

MOLECULAR STRUCTURE AND THEORIES OF BONDING

orbital:-

The 3-dimensional space around the nucleus of an atom, where in the probability of finding an e⁻ is maximum is known as "orbital."

Shapes & Geometry of diff. atomic orbital.

	<u>shape</u>	<u>Geometry</u>
1) s-orbital	spherical in shape.	(○)
2) p-orbital	Dumb-bell (2-lobes)	(J)
3) d-orbital	Double dumb-bell (4-lobes)	(*)
4) f-orbital	Four fold dumb-bell (8-lobes)	(—)

→ A single orbital can accommodate a maximum of 2 e⁻'s with opposite spins.

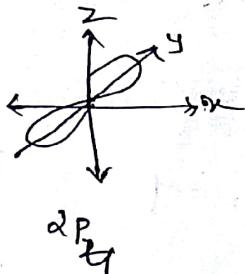
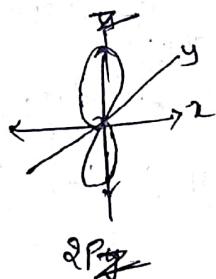
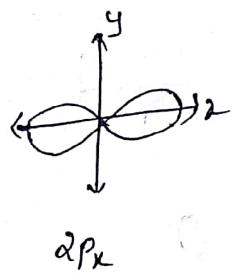
Ex:-

- 1) s-subshell - $\boxed{1v}$ → 1 orbital & 2 e⁻'s.
- 2) p-subshell - $\boxed{1v} \boxed{1v} \boxed{1v}$ → 3 orbitals & 6 e⁻'s.
- 3) d-subshell - $\boxed{1v} \boxed{1p} \boxed{1d} \boxed{1f} \boxed{1g}$ → 5 orbitals & 10 e⁻'s.

S-orbital!:-

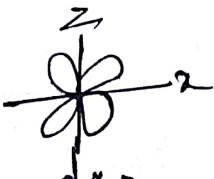


p-orbital!:-



→ The 2 dumbbells of p-orbitals have opposite phase signs.
the area where the change of phase signs take place
is known as a node.

d-orbital!:-



* Molecular
Molec
Ove

* Molecular orbitals!

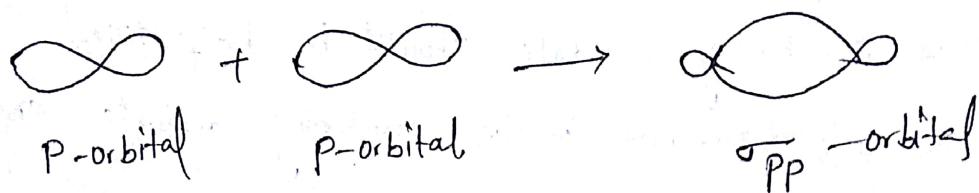
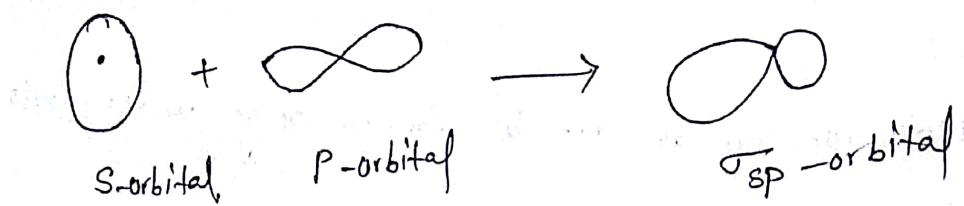
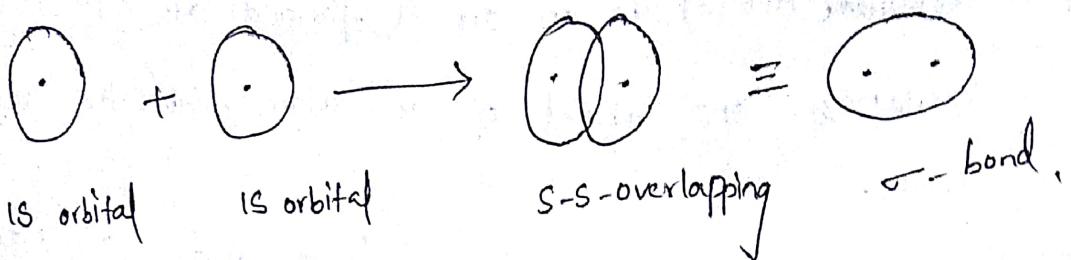
- Molecular orbital is an orbital formed due to the overlap of one orbital of an atom with the orbital of another.
- Thus MO represents a covalent bond and contains only $2\bar{e}'s$.
- A molecular orbital can be formed only under following conditions:
 - ① The combining orbitals should be half-filled.
 - ② The $\bar{e}'s$ present in the combining orbitals should have opposite spins.
 - ③ The combining orbitals are properly aligned to ensure that the overlap is effective.

* Types of MO's

They are 2 types 1) σ 2) π .



- It is formed due to the parallel end to end overlap orbitals.
- 'σ' bonds can be formed by the overlap of two s orbitals (or) by one s-orbital and p-orbital (or) by 2 p-orbitals

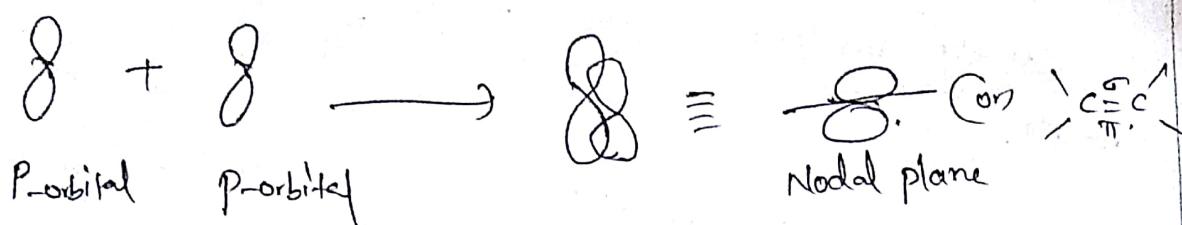
Q1-π-Bond :-

It is formed due to the parallel overlap of p orbitals.

The π 's associated with π bonds are called pi's.

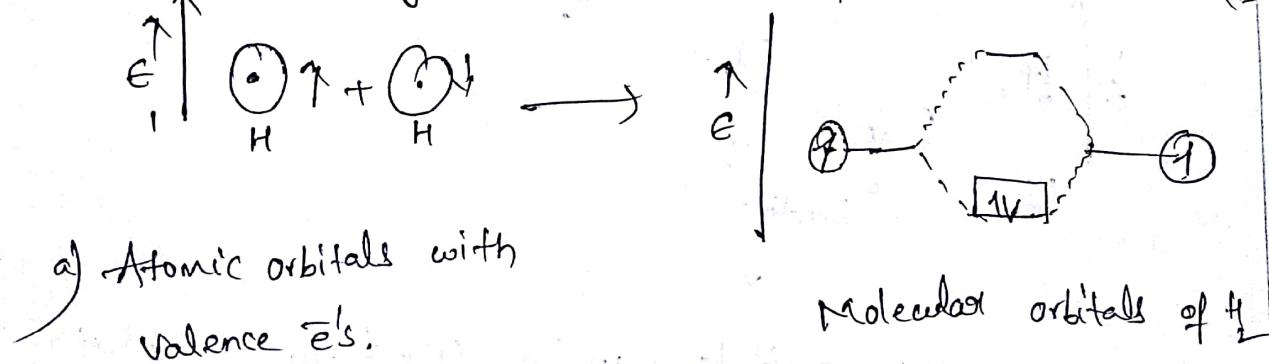
Since the bonds are formed by overlap of p orbitals which have 2 lobes, the hybrid orbital also has two lobes, each one of the lobes lies on either side of the plane.

π ϵ 's are of high energy & are also loosely held, hence these are easily broken than σ ϵ 's. The atoms cannot rotate around the π bond, due to which the alkenes can exist as cis-trans isomers.



Molecular orbital theory:-

- It was proposed by Hund - Mulliken theory.
- Atomic orbitals containing valence e⁻s combine together & form a Molecular orbital.
- Bonding molecular is + is → Bonding M.O.
- 2 atomic orbitals combined together & form 2 M.O.
- In that lowest energy M.O. will contain e⁻ pair which is called B.



- Bonding orbital has lower energy than that of the atomic orbitals from which it is formed.
- This orbital is formed when the lobes of the 2 atomic orbitals have same sign.

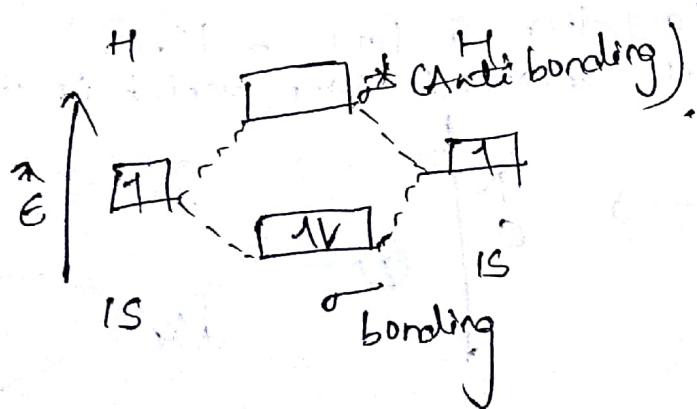
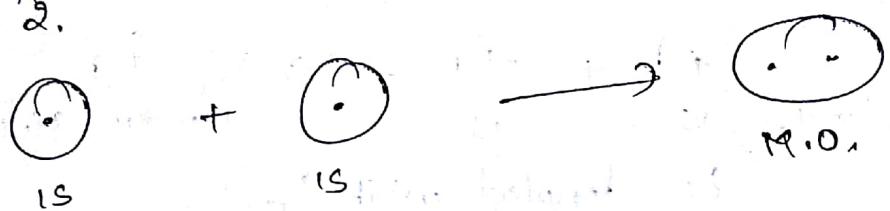
3) Bonding orbitals are usually stable because of the high density available at the nuclei of two atomic orbitals.

Anti bonding Molecular orbital :-

→ 2 atomic orbitals combine together & form $2^{\text{M.O.}}$. In that higher energy M.O. is vacant. It is called Anti bonding Molecular orbitals.

which is denoted as σ^* .

Eg:- H_2 .



These molecular orbitals can be used to calculate the geometry, energy levels & other properties.

Let us represent the lowest energy M.O. as σ & highest energy M.O. is σ^* .

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12ene :-

Line Diagram	M.O Structure	Nature	No. of Nodes
		A.B.M.O	5
		A.B.M.O	4
		A.B.M.O	3
		B.M.O	2
		B.M.O	1
		B.M.O	0

wave function

$$\Psi = c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 + c_4 \psi_4 + c_5 \psi_5 + c_6 \psi_6 \rightarrow \Psi_1 \text{ to } \Psi_6$$

Ground State :-

$$\psi_1^2 \psi_2^2 \psi_3^2 \psi_4^0 \psi_5^0 \psi_6^0$$

= wave function
of $6P_z$ orbita

$$\text{Excited State} : \quad \psi_1^2 \psi_2^2 \psi_3^1 \psi_4^1 \psi_5^0 \psi_6^0 \rightarrow c_1 + c_2 = \text{coefficient of each M.O.}$$

Benzene :-

(4)

M.O	Line Diagram	M.O Structure	Nature	No. of Nodes
Ψ_6			A.B.M.O	5
Ψ_5			A.B.M.O	4
Ψ_4			A.B.M.O	3
Ψ_3			B.M.O	2
Ψ_2			B.M.O	1
Ψ_1			B.M.O	0

wave function

$$\Psi = c_1 \Psi_1 + c_2 \Psi_2 + c_3 \Psi_3 + c_4 \Psi_4 + c_5 \Psi_5 + c_6 \Psi_6 \rightarrow \Psi_1 \text{ to } \Psi_6$$

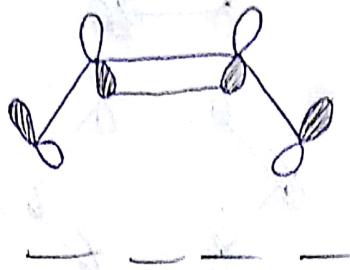
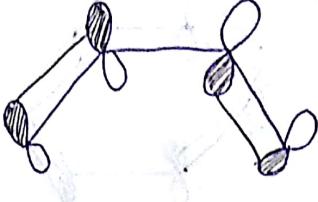
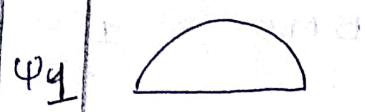
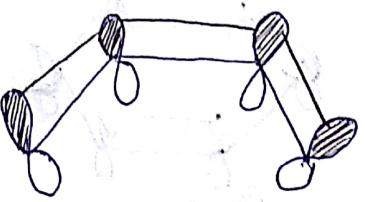
Ground State :-

$$\Psi^2 \Psi_2^2 \Psi_3^2 \Psi_4^0 \Psi_5^0 \Psi_6^0$$

= wave func
of $6P_z$ or

$$\text{Excited State} : \Psi_1^2 \Psi_2^2 \Psi_3^1 \Psi_4^1 \Psi_5^0 \Psi_6^0 \rightarrow c_1 + c_2 = \text{coefficient of each M.O.}$$

1.3 Butadiene :- $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$

M.O	Line Diagram	M.O Structure	Nature	M.O. of Nodes
Ψ_4			A.B.M.O	3
Ψ_3			A.B.M.O	2
Ψ_2			B.M.O	1
Ψ_1			B.M.O	0

Ground state :- $\Psi_1^2 \Psi_2^2 \Psi_3^0 \Psi_4^0$: Excited state = $\Psi_1^2 \Psi_2^1 \Psi_3^1 \Psi_4^0$

wave function :- $\Psi = c_1 \Psi_1 + c_2 \Psi_2 + c_3 \Psi_3 + c_4 \Psi_4$

Ψ_1 to Ψ_4 are wave functions of four p_z orbitals

c_1 to c_4 are respective coefficients of each M.O.

Benzene:- Butadiene

$\Psi_1 \rightarrow$ Lowest energy level no internuclear nodes in b/n.

$\Psi_2 \rightarrow$ Next higher energy one internuclear node in b/n 2nd & 3rd carbon.

$\Psi_3 \rightarrow$ Next higher energy, internuclear nodes b/n all carbons 1 & 2nd and 3 & 4 carbons are antibonding atoms 2 and 3 are bonding.

$\Psi_4 \rightarrow$ Highest energy, 3 internuclear nodes b/n all carbons resulting total antibonding.

Benzene:-

→ Although all these orbitals (Ψ_1, Ψ_2, Ψ_3) do not appear equivalent, they have same energy & predominantly of bonding character.

→ Ψ_4, Ψ_5, Ψ_6 have 3 internuclear nodal surfaces.

→ These orbitals have equal energy though they do not resemble each other containing predominantly antibonding character.

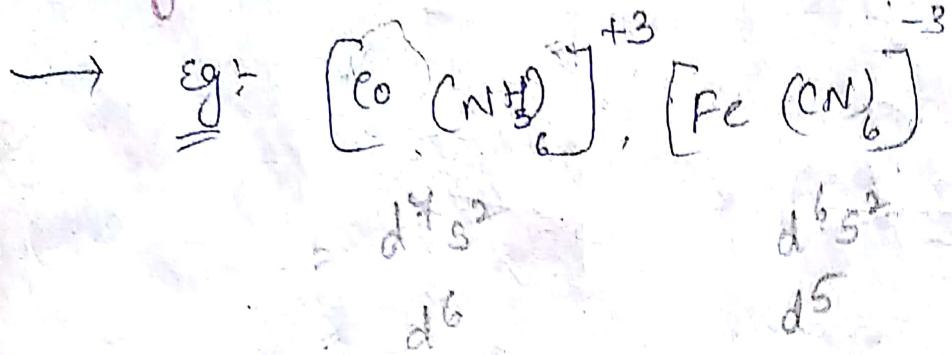
CFT: (Crystal field theory)

This theory was introduced by Bethe and VanVleck to explain the colour and magnetic properties of crystals & solids hence, it is called as CFT.

Salient features of CFT:-

- According to CFT a complex has a combination of central ion surrounded by other ions or molecules with electrical dipoles called ligands. This theory consider these ligands as point charges or point dipoles.
- The bonding between the metal cation and ligand arise due to electrostatic attraction between the nucleus of the metal cation and the partial negative charge present on the ligand.
- The bond between the metal and ligand is purely ionic.
- The interaction betw. the electrons of the cation and lone pair electrons of the ligand is entirely repulsive.
- These repulsive forces are responsible for the splitting of d-orbital of the metal cation.
- The d-orbital which are degenerate (same energy) in a free metal ion have their degeneracy destroyed by the approaching ligands during the formation of a complex.
- CFT does not consider the overlapping between metal orbitals & ligand orbitals.

① Regular oh Geometry:



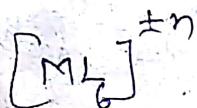
→ In case of free Metal ion all the 5 d-orbitals are degenerate → having same energy.

→ i.e. these have same energy.

→ Let us consider an o.h complex $[\text{ML}_6]^{\pm n}$ in which the central Metal cation $\text{M}^{\pm n}$

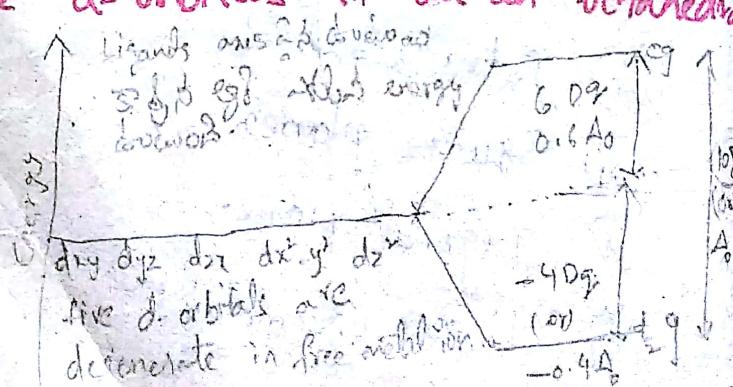
→ placed at the centre of the oh & is surrounded by 6 Ligands.

→ which are present at the 6 corners



→ All the bonds b/w the M & the ligands are in same distance in Regular oh Geometry.

splitting of the d-orbitals in ~~an octahedral~~ complex:



→ In octahedral complex 6 ligands approach to the metal ion along the $x, y, z \ & -x, -y, -z$ directions.

→ since the lobes of the two eg orbitals i.e $d_{x^2-y^2}, d_{z^2}$ point directly at the path of the approaching ligand.

→ The es in eg orbitals experience greater repulsion from the ligands than those in $3 t_{2g}$ orbitals. i.e., $d_{xy}, d_{yz} \ \& d_{zx}$.

→ These lobes directed in space b/w the path of the approaching ligands. Hence, the energy of the eg orbitals are increased & energy of the t_{2g} orbitals are decreased.

→ Thus, the 5d orbitals which are degenerate are splitting to 2 levels under influence of approaching ligands.

→ The eg which is doubly degenerate possess higher energy & the t_{2g} or level which is triply degenerate possesses lowest energy.

→ The splitting of 5d orbitals into eg & t_{2g} by approaching of ligand is called crystal field splitting or energy level splitting.

→ The energy difference b/w σ_g & σ_u level is denoted by $10 Dq \cos \Delta_0$. E is called as crystal field's splitting energy in o.h. geom.

If tetragonally distorted o.h. geometry!

- If 2 trans ligands along 2 axis of o.h. complex $[ML_6]$ are moved either towards the metal ion (or away from the metal ion).
- The resulting complex is said to be 'tetragonal distorted o.h. geometry'.
- D^+ is defined as any deviation from regular o.h. complex is known as distorted o.h. complexes.
- There are 2 types of distorted o.h. complexes.
 - one is compressed o.h. (or shortened) elongated o.h (or stretched)



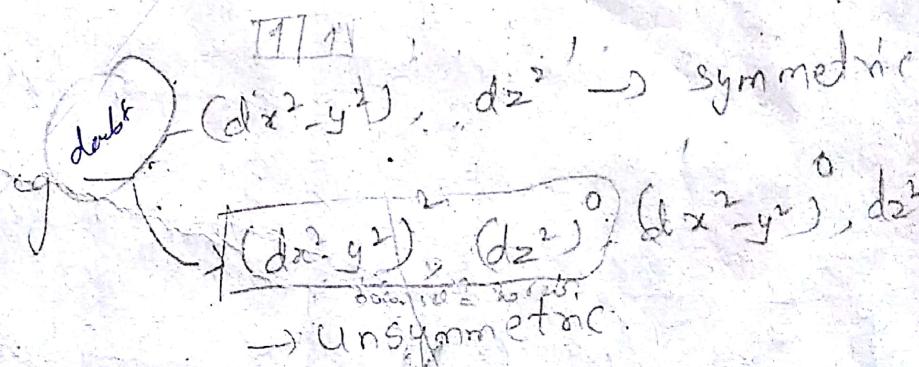
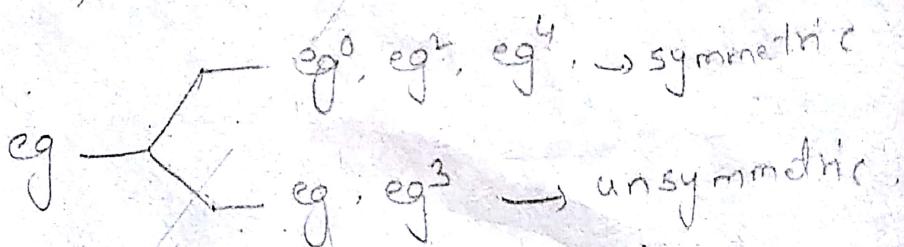
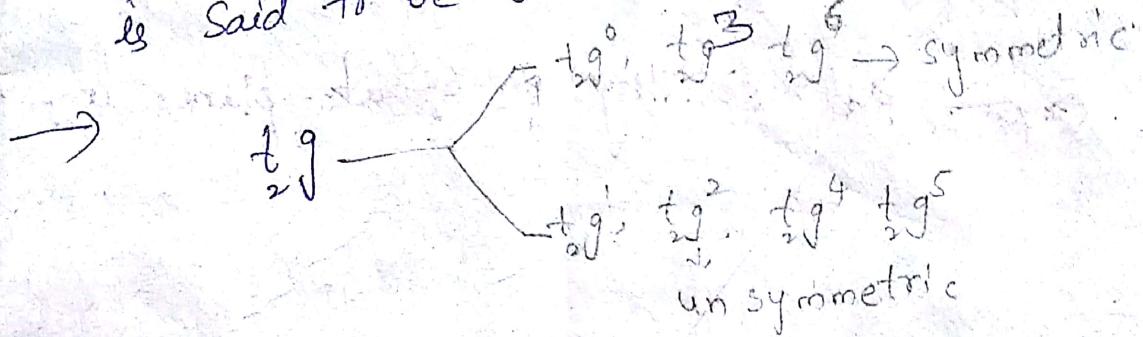
* John Teller Theorem:

- 1 Any non-linear molecular system possessing degenerate electronic state will be unstable.

& will undergo distortion to result in V-shape

system of low symmetry, low energy & thus the degeneracy is removed.

→ The decrease of energy due to distortion is said to be Jahn-Teller stabilization energy



t_{1g} - sym

\times t_{1g} - unsym

Conditions for distortion:

t_{2g} symmetric, eg symmetric → No distortion

t_{2g} unsymmetric, eg symmetric → slight distortion

t_{2g} unsym., eg unsym. → strong distortion

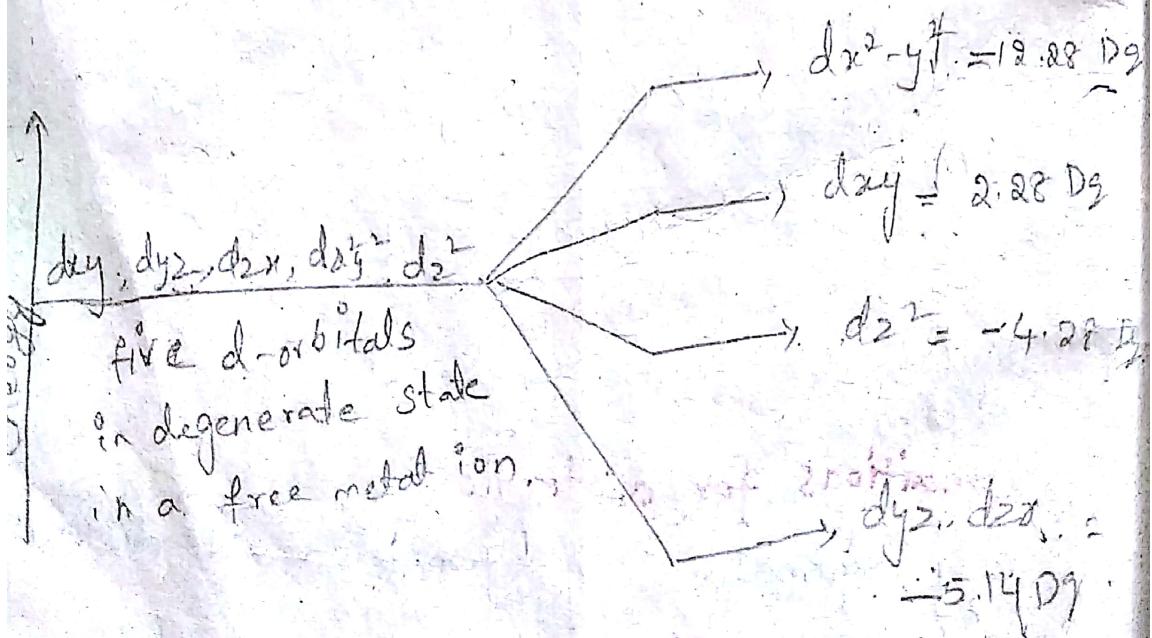
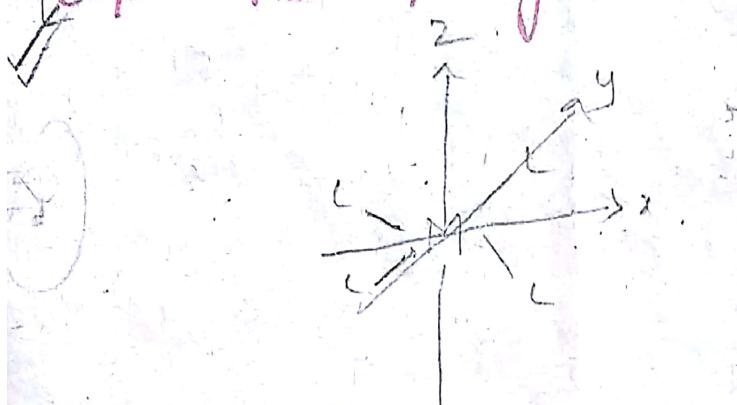
t_{2g} sym., eg unsym. →



$t_g \rightarrow [IV. IV. IV] sy$ } sharing
 $e_g \rightarrow [IV. I] un$ } distortion

→ Due to distortion the degeneracy state is lifted & energy levels get separated.

Crystal field splitting in square planar complex



→ In square planar complexes we have 4 ligands on x & y axis & 2 ligands are completely removed on z-axis.

→ In such a case $d_{x^2-y^2}$ orbital which is oriented along the $x \& y$ axis experience from 4 ligands & it attains higher energy equivalent to $+2.28 Dq$.

→ The d_{xy} orbital is oriented in b/n $x \& y$ axis, it experience least repulsion & energy equivalent to $-2.28 Dq$.

→ The d_{z^2} & d_{x^2} & d_{yz} orbitals have energy equals to $-4.28 Dq$ & -5.14 respectively.

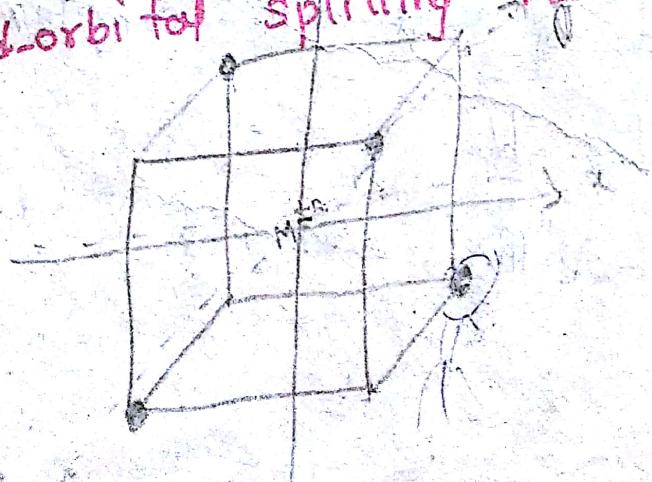
→ The energy difference b/n $d_{x^2-y^2}$ & d_{z^2} d_{yz} is called as square planar split energy, & it is denoted by Δ_{sp}

Energy order:

$$d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{x^2}$$

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d-orbital splitting tetrahedra Geometr

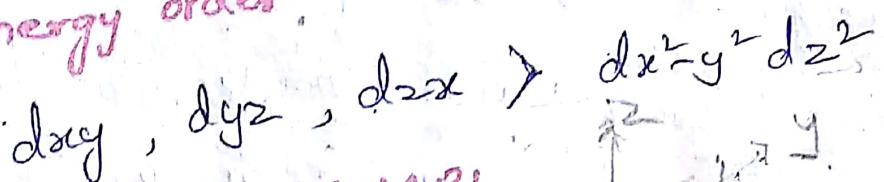


- d_{xy}, d_{yz}, d_{zx}
d_{xz}, d_{y²}, d_{z²}
 $d_{x^2-y^2}$, d_{z^2}
 $\Delta E = 6Dq$
 $\rightarrow 0.6 \text{ Å}$
- A tetrahedral placed in a cube in which centre of the cube is the metal ion M^{+n} is present.
 - from the above observation the d-orbital of d_{xy}, d_{yz}, d_{zx} are near to the 4 ligands.
 - whereas d-orbital of $d_{x^2-y^2}, d_{z^2}$ orbitals are away from the 4 ligands.
 - t₂ orbitals of metal ion interact with 4 ligand orbitals & get more energy than e' orbitals.
 - thus the energy of t₂ orbitals will be \uparrow while that of e' orbitals will be decreased.
 - The splitting of d-orbitals in a tetrahedral complex is reverse of that of o.h. - complex.
 - The energy diff. b/w t₂ & e' is called crystal field splitting & is denoted with Δt .

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- In tetrahedral complex the d-orbitals are not interacting directly with the 4 ligands
 - So, splitting energy of d-orbitals is less than that in the O.H. complex.

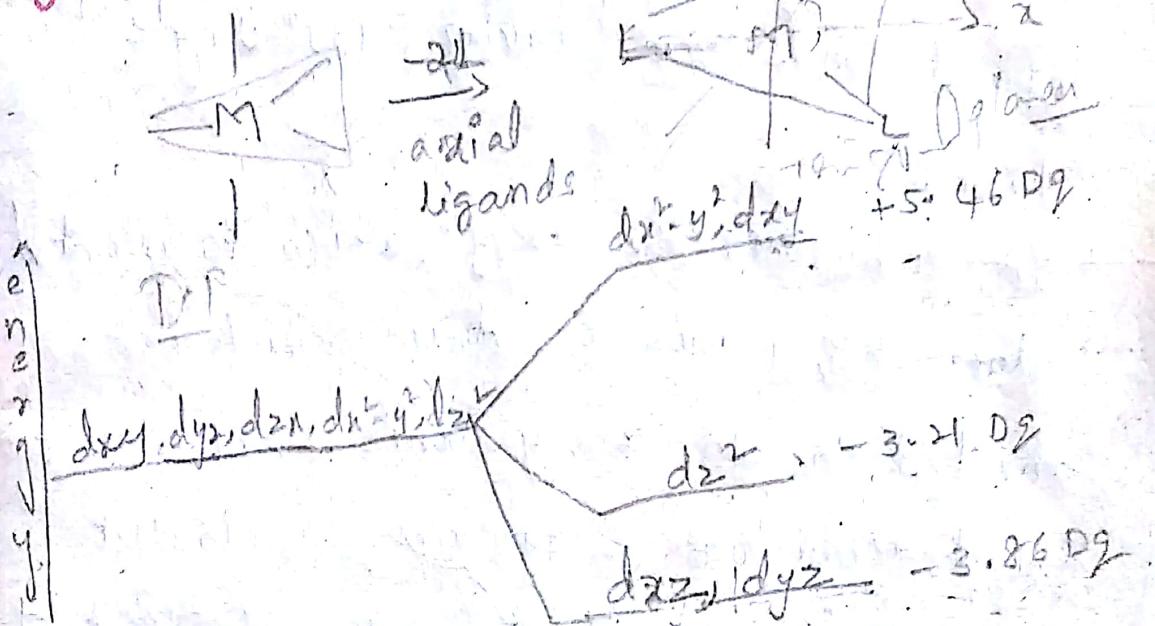
→ i.e., $\Delta_t = \frac{4}{9} \Delta_o$

Energy order:



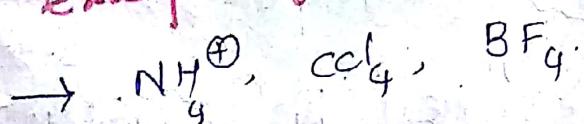
more stability.

* 6. TRIGONAL PLANAR!



Examples of tetrahedral complexes:

(Rama Lingam)



Trigonal planar complex is resultant from trigonal bipyramidal complexes. By completely removal of 2 trans (org) axial ligands in trigonal planar $\rightarrow \text{SP}^3 \text{d}^2$

~~Date~~

Water Treatment :-

Introduction:-

→ Water is the most wonderfull abundant and useful compound for all living Organisms (humans, animals, and plants).

→ Not only essential for living Organisms it occupies the unique positions in industries like Textile, paper, pharmaceutical industries and domestic purposes.

Sources of Water:-

→ Main sources of water are

1. Rain water :-

→ Rain water is the purest form of water

→ Since it is obtained as a result of evaporation

from the surface water during rain fall, it desenters dissolved gases like CO_2 , NO_2 , SO_2 , etc.

2. River water :-

* Rivers are fed by rain and spring water.

* River water also contains the organic matter formed by the decomposition of plants and other impurities.

3. Sea water:-

* This is most impure form of Natural water

* Sea water contains 3.5% saline salts out of which

about 2.5% of NaCl.

* Sea water also contains bycarbonates of Ca^{2+} , Mg^{2+} , K^+ .

4. Spring and well water:-

* It is general clear appearance due to the filtering action of soil.

* But contains more of the desirable salts.

* But less organic impurity.

5. Impurities in water:-

The natural water is usually contaminated by different types of impurities like-

Chemical impurities, physical impurities, biological impurities.

a) chemical impurities:

i. Dissolved gases: * Natural water contains deserved atmospheric CO_2 , deserved O_2 in industrial water induces corrosion reaction.

* Dissolved NH_3 in water arises from decomposition of Nitrogenous or Organic matter.

ii) Minerals: These includes mineral acids, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{2+} , CO_3^{2-} , Mn^{2+} , HCO_3^- , Cl^- , SO_4^{2-} , F^- , SiO_2 etc.

b) physical impurities:

i. colour: It is caused by metallic substances like salts of iron, Mn^{2+} , algae, Industrial efflu.

Eg: Yellowish red indicates the presence of iron.

iii) Turbidity :- It is due to the colloidal or finely divided solid suspension such as clay, finely divided matter and microorganisms.

iv) Impure taste :-

v) Taste :- Bitter taste is due to presence of algae, bacteria, fungi.

c) Biological impurities :-

Micro organisms like algae, fungi, bacteria which offend from slime thereby causing corrosion

6. Dissadvantages of impure water for industrial purposes

i) Paper industry: Dissolved impurities react with the chemicals used to give paper a glossy surface affecting the colour of paper

ii) Textile industry: Dissolved salts react with dyes to form undesirable precipitates. produce will adhere to be fabric and shared the colour, and cause spots on the fabrics.

iii) Sugar industry : Water for sugar & refineries must be free from sulphides, carbonates, nitrates, and bacteria. causes crystallinity of sugar.

iv) Bakeries :-

presence of organic matter is harmful and it may effect the action of yeast.

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IV. Boilers :- Dissolved salts in water produce scale and scale and caustic embrittlement during the steam generation in boilers.

Types of water :-

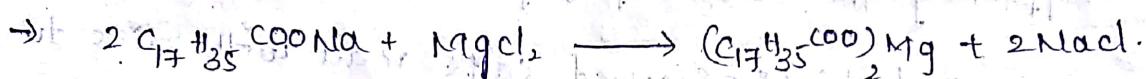
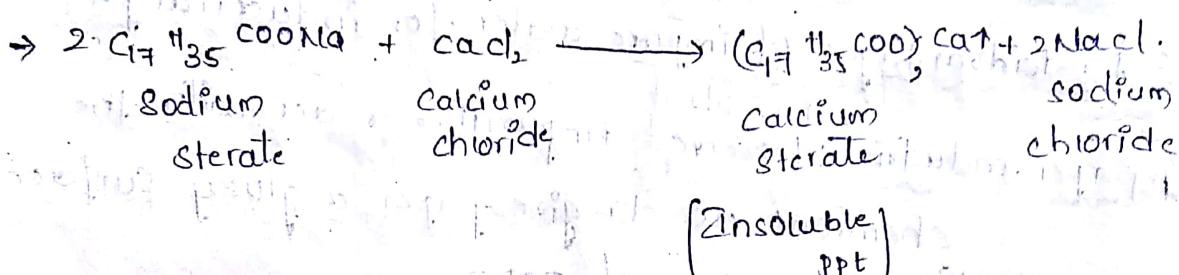
There are two types of water

1. Hard water
2. Soft water

1. Hard water :-

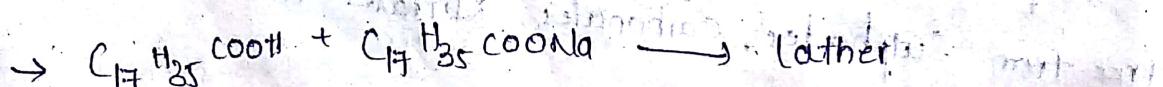
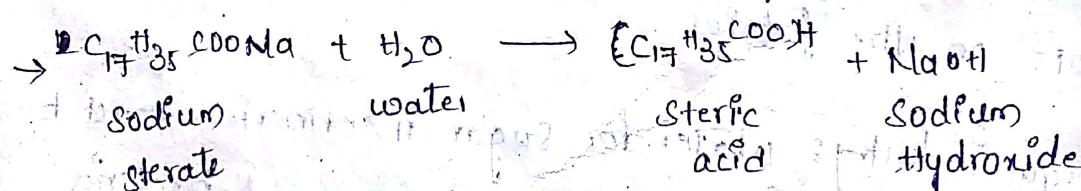
→ It doesn't produce lathering soap solution

→ It forms insoluble ppt



2. Soft water :-

→ Water which produces lathering soap solution.



Hardness of water :-

→ It is a characteristic property of water

→ The water which prevents the lathering soap solution

(Q) Lather prevention capacity is called hardness of water

→ This is due to the presence of Bi^{+3} , Cs^+ , N^+ or Ca^{+2} , Mg^{+2} and other heavy metal ions.

$\text{Ca}(\text{HCO}_3)_2$, CaCl_2 , MgCl_2 , $\text{Ca}(\text{NO}_3)_2$, CaSO_4

Types of hardness

1. Temporary hardness:- It is also called carbonate hardness

and alkaline hardness.

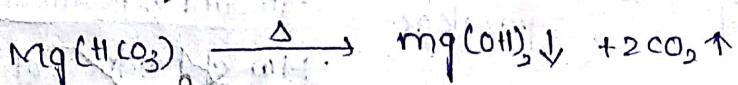
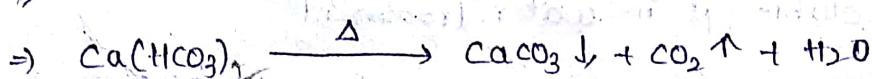
→ It is caused due to the presence of bicarbonates of Ca , Mg , and other heavy metal ions i.e.

i.e. $\text{Ca}(\text{HCO}_3)$, $\text{Mg}(\text{HCO}_3)$

→ Temporary hardness is removed by simple boiling of water

→ While heating bicarbonates are converted into carbonates and hydroxides [insoluble ppt]

→



→ This insoluble ppt deposited as a crust at the bottom of the vessel

2. permanent hardness:-

It is also called as non-carbonate or non-alkaline hardness

→ It is caused due to the presence of Cl^- , Nitrates, Sulphates of Ca^{+2} , Mg^{+2} and other heavy metal ions.

i.e. CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, CaSO_4

MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, MgSO_4

→ Like temporary hardness, permanent hardness cannot be removed by simple boiling but these can be removed by

internal and external treatment of water

Types of H ₂ O	Hardness
Soft H ₂ O	0-70 ppm
Hard H ₂ O	70-150 ppm
Moderate Hard H ₂ O	150-300 ppm
Very hard H ₂ O	above 300 ppm

Degree of hardness or experience of hardness of water

p

→ The hardness of water calculated in terms of CaCO₃ equivalence

→ It is expressed in CaCO₃ equivalence because of two reasons.

1. Its molecular wt is 100 easy for calculations.

2. It is most insoluble ppt in water treatment.

Hardness in terms of CaCO₃ equivalence = $\frac{\text{Amount of hardness}}{\text{Mw of hardness salt}} \times 100$

Salt

Units of hardness :-

1. ppm

2. mg/l

3. ‰ Clark

4. °french

1 parts per million :-

No. of parts of hardness causing salts in CaCO₃ equivalent present in 10⁶ parts [1 million parts] of water

One ppm = One parts hardness causing salts in CaCO₃ equivalent present in 10⁶ parts of water

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2. Milli gram per litre: It is the no. of parts or milli gram of CaCO_3 equivalent hardness present per one litre of water.

$1 \text{ mg/lit} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness present per One litre of water}$

3. Degree Clark: It is the no. of grains of CaCO_3 equivalent hardness present per Gallon ($70,000$) of water.

$1^\circ \text{ Clark} = 1 \text{ grain of } \text{CaCO}_3 \text{ equivalent hardness per gallon of water or } 70,000 \text{ parts of water}$

4. Degree French: It is no. of parts of CaCO_3 equivalent hardness present per 10^3 parts of water.

$1^\circ \text{ French} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness per } 10^3 \text{ parts of water}$

$$1 \text{ ppm} = 1 \text{ mg/lit} = 0.07^\circ \text{ cl} = 0.01^\circ \text{ Fr}$$

10-08-17

Estimation of hardness of water by using EDTA Method:

→ It is a complexometric method in this method EDTA is the reagent.

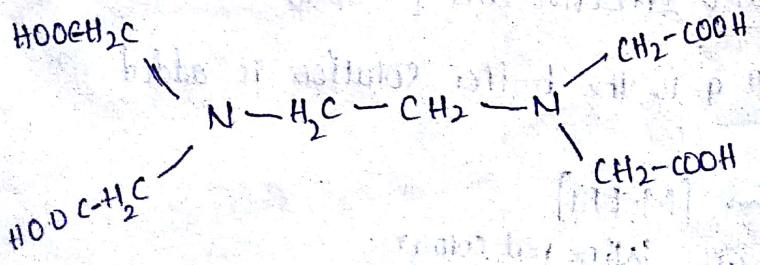
→ EDTA forms the complexes at different pH.

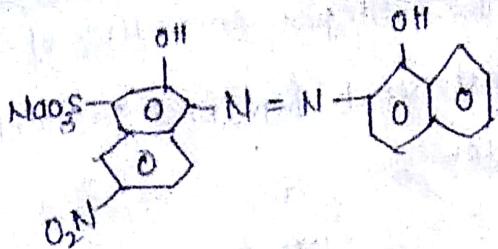
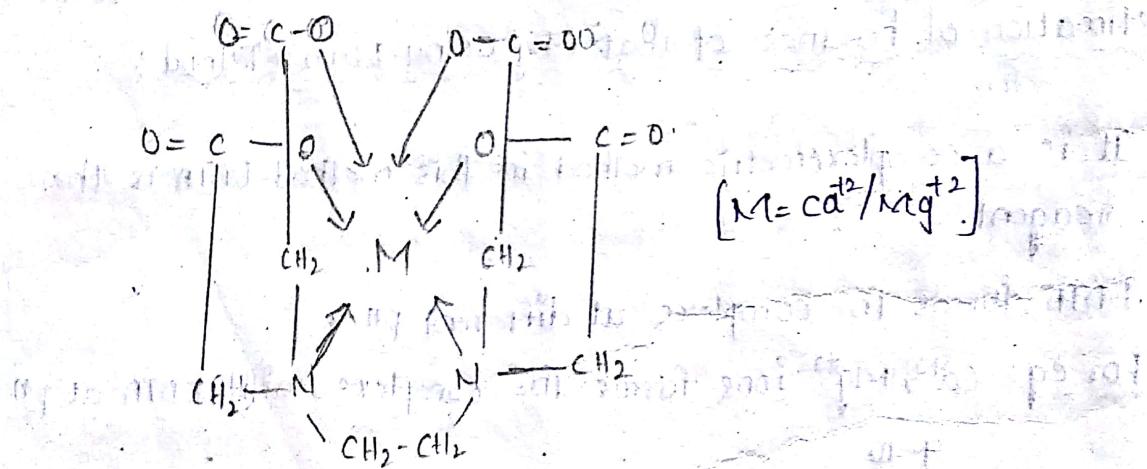
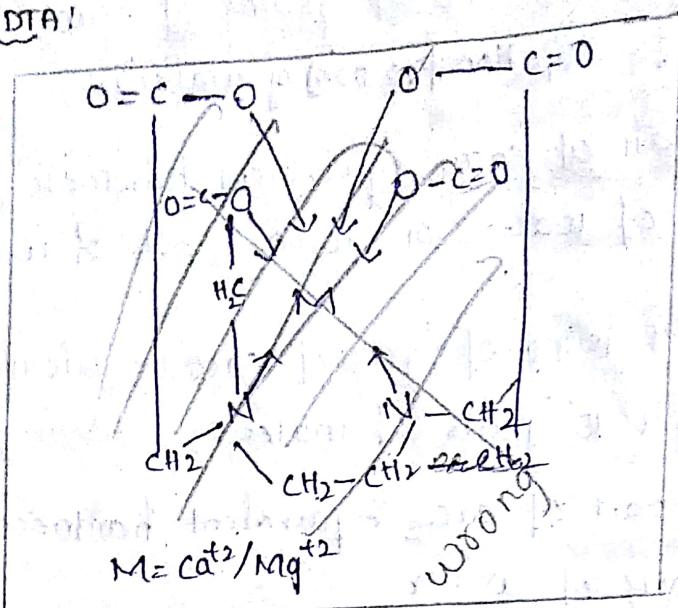
For e.g.: $\text{Ca}^{2+}, \text{Mg}^{2+}$ ions form the complexes with EDTA at pH 9-10.

→ To maintain the pH 9-10 buffer solution added $(\text{NH}_4)_2\text{HPO}_4 + \text{NH}_4\text{Cl}$

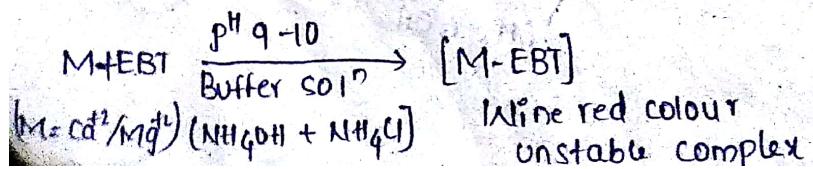
→ In this method Eriochrome Black-T is an indicator.

EDTA:



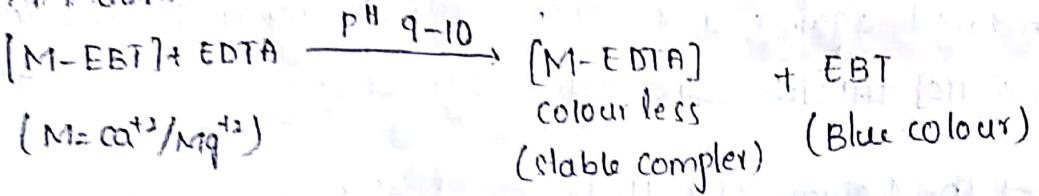
EBT:Metal EDTA:Principle:-

- When hard water treated with EBT indicator it forms M-EBT complex which is in wine red colour and unstable complex.
- Here the EBT is also effective and pH. 9-10
- To maintain the pH 9-10 the buffer solution is added



The wine red colour solution is titrated against $\text{M}-\text{EDTA}$ and it forms $(\text{M}-\text{EDTA})$ complex which colourless and stable complex and it releases the free EBT indicator which is in blue colour.

$\text{M}-\text{EDTA}$



procedure:-

preparation of standard hardwater: Dissolve one gram of pure and dry CaCO_3 in minimum quantity dilute HCl and evaporate the solution to dryness (or) water bath.

→ Dissolve the residue in distilled water to make one litre solution in a standard flask or volumetric flask.

⇒ 1 gram of pure & dry CaCO_3 → add minimum quantity of HCl.

→ evaporated in water bath → Residue is form → This residue dissolved in 1lit of distilled water by using standard flask

Molarity of standard hardwater (M_1)

$$M_1 = \frac{1}{100} \times \frac{1}{V(\text{lit})}$$

$$M_1 = 0.01$$

standardisation EDTA solution:- take 20ml of standard hardwater

Take 20ml of hard water in a conical flask + 20ml of buffer solution + 2/3 drops of EBT and EDTA titrate.

$[\text{M}-\text{EDTA}] + \text{EBT}$ initial colourless Blue colour

→ Pipette out 20ml of standard hard water solution into a conical flask add 2ml of buffer solution and 3 drops of EBT indicator

→ The wine red colour solution present in conical flask is titrated against with EDTA solution, [which is taken in a burette] till the wine red colour changes to blue colour

→ Let the volume of EDTA is x ml

$$M_1 V_1 = M_2 V_2$$

(STHW) (EDTA)

$$M_1 = \frac{M_2 V_2}{V_1} \text{ molarity of standard hard water} = 0.01 \text{ M}$$

$$V_1 = \text{volume of STHW} = 20 \text{ ml}$$

$$M_2 = \text{molarity of EDTA} = ?$$

$$V_2 = \text{volume of EDTA} = x \text{ ml}$$

$$M_2 = \frac{M_1 V_1}{V_2}$$

$$M_2 = \frac{0.01 \times 20}{x}$$

Standardisation of total hardness :-

→ pipette out 20ml of the water sample into a clean conical flask and add 2ml of buffer solution and 3 drops of EBT indicator and titrate this against with EDTA solution (which is taken in a burette) till the wine red colour changes to blue colour

→ let the volume EDTA is y ml

$$M_2 V_2 = M_3 V_3$$

(EDTA) (Hard water sample)

$$M_3 = \text{Molarity of EDTA}$$

$$V_2 = \text{volume of EDTA} = 1 \text{ ml}$$

$$M_3 = \text{Molarity of hard water sample} = ?$$

$$V_3 = \text{volume of hard water sample} = 20 \text{ ml}$$

Total h

$$\text{Total hardness water} = M_3 \times 10^5 \text{ ppm}$$

Standardisation of permanent hardness:

→ Pipette out 100ml of hard water sample (Tap water) in a beaker and boil it till the volume reduced to 20ml. Cool the solution and filtered the water into a conical flask and add 2ml of buffer solution and add 3 drops of EBT indicator and titrate with EDTA till a blue colour end point is obtained.

→ Take the reading as 'z'ml

$$M_1 V_1 = M_4 V_4$$

(EDTA) (mls after heating)

M_1 = molarity of EDTA

V_1 = volume of EDTA

M_4 = molarity of hard water soln after heating

V_4 = volume of hard water soln after heating

$$\text{permanent hardness of water} = M_4 \times 10^5 \text{ ppm}$$

Calculation temporary hardness:-

$$\text{Total hardness} = \text{Temporary hardness} + \text{permanent hardness}$$

$$\text{Temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$

18-08-17

Portable water:-

→ The water which is used for drinking purpose (or) safe to

drink is called as portable water

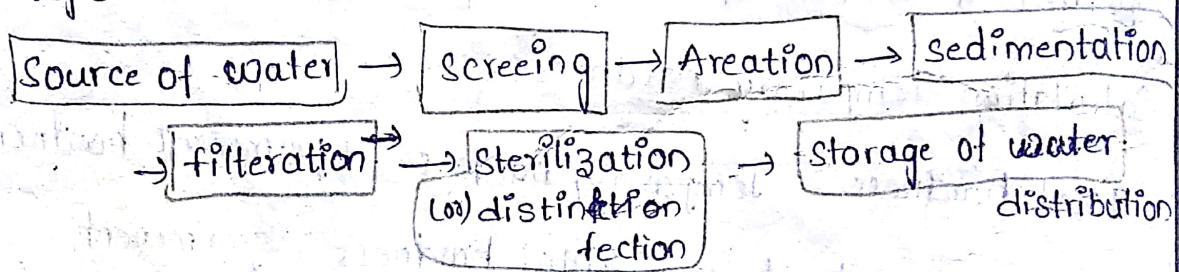
→ Safety of

Specification:-

- It is colourless, odourless
- It should be good in taste
- The optimum hardness of the water must be 125 ppm
- Turbidity of water must not exceed 25 ppm
- Water must be free from py. pathogenic bacteria and disorder gas like H_2S
- The total dissolved salts in water must not exceed 500 ppm
- Water must be free from heavy-metals like lead, chromium and manganese
- The pH of water should be 7-8.5

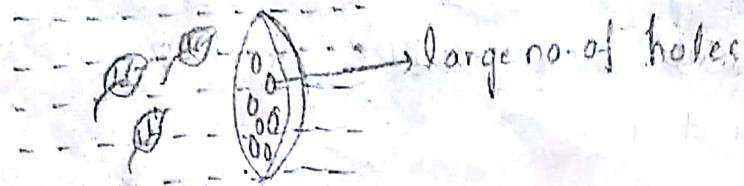
Treatment of water for domestic Supply :-

- It involves in the removal of colloidal impurities, suspended impurities and pathogenic bacteria in water
- Treatment of water for domestic supply involves following steps.



Screening:-

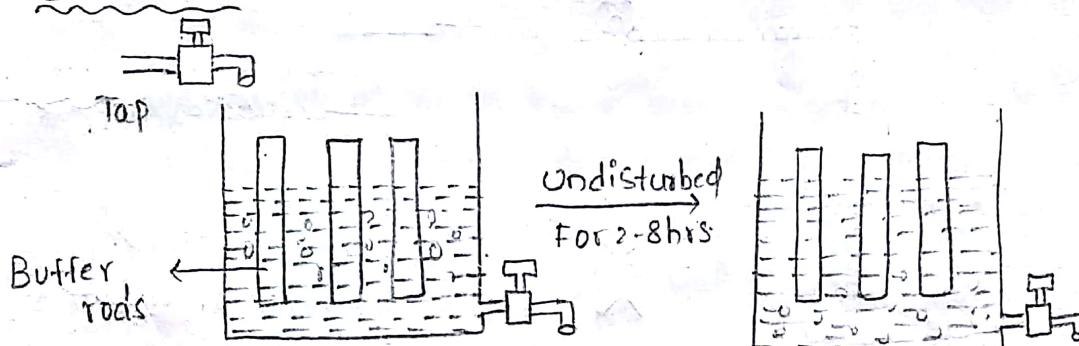
- The water is passed through the screen which is having large no. of holes
- While passing it involves removal of floating materials like leaves, wooden pieces



Aeration:-

- The water is then subjected to aeration.
- Which helps in exchange of gases between water and air
 - Increases the oxygen content
 - It removes impurities like iron, manganese in the form of their hydroxides

Sedimentation:-



In this process the water is passed through the cans.

- It is left undisturbed for 2-8 hours.
- Settlement of particles at the bottom of the tank due to gravitational force.

Sedimentation with Coagulation:-

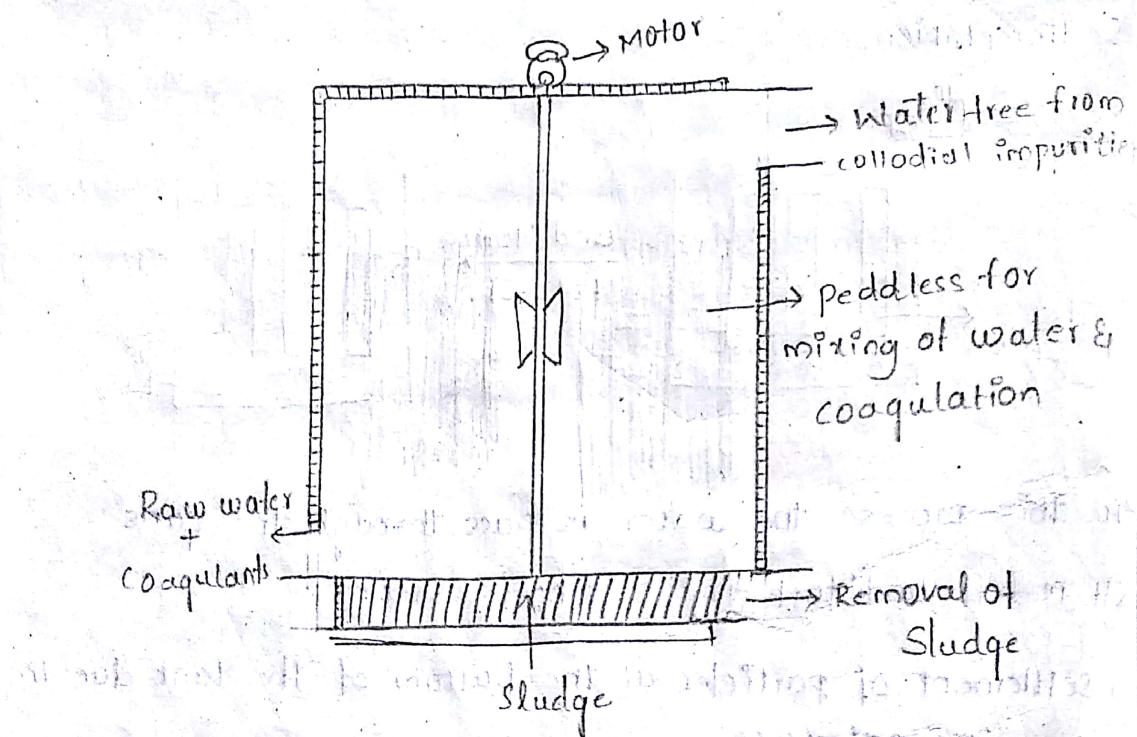
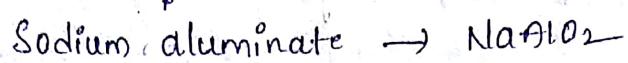
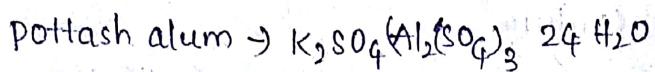
The suspended and colloidal impurities allowed to settle under gravitation

- The basic principle of this treatment is to allow water to flow at a very slow velocity so that the heavier particles are settled down.

→ For setting of fine particle coagulants like alum, sodium aluminate are added which produces gelatinous ppt called floc.

→ It observes the absorb the colloidal and suspended impurities in water.

→ The following sedimentation tank used for the removal of colloidal impurities.



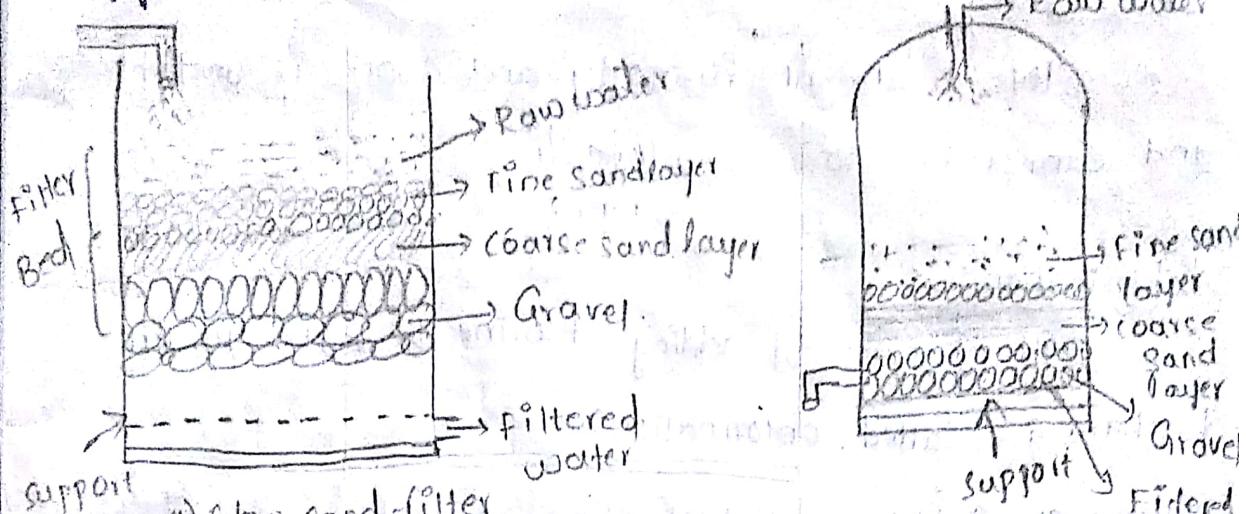
Filtration:-

It involves removal of colloidal particles which are not removed in sedimentation process. In these two types of sand filters are used

1. Slow sand filter

2. Rapid sand filter

→ In case of rapid sand filter filtration becomes fast when compared to slow sand filter due to application



a) slow sand filter

Sterilization and disinfection:-

→ It involves destruction of pathogenic bacteria from water sample

→ Three methods are adapted for sterilization and disinfection

1. Boiling

2. Ozonolysis

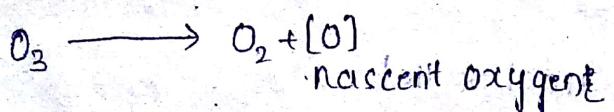
3. By Chlorination.

1. By boiling :-

By boiling - water about 20-30 mins bacteria are killed this process is adapted for domestic purpose but not industrial purpose

2. By adding ozone :-

When ozone is passed into water it decomposes into O_2 and nascent oxygen (O)



→ Nascent oxygen acts as disinfectant [which kills bacteria]

→ O_3 is an unstable isotope of oxygen

Disadvantage :-

This treatment is costly and ozone is unstable and cannot be stored for a long time

3. Chlorination :-

The process of adding chlorine to water to kill bacteria is called chlorination

→ There are 3 types of chlorinating reagents are used:-

1. By passing chloramine

2. By adding bleaching powder

3. By adding chlorine

1. chloramine:



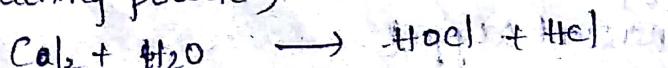
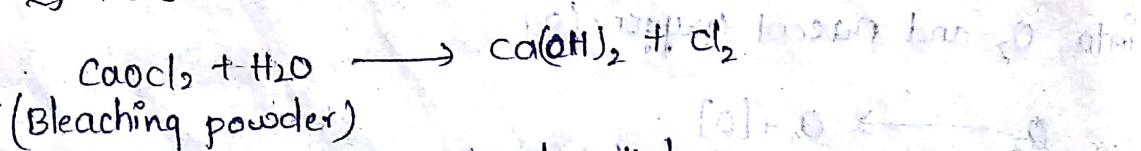
Hypo chlorous
acid

(disinfectant)

→ Chlorine gas is mixed with ammonia in the ratio 2:1 to form a stable chloro-ammine further it reacts with water to form hypo chlorous acid and ammonia (NH_3)

→ HOCl acts as disinfectant

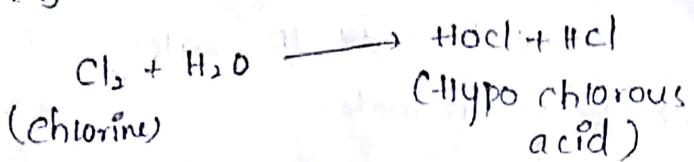
2. By adding bleaching powder:-



(Hypo chlorous
acid)

→ Here HCl acts as disinfectant which kills bacteria.

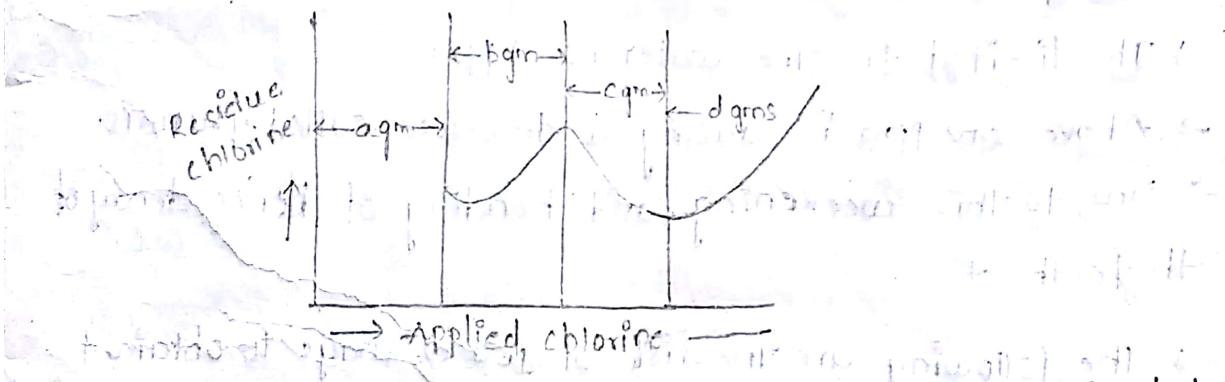
3. By adding chlorine:-



→ Chlorine after reacting with bacteria excess amount of chlorine remains in water as residual chlorine which cause bad taste, odour, and toxic to human beings.

Break point of chlorination :-

→ The process of adding required amount of chlorine to kill bacteria is called break point of chlorination.



→ The water sample is treated with chlorine and estimated for the residual chlorine in water and plotted a graph as showed above which gives the "Break point of chlorination"

From graph it is clear that a gms of chlorine

* a gms of chlorine added oxidises reducing impurities of H_2O

* b gms of Cl_2 added forms chloramines and other chloro compounds

* c gms of Cl_2 added causes destruction of bacteria.

* d gms of chlorine is residual chlorine

* c gms is the break point for the addition of chlorine to water. This is called "Break point of chlorination".

Advantages :-

- It removes colour, taste and organic impurities.
- It destroys all disease-causing bacteria in water.
- It prevents growth of weeds in water.

Dechlorination process :-

→ Removal of excess chlorine from water sample is called dechlorination. It can be done by SO_2 [Sulphur dioxide]



26-08-17

Defluoridation :-

→ Fluorine is most active element found in naturally occurring rocks. The

- The limited fluorine water is 1 ppm
- Above one ppm is causing a disease called fluorosis
- Due to this weakening and bending of bones decay of teeth etc.
- The following are the list of ways to obtain drinking water without fluorine

1. Reverse osmosis filtration.

2. Activated aluminium defluoridation.

3. Distilled water

- Defluoridation methods are divided into 3 basic types depending upon the mode of action.

1. Based on some kind of chemical reaction with fluoride
- Nalgonda Technique

2. Based on absorption process of bone charcoal, tricalcium phosphate, activated carbon, Tamarind gel

→ In this process NaOH cause 'dissolution' of lime
This phenomenon is called 'caustic embrittlement'

'prevention':

→ By using NaPO_4 instead of sodium carbonate in lime

Soda process

Treatment of boiler feed - the :-



Internal treatment

1. Colloidal conditioning.
2. Phosphate conditioning
3. Calgon-conditioning

External treatment

1. Zeolite process
2. Ion-exchange process
3. Lime soda process

Internal treatment:-

Removal of hardness causing salts with in the boiler

• Colloidal conditioning:

In low pressure boilers scale formation can be prevented by adding substances like kerosene and Agar agar

These substances get absorbed over scale forming salts

and results formation of soft, loose, non-sticky ppt (Sludge)

which can be easily removed by using bottom wire brush head

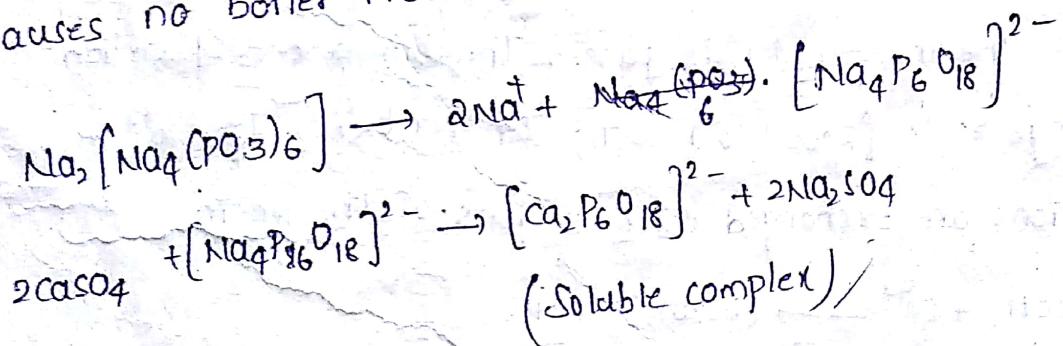
and Blow down operations.

2. phosphate conditioning:

- In high pressure boilers, scale formation can be avoided by adding Na_3PO_4 which reacts with hardness causing salts (causing) to salts forming sludge, soft, loose, and non-sticky ppt of esp. calcium phosphate.
- ~~sludge + sludge~~ Magnesium phosphate which can be easily removed by wire brushes and Blow down operation.

3. Calgon conditioning:-

- It is sodium hexa meta phosphate $[\text{Na}_5(\text{Na}_4(\text{PO}_3)_6)]$ in this process scale formation can be prevented by adding Calgon.
- 0.5-5 ppm calgon prevents scale formation
- This forms soluble complex compounds with CaSO_4 which causes no boiler troubles.



→ The treatment of boiler water with calgon is called

Calgon-conditioning.

External treatments-

Removal of hardness causing salts from the water outside of boiler

In exchange process & (or) Deionisation (or) Demineralisation process:-

It involves exchange in cation of H⁺s with H⁺ ions and anions of H⁺s with OH⁻ ions, for this two types of ion exchange resins are used.

(i) cation exchange resin

(ii) Anion exchange resin

Principle:-

Ion exchange resins are insoluble, cross-linked, longchain organic polymers and the functional groups attached to the chains can exchange hardness producing cations and anions present in water.

Process:-

This process involves the following steps:-

Step 1:- The hard water is passed through a bed of cation exchange resin [R-COOH (or) -SO₃H] of tank A'. The Ca²⁺ and Mg²⁺ ions are exchanged with H⁺ ions of the resin.



→ Thus hardness producing cations [Ca²⁺ and Mg²⁺] are removed.

→ The water (containing) coming out contains Cl⁻, SO₄²⁻, HCO₃⁻
→ Styrene dimethyl benzene copolymer is used as cation exchange resin.

Step 2:-

→ The hard water is then passed through a bed of anion exchange resin [R-OH (or) R-NH₂] of tank B'.

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→ The Cl^- , SO_4^{2-} , HCO_3^- ions are exchanged with OH^- ions of the resin.

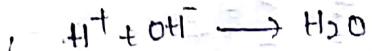


→ p

→ Thus hardness producing anions [Cl^- , SO_4^{2-} , HCO_3^-] are removed.

Step 3:-

→ The H^+ ions produced in 'tank A' combined with OH^- produced in 'tank B' to form water



→ Thus this process removes all types of hardness producing cations and anions present in water.

→ The resulting water is known as "De-mineralised" (or)
"De-ionised water".

→ When water sample is completely de-ionised, it has the tendency to absorb gases like CO_2 , O_2 etc.. from atmosphere which cause boiler corrosion

→ Hence De-ionisation must be followed by de-gasification.

→ Phenol formaldehyde (or) Amine formaldehyde is used as an ion exchange resin.

Regeneration of resins :-

→ With constant use, the resins get exhausted

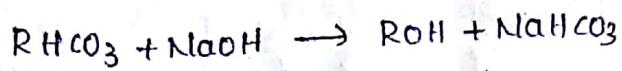
→ This can be regenerated as follows

(1) The exhausted cation exchange resin can be regenerated by passing dil. HCl

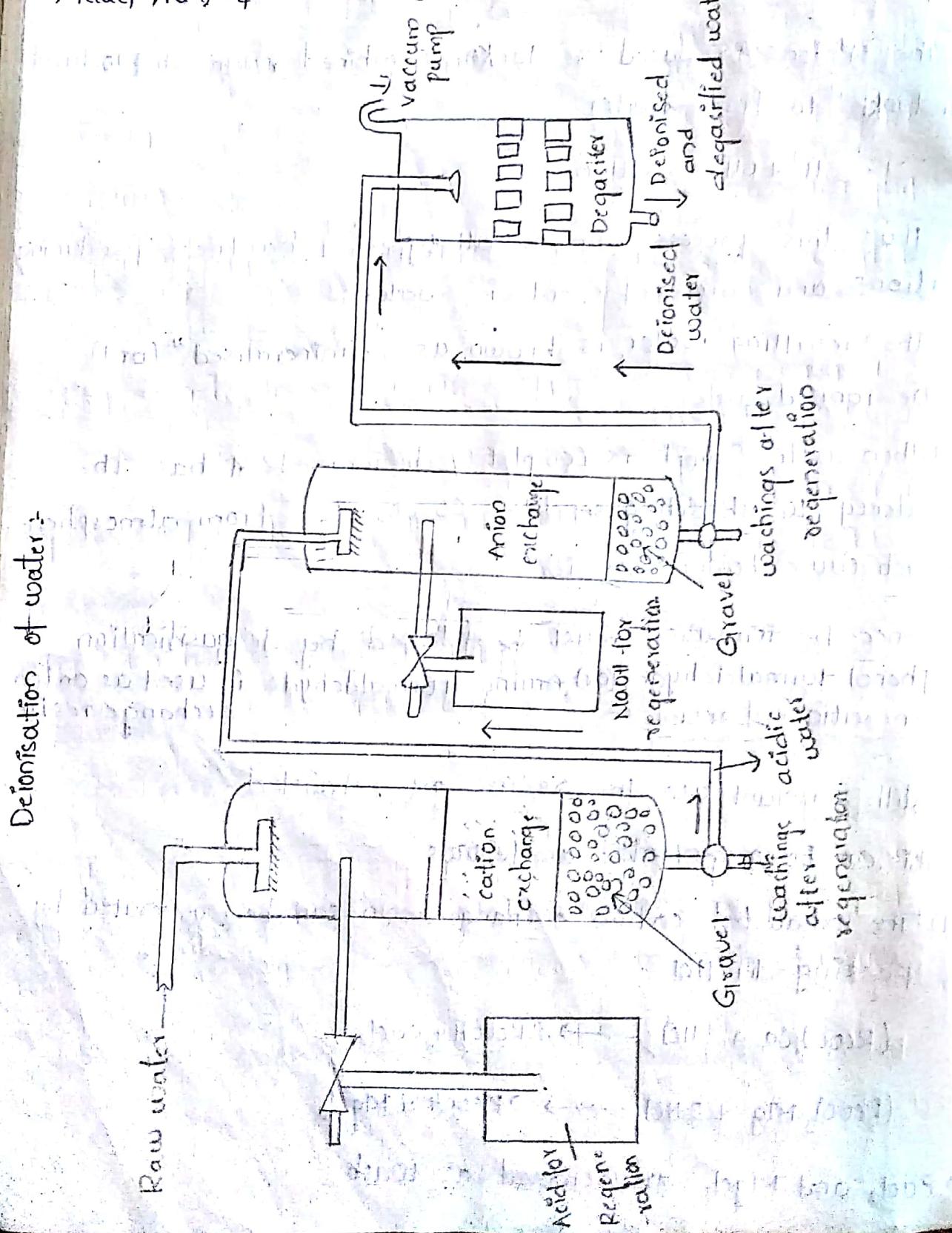


→ CaCl_2 and MgCl_2 are removed as wash

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(Q) The exhausted anion exchange resin can be regenerated by passing dil. NaOH



→ NaCl, Na₂SO₄ and NaHCO₃ are removed as wash



Advantages:-

- Highly acidic or Alkaline water Samples can be purified by this process
- The hardness possessed by de-ionised water is 2ppm
- The de-ionised water is most suitable for high pressure boilers.

Disadvantages:-

- The ion exchanging resins are expensive, hence the cost of purification is high.

- Raw water should contain turbidity below 10 ppm otherwise pores in the resin will be blocked and output of the process is reduced.

Molecular weights of compounds:-

$$\text{CaCl}_2 = 111$$

$$\text{MgCl}_2 = 95$$

$$\text{CaSO}_4 = 136$$

$$\text{MgSO}_4 = 120$$

$$\text{Ca}(\text{NO}_3)_2 = 164$$

$$\text{Mg}(\text{NO}_3)_2 = 148$$

$$\text{CaCO}_3 = 100$$

$$\text{Ca}(\text{HCO}_3)_2 = 162$$

$$\text{Mg}(\text{HCO}_3)_2 = 146$$

$$\text{HCl} = 36.5$$

$$\text{H}_2\text{SO}_4 = 98$$

$$\text{MgCO}_3 = 84$$

Q) A sample of hardwater contains the following dissolved salts per litre: $\text{CaCl}_2 = 111 \text{ mg's}$, $\text{CaSO}_4 = 1.36 \text{ mg's}$, $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ mg's}$, Silica = 40 mg's, turbidity = 10 mg's.

Calculate the temporary, permanent hardness of the water

in ppm, $^{\circ}\text{Cl}$, $^{\circ}\text{Fr}$:

Calculation of H.C.S

Sol:

H.C.salt	Quality of H.C.s (mg's)	M.wt of H.C.s	Equivalent of CaCO_3
CaCl_2	111	111	$\frac{111}{111} \times 100 = 100 \text{ mg/lit}$
CaSO_4	1.36	136	$\frac{1.36}{136} \times 100 = 1 \text{ mg/lit}$
$\text{Ca}(\text{HCO}_3)_2$	16.2	162	$\frac{16.2}{162} \times 100 = 10 \text{ mg/lit}$
$\text{Mg}(\text{HCO}_3)_2$	14.6	146	$\frac{14.6}{146} \times 100 = 10 \text{ mg/lit}$

$$\text{Temporary hardness} = 10 + 10 = 20 \text{ ppm} = \frac{20 \times 0.07}{20 \times 0.1} = 1.4^{\circ}\text{Cl}$$

$$\text{permanent hardness} = 100 + 1 = 101 \text{ ppm} = \frac{101 \times 0.07}{101 \times 0.1} = 7.07^{\circ}\text{Cl}$$

$$\text{Total hardness} = 20 + 101 = 121 \text{ ppm}$$

$$= 121 \times 0.07 = 8.47^{\circ}\text{Cl}$$

$$= 121 \times 0.1 = 12.1^{\circ}\text{Fr}$$

2) calculate the temporary, permanent hardness in $^{\circ}\text{Fr}$, of a water sample collected in Nalgonda district the analysis water is as follows: $\text{CaCl}_2 = 16.2 \text{ ppm}$, $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm}$, $\text{CaSO}_4 = 13.6 \text{ ppm}$, $\text{MgSO}_4 = 12 \text{ ppm}$, $\text{NaCl} = 9.5 \text{ ppm}$?

H.C.S.	Quality of H.C.S (mgs)	M.wt of H.C.S	Equivalent of CaCO_3
$\text{Ca}(\text{HCO}_3)_2$	16.2	162	$\frac{16.2}{162} \times 100 = 10 \text{ mg/lit}$
$\text{Mg}(\text{HCO}_3)_2$	14.6	146	$\frac{14.6}{146} \times 100 = 10 \text{ mg/lit}$
CaSO_4	13.6	136	$\frac{13.6}{136} \times 100 = 10 \text{ mg/lit}$
MgSO_4	12	120	$\frac{12}{120} \times 100 = 10 \text{ mg/lit}$
MgCl_2	9.5	95	$\frac{9.5}{95} \times 100 = 10 \text{ mg/lit}$

Temporary hardness = $10 + 10 = 20 \text{ ppm}$
 (bicarbonates)

$$= 20 \times 0.1 = 2^{\circ}\text{F.L.}$$

Permanent hardness = $10 + 10 + 10 = 30 \text{ ppm}$
 (Bi, C, N, S)

$$= 30 \times 0.1 = 3^{\circ}\text{F.L.}$$

Q3) One litre of water from an underground reservoir in Nalgonda, in Telangana, found to have the following dissolved salts $\text{Mg}(\text{HCO}_3)_2 = 0.0146 \text{ gms}$, $\text{Ca}(\text{HCO}_3)_2 = 0.081 \text{ gms}$, $\text{MgSO}_4 = 0.0012 \text{ gms}$, $\text{CaSO}_4 = 0.0136$, $\text{NaCl} = 0.0585 \text{ gms}$. Organic impurities 100 mgs.
 Calculate the temporary, permanent hardness of water in °F.L.

H.C.S.	Quality of H.C.S (mgs)	M.wt of H.C.S	Equivalent of CaCO_3
$\text{Mg}(\text{HCO}_3)_2$	$0.0146 \times 1000 = 14.6$	146	$\frac{14.6}{146} \times 100 = 10 \text{ mg/lit}$
$\text{Ca}(\text{HCO}_3)_2$	$0.081 \times 1000 = 81$	162	$\frac{81}{162} \times 100 = 50 \text{ ppm}$
MgSO_4	$0.0012 \times 1000 = 1.2$	120	$\frac{1.2}{120} \times 100 = 1 \text{ ppm (or) } 1 \text{ mg/lit}$
CaSO_4	$0.0136 \times 1000 = 13.6$	136	$\frac{13.6}{136} \times 100 = 10 \text{ ppm}$
NaCl	$0.0585 \times 1000 = 58.5$		

Temporary hardness $\Rightarrow 50 + 10 = 60 \text{ ppm} = 60 \times 0.1 = 6^\circ \text{P}$.

Q) One gram of CaCO_3 was dissolved in HCl and solution was made up to one litre with distilled water. 50ml of the above solution required, 30ml EDTA solution for titration. 50ml H.W.S required, 40ml of same solution of EDTA for titration. 50ml H.W.S after boiling ^(or) heating filtering required 30ml of same EDTA solution for titration. Calculate the temporary hardness of water?

Soln

$$M_1 = \frac{wt}{M \cdot wt} \times \frac{1}{V(\text{lit})}$$

$$= \frac{1}{100} \times \frac{1}{1}$$

$$\boxed{M_1 = 0.01 \text{ M}}$$

Step 1:

$$M_1 V_1 = M_2 V_2 \quad (\text{EDTA})$$

$$(H.W.S) \quad M_1 = 0.01, V_1 = 50 \text{ ml}, V_2 = 30 \text{ ml}, M_2 = ?$$

$$M_2 = \frac{M_1 V_1}{V_2}$$

$$M_2 = \frac{0.01 \times 50}{30}$$

$$\boxed{M_2 = 0.016 \text{ M}}$$

Step 2:

$$M_2 V_2 = M_3 V_3 \quad (\text{H.W.S})$$

$$M_2 = 0.016, V_2 = 40 \text{ ml}, V_3 = 50 \text{ ml}, M_3 = ?$$

$$M_3 = \frac{M_2 V_2}{V_3}$$

$$M_3 = \frac{0.016 \times 40}{50}$$

$$\boxed{M_3 = 0.0128 \text{ M}}$$

$$\text{Total hardness} = M_2 \times 100 \times 10^3 \text{ ppm}$$

$$= 0.0128 \times 100 \times 1000 \text{ ppm}$$

$$= 1280 \text{ ppm}$$

Step 3: (EDTA) $M_2 V_2 = M_4 V_4$ (Hence after S)

$$\Rightarrow M_2 = 0.016, V_2 = 30 \text{ ml}, V_4 = 50 \text{ ml}, M_4 = ?$$

$$M_4 = \frac{M_2 V_2}{V_4}$$

$$M_4 = \frac{0.016 \times 30}{50}$$

$$M_4 = 9.6 \times 10^{-3} \text{ M}$$

$$\text{permanent hardness} = M_4 \times 10^5 \text{ ppm}$$

$$= 9.6 \times 10^{-3} \times 10^5$$

$$= 9.6 \times 10^2$$

$$= 960 \text{ ppm}$$

$$\text{Temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$
$$= 1280 - 960$$
$$= 320 \text{ ppm}$$

~~Desalination of brakish water:-~~

→ water containing high concentrations of dissolved solids with a brakish taste is called brakish water.

→ Sea water is an example of brakish water containing about 3.5% dissolved salts.

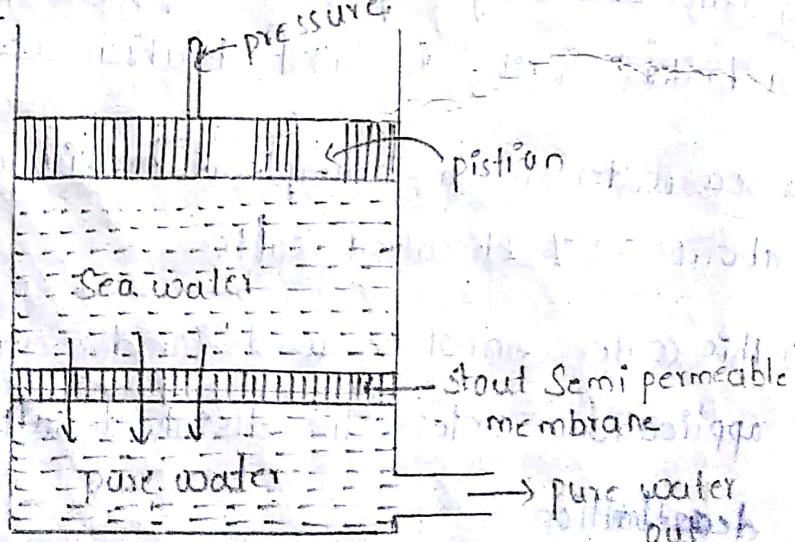
→ This water cannot be used for domestic and industrial applications unless the dissolved salts are removed by desalination.

desalination:

Reverse Osmosis

- When 2 solutions of unequal concentration are separated by semi-permeable membrane which
- Which doesn't permit the passage of dissolved solid particles (molecules and ions)
- Flow of solvent takes place from the dilute solution to concentrated solution this is called Osmosis.
- If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side of the solvent, the solvent is forced to move from higher concentration to lower concentrated side across.
- Thus, the solvent flow is reversed hence this method is called reverse osmosis.
- Thus, reverse osmosis pure water is separated from the contaminated water
- This membrane filtration is called super filtration (or) Hyperfiltration.

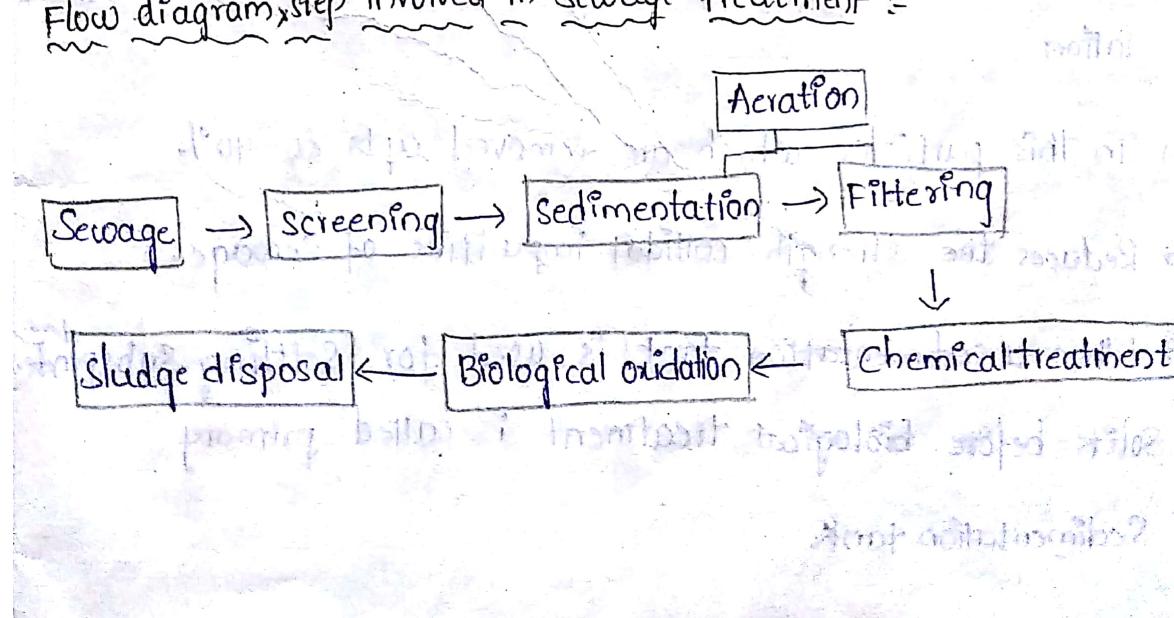
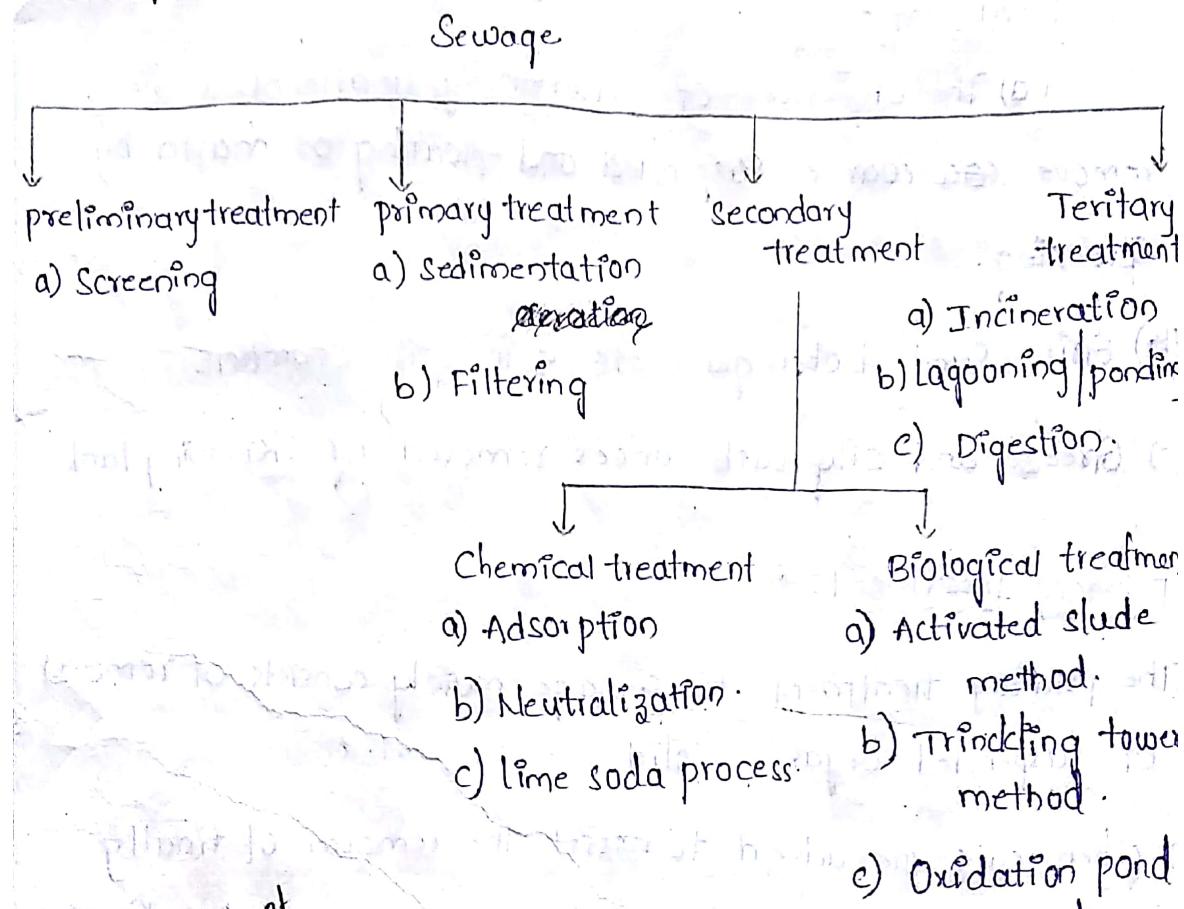
Reverse osmosis cell:-



Advantages :-

- cost of purification of water is less and maintenance cost is less.
- This water can be used for high pressure boilers.
- Both ionic and non-ionic, colloidal, high molecule weight, organic matter is removed by from the water sample.

Sewage Water-Steps involved in treatment of sewage :-

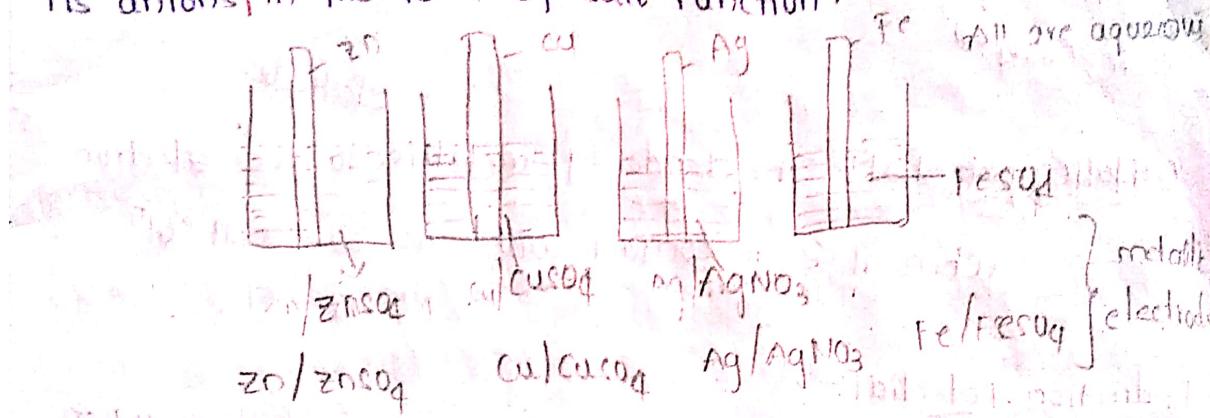


Electrochemistry

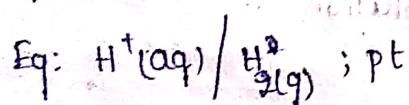
UNIT-III

Electrochemistry:

Electrode: When a metal is dipped in its own salt solution or if gaseous non metal is contact with solution containing its anions in the form of salt function.



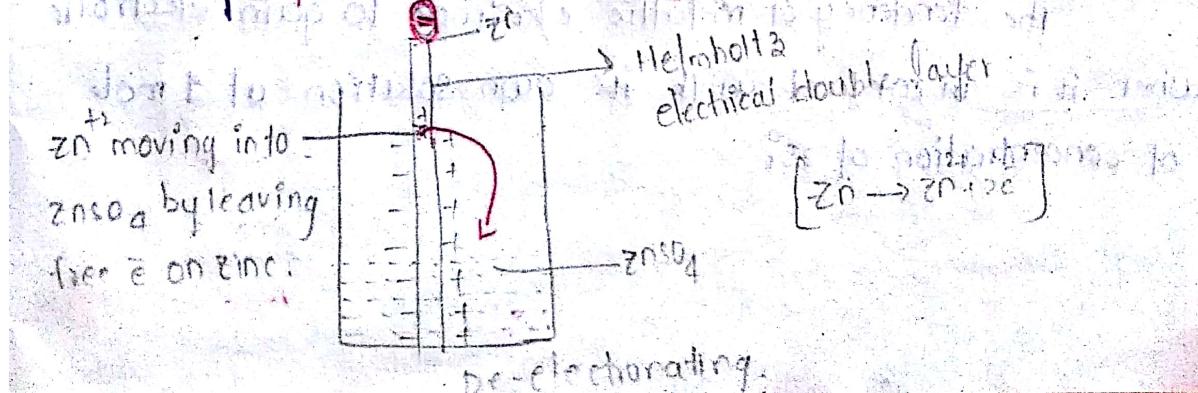
→ Non metallic electrode

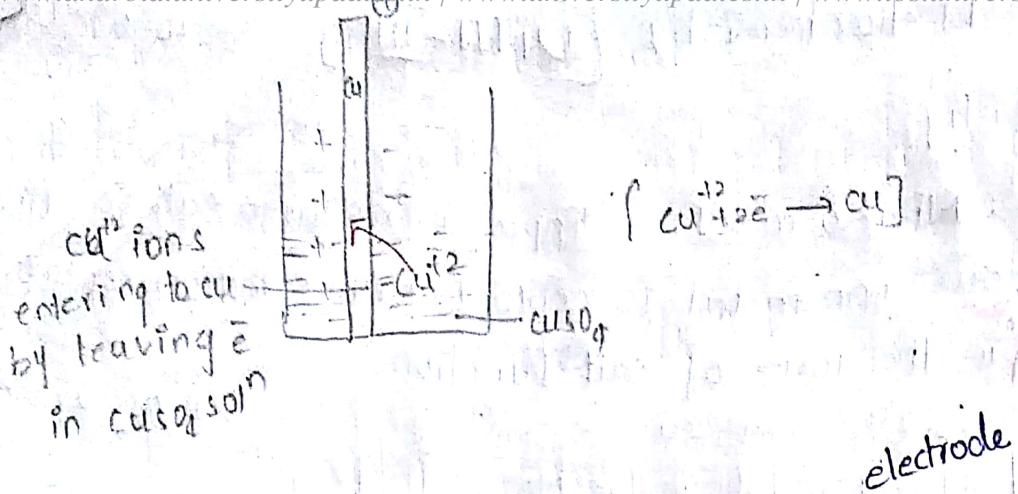


→ Hydrogen electrode

Electrode potential (E):

The tendency of metallic electrode to loose or gain of electron when it is contact with its own salt solution or when it is polarized by CO_2 .
 A difference of potential between metal and its salt solution arises due to formation of helmholtz electrical double layer is called electrode potential.





Oxidation potential: The tendency metallic to loose electron when it is in contact with its own salt soln

Reduction potential:

The tendency of metallic electrode to gain electron when it is in contact with its own salt solution

Standard electrode potential e° :

The tendency of metallic electrode to loose or gain of electron when it is contact with its own salt solution of 1M concentration at 25°C .

Standard oxidation potential:

The tendency of metallic electrode to loose electron when it is contact with its own salt solution of 1 mole concentration at 25°C .

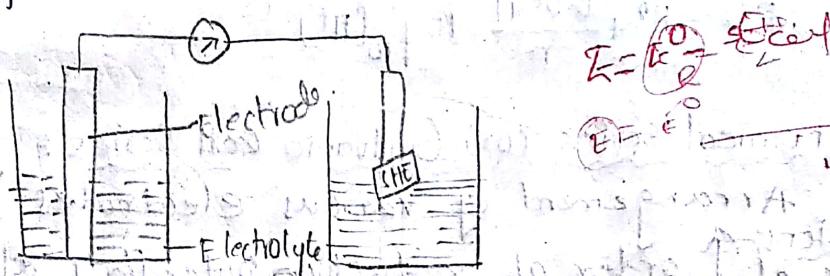
Standard reduction potential:

The tendency of metallic electrode to gain electron when it is in contact with its own solution of 1 mole of concentration of 25°C .

Measurement :-

Absolute electrode potential cannot determine directly but we can measure difference of potential between two electrodes using potentiometer

- In order to determine single electrode potential, standard electrode potential of hydrogen electrode has been ~~arbitrarily~~ arbitrarily fixed at zero.
- For measuring electrode potential, the electrode whose potential is to be determined is coupled with standard hydrogen electrode and E-cell is measured.
- Since (SHE) potential is zero, the E-cell value is the electrode potential of second electrode.

Nernst equation :-

- The concentration effect i.e. when the conc is not 1M the EMF of the electrode alters.

→ To calculate the potential of the standard electrode, Nernst equation is used, as is given below

$$E = E_0 - \frac{RT}{nF} \log_{10}(H^+)$$

where E_0 = standard electrode potential (or) equation

R = gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

T = absolute temperature

F = faraday (96500 coul)

n = Valency of ion.

E = single electrode potential.

Substituting all the values we get potential of the cell at 25°C .

$$E = E^{\circ} - \frac{0.0591}{n} \log_{10} [\text{H}^+]$$

$$E = E^{\circ} - 0.0591 \log_{10} [\text{H}^+]$$

$E = E^{\circ} - 0.0591 \text{ pH}$. This is the equation for a half cell where oxidation occurs. In case standard hydrogen electrode used as reduction electrode, the E.M.F. (E) will be measured by reversing the sign of E (E°) so

$$E = -E^{\circ} + \frac{0.0591}{n} \log_{10} [\text{H}^+]$$

Electrochemical Series (or) Galvanic Cell Series:

Def:- Arrangement of various electrodes in their Applications.

→ Order of reduction potentials at unit molal conc. at 25°C , using hydrogen electrode as reference electrode.

→ The relative corrosion tendencies of the metals and alloys.

→ To predict replacement tendencies of metals.

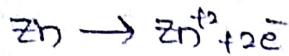
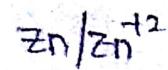
→ Relative ease of oxidation (or) refection of the metals.

→ To calculate the equilibrium constant.

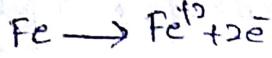
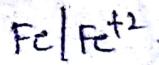
→ Predicting the spontaneity of redox reactions.

→ It is used to predict relative corrosion tendencies oxidizing of Standard Oxidation potential at 25°C :- Reducing Power.

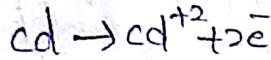
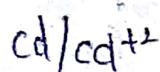
Electrode	Halfcell representation	E° volts.	Cathode
Li/Li^+	$\text{Li} \rightarrow \text{Li}^+ + e^-$	+3.045	the
K/K^+	$\text{K} \rightarrow \text{K}^+ + e^-$	+2.925	active anode
Ca/Ca^{2+}	$\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$	+2.87	
Na/Na^+	$\text{Na} \rightarrow \text{Na}^+ + e^-$	+2.714	
Mg^{2+}/Mg	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	+2.37	



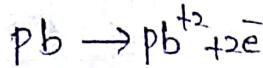
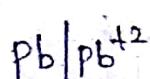
+0.763



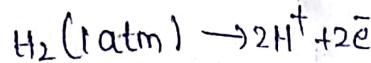
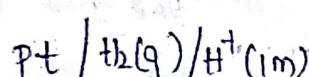
+0.440



0.403

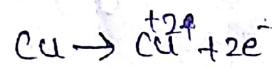
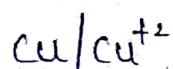


0.126

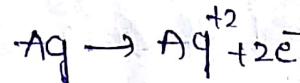
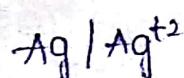


0.000

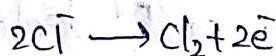
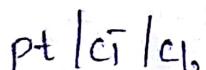
(1 atm)



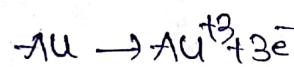
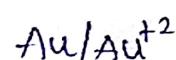
-0.337



-0.799



-1.36



-1.50

Active
anodeNoble
cathode

Types of electrodes:-

Construction & Functioning of SHE, Calomel, Glass electrodes

SHE:-

Reference electrodes:-

- This is an electrode which has a stable and a well-known potential used to determine the potential of other electrode.

- Reference electrodes acts as either anodic half of (or) cathodic half cell depending on the nature of the other half cell used.



2) Standard calomel electrode (SCE):-

standard calomel electrode is a secondary reference electrode which is used for cell

Potential measurements

The calomel electrode consists of a glass tube having two side tubes. A small quantity of pure mercury is placed at the bottom of the vessel and is covered with a paste of Hg and Hg_2Cl_2 , KCl solution of known concentration is filled through side tube. Shown on the right side of the vessel. The KCl sol. is filled in the left side tube which helps to make a connection through a salt bridge with the other electrode, which potential has to be determined.

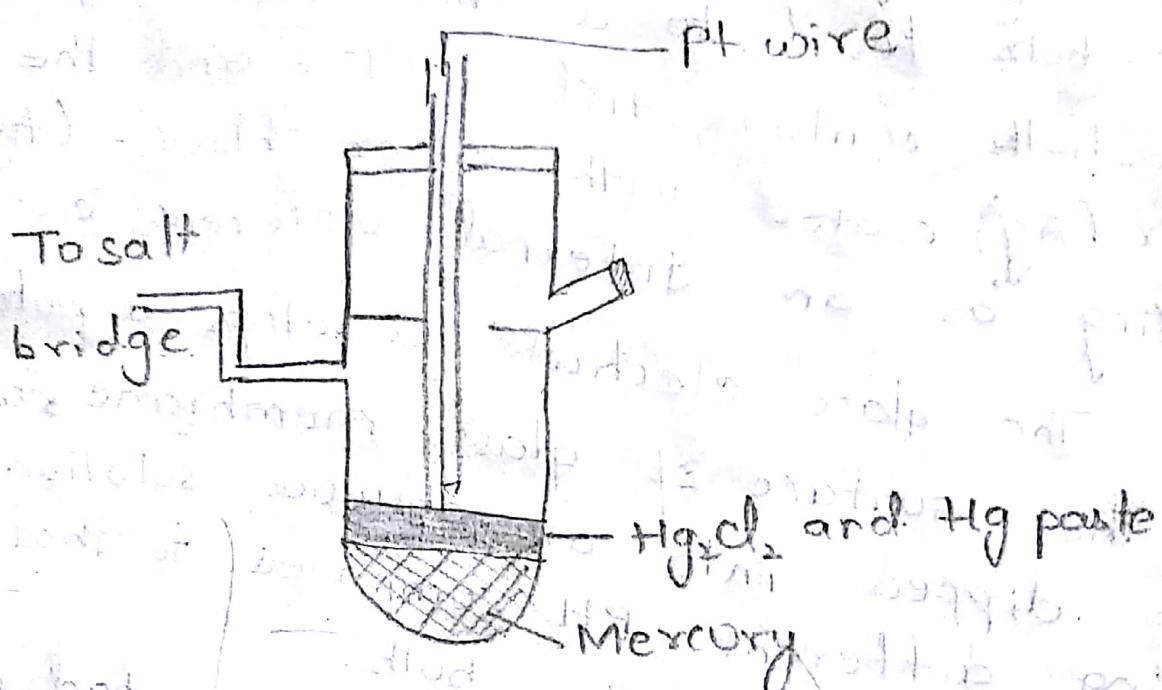
A 'Pt' wire is sealed into a glass tube as shown in the fig which is in contact with Hg. When the cell is set up it is immersed in the given solution.

→ To determine potential measurements the potential of calomel depends upon concentration of KCl.

→ Saturated KCl electrode potential = 0.24V.

→ 1m KCl electrode potential = 0.28V.

→ 0.1m KCl electrode potential = 0.33V.



Calomel electrode

The electrode reaction is: $\frac{1}{2} \text{Hg}_2\text{Cl}_2 + \text{e}^- \rightarrow \text{Hg} + \text{Cl}^-$

Electrode representation: $\text{Pt} | \text{Hg}, \text{Hg}_2\text{Cl}_2 / \text{Cl}^-$.

Nernst's expression: $E = E^\circ - 0.0591 \log [\text{Cl}^-]$.

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

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{hydrogen}}$$

$$E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = 0.242 + 0.0591 \text{ pH}$$

$$\boxed{P\text{H} = \frac{E_{\text{cell}} - 0.242}{0.0591}}$$

Glass Electrode:

The glass electrode of an electric conducting glass membrane in the form of thin bulb fused to a thick walled tube. The bulb contains HCl solution and the silver (Ag) coated with silver chloride (AgCl) working as an internal reference electrode.

The glass electrode develops a potential at the surface of glass membrane, when it is dipped into an aqueous solution having different pH compared to that of the solution with the bulb.

The glass electrode represented as:

$\text{Ag}/\text{AgCl}, \text{HCl (0.1M)}/\text{glass}$.

The potential is related to the transform of H^+ ions through the glass membrane between solutions of H^+ ion concentration of external solution (c_1) and internal solution (c_2)

(Reference electrode-1 / solution to be analysed (c_1) // Internal standard solution)

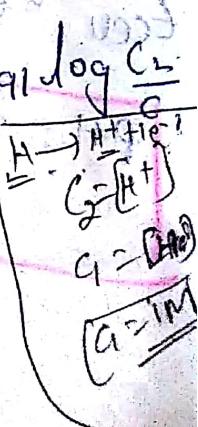
(c_2) / Reference electrode-2)

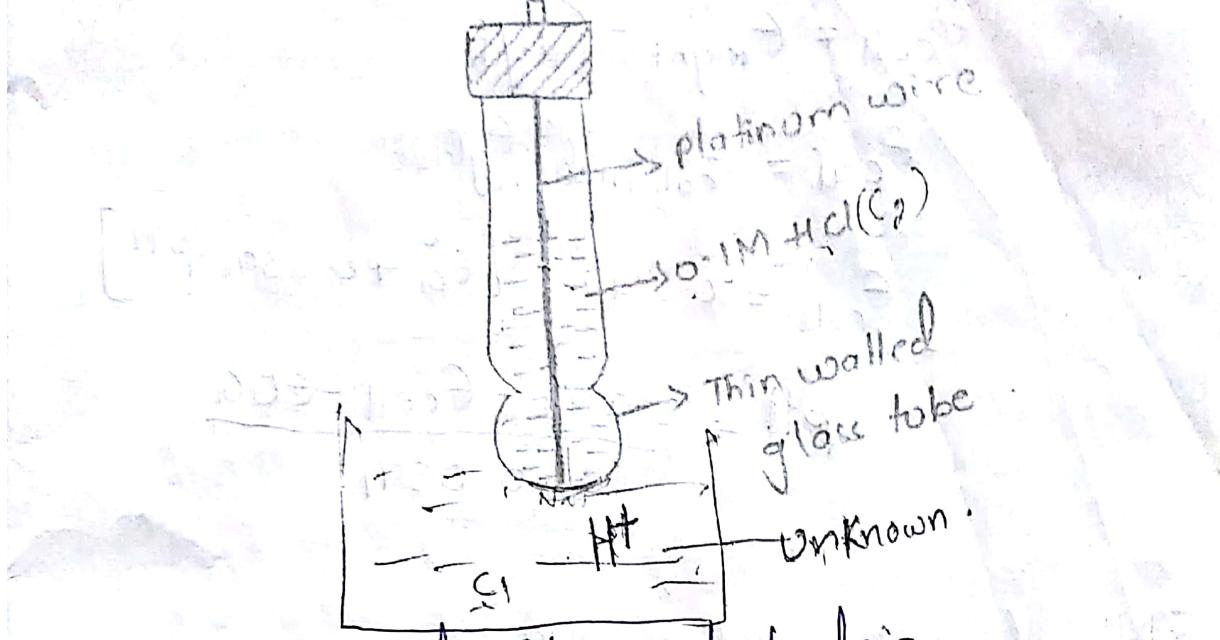
Nernst Equation

$$E = E^\circ - 0.0591 \log \frac{C_2}{C_1}$$

Potential of glass electrode

$$E_g = E_g^\circ + 0.0591 \text{ pH}$$





Advantages of Glass electrode:-

- It is used to determine pH of the solution
- It is used to determine concentration of number of cations
- The results are accurate
- The results are not easily poisoned.

Determination of pH by using glass electrode:-

To determine the pH of unknown solution the glass electrode dipped in the solution whose pH is to determine. It is then combined with a reference electrode saturated calomel electrode to determine total emf of the cell.

The cell represented as:-

$\text{Ag}/\text{AgCl}/0.1\text{N HCl}/\text{glass}/\text{solution of}$
 $\text{Unknown } p\text{H} // \text{saturated calomel electrode}$

$$\epsilon_{\text{cell}} = \epsilon_{\text{Right}} - \epsilon_{\text{Left}}$$

$$\epsilon_{\text{cell}} = \epsilon_{\text{calomel}} - \epsilon_{\text{glass}}$$

$$\epsilon_{\text{cell}} = 0.242 - [\epsilon_{\text{G}}^{\circ} + 0.0591 \text{ pH}]$$

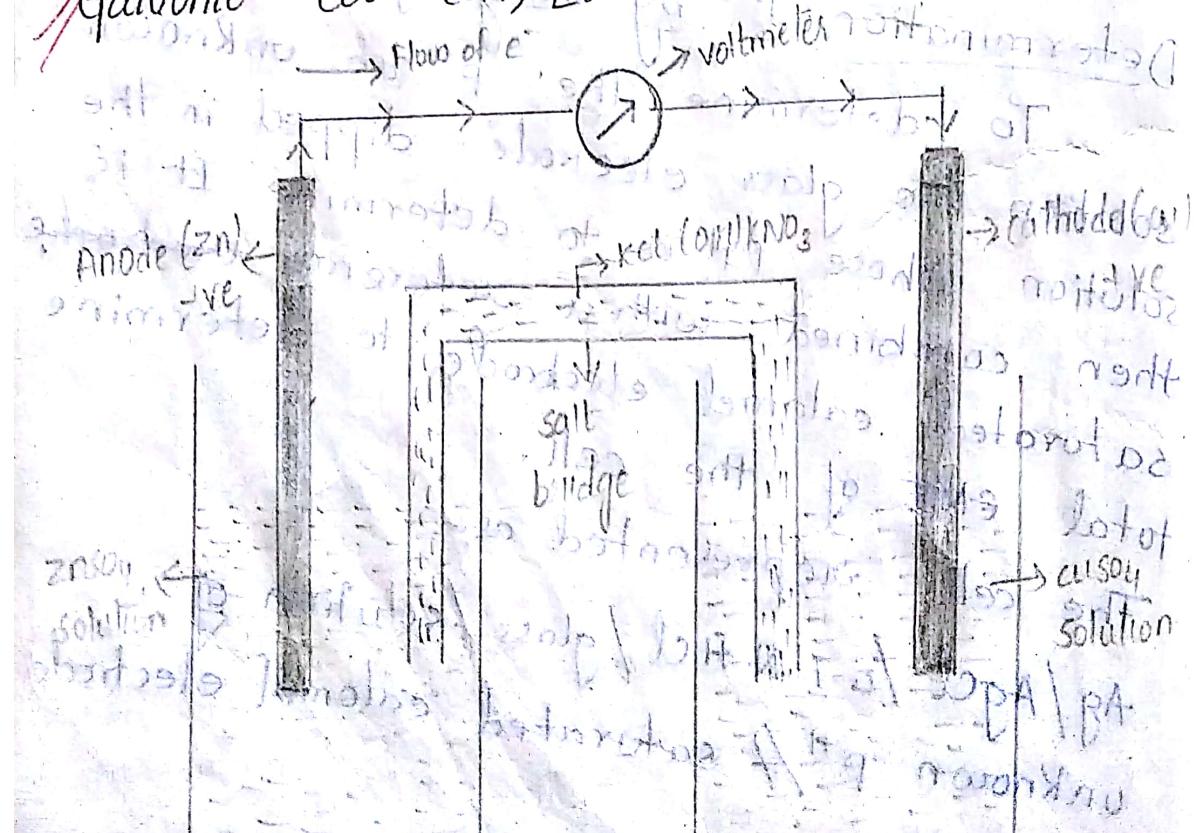
$$\text{pH} = \frac{0.242 - \epsilon_{\text{cell}} - \epsilon_{\text{G}}^{\circ}}{0.0591}$$

EMF: (Electro Motive Force) ϵ

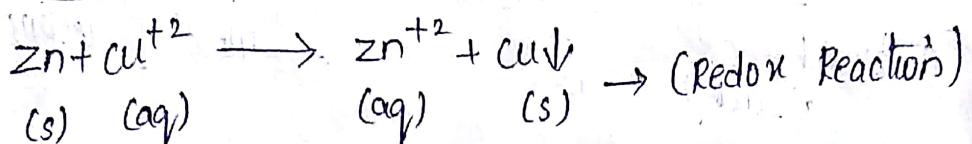
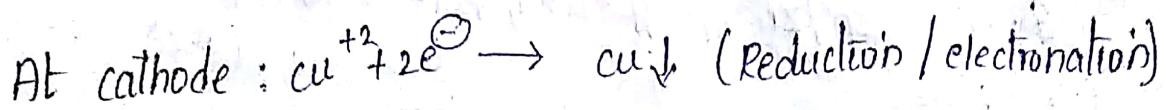
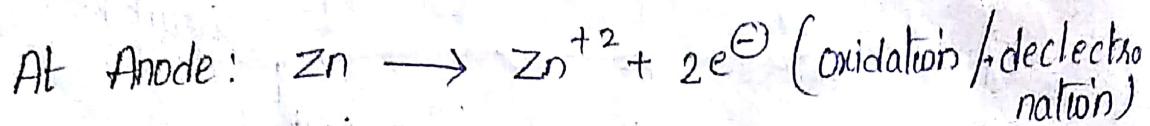
Standard emf.

The measurement of emf in standard conditions (temp = 25°C; conc = 1M; pressure = 1 atm) is called standard emf denoted by ϵ_0 .

Galvanic Cell (or) Electrochemical Cell



Cell reactions :



→ The electrochemical cell is also called Galvanic cell in this, chemical energy is converted into Electric energy.

→ A typical ex. of electrochemical cell (or) Galvanic cell is Daniel cell.

→ In this cell Zn electrode is dipped in ZnSO_4 solution in one container & Cu electrode is dipped in CuSO_4 solution in another container.

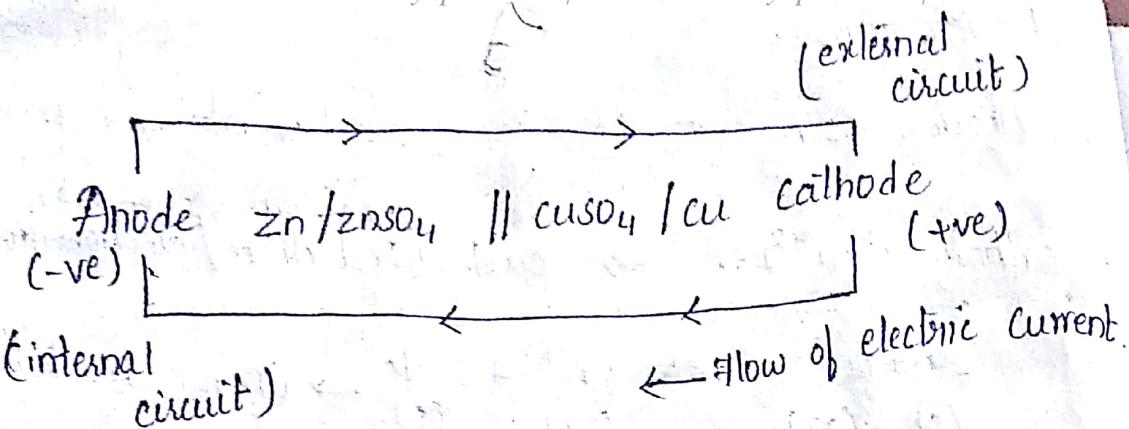
→ In this each container may be regarded as Half cell (The electrode which is dipped in its own solution (or) own metal ions is called Half cell)

→ In this the Zinc rod acts as Anode having -ve charge. (At this electrode the current leaves the cell) & Cu electrode acts as cathode having +ve charge. (At this electrode current enters into the cell)

→ These two electrodes are connected to Voltmeter.

→ To measure potential difference (e.m.f)

→ These two half cells are connected through salt bridge to maintain equilibrium by passing solvent particles.



→ The anodic half electrode follows symbol of metal represented by metal ion

Functions of Salt bridge

- Salt Bridge is a inverted 'V' shape glass tube filled with KCl (potassium chloride) or KNO_3 (because of its high solubility and equal mobility)
- To prevent the direct contact between two reactants.
- It does not allow any chemical reaction between the two solutions
- It maintains electrical neutrality
- It prevents the accumulation of charge at electrodes and provides free flow of electrons through the internal circuit

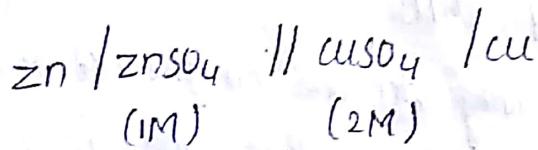
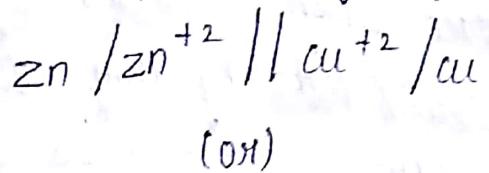
→ The denoted

Cell Notation (or) Cell Representation

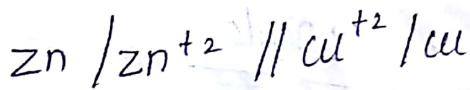
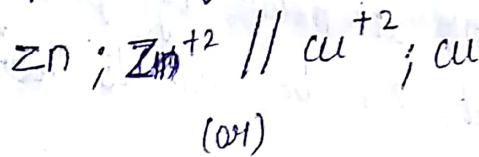
- The salt bridge which connects two half cells is represented by a double vertical line (||).
- The anodic half cell is written on left hand side and the cathode half is written on right hand side.



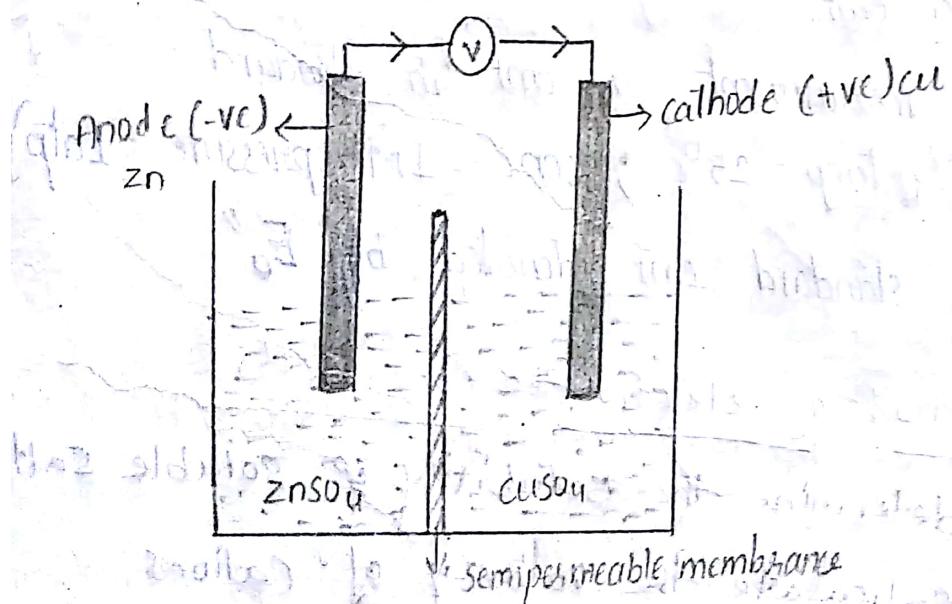
→ The anodic half cell is represented by symbol of electrode followed by symbol of metal ion and the cathodic half cell is represented by symbol of electrode followed by symbol of metal ion followed by symbol of electrode



→ The phase boundary of each electrode is denoted by a single vertical lines (or) semi colons



Daniel Cell:



→ E.M.F of Daniel cell is 1.09V

Batteries

Batteries are portable storage devices, which store thermal energy and converts into electric energy.

→ Batteries are worked based on the principle of electrochemical cell

→ Batteries consist of a several no. of electrochemical cells connected in Series.

→ Batteries are commercial electrochemical cells which are used as a source of direct electric current at constant voltages.

→ The following requirements should be present in a battery.

(i). High capacity.

(ii). High energy efficiency.

→ The % of efficiency =
$$\frac{\text{Energy released during discharge}}{\text{Energy required for charging}}$$

(iii) Long self life is required.

(iv). Releable in electricity generator.

Classification

Based on the recharging capacities the batteries can be classified into 2 types they are;

1) Primary cells (or) Primary batteries

2) Secondary cells (or) Secondary batteries.

Primary cells :-

In this cells the cell reaction is not reversible. It means the reactants can be converted into products, during that time it produces electricity.

→ After one time electricity production the battery becomes dead.

→ These are also called as non-rechargeable batteries.

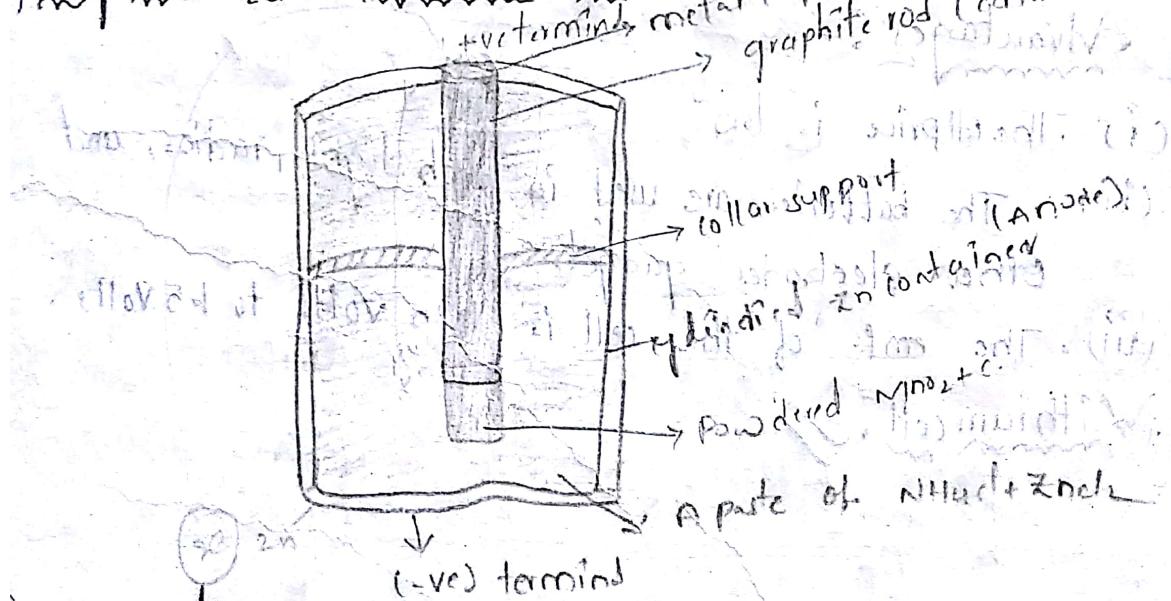
Example :-

(i) Dry cell (or) Leclanche cell.

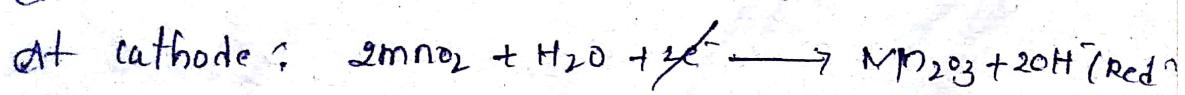
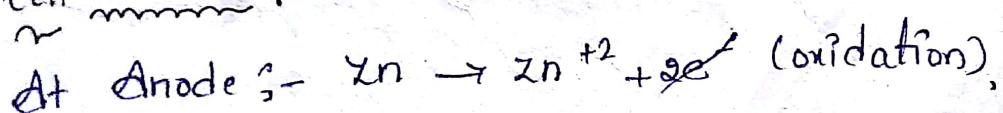
(ii) Alkaline cell.

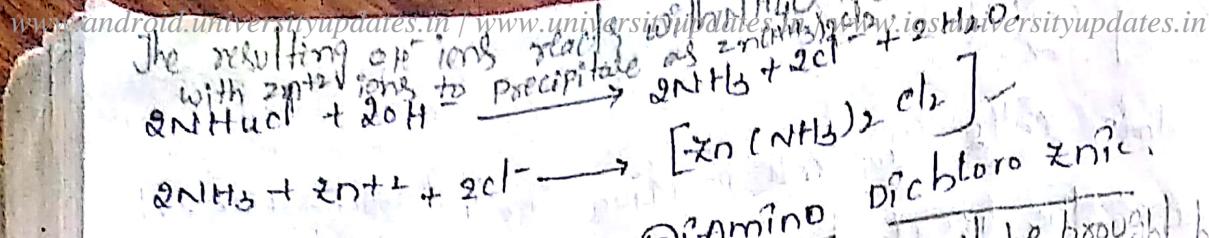
(iii) Lithium cell.

Dry cell (or) Leclanche cell



Cell reaction :-





① Construction:- the exhausted cell cannot be brought back to the original state in container which

Dry cell consists of a cylindrical rod is placed below acts as anode and a graphite rod is placed above the container which acts as cathode which is placed carefully by not touching to the ground.

→ The gap between the cathode and anode is filled with a paste of Ammonium chloride and zinc chloride

→ The graphite rod is coated with powdered MnO_2 and carbon.

→ the rod is inserted with collar support.

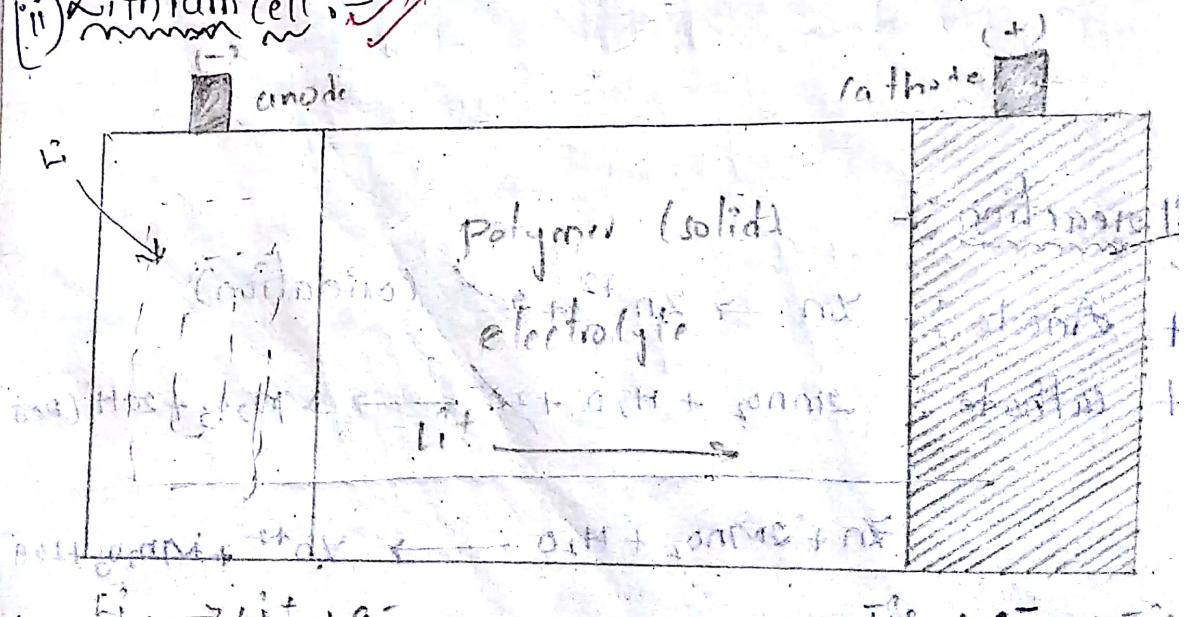
③ Advantages :- Dry cell representation: $\text{Zn}|\text{Zn}^{2+}, \text{NH}_4^+/\text{Hg}$

(i) The price is low.

(ii). The batteries are used in torch light, radios, and other electronic gadgets.

(iii). The emf of this cell is 1.25 volts to 1.5 volts

(ii) Lithium cell:



In Lithium cell Lithium acts as Anode because of its light weight and high conductivity.

→ Based on the physical state of cathode these are classified into two types.

(i) Lithium cells with solid cathode :-

Ex:- Li-MnO₂ cell.

Anode : Li.

Cathode : MnO₂.

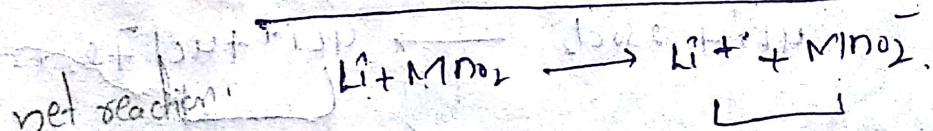
Electrolyte : LiBF₄ salt in a solution of propylene carbonate.

EMF : 3 Volts.

Cell Reactions :-

At Anode : Li → Li⁺ + e⁻ [oxidation].

At Cathode : MnO₂ + e⁻ → MnO₂⁻ [Reduction].



Applications :-

- 1) The cylindrical cells are used in wall clocks, remotes, transistor radios etc..
- 2) Coin type cells are used in watches, calculators etc..

Lithium cells with liquid cathode :-

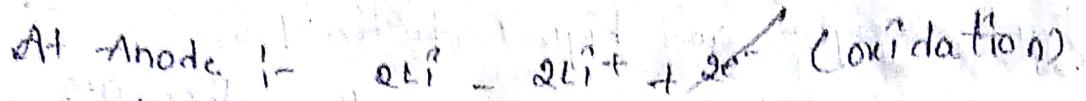
Ex:- Li-SO₂ cell.

Anode - Li

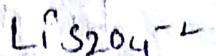
Cathode - SO₂

Electrolyte - (propylene carbonate) LiClO₂

EMF - 3.8 volts

Cell Reactions:

Li^{+2} Li-SO₂ cell.

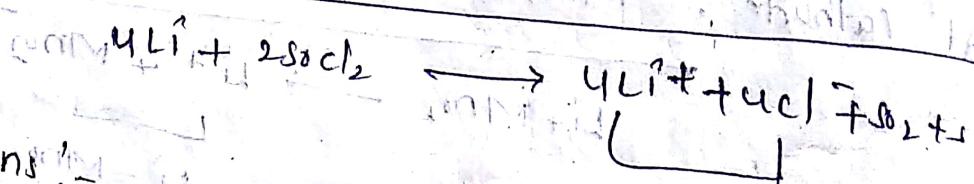
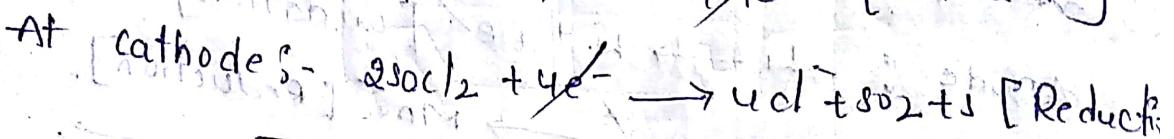
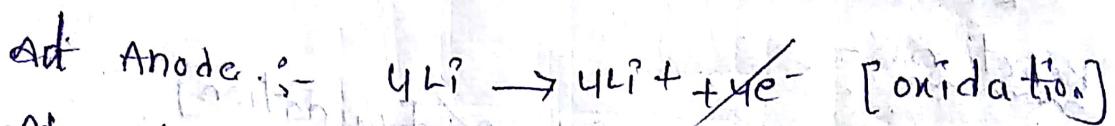


Anode - Li

Cathode -

Electrolyte - SO_2 soln. in H_2O

Emf - 3.8V.

Applications:

- These cells are used for low current applications.
- These batteries are used in electrical circuit boards.



P. CORROSION AND ITS CONTROL

UNIT-3

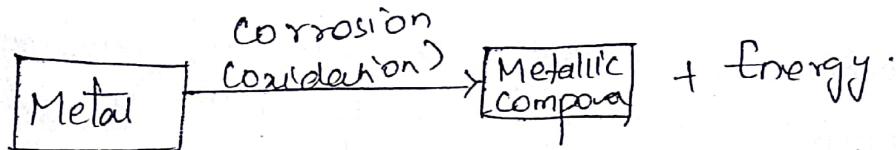
PART-3

Introduction:-

The surfaces of all metals begin to decay even they exposed air, H_2O (or) any other liquid, as a result of it they are converted to oxides, carbonates and hydrides. This process is called corrosion.

e.g.- Formation of reddish brown layer on surface of iron.

Formation of green film of basic carbonate $[CuCO_3 + Cu(OH)_2]$ on surface of copper.



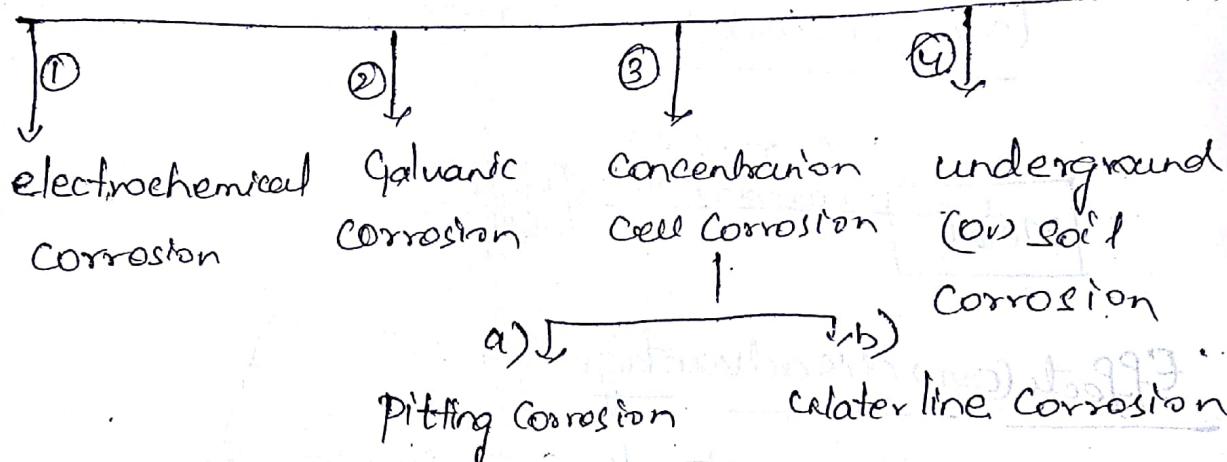
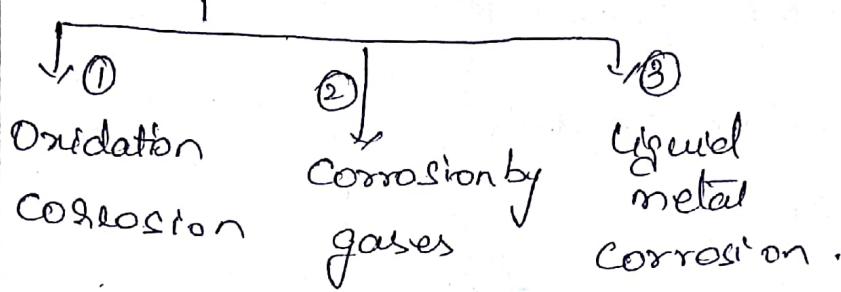
Effects (or) disadvantages of Corrosion:-

- Valuable properties like conductivity, malleability, ductility lost due to corrosion.
- Life Span of metallic parts and machines are reduced
- The failure of machinery takes place due to loss of useful properties of metals.
- It leads to more wastage of metal.

Types of Corrosion

Dry/chemical
Corrosion

Wet/electrochemicals
Corrosion



Stress corrosion Intragranular
Corrosion

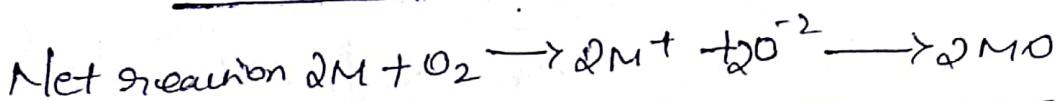
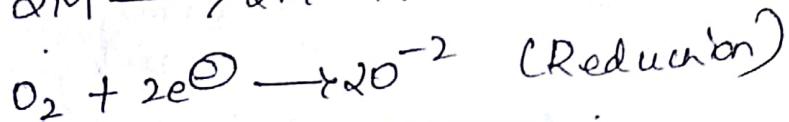
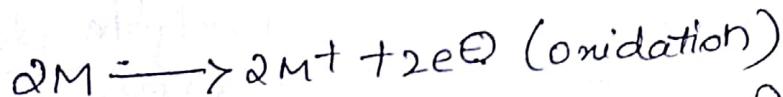
Dry Gas chemical Corrosion -

This type of corrosion occurs when metal is exposed to gases like O_2 , N_2 , SO_2 , halogens leads to a chemical action between metal and gases.

This is classified as

- Oxidation corrosion.
- Corrosion by other gases
- Liquid metal corrosion.

a) Oxidation Corrosion :- Direct attack of oxygen on surface of metal is called oxidation corrosion.

Mechanism of Oxidation Corrosion :-

The oxidation of a metal occurs first then the e^- are accepted by the metal leads to formation of Metal Oxide scale



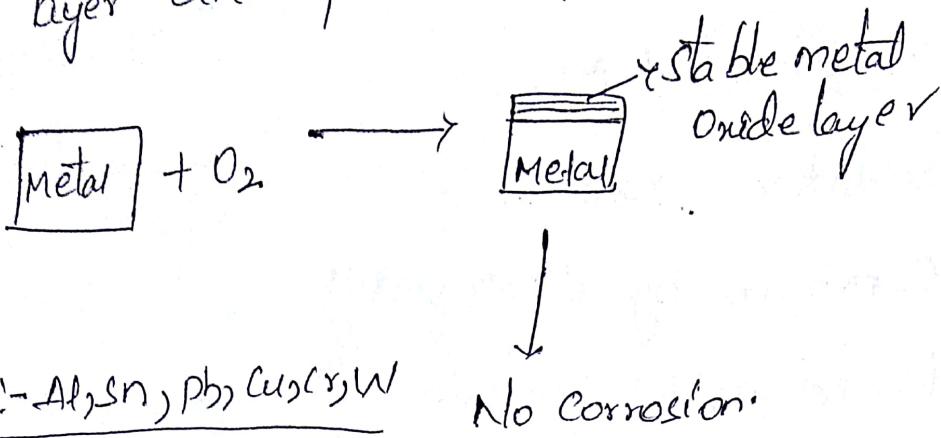
(M) = metal

Metal Oxide Scale

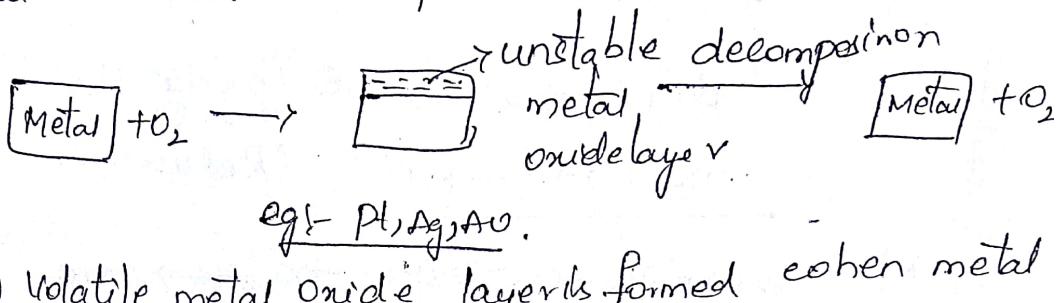
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The absorption of O_2 and formation of OC a different ways in different metals.

① A pure metal reacts with O_2 form a stable oxide layer. This acts as film and protects byer and prevents further corrosion.

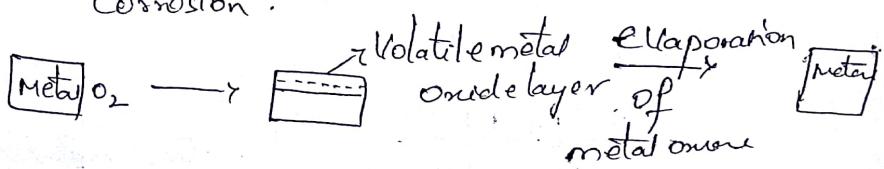


② Metal reacts O_2 to form a metal oxide layer but it shows decomposition of metal oxide.

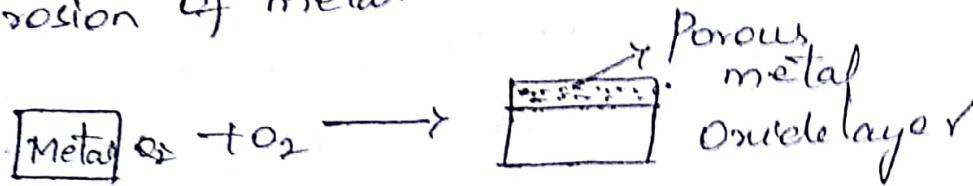


③ A volatile metal oxide layer is formed when metal reacts with O_2 and once formed undergoes evaporation. eg MnO_3 .

which leads to again exposure of metal for corrosion.



4) \rightarrow porous metal oxide layer is formed in case of
Some metals even metal reacts with O_2 . A porous
metal oxide contains cracks; through these cracks
 O_2 enters the depth of metal and causes a total
corrosion of metal.



Porous metal oxide layer



Further attack through pores
and cracks.

e.g.: - Alkali and Alkaline earth metals (Li, K, Na, Mg, Ba).

To explain the extent of corrosion Pilling Bedworth
proposed a rule:-

He has proposed a specific volume ratio: - It is
a ratio of Volume of metal oxide to volume of metal

$$\text{i.e. Specific volume ratio} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

From this

(i) if the volume of metal oxide layer is greater
than volume of metal, then we can say metal-
oxide layer formed is more. So mostly metal is not

metal oxide layer is formed in case of free gas. So it acts as protective layer and no further corrosion.

PART-3

DING

- ii) if the volume of metal oxide layer formed is less than the volume of metal, so that metal has a chance to react with O_2 . So that corrosion occurs. eg:- Alkali & Alkaline earth metals.

Speci Volume lation	3.6	2.0	1.6
Metu	W	Cr	Ni

Of the 'W' acts as more protective and no further corrosion.

b) Corrosion by other gases:-

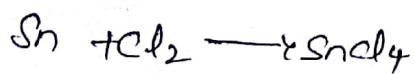
The gases like SO_2 , CO_2 , Cl_2 , H_2S & F_2 also causes a chemical corrosion.

With different examples we can explain.

→ Attack of Cl_2 gas on the surface of 'Ag' metal leads to formation of $AgCl$. The layer ' $AgCl$ ' is non-porous hence it is protective.

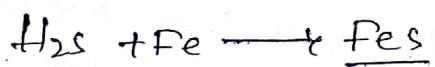
→ If corrosion layer is less volume then cracks forms

eg:- Attack of Cl_2 on Sn



Thus cracks developed \rightarrow Cl_2 gas moves
cracks and leads to total corrosion of metal.

Another example :- Attack of H_2s on surfaces



c) Liquid metal corrosion:-

This type of corrosion is developed by the flowing of liquid metal on surface of metal.

WET (Ox) Electrochemical Corrosion:-

This type of corrosion takes place under wet (Ox) moist conditions. This is most common type than Dry corrosion.

1. Cathodic and anodic areas are separated by conductive medium.
2. At anode oxidation occurs $\text{M} \rightarrow \text{M}^+ + \text{e}^-$
3. During cathodic reaction either H^+ (or) O_2 & H_2o Consumes e^- and converted to OH^- (or) O^{2-} .
4. The diffusion of M^+ & non metallic ions (OH^- O^{2-}) towards respective electrode then corrosion product formed between anode & cathodic area.

①

DDING.

→ Wet corrosion takes place by

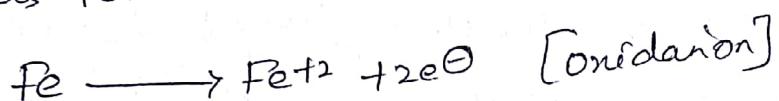
a) Evolution of H_2 .

b) Evolution of O_2

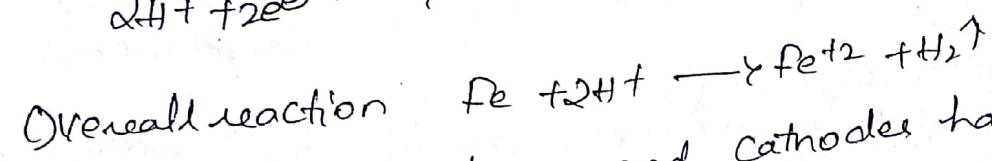
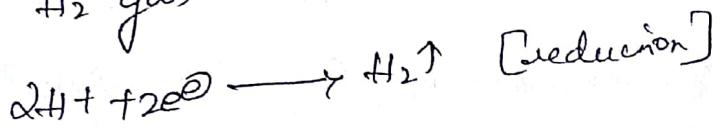
a) Evolution of H_2 :-

This type of corrosion occurs in acidic medium.

At Anode Fe^{+2} undergoes oxidation to liberate ferrous ions.

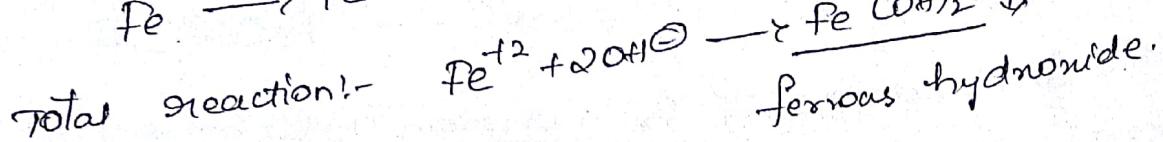
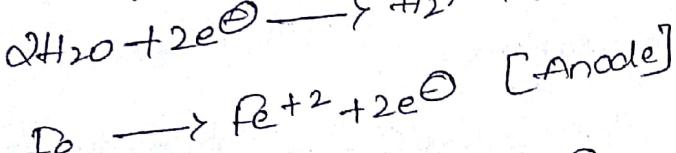
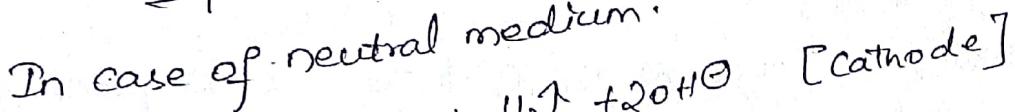


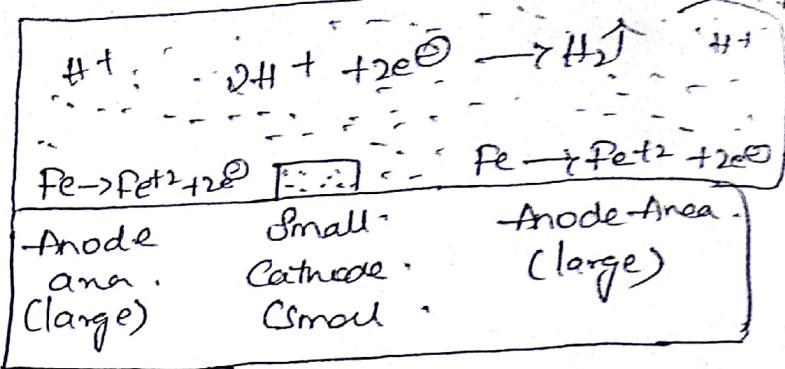
The e^- flow from anodic area to cathodic area
enhances acidic environment present and eliminates
as H_2 gas



In this Anodes are large and cathodes have small
Surface area.

In case of neutral medium.

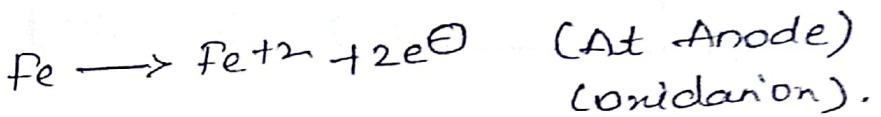




b) Absorption of O₂ :-

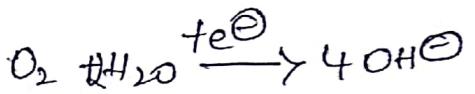
Due to the absorption of O₂ on Surface of 'Fe' rod rusting takes place. first due to exposure of 'Fe' rod to O₂ Fe Iron oxide layer forms.

The following reactions takes place during rusting of iron.

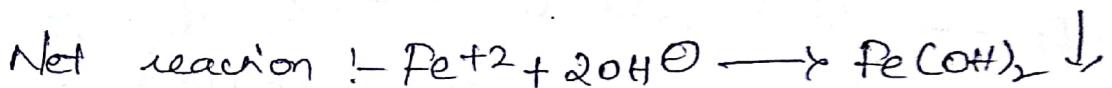


At cathode e⁻ were accepted by water and O₂

to generate OH⁻ ions.

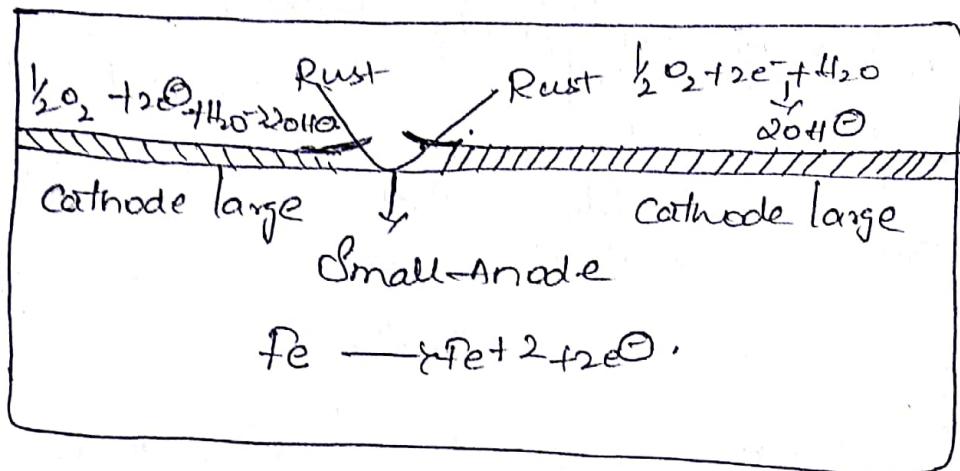
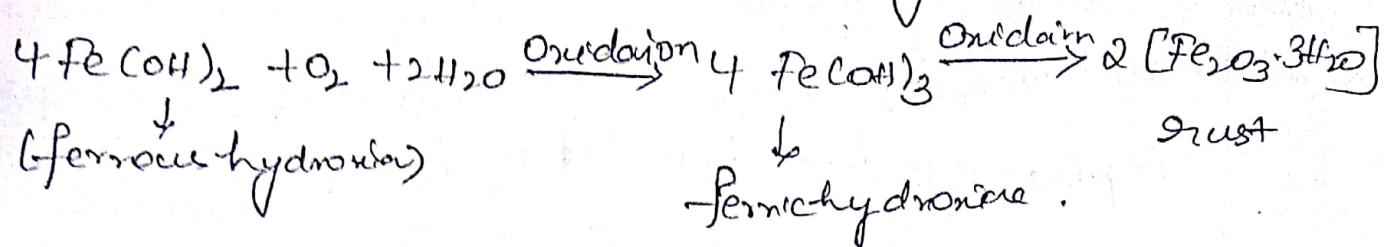


when the amount of O₂ increases it proceeds for further oxidation.



In presence of O₂ Corrosion occurs at Anode and rust at Cathode.

enough O₂ is present ferrous hydroxide easily oxidised to ferric hydroxide and then hydrated ferric oxide which is nothing but rust.



Differences b/w chemical and electrochemical corrosion.

Dry (or) chemical
corrosion.

(Wet or) electrochemical
corrosion

- 1. This corrosion occurs at dry condition.
- 2. Corrosion is uniform
- 3. It is a slow process
- 4. It is explained by a absorption mechanism.
- 5. Corrosion products are produced where corrosion occurs
- This corrosion occurs in every condition in presence of electrolyte medium.
- Corrosion is not uniform
- It is a rapid process.
- It is explained by electro-chemical reactions.
- Corrosion occurs at Anode, and corrosion product occurs in b/w Cathode & Anode.

Confirmation mechanism of corrosion :-

The mechanism of electrochemical corrosion can be confirmed by,

- 1) Phenolphthalein (Indicates presence of OH^-) if OH^- ions are present shows pink colour.
- 2) Potassium Ferrocyanide (Fe^{+2} indicates presence of OH^- ions) if Fe^{+2} ions are present indicates presence of blue colour.

Galvanic (or Bimetallic) Corrosion:-

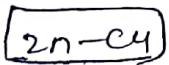
when two dissimilar are connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called a

Galvanic Corrosion.

e.g. Zn & Cu are connected exposed to corroding environment
Zn becomes anodic because of higher position in an electrochemical series.

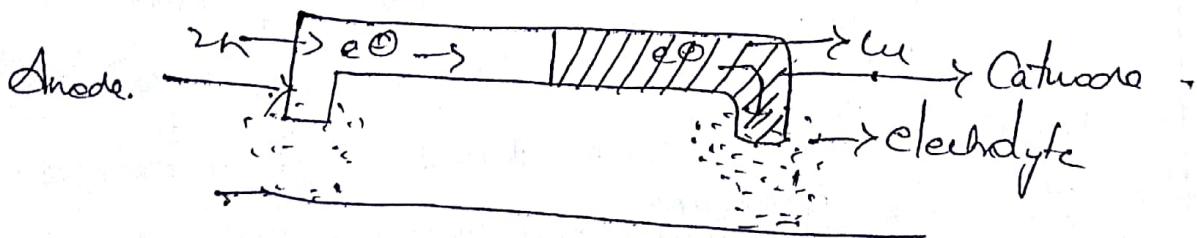
'Zn' or undergoes oxidation and 'Cu' undergoes reduction.

In a similar way 'Fe' and 'Cu' exposed to corroding environment. 'Fe' will undergo corrosion because it acts as anode.



Anodic Metal $\rightarrow \text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}^-$ (Oxidation)

Cathodic Metal $\rightarrow \text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$ (Reduction).



e.g. → Steel screws in brass Marine hardware.

Steel pipe connected to copper plumbing

Highest active anode / Corrosion

Magnesium

Magnesium Alloys

Zinc

Aluminium

Low 'C' steel

Cast iron

Stainless Steel (Aisi 316)

Lead-tin alloys

Lead

Tin

Brass

Copper

Bronze

Copper-Nickel alloys

Silver

Stainless Steel

Graphite

Titanium

Gold

Platinum

Concentration cell corrosion :-

- This type of corrosion mainly arises due to
1. difference in a concentration of metal ions
 2. difference in a temperature.
 3. difference in a exposure to air/O₂.

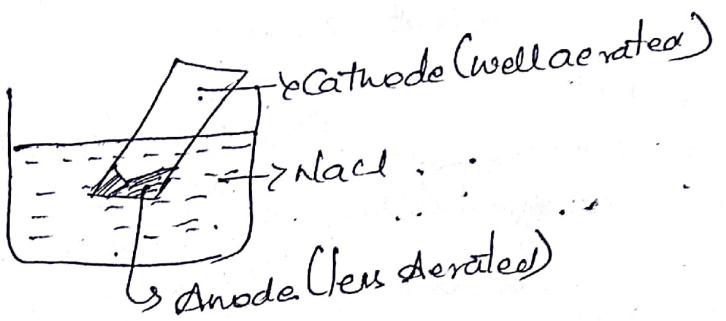
Most Common type Concentration cell Corrosion is due to differential aeration.

when a metal exposed to air poorly Oxygenated part acts as a Anode and Other part which exposed to air acts as Cathode

Differential aeration Corrosion -

This can be occurred in different ways:-

- a) partial immersion of metal in a Solution :-



'Zn' rod immersed deep in NaCl = Anode

'Zn' rod above NaCl = Cathode

A beaker is filled with NaCl solution. In that 'Zn' rod is dipped. Half of 'Zn' rod exposed to air acts as Cathode and another which is not exposed acts as Anode.

At Anode: $2n \rightarrow 2n^{+2} + 2e^-$

At Cathode:- $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$



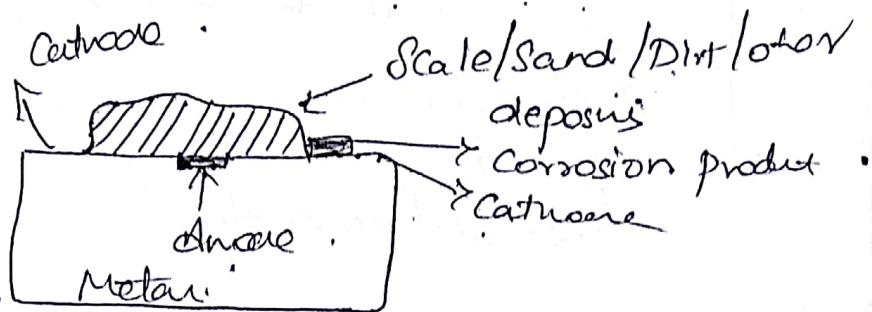
Cathodic product

formed at Anode.

b) Accumulation of dirt, Sand, Scale and other Contaminants

when the dirt, Sand, Scale and other Contaminations deposited on Surface of metal. The metal under deposit is exposed to less O_2 Supply becomes Anodic and remain part of metal acts as Cathodic.

Corrosion product is formed in between the Cathodic and Anodic areas.



c) Pitting Corrosion

This type of Corrosion is developed as cavity pinholes, pitting developed on Surface of a protective film.

The cracks developed less exposed to air / less oxygenated part acts as Anode

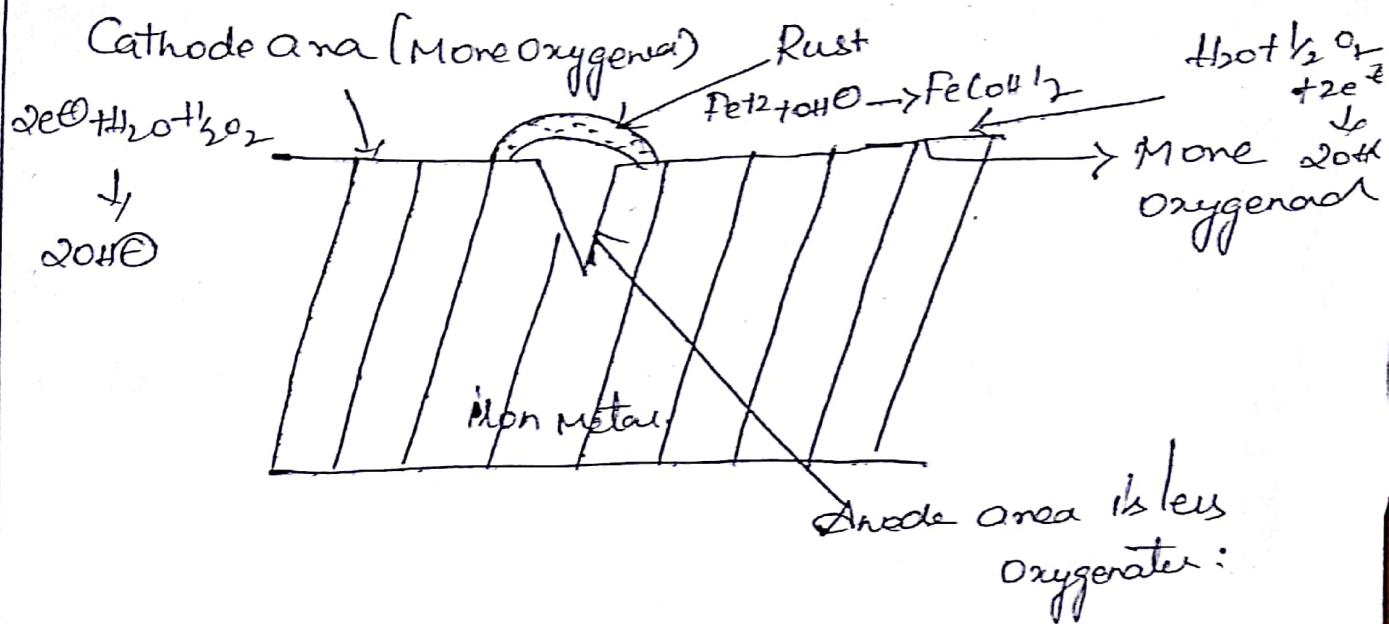
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The space which is more exposed to air in cracks or pinholes behaves as Cathode.

The corrosion product formed in between Cathode and Anod areas.

Cracking of a protective film is caused by

- (1) Surface roughness
- (2) Scratches / cut edges
- (3) Sliding under load.



Underground Corrosion:-

This corrosion is otherwise called as Soil Corrosion.

The corrosive nature of soil is due to

1. acidity of soil
2. Degree of aeration
3. Soil texture.
4. Moisture and Salt conc. present in soil.

As per as particle size they are classified as

a) Gravely (or) Sandy Soils:-

They are very porous and strongly aerated and corrosion occurs similar to wet condition.

b) Water logged Soils:-

They have a very small amount of free O₂ available. Here rate of corrosion depends on pH of soil and presence of salts and O₂ in soil.

c) Intermediate character Soil:-

Here soil is fine gravel, sand & silt may be produced. Here corrosion due to differential aeration.

d) Intergranular corrosion:-

This corrosion occurs along grain boundaries.

The typical example of this corrosion is welding of stainless steel done by deposition of Chromium Carbide at the grain boundaries which makes grain boundaries.

→ Intergranular corrosion (IGC), also known as intergranular attack (IGA).

→ Grain boundaries are developed due to some impurities. Boundary of grain acts as Anode and centre of grain is cathode.

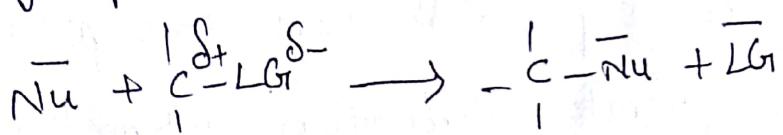
RXⁿ MECHANISMSubstitution reaction:

Substitution RX^n is a rx^n in which an atom(or) group in a molecule is replaced by another.

Eg:- Nucleophilic substitution.

NUCLEOPHILIC SUBSTITUTION

The Nucleophilic rx^n 's occur when an electron rich species the Nucleophile (Nu) reacts at an electrophilic saturated carbon atom attached to an electronegative group the leaving group (LG) that can be displaced in this rx^n .



The electrophilic carbon contain the polar σ bond due to presence of an electronegative substituent (LG) (esp c-cl, c-I, c-O, etc).

This rx^n allow the interconversion of functional groups

Nucleophilic Substitution goes in two ways.

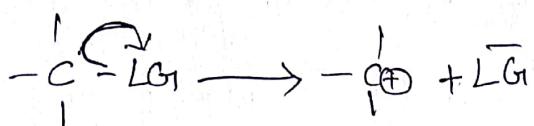
i) $\text{S}^{\text{N}}1$ mechanism

ii) $\text{S}^{\text{N}}2$ mechanism.

* S_N^1 - mechanism:

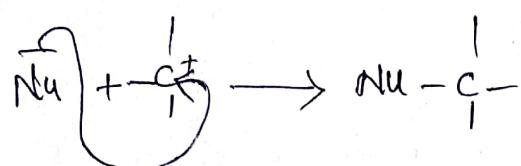
- S_N^1 - indicates a substitution nucleophilic, unimolecular rx^t
- $$\text{rate} = K [R-LG]$$
- which is a rate determining step (RDS) depend on the decomposition of a single unimolecular species.
- The S_N^1 goes by 2 steps.

Step-1

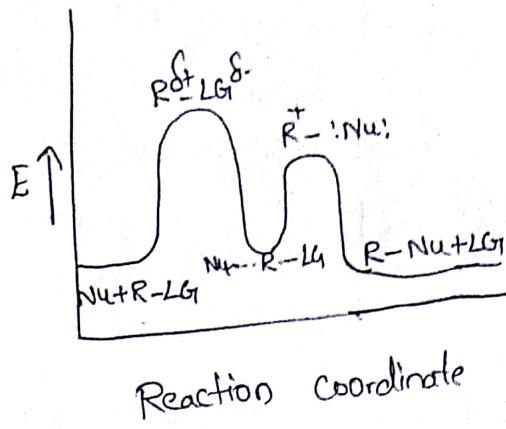


→ It is a slow step process. Here loss of the leaving group LG^- to generate carbocation intermediate.

Step-2

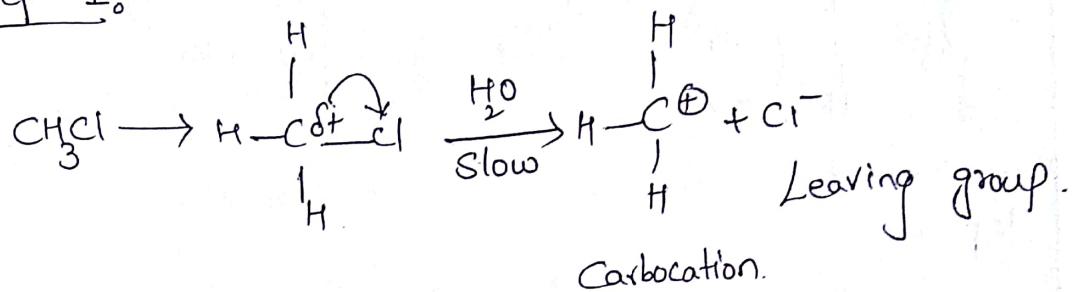


- Rapid attack of the nucleophile (Nu^-) on the electrophilic carbon (Carbocation) to form a New bond.
- S_N^1 mechanism is a multistep process produces several transition states.
- In the above rx^t 2 T.S were produced.



Eg: S_N^1 mechanism of alkyl halides in presence of H_2O

Step-1°:-



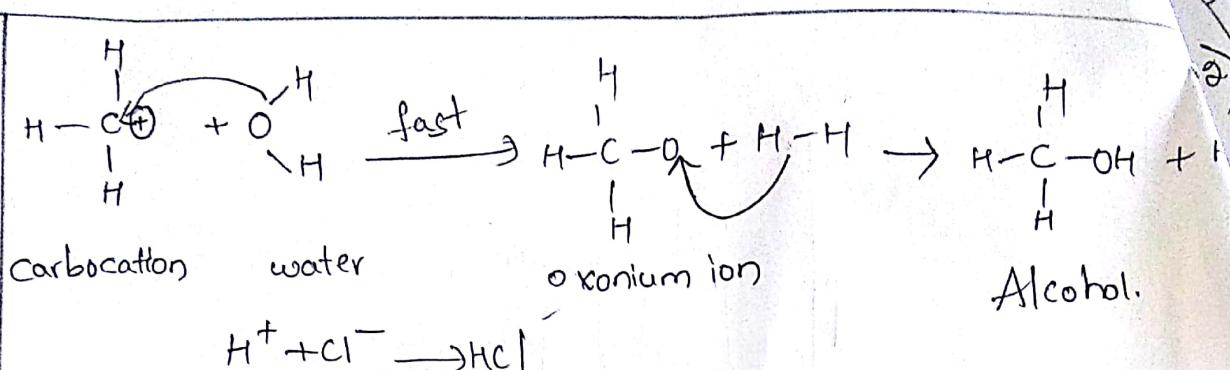
Carbocation.

In this step cleavage of polar C-Cl bond allows the loss of the good leaving group, the chloride ion to give Carbocation intermediate.

This is rate determining step.

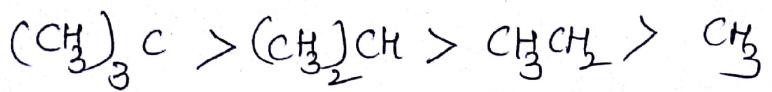
Step-2°:-

Attack of the Nucleophile, (the lone pair of \bar{e} 's on oxygen atom of water molecule) on the electrophilic Carbocation creating oxonium species.

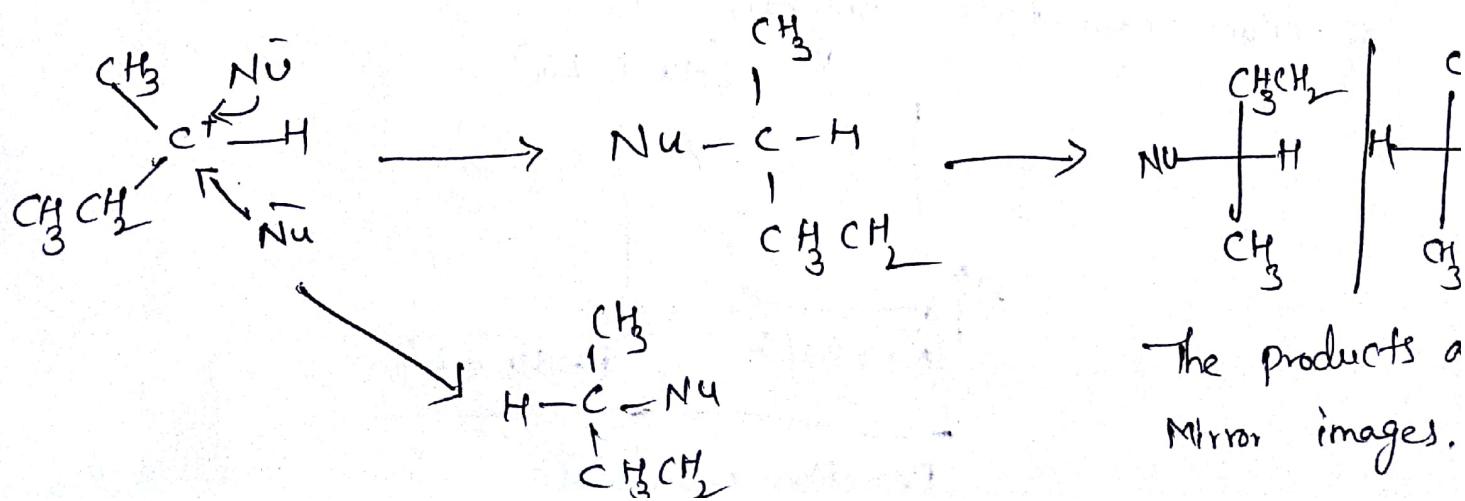
Ex-2:-Step-1:-Step-2:-

* Factors affecting $\text{S}^{\text{N}}\text{I}$ Mechanism!

1. Nature of Carbocation formed!
- The more stable the Carbocation is, the faster the $\text{S}^{\text{N}}\text{I}$ rxn will be.
- The Nature of Substituent on carbocation plays an important role.



- x 2) Leaving group (LG): LG has strong influence on S_N^1 reaction, because the cleavage of C-LG bond is the rate determining step.
- The more electronegative the LG, the faster the S_N^1 mechanism.
- 3) Nature of Nu^- : It has least influence on rate of rxn because it is not the rate determining step but however the more reactive the Nu is, the more likely an S_N^1 mechanism becomes.
- 4) Solvent: Polar solvents can stabilise carbocations which can favour the S_N^1 rxn. [e.g. H_2O , R_2OH , etc]
- 5) Stereochemistry: In an S_N^1 mechanism, the Nu attacks the planar carbocation with equal probability of attack on the each face. Hence there will be a loss of stereoselectivity at the reactive centre as both products will be



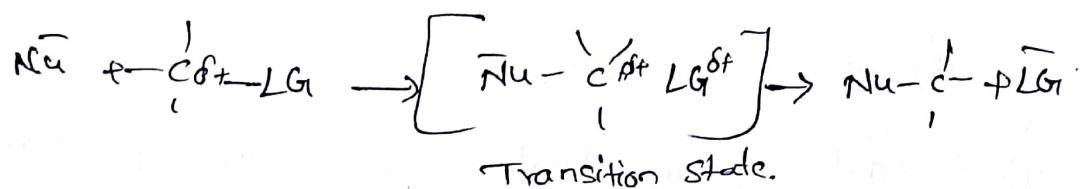
(iii)

 SN^2 Mechanism

SN^2 indicates a substitution, nucleophilic bimolecular rxn with the expression for rate. = $k [Nu] [R-LG]$ which shows that the rate determining step involves an interaction b/w 2 species, the nucleophile & the organic substrate.

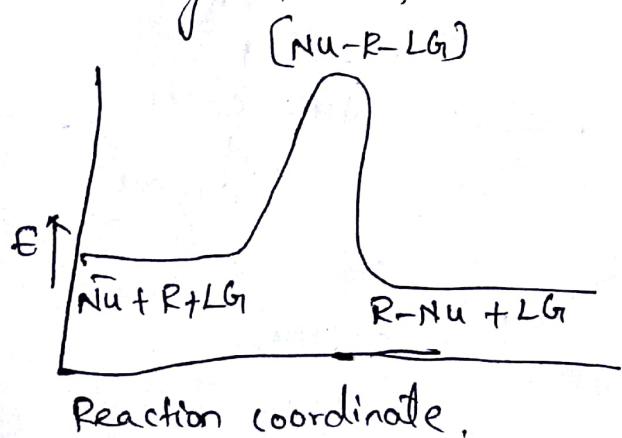
This SN^2 mechanism is one step (single step process).

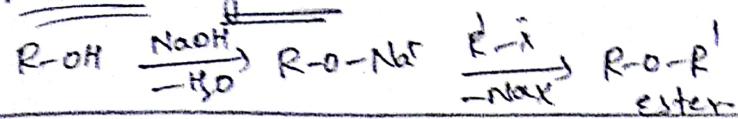
The general mechanism is



The nucleophile attacks the carbon with partial positive charge resulting carbon-nucleophile bond producing the T.S. The C-LG bond breaks and the product is produced.

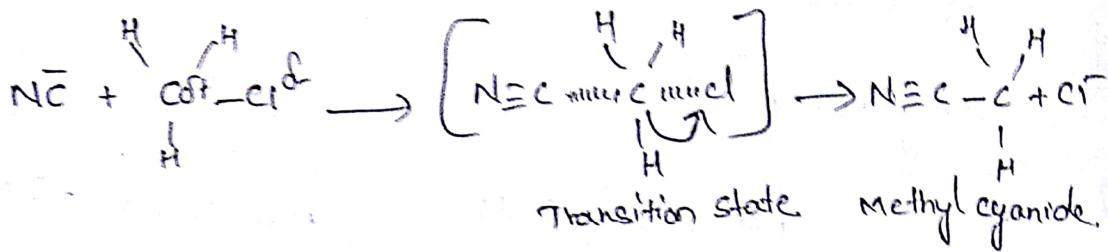
SN^2 mechanism is a single step mechanism and proceeds with intermediates and a single T.S, in which the central carbon 'c' is partially bonded to five groups. The reaction coordinate diagram is,





(14)

Ex: Rxn of an alkyl halide with HCN gives alkyl cyanide.



factors influencing S_{N}^2 mechanism:-

In S_{N}^2 rxns the T.S has 5 groups around the central carbon atom which produces steric requirements at this centre and more smaller groups will favour S_{N}^2 rxn by making it easier to achieve T.S.

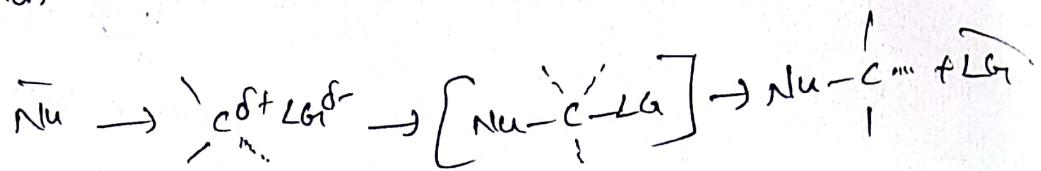
Hence - $\text{CH}_3 > \text{CH}_2\text{CH}_3 \rightarrow (\text{CH}_3)_2\text{CH} \rightarrow \text{C}(\text{CH}_3)_3$. If the steric crowding increases around the electrophilic centre, the rate of rxn decreases.

The breaking of C-LG is rate determining. If the LG is active, then the rate of S_{N}^2 rxn increases.

The nature of Nu is very important in an S_{N}^2 mechanism. The more reactive the nucleophile, the more likely the rxn of S_{N}^2 .

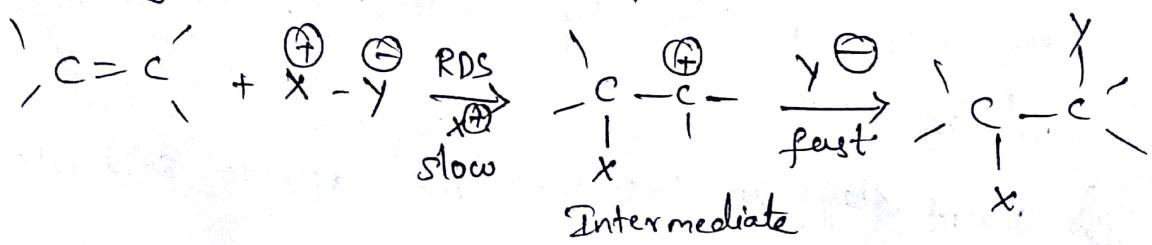
Solvent plays an important role. aprotic solvents can be used.

5) stereochemistry :- when the $\bar{N}u$ attacks in a S_N^2 mechanism it is on the opposite side to the position of the LG , as a result the rxn will proceed with a inversion of configuration is



* Electrophilic Addition Reactions

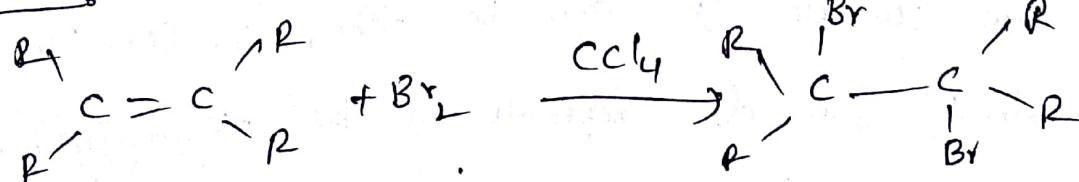
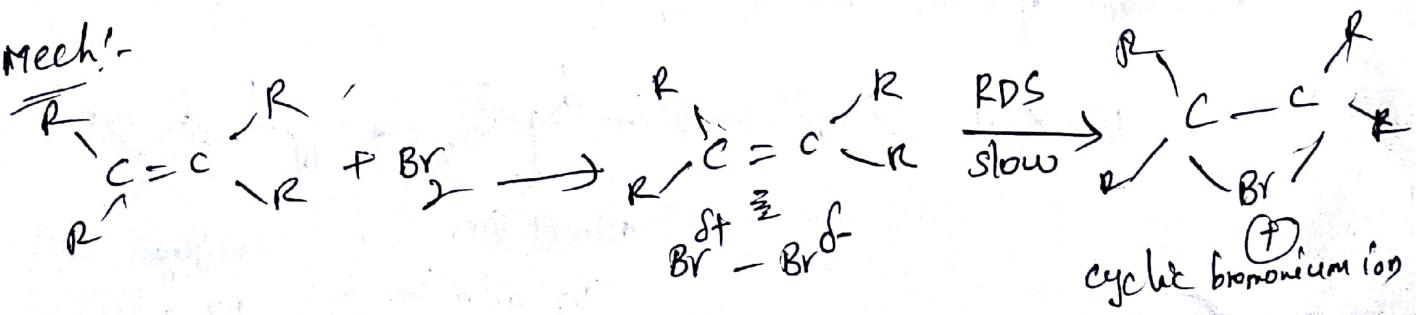
- Electrophilic addition rxn's can be defined as the chemical rxn's in which the electrophile is added to an π rich carbon atom, specially alkenes containing $\pi\text{-e}^-$'s & get attached to the double bonded carbon.
- Hydrogenation, hydrohalogenation alkenes are some common electrophilic addition rxn's of alkenes.
- (or)
- In an unsaturated system as the $\pi\text{-e}^-$'s are loosely held they can attract an electrophile which is electron deficient. Hence, the electrophilic addition rxn's are mainly seen in 'alkenes'.

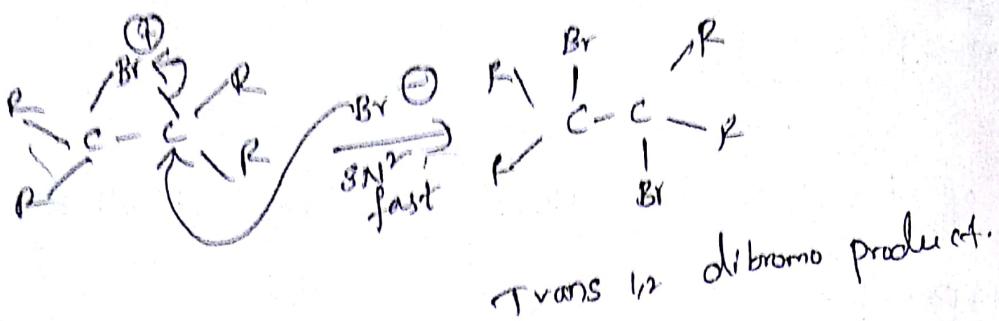


Addition of Bromine :-

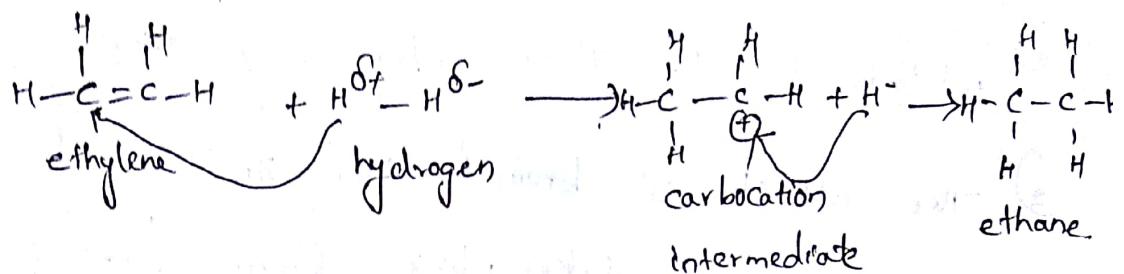
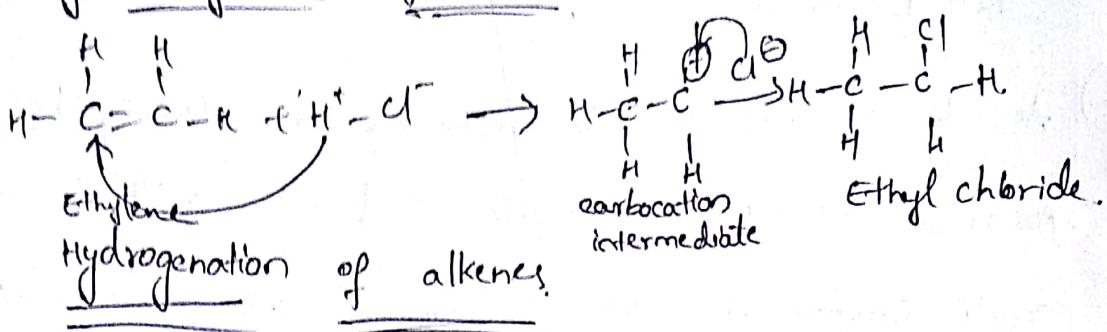
→ Addⁿ of Bromine to alkenes is stereoselective & stereospecific.

- 1) The alkene on rxn with bromine gives Trans 1,2 dibromo-addⁿ product.
- 2) As the $\pi\pi^*$'s of the alkenes are loosely held, it polarise bromine molecule & forms a π -complex. cyclic bromonium ion is formed as an intermediate & which is the Rate determining step.
- 3) The attack of bromide ion (Br^-) on the cyclic bromonium ion takes place from rare C or back side because the cyclic bromonium ion hinders (stopping) the approach of Br^- from the front side.
Hence trans dibromo product is formed

 RX^n :-Mech:-

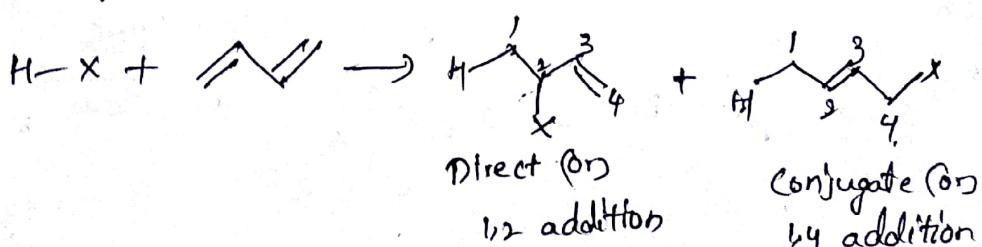


Ex:- Hydrohalogenation of alkene.

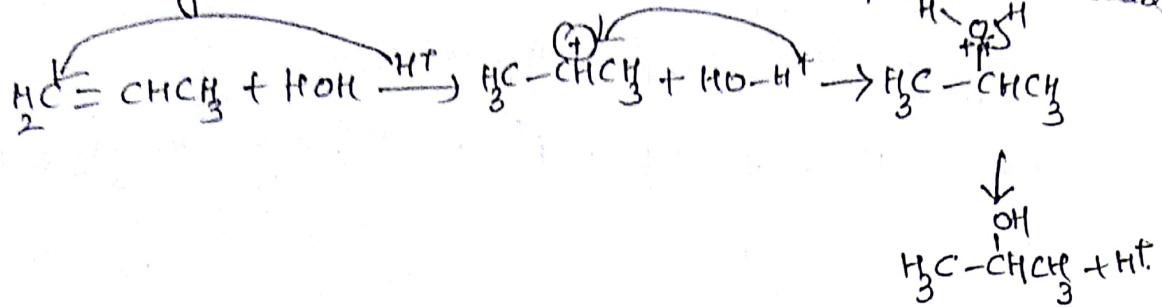


Ex:- Electrophilic addition to conjugated Dienes.

- conjugated dienes have double bonds in alternate manner & conjugated dienes are stable due to delocalisation of pi-electrons. Since there are two double bonds, two modes of addition are possible. It can be either 1,2 or 1,4 addn?
- the product formed depends on the thermodynamic conditions of the rxn.



Ex-4. Dehydration of propene with H_2O in presence of an acid.



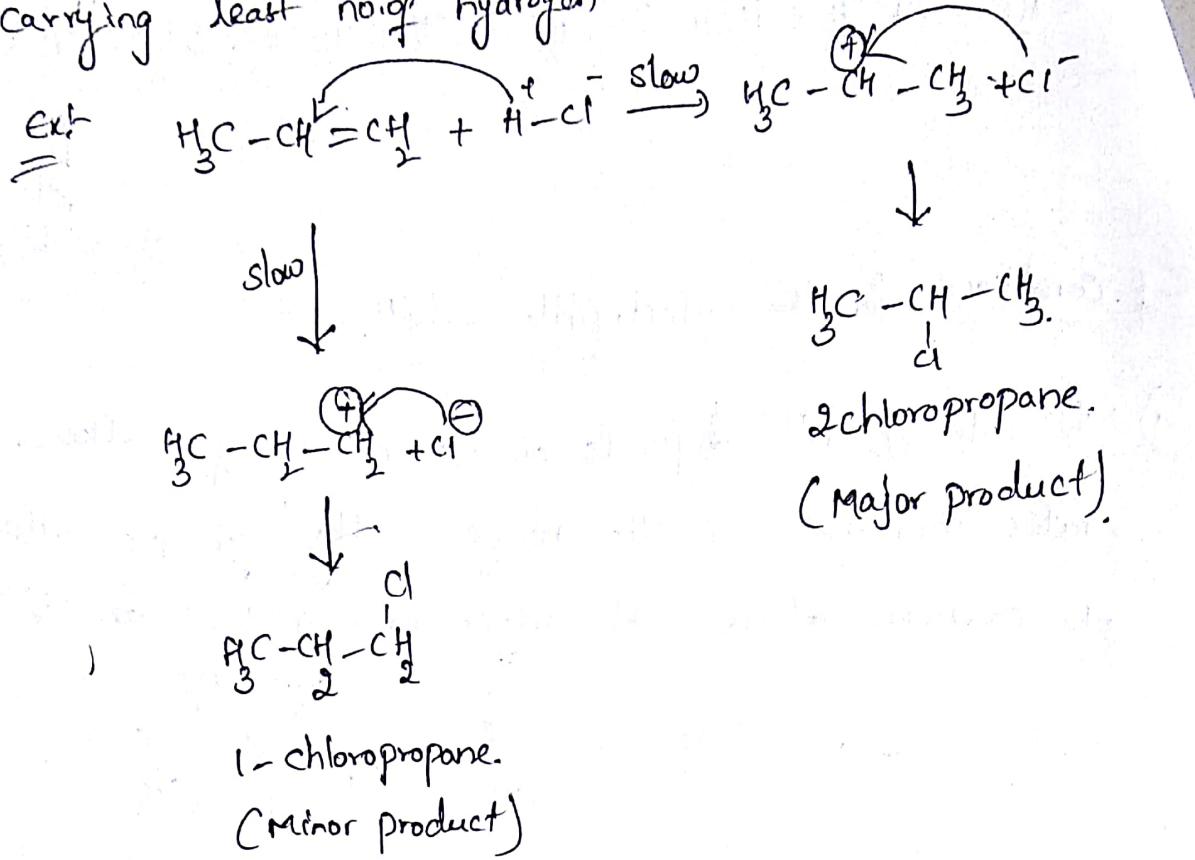
* Conditions for the electrophile addn:-

- 1) The rate of rxn depends on the nature of alkene. Rxn rates increase as the no. of alkyl groups attached to carbon atoms at either end of the double bond.
- 2) Nature of halogen on the hydrogen halides determines the rate of rxn. For e.g.:- $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.
- 3) The stability of carbocation \uparrow ses, the rate of rxn. I.e. If the stability of carbocation \uparrow ses, the activation energy \downarrow ses & the rxn becomes faster.

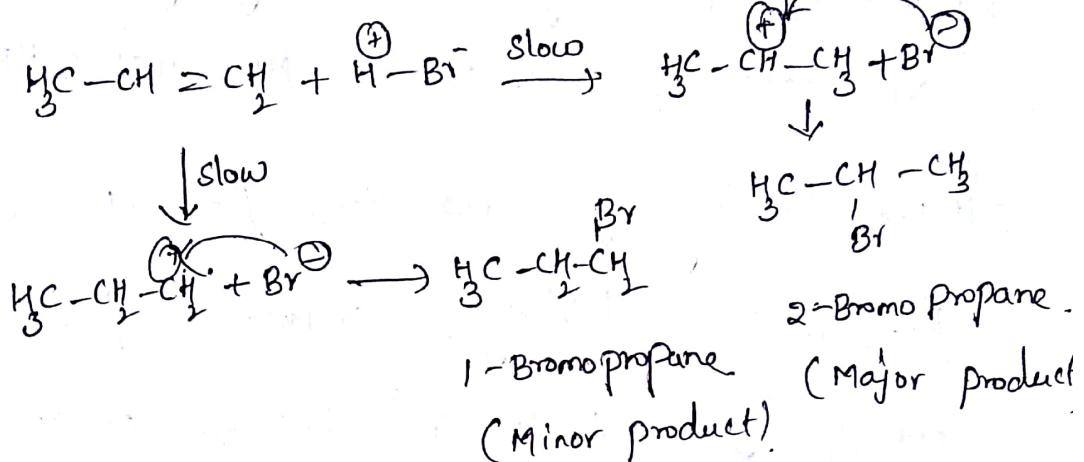
* Markovnikov's rule

- Markovnikov's rule is used to direct the possible product in electrophile addn as an unsymmetrical alkene
- According to markovnikov's rule the negative part of the

attacking reagent attaches itself to the carbon atom carrying least no. of hydrogen atoms.



Ex-2.



* Anti Markovnikov's Addition

→ It describes the regiochemistry where the substituent is bonded to a less substituted carbon, rather than more substituted carbon.

→ It is explained by M.S Kharash.

Conditions for Anti Markovnikov's rule

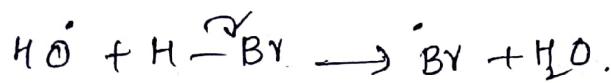
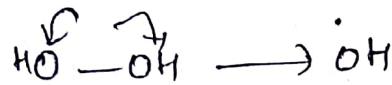
- 1) This rxn occurs only in presence of HBr not in presence of HI & HCl.
- 2) There must be a peroxide for initiation usually H_2O_2 is used.
- The rxn in presence of peroxide & HI or HCl cannot take place because this rxn is unfavourable.

Mechanism of Anti Markovnikov's rxn:-

- This rxn proceeds in 2 steps.
- 1) Initiation.
 - 2) Propagation.

a) Initiation:-

- H_2O_2 being unstable undergoes homolytic cleavage to produce free radicals.
- which attack, HBr and produces more stable bromine free radical.

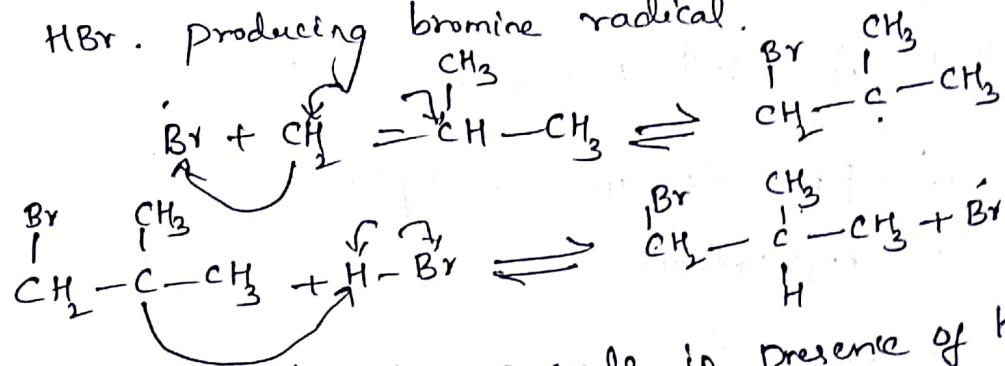


Propagation:- The bromine radical will attack the substituted carbon atom of alkene producing ... it is substitution radical which is more stable when with methyl groups etc.

Compounds having
organometallic c...
Recd/

→ due to induction & hyperconjugation.

→ the carbon radical formed will attack the hydrogen of HBr. producing bromine radical.



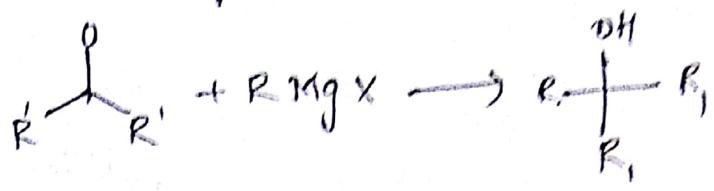
→ Markovnikov's rxn also proceeds in presence of H_2O_2 by radical way with HCl & H.I.

* Grignard Addition on carbonyl Compounds.

→ The grignard rxn named after Victor Grignard who proposed the mechanism & awarded Nobel prize (1912) is an organometallic chemical rxn in which alkyl, vinyl, or aryl Magnesium halides added to a carbonyl group in an aldehyde (or) ketone.

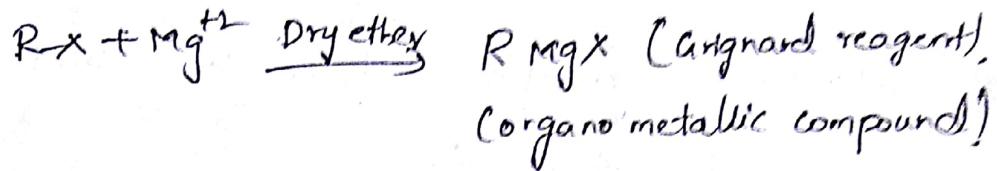
This is a very important rxn to formation of C-C bonds.

Compounds having carbon & metal bonding called as organometallic compound.



Mechanism of rxn

→ Grignard reagent

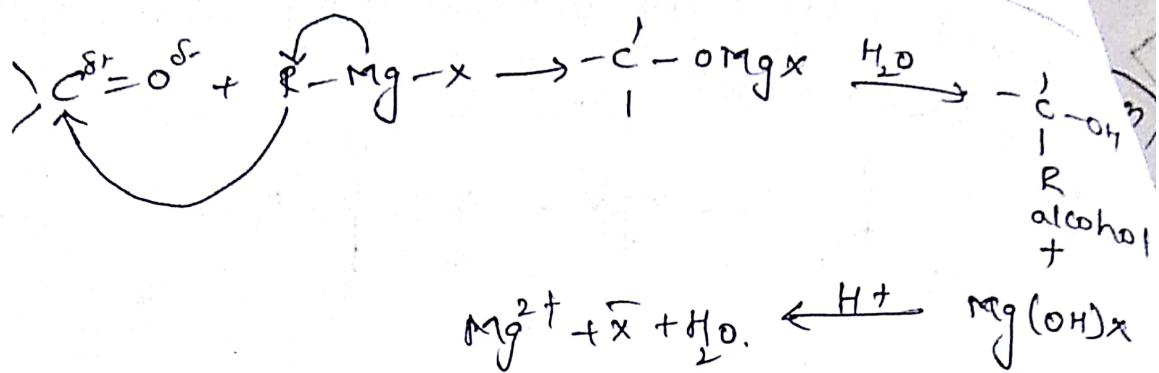


→ This reagent react with a variety of carbonyl compounds to produce the corresponding hydroxy compounds.

→ The carbon-Mg bond of the Grignard reagent is a highly polar bond, carbon being negative relatively to electropositive Mg, during the addn of carbonyl group.

→ The organic group becomes attached to carbon and Mg to oxygen resulting the product Mg salt of weakly acidic alcohol which is easily converted to alcohol itself.

→ The biproduct Mg(OH)_x is a gelatinous material, difficult to handle hence HCl/H₂SO₄ is commonly used instead of water, so that water soluble Mg salt is formed.

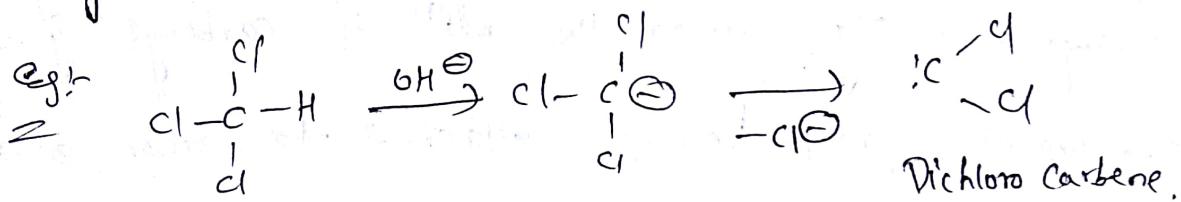


Elimination Reactions!-

- Removal of atoms or groups from the substrate are known as Elimination rxns.
- They are divided in to 3 steps.

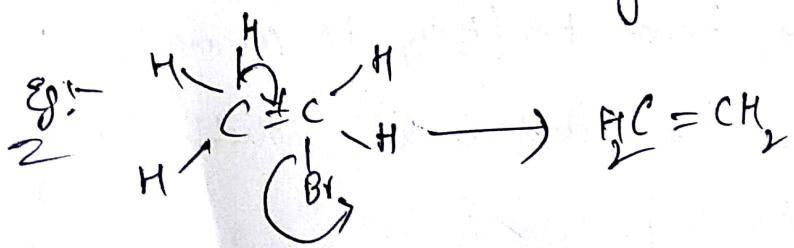
1) 1,1 (or) α-elimination!-

- Both the atoms are removed from the same carbon to give reactive species such as carbene.



2) 1,2 (or) β-elimination!-

- In this the leaving groups are present at 1,2 positions in the vicinal carbons to give an unsaturated product



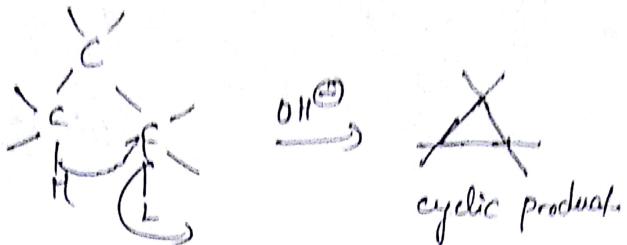
for β -elimination
where in the probability of finding
intermediate orbital

(q)

β -elimination:

In these eliminations the leaving group are present
in β positions to give a cyclic product.

e.g:-



Most of the elimination rxns are β -elimination rxns.

β -eliminations:

They are of 3 types

E_1 (or) unimolecular elimination reactions.

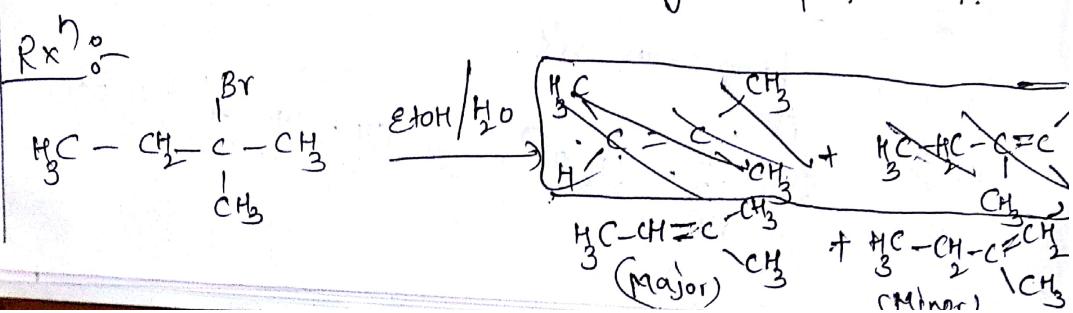
E_2 (or) Bimolecular elimination rxns.

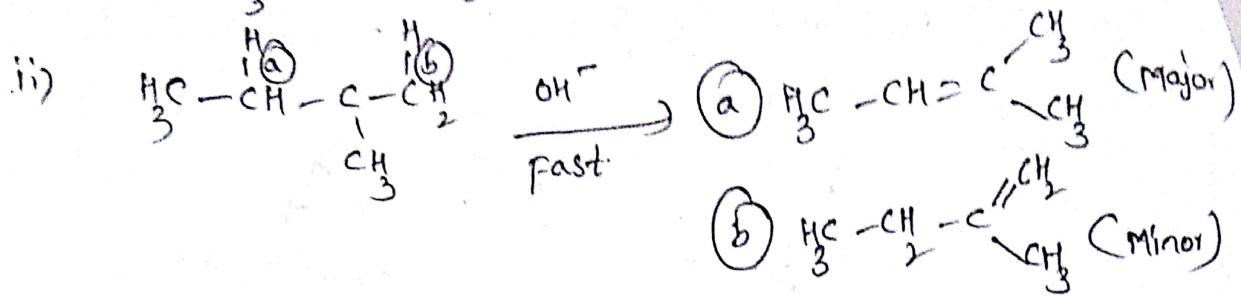
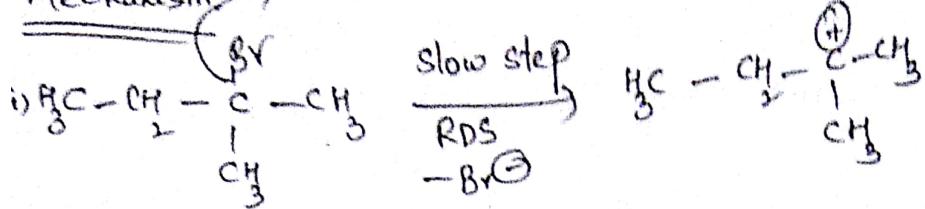
E_{1cB} elimination rxns.

E_1 (or) unimolecular elimination rxns:-

It is a 2 step process.

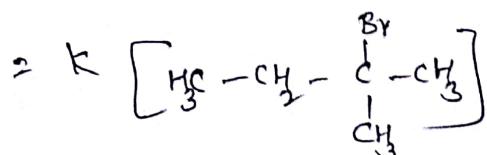
The two step process involves a carbocation intermediate
then it lose electrophile (CH_3^+) to give E_1 product.



Mechanism →

Rate = Rate constant × substrate

$$\text{Rate} = K [\text{substrate}]$$



with respect to reactivity of alkyl halide $3^\circ > 2^\circ > 1^\circ$

factors governing E_1 -elimination:-

substitution at α -carbon.

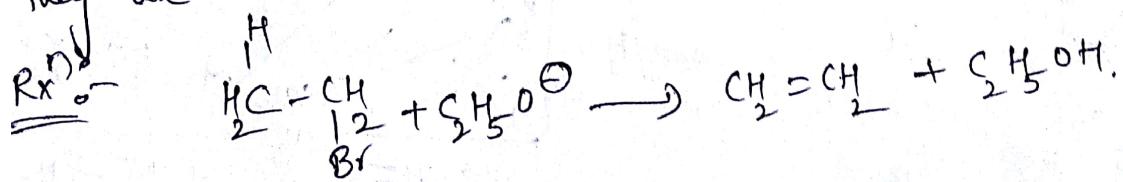
Substitution at β -carbon.

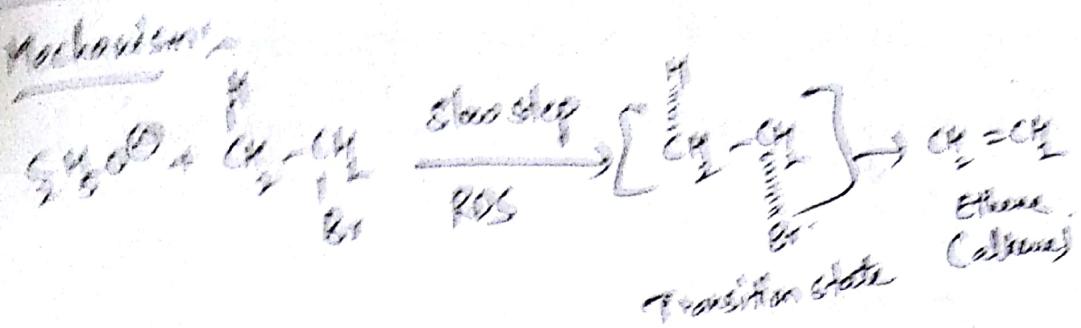
Benzyl (or) Allyl system readily gives E_1 , p.t.l.

In the presence of heat also favours E_1 elimination.

 E_2 -elimination

They are bimolecular rxns.





- the rate of ethene formation is proportional to the concentration of Ethyl bromide as well as Sodium hydroxide.
- In the mechanism the base abstracts a proton from the P-carbon & simultaneously the leaving group departs from the S-carbon along with the pair of bonding electrons.

* factors affecting:-

- 1) The rate of E₂-rd increases with increasing strength of base.
- 2) E₂-rd usually require strong negatively charged bases like OH⁻, OR⁻ etc.
- 3) The better LG, the faster the rd which follows the order F < Cl < Br < I.

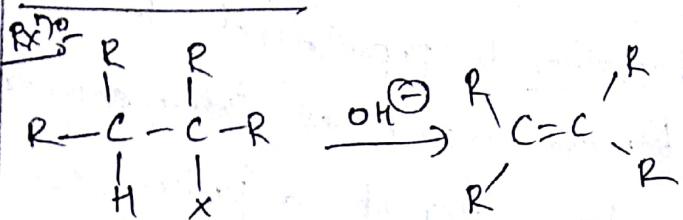
* Energy profile diagram:-

- The energy changes that accompany a chemical rxn are represented in the form of an

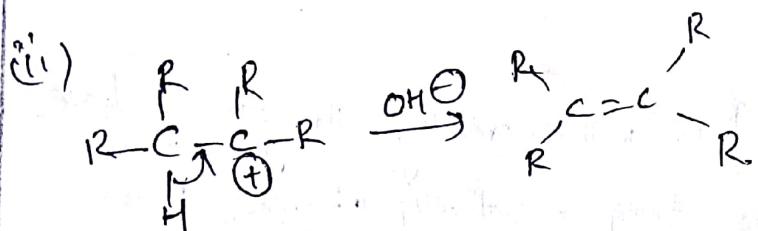
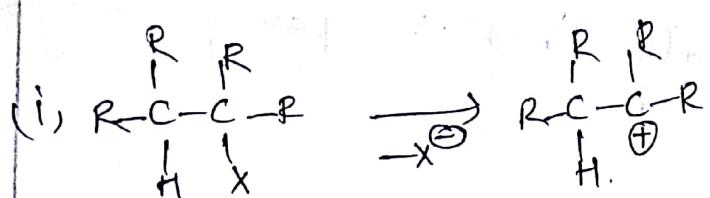
energy diagrams with potential energy plotted against Rx^n pathway which is known as energy profile diagram.

Eliminations:-

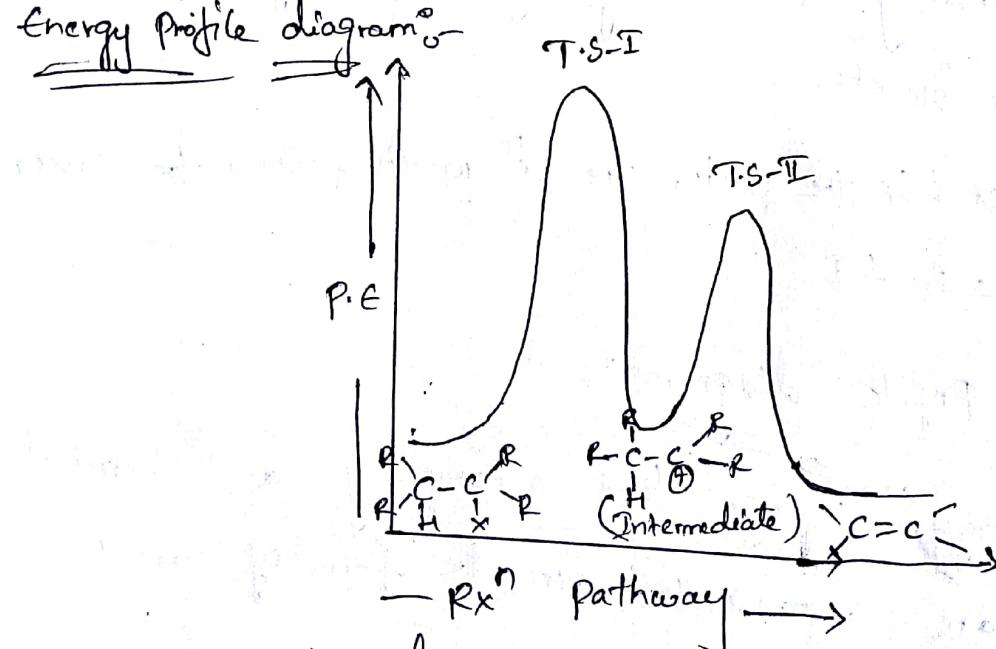
* $E_i - \text{Elimination!}$



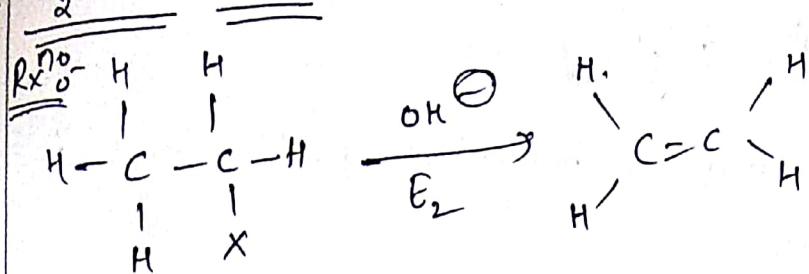
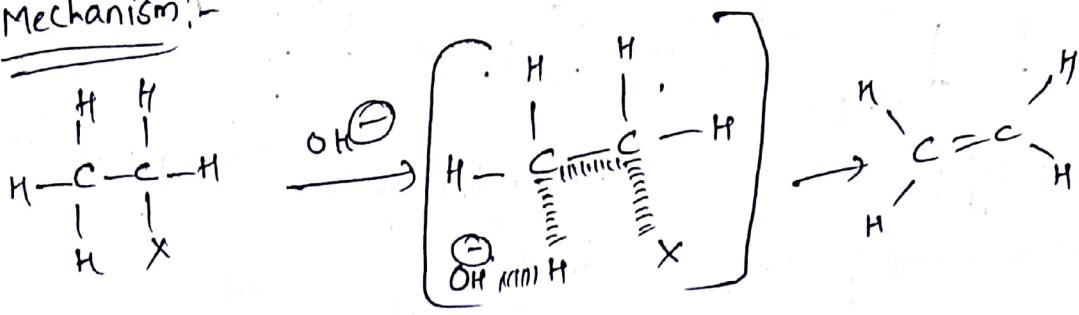
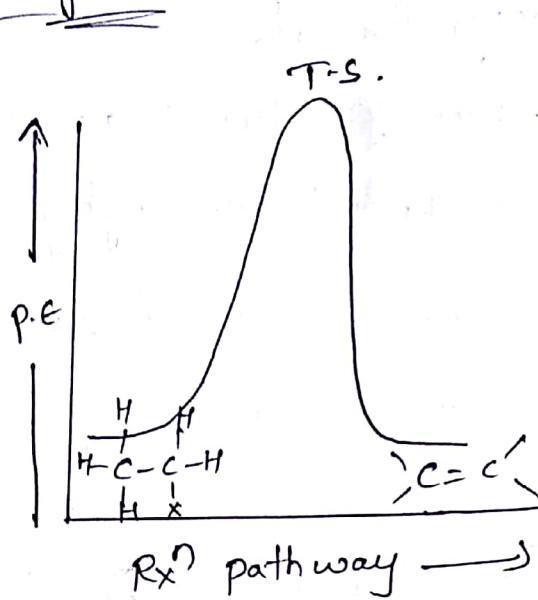
Mechanism:-



* Energy Profile diagram:-



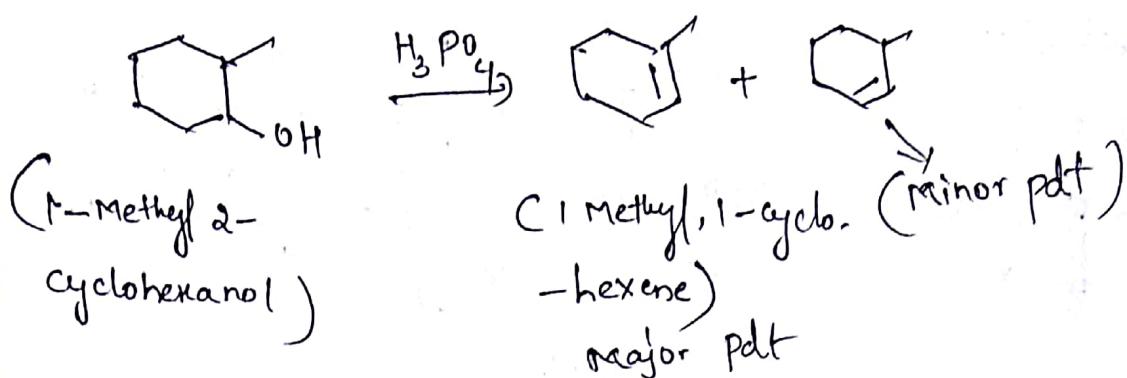
→ The energy Profile diagram of E_i, rx^n shows that the intermediate is formed in this Rx^n & it involves 2 transition states.

E_2 - elimination! -Mechanism! -* Energy profile diagramZaitsev (Saytzeff) Rule (or Saytzev's Rule)

- When alkyl halides have 2 or more diff. carbons more than one alkene is produced.
- In such cases, the major product is the more stable

Product with more substituted double bond. This rule is called Saytzeff rule.

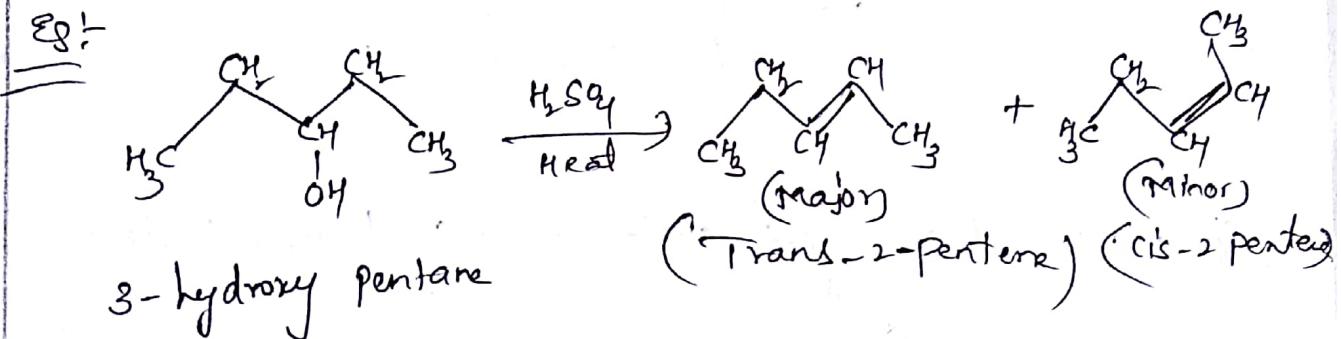
→ The stability of more substituted double bond is due to hyperconjugation.



→ This rxn is dehydration rxn.

→ In this dehydration of alcohols preference of elimination is given to the product with highly substituted (or) stable alkene which is called Zaitsev's / Saytzeff's pdt.

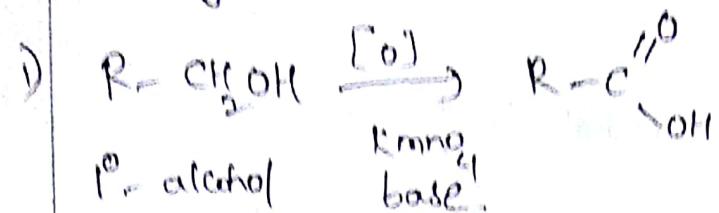
→ The products are stereoisomers.



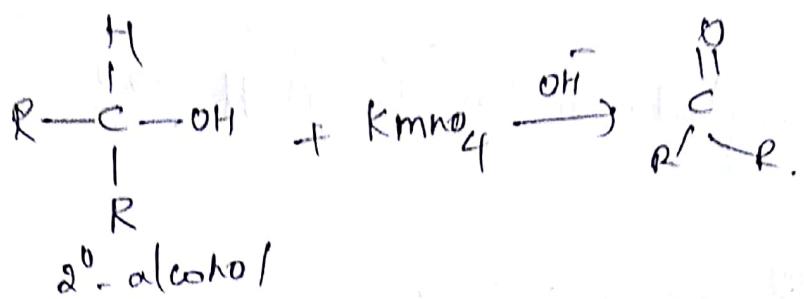
OXIDATION REACTIONS OF KMNO₄

i) with alcohols :-

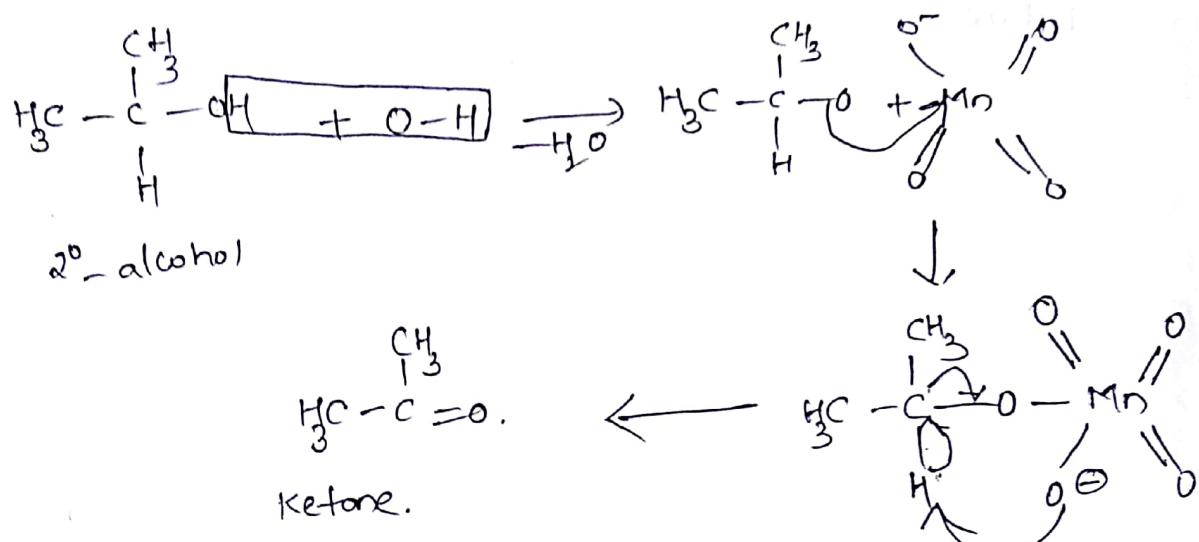
a) primary alcohols :- it gives an acid.



b) Secondary alcohols :- 2° alcohol undergo oxidation to produce ketones.



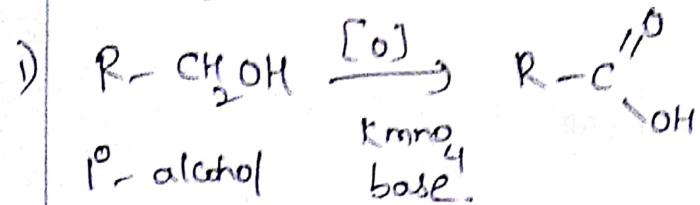
Mechanism :-



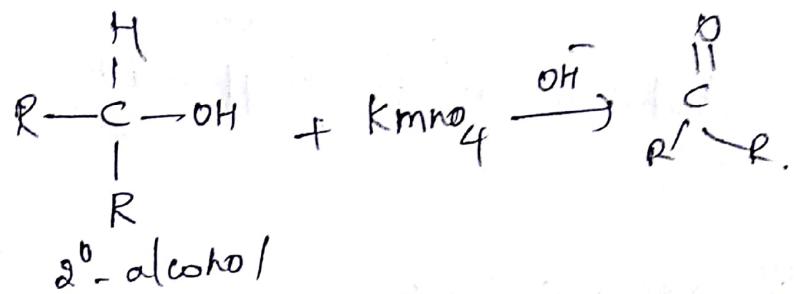
OXIDATION REACTIONS OF KMNO₄

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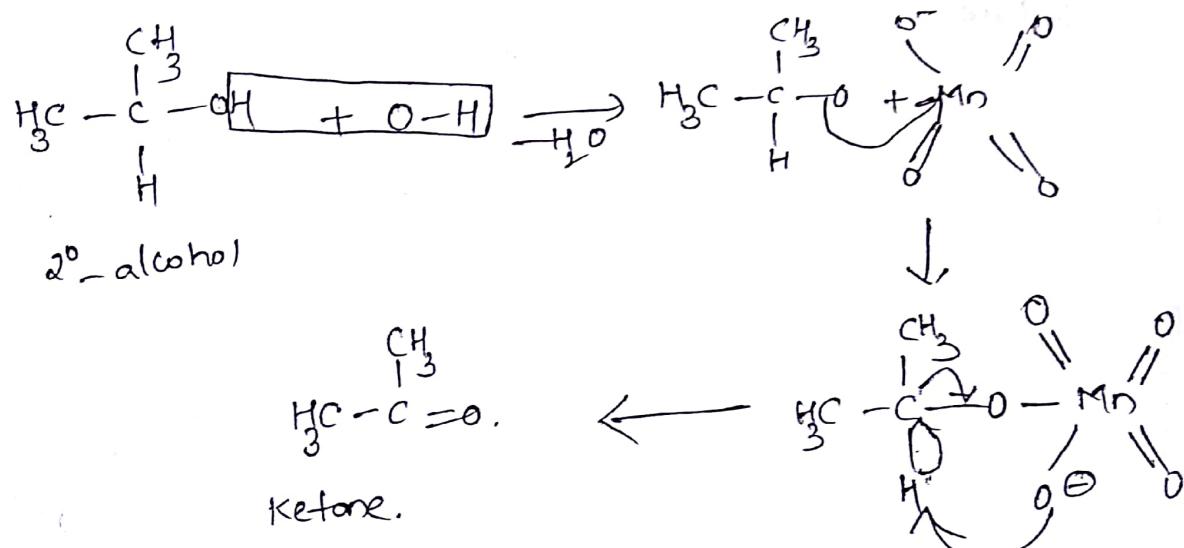
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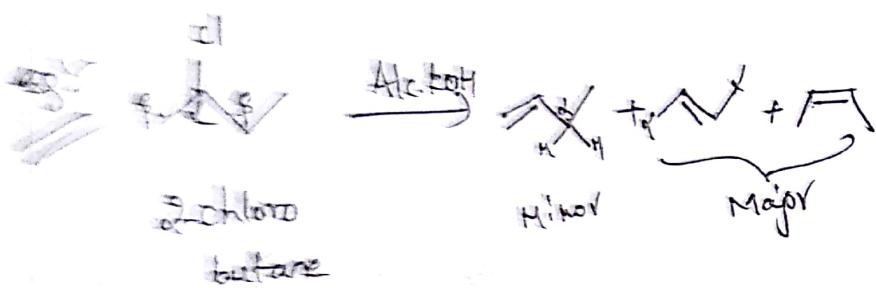
Mechanism:-



OXIDATION BY CHROMIC ACID:-

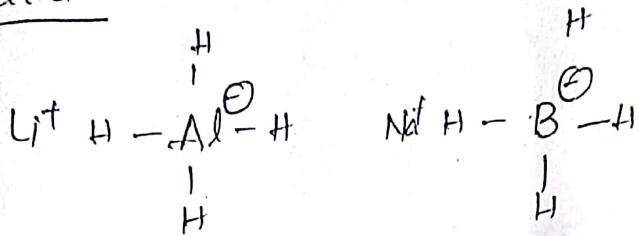
- Jones oxidation is carried out by Jones Reagent $[CrO_3 + H_2O]$
- $\text{^{\circ}}$ alcohol is dissolved in acetone & treated with chromic acid. The chromic acid oxidises $\text{^{\circ}}$ alcohol to carboxylic acids.
- Jones Reagent oxidises $\text{^{\circ}}$ alcohol to ketones
- $\text{^{\circ}}$ and $\text{^{\prime\prime}}$ oxidation occurs in acid medium, whereas KMnO_4 oxidation occurs in basic medium.

Elimination Rxn "Dehydrohalogenation" (Saytzeff rule)



Reduction of Carbonyl Compounds using LiAlH_4 and NaBH_4 .

Structure



Lithium Aluminum hydride.

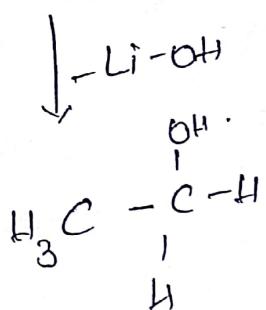
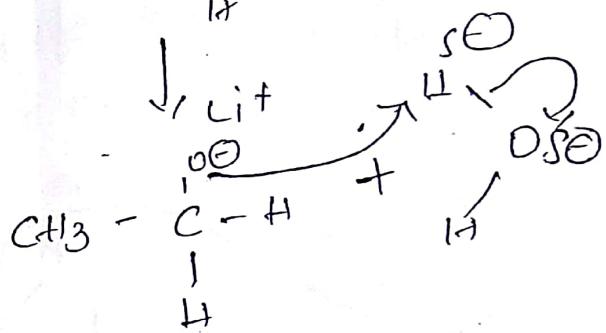
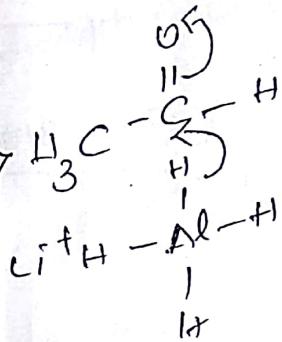
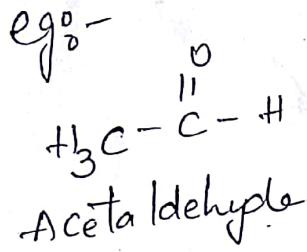
Sodium Boro hydride.

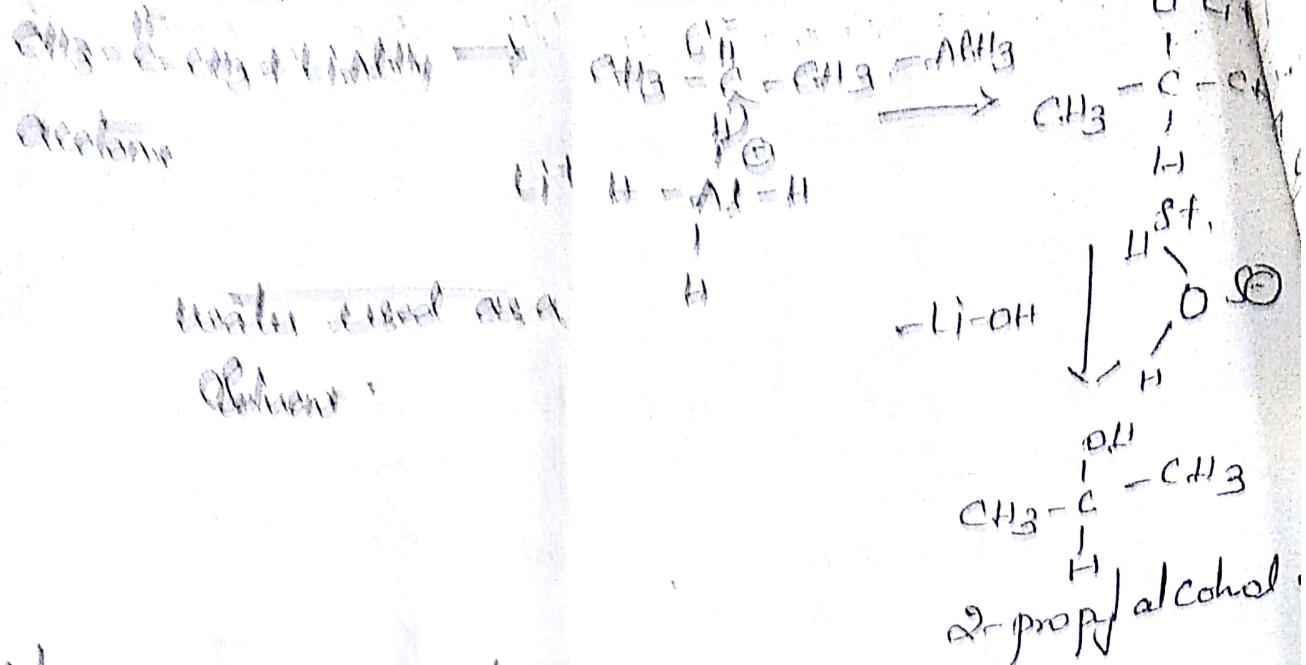
 LiAlH_4

$\text{Al}-\text{H}$ bond of LiAlH_4 is more polar making it a strong reducing agent.

making LiAlH_4

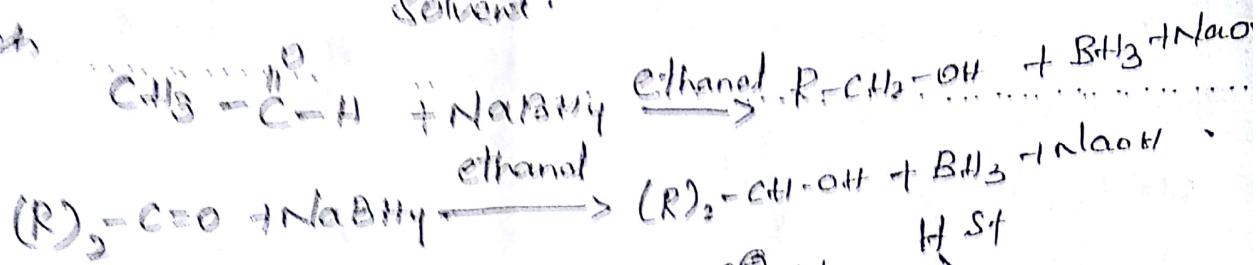
The addition of hydride anion from LiAlH_4 to aldehydes and ketones yields alcohol.



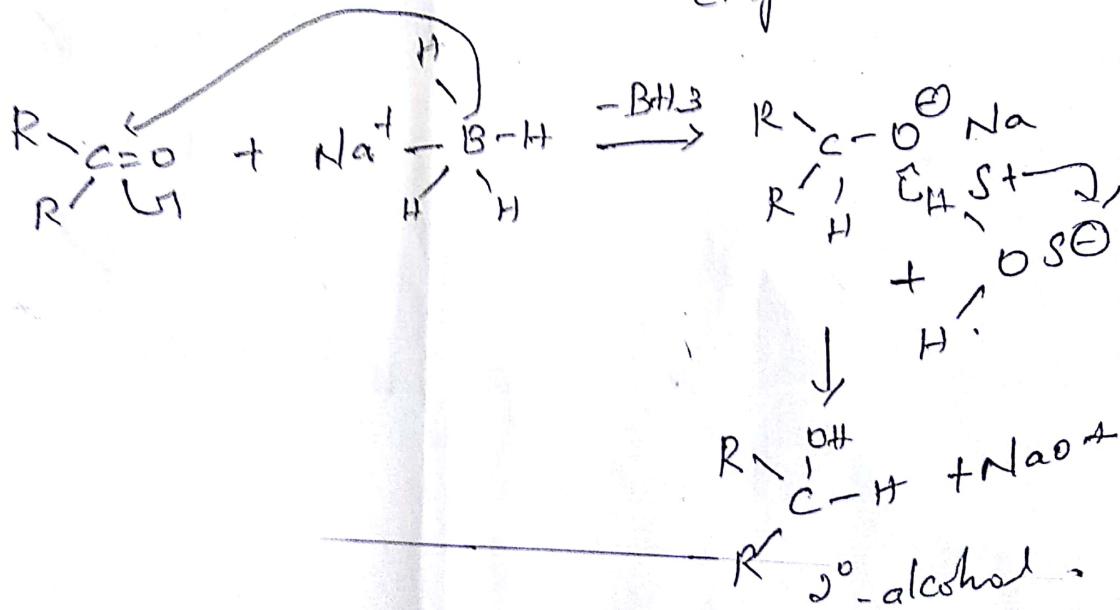
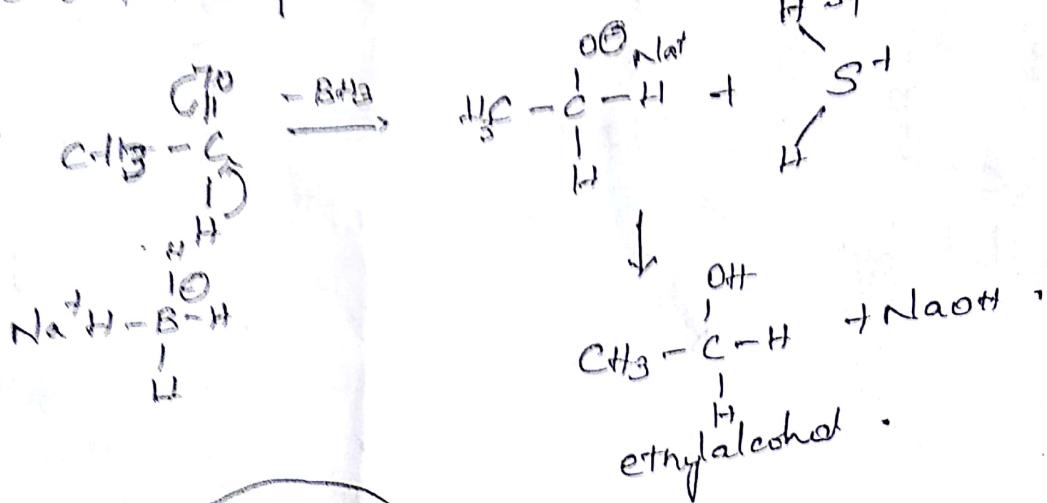


NaBHy :- Methanol used as a
Solvent.

Mech

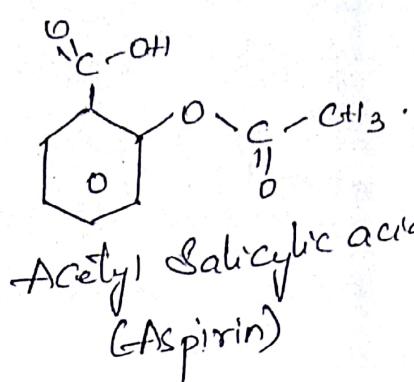


Mechanism

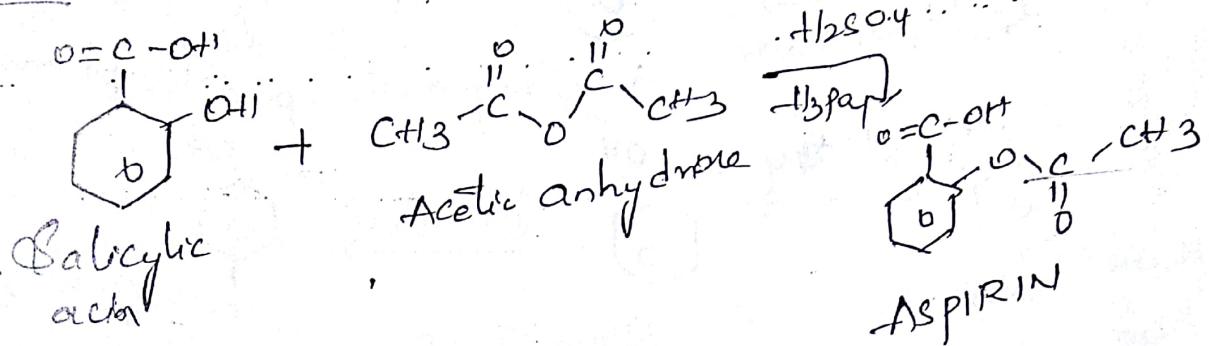


(12)

It is also known as Acetyl Salicylic acid. Aspirin given shortly after a heart attack decreases the risk of death.



Synthesis :-



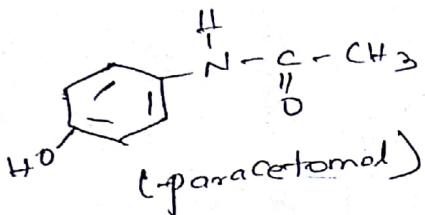
ASPIRIN is synthesised by esterification of Salicylic acid with acetic anhydride in presence of $\text{Al}_2\text{O}_3/\text{HgPO}_4$ which acts as catalyst.

Applications :-

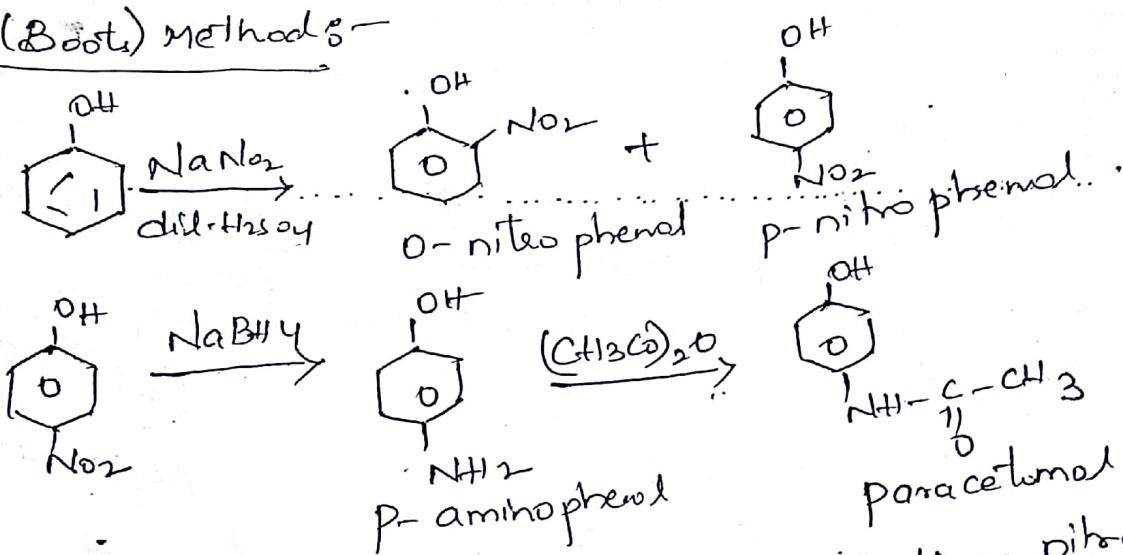
- 1) It is used to control the fever.
- 2) Treatment for certain types of Headaches.
- 3) It is used for prevention of some cancers.
- 4) It is used after high and low stroke.
- 5) Aspirin is used after heart attacks.

Paracetamol :-

It is also known as acetaminophen (as) ApAP is a medicine was discovered in 1873.



Conditions for opt symmetry
Plane of sym two identical halves
-ance, P these

Synthesis:-Original (Boots) method :-

It involves nitration of phenol with Sodium nitrate which gives rise to Ortho and para nitro phenol. O-nitro phenol is distilled off and p-nitrophenol treated with NaBH4 and acetic anhydride gives a paracetamol.

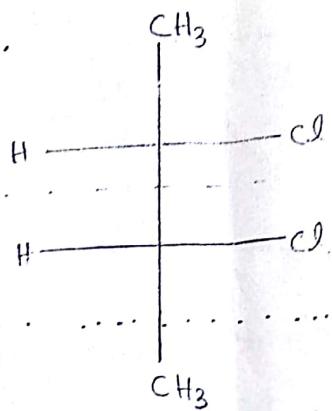
Applications :-

- 1) Reducing fever.
- 2) For pain relief
- 3) Low back pain
- 4) To reduce the dental pain

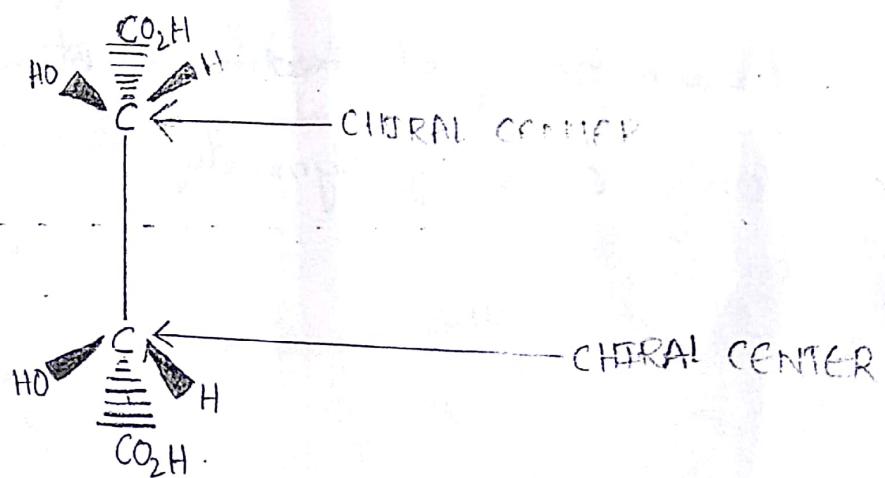
Q) Symmetry

a) Plane of symmetry: The plane that splits an object in two identical halves is called a plane of symmetry. For instance, palm of our hand cannot be divided into two equal halves and hence it does not have a plane of symmetry.

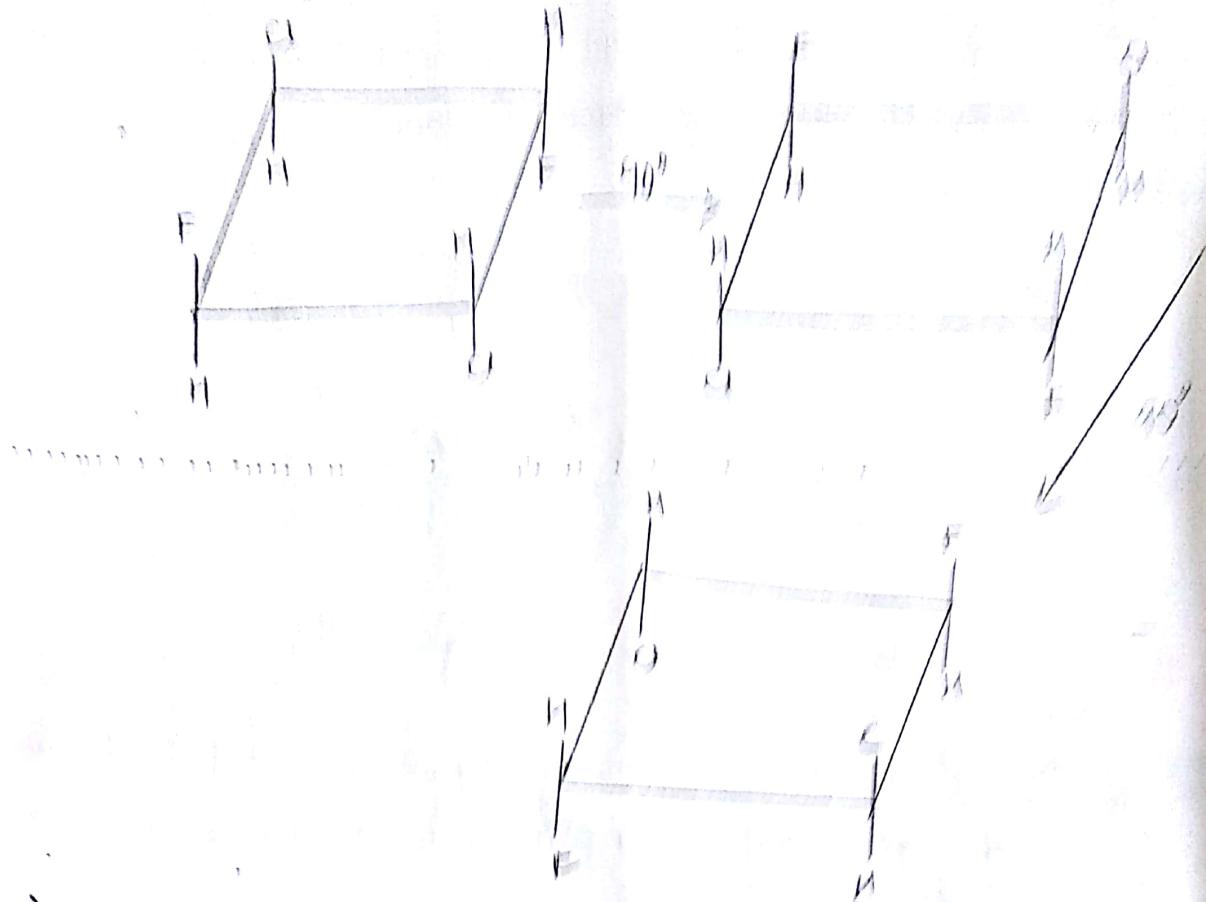
Therefore, it is chiral.



b) Center of symmetry: It is a point in a molecule. A line drawn through this point from any atom or group to the end res in the presence of identical group or atom at the opposite end.



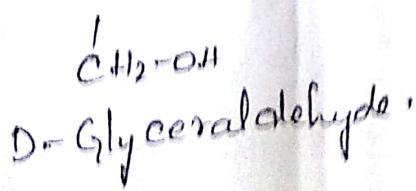
by an angle of $60^\circ/\text{min}$ through an angle of 60° across a plane which stands perpendicular to this axis results in an identical structure; this would be an operation of symmetry of the molecule.



2)

Chirality:

A carbon should be surrounded by four different groups. It should be tetrahedral in nature. It should have only one axis of symmetry.

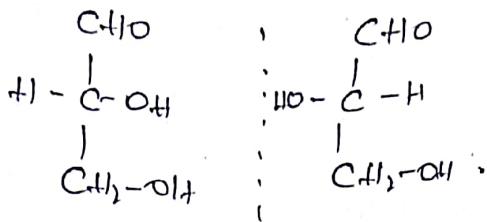


(19)

3) Enantiomers :-

These are a isomers which are neither & non-Superimposable mirror images.

→ They have identical physical properties but different rotation of plane polarised light.



Absolute Configuration :-

Cahn-Ingold-Prelog proposed a rule called Sequence rule and assigned R (means rectus) for dextro-rotatory and S (sinister means left) to levorotatory.

The salient features of Sequence rule are as :-

1. Order of priority :-

The atom with highest atomic number will get first priority.

I > Br > Cl > F > O > N > C > H.

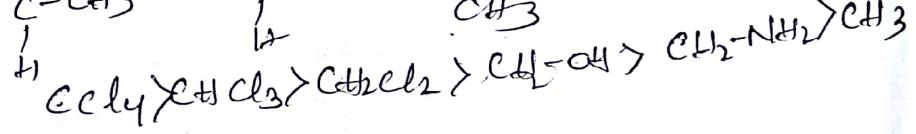
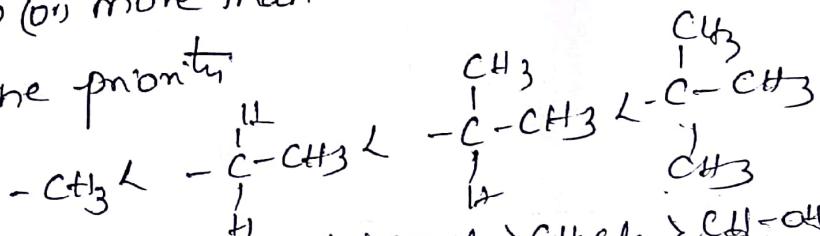
I > Br > Cl > F > O > N > C > H.

Isotopes with higher atomic number will get priority.

^{3}H > ^{2}H > ^{1}H

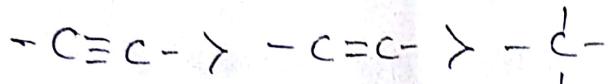
3. if two or more than two similar atoms are present

then the priority

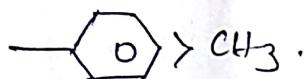


Order of Priority :-

4. If C is surrounded by Multiple bonded System

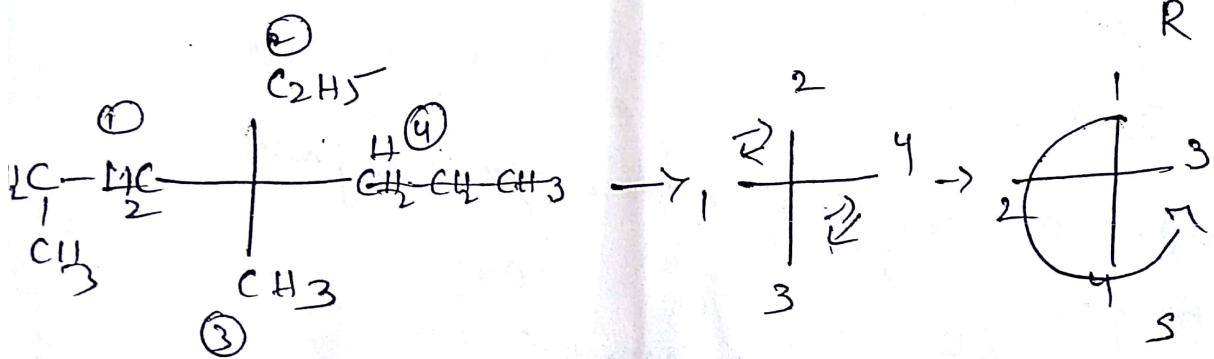
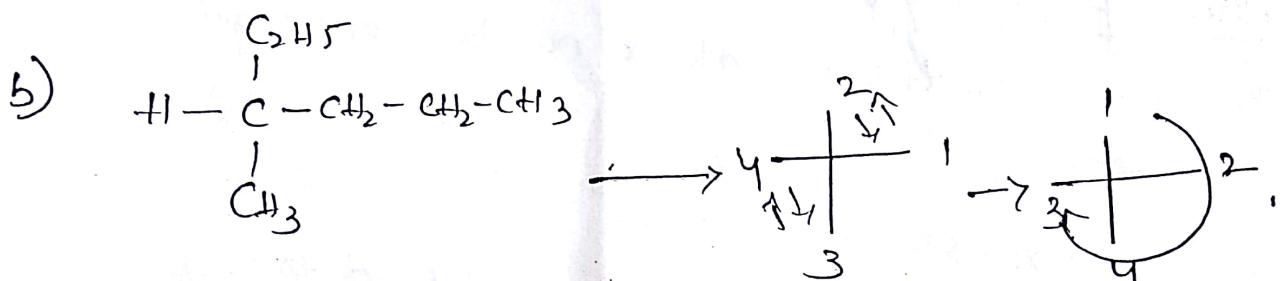
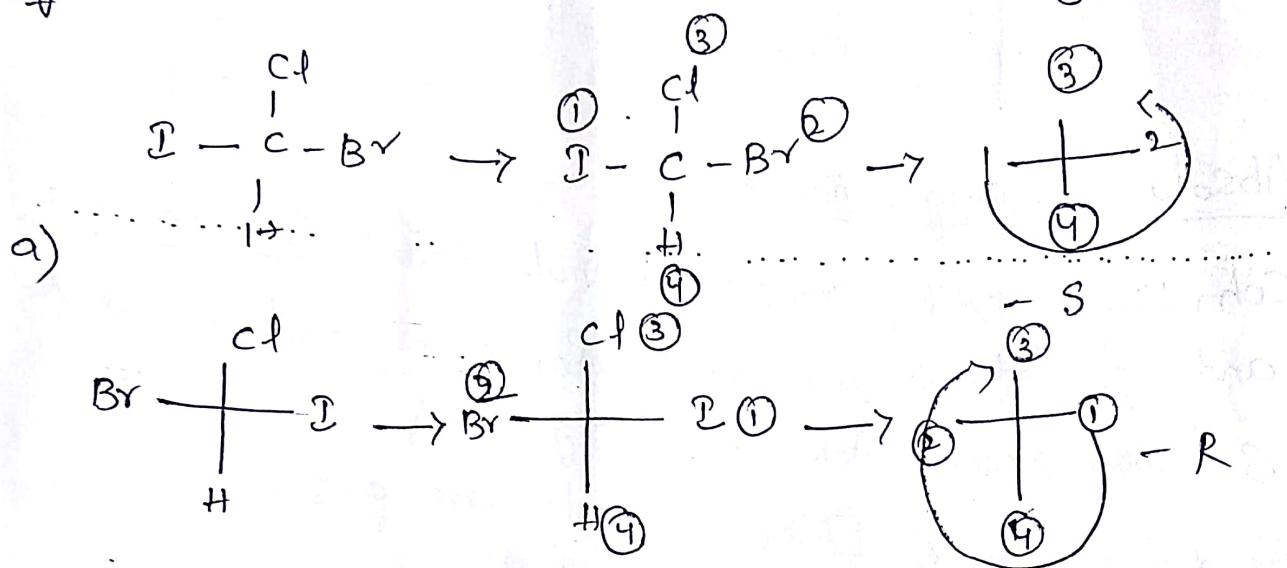


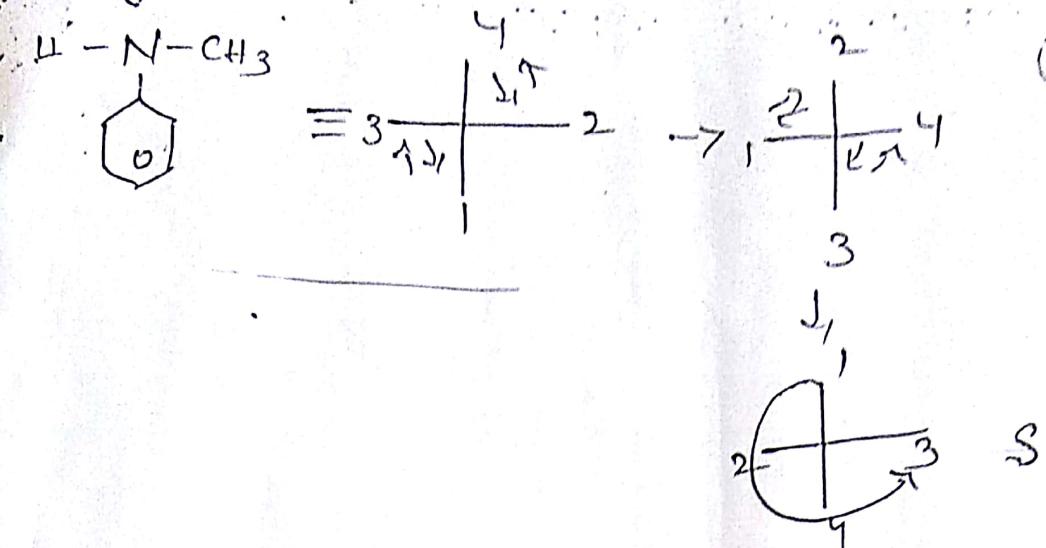
5. Cyclic group must be given priority over acyclic group



S5

Eg:-

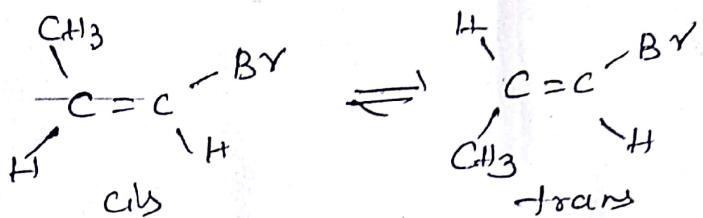




Nomenclature In geometrical Isomerism :-

Cis-trans Configuration :- if two similar groups are on same side of restricted bond the configuration is cis,

otherwise trans.



E/Z Configuration:-

if two senior groups are on same side of the restricted bond i.e called Z-cis.

if opposite side called E-trans.

Sequence rules:-

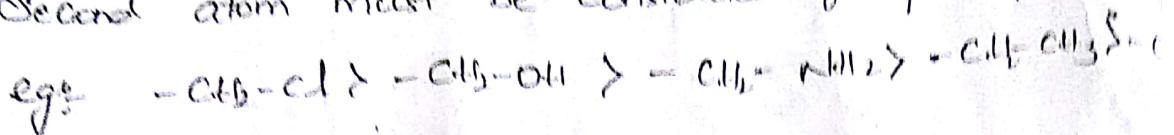
1) when C=C is attached with four different groups
the group with highest atomic number given first
Priority:

e.g. I > Br > Cl > S > F > O > N > C > H.

2) The higher mass isopeks get full priority.

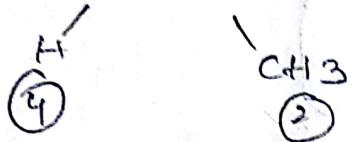
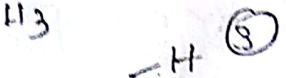
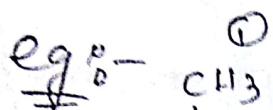
T > D > H

3) if the first atom of all groups are similar then
Second atom must be considered for priority.

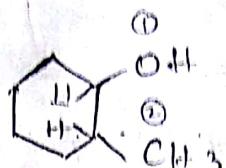


4) $\equiv > = > -$

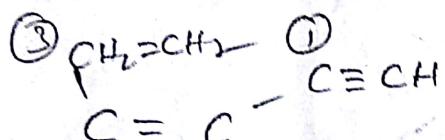
5) Bond pair must be given priority over lone pair.



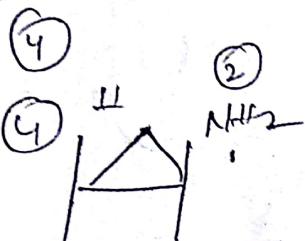
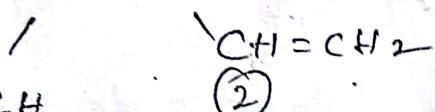
Trans (E)



CH₂ C₂



cis (Z)



cis (Z)

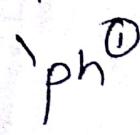
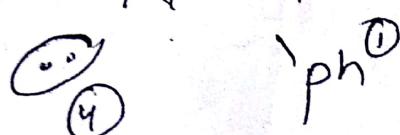
②



①



Trans (E)



Lambert-Beer's law

ELECTRONIC SPECTROSCOPY

In UV-visible Spectroscopy, sample interacted with UV-visible range of Electromagnetic radiation (200 nm - 800 nm).

UV-visible (region) range of radiation brings about change in position of electrons in molecule, i.e. electronic energies of molecule. Therefore also called as Electronic Spectroscopy. UV-visible is more energetic, therefore transition always accompanied by rotational, vibrational transitions of a molecule.

The participating e⁻s in electronic transitions are valence e⁻s & non bonding e⁻s (lone pair e⁻s) of molecule.

UV range : 200 - 400 nm.

VISIBLE : 400 - 800 nm.

Source for UV radiation : H₂/O₂ lamp.

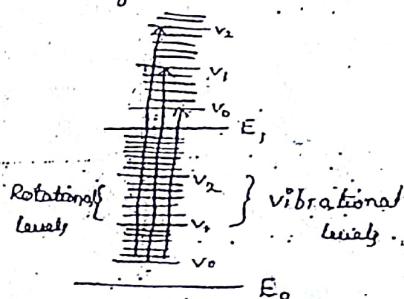
Source for vis radiation : Tungsten filament.

The UV spectrum may be divided into:

1. Far (or vacuum) UV — 10 - 200 nm

2. Neod or quartz UV — 200 - 380 nm

A molecule contains electronic, vibrational & rotational energy levels. Each electronic level within a molecule, is associated with a host of vibrational levels with less energy separation and each vibrational level is again associated with a set of rotational levels with even less energy separations.



Selection rules

Selection rules are statements which predict whether the transition is allowed or forbidden.

Allowed transition : Transitions which are taking place which have high probability are allowed transitions. Takes place in short time and bands in the spectrum appears with more intense. $E_{max} \geq 10^4$

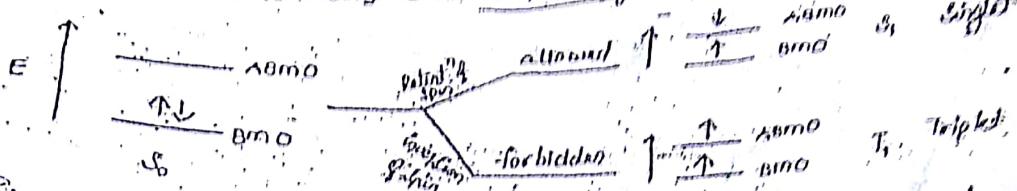
forbidden transitions: Electrons having long path with low probability are called forbidden electrons. Thus, anti-bonding transitions are forbidden transitions. Thus, anti-bonding transitions are forbidden.

(c) Overlapping exclusion rule:

In electronic transitions if participating molecular orbitals are in same plane, overlapping between them will be maximum & the bonding is allowed.

If participating orbitals are in different planes, overlapping b/w orbitals is poor & thus electronic transitions are forbidden.

(d) Spin exclusion rule: Transitions with retention of spin are allowed bondings, while electronic transitions with inversion of spin are forbidden transitions.



During electronic transition, if multiplicity is retained = allowed.

During electronic transition, if multiplicity is changed = forbidden.

(e) Symmetry criteria or symmetry exclusion rule:

In electronic transitions between participating mo's, if symmetry characteristics are same, transitions are forbidden, if symmetry characteristics is different transitions are allowed.

(f) Parity exclusion rule:

Electronic transitions $g \rightarrow g$, $u \rightarrow u$ mo's are forbidden.

$g - u$ & $u - g$ are allowed.

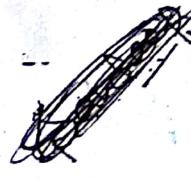
Ex: $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$ — forbidden.

$\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$ — allowed.

This rule is valid only if the molecules have centre of inversion.

Molecular orbitals C: designation

σ	σ	g	g
σ^*	A	u	u
π	A	u	u
π^*	S	g	g



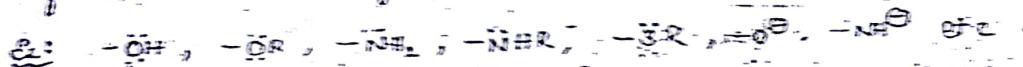
TermsChromophore

Unsubstituted group responsible for absorption other than range of radiation (200-400nm) is called chromophore.

Auxochrome:

The group with intensity absorption wavelength of chromophore & called Auxochrome.

Auxochrome itself cannot absorb radiation. Group carrying longevity of $\pi\pi^*$ or $-ve$ charge acts as auxochrome.



Effect of auxochrome on chromophore shifts the Or-Vis band to longer wavelength called bathochromic shift.



$$\lambda_{max} = 255 \text{ nm}$$

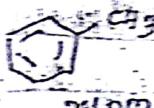
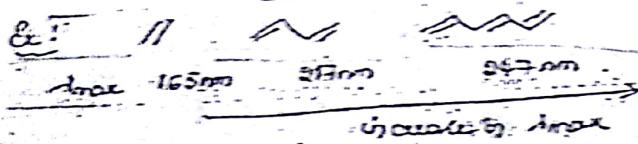
$$\lambda_{max} = 270 \text{ nm}$$

Bathochromic shift (or) Red Shift

Shift in Or-Vis bands towards higher wavelength in Or-Vis spectrum is called bathochromic shift.

Shift in Or-Vis band towards right in Or-Vis spectrum is

Called Bathochromic shift.



$$\lambda_{max} = 255 \text{ nm}$$

$$\lambda_{max} = 265 \text{ nm}$$

Hypsochromic shift (or) Blue shift

Shift in bands towards lower wavelength in Or-Vis spectrum is

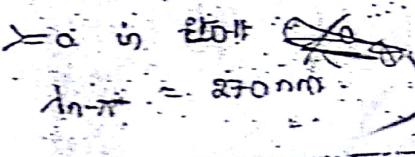
Called Hypsochromic shift.

(Or)

Shift in band towards left in UV-VIS spectrum is Blue shift.

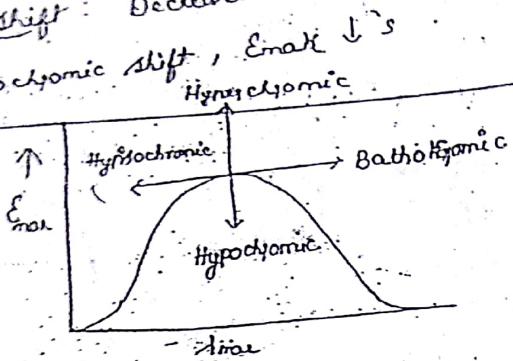
$\text{X} = \text{O}$ in n -butane

$$\lambda_{n-\pi^*} = 279 \text{ nm}$$



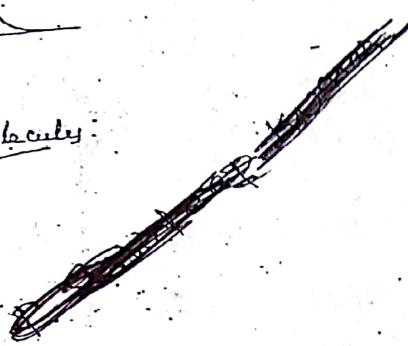
Hypsochromic shift : Increase in intensity of UV-vis band is called Hypsochromic shift, Emax ↑'s

Hypsochromic shift : Decrease in intensity of UV-vis band is called Hypsochromic shift, Emax ↓'s



Types of electronic transitions in molecules:

1. $\sigma \rightarrow \sigma^*$ transition
2. $n \rightarrow \sigma^*$
3. $\pi \rightarrow \pi^*$
4. $\pi \rightarrow \pi^*$



1. $\sigma \rightarrow \sigma^*$ transition : The transition of an e⁻ from a bonding sigma orbital of a molecule to the higher-energy antibonding sigma orbital is σ transition. The energy required for this transition is very high, because σ bonds are very strong bonds. These transitions can occur in such compds in which all the e⁻'s are involved in sigma bonds and there are no lone pairs of electrons. For example, in alkanes or saturated hydrocarbons in which valency shell of only most electrons are involved in single bonds. Since sigma bonds, the $\sigma \rightarrow \sigma^*$ transition is a high energy process and so relative to the other possible transitions, the energy required to induce $\sigma \rightarrow \sigma^*$ transition is large, these transitions require very short wavelength or high energy UV light of 150nm. Such transitions are studied in vacuum UV region since below 200nm oxygen present in the air begins to absorb.

2. $n \rightarrow \sigma^*$ transition : Saturated Compds containing atoms with unshared e⁻ pairs such as oxygen, nitrogen, sulphur, or the halogens, or non-bonding e⁻'s are capable of n → σ* transition, needs less energy than the σ → σ* transition.

In the case of alkyl halides, the energy required for n → σ* transition decreases with ↑ in the size of the halogen atom or ↓ in t

electronegativity of the atom.

Becoz of greater electronegativity of chlorine than iodine, the $n - e^-$'s on iodine atom are comparatively difficult to excite. The $n - e^-$'s on iodine atoms are loosely bound. Now let us compare $n \rightarrow \sigma^*$ transition in methyl chloride and methyl iodide. The $n - e^-$'s of chlorine in methyl chloride are more attracted towards chlorine bcoz it has high electronegativity value. Hence comparatively more energy will be required for excitation of $n - e^-$, i.e. for $n \rightarrow \sigma^*$ transition. More energy means lesser wavelength (λ) value. Hence λ_{max} for methyl chloride is $\lambda_{max} = 173$ nm, λ_{max} for CH_3I is $\lambda_{max} = 259$ nm; bcoz $n - e^-$'s on iodine atom are loosely bound. This indicates that, for Methyl Iodide comparatively less energy is required for $n \rightarrow \sigma^*$ transition than methyl chloride; $n \rightarrow \sigma^*$ transition is more probable in case of methyl iodide.

$n \rightarrow \pi^*$ transitions are sensitive to H-bonding. for example, alcohols and amines form hydrogen bonds with the solvent molecules. Such association occurs bcoz of the presence of non-bonding $n - e^-$ s on the hydroxyl atoms present in these compds. So greater energy will be required for $n \rightarrow \pi^*$ transitions. In other words, hydrogen bonding shifts the absorption towards shorter wavelength. The non-bonding $n - e^-$ s on nitrogen atoms in amines are loosely bound as compared to the $n - e^-$ s on oxygen atom in alcohols bcoz of higher EN of oxygen than nitrogen. Since $n \rightarrow \pi^*$ transition is more probable in amines than alcohols, the amines absorb at higher λ as compared to alcohols.

3. $\pi \rightarrow \pi^*$ transitions: The transition require the presence of an unsaturated functional group to provide the π orbitals.

The $\pi - \pi^*$ transition corresponds to the promotion of an electron from a bonding π orbital to an antibonding π^* orbital available in compounds with unsaturated centers such as simple alkenes, aromatics, carbonyl compds etc. Since the excitation of $\pi - e^-$ requires lesser energy than $n \rightarrow \sigma^*$ transition, this type of transition occurs at longer λ.

Here the $\pi - e^-$ of the double bond excites to π^* antibonding orbital. Hence Compds containing double bonds or triple bonds (e.g.: aromatic compds, alkenes, alkynes, carbonyl compds such as aldehydes & ketones, etc., undergo $\pi \rightarrow \pi^*$ transition).

In simple alkenes, the lowest energy transition is the $\pi - \pi^*$ transition and an absorption band at about 170-190 nm in unconjugated alkenes; is due to this transition Ethene absorbs at about 165 nm. It is due to this transition. Ethene linkage produces a bathochromic shift. Introduction of alkyl gp. to olefinic linkage produces a bathochromic shift.

higher

 $T > D > 1$

first

d σ

- Ct

 $= >$

our

1. $n \rightarrow \pi^*$ transitions: Bands attributed to $n \rightarrow \pi^*$ transitions are known as R-bands. In this an e^- of unpaired σ pair on a hetero atom such as oxygen, nitrogen or sulphur is excited to π^* antibonding orbital. This transition involves least amount of energy among all. The transitions and hence the transition gives rise to an absorption band at longer λ . The $n \rightarrow \pi^*$ transitions exhibit a weak band in IR absorption spectrum. In saturated ketones, e.g.: the $n \rightarrow \pi^*$ transition around 280 nm is the lowest-energy transition. This is forbidden by symmetry consideration. Saturated aldehydes & ketones exhibit an absorption of low intensity around 285 nm because of $n \rightarrow \pi^*$ transition.

Solvent and Structural influence on absorption maxima (λ_{max})

1. Nature of chromophore
2. Presence of autochrome
3. Conjugation of chromophore
4. Nature of solvent
5. Nature of substituents
6. Steric factors

i. Nature of chromophore

Dane \approx λ_{max}
217 nm

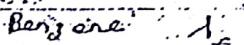
Carbonyl, C=O $188 \text{ nm } (\pi-\pi^*)$

$229 \text{ nm } (n-\pi^*)$



$231 \text{ nm } (\pi-\pi^*)$

$335 \text{ nm } (n-\pi^*)$



180 nm

204 nm

255 nm

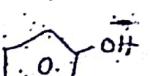
Depending upon the nature of the chromophore, the λ_{max} varies.

2. Presence of autochrome

Presence of autochrome enhances absorption wavelength (λ_{max})



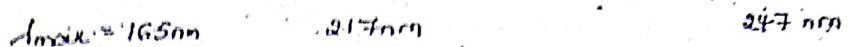
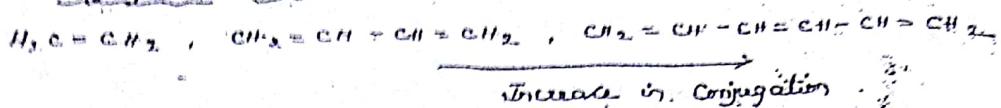
$\lambda = 255 \text{ nm}$



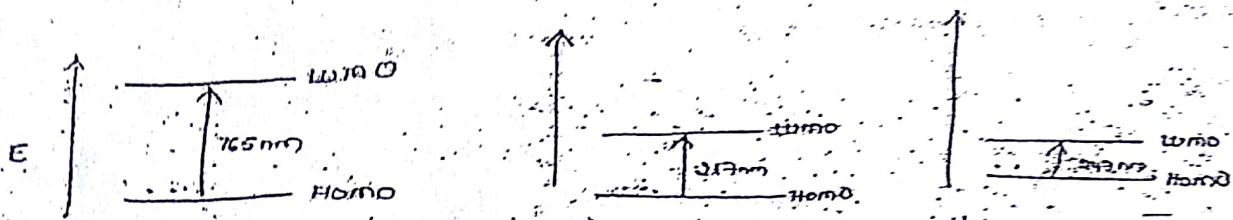
$\lambda = 287 \text{ nm}$

Change in λ_{max} due to the presence of off to diaryl chromophore.
In aromatic am chromophore shifts the $\pi-\pi^*$ band
to red shift.

Effect of chromophore



↑ in Conjugation increases the absorption wavelength (λ_{max}).
This is explained as - follow -
↑ in Conjugation ↓'s the HOMO-LUMO gap which increases λ_{max} .



Nature of solvent

Ex: Crotonaldehyde

	$\lambda_{\pi-\pi^*}$	$\lambda_{\pi-\pi^*}$
Isooctane	214 nm	329 nm
EtOH	220 nm	322 nm

From the above data, we can say that there is effect of solvent on λ_{max} .

In polar solvent, due to H-bonding $n-\pi^*$ energy gap ↑'s, absorption wavelength is small — Hypsochromic shift.

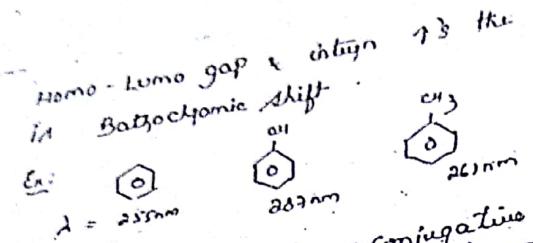
In polar solvents, $\pi-\pi^*$ energy gap ↓'s due to interaction between π^* & polar solvent, λ_{max} ↑'s — bathochromic shift.

Nature of substituents

→ Hyperconjugative substituents. Ex: $-R$.

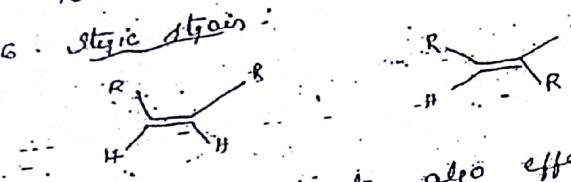
→ presence of hyperconjugative gss on chromophore it's the

www.android.universityupdates.in / www.universityupdates.in / www.ios.universityupdates.in



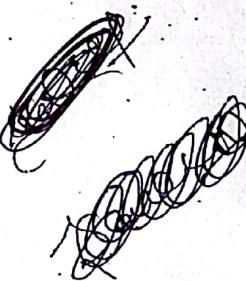
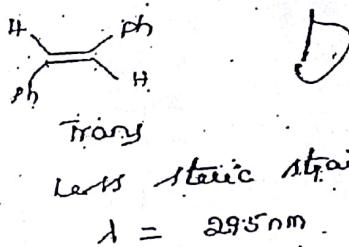
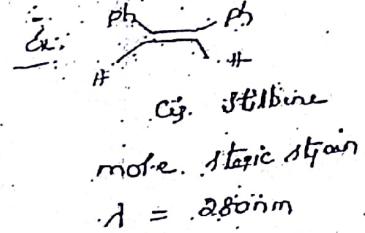
Influence of hyperconjugative groups on absorption compared to aurochromic groups

6. Steric strain:



Steric strain in a molecule also affects the absorption. Isomers which are having steric crowding shows peak at smaller absorption wavelength while isomers which is free from steric crowding shows peak at higher max.

Steric strain & the Homo-Lumo gap



In general trans isomers show more than cis isomers.

- In general, polar solvents tend to shift the position of the bands & diminish the vibrational structure of bands. Non polar solvents produce little change in the bands compared to the gas phase spectra.
- The vibrational structure of $n \rightarrow \pi^*$ bands is completely blurred in polar solvents.
- The vibrational structure of $\pi - \pi^*$ bands is retained even in polar solvents.

Benzene and its derivatives

benzene gives 3 absorption bands in the UV region. These bands occur at 184nm ($\epsilon_{max} 60,000$) 204nm ($\epsilon_{max} 7100$) 254nm ($\epsilon_{max} 204$). The de absorptions are seen in hexane solution.

is occur due to $\pi \rightarrow \pi^*$ transitions.

band occurring at 184nm is due to symmetry allowed.

the band at 204nm is the result of forbidden transition.

" symmetrical benzene molecule "

→ Benzene absorbs strongly at 184nm & weakly at 254nm in cyclohexane. The band at 204nm is very broad absorption band occurring from $260 - 270\text{nm}$ & consists of a series of multiple peaks or fine structure.

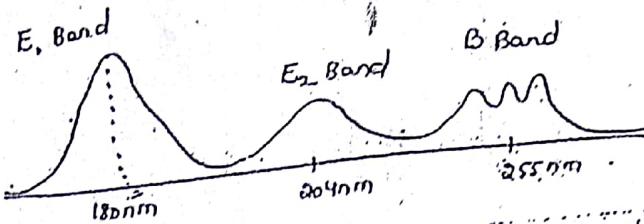
→ The multiple peaks or fine structure are the result of the vibrational subbands and their influence on electronic transitions. ($\pi \rightarrow \pi^*$).

→ Substitution of an alkyl group on the benzene ring shifts the absorption and to longer wavelength due to hyperconjugation.

→ Substitution is supposed to polarize the benzene ring both by resonance & inductive effect.

→ A substituent with +ve inductive effect lowers the ionization energy of the substituted benzene, while one with -ve inductive effect raises it.

→ E₁, E₂, B bands are possible bands for Benzene chromophore.



$$\epsilon_{max(E_1)} > \epsilon_{max(E_2)} > \epsilon_{max(B)}$$

E₁ = allowed band.

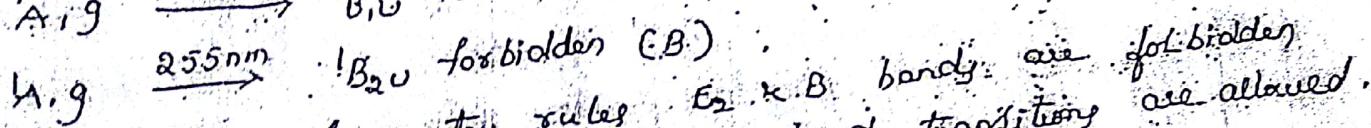
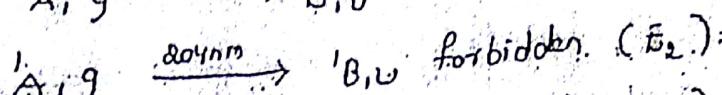
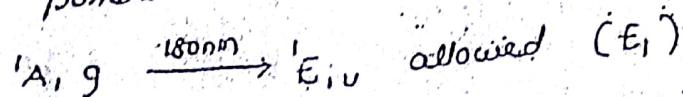
E₂ & B = forbidden band.

The fine splitting of B band is due to resolution of various vibrational transitions.

Vibrational transitions are characteristic band of aromatic chromophores.

B band is highly characteristic band of aromatic chromophores. B band is highly characteristic band of aromatic chromophores. B band is highly characteristic band of aromatic chromophores. B band is highly characteristic band of aromatic chromophores.

The possible electronic transitions in benzene w.r.t. Group theory rotation.



According to symmetry rules E₂ & B bands are forbidden. E₁ band transitions are allowed & appears with low intensity.

→ The vibrational fine splitting is due to the transitions among the vibrational levels.

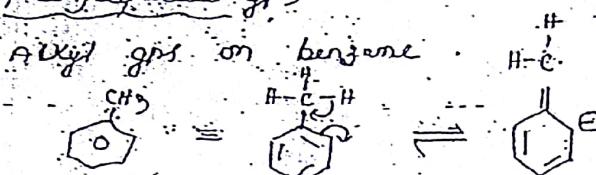
Substituent effects on Aromatic chromophore

Hückel Conjugative grp -

Auxochromic grp -

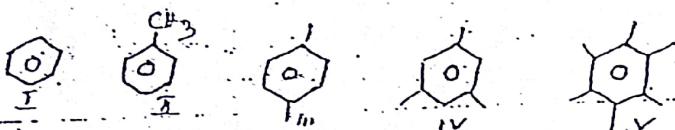
Chromophoric grp -

Hückel Conjugative grp



Hückel conjugative grp on aromatic chromophore grp shifts the σ-ν bands towards higher wavelength but the shift in band is very less bcoz the Hückel conjugative grp are less effective.

Influence of alkyl grp on E₁ bond is almost neglected, mainly E₂ & B bands are effected.



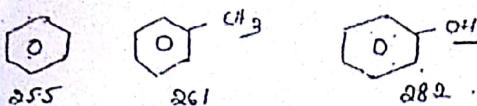
$$\lambda_1 < \lambda_2 < \lambda_3 < \lambda_4 < \lambda_5$$

with π in alkyl grp, the absorption wavelength increases.

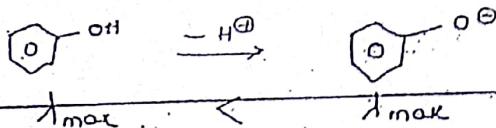
2. Auxochromic grp



The auxochromic grp are more efficient in e⁻ transfer when compared to Hückel conjugative grp. The energy gap between Homo & Lumo is smaller. Strong bathochromic shift of E₂ & B bands are observed when compared to hypsochromic group shift in absorption wavelength.



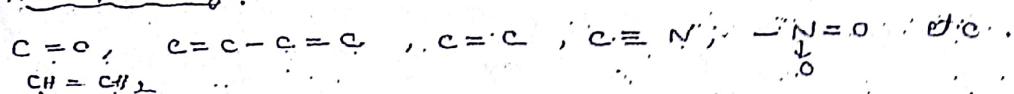
Longer absorption wavelength of phenol of aromatic gp is due to the presence of efficient auxochromic gp.



Due to strong π -donating character, the absorption λ_{max} of phenoxy ion is more than phenol.

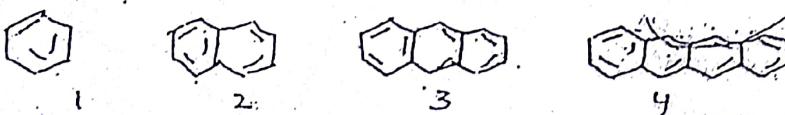
Dissolving phenol in alkali, the bathochromic shift is observed due to formation of phenoxy.

chromophoric grps



→ presence of chromophoric grps. on aromatic skeleton increases conjugation in ligand decreases energy gaps & result is \uparrow in λ_{max} . As a result, shift in bands & Bathochromic shift.

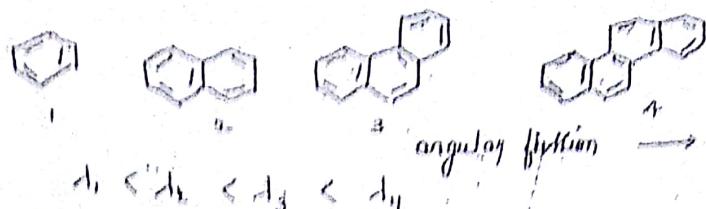
Benzene & its derivative & polycyclic aromatics



$$\lambda_{\text{max}} = \lambda_1 < \lambda_2 < \lambda_3 < \lambda_4$$

Linear fusing of aromatic rings is called acenes. In acenes, with \uparrow in no. of benzene rings $\lambda_{\text{max}} \uparrow$, due to \uparrow in conjugation or delocalisation of π system, shift in bands in bathochromic.

In these systems E_{g} & B bands appear with fine splitting. In E_{g} & B bands strong bathochromic shift is observed in E_{g} than B band.



Compared to linear ring system, the increase in area is small.

b) Carter of angular ring fission:

Angularly fused polycyclic aromatic, called phrenes".

The decrease in Area, μm^2 , benzene, using fission in phrenes is smaller compared to acenes.

→ In phrenes UV-vis spectrum $\pi \rightarrow \pi^*$ bonds are slightly overlapping & makes the absorption complex. ∴ very difficult to predict Area of $\pi\pi^*$ bands.

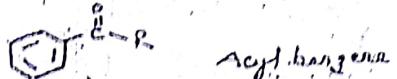
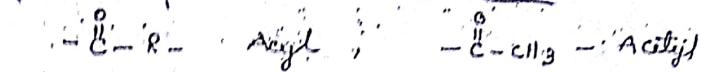
Compound A_E A_{E_2} A_B

Benzene 1.180 2.04 2.55

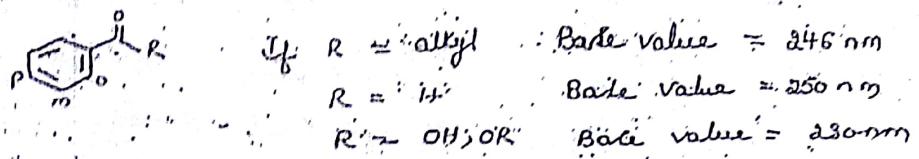
Naphthalene 2.41 2.86 315nm

Anthracene 3.56 3.75 $E_{\pi\pi^*}$ are merged

Scott's Rule for acyl Benzenes



By applying Scott's rule: The Area of $\pi\pi^*$ bond is predicted for acyl benzenes.



Substitution ortho meta para

Alkyl 3 3 10

$\text{OH} ; \text{OR}$ 7 7 25

Cl 0 0 10

Br 2 2 15

$-\text{O}^\ominus$ 11 20 18

NH_2 13 13 58

$>\text{N}-$ 20 20 85



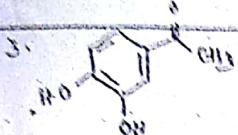
Basic value = 246 nm

Acet = 246 nm



Basic value = 246 nm

O = OR = 246 nm



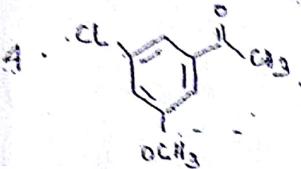
m-OH = 246

p-OH = 25

238 nm

O-alkyl = 246 nm

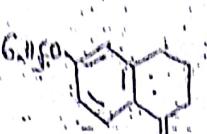
246 nm

249 nm

m-Cl = 246

m-OCH₃ = 25

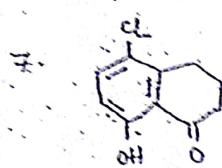
m-Cl = 253 nm

238 nm

246 nm

J. O-alkyl = 25

P-OR = 253 nm

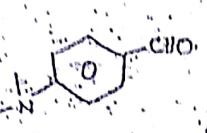
239 nm

246 nm

O-OH = 25

O-alkyl = 25

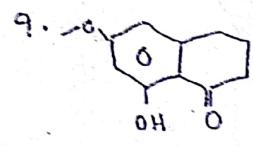
m-Cl = 256

238 nm

246 nm

J. O-alkyl = 25

P-OR = 253 nm

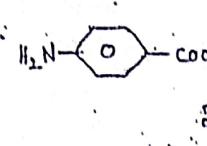
239 nm

246 nm

O-OH = 25

O-alkyl = 25

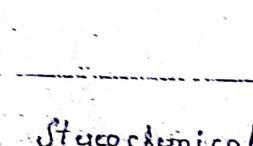
P-OR = 256

238 nm

250 nm

R-NH₂ = 25

235 nm

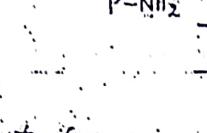
233.5 nm

246 nm

O-OH = 25

O-alkyl = 25

P-OR = 256

238 nm

230 nm

P-NH₂ = 58

288 nm

233.5 nm

Stycochemical factors in electronic spectroscopy:

1. Styic hindrance:

Styic outer crowding distorts the geometry of the chromophore.

Third conjugation is reduced by reduction in π -orbital overlap etc.

Biphenyl & Substituted Biphenyls:

When the biphenyls are in plane then free delocalisation of π system takes place, and effective resonance is J_{eff} , small Homoo-Lumo gap, & large ΔE_{max} .



Planar bond

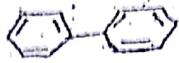


In plane

Phenyl is out of plane arrangement strained delocalization of

It attain a large gap & smaller strain is observed.
In the substituents are at ortho position of phenyl, biphenyl
is formed. That means two phenyls are almost 90° to
each other in separation.

With the bulkiness of the substituents preference of 1° arrangement
is more. Steric crowding is increasing & strain is decreasing.
Due to deviation from planarity.



perpendicularity

Biphenyl has $\lambda_{max} = 248\text{nm}$

Both cis and trans isomers are considered; trans isomer shows
high strain than cis isomer, becoz in trans form, effective π -orbital
overlap is less, so change in strain is observed.

(a) $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH}_2 - \text{C}_6\text{H}_5$

$\text{HOOC} - \text{C}_6\text{H}_4 - \text{CH}_2 - \text{CH}_2 - \text{C}_6\text{H}_4 - \text{COOH}$

cis. $\lambda_{max} = 262\text{nm}$

$\text{Et}_2\text{C} = \text{C}^{\prime\prime}$

$\text{H} - \text{C}^{\prime\prime} - \text{COOH}$

Trans. $\lambda_{max} = 272\text{nm}$

Due to greater crowding in the cis form the geometry of the
allene chromophore is disturbed.

Angular Distortion & Cross Configuration

The Woodward rules for Conjugate dienes & Carbonyl Compds
give reliable results only when there is absence of strain
around the chromophore.

Chromophore distortion may occur by ring strain or by
the introduction of additional conjugation other than at the
end of chromophore (cross conjugation).



For this structure expected $\lambda_{max} = 237\text{nm}$, but distortion of chromophore

try it to absorb at 220nm.

⑧

Ans:  strain in the molecule.

$\lambda_{\text{max}} = 234 \text{ nm}$, $\lambda_{\text{obs}} = 220 \text{ nm}$, 14 unit difference.
So not accepted.

g.c. strain:

deviation of angle is angle strain.

Ex:



Cyclopropane

$$109.28 - 60 = 48.2^\circ$$



Cyclopentane

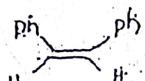


Cyclobutane

ii - Trans isomerism:

Since geometrical isomers differ in the spatial arrangement of groups about a plane, the λ_{max} will be different. The trans isomers about a plane, the λ_{max} will be different. The trans isomers are normally more elongated than the cis isomers. So the trans isomers are more for trans than cis form. Steric effects are also considered and based on that also trans form have more λ_{max} .

Ex: 1. Cis 1,4-butadiene



$\lambda_{\text{max}} 280 \text{ nm}$

Trans stilbene



290 nm

2. Cis acrylic acid

Trans acrylic acid

Application of electronic spectra of Metal Complexes: = d-d transition

Spectra of first row transition metal aqua complexes.

The electronic spectra of transition metal complexes is generally due to promotion of a d-orbital ϵ to another d-orbital. These transitions are known as d-d transitions.

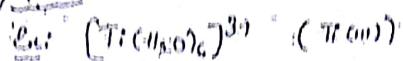
Quantum mechanically these transitions are forbidden, however experimentally we observe these transitions due to the mixing of vibrational energy levels & hence known as vibrationally coupled electronic transitions.

Complete
d band
sym

Spectra of first-row transition metal aqua-complexes

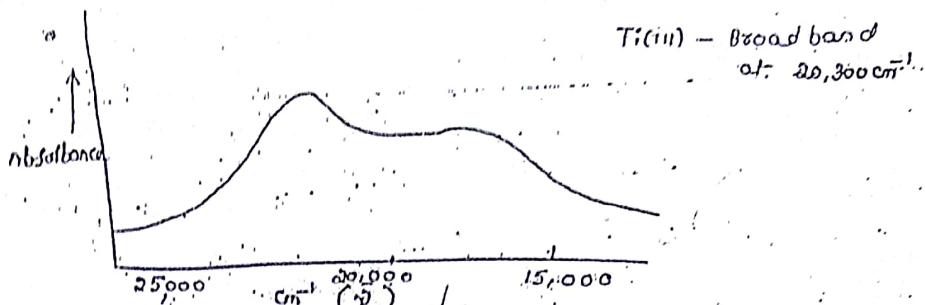
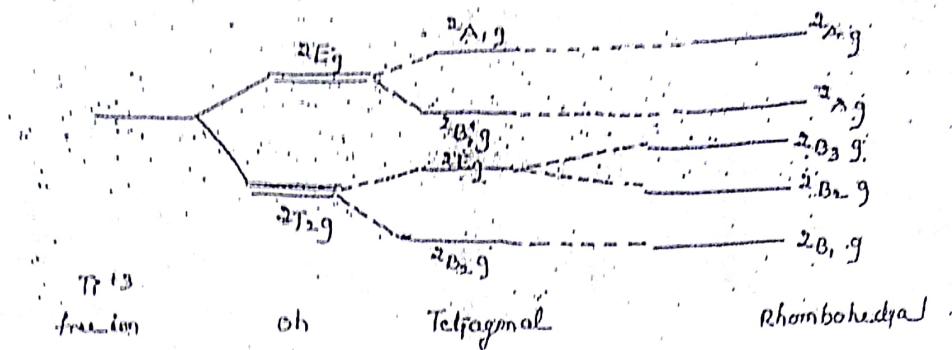
The electronic spectra of transition metal complexes of first row transition metals can be discussed in terms of d-orbital splitting when ligands approach towards the central metal ion due to electrostatic repulsion energy the d-orbital will split into two levels.

d¹ Configuration



The ground state of Ti^{3+} is t^2g^3 .

The ground state of Ti^{3+} is t^2g^3 . When one e⁻ is promoted to eg orbital it is $t^2g^2e_g^1$. When the symbol t^2g is written before e_g orbital it is represented as $t^2g^1e_g^1$ by writing the symbol t^2g before e_g orbital. Thus the electronic transition in Ti^{3+} is represented by $t^2g \rightarrow t^2g$ except one electron.



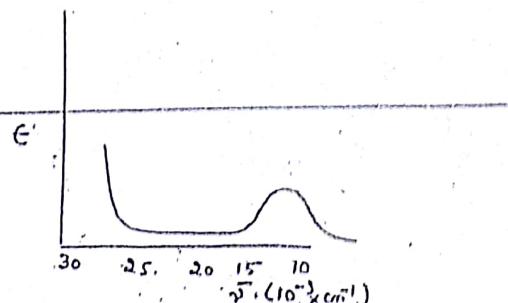
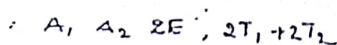
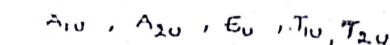
The electronic absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

d⁹ : Ex: Cu(II)

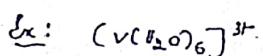
The 6-coordination Cu^{+2} (d^9) complexes are very sensitive to Jahn-Teller effect i.e. undergo distortion from regular oh geometry to tetragonal type. An absorption band is due to $t^2g \rightarrow t^2g$.

Complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ has a pale blue colour & exhibits a odd band with peak at $9,400 \text{ cm}^{-1}$ & $10,600 \text{ cm}^{-1}$. (9)

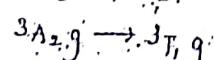
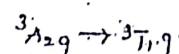
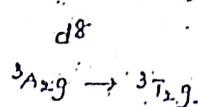
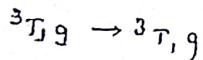
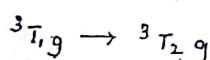
Term symbol is 2D



$\sim v^{+3}$) and d^8 $[(\text{Ni}(\text{H}_2\text{O})_6)]^{2+}$



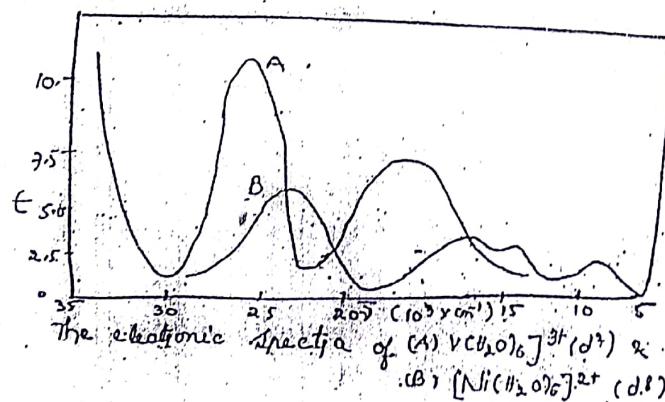
Both d^2 & d^8 exhibit spin allowed bands.



$\text{V}^{(3+)}$ exhibit bands at $17,800 \text{ cm}^{-1}$ & $25,700 \text{ cm}^{-1}$. The first band is due to $^3T_1, g \rightarrow ^3T_2, g$ transition.

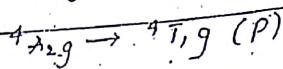
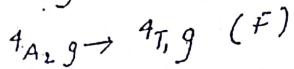
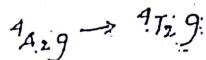
The ground state term of $\text{V}^{(3+)}$ is 3F & excited states are 1D , 3P , 1S , 1S . The 3F term splits into above transitions of energies.

Green Coloured (Ni^{2+}) aquo complexes give the bands at following position 8700 cm^{-1} , $14,500 \text{ cm}^{-1}$ & $25,300 \text{ cm}^{-1}$.



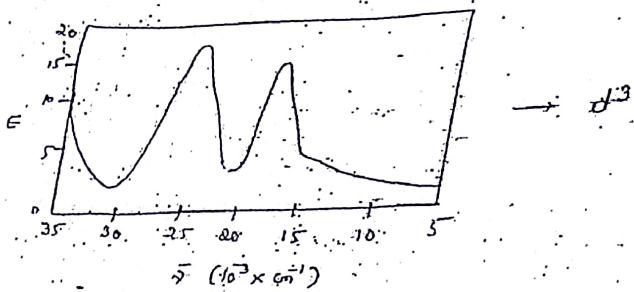
$d^3 \times d^7$ Ex: $\text{Cr}(\text{III})$ i.e. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ for d^3

The d^3 oh transitions are



The bands are at $17,400 \text{ cm}^{-1}$, $24,600 \text{ cm}^{-1}$ & the 3rd weak bc at $37,800 \text{ cm}^{-1}$.

The ground state is $4F$ & the excited states are $4P$, $2G$, $2F$.



$\text{Co}(\text{II})$ for d^7 system.

$4T_{1g}$ (of $4F$) ground state in octahedral stereochemistry can be considered. A large no: of $\text{Co}(\text{II})$ oh complexes are known. In this case electronic spectra is not straight forward, due to the occurrence of a multiple band pattern where a band due to $4T_{1g} \rightarrow 4T_{1g} (\text{P})$ transition would normally occur. The multiplicity of bands may be due to other terms.

$\text{Co}(\text{II})$ gives bands at $8,000 \text{ cm}^{-1}$ $4T_{2g} (\text{F}) \leftarrow 4T_{1g} (\text{F})$

$19,600 \text{ cm}^{-1}$

$4A_{2g} (\text{F}) \leftarrow 4T_{1g} (\text{F})$

$21,600 \text{ cm}^{-1}$

$4T_{1g} (\text{P}) \leftarrow 4T_{1g} (\text{F})$

$14,500 \text{ cm}^{-1}$

$3T_{1g} (\text{F}) \leftarrow 4T_{1g} (\text{F})$

$23,300 \text{ cm}^{-1}$

$3T_{1g} (\text{P}) \leftarrow 3A_{2g} (\text{F})$

$3T_{1g} (\text{P}) \leftarrow 3A_{2g} (\text{F})$

①

Electronic spectra of metal complexes:-

Ex:- Hexa aquo metal complexes:

~~1) d⁷ complex: ex: $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$~~

Valence e⁻ configuration of $\text{Ti(OH}_2\text{)}_6$ state = $d^2 s^2$

Ti ion in +3 state = d^1

The term symbol for d^1 configuration is,

+2	+1	0	-1	-2
1				

$L = 2, \therefore$ Term symbol is = D

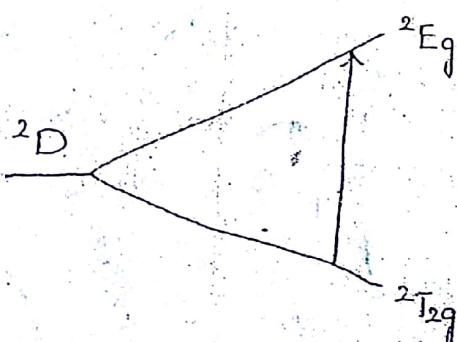
$L = 0 \ 1 \ 2 \ 3 \ 4$
Term = S P D F G

The general symbol for Term is " $_{2s+1}^L$ "

where, $2s+1$ is multiplicity. $2s+1 = 2 \times \frac{1}{2} + 1 = 2$.

∴ Term is 2D

The term D is splitted in to two energy levels, same as in case of d-orbital splitting.



The transition is from $^2T_{2g} \rightarrow ^2E_g$.