Rightarrow$  Two double bond

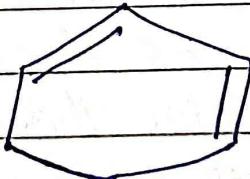
(ii) Homocyclic conjugated diene  $\therefore$  It is a cyclic diene in which double bonds in conjugation or alternative positions of bonds in one ring is Homocyclic C.d.  
Note  $\div$  same double bond too

Ex  $\therefore$

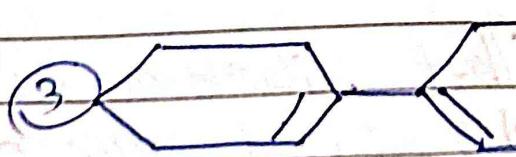
①



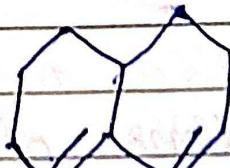
②



③



④



⑤



alternative bond  
must be

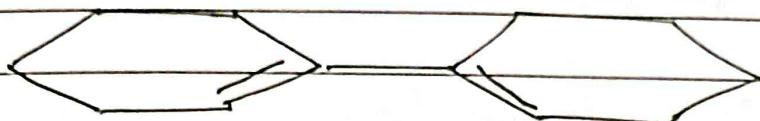
(iii)

Heteroannular conjugated diene :-

Trans double bond Sis  $\rightarrow$  [ trans  $\rightarrow$  ]  
 in any diene called  
 Heteroannular conjugated diene

Ex :-

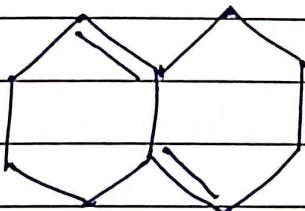
(i)



trans double bond

Heteroannular

(ii)

trans double bond  
Heteroannular

Note :- anywhere become Homocyclic and  
 Heteroannular diene them we take  
 only homocyclic because it's wavelength  
 is greater than Heteroannular.

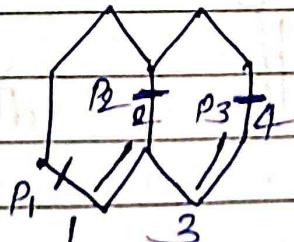
Homo  $\rightarrow$  253 nmHetero  $\rightarrow$  214 nm

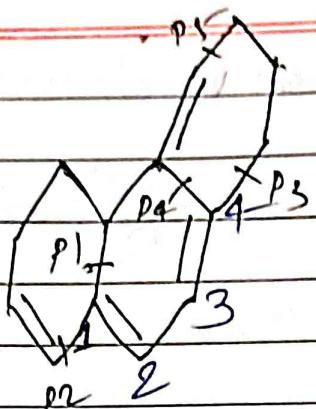
(iv)

Each alkyl substituent or ring residue :-  
 which diene has alkyl group  
 like :-  $\text{H}_3\text{C}$ ,  $\text{CH}_3$ ,  $\text{CH}_2$ ,

\*

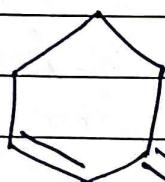
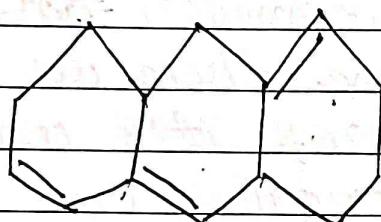
Ring residue :-

Those  $\text{P}_1$ ,  $\text{P}_2$ ,  $\text{P}_3$  is residue

Ex  $\Rightarrow$  $p_1, p_2, p_3, p_4, p_5$  is residue

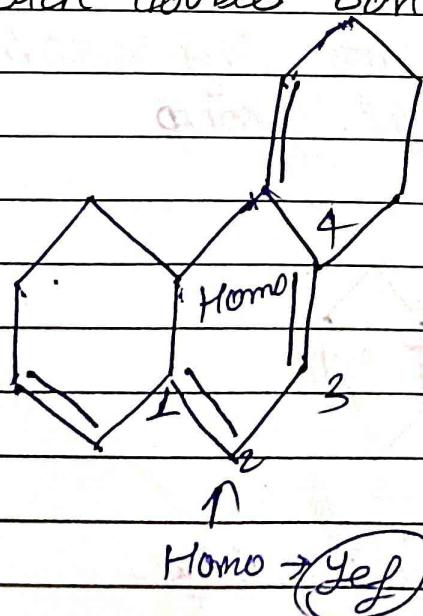
(v)

Exocyclic double bond :-

Exo  $\rightarrow$  External  $\rightarrow$  out of ring  
Cyclic  $\rightarrow$  ring $\rightarrow$  exocyclic double bond $\rightarrow$  exocyclic double bond

Two exocyclic bond

(vi) Each double bond extending conjugation.

There are homo and heteroannular  
homo conjugation

$\leftarrow$  Homo cycle & double bond  
 $\leftarrow$  3 to 1 or 4 to 2  
double bond  $\leftarrow$  5 to 4  
extending conjugation

EAT 1

## \* Woodward Fieser rule :

### (a) Parent Values

- (i) Acyclic Conjugated diene 217 nm
- (ii) Homoaannular Conjugated diene 253 nm
- (iii) Heteroannular Conjugated diene 214 nm

### (b) Increment's :

- i) Each alkyl substituent or ring residue 5 nm
- ii) Exocyclic double bond 5 nm
- iii) Each double bond extending conjugation 30

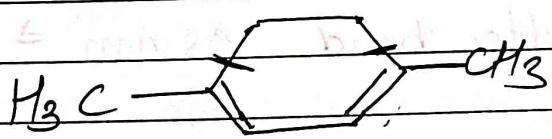
(c) Auxochromes:	-OR	6 nm
	-SR	30 nm
	-Cl, Br	5 nm
	-NR <sub>2</sub>	60 nm
	-OCOCH <sub>3</sub>	0 nm

Exemple - 103  $\Rightarrow$  CH<sub>3</sub>—CH=CH—CH=CH—CH<sub>3</sub>

Acyclic Conjugated diene = 217

Alkyl substituent diene  $\Rightarrow 2 \times 5 = 10$

227 nm



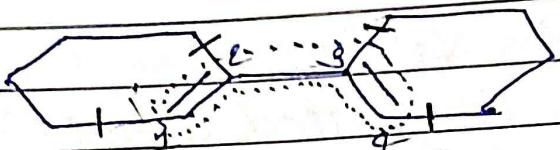
Homoannular  $\rightarrow$  253 nm 253

Alkyl C=C  $\Rightarrow 2 \times 5 = 10$  10

Two ring residue  $\Rightarrow 2 \times 5 = 10$  10

873 nm

Ex = 105  $\Rightarrow$  Compute  $\lambda_{max}$  for the compound:



heterocyclic diene

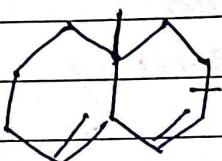
four ring residue

$$214 \text{ nm} = 214$$

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

$$[234 \text{ nm}]$$

Ex = 106 Calculate  $\lambda_{max}$



heterocyclic diene

ring residue 3

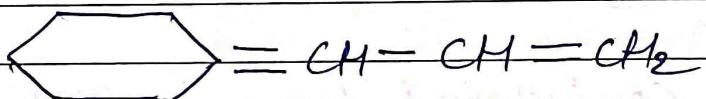
$$214 \text{ nm} \Rightarrow 214$$

$$3 \times 5 = 15 \Rightarrow 15$$

one exocyclic double bond 5 nm

$$[234 \text{ nm}]$$

Example 107 Calculate  $\lambda_{max}$



Acyclic diene

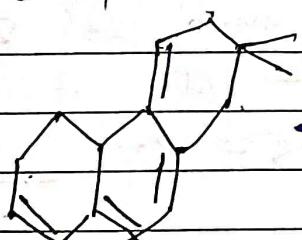
$$217 \text{ nm} \Rightarrow 217$$

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

one exocyclic double bond 05 nm  $\Rightarrow 5$

$$232 \text{ nm}$$

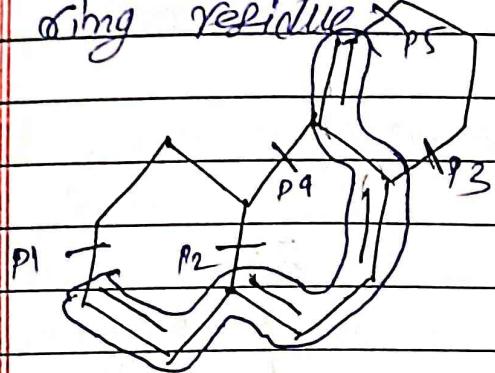
Ex = 108 Compute  $\lambda_{max}$



There is heterocyclic and homocyclic diene  
best we take homocyclic

Homoannular diene = 253 nm

rings residue



Homoannular diene = 253 nm

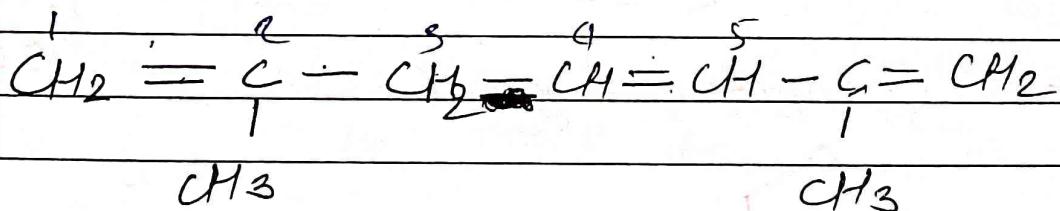
rings residue  $5 \times 5 = 25$

with 3 exocyclic double bond  $3 \times 5 = 15$

(Homoan) double bond extending conjugation  $= 2 \times 30 = 60$

$$\begin{array}{r}
 253 \\
 25 \\
 15 \\
 60 \\
 \hline
 353 \text{ nm}
 \end{array}$$

problem 1.5 Calculate  $\lambda_{\max}$



Acyclic diene Conjugated  $\lambda_{\max} = 217 \text{ nm}$

Two alkene sub  $2 \times 5 = 10$

~~exocyclic~~  $\geq 1$  double bond  $30 \times 1 = 30$   
double bond extending  $\geq$

217

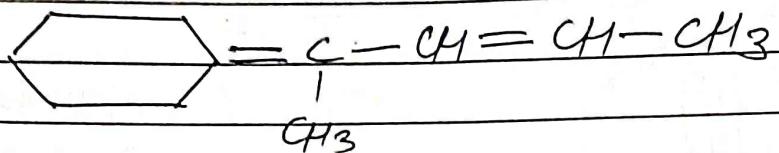
10

30

257 nm

Problem 106 Calculate  $\lambda_{max}$  for the following Compounds:

(i)



(ii)

Acyclic  $\Rightarrow 217 \text{ nm}$ 

217

10

(iii)

2 Alkyl Sub  $\Rightarrow 2 \times 5 = 10$ 

10

(iv)

2 ring residue  $\Rightarrow 2 \times 5 = 10$ 

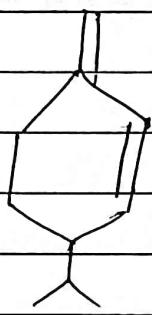
5

exocyclic double bond  $\Rightarrow 1 = 5$ 

5

 $242 \text{ nm}$  $\text{CH}_2$ 

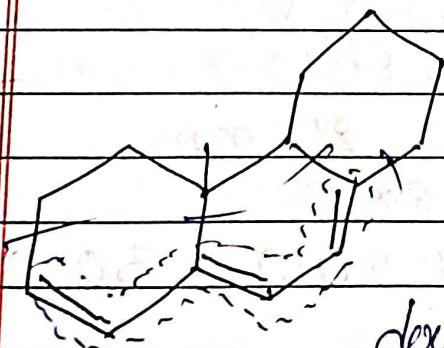
(v)

(i) heteroannular  $214 \text{ nm}$ (ii) ring residue  $\Rightarrow 2 = 2 \times 5 = 10$ (iii) one exocyclic double bond  $\Rightarrow 1 \times 5 = 5$ 

(iv) 214

10

5

 $289 \text{ nm}$ Problem 107  $\Rightarrow$  Compute  $\lambda_{max}$ Homoannular  $\Rightarrow 253 \text{ nm}$ 4 ring residue  $\Rightarrow 4 \times 5 = 20 \text{ nm}$ Two exocyclic double bonds  $\Rightarrow 2 \times 5 = 10$   
double bond extending(Homo)  
aromaticConjugation  $\Rightarrow 30 \times 1 = 30$ 

253

20

10

30

 $313 \text{ nm}$

## Application of IR Spectro

\* Factors affecting wave number value ( $\bar{\nu}$ ) or vibrational frequency

① Electronic Effect: Electronic effects include inductive effect, mesomeric effect, field effect etc. under the influence of electronic effects, force constant or the bond strength changes and its absorption frequency shifts from normal value. The introduction of a group which results into +I effect, causes lengthening or weakening of the bond hence the value of  $K$  is lowered and wave number of absorption decreases.

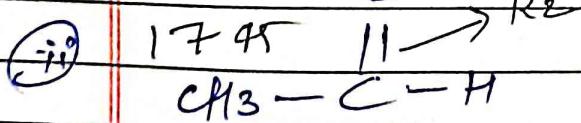
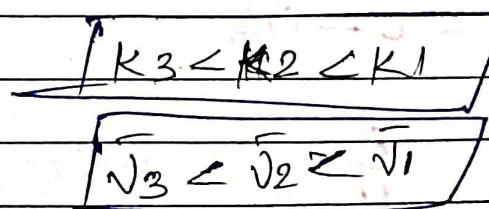
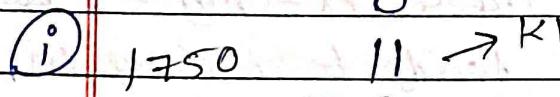
$50 - 12500 \text{ cm}^{-1} = \bar{\nu}$  range of IR region

polyatomic molecule + change in bonding

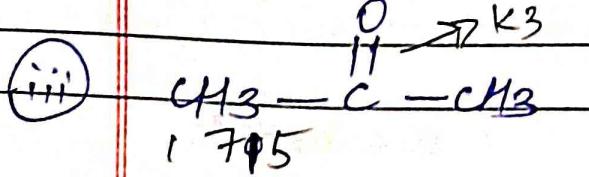
Sto effect  $\rightarrow$  Bonding

\* The wave no for  $C=O$  in  $HCHO, CH_3CHO$  and  $CH_3COCH_3$

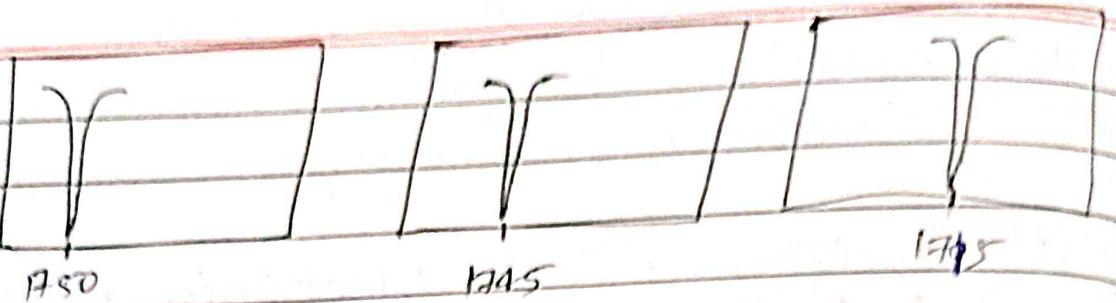
Ex  $\Rightarrow$  i)  $\bar{\nu} (HCHO) = 1750 \text{ cm}^{-1}$  is not same but it's  
 ii)  $\bar{\nu} (CH_3CHO) = 1745 \text{ cm}^{-1}$   $175, 178, 1715 \text{ cm}^{-1}$  Explain  
 iii)  $\bar{\nu} (CH_3COCH_3) = 1715 \text{ cm}^{-1}$



I+ effect leads to Decrease in  $\bar{\nu}$  wavenumber



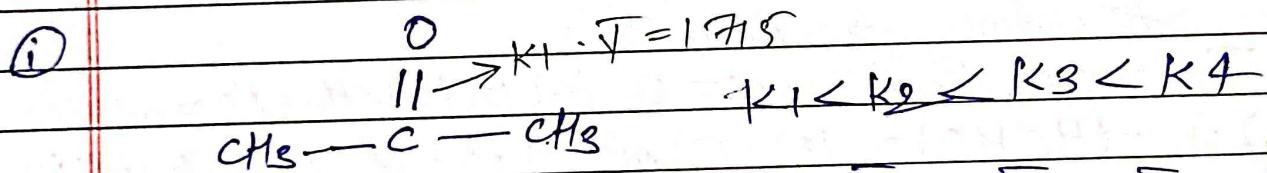
I- effect leads to increase in  $\bar{\nu}$



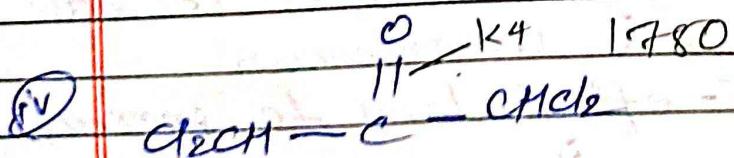
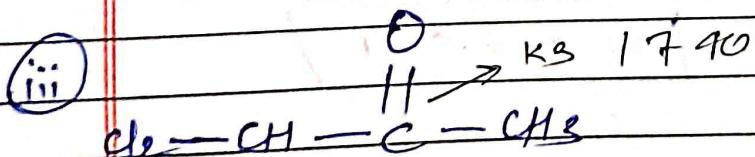
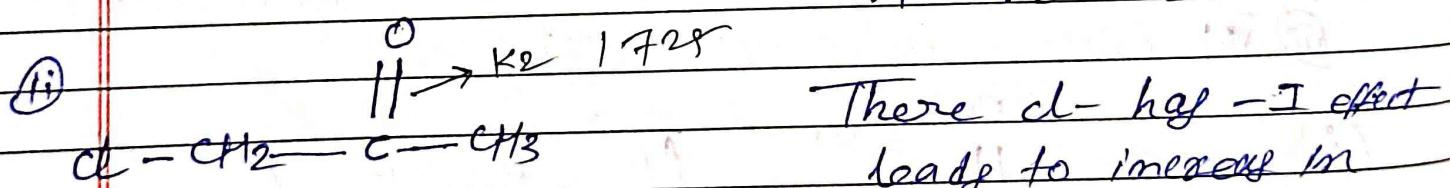
\* +I effect : It effect decreases in wave number and decreases Bond order and value of  $K$  hence  $\bar{v}$  also decrease.

\* -I effect : electron with drawing inductive effect which results into increase of bond order hence value of  $K$  increases. Hence  $\bar{v}$  also increases.

- Ex  $\Rightarrow$
- i)  $\text{CH}_3\text{COCH}_3$   $1715 \text{ cm}^{-1}$
  - ii)  $\text{ClCH}_2\text{COCH}_3$   $1725 \text{ cm}^{-1}$
  - iii)  $\text{Cl}_2\text{CHCOCH}_3$   $1740$
  - iv)  $\text{Cl}_2\text{CHCOCHCl}_2$   $1750$



$$\bar{v}_1 < \bar{v}_2 < \bar{v}_3 < \bar{v}_4$$

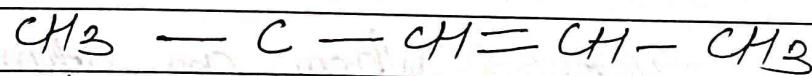
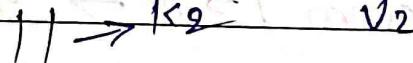
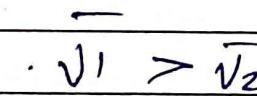


(2) Effect of conjugation : Conjugation leads decrease bond order and conjugation leads to decrease  $K$  value and hence conjugation leads to decrease wave number.

(i)



(ii)

 $\hookrightarrow$  conjugation $C=O$  bond order weakvalue of  $K$  decrease  
hence  $\bar{v}$  decreased

(3)

Hydrogen-bonding : Infrared technique is used to distinguish between two types of H-bonds  $\Rightarrow$  i) intermolecular ii) intramolecular H-bond  $\rightarrow$

additonal signal is of H-bond

H-bond

Conformational

H-bond

broad signal

intermolecular

H-bond

Sharp/intense signal

- \* Nuclear Magnetic Resonance or Magnetic Resonance Spectroscopy,  
or proton Magnetic Resonance → Also known as Radio frequency spectroscopy
- \* Magnetic nucleus = Charge + Spin → Magnetic

$n$	$p$	
odd	odd	$\rightarrow N \rightarrow$ magnetic
odd	even	$\rightarrow N \rightarrow$ magnetic
even	odd	$\rightarrow N \rightarrow$ magnetic
even	even	$\rightarrow N \rightarrow$ not magnetic

- \* Magnetic nucleus = When an atom acquires charge and produces nuclear spin, it is called Magnetic nuclei.

Ex) C :  $n = 6$  even       $p = 6$  even  $\rightarrow$  Not magnetic

13

C  $\rightarrow$  Magnetic

M  $\rightarrow$  simple possible nucleus Magnetic

H  $\rightarrow$  Simple possible nucleus Mag

$$\begin{array}{l} M \rightarrow \\ n=0 \\ p=1 \end{array}$$

- \* Nucleus of a hydrogen atom is called a proton as it has only one proton in it.

∴ The nucleus of a hydrogen atom is called a proton as it has only one proton in it.

\* What is precessional motion?

$\Rightarrow$  A form of motion that occurs when a torque is applied to a rotating body in such a way that it tends to change the direction of its axis of rotation like : earth

Precessional motion & external mag field

$$\boxed{\nabla \times H_0}$$

\* CH<sub>4</sub>

C	$\rightarrow$	Magnetic
H	$\rightarrow$	Magnetic
O	$\rightarrow$	Magnetic

Step 1

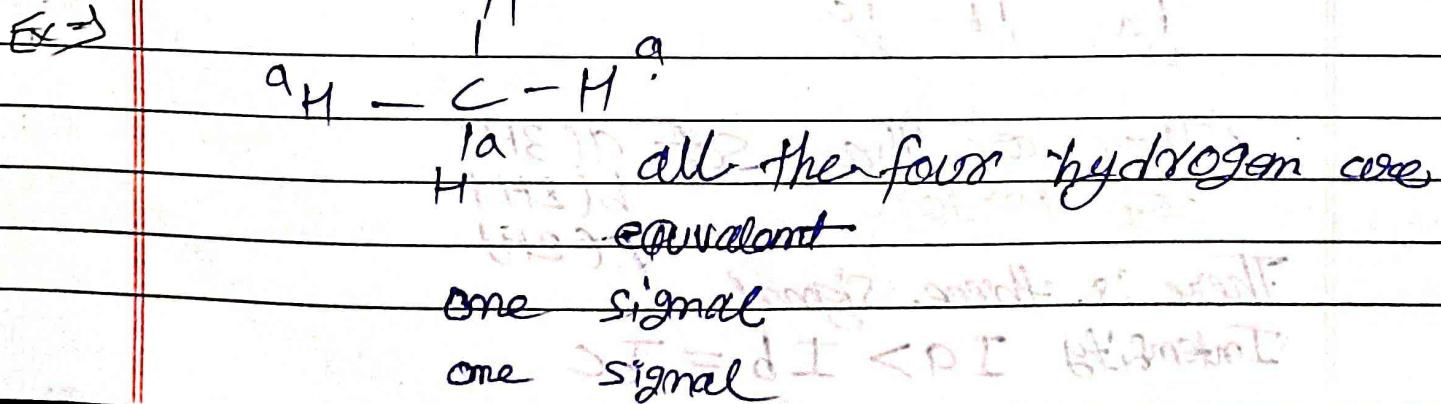
\* Chemical environment

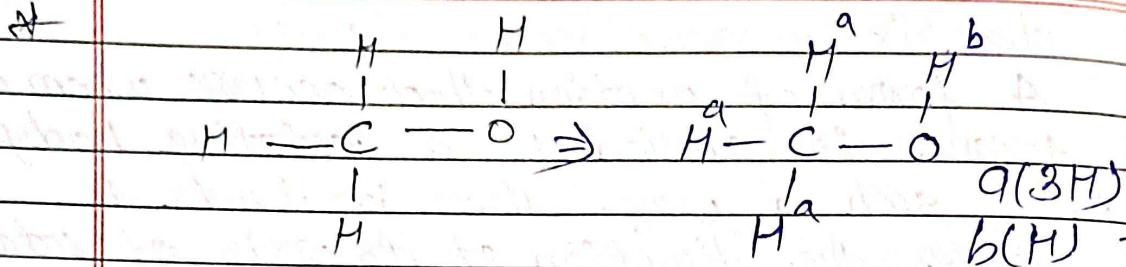
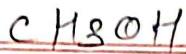
Same  $\rightarrow$  equivalent

not same  $\rightarrow$  not equivalent

2 \* Number of signal = n of different sets of protons

3 \* The intensity of signal  $\propto$  number of hydrogens or number of hydrogens in that set

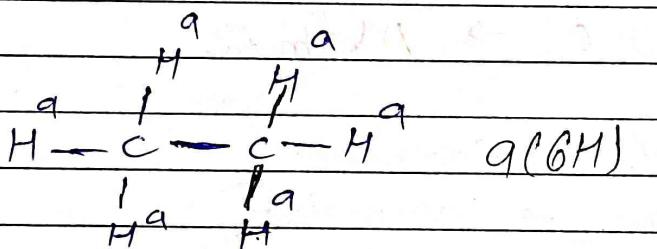
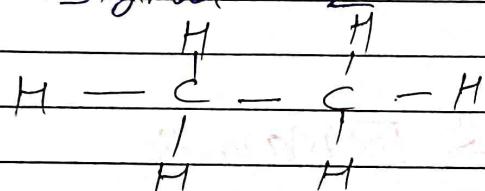




There are two set of proton  $a, b$

$a(3\text{H}) \rightarrow$  equivalent | Intensity  $I_a > I_b$   
 $b(\text{H}) \rightarrow$  No equivalent

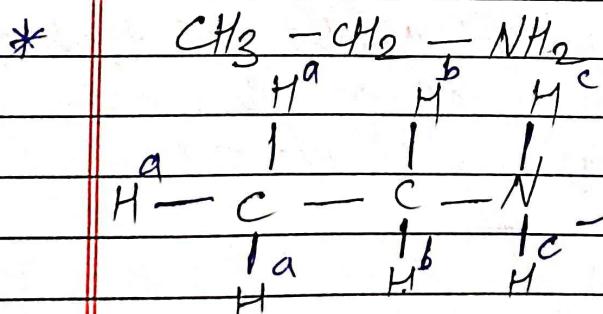
signal  $\rightarrow 2$



There all are equivalent

There is one set of proton  $a(6\text{H})$

There is one signal



because  
me

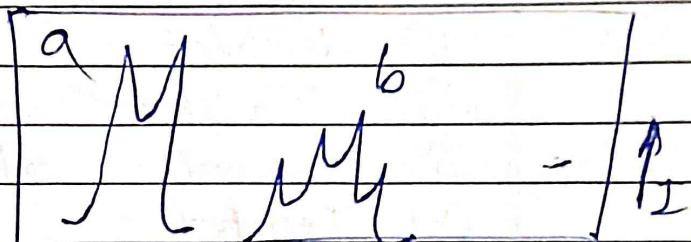
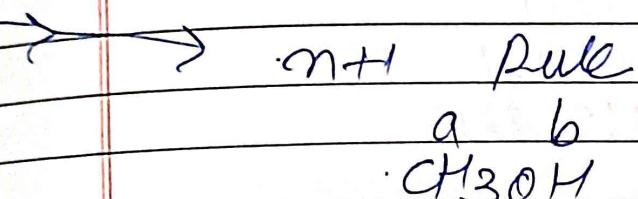
There are Three set  $a(3\text{H})$   
of proton

$b(2\text{H})$   
 $c(2\text{H})$

There is three signal

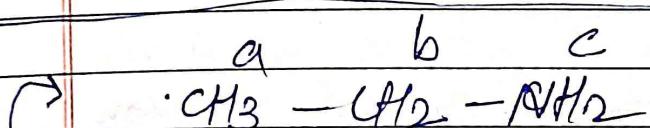
Intensity  $I_a > I_b = I_c$

\*  $\text{PMR} \rightarrow \text{Proton nuclear magnetic resonance}$   
 proton magnetic resonance is the part of Nuclear Magnetic Resonance for Hydrogen



for a  $\rightarrow n=1, n+1=2$  doublet

for b  $\rightarrow n=3, n+1=4$  quartet.



for a,  $n=2, n+1=3$

Triplet signal

for c,  $n=2, n+1=3$

Triplet signal  
 i.e.  $2^0$  of a singlet is  $(n_1+1)(n_2+1)$  times it,

for b  $\rightarrow n_1=3$   ~~$= 3+1$~~   $(n_1+1)(n_2+1)$

because two there  $n_2=2$   
 neighbours

$$n_1 = 3 \quad (3+1)(2+1)$$

$$= 12 \text{ signals}$$

There is multiplet signal with 12 peaks

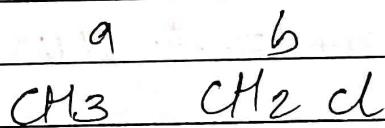
## ~~Principle of M.R.S.~~

### Multiplet

#### Type of signal

- i) singlet  $\rightarrow 1:1$
- ii) doublet  $\rightarrow 1:2:1$
- iii) Triplet  $\rightarrow 1:3:3:1$
- iv) quartet  $\rightarrow 1:4:6:4:1$
- v) Pentet

\*  $n+1$  Rule



for 'a' set  $n = n/8$  no of proton  
presence on the methine atom

$$n = 2$$

$$n+1 = m = 2+1$$

$$n = 3$$

n of Peaks of the signal is 3  
 $1:0 =$  triplet

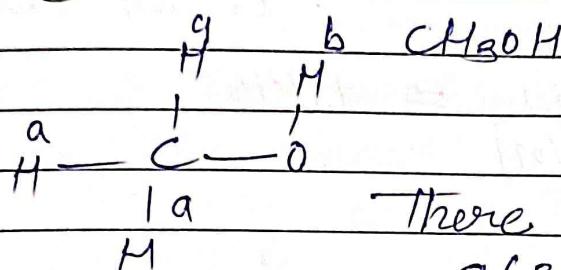
for 'b' set

$$n = 3$$

$$n = n+1$$

$$n = 4$$

no of peaks in the signal is 4  
i.e. signal quartet



There are two sets of protons  
 $a(3H)$   $\rightarrow$  equivalent  
 $b(1H)$   $\rightarrow$  Not equivalent

signal = 2

Intensity  $I_a > I_b$

$n+1$  rule  $\rightarrow$  for  $a \doteq n=1$   $n+1=2$

[doublet]

for  $b \rightarrow n=3$   $n+1=4$

[quartet]

Note :-

left

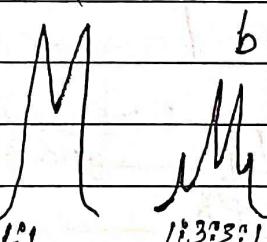
a-

right

first Intensity

2:1:0:1 0:1:1:0:1

left side  $\rightarrow$  strong



Here  $I_a > I_b$

\* proton is exposed to a magnetic field ( $H_0$ ),  
two energy state are possible.  $I = -\frac{1}{2}$

Energy is more  $\rightarrow$  aligned against = unstable  $E_2$   
flipping  $\downarrow$  E

Energy is less  $\rightarrow$  aligned with = stable  $E_1$   
 $I = +\frac{1}{2}$

Energy of proton  $\Rightarrow E = -KI'Ho$   
 $\hookrightarrow$  spin orientation

$$\Delta E = E_2 - E_1 = \pm I K H_0$$

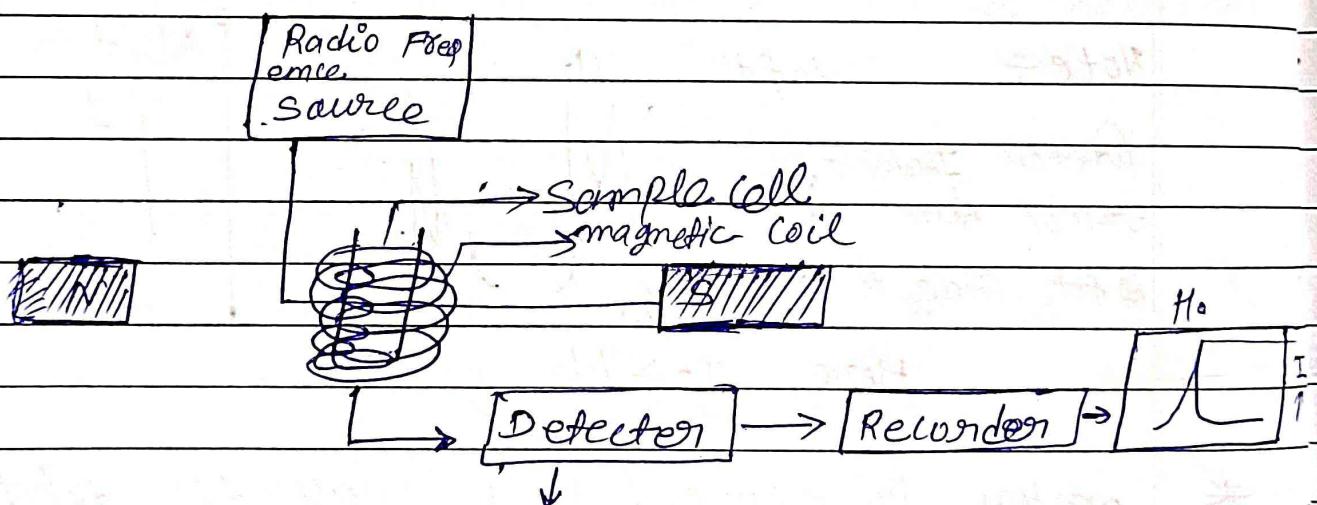
$$\Delta E = \pm K H_0 I$$

$$I = +\frac{1}{2}, -\frac{1}{2}$$

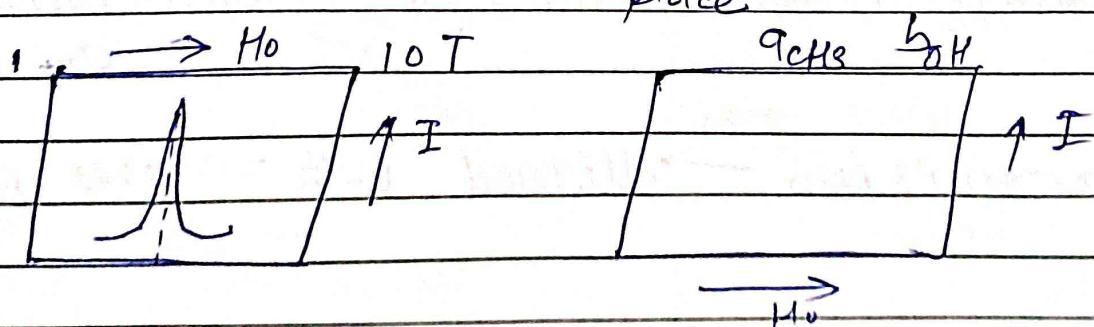
$$I' = +\frac{1}{2}, E_1 = -\frac{1}{2} \cdot K H_0$$

$$I' = -\frac{1}{2}, E_2 = +\frac{1}{2} K H_0$$

\* At some  $H_0$  resonance between sample and energy source then abs. of energy  $\Rightarrow$  flipping of proton.  $E_1$  to  $E_2$



Detector detects the  $H_0$  value at which flipping takes place.



## Shielding & deshielding

magnetic field experienced by the proton  
(magnetic nucleus)

External magnetic field

shielding of proton from External  
magnetic field

Up field shift :

Higher value of external magnetic field  
is to be applied to proton for its  
flipping is called up field shift

shielding is directly proportional to  $n$  or  
electron density

shielding leads to up field shift

\* Magnetic field experienced by the proton (magnetic  
field)  $>$  Applied External magnetic field ( $H_0$ )

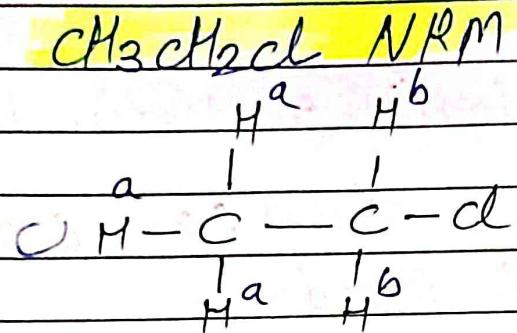
deshielding of proton from external magnetic  
field

\* down field shift : lower value of external  
magnetic field is to be applied to  
proton for the flipping is called Down field  
shift.

deshielding &  
electron density

deshielding leads to down field shift

\* Discuss & and explain  $\text{CH}_3\text{CH}_2\text{Cl NMR}$ .  
nucleus.



① Set of proton = 2

i) a (3H)  $\rightarrow$  equivalent

ii) b (2H)  $\rightarrow$  not equivalent

② No of signal = two = 2

③ Intensity of signal = Ia > Ib

because a set has more proton than b

④ n+1 rule  $\rightarrow$  for Set a (3H)  $n = 2$

$$\therefore n+1 = 2+1 = 3$$

Signal  $\rightarrow$  triplet signal with three peaks  
 $1:3:3:1$

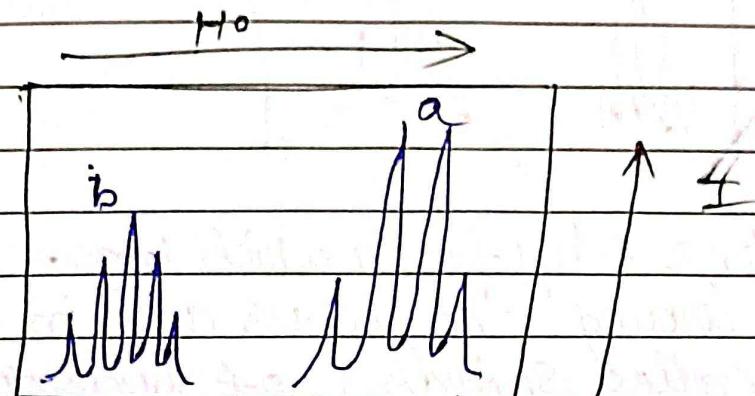
for Set b (3),  $n = 3$

n+1 rule  $\rightarrow n+1 \Rightarrow 3+1 = 4$   
 signal quartet  $1:4:6:4:1$   
 signal with four peaks

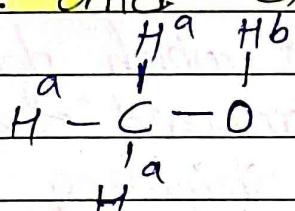
⑤ Position of signal :

shielding for a  $\rightarrow$  up field shift because a is away from chlorine.

deshielding for b  $\rightarrow$  down field shift because b is near from chlorine.



\* Discuss and explain  $\text{CH}_3\text{OH}$  NMR nucleus.



① Sets of protons  $\rightarrow$  2

a(3H)  $\rightarrow$  equivalent

b(1H)  $\rightarrow$  not equivalent

② Intensity  $\therefore I_a > I_b$  because a has more proton than b

③ No. of signals  $\rightarrow$  Two

④  $n+1$  rule  $\rightarrow$  for a,  $n=1 \rightarrow n+1=2$

doublet  $\rightarrow 1:2:1$

for b  $\rightarrow n=3, n+1=3+1=4$

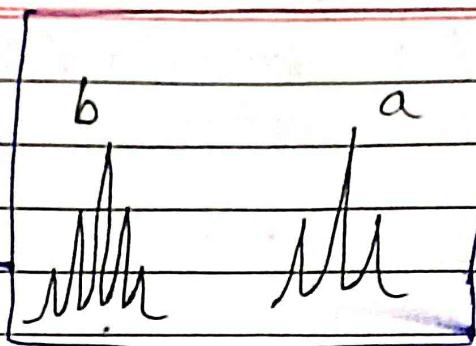
quartet  $\rightarrow 1:4:6:4:1$

⑤ Position of electrons  $\therefore$  Shielding for a  $\rightarrow$  up field shift because a has more electron density as compare to b  
deshielding for b  $\rightarrow$  down field shift because b has less electron density as compare to a

D.F.S

 $\xrightarrow{H_0}$ 

U.F.S

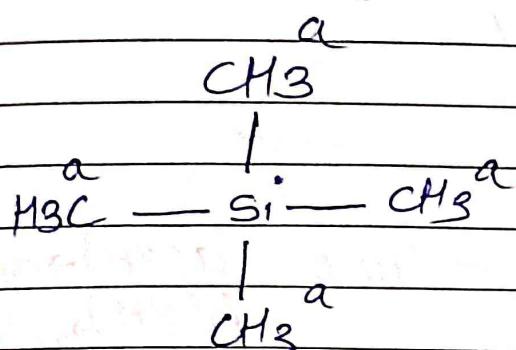


- \* Shielding : Any factor which increase the electron density around the nucleus and increase it's shielding this is called shielding of nucleus . Shielding is directly proportional to electron density and shielding leads to up field shift .
- \* Deshielding : Any factor which decrease of the electron density around the nucleus and decrease it's shielding ~~is~~ they is called deshielding of nucleus . Deshielding is indirectly proportional to electron density and deshielding leads to down field shift .
- \* Up field shift : Higher value of external magnetic field is to be applied to proton for the flipping is called up field shift .
- \* Down field shift : lower value of external magnetic field is to be applied to proton for the flipping is called up field shift .
- \* Chemical shift : It is the distance between of the signal of sample from the signal of TMS . chemical shift is represented by  $\delta$  , It's unit is ppm ; chemical shift increase towards left .

+

## Chemical Shift

Tetra methyl Silane (TMS)



character

property

i) Inert gas

i) Does not react

ii) Volatile (विस्फुल)

ii) Evaporates on its own

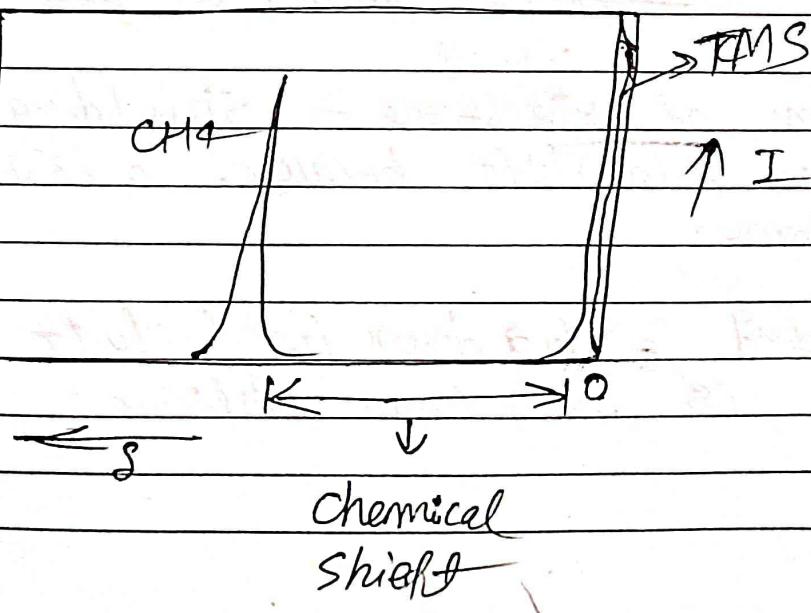
iii) 12 equivalent protons

iii) One signal with high Integrity

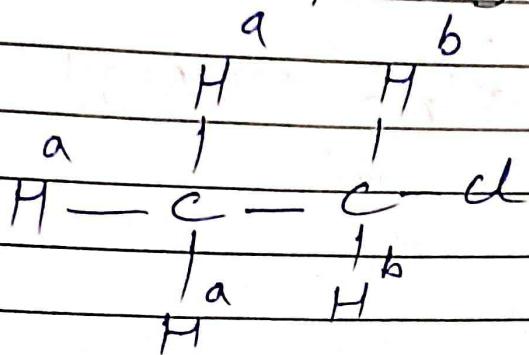
iv) Maximum shielding of proton

iv) Maximum up field shift

$\rightarrow H_0$



\* Draw NMR of  $\text{CH}_3\text{CH}_2\text{Cl}$



- 1 no of sets of proton = Two  $a(3H) \rightarrow$  equivalent  
 $b(2H) \rightarrow$  non-equivalent

- ② No of signal = 2

- ③ Intensity of signal =  $I_a > I_b$  because a set has more proton than b

- ④  $n+1$  rule  $\rightarrow$  for set  $a \rightarrow n=2$

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

Signal Triplet with three peaks

~~183031~~ 10201

for set b  $\rightarrow n=3$   $n+1 = 3+1 = 4$

~~Partlet~~ 1:3:3:1

~~transient~~ with four peaks

## signals

- ⑤ position of ~~chlorine~~ : shielding for a  $\rightarrow$  up field shift because a is away from chlorine.

deshielding for  $\delta \rightarrow$  down field shift because  
 $\alpha$  is near from chlorine.

Down field shift

 $H^0$ 

Upfield shift

TMS

I

a

b

b

a

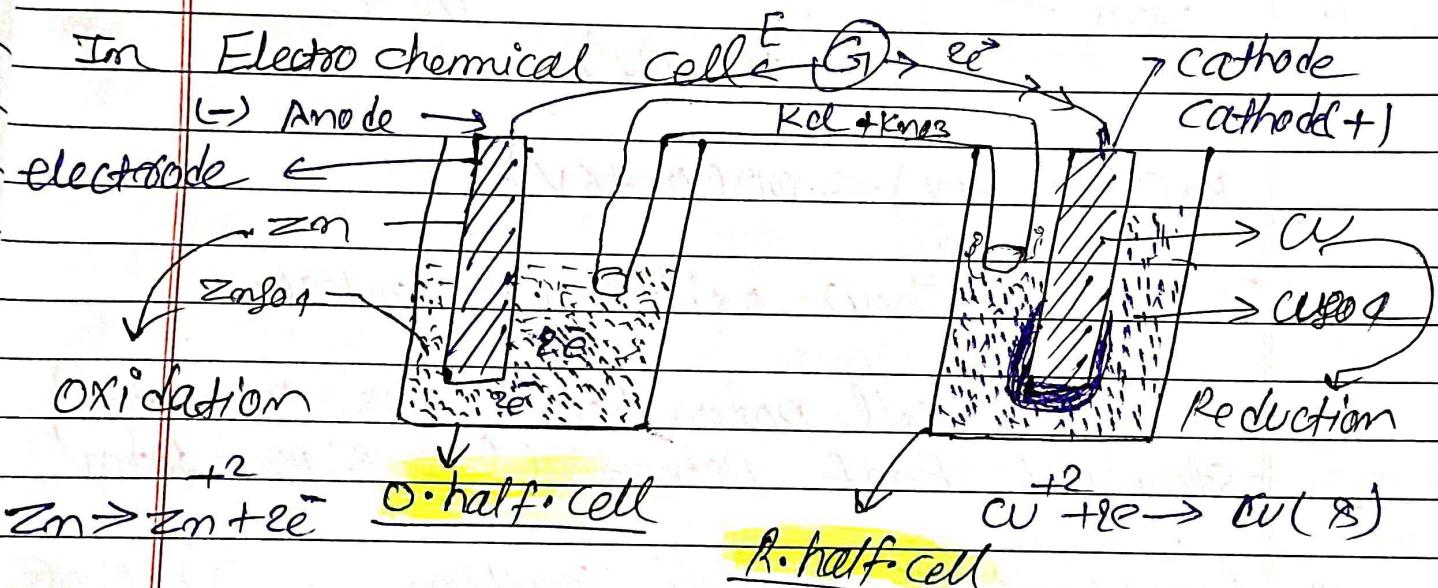
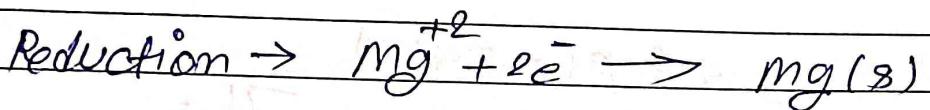
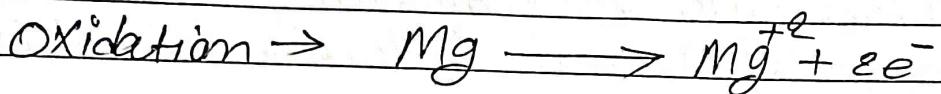
S

 $\delta_b > \delta_a$

## Chapter - 5

(उत्तमिका) Oxidation  $\rightarrow$  loose of electrons (संकरित विचार)

(उत्तमिका) Reduction  $\rightarrow$  gain of electrons (संवर्धित विचार)



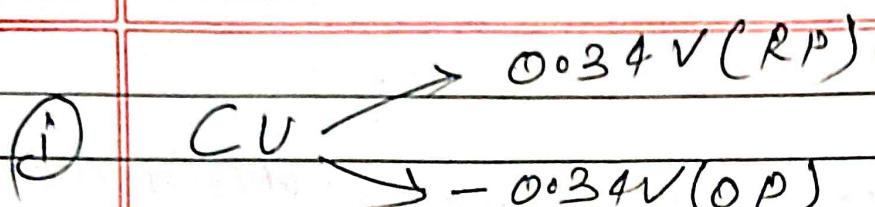
Electrode potential  
oxidation potential      reduction potential

Note :-

$$\text{Oxidation potential} = -\text{Reduction potential}$$

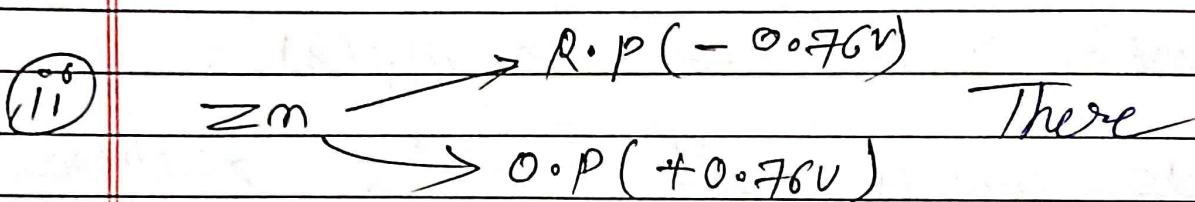
$$\text{Reduction potential} = -\text{Oxidation potential}$$

Note :- In any element if we compare both in terms of potential then if Reduction potential is more than Oxidation potential there will be Reduction potential if Oxidation potential is more than Reduction potential then will be Oxidation potential.



$$0.34(RP) > -0.34(OP)$$

There will be Reduction potential. It means Cu will show Reduction potential.



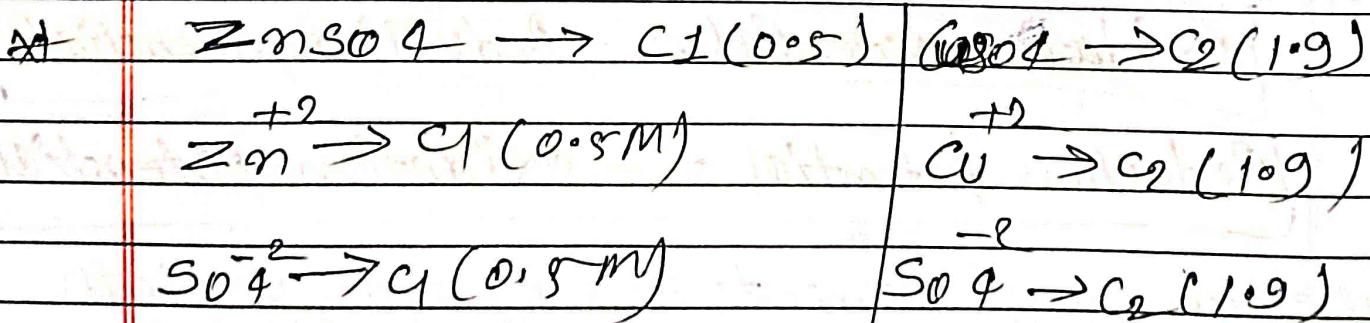
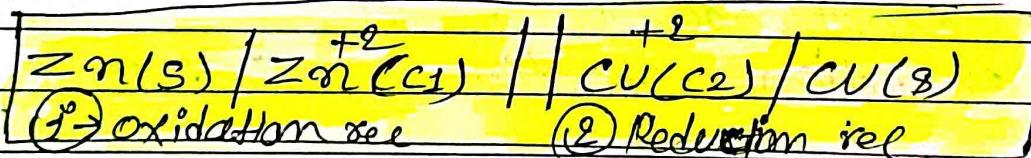
$$R.P (-0.76V) < O.P (0.76V)$$

will

There  $Zn^+$  show oxidation potential.

Standard cell potential ( $T=25^\circ$   $P_{O_2} = 1\text{ atm}$ )  
 Standard Emf potential ( $T=25^\circ$   $P_{O_2} = 1\text{ atm}$ )

### \* Representation of Cell reaction



Note  $\rightarrow$  Electrode Potential = Emf ] = cell potential  
 $SEP = E^\circ$

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\* Note  $\therefore E^\circ_{Zn}, Zn^{+2} = 0.76$

$\downarrow$   
oxidation reaction so that the given value of  $Zn$  that is  $0.76$  is  $SOP = 0.76$   
 $E^\circ_{Ag, Ag^+} = -0.80V$

$E^\circ_{Ag, Ag^+} \rightarrow$  oxidation reaction so that the given value of  $Zn$  that is  $(-0.80V)$

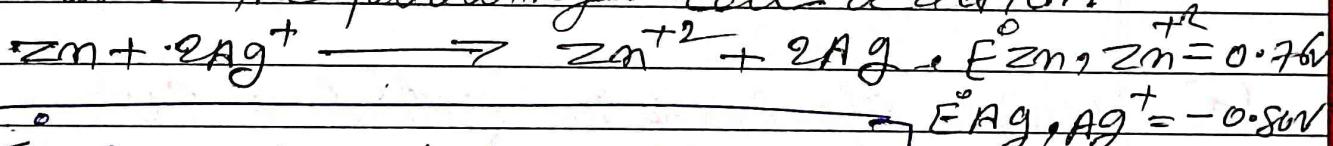
Oxidation real + Reduction real  $\rightarrow$  Redox Reac

Note  $\therefore$  First Reduction Potential of cathode

\* formula

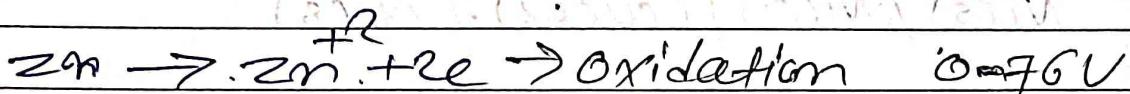
Std Emf = SRP Cathode - SRP anode

\* Calculate the std emf of a cell which involves the following cell reaction

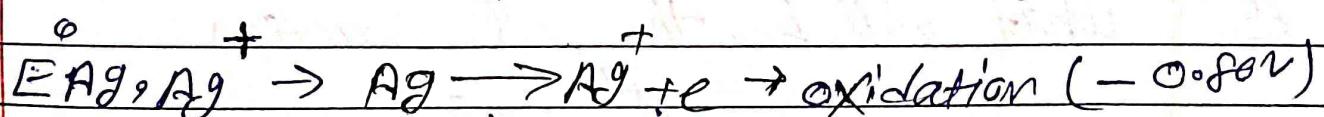


ans  $\Rightarrow$  Emf = SRP cathode - SRP anode

$E^\circ_{Zn, Zn^{+2}} = 0.76V$  /  $Zn \rightarrow$  anode  
 $Ag \rightarrow$  cathode



Std Reduction Potential  $(-0.80V)$



Std Reduction P  $\Rightarrow +0.80V$

$$\text{Emf} = (0.80) - (-0.76V)$$

$$= 0.80 + 0.76$$

$$= 1.56V$$

\* A cell is prepared by dipping Cu rod in one molar  $\text{CuSO}_4$  solution and Ni rod in 1 molar  $\text{NiSO}_4$  soln. The SRP of Cu is  $0.34\text{ V}$  and SRP of Ni is  $-0.28\text{ V}$

- (a) which electrode is cathode
- (b) Representation of cell
- (c) what will be the cell reaction
- (d) Calculate std emf of the cell.

Sol:

1M  $\text{CuSO}_4$

1M  $\text{NiSO}_4$

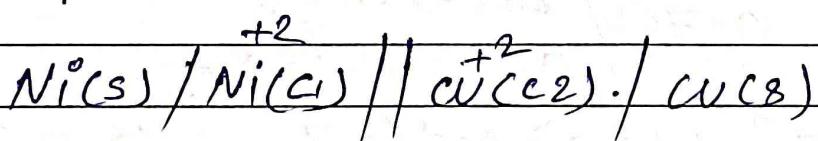
SRP of Cu =  $0.34\text{ V}$

SRP of Ni =  $-0.28\text{ V}$

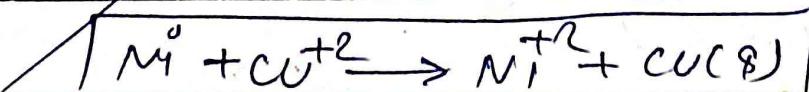
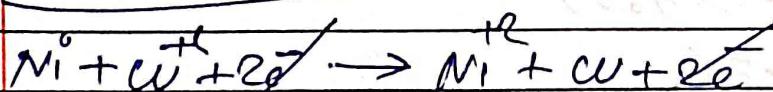
SRP of Cu > SRP of Ni  $\therefore$  it means  
 $\text{Cu} \rightarrow \text{cathode}$

- (a) which electrode is cathode  $\rightarrow$  Cu

- (b) Representation of cell  $\rightarrow$



- (c) what will be the cell reaction



Q) Calculate std emf of this cell :-

$$\text{E}_{\text{cell}} = \text{SRP (cathode)} - \text{SRP of anode}$$

$$\text{Emf} = 0.34 - (-0.28 \text{ V})$$

$$\text{Emf} = 0.34 + 0.28 \text{ V}$$

$$\boxed{\text{Emf} = 0.62 \text{ V}}$$

Note : Now, we found Emf  $\rightarrow$  standard Emf but if we will find have to find only Emf than we use Nernst equation

$$E = E^{\circ} - \frac{0.0591}{n} \log \left[ \frac{P_x}{P_y} \right]$$

Where  $n \rightarrow$  no of electron

$P \rightarrow$  Product

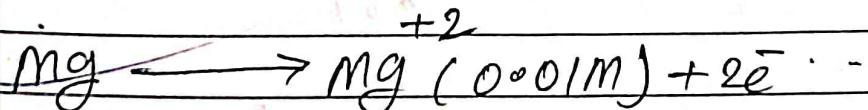
$R \rightarrow$  Reactant

$x \rightarrow$  no of coefficient with product

$y \rightarrow$  no of coefficient with reactant

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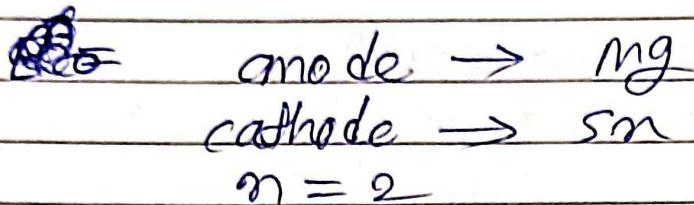
\* calculate Emf of the following



$$\begin{array}{l} \text{E}^{\circ} \text{ Mg, Mg}^{+2} = 0.34 \text{ V} \rightarrow \text{SOP} \\ \text{F}^{\circ} \text{ Sn}^{+2}, \text{Sn} = -0.136 \text{ V} \rightarrow \text{SRP} \end{array}$$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[P]_y}{[P]_x}$$

$$E^\circ = SRP_{\text{cathode}} - SRP_{\text{anode}}$$



$$SOP \text{ of } Mg = 2.34V$$

$$\text{so that } SRP \text{ of } Mg = -2.34V$$

$$SRP \text{ of } Sn = -0.1366V \Rightarrow -0.136V$$

$$E^\circ = (-0.136) - (-2.34)$$

$$E^\circ = -0.136 + 2.34$$

$$E^\circ = 2.204$$

so that Nernst eq<sup>n</sup>

$$E = 2.204 - \frac{0.0591}{2} \log \frac{[Mg]^+ [Sn]}{[Mg]^2 [Sn^{2+}]}$$

$$E = 2.204 - \frac{0.0591}{2} \log \frac{[0.01][1]}{[1][0.1]}$$

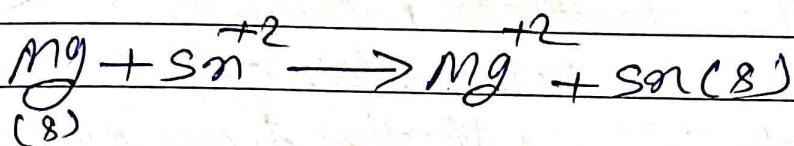
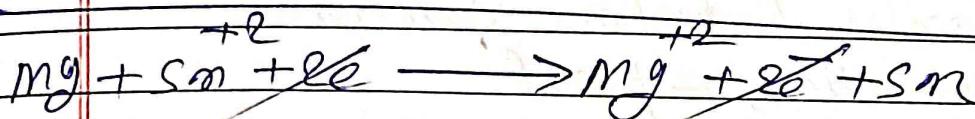
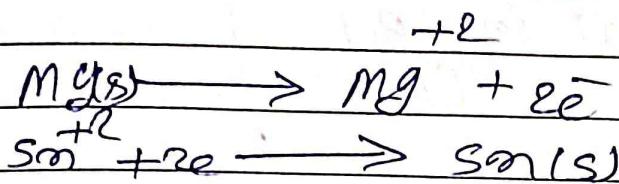
$$E = 2.204 - \frac{0.0591}{2} \log \frac{0.01}{0.1}$$

$$E = 2.204 - \frac{0.0591}{2} \times (-1)$$

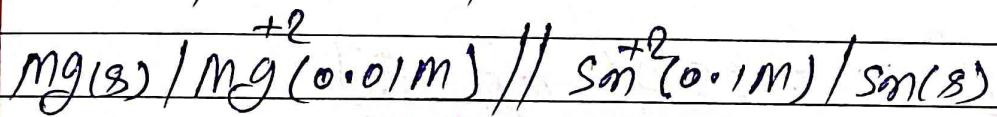
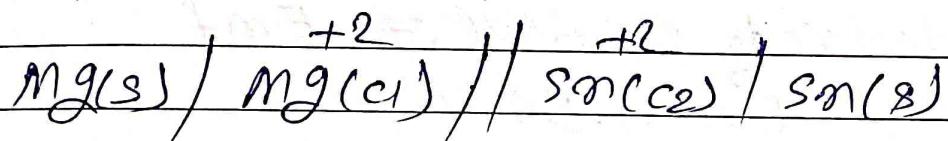
$$E = 2.204 - 0.0591 \Rightarrow E = 2.234V$$

(a) which is cathode  $\rightarrow \text{Sn}$

(b) cell reaction



(c) representation of cell :-



\* calculate the electrode potential of copper wire electrode dipped in 0.1M  $\text{CuSO}_4$  solution at  $25^\circ$  given reduction potential of Cu electrode is  $0.310\text{V}$ .

Ans  $\Rightarrow$  Given value of  $\text{Cu}^{+2}(0.1\text{M})$

~~Impact player  
Surprise  
But is it~~

~~0.10  
100  
1/10~~

~~②~~

~~③~~

Nernst equation for Half cell reaction

$$E = E^{\circ} - \frac{0.0591}{\infty} \log \left[ \frac{P}{R} \right]$$

Take only Reduction reaction

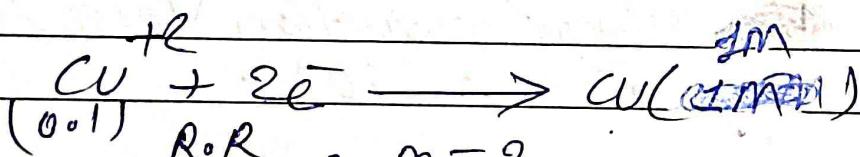
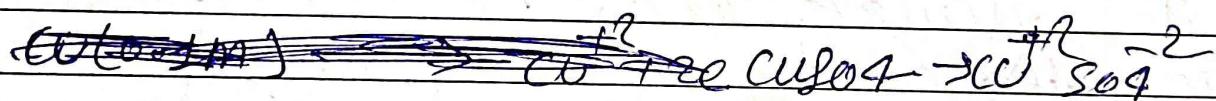
Electrode potential, = Emf

\* Calculate the electrode potential of a copper wire dipped in 0.1 molar copper sulphate solution at 25°C. At this temperature, the standard electrode potential of copper is 0.31 volt.

electrode potential =  $E_{m.f}$

$$E = 0.39 \text{ V}$$

$$E = E^{\circ} - \frac{0.0591}{n} \log \left[ \frac{P}{R} \right]$$



$$R = e^{+l} (\cos l)$$

$$P = C_U(\overline{1M})$$

$$F = 0.34 - \frac{0.0591}{2} \log \frac{0.1}{0.1}$$

$$E = 0.39 - \frac{0.059}{z} x + 1$$

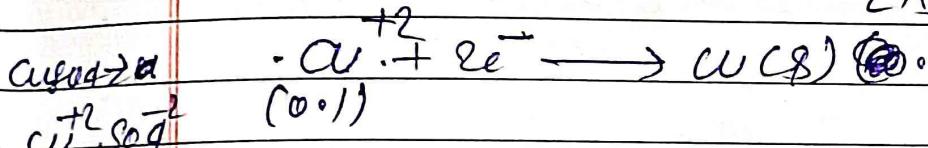
$$F = 0.34 + 0.02955$$

$$F = 0.31048 \text{ volt}$$

\* calculate the standard electrode potential of a Cu electrode dipped in 0.1 M CuSO<sub>4</sub> sol at 25°C if the electrode potential of what =? Reduction potential of Cu = 0.310 V electrode.

ans  $\Rightarrow E = E^{\circ} - \frac{0.0591}{2} \log \frac{P}{[R]}$

$$E^{\circ} = E + \frac{0.0591}{2} \log \frac{P}{[R]}$$

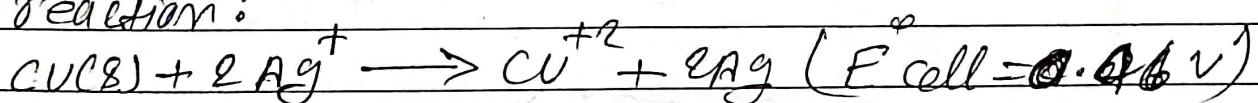


$$E^{\circ} = 0.310 + \frac{0.0591}{2} \log \frac{1}{0.1}$$

$$E^{\circ} = 0.310 + 0.02955$$

$$\boxed{E^{\circ} = 0.33955 \text{ volt}}$$

\* calculate the equilibrium constant for the reaction:



ans Note ∵ at equilibrium  $[E = 0]$   $\log \frac{P}{R} = \log K$

$$E^{\circ} = E^{\circ} - \frac{0.0591}{2} \log K$$

$$0 = 0.46 - \frac{0.0591}{2} \log K$$

$$0 = 0.46 - 0.02955 \log K \Rightarrow 0.02955 \log K = 0.46$$

~~$$\log K = \frac{0.46}{0.02955} = 15.56$$~~

$$K = \text{antilog } 15.5668 \text{ or } 1.368 \times 10^{15}$$

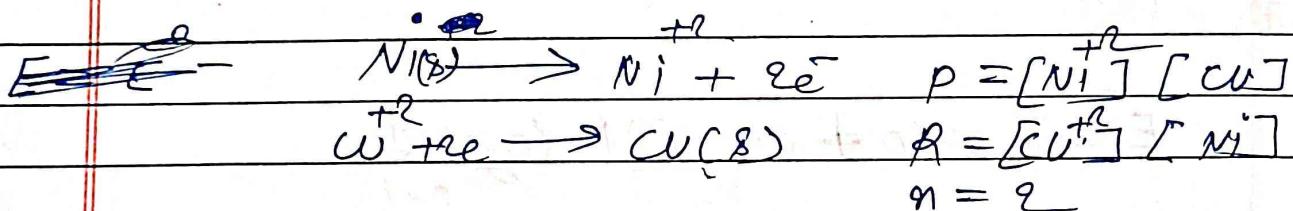
\* Calculate the standard electrode potential of  $\text{Ni}^{+2}/\text{Ni}^{\circ}$  electrode if the cell potential of the cell:  $\text{Ni}^{\circ}/\text{Ni}^{+2}(0.01\text{M})/\text{Cu}^{+2}(0.1\text{M})/\text{Cu}^{\circ}$  is  $0.59\text{V}$ . Given:  $E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} = 0.34\text{V}$

$$\text{Given } E^{\circ} = 0.34\text{V}$$

∴  $E^{\circ}$  of  $\text{Ni}^{\circ}$  = ?

$$E^{\circ} = \text{SRP of cathode} - \text{SRP of anode}$$

$$\therefore \text{Nernst eqn} \Rightarrow E^{\circ} = E^{\circ} - \frac{0.0591}{2} \log \left[ \frac{P_{\text{Cu}}}{P_{\text{Ni}}} \right]$$



$$0.34 = E^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Ni}^{\circ}][\text{Cu}]}{[\text{Cu}^{+2}][\text{Ni}^{\circ}]}$$

$$0.34 = E^{\circ} - \frac{0.0591}{2} \log \frac{0.01}{0.1} \times 1$$

$$0.34 = E^{\circ} - \frac{0.0591}{2} \log \frac{0.01}{0.1}$$

$$0.34 = E^{\circ} - \frac{0.0591}{2} \times -1$$

$$0.34 = E^{\circ} + \frac{0.0591}{2}$$

$$E^{\circ} = 0.34 - 0.02955$$

$$E^{\circ} = 0.31045\text{V}$$

End

So that  $E^{\circ}$  for  $\text{Ni}^{\circ}$

$$E = SAP_{\text{cathode}} - SRP_{\text{anode}}$$

$$0.31045 = 0.34 - SRP_{\text{anode}}$$

$$SRP_{\text{anode}} = 0.34 - 0.31045$$

$$[SAP_{\text{anode}} = 0.02955]$$

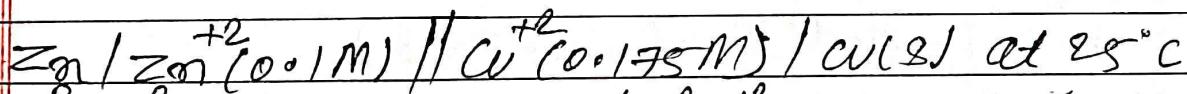


$$E = SRP_{\text{cathode}} - SRP_{\text{anode}}$$

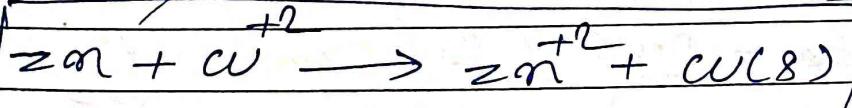
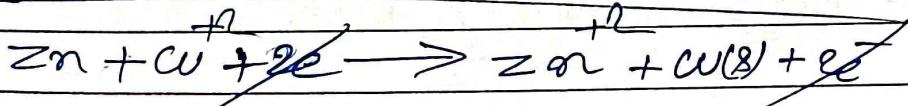
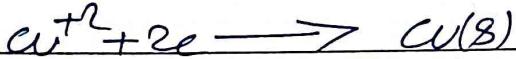
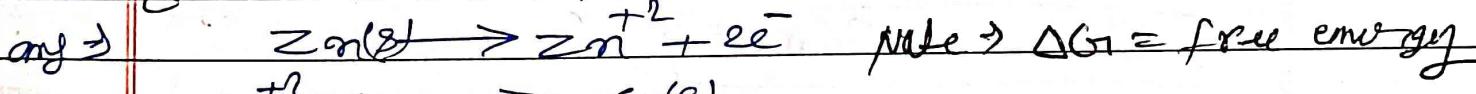
$$R = 0.34 - 0.02955$$

$$E \text{ of Ni} \Rightarrow 0.31045^\circ V$$

\* Write down the cell reaction of following cell



$$E_{Zn^{+2}/Zn} = -0.76V \text{ and } E^\circ_{Cu^{+2}/Cu} = 0.34V, \text{ calculate } \Delta G_f$$



$$\Delta G_f = -m.f E_{\text{cell}} \quad E^\circ = (0.34) + (-0.76V)$$

$$E^\circ = 1.10 V$$

$$E = 1.10 - \frac{0.0591}{2} \log \frac{0.1}{0.175} \quad \left. \right\} \Delta G_f = -2 \times 96500 \times 1.107$$

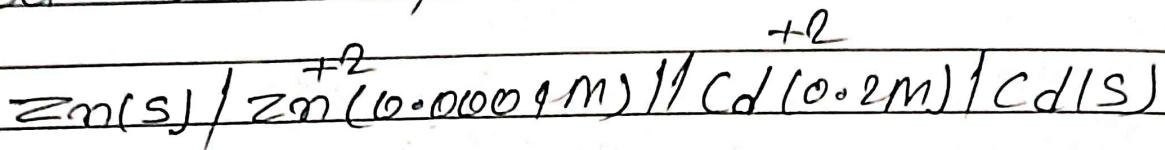
$$E = 1.10 + 0.00718$$

$$[E = 1.107 V]$$

$$\Delta G_f = -213681 \text{ kJ/mol}$$

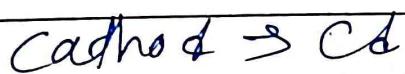
#

Calculate the cell emf and the value of free energy change for the cell reaction at  $25^\circ\text{C}$  for the cell:



$E^\circ$  value at  $25^\circ\text{C}$ :  $\text{Zn}^{+2}/\text{Zn} = -0.763\text{V}$ ;  $\text{Cd/Cd} = -0.403\text{V}$

$$E = \text{SRP cathod} - \text{SRP of anode} \quad \text{Zn} \rightarrow \text{Zn}^{+2} + 2e^-$$



$$\text{SRP of Cd} = -0.403\text{V}$$

$$\text{SRP of Zn} = -0.763\text{V}$$

$$E^\circ = [-0.403] - (-0.763)$$

$$E^\circ = -0.403 + 0.763$$

$$E^\circ = 0.360\text{V}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{P}{[R]}$$

$$E = 0.360 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{+2}][\text{Cd}]}{[\text{Zn}][\text{Cd}^{+2}]}$$

$$E = 0.360 - \frac{0.0591}{2} \log \frac{0.0001}{0.2}$$

$$E = 0.36 - 0.02955 \times -2.69897$$

$$E = 0.36 + 0.07975$$

$$E = 0.439754\text{V}$$

## Thermodynamic functions

\* change in Gibbs free energy =

$$\boxed{\Delta G_1 = -nFE}$$

\* change in Entropy  $\Rightarrow \boxed{\Delta G_1 = -nFE}$  KJ/mol

\* change in Entropy  $\Rightarrow \Delta S = -\left(\frac{d\Delta G_1}{dT}\right) \times$

$$\text{or } \boxed{\Delta S = nF\left(\frac{dE}{dT}\right)}$$

$$\boxed{T\left(\frac{dE}{dT}\right) = \frac{E_2 - E_1}{T_2 - T_1}}$$

Enthalpy  $\Rightarrow \boxed{\Delta H = nFT\left(\frac{dE}{dT}\right) - nFE}$  KJ/mol

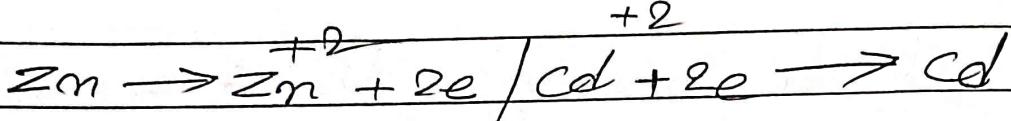
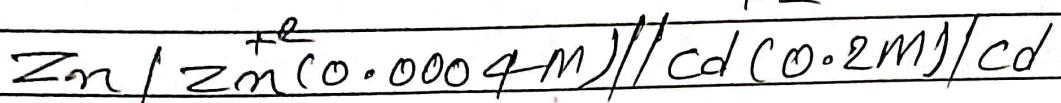
\*  $\boxed{\Delta G_1 = \Delta H - T\Delta S}$

\*  $\boxed{\Delta G_1 = -nFE}$   $\boxed{\Delta G_1 = \Delta H - T\Delta S}$  KJ/mol

$$\boxed{\Delta S = nF\left(\frac{dE}{dT}\right)} \text{ JK}^{-1}\text{mol}^{-1}$$

$$\boxed{\Delta H = nFT\left(\frac{dE}{dT}\right) - nFE}$$

\* Calculate the value of  $\Delta G_f$  or free energy change involved in the following cell reaction at  $25^\circ C$

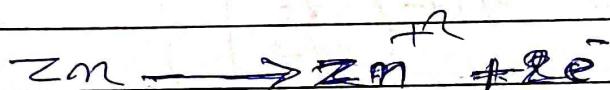


$$\Delta G_f = -nFE$$

$$F = 96500 \text{ C}$$

$$\boxed{\Delta G_f = -nFE_{cell}}$$

$$\boxed{F = 96500 \text{ C}}$$



$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Zn}^{+2}][\text{Cd}]}{[\text{Cd}^{+2}][\text{Zn}]}$$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{0.0004}{0.2}$$

$$E = E^\circ - \frac{0.0591}{2} \times -2.698$$

$$E = E^\circ - 0.02955 \times -2.698$$

$$E = E^\circ + 0.07972$$

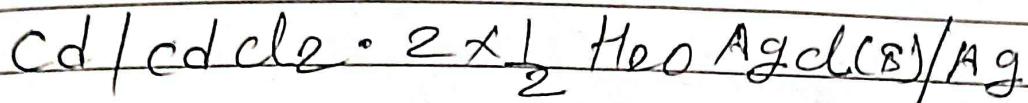
$$\boxed{E = E^\circ + 0.07972}$$

$$\Delta G_f = - \times 2 \times 96500 \times (E^\circ + 0.07972)$$

$$\Delta G_f = -E^\circ 193000 - 15385.96$$

$$\boxed{\Delta G_f = -193000E^\circ - 15385.96}$$

## Emf of a cell



$$E_1 = 0.6753 \text{ V at } 25^\circ\text{C}$$

$E_2 = 0.6915 \text{ V at } 0^\circ\text{C}$  calculate  $\Delta G_1, \Delta H, \Delta S$  for the cell.  $T_2$

Sol:  $\Delta G = -nFE$

$$\Delta G = -2 \times 96500 \times 0.6753$$

$$\boxed{\Delta G = -130332.9 \text{ J}}$$

$$\boxed{\Delta G = -130.33 \text{ kJ/mol}}$$

$$\boxed{\Delta S = nF \left( \frac{dE}{dT} \right)}$$

$$\frac{dE}{dT} = \frac{E_2 - E_1}{T_2 - T_1}$$

$$\frac{dE}{dT} = \frac{0.6915 - 0.6753}{273 - 298}$$

$$T_1 = 25^\circ\text{C} \rightarrow 273 + 25 = \boxed{298}$$

$$= 298 \text{ K}$$

$$T_2 = 0^\circ\text{C}$$

$$T_2 = 273 + 0 = 273 \text{ K}$$

$$\frac{dE}{dT} = \frac{0.0162}{-25}$$

$$\boxed{\frac{dE}{dT} = -0.000648}$$

$$\Delta S = 2 \times 96500 \times -0.000648$$

$$\boxed{\Delta S = -125.064 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = \Delta G + T\Delta S$$

$$\Delta H = (-130333) + (-125.064) \times (25 + 273)$$

$$\Delta H = (-130) - (125.064 \times 298)$$

~~$$\Delta H = -130333 + (-32869.27)$$~~

~~$$\Delta H = -167608.7 \text{ J}$$~~

$$\boxed{\Delta H = 167608.7 \text{ J}}$$

$$\boxed{\text{J K}^{-1} \text{ mol}^{-1}}$$

Note: Free energy change =  $\Delta G$

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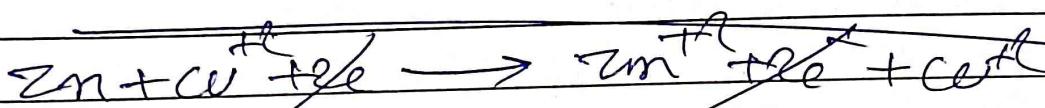
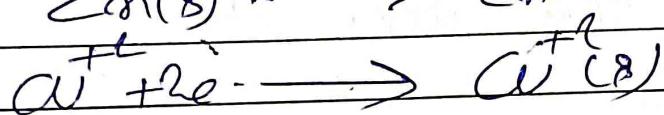
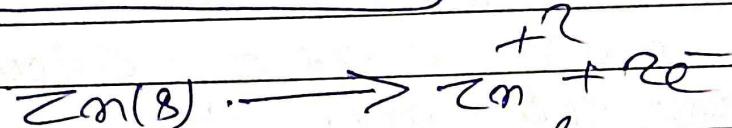
\*

Cell reaction

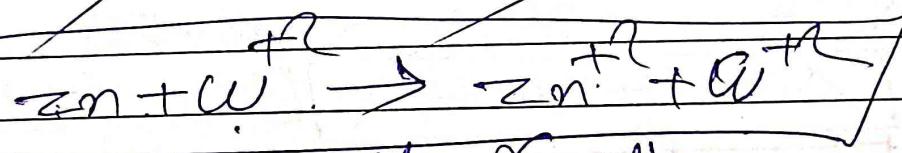
$\Delta G =$

$$\Delta G = -nFE_{cell}$$

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



all reaction



Cell reaction

$$E^\circ = SRP_{cathode} - SRP_{anode}$$

$$E^\circ = (0.34) - (-0.76)$$

$$E^\circ = 0.34 + 0.76$$

$$\boxed{E^\circ = 1.10V}$$

$$\Delta G = -2 \times 96500 \times 1.10V$$

$$\Delta G^\circ = 212300 \text{ J} \quad \text{(crossed out)}$$

$$\boxed{\Delta G^\circ = 212300 \text{ kJ/mol}}$$

## \* Acid base equilibria

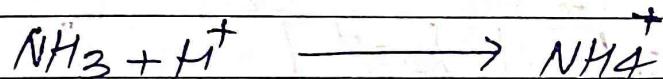
Azotomies concept :

Acid = which donate  $H^+$  ion eg.  $\Rightarrow HCl$

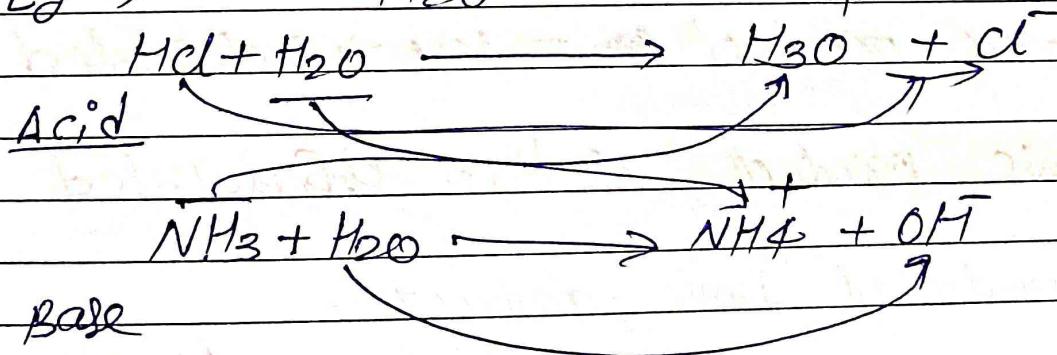
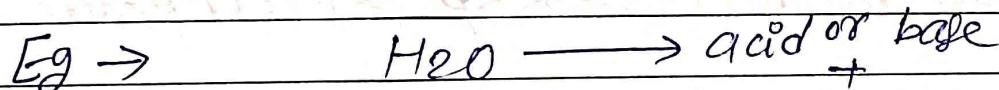
Base = which can donate  $OH^-$  ion Eg.  $= NaOH$   
(and accept  $H^+$ )

## \* Brønsted lowry concept :

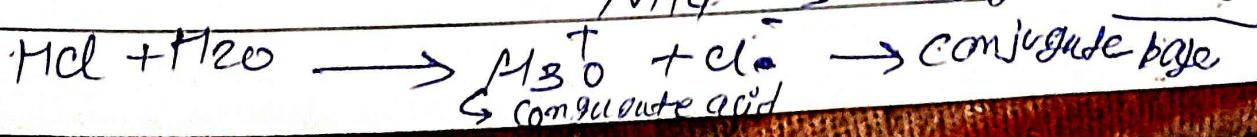
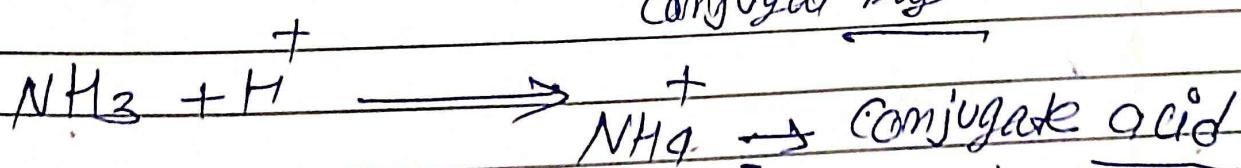
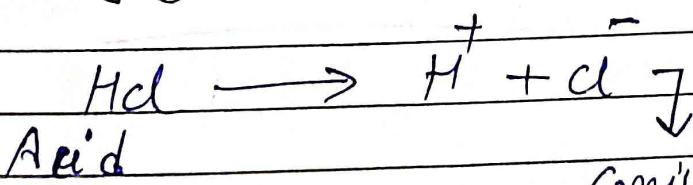
$NH_3 \rightarrow$  Base is a substance which can accept  $H^+$  ion



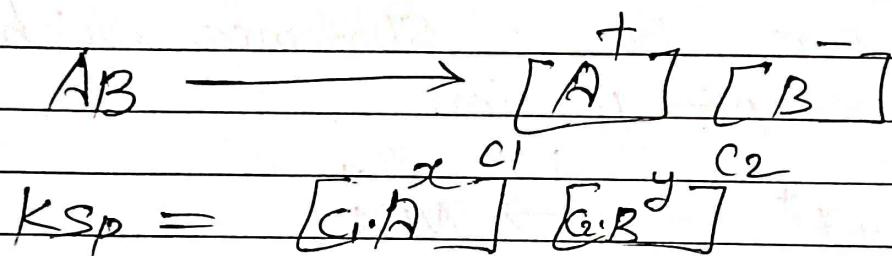
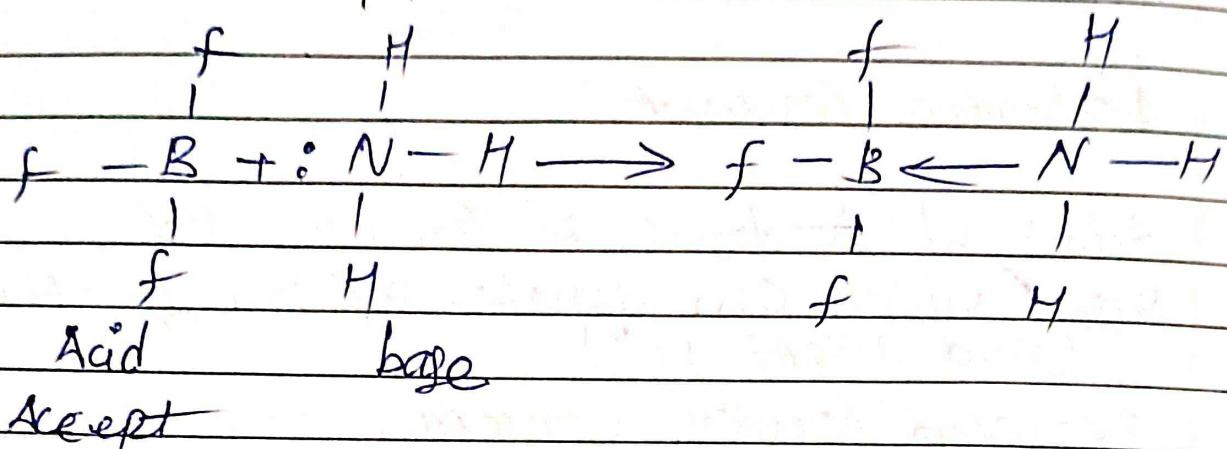
\* Amphoteric Compound = which are acid and base different - different times.



## \* Conjugate Acid base Pairs :



\* Lewis Concept :



Ionic product  $\rightarrow$

Ionic product  $> K_{\text{sp}} \rightarrow$  precipitate

Ionic product  $= K_{\text{sp}} \rightarrow$  saturated sol.

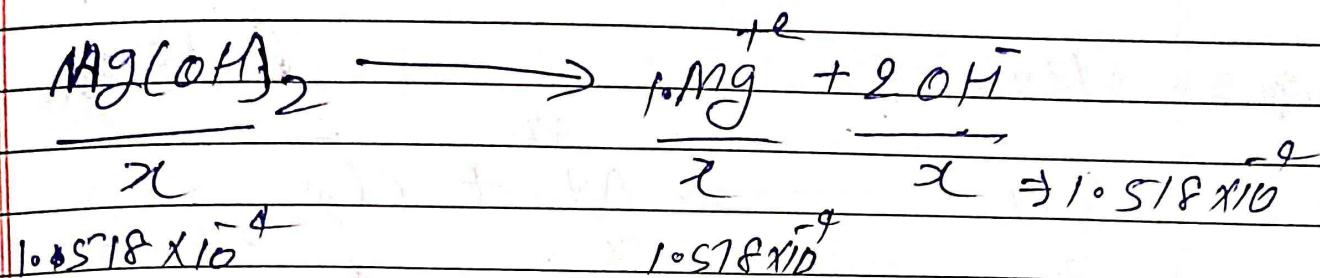
Ionic product  $< K_{\text{sp}}$  ~~saturated~~

formula of Ionic product =

$$\text{Ionic product} = [\text{G}\cdot\text{A}]^x [\text{G}\cdot\text{B}]^y$$

\* The solubility of  $Mg(OH)_2$  is  $1.518 \times 10^{-4}$  mol/L at 285 K.  $K_{sp} = ?$

Sol: Concentration of  $Mg(OH)_2$  =  $1.518 \times 10^{-4}$



$$K_{sp} = [C_1 \cdot A]^{+y} [C_2 \cdot B]^y$$

$$K_{sp} = [1.518 \times 10^{-4}]^{\frac{1}{2}} [OH^-]^{\frac{2}{2}}$$

$$K_{sp} = 1 \times 1.518 \times 10^{-4} \times (2 \times 1.518 \times 10^{-4})^{\frac{1}{2}}$$

$$K_{sp} = 1.0518 \times 10^{-4} \times \cancel{36.86} \times 10^{-8}$$

~~$1.0518 \times 10^{-4} \times 36.86 \times 10^{-8}$~~

~~$1.0518 \times 10^{-4} \times 36.86 \times 10^{-8}$~~ 

$$= 13.991 \times 10^{-12}$$

~~$1.0518 \times 10^{-4} \times 36.86 \times 10^{-8}$~~ 

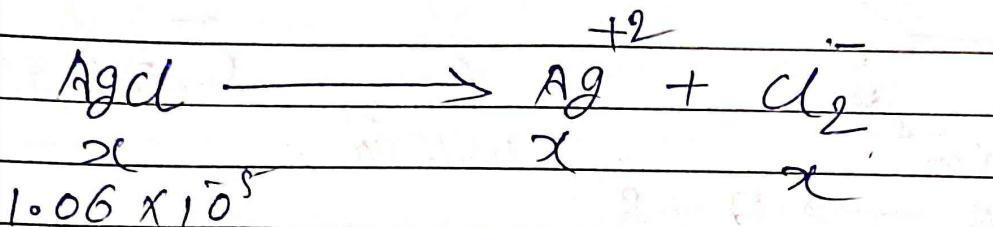
$$= 14 \times 10^{-12}$$

~~$1.0518 \times 10^{-4} \times 36.86 \times 10^{-8}$~~ 

$$K_{sp} = 1.4 \times 10^{-12} \text{ mol/L}$$

\* The solubility of  $\text{AgCl}$  in water at  $25^\circ\text{C}$  is  $1.06 \times 10^{-5} \text{ mol/L}$ . Calculate the solubility product of  $\text{AgCl}$  at this temperature.

$$\text{Ans} \Rightarrow K_{\text{sp}} = ?$$



$$K_{\text{sp}} = [c_1 \text{Ag}] \cdot [c_2 \text{Cl}]$$

$$K_{\text{sp}} = (1.06 \times 10^{-5}) (1.06 \times 10^{-5})$$

$$K_{\text{sp}} = 1.1236 \times 10^{-10}$$

$$K_{\text{sp}} = 1.1236 \times 10^{-10}$$

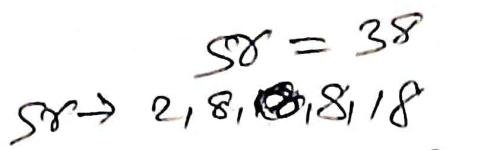
$$K_{\text{sp}} = 1.1236 \times 10^{-10}$$

### Strontium

\* The solubility of ~~strontium~~ chloride  $\text{SrF}_2$   $1.2 \times 10^{-2} \text{ g/L}$  calculate the solubility product of this room temperature.

$\text{Ans} \Rightarrow$  When given temperature than give Mo of  $\text{SrF}_2$  with given concentration

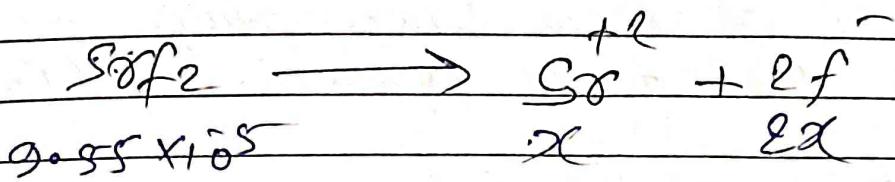
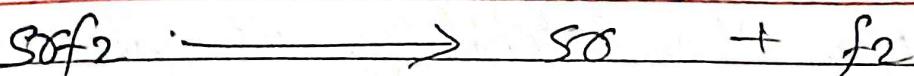
$$= \frac{1.2 \times 10^{-2}}{125.6} \Rightarrow 9.55 \times 10^{-5} \text{ mol/L}$$



<sup>+2</sup>  
SO

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$$K_{sp} = [9.55 \times 10^5] \times [2x]^2$$

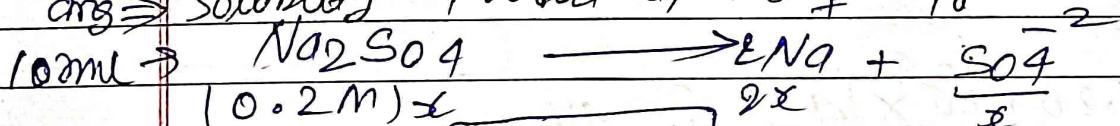
$$K_{sp} = [9.55 \times 10^5] [364.81]$$

$$K_{sp} = 3483.9 \times 10^{-15}$$

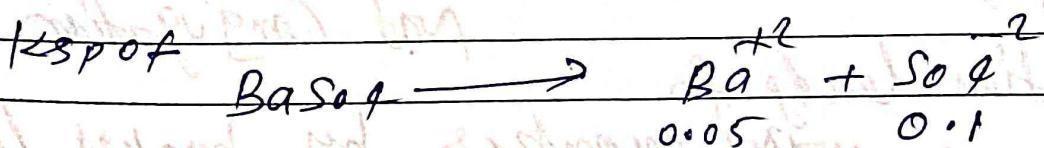
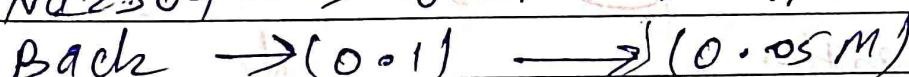
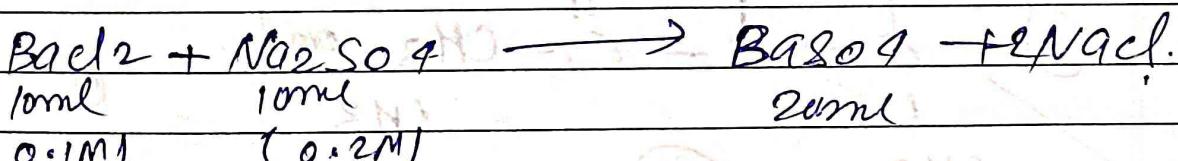
$$K_{sp} = 3.48 \times 10^{-12} \text{ mol/l}$$

\* When 10ml of 0.2M Solution  $Na_2SO_4$  is mixed with 10ml of 0.1M  $BaCl_2$  will a precipitate of  $BaSO_4$  be formed or not?

Ans  $\Rightarrow$  Solubility product of  $BaSO_4 = 10^{-10}$



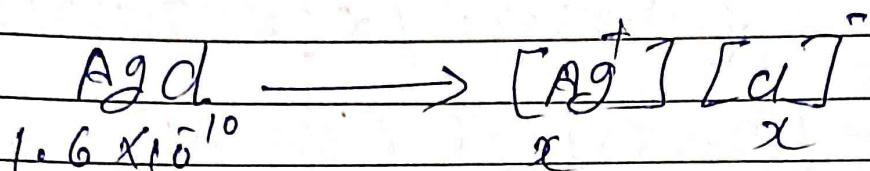
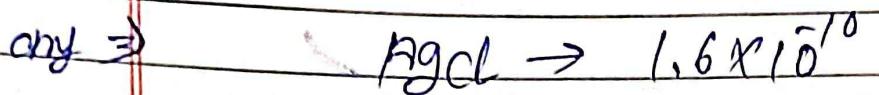
$$\text{Given } K_{sp} = 10^{-10}$$



$$K_{sp} = [0.05][0.1] \quad K_{sp} = 5 \times 10^{-5} \text{ mol/l}$$

There will be precipitate cause of  $[K_{sp} < IP]$

\* Calculate the solubility of silver chloride in water at room temperature if solubility product of  $\text{AgCl}$  is  $1.6 \times 10^{-10}$



$$x = \sqrt{1.6 \times 10^{-10}}$$

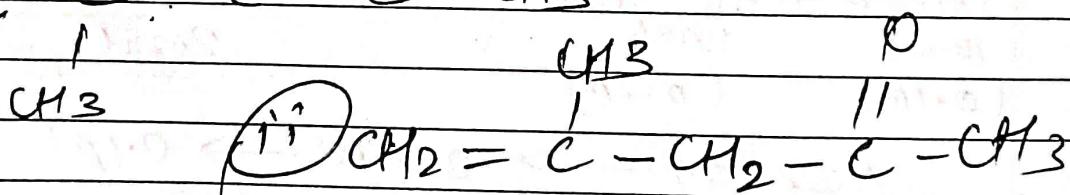
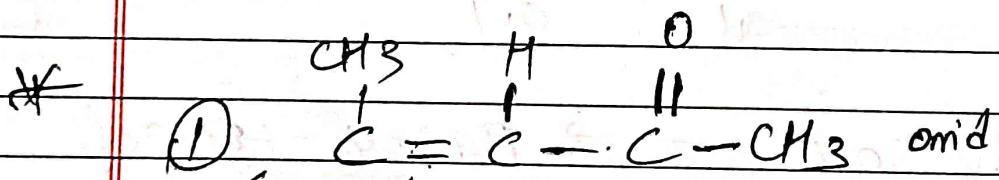
$$x = 1.26 \times 10^{-5} \text{ mol/L}$$

Solubility of  $\text{AgCl}$  at room temperature

$$\text{M}_0 \\ \text{AgCl} = 143.5$$

$$= 1.26 \times 10^{-5} \times 143.5 \text{ g/L}$$

$$\Rightarrow 0.0018 \text{ g/litre}$$



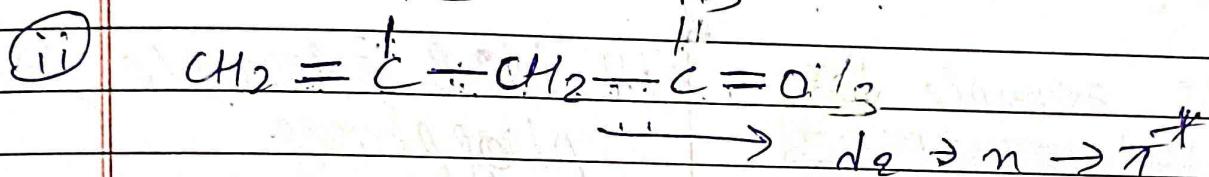
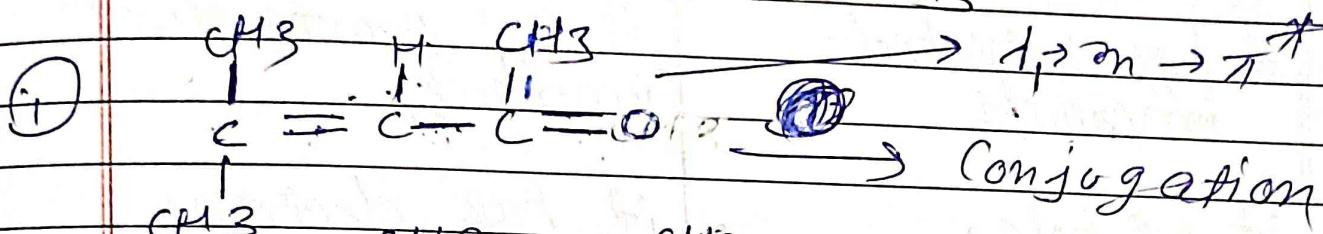
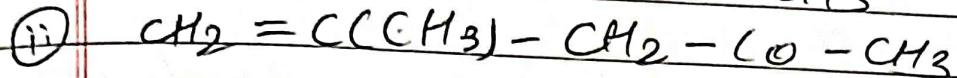
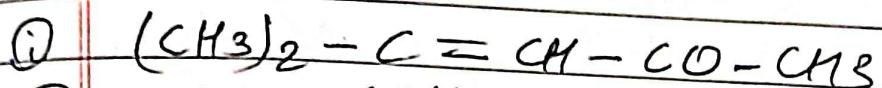
Conjugation

Mad Conjugation

Conjugation leads to decrease in wave number by hooker law

$$\text{iii} > \text{ii}$$

\* why the value of wavelength for  $n \rightarrow \pi^*$  transition in the following molecules is different?



$d_1 \rightarrow$  Conjugation  $\rightarrow$  Conjugation leads to decrease in energy gap  $\Delta E$   
so that less energy ~~is~~ in  $\rightarrow$

Molecule  
for  $n \rightarrow \pi^*$  transition we know  
that  $E = \frac{1}{d}$  less than I more

ii) in second molecule there is no any conjugation so that more energy for  $n \rightarrow \pi^*$  transition than molecule i)  
so that I wavelength less than molecule i)

$$I > I_2$$

\* Difference between n type and p type Semiconductors.

P type

- (i) it has trivalent impurity
- (ii) it has hole.
- (iii) its example is ~~phosphorus~~  
Aluminum
- (iv) Holes are the majority charge carriers

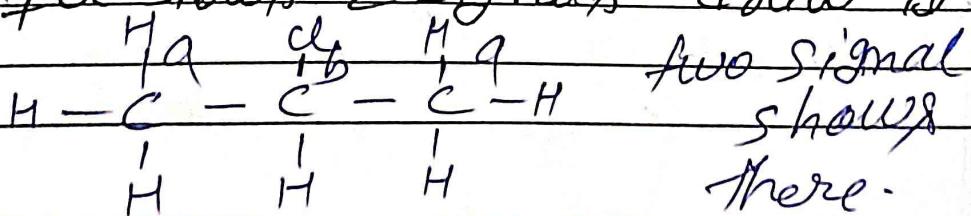
N type

- it has pentavalent impurity
- it has electron.
- (iii) its example is phosphorous
- electrons are the majority charge carriers.

\* Does temperature influence the conductivity of n type semiconductor? Discuss.

Ans ⇒ As the temperature increases, more electrons get the energy to jump from conduction band to valence band, and thereby the therefore conductivity of the semiconductor increases.

\* Discuss the high resolution NMR of  $C_3H_7Cl$  shows 2 signals draw it.



## \* Coupling Constants :-

Coupling Constants are important NMR parameters that provide complementary structural information to chemical shifts.

# Phase diagram of two Component System

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\* Finger print Region : The region below 1500 cm<sup>-1</sup> of IR is called Big finger print Region.

(1) Stretching :

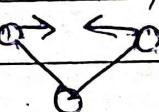
- i) Symmetric
- ii) Asymmetric

i) Symmetric : Movement of atoms w.r.t to Asymmetric if particular atom is in the same directions.

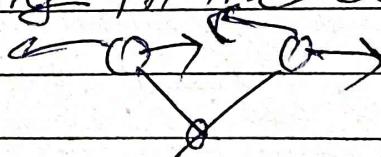


ii) Asymmetric : one atom approaches the central atom while the other departs from it.

(2) Bending or Scissoring : When two atoms approach each other.

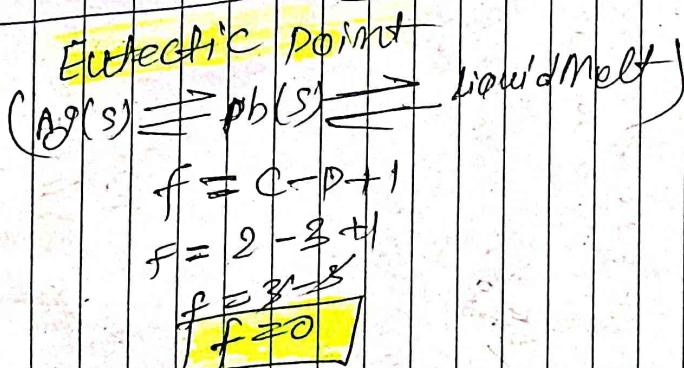
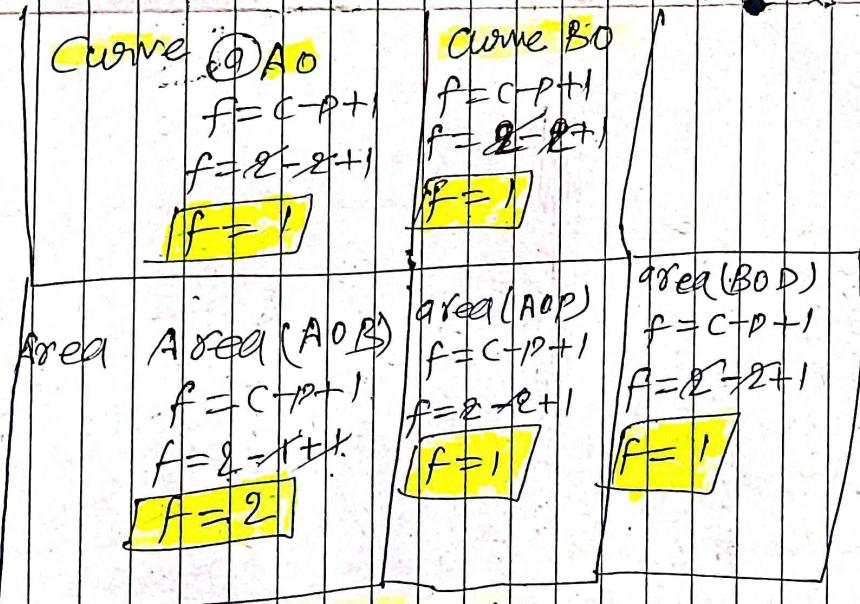
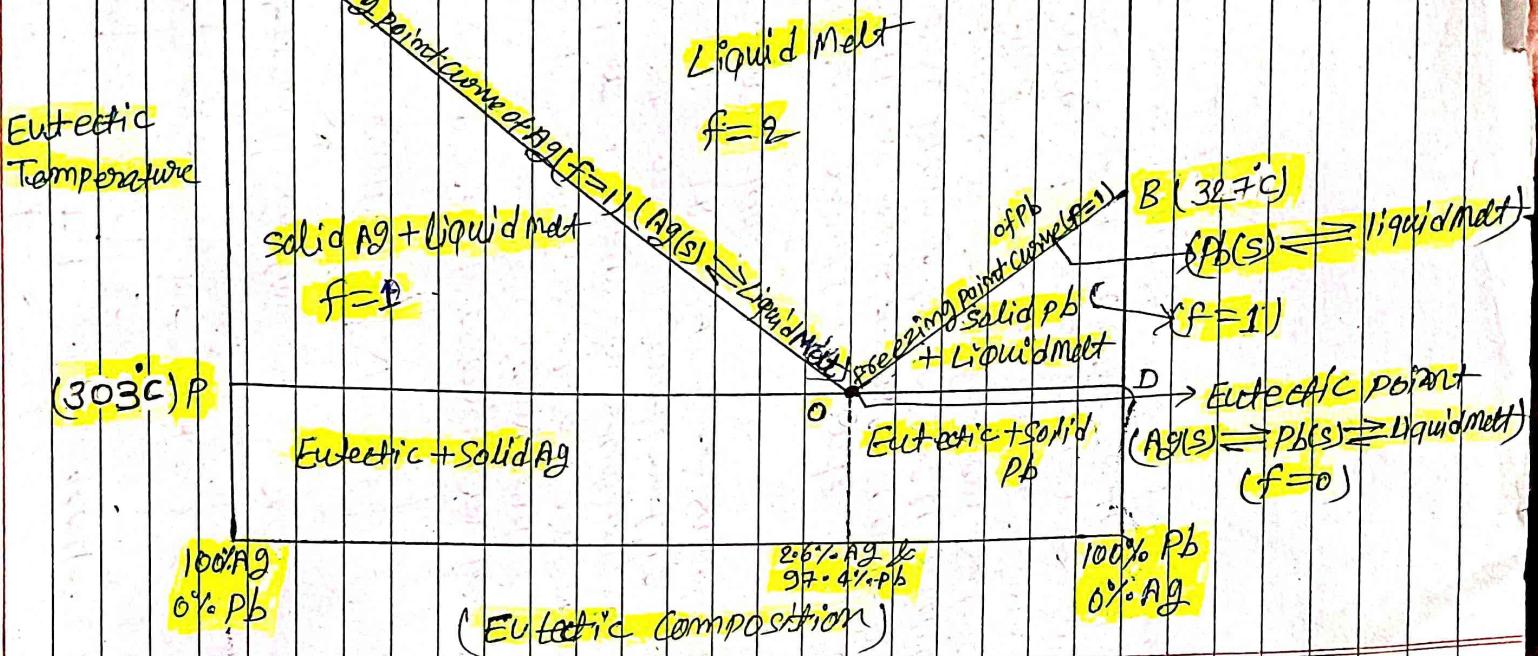


(3) Rocking : When the atoms in the same direction



(4) Wagging : when two atoms move above or below the plane w.r.t central atom

(d) Twisting : one of the atom move up and other moves below the plane w.r.t central atom.



\* Define IR  $\xrightarrow{\lambda}$

0.8 μ

2.5 μ

1 →  
15 μ

200 μ

Near infrared Region	infrared Region	far infrared Region
----------------------	-----------------	---------------------

12500  $\text{cm}^{-1}$       4000  $\text{cm}^{-1}$       667  $\text{cm}^{-1}$       50  $\text{cm}^{-1}$

Wave number  $\xrightarrow{\nu = \frac{1}{\lambda}}$

Infrared (IR) Spectroscopy can be used to identify a particular compound or to predict the structure of an unknown compound. It helps in studying the presence of many functional groups by comparing the IR spectra of sample with the standard table.

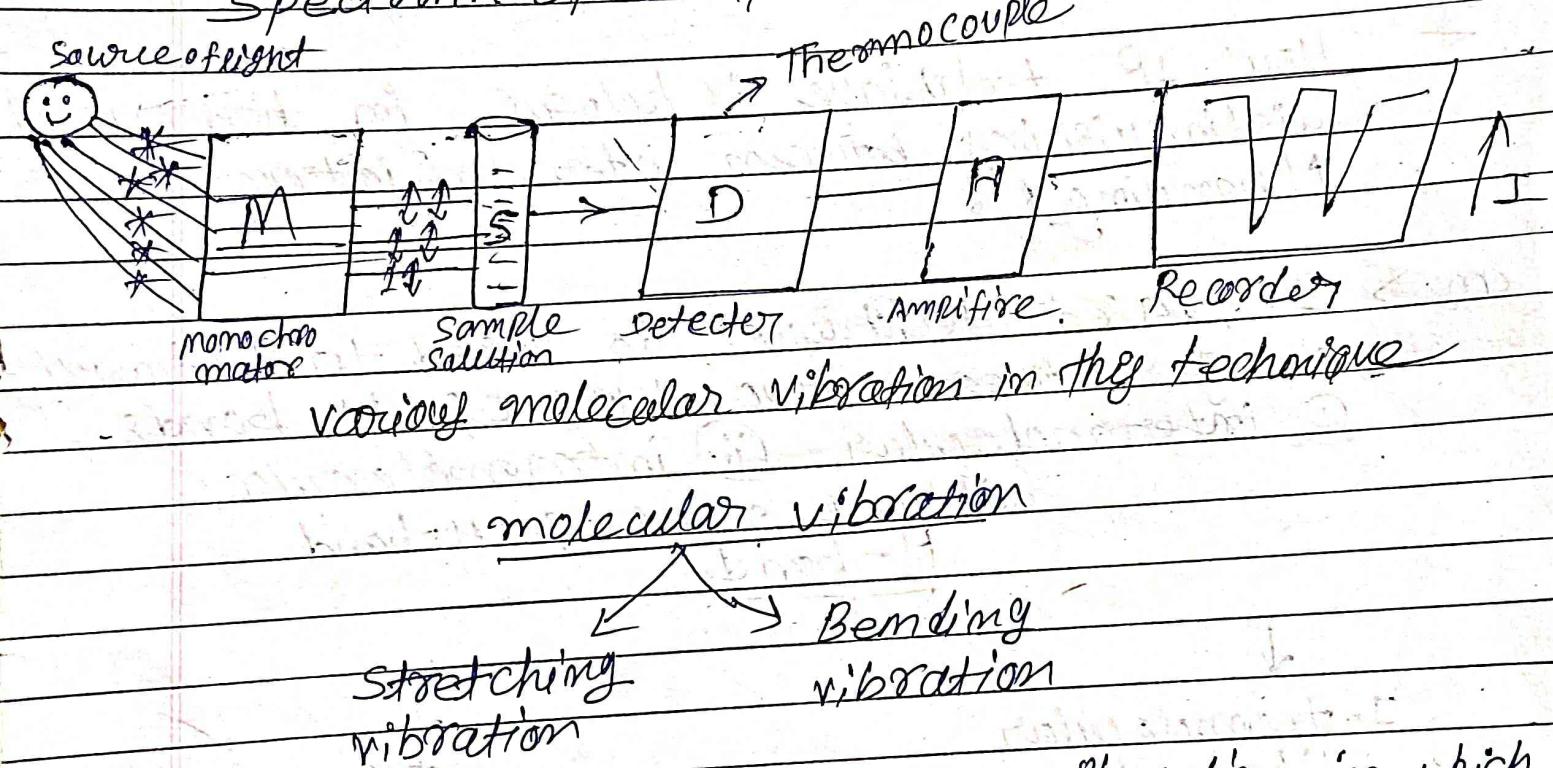
The infrared region extends from 0.8 μ to 200 μ in wavelength (12500 to 50  $\text{cm}^{-1}$ ). The region from 0.8 to 2.5 μ is called near infrared region and from 15 μ to 200 μ is called far infrared region.

The ordinary infrared region extends from 2.5 μ to 15 μ (4000  $\text{cm}^{-1}$  to 667  $\text{cm}^{-1}$ ). This is most important region for an organic chemist.

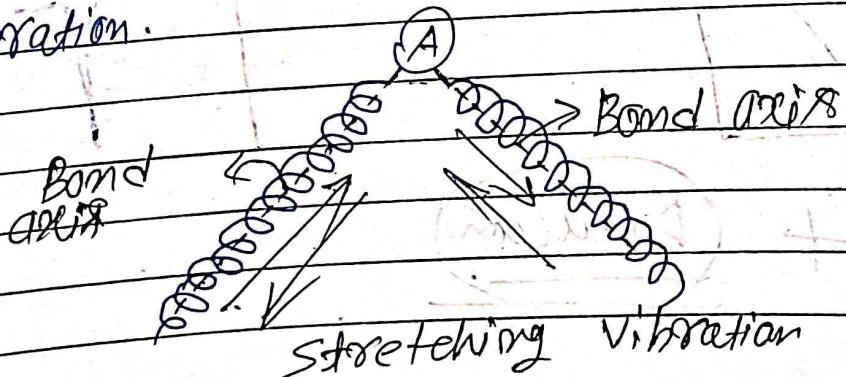
Q. Define IR Spectroscopy. Discuss various molecular vibration in this technique.

n IR Spectroscopy is an instrument.

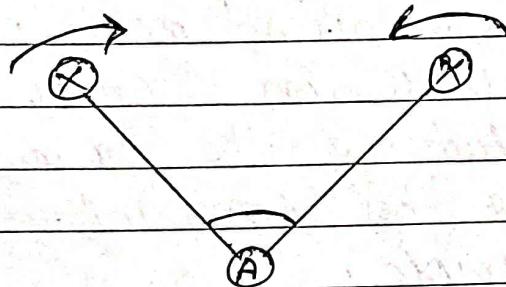
Sol: (IR) Infrared Spectroscopy can be used to identify a compound or to predict the structure of an unknown compound and it also helps in studying the presence of many functional groups by comparing the IR spectrum of sample.



i) stretching vibration: That vibration in which distance between two atoms increases or decreases but the atoms remain in the same bond axis are known as stretching vibration.



ii) Bending vibration : That vibration in which positions of atoms changes and bond angle of atom changes but internuclear distance does not change are known as Bending vibration.



\* How IR technique is helpful in distinguishing between inter and intramolecular H bonding.

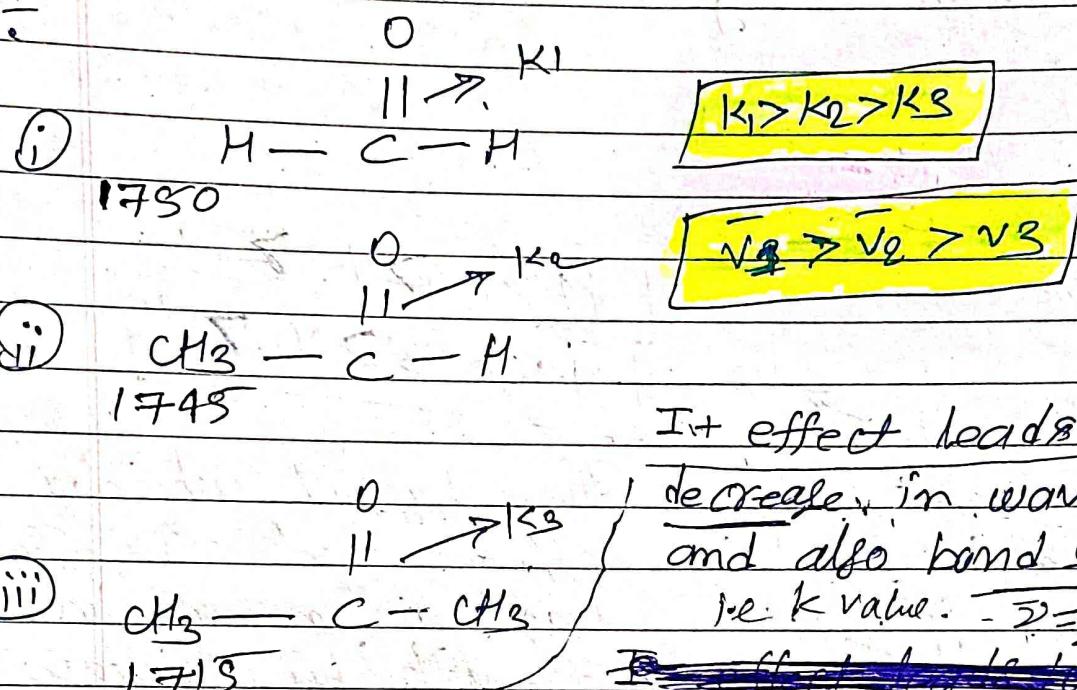
⇒ Infrared technique is used to distinguish between two types of H-bonds

i) intermolecular ii) intramolecular  
additional signal of H-bond  
H-bond



\* The wave no for C=O in HCHO, CH<sub>3</sub>CHO and CH<sub>3</sub>COCH<sub>3</sub> is not same but is 1750, 1745 and 1715 cm<sup>-1</sup> respectively. Explain.

Sol :



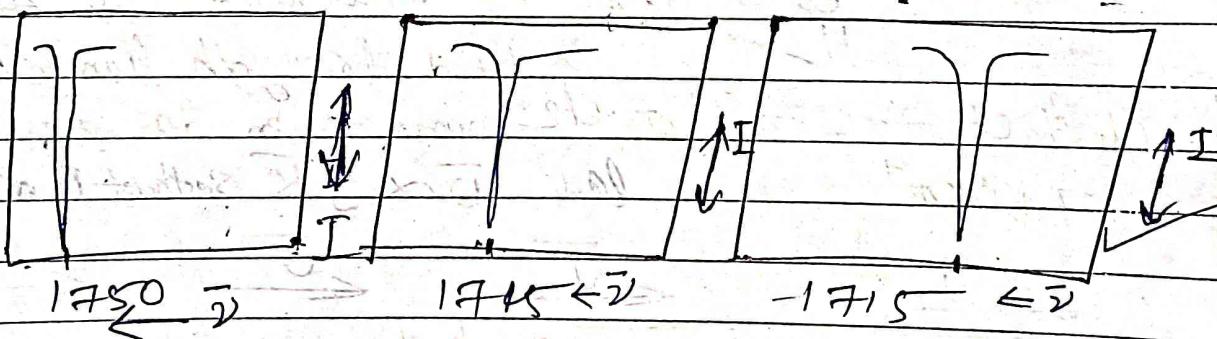
+I effect leads to

decrease in wave number  
and also bond strength

$$\text{i.e. } k \text{ value. } \bar{\nu} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

~~Effect due to increase in mass and all~~

~~increase in bond strength K~~



+I effect leads to decrease in bond strength (by Hooke's law)

$$\bar{\nu} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

$\bar{\nu} \propto \sqrt{k}$  so that

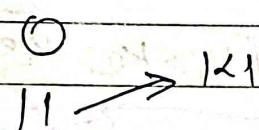
wave number decreases

\* The wave no for  $C=O$  in  $CH_3COCH_3$ ,  $ClCH_2COCH_3$ ,  $Cl_2CH_2COCH_3$  and  $Cl_3COCOCHCl_2$  is not same but is 1715, 1725, 1740 and 1750  $\text{cm}^{-1}$  respectively. Explain

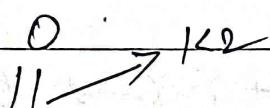
Ans →



$1715 \text{ cm}^{-1}$



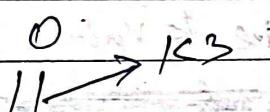
$$K_4 > K_3 > K_2 > K_1$$



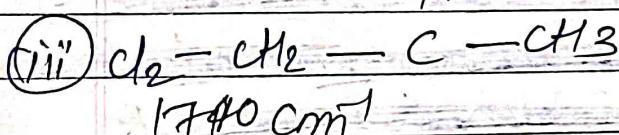
$$\sqrt{4} > \sqrt{3} > \sqrt{2} > \sqrt{1}$$



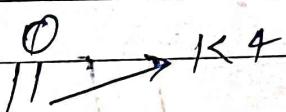
$1725 \text{ cm}^{-1}$



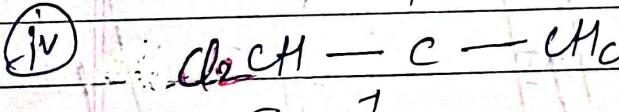
There has  $Cl$  which is  $-I$  effect and  $-I$  effect leads to increase in bond strength hence wave number increased by Hooke's law cause of  $\bar{V} \propto f^2$



$1740 \text{ cm}^{-1}$



+ I effect leads to decrease in bond strength hence wave number decreased by Hooke's law  $\bar{V} \propto f^2$  so that  $\bar{V} \propto f^2$



$1750 \text{ cm}^{-1}$

low

$\bar{V} \propto f^2$

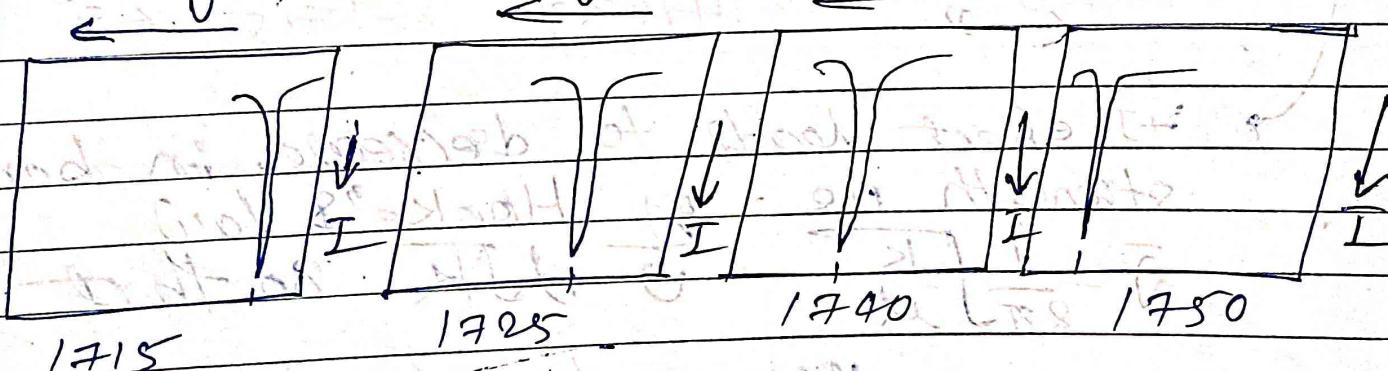
$f$

$J$

$J'$

$J''$

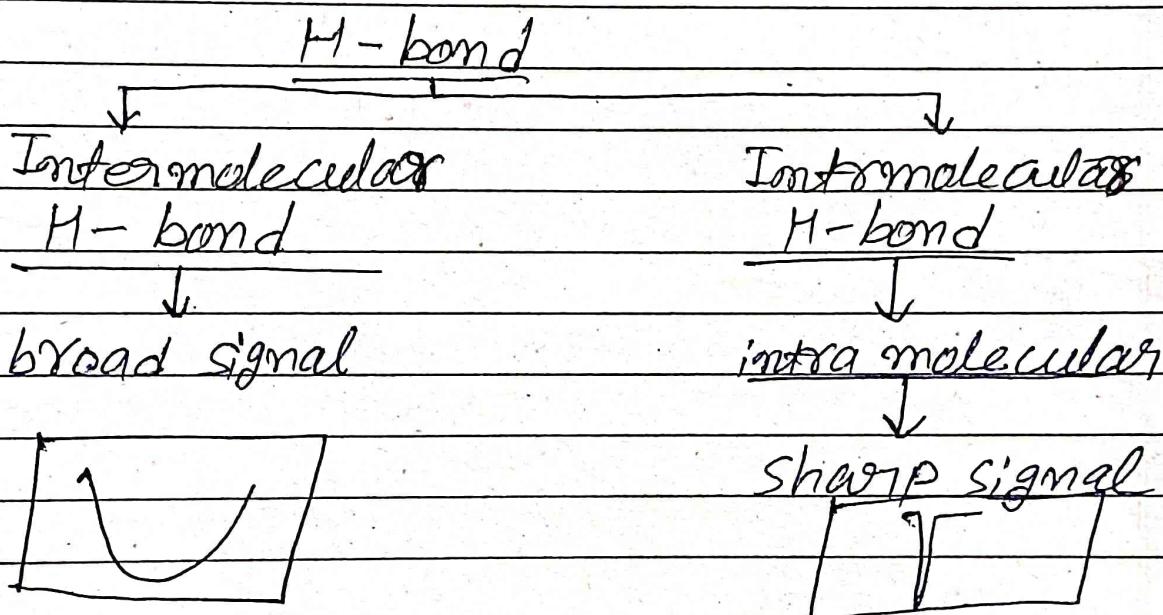
$J'''$



\* How IR technique is helpful in distinguishing between inter and intramolecular H-bonding.

Ans  $\Rightarrow$  Infrared technique is used to distinguishing between two types of H-bond  
 (i) intermolecular (ii) intramolecular

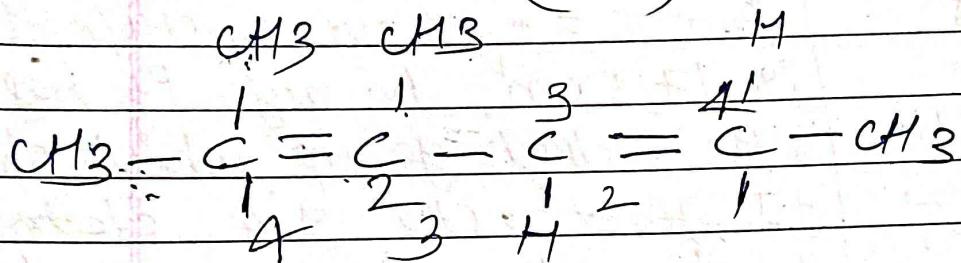
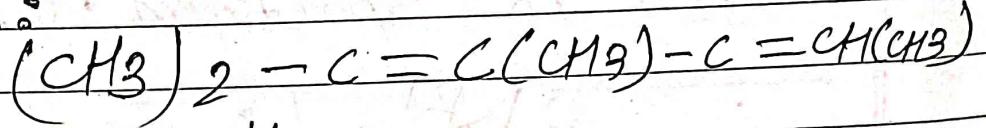
additional signal of H-bond



Dilution reduces the intermolecular H-bond  
 But it has no effect on intramolecular H-bond. So if the sample is analysed after the dilution and if it shows diminishing of the band, it results that band at lower  $\nu$  value was because of intermolecular H-bond. But if after dilution, sample does not show any effect on the band ~~disappearing~~, it results that band is because of intramolecular H-bond.

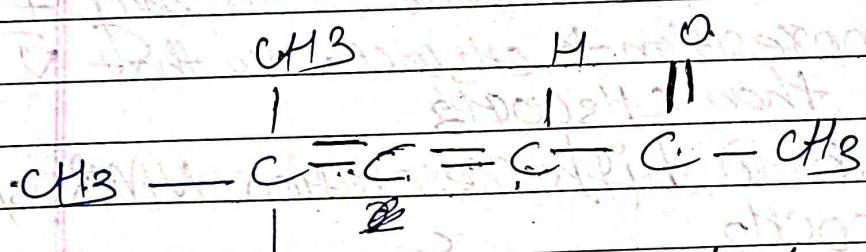
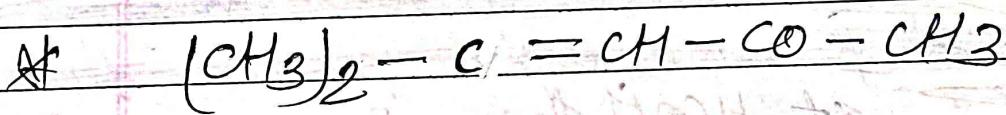
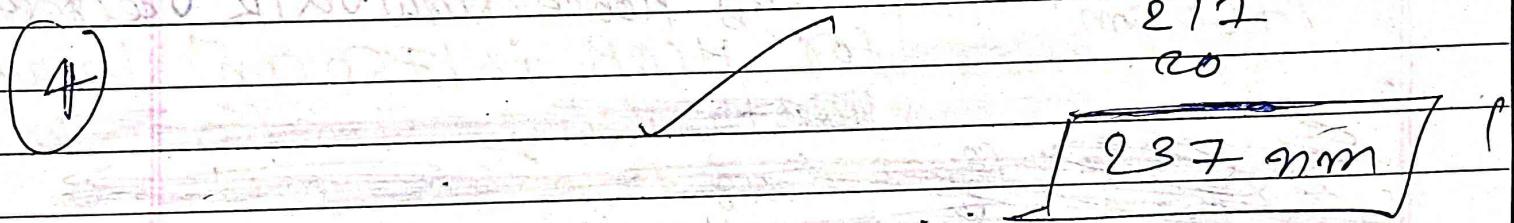
This is so because dilution reduces intermolecular H-bond but it has no effect on intermolecular H-bond.

\* By using Woodward Fieser rule, calculate the wavelength absorbed by the following:



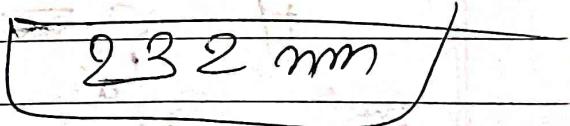
Acyclic conjugated diene = 217 nm

alkyl substituent  $\geq 4 \times 5 = 20$  nm



Acyclic conjugated ~~diene~~ dicone = 217 nm

alkyl substituent  $3 \times 5 = 15$  nm

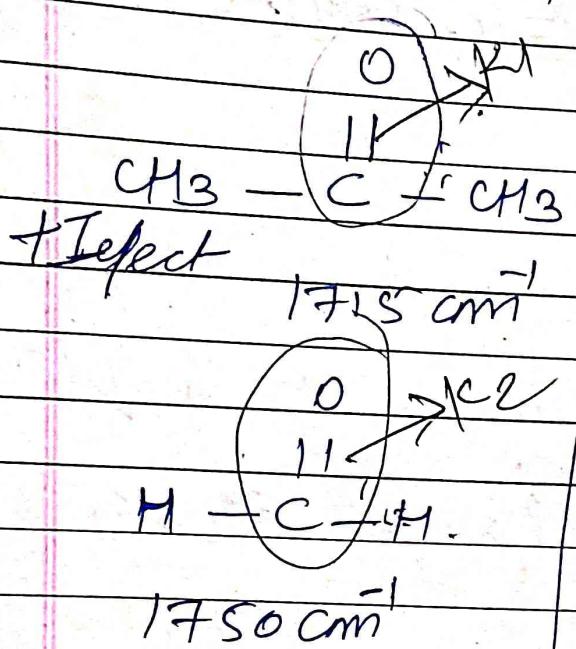


Leave it

Leo

Leave it

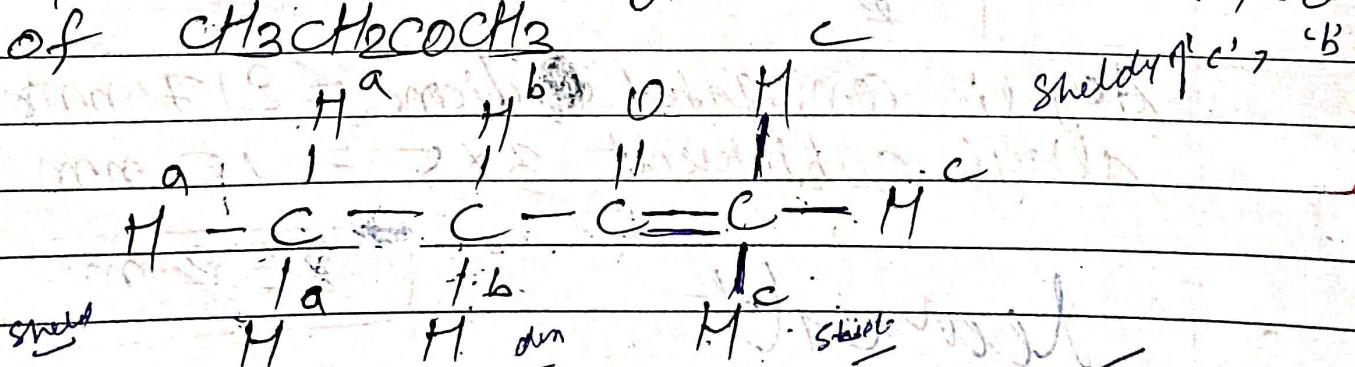
\* Wave no for  $C=O$  group in  $\text{CH}_3\text{COCH}_3$  is  $1715 \text{ cm}^{-1}$ , whereas for  $\text{HCOH}$  is  $1750 \text{ cm}^{-1}$ , in IR spectrum. Why?



for  $C=O$  group in  $\text{CH}_3\text{COCH}_3$  is  $1715 \text{ cm}^{-1}$  because it has  $\text{CH}_3$  alkyl group which show +I effect,  $\text{CH}_3$  give electron density to carbon so that  $C=O$  bond strength is decreasing hence wave number decrease than  $\text{HCOH}$ , by Hooke's law  $\propto 1/k$  decrease for  $\text{HCOH}$  is  $1750 \text{ cm}^{-1}$  because ~~it has +I effect so~~

~~that  $\propto 1/k$  effect leads to increase C=O bond strength so that wave number increases due to more electron density than  $\text{CH}_3\text{COCH}_3$ .~~ at  $\text{HCOH}$  there is no any +I effect as compression to  $\text{CH}_3\text{COCH}_3$  so that  $\nu$  of  $\text{HCOH}$  is greater than  $\text{CH}_3\text{COCH}_3$

\* Explain and draw high resolution NMR spectra of  $\text{CH}_3\text{CH}_2\text{COCH}_3$



① no of sets of protons = 3 ✓

a (3H)

b (2H)

c (3H)

② no of signal  $\rightarrow$  3 ✓

③ Intensity of signal  $\rightarrow I_a = I_c > I_b$   
because a and c set has more proton than b

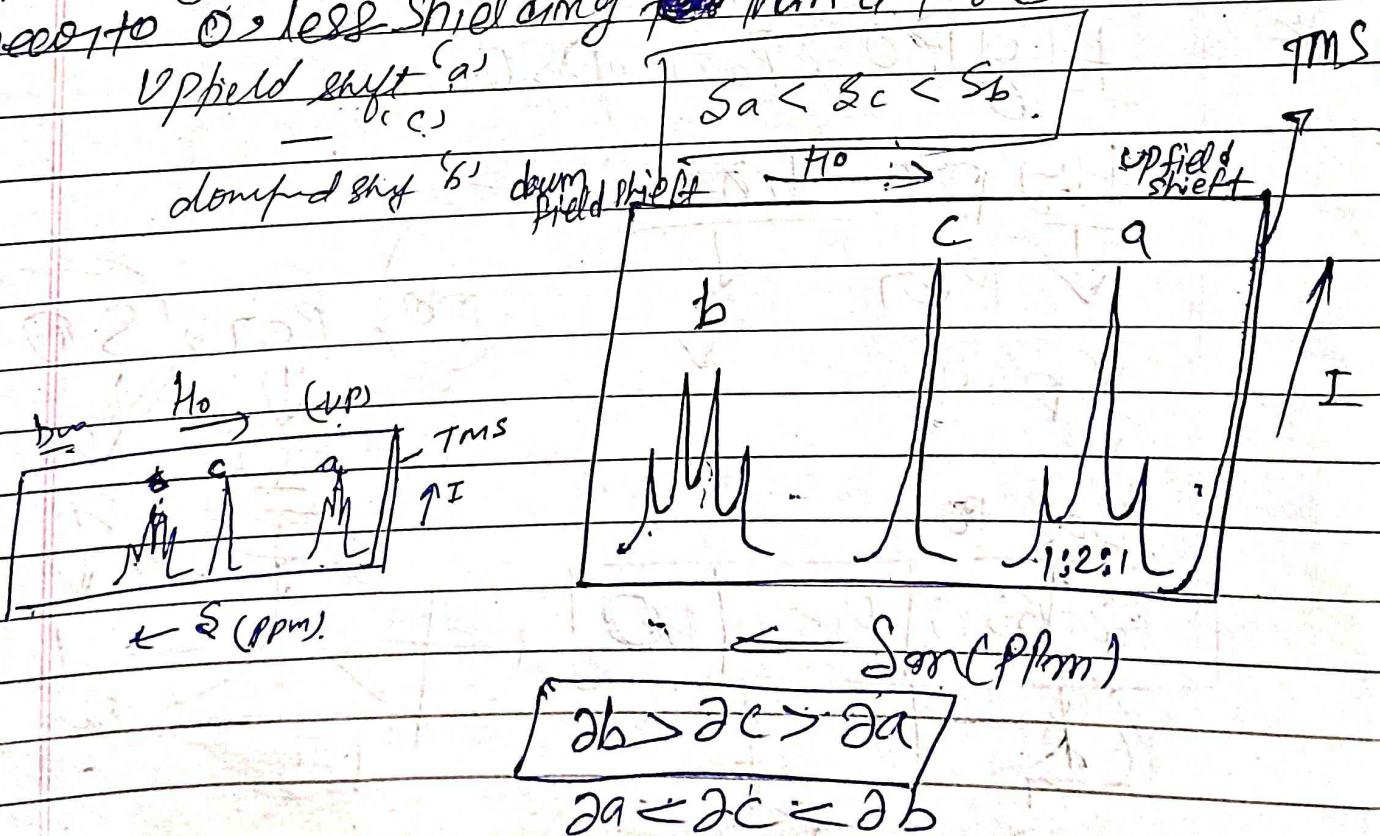
④ n+1 rule  $\rightarrow$  for set a  $\Rightarrow n=2$  ✓

$$n+1 \Rightarrow 2+1=3 \quad \text{TOPIC} \quad 1:2:1$$

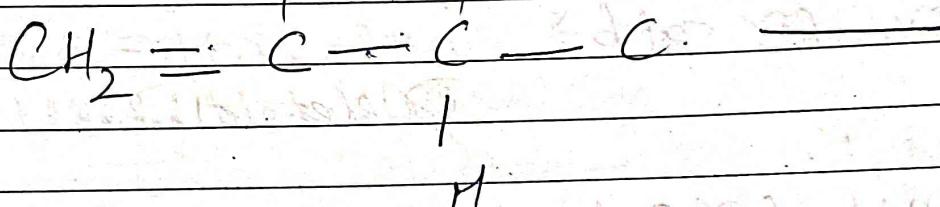
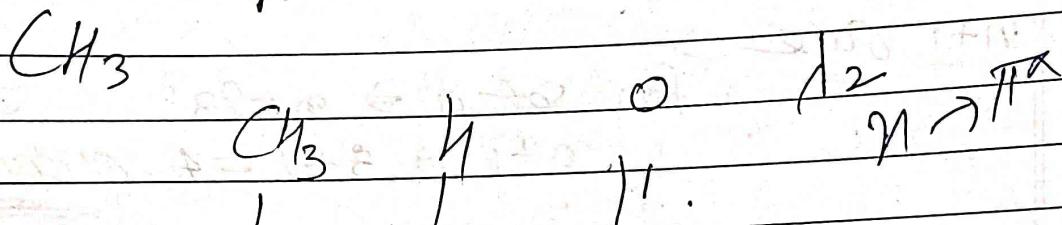
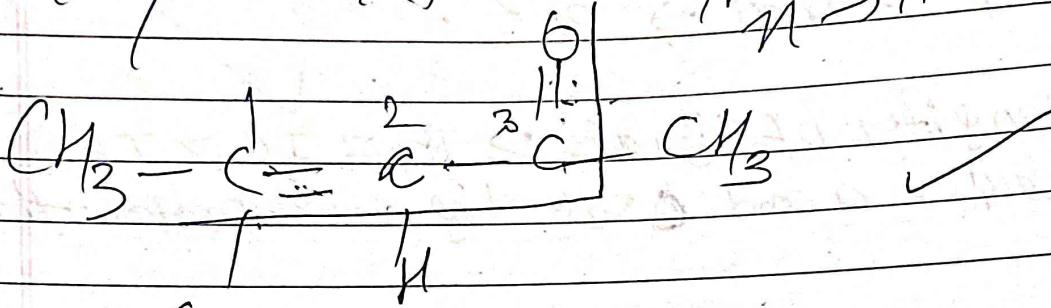
n+1 rule for set b  $\rightarrow n=2, n+1 = 3$  ✓  
~~TOPIC~~ 1:3:3:1

for  
n+1 for set c  $\rightarrow n=0, n+1 = 1$   
~~TOPIC~~ singlet

⑤ position of signal  $\div$  shielding for a  $\rightarrow$  up field shift because a is away from O  
deshielding for b  $\rightarrow$  down field shift because b is near to O, less shielding than a for c



~~A 2 / MSTJ~~



Conjugation  $\rightarrow \Delta E$  bet gd & excited  
state dec. ie less energy is abs  
for excitation  $\rightarrow$  longer d.abs

Hypo, perhaps

## Hypochromic

J Per

PSO

10

Per

A simple line drawing of a smiling face. It has large, circular eyes with thick outlines and small pupils. The mouth is a wide, open U-shape with a single vertical line inside representing a tongue or a smile. The entire face is enclosed in a roughly circular outline.

Ba Po

baksö | per | po

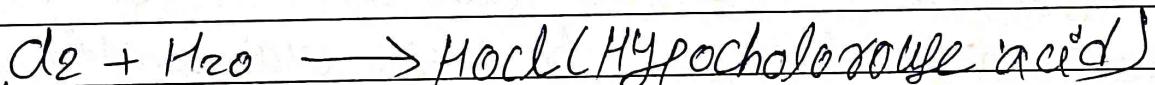
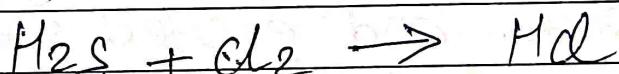
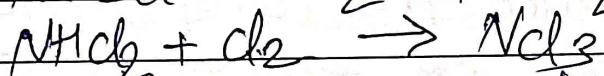
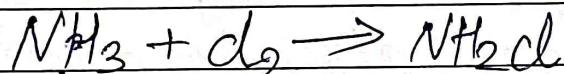
D

5

\* How water can be disinfected by chlorination?

$\Rightarrow$  Chlorination is the process of adding chlorine to water, this method is used to kill bacteria, viruses and microbes in water.

~~NH<sub>3</sub>~~ ~~bacteria~~  $\rightarrow$  Nitrogen bacteria  
 $\rightarrow$  Sulphur bacteria



$\downarrow$  (break point chlorination)

\* Break point chlorination: A point of time when  $NH_3$  is completely converted into  $NH_2$  and  $H_2S$  is completely converted into  $HCl$  and  $HOCl$  when we add more chlorine to water that makes  $HOCl$  this point called v chlorination.

Break point

## Q Define chromophore

Chromophore : Chromophore is a unsaturated molecule group which absorb UV energy and shows electronic transition and responsible for colour.

Ex  $\Rightarrow$   $\text{CH}_2 = \text{CH}_2$ ,



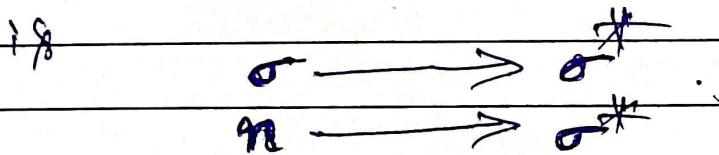
\* Define Auxochromes : Auxochrome is a molecule which absorb UV energy and shows electronic transition if ~~it is~~ is a group which has lone pair. lone pairs on auxochrome extend the conjugation. It leads to decrease in energy gap between ground state and excited state. Energy required for electronic transition decreases. Hence because wavelength is inversely proportional to energy so that wavelength absorb increases. Ex  $\Rightarrow$

\* How presence of an auxochrome leads to bathochromic shift?

$\Rightarrow$  because auxochrome has lone pairs, lone pairs on auxochrome extend the conjugation. Conjugation leads to decrease in energy gap b/w ground state to excited state so that wavelength absorb increases it leads to bathochromic shift

Ques Are  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  chromophore? Why?  
 , Name the electronic transition shown by these. Do these need same energy for this transition? Justify

Ans No, this is not a chromophore because it have lone pair so that it is not a Chromophore.  
 electronic transition shown by these molecule



No electronic transition shown by molecule.

No, these need not same energy.  
 Rather these need different different energy because chlorine is more electronegative than Br so that it need more energy and less wavelength the Br and Br needs less energy and more wavelength than chlorine.

\* All tetrahedral complexes are high spin complexes wh?

→ because in comparison to strong ~~field~~ field ligands and weak field ligands there is ~~not~~ a bigger energy difference between  $t_{2g}$  set and  $e_g$  set. However tetrahedral splitting is always much smaller than octahedral splitting thus all the tetrahedral complexes have high spin.



Expt. No. ....

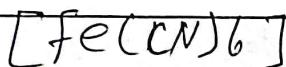
Page No. ....

or detached oral

Date \_\_\_\_\_

\* Explain crystal field splitting in octahedral complex  $[\text{Fe}(\text{CN})_6]^{4-}$ . Also calculate CFSE in  $d^3$  and  $d^6$  or  $d^7$  of tetrahedral or octahedral complex

$\rightarrow$  Octahedral =  $d^6$



$$x + (-1)x6 = -4$$

$$x - 6 = -4$$

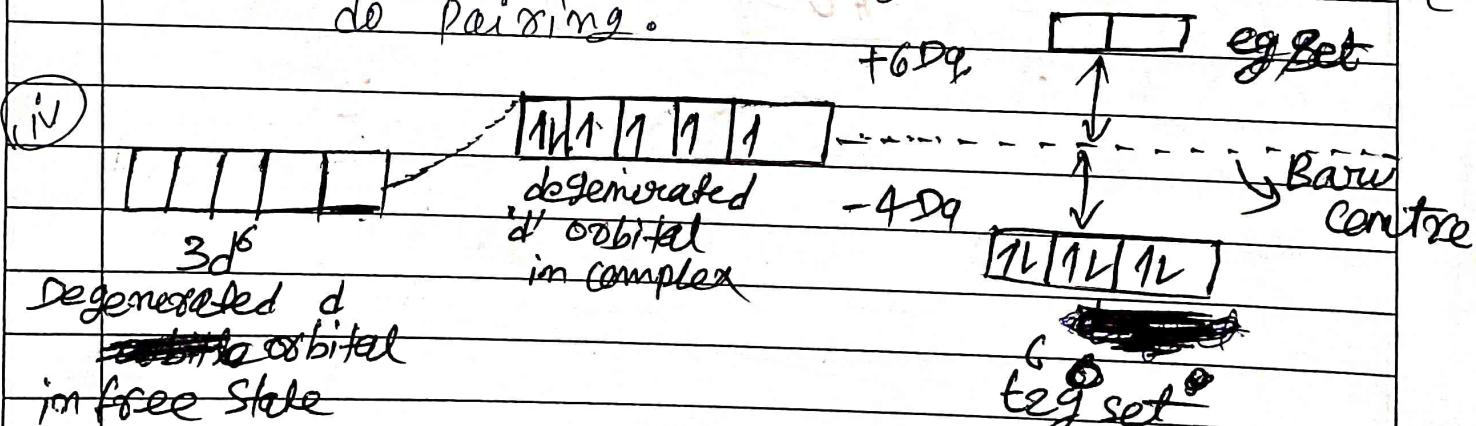
$$x = -4 + 6 \quad x = +2 \Rightarrow \boxed{\text{Fe} = +2}$$

(ii)  $\text{Fe}(26) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 \rightarrow \text{8 pairs}$

$\text{Fe}^{+4}(26) \rightarrow 1s^2 2s^2 2p^6 2s^2 3p^6 4s^0 3d^6$

$\text{Fe}^{+4}(26) = \boxed{1s^2 3d^6}$

(iii) CN  $\Rightarrow$  it is strong field ligand so that it will do pairing.



$$\text{CFSE} \rightarrow x \times (+6Dq) + y(-4Dq) + z \times p$$

$$\text{CFSE} \rightarrow 0(6Dq) + 6(-4Dq) + 2p$$

$$\boxed{\text{CFSE} = -24Dq + 2p}$$

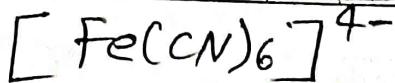
N.o. of unpaired electrons

Teacher's Signature \_\_\_\_\_

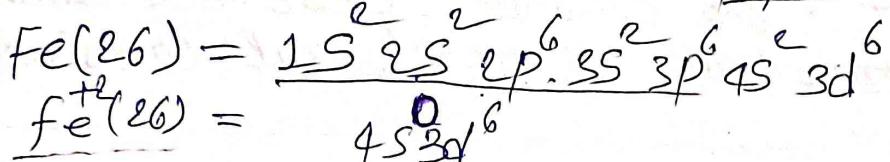
is 0 so that this is diamagnetic in nature

$x, y \rightarrow \text{No. of electrons}$   
 $z = \text{no. of pairs}$   
 $p = \text{pairing energy}$

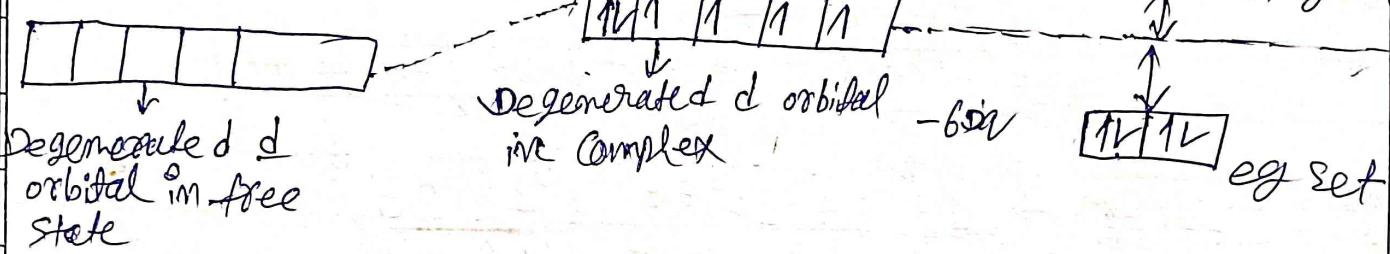
For tetrahedral



i)  $x + (-1)x6 = -4 \quad x = +2$   
 $x - 6 = -4 \quad \boxed{\text{Fe} = +2}$



iii) CN  $\rightarrow$  it is strong field ligand it will do pairing.



$$\text{CFSE} = +4Dq(2) + 4(-6Dq) + 1 \times p$$

$$\text{CFSE} = +8Dq - 24Dq + p$$

$$\boxed{\text{CFSE} = -16Dq + p}$$

$$8Dq + 16Dq - 24Dq + p > 0$$

$$-8Dq + 16Dq - 24Dq + p < 0$$

$$8Dq + 16Dq - 24Dq + p < 0$$

CFSE in d<sup>3</sup>, d<sup>2</sup> of tetrahedral

for w.f.l (weak field ligand)

d<sup>3</sup> → w.f.l

+4Dq [ ] +2g set

[ ]

- [ ] - - - - - - - - - -

-6Dq

[ ]

CFSE = eg set

$$1(4Dq) + 2(-6Dq) + 0 \times p$$

$$CFSE = 4Dq - 12Dq$$

$$CFSE = -8Dq$$

S.f.l

+4Dq [ ] +2g set

d<sup>2</sup>

[ ]

- [ ] - - - - - - - - - -

-6Dq

[ ]

$$CFSE = 0(+4Dq) + 3(-6Dq) + 1(p) \quad \text{eg set}$$

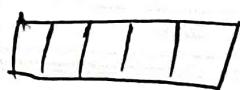
$$CFSE = -18Dq + p$$

~~d~~

$d^6 \rightarrow$  for

W.F.C  
+4Dq

~~1H1 H1 H1~~ feg set



-6Dq



~~1L1~~ eg set

$$C.F.S.E \rightarrow 3(4Dq) + 3(-6Dq) + 0(P)$$

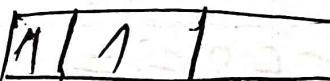
$$C.F.S.E = 12Dq - 18Dq.$$

=

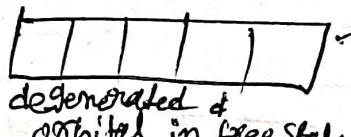
$-6Dq$

for S.f.C

$d^6$   
+4Dq



feg set



Degenerated d orbital in complex

-6Dq



Bare centre

~~1L1~~ eg set

$$C.F.S.E = 2(4Dq) + 4(-6Dq) + 0(P)$$

$$= 8Dq + (-24Dq) + P$$

$$= 8Dq - 24Dq + P$$

$$= -16Dq + P$$

$d^4 \rightarrow$  W.F.C

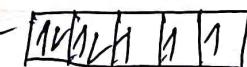
+4Dq



feg set



Degenerated d orbital in free state



Degenerated d orbital in complex

-6Dq



Bare centre

$$C.F.S.E = 12Dq + 24Dq + 0 \times P$$

$$C.F.S.E = -12Dq$$

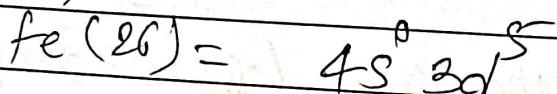
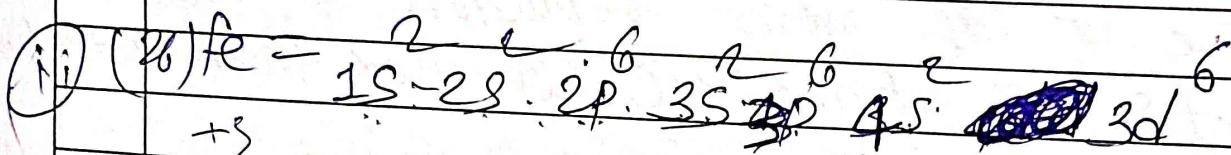
~~1L1~~ eg set

and  $[\text{Fe}(\text{CN})_6]$

$$\text{i) } x + (6x - 1) = 3$$

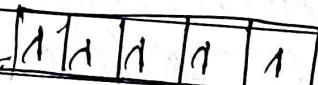
$$x = +6 - 3$$

$$\boxed{x = +3}$$



iii) CN  $\rightarrow$  It is strong field ligand  
so they ~~don't~~ do pairing.

+6 Dq  $\downarrow$  ~~get~~



-4 Dg

$\boxed{11111}$

+2g set

CFSE  $\rightarrow$   $-20Dq + 9 \times p$

~~CFSE~~ CFSE  $\rightarrow$   $-20Dq + 2p$

Paramagnetic because 1 orbital has one unpaired electron.

fr. One unpaired electron so that

that is paramagnetic

\* List any two reasons for less crystal field splitting in tetrahedral complexes than in octahedral complexes.

Ans) i) Octahedral complexes have more ligands in comparison to tetrahedral so that octahedral has more negative charge due to more ligands therefore it has more repulsion so that less CFS in tetrahedral complex than octahed.

ii) d orbital of tetrahedral less strongly interact with ligands and d orbitals of octahedral more strongly interact with ligands so that less crystal field splitting in ~~tetrahedral~~ than octahedral compa.

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$$d \rightarrow 5: f_{\text{c}} + 4 Dg \quad [1/1/1] \text{ deg set}$$

degenerated d orbital in free space

$$\text{CFSE} = 12Dg - 24Dg + 0 \\ = -12Dg$$

\*  $d^5$  in octahedral

$$\text{for O.f.L} \quad \begin{matrix} \text{eg set} \\ [1/1] \end{matrix} \\ + 6 Dg \quad \begin{matrix} \text{N} \\ [1/1/1/1/1] \end{matrix}$$

degenerated d orbital in free state

$$\text{CFSE} = 12Dg - 12Dg + P$$

$$= -4Dg + P$$

for  $\rightarrow S.p.L$   $[1/1]$  eg set

$$+ 6 Dg$$

$$\begin{matrix} \text{N} \\ [1/1/1/1/1] \end{matrix} \quad \begin{matrix} \text{f} \\ \downarrow \end{matrix} \quad \begin{matrix} \text{eg set} \\ [1/1/1/1/1] \end{matrix}$$

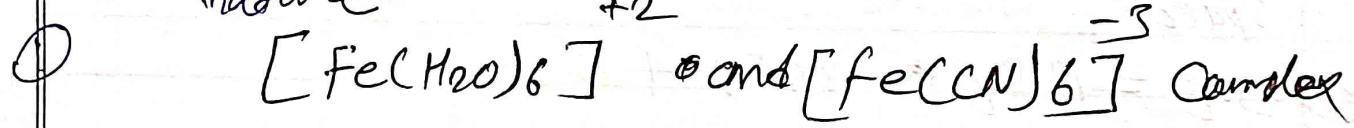
$$- 4Dg$$

$$\boxed{\text{CFSE} = -4Dg + EP}$$

Teacher's Signature \_\_\_\_\_

(8)

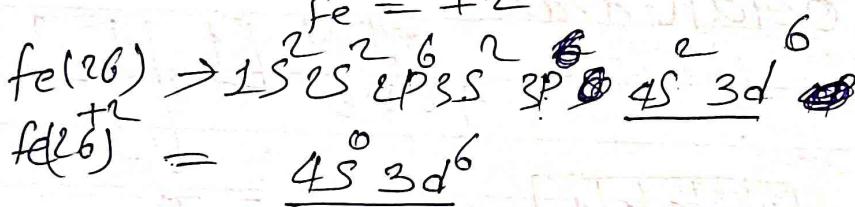
- \* Crystal field theory: crystal field theory is a bonding model that explains many important properties of transition-metal complexes, including their colour, magnetism, structure, stability and reactivity. The central assumption of CFT is that metal-ligand interactions are purely electrostatic in nature +2



$$x + 6 \times 0 = +2$$

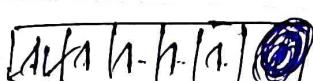
$$x = +2$$

$$\text{Fe} = +2$$

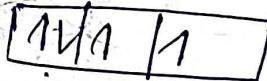


(iii)  $\text{H}_2\text{O}$  is a weak field ligand ~~so it does not pairing~~

$$+6Dq \quad \boxed{1 \ 1} \quad \text{Set}$$

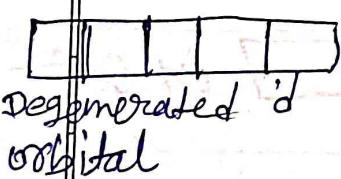


$$-4Dq$$



Bowl  
Centre

2 Set



$$\text{CFSE} \rightarrow 2(6Dq) + 4(-4Dq) + 0 \times p \quad \begin{matrix} \text{Total number of} \\ \text{unpaired electrons} \end{matrix}$$

$$= 12Dq - 16Dq + 0 \quad \text{is } +80 \text{ f.e.s}$$

$$\Rightarrow -4Dq \quad \text{paramagnetic in behaviour}$$