

# UNIT-1: MOLECULAR STRUCTURE AND THEORIES OF BONDING

## \* VALENCE BOND THEORY

This theory was given by Hietler and London in 1927. Then further extended by Slater and Pauling.

### POSTULATES OF VALENCE BOND THEORY :

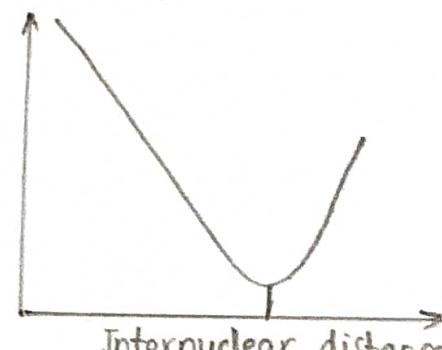
1. Atoms unite or combine to form molecule and retain their identity.
2. The atomic orbitals with unpaired electron overlap and the spin of two electrons get mutually neutralised resulting in the formation of coherant bond. covalent bond.
3. If the atomic orbitals poses more than one unpaired electron, then more than one bond can be formed.
4. Electrons which are already paired in the valency shell, do not participate in the formation of bond.
5. The strength of the covalent bond depends on the strength which two combining atomic orbital overlap in space.
6. The strength of overlap of two atomic orbitals is represented by wave weight function  $\Psi_A$  and  $\Psi_B$  where A and B are respective atoms.
7. It is expressed quantitatively by S.

$$S = \int \Psi_A \Psi_B dV$$

when  $S > 0$ , bond is formed.

$S < 0$ , repulsion between nuclei.

$S = 0$



8. The overlapping atomic orbitals may differ. The two types of overlapping orbitals are ' $\Sigma$ ' and ' $\Pi$ '. (sigma and pi).

### LIMITATIONS OF VALENCE BAND THEORY:

1. It considers only the outermost orbitals of an atom to take part in the formation of bond.
2. The theory cannot explain paramagnetic nature of oxygen molecule.

3. It cannot explain the electronic spectra of the molecule  $\text{H}_2\text{Mg}$ .

### \* MOLECULAR ORBITAL THEORY: WAVELET AND ENERGY LEVELS

1. The theory was proposed by Hund and Mulliken to explain the bonding in molecules.

2. Molecule is considered as group of nuclei containing orbitals.

The electrons of the atoms are not confined to individual atoms but treated as a whole molecule.

3. All the electrons are distributed around the single nucleus in different energy levels. They are called atomic orbitals and they are monocentric.

4. When the electrons are distributed around the group of nuclei in different energy levels. They are called molecular orbitals and they are polycentric.

5. Each orbital in the molecule described by a wave function. The value of wave function obtained by linear combination of atomic orbital.

6. Each molecular orbital contains definite amount of energy. It can be calculated by applying Schrodinger Wave Equation.

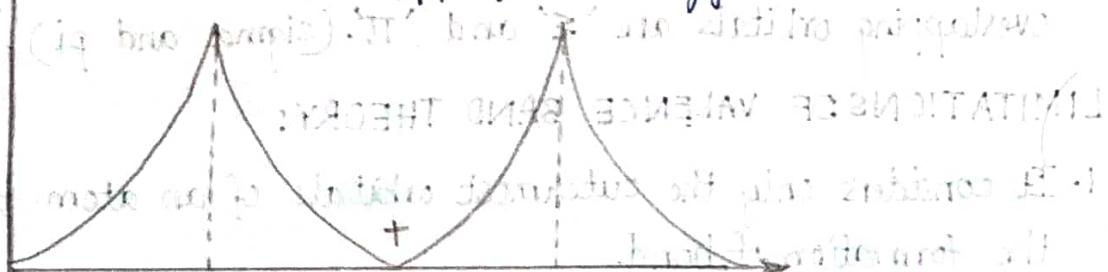
7. The size, shape and energy of molecular orbital depends upon that of corresponding atomic orbital.

8. The electrons are filled in the molecular orbital, by the rule suggested by Aufbau, Hunds and Pauli's.

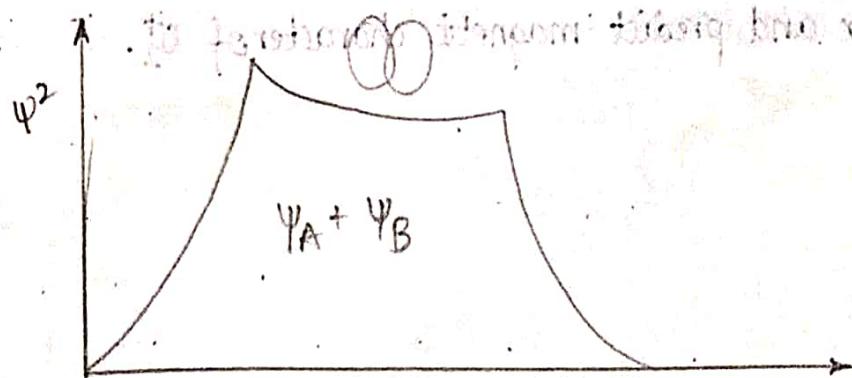
9. Atomic orbitals with same symmetry and comparable energy may combine to form molecular orbital.

BMO:

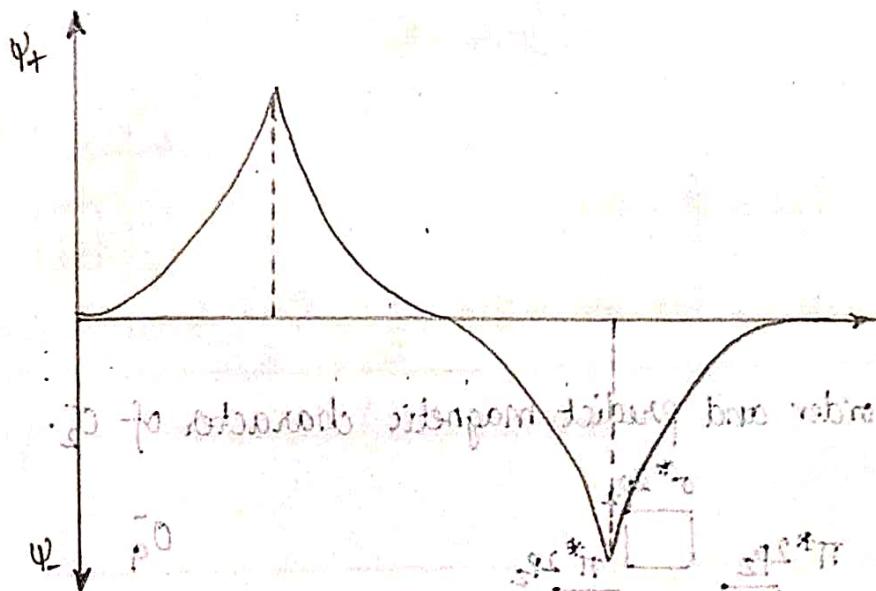
constructive overlapping (low energy)



When two atomic orbitals overlap, they form a bonding molecular orbital.



ABMO:



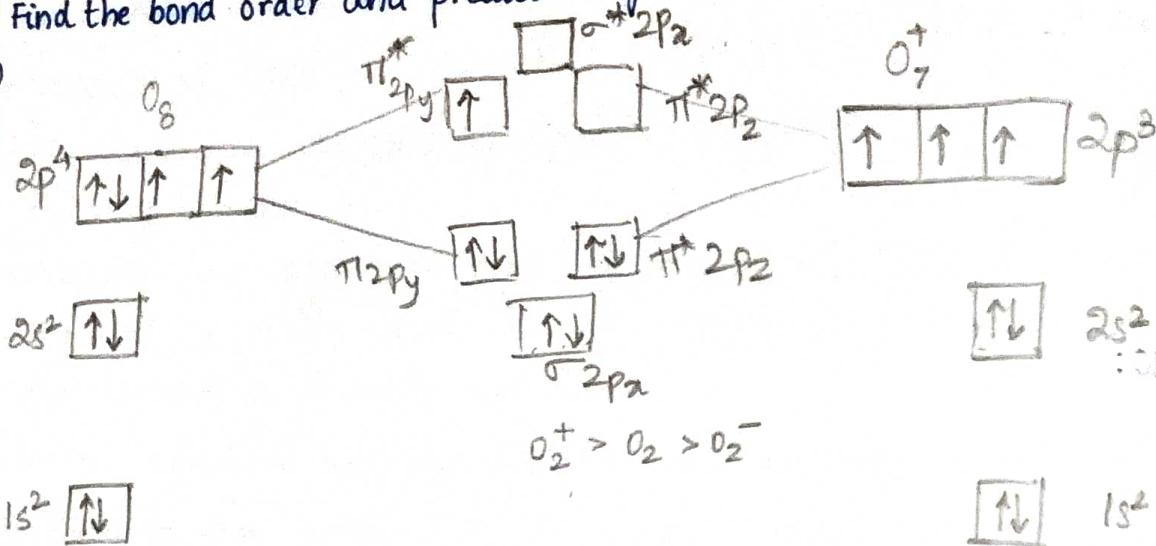
#### \* Rules of LCAO: (Linear Combination of Atomic Orbital)

- ① The combining orbitals must have roughly same energy.
- ② The orbitals must overlap as much as possible. This is done only when the atoms are close enough and radial distribution of 2 atoms are similar.
- ③ In order to produce bonding and antibonding molecular orbitals, either the symmetry of 2 atomic orbitals must remain unchanged when rotated about the internuclear axis, or both atomic orbitals should change symmetry in identical manner.
- ④ Aufbau Principle is used to fill the atomic orbitals with lowest energy. Each orbital may get maximum of two electrons.
- ⑤ Hund's rule and Pauli's rule must be followed in filling of the atomic orbitals.

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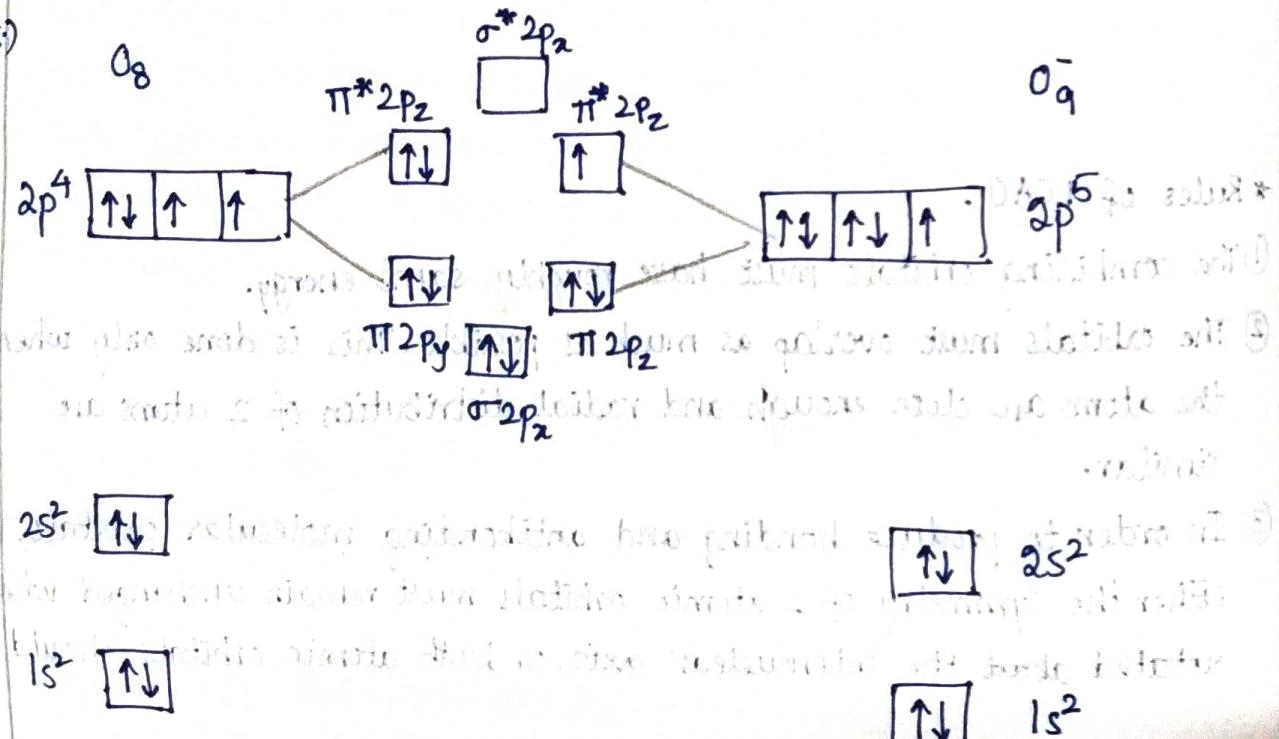
1Q. Find the bond order and predict magnetic character of  $O_2^+$ .

Ans)



2Q. Find the bond order and predict magnetic character of  $O_2^-$ .

Ans)

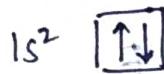
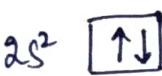
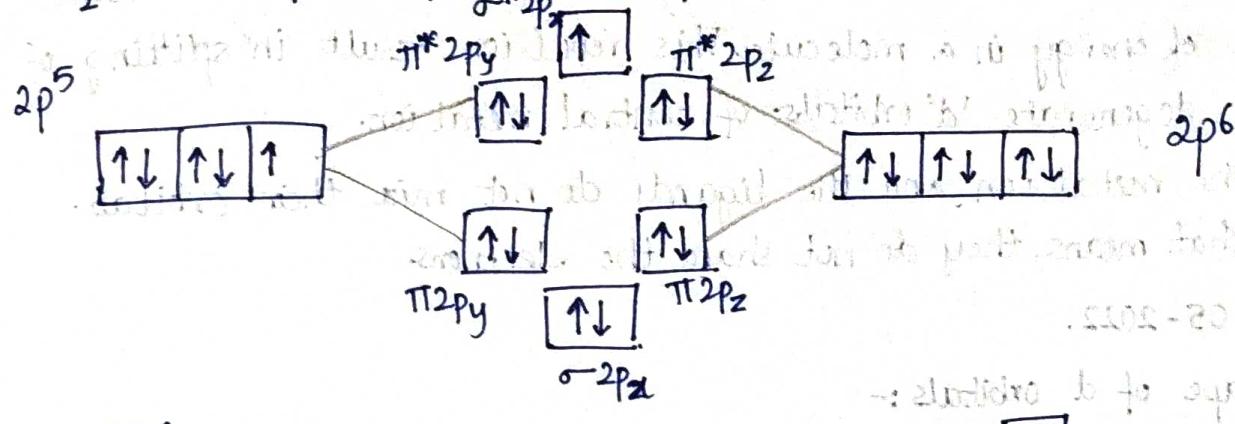


$$\text{Bond Order} = \frac{6 - 3}{2} = \frac{3}{2} = 1.5$$

Magnetic Character = Paramagnetic

36. Find the bond order and predict magnetic character of  $F_2^-$ .

$$\text{Ans: } F_2 = \cancel{1s^2} \cancel{2s^2} \cancel{2p^6} \cancel{3s^2} \cancel{3p^6} \cancel{4s^1} \cancel{1s^2} \cancel{2s^2} \cancel{2p^5}$$



$$\text{Bond Order} = \frac{6-5}{2} = \frac{1}{2} = 0.5$$

Magnetic Character = Paramagnetic.



## \* CRYSTAL FIELD THEORY :-

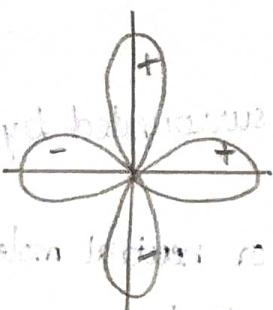
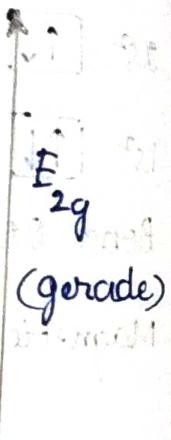
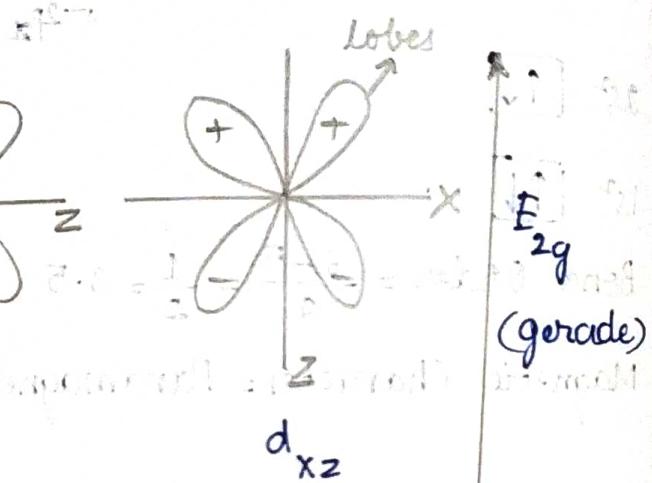
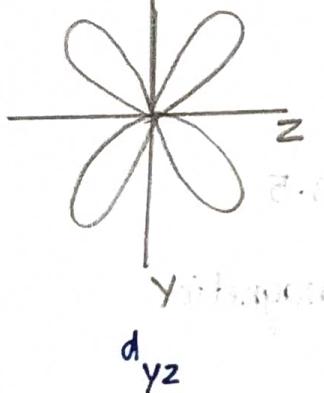
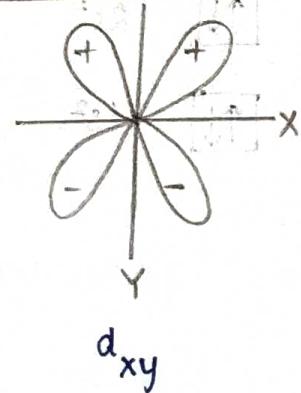
- ① Any complex is a combination of central metal surrounded by ligands or molecules.
- ② Ligands can be either negatively charged ions or neutral molecule. Hence, they are considered as point charges or point dipole.
- ③ If the ligands are negatively charged, they approach closer to the central metal ion with negative charge dipole.
- ④ If the ligands are neutral molecules, they approach closer to the central metal ion with dipole.
- ⑤ CFT considered electrostatic induction interaction between metal and ligands. These interactions are
  - a) an electrostatic interaction between the nucleus and negatively charged ions that affects in overall decrease of energy in the molecule. It leads to purely ionic bond between the central metal ion and ligand.

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- (b) an electrostatic repulsion between the valency shell of an electron of a metal and ligands causes overall increase of energy in a molecule. This repulsion result in splitting of degenerate 'd' orbitals of central metal ion.
- ⑥ The metal ion and the ligands do not mix their orbitals. That means, they do not share the electrons.

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\* Shape of d orbitals:-



### SPLITTING IN OCTAHEDRAL COMPLEXES:

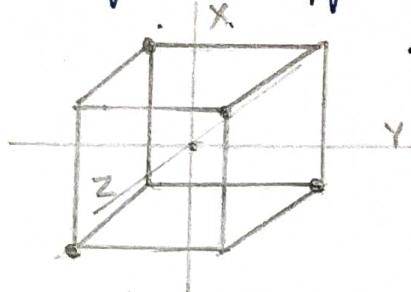
- In the octahedral complex, metal is at the centre of the complex and the ligands are at the corners.
- The direction of x, y, and z point to three adjacent corners of the octahedron.
- The lobes of  $E_g$  orbitals ( $d_{x^2-y^2}$  and  $d_{z^2}$ ) points along the axes x, y and z.
- The lobes of  $E_g$  orbitals points in between the axes. It follows that the approach of 6 ligands along x, y, z, -x, -y, -z, this direction will

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increase the energy.

SPLITTING IN TETRAHEDRAL COMPLEXES :- (always high spin)

A regular tetrahedron is a cube. One atom is at the centre of the cube and 4 ligands occupy 4 corners of the cube alternatively.



- The direction of x, y, and z point to the center of the faces of the cube. The  $E_g$  orbital points along x, y and z. The  $E_{2g}$  orbitals point between x, y and z.

- The direction of approach does not co-incide exactly with either  $E_g$  or  $E_{2g}$  orbital.
- The angle between  $E_g$  orbital, central metal ion and ligand is  $54^\circ 44'$ .
- The angle between  $E_{2g}$  orbital, central metal ion and ligand is  $35^\circ 16'$ .
- Thus the  $E_{2g}$  orbitals are nearer to the ligands than the  $E_g$  orbital.
- The approach of the ligand raises the energy of both the sets of orbitals.
- The energy of  $E_{2g}$  orbitals raise the most because they are more near.

FACTORS OF  $\Delta_t = \frac{4}{9} \Delta_0$  :-

① The ligand field strength is 4 in case of tetrahedron whereas it is 6 in case of octahedron.

② The direction of the orbital does not co-incide with the direction of the ligands. This further reduces, the splitting by  $\frac{2}{3} \Delta_0$ .

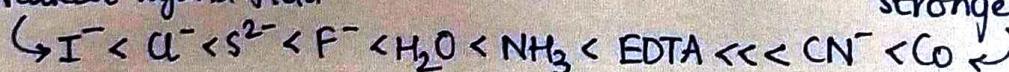
$$\Delta_t = \frac{2}{3} \times \frac{2}{3} \Delta_0$$

$$= \frac{4}{9} \Delta_0 = 0.45 \Delta_0$$

$\therefore \Delta_t$  is very very small, the complex will always have a high spin.

ELECTROCHEMICAL SERIES :

Weakest ligand field



high spin

strongest ligand field

low spin

## UNIT-2 : WATER AND ITS TREATMENT

Hardness can be classified into two categories:

- i) carbonate / bicarbonate → temporary hardness.
- ii) Non-carbonate → hard water.

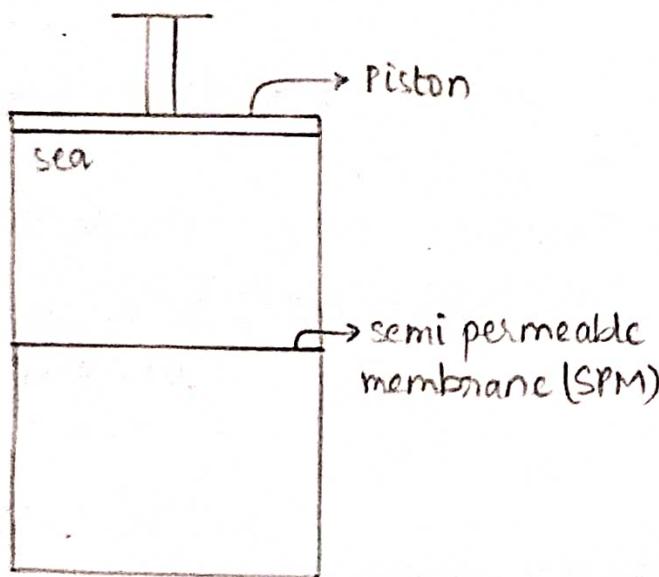
Purification method

**Ion Exchange Process / Demineralisation Process :**

Advantage:

Osmosis : It is the process when the flow of solvents moves from lower concentration side to higher concentration side.

If hydrostatic pressure in excess to the osmotic pressure is applied, the flow of solvent is reversed, i-e. solvent forced to flow from higher concentration side to lower concentration side.



Advantages: -

2. It removes colloidal silica that can't be removed by ~~conventional~~  
Ion Exchange Process.
3. The maintenance is entirely depends on the replacement of semi-permeable membrane.
4. The lifetime of semi-permeable membrane is quite high which is 2 years.
5. The replacement takes place within few minutes.

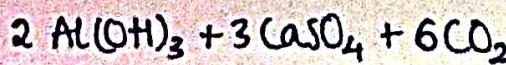
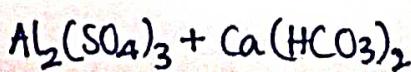
## \* Drinking Water / Municipal Water / Potable Water:

Drinking water must satisfy the following criteria:-

- 1) It should be sparkling clean.
- 2) pleasant in taste.
- 3) It should be perfectly cool.
- 4) Turbidity should be below 10 ppm.
- 5) Free from objectional gases such as  $H_2S$ .
- 6)  $Pb^{+2}$ ,  $As^{+2}$ ,  $Cu^{+2}$  for toxic. insoluble for availability of calcium sulphate.
- 7) Alkalinity should not be high.
- 8) pH should be close to 8.

## \* Purification :

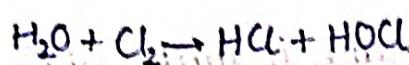
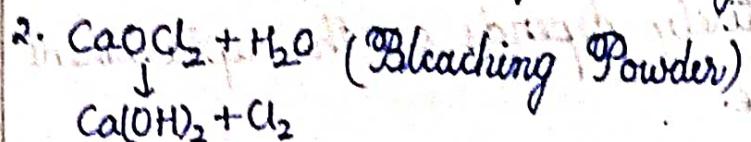
1. Screening: purifying and removing suspended impurities.
2. Sedimentation:
  - coagulant:
  - 1. Eg: Potash Alum ( $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ ) used when water is alkaline.
  - 2. Eg: Sodium Aluminate ( $NaAlO_2$ ) used when water is not alkaline.



## 3. Filtration :

## 4\* Removal of micro-organisation:

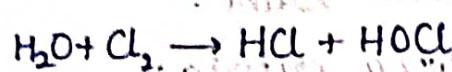
1. Removal as micro organism by boiling.



$\text{HOCl} + \text{Germs} \rightarrow \text{killed.}$

Hypochlorous acid Drawback: Water is somewhat harder.

3. Chlorination



Filtration

Germs + HOCl → Germs killed.

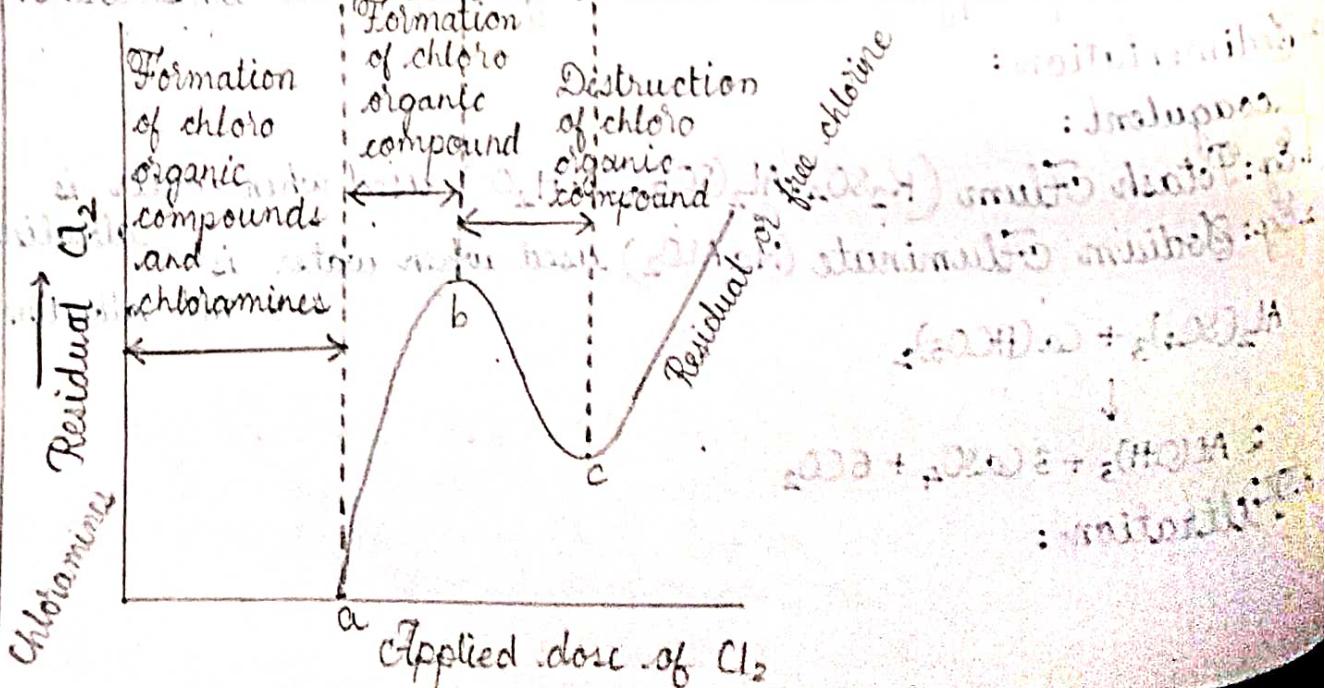
## 5\* Breakpoint of Chlorination:

(Free or residual  $\text{Cl}_2$ )

Involves in addition of sufficient amount of chlorine to oxidize  
① organic matter.

② reducing substance.

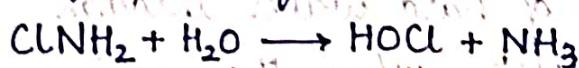
③ Free ammonia in raw water leaving water mainly with  $\text{Cl}_2$



- \* Advantages of break point of chlorination:
- It oxidises completely organic compound such as  $\text{NH}_3$ .
  - It removes colour from water due to presence of organic matter.
  - It destroys all disease producing bacteria.
  - It removes both taste and odour from water.
  - It prevents the formation of weeds in water.

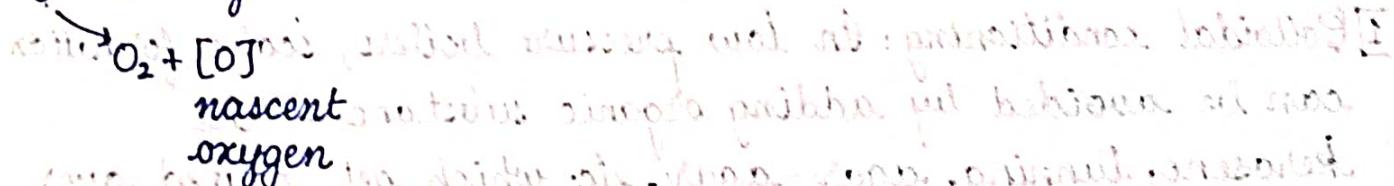
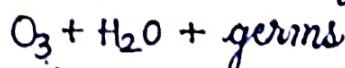
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- \* Disinfection by  $\text{ClNH}_2$  (chloramine):



**Chloramine**      **Germicide**  
                           (Hypochlorous acid)

Disinfectant = Ozone (a very unstable, light-blueish gas)



Internal treatment of boiler feed water

1. colloidal conditioning

2. phosphate conditioning

3. Calgon conditioning  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$

In weak-acid point of action for coagulation flow starts

to pH 7.0 to 7.5 aluminum silicate ions form

and iron hydroxide precipitate forms.

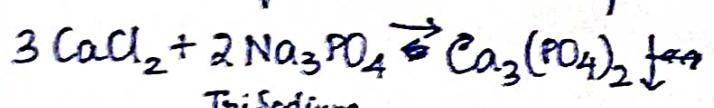


(hard water)

- \* Prevention of Scale Formation should be experimental.
- ① Internal treatment of water :-
 

In this process, water is prohibited original character by complexing or converting into more soluble salts by adding appropriate agents. An internal treatment is accomplished by adding proper chemical to the boiling water either

    - ② to precipitate the scale forming impurities in the form of sludges, which can be removed by the blow-down operation (it is partial removal of hard water through the top at the bottom of the boiler), when the exchange of hardness in the boiler becomes alarmingly high
    - ③ to convert them into compounds which will stay in dissolved form in water.
  - ② Colloidal conditioning : In low pressure boilers, scale formation can be avoided by adding organic substances like kerosene, tanning, agar-agar, etc. which get coated over the scale forming precipitates thereby yielding non-sticky and loose deposits which can be easily removed by blow-down operation.
  - ③ Phosphate conditioning : In high pressure boilers, scale formation can be avoided by addition of sodium phosphate, which reacts with hardness of water forming non-sticky or non-adherent and easily removable soft sludge of calcium and magnesium phosphate which can be removed by blow-down operation.

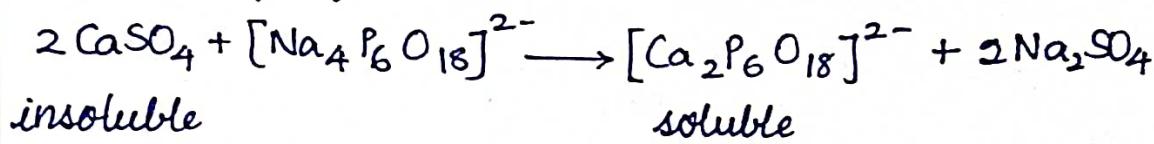


Tri Sodium  
Phosphate

+ 6 NaCl

$\Rightarrow \text{NaH}_2\text{PO}_4$  (acid)

3] Calgon conditioning : It involves addition of Sodium Hexa meta phosphate in boiling water which prevents scale and sludge formation and convert them into soluble complexes.



\* Hardness =  $\frac{\text{Amount of hardness causing } x \text{ substance}}{\text{Molecular weight of CaCO}_3 \text{ mole. of "x" weight}}$

Q. The analysis of water gives following results.

Sample 1 : 10 mg/L of calcium sulphate.

Ans.) Molecular weight of  $\text{CaSO}_4 = 40 + 32 + 4(16) = 40 + 32 + 64 = 136$

$$\text{Hardness} = \frac{10 \times \frac{100}{136}}{1000} = \frac{1000}{136} = 7.35 \text{ mg/L}$$

$$= 7.35 \text{ ppm}$$

$$= 735 \times 0.07^{\circ}\text{Cl}$$

$$= 735 \times 0.1^{\circ}\text{Fr}$$

\* ppm =  $\frac{1}{10^6}$

1 million =  $10^6$

Sample 2 contains 10 mg/L of magnesium bicarbonate.

Ans.) Molecular weight of  $\text{Mg}(\text{HCO}_3)_2 = 24 + 2(1) + 2(12) + 6(16)$   
 $= 24 + 2 + 24 + 96$   
 $= 146$

Hardness =

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Lab No 16-0

Sample 3 contains 10mg of  $MgSO_4$  in 10 ml of dilute HCl

After adding 10ml of dilute HCl, white precipitate of  $Mg(OH)_2$  is formed. This is washed with water and dried.

Weight of  $Mg(OH)_2$  = 0.01 g

Weight of  $Mg(OH)_2$  = 0.01 g  
Molar mass of  $Mg(OH)_2$  = 58.32 g/mol  
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Molar mass of  $Mg(OH)_2$  = 58.32 g/mol  
 $\frac{58.32}{58.32} \times 100 = 100\%$

100% = 100 mg of  $Mg(OH)_2$  = 100 mg of  $Mg(OH)_2$

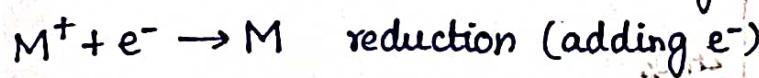
100 mg of  $Mg(OH)_2$  = 100 mg of  $Mg(OH)_2$

100 mg of  $Mg(OH)_2$  = 100 mg of  $Mg(OH)_2$   
 $(MgO) + (OH) + 2H + SO_4 = MgSO_4 + H_2O$

Molar mass of  $Mg(OH)_2$  = 58.32 g/mol

$$\frac{58.32}{58.32} \times 100 = 100\%$$

# UNIT-3: ELECTROCHEMISTRY



**ELECTROCHEMICAL CELL :** The device which converts electrical energy into chemical energy and vice versa is known as Electrochemical cell. Based on electron active energy. These devices are classified into 2 categories:-

1) Electrolytic cell.

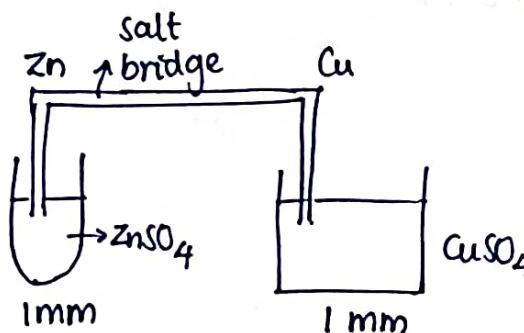
2) Galvanic Cell

Chemical cell  
Concentration cell

Voltaic Cell

1) Electrolytic Cell: The device in which chemical changes occur in presence of electricity or in presence of applied electrical energy are called electrolytic cell.

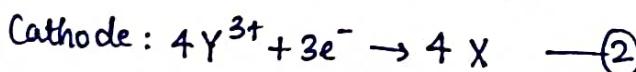
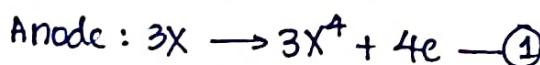
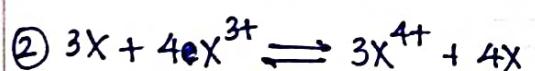
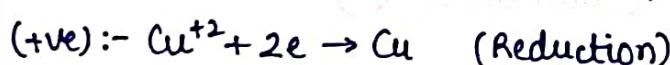
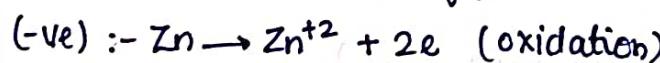
2) Galvanic Cell: The device in which electrical energy is generated on account of chemical reaction are called as galvanic cell.



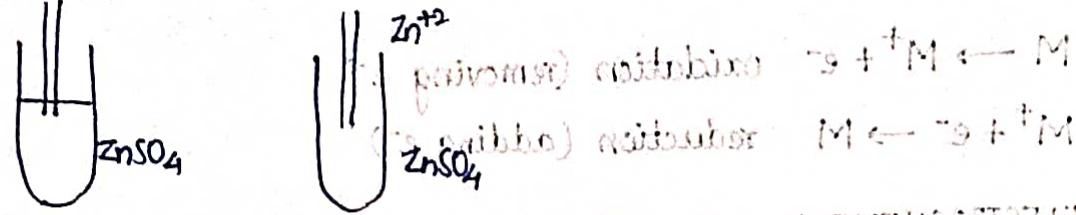
**Redox Reaction:** The reaction in which oxidation and reduction takes places.



Write the reaction taking place at anode and cathode.

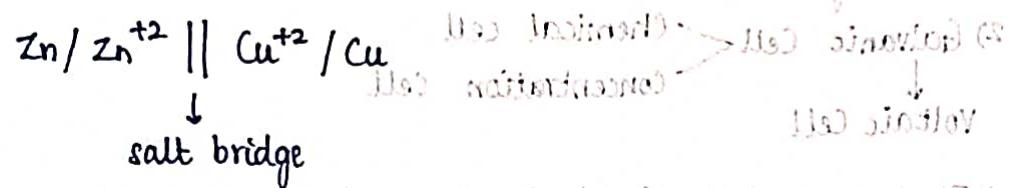


## ELECTROCHEMICAL CELL: E-TIVU



\* **discrete origin of Electrode Potential:**

$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$  } for calculations  
 $= E_{\text{cathode}} - E_{\text{anode}}$



**Standard  $E^{\circ} = 0.76$**

**Reduction Potential of  $\text{Zn}/\text{Zn}^{2+}$  is  $-0.76$ .**

Oxidation Potential of  $\text{Zn}/\text{Zn}^{2+}$  is  $+0.76$ .

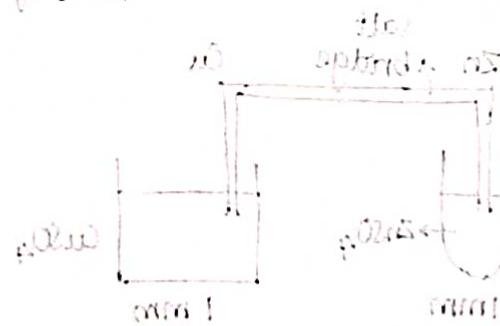
Increase in balancing of  $\text{Cu}^{2+}/\text{Cu}$  oxidation state in acidic salt :  $\text{H}_2\text{O}$  involved (2)

RP of  $\text{Cu}^{2+}/\text{Cu}$  is  $-0.34$ .  
 OP of  $\text{Cu}^{2+}/\text{Cu}$  is  $+0.34$ .

**Standard  $E^{\circ} = -0.76$**

$E_{\text{cell}} = 0.34 - (-0.76)$

$E_{\text{cell}} = 1.10 \text{ V}$



### \* NERNST EQUATION

It is a derivation of mathematical relationship between cell potential, concentration of solution and temperature.

For eg: For reduction reaction, the <sup>rn</sup> equation can be written as



Nernst Equation  $E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{\{M^t\}}{\{M^{nt}\}}$  (Addition of  $t$ )

where  $E$  = cell potential

$E^{\circ}$  = Standard electrode potential

$R$  = Gas Constant =  $8.314 \text{ J/Kmol}$

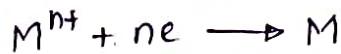
$n$  = number of electrons involved in reaction

$F$  = Faraday's constant (16500 C)

$\{M^{n+}\}$  = Concentration of electrolytic solution

$\{M\}$  = Activity of  $M\{1\}$  (Solid is 1).

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



For solid  $\Rightarrow |M| = 1$  and will be retained.

$$E = E^\circ - \frac{0.0591}{n} \log \frac{|M|}{|M^+|}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{|1|}{|M^+|}$$



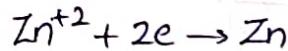
$$E = E^\circ - \frac{0.0591}{n} \log \frac{|M^+|}{|M|}$$

$$\therefore |M| = 1$$

$$E = E^\circ - \frac{0.0591}{n} \log |M^+|$$

- Q. A zinc rod is dipped in 0.1M of  $ZnSO_4$  solution. Calculate the electrode potential  $E_{Zn^{+2}/Zn}^\circ = -0.76$  V.

Ans)



$$E = -0.76 - \frac{0.0591}{2} \log \frac{1}{0.1}$$

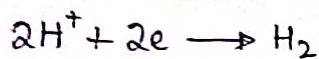
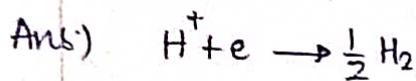
$$= -0.76 - 0.0295 (1)$$

$$= -0.7895$$

$$\approx -0.8$$

28. Calculate the pH of the following solution half cell  $\text{H}_2 \uparrow / \text{H}_2\text{SO}_4$ .  
The oxidation electrode potential is 0.3 V.

$\text{Hg}_2\text{Cl}_2$  (preferred)



$$\text{pH} = -\log |\text{H}^+|$$

$E^\circ$  will always be zero for hydrogen.

$$E = 0 - \frac{0.0591}{2} \log \left| \frac{1}{\text{M}^+} \right|$$

$$-0.3 = 0.0295 \log \left| \frac{1}{\text{M}^+} \right|$$

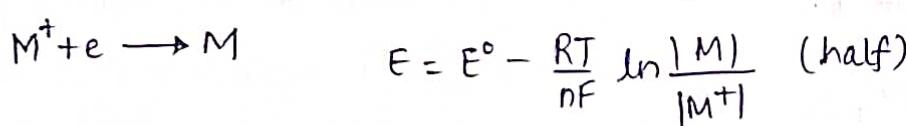
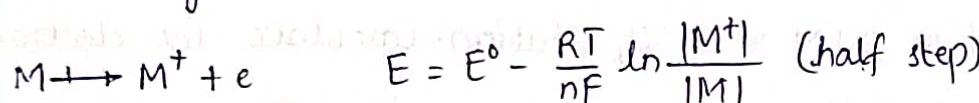
$$\frac{0.3}{0.0295} = -\log \left| \frac{1}{\text{M}^+} \right|$$

$$10 = \log |\text{M}^+|^2$$

$$10 = 2 \log |\text{M}^+|$$

$$\frac{10}{2} = \log |\text{M}^+|$$

$$\log |\text{M}^+| = 5$$



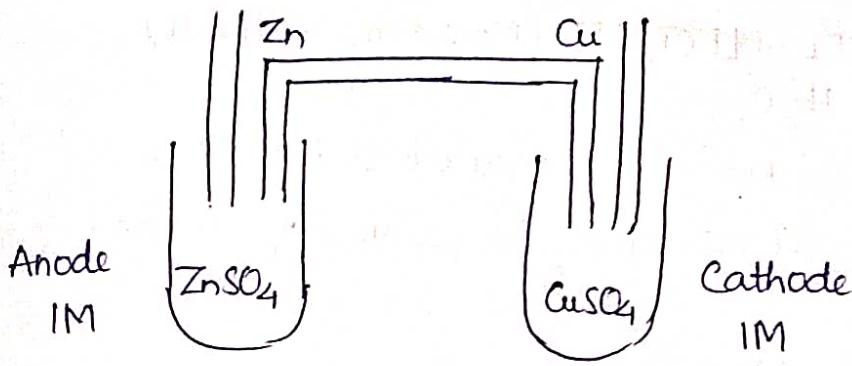
$$E_{\text{cell}} = E^\circ - \frac{RT}{nF} \ln \frac{|\text{M}|}{|\text{M}^+|} - \left( E^\circ - \frac{RT}{nF} \ln \frac{|\text{M}^+|}{|\text{M}|} \right)$$

Under standard condition

$$E_{\text{cell}} = E_{\text{st}}^\circ - E_{\text{oxt}}^\circ - \underbrace{\frac{RT}{nF} \ln \left( \frac{|\text{M}|}{|\text{M}^+|} \cdot \frac{|\text{M}^+|}{|\text{M}|} \right)}_{=0}$$

$$E_{\text{cell}} = E_{\text{st}}^\circ - E_{\text{oxt}}^\circ$$

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At standard condition,

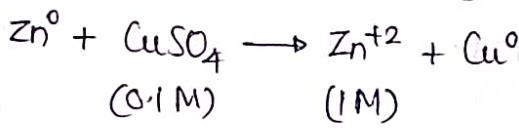
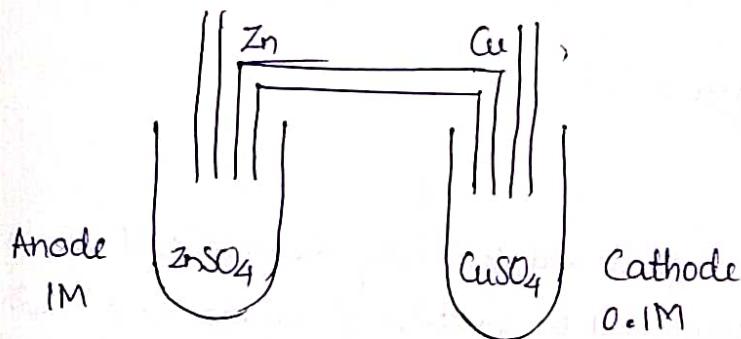


$$E^\circ = -0.76 \text{ V}$$

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

$$\begin{aligned} E^\circ &= E_{\text{right}} - E_{\text{left}} = E_{\text{cathode}} - E_{\text{anode}} \\ &= 0.34 - (-0.76) \end{aligned}$$

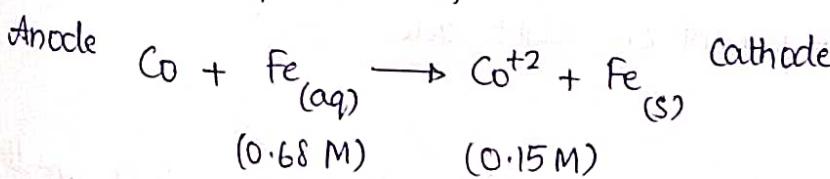
$$E^\circ = 1.10 \text{ V} //$$



(0.1 M) (1 M)

$$\ln \frac{1 [Zn^{+2}] [Cu^0]}{0.1 [Cu^{+2}] [Zn^0]} = \ln \frac{Zn^{+2} | 1 |}{Cu^{+2} | 0.1 |} = \ln 10 = 1 //$$

Calculate the potential of cell



(0.68 M) (0.15 M)

$$E^\circ_{Fe^{+2}/Fe} = 0.44 \text{ V}$$

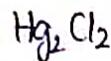
$$E^\circ_{Co^{+2}/Co} = -0.28$$

$\Delta G = \text{Gibbs Free Energy}$

$$= -nFE^\circ$$

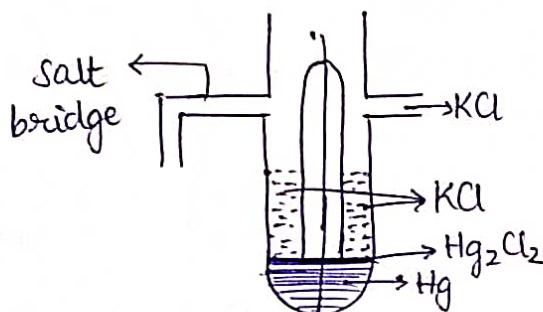
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## Reference Electrode $\Rightarrow$ CALOMEL ELECTRODE (Mercurous Chloride)



An electrode whose potential is known and constant is known as Reference Electrode. It is used for determining the potential of unknown electrode. They can be of five types:-

- 1) Hydrogen electrode (standard)
- 2) Calomel electrode (metal / metal salt ion electrode)
- 3) Redox Electrode (quinhydrion electrode)
- 4) Glass electrode (ion selective electrode)
- 5) Metal / Metal salt electrode



### Construction :

- An electrode of this type consists of a metal and sparingly soluble salt of the same metal which is dipped in (or) immersed in solution of soluble salt having same anion. It is represented as  $\text{Hg}_{(s)}, \text{Hg}_2\text{Cl}_{2(l)} / \text{KCl}$ .
- Hg of high purity is placed at the bottom of the glass tube with the side tube on both the sides. It is connected to the outer circuit by means of this Platinum wire sealed in glass tube. The surface is covered with a paste of Mercurous Chloride. A saturated normal or decinormal KCl is introduced through the side of the tube present on right side.

### Working :

- If this electrode acts as anode, i.e. when oxidation is taking place on this, the electrode gives  $\text{Hg}_2\text{Cl}_2 \rightarrow \text{Hg}^{+2} + \text{Cl}^-$  with the liberation of free electrons. These  $\text{Hg}^{+2}$  ions combine with the chloride present in KCl to form sparingly soluble  $\text{Hg}_2\text{Cl}_2$  which results in dropping concentration of chloride ion.
- On the other end, when the electrode acts as cathode, i.e. reduction is

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taking place on this, it results in increase in concentration of chloride ion. Hence, the calomel electrode is reversible w.r.t. chloride ion.

- The electrode is connected with side tube (to the left) to a salt bridge, the potential of which needs to be determined. The potential of calomel electrode depends upon the concentration of KCl filled in the electrode.
- The potential of calomel electrode is

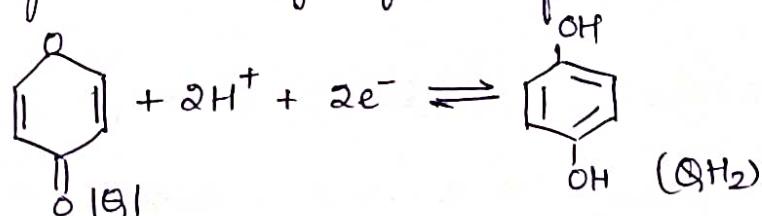
$$1 \text{ N KCl} = 0.28 \text{ V}$$

$$0.1 \text{ N KCl} = 0.33 \text{ V}$$

$$\text{Saturated KCl} = 0.2415 \text{ V}$$

#### \* QUINHYDRON ELECTRODE :

Quinhydrone and Hydroquinone form reversible redox reaction.



Construction:

- Add a pinch of Quinhydrone powder to the solution and immerse the Platinum electrode in it. Potential E develops when inert electrode Platinum is immersed in the solution, is given by last equation:

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{QH}_2]}{[\text{Q}] [\text{H}^+]^2}$$

$$= E^\circ - \frac{0.0591}{2} \log \frac{1}{[\text{H}^+]^2}$$

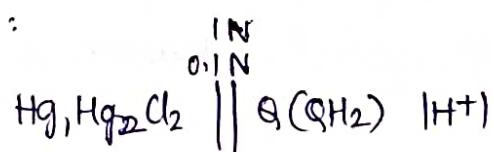
$$= E^\circ - \frac{0.0591}{2} \log [\text{H}^+]^{-2}$$

$$= E^\circ - \frac{0.0591}{2} (-2) \log [\text{H}^+]$$

$$= E^\circ - 0.0591 \text{ pH}$$

$$= 0.0699 - 0.0591 \text{ pH}$$

standard potential



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

$$= 0.06999 - 0.0591 \text{ pH} - 0.2415$$

$$= 0.4575 - 0.0591 \text{ pH}$$

$$\text{pH} = \frac{E_{\text{cell}} - 0.4575}{0.0591}$$

→ The first step is to identify the main components of the system. In this case, the system consists of a pump, a tank, and a flow line. The pump is located at the bottom of the tank, and the flow line connects the pump to the top of the tank. The flow line has a valve that can be controlled to regulate the flow rate.

→ The second step is to determine the desired operating conditions. This includes specifying the desired flow rate, the desired pressure at the pump inlet, and the desired temperature of the fluid.

→ The third step is to select appropriate control valves. In this case, a valve is selected to regulate the flow rate. The valve is located on the flow line between the pump and the tank.

→ The fourth step is to calculate the required valve size. This involves determining the flow rate, the pressure drop across the valve, and the valve characteristics.

→ The fifth step is to select the appropriate valve type. In this case, a globe valve is selected due to its linear flow characteristic.

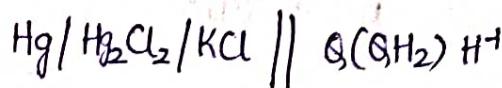
→ The sixth step is to calculate the required valve size. This involves determining the flow rate, the pressure drop across the valve, and the valve characteristics.

→ The seventh step is to select the appropriate valve type. In this case, a globe valve is selected due to its linear flow characteristic.

→ The eighth step is to calculate the required valve size. This involves determining the flow rate, the pressure drop across the valve, and the valve characteristics.

→ The ninth step is to select the appropriate valve type. In this case, a globe valve is selected due to its linear flow characteristic.

- 1Q. Find the pH of solution in a Hydroquinon half cell which was coupled with standard calomel electrode. The emf of combined cell = 0.123V at 25°C.



Ans.) We know that  $\text{pH} = \frac{E_{\text{cell}}}{0.0591}$

$$0.0591 \text{ pH} = 0.459 - E_{\text{cell}}$$

$$\text{pH} = \frac{0.459 - E_{\text{cell}}}{0.0591}$$

$$\text{pH} = \frac{0.459 - 0.123}{0.0591}$$

$$\boxed{\text{pH} = 5.6}$$

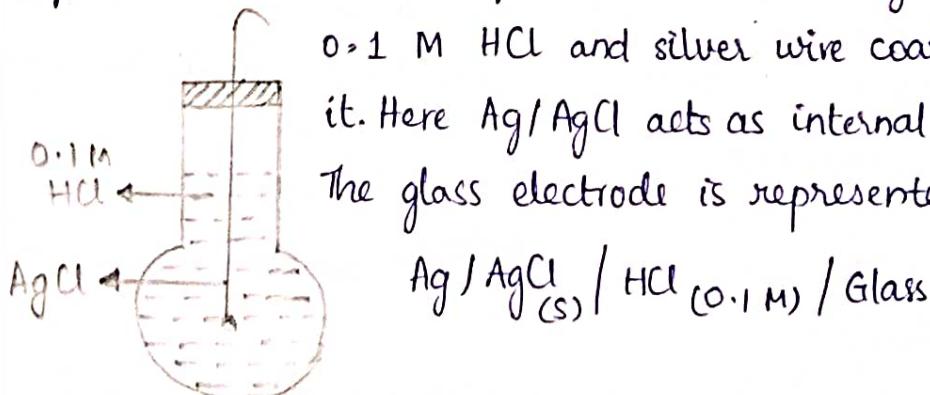
### \* GLASS ELECTRODE (ion selective electrode) :

CONSTRUCTION :-

The glass electrode is made up of spatial glass called corning glass containing  $\text{Na}_2\text{O}$  (22%),  $\text{SiO}_2$  (72%) containing of relatively low melting point and high electrical conductivity. It consists of thin glass bulb filled with

0.1 M HCl and silver wire coated with AgCl immersed in it. Here Ag/AgCl acts as internal reference electrode.

The glass electrode is represented as below:-

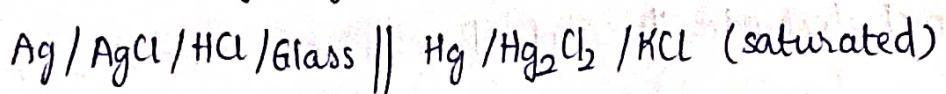


### WORKING :

When the glass electrode is immersed in another solution whose pH value is to be determined, a potential is developed over there between two surfaces of the membranes. The potential difference developed is proportional to the pH of the solution. The glass membrane functions as ion exchange resin and equilibrium is established between the sodium ion in the glass and the H ion in the solution. For a particular type of glass, the potential difference varies with concentration of  $\text{H}^+$  solution.

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



$$E^{\circ} = 0.2415$$

$$E_{\text{cell}} = 0.2415 - (E_g^{\circ} - 0.0591 \text{ pH})$$

$$0.0591 \text{ pH} = 0.2415 - E^{\circ} - E_{\text{cell}}$$

$$\boxed{\text{pH} = \frac{0.2415 - E_g^{\circ} - E_{\text{cell}}}{0.0591}}$$

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### \* BATTERIES :

A battery is a galvanic cell or series of combined galvanic cells that can be used as a source of direct electric current at a constant voltage.

1) Primary batteries

2) Secondary batteries

a) Fuel Cell ↗

→ Primary batteries: They act as galvanic cell.

→ Secondary batteries: They act as both galvanic cell and electronic cell.

2) They can be reused.

3) They are not rechargeable.

4) It has lifespan of 2 years.

5) Eg: Ni-Cd cell, Li-ion cell.

### Primary batteries (continuation).

2) They cannot be reused if they are discharged once.

3) They are not rechargeable.

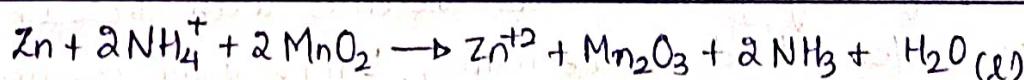
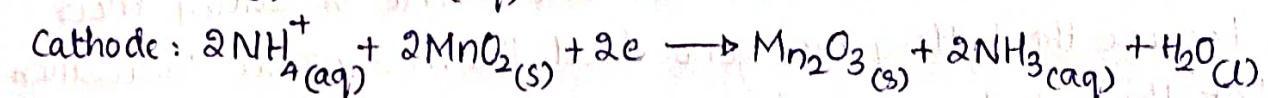
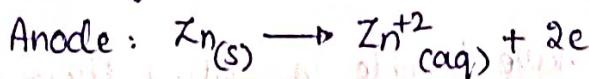
4) It has short life span of 6 months.

5) Eg: Dry cell, Li MnO<sub>2</sub> cell.

The dry cell is without any fluid component.

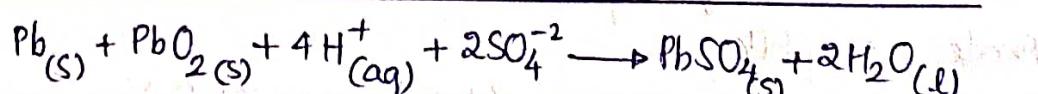
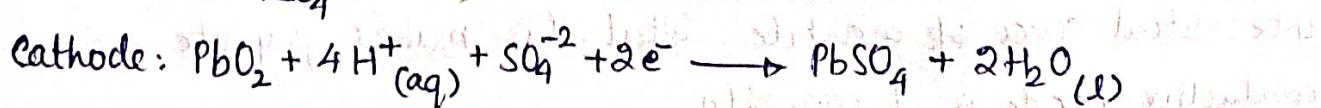
#### Leclanche Cell / Dry Cell

The anode of the cell consists of Zn that is in contact with MnO<sub>2</sub> and is in contact with electrolyte. The electrolyte filled in is NH<sub>4</sub>Cl + ZnCl<sub>2</sub> in water, to which starch is added to thicken the solution to a paste-like consistency so that less chances to leak.



#### \* Lead Storage Battery

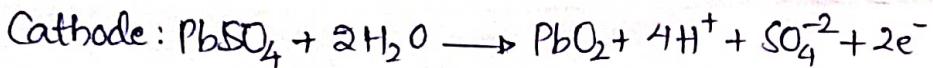
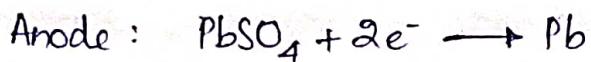
The lead storage battery is commonly used in automobiles. It consists of 6 identical cells joined in series. Each cell has lead anode and cathode is made up of PbO<sub>2</sub> (lead dioxide). Both cathode and anode are immersed in aqueous sulphuric acid which acts as electrolyte. The cell reaction can be written as:-



→ Under normal operating condition, each cell produces 2 V and a total of 12 V from the six cells used in series to ignite the engine of the automobile. The net storage battery can deliver large amount of current for short duration of time; that helps to start the engine.

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Unlike dry cell, ~~lead~~ storage battery is rechargeable. Recharging the battery means reversing the normal electrochemical reaction at cathode and anode.



Because

① ~~First~~, the battery consumes  $\text{H}_2\text{SO}_4$  as electrolyte, the degree or extent upto which the battery is used can be checked by measuring the density of electrolyte with the help of hydrometer. The density of fluid electrolyte  $\text{H}_2\text{SO}_4$  in good condition, i.e. when battery is fully charged would be greater than or equal to  $1.2 \text{ g/mL}$  or  $1.2 \text{ g/cm}^3$ .

② People living in cold climate sometimes have trouble in starting their vehicle because the battery has gone dead. Thermodynamic calculation shows that the emf of many galvanic cells decreases with decrease in temperature. However, for a lead storage battery, temperature coefficient is about  $1.5 \times 10^{-4} \text{ V/}^\circ\text{C}$  i.e. there is decrease in voltage of  $1.5 \times 10^{-4} \text{ V}$  per degree. Thus even allowing ~~the~~ <sup>only</sup> temperature about  $40^\circ$  degrees, the decrease in voltage amount is  $1.6 \times 10^{-3} \text{ V}$  which is about  $\frac{1.6 \times 10^{-3} \text{ V}}{12 \text{ V}} \times 100\% = 0.05\%$ .

#### \* LITHIUM BATTERY:

→ There are secondary cells. In this,

~~in this~~, cathode consists of layered graphite into which the lithium ion is intercalated. Intercalation keeps the small ions like lithium ion in interstitial space of graphite crystal. This makes graphite more conductive. Anode is of graphite.

Anode : graphite

Cathode : oxide of Lithium ( $\text{LiCO}_2$  or  $\text{LiNiO}_2$ )

Electrolyte:  $\text{Li PF}_4$ ,  $\text{LiBF}_4$ .

The cell reaction involved during discharge at anode

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## Unit - 1 Electrochemical Series (Obj.)

1. Strongest ligand : Co

2. Bond Order :  $O_2 = 2$ ,  $F_2 = 1$ ,  $N_2 = 3$ .

3. One part of  $CaCO_3$  is equivalent to  $10^5$  at water.

• Clark, ppm, °French

0.07

$\times 10^6$

$10^5$

4. Bonding molecular orbital

i) Constructive interference ✓

ii) Destructive interference

iii) Both i) and ii)

iv) By combination of atomic orbitals of 2 negative ions.

5.  $CaCl_2$  and  $Mg(HCO_3)_2$

i) Temp: hardness

ii) Permanent hardness

iii) Perm. & Temp.

iv) Temp. & Perm.

6. Germicide used in purification process is HOCl (hypochlorous acid).

7.  $Zn/Zn^{+2} \parallel Cu^{+2}/Cu^0$

a) Zn is getting reduced.

b) Cu is getting oxidised.

c) Zn is getting oxidised.

d) Cu is neutral.

8. Cell reaction is reversible in secondary cell.

\*  $O_2, N_2$  Molecular Orbital Energy Diagram.

\* Octahedral and Tetrahedral Splitting.

\* CFSE.

i)  $[Co(NH_3)_6]^{+3}$  low spin

ii)  $[Co(CN)_6]^{-3}$  low spin.

iii)  $[CoF_6]^{-3}$  high spin

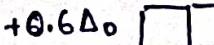
iv)  $[Fe(H_2O)_6]^{+2}$  high spin

v)  $[Co(H_2O)_6]^{+3}$  high spin

A) i)  $Co_{(27)} = d^7 s^2$

$Co^{+2} = d^6 s^0$

$\uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow$

$+0.6\Delta_0$   eg

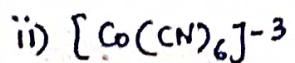
$= -0.4(6)$

$= -2.4\Delta_0$

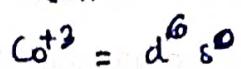
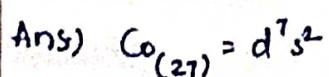
$-0.4\Delta_0$  

$t_{2g}$

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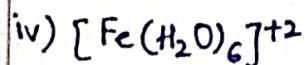
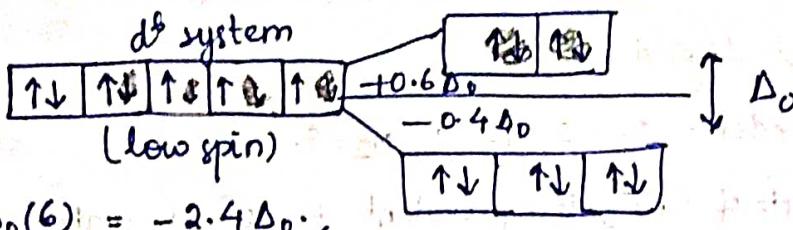


$$x + 6(-1) = -3 \Rightarrow x = -3 + 6 \Rightarrow x = 3$$

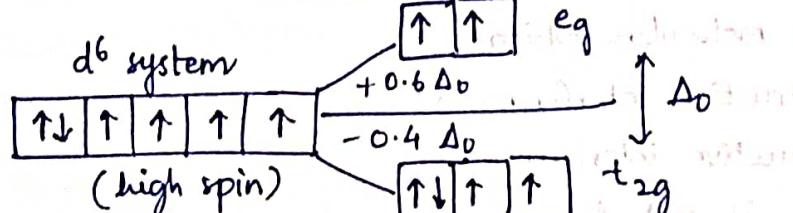
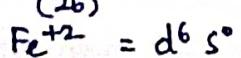
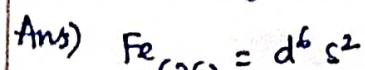


CFSE =

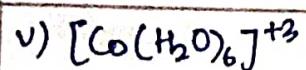
$$= 0.6\Delta_0(4) - 0.4\Delta_0(6) = -2.4\Delta_0 //$$



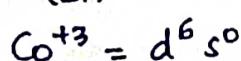
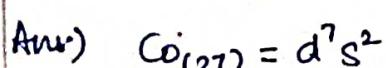
$$x + 6(0) = 2 \Rightarrow x = 2$$



$$\text{CFSE} = +0.6\Delta_0(2) - 0.4(4) = 1.2 - 1.6 = -0.4\Delta_0 //$$



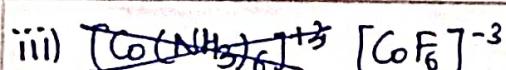
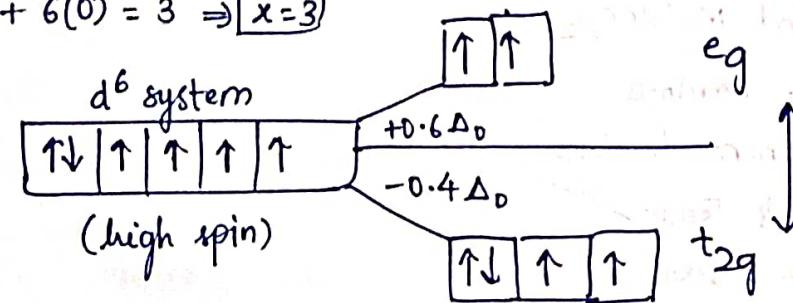
$$x + 6(0) = 3 \Rightarrow x = 3$$



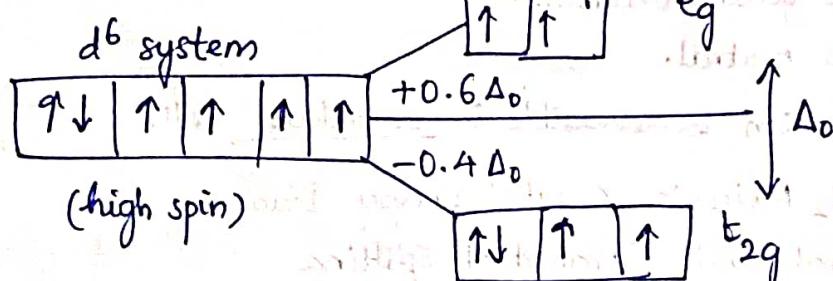
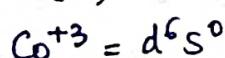
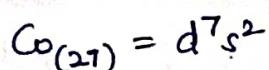
CFSE =  $0.6\Delta_0(2)$

$$+ (-0.4\Delta_0)(4)$$

$$= 1.2\Delta_0 - 1.6\Delta_0 = -0.4\Delta_0 //$$



$$x + 6(-1) = -3 \Rightarrow x = 3$$



Q.  $\Delta_0$  depends on these factor(s):

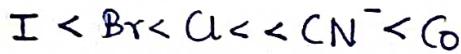
1. Nature of ligands (✓)
2. Charge on central metal ion.
3. From which d series central metal belongs

$$\begin{aligned}\mu &= n(n+2) \\ &= 4(4+2) \\ &= \sqrt{24} = 2\sqrt{6}\end{aligned}$$

- Q.  $[\text{Co}(\text{NH}_3)_6]^{+3}$  strong ligand
- A) No. of unpaired electrons  $n=0$  due to low spin.  $\therefore \mu=0$ .
- Q.  $[\text{CoF}_6]^{3-}$   $x+6(-1)=-3 \Rightarrow x=-3+6 \Rightarrow x=3$
- A)  $\mu=\sqrt{4(4+2)}=2\sqrt{6}$ .
- Q.  $[\text{Cr}(\text{NH}_3)_6]^{+3}$ . Calculate CFSE &  $\mu$ . (low spin complex)
- A)  $x+6(0)=3 \Rightarrow x=3$
- $$C_s^{(24)} = d^4 s^2$$
- $$\text{Cr}^{+3} = d^3 s^0$$
- $d^3$  system
- 
- $$\text{CFSE} = -0.4 \Delta_0 (3) = -1.2 \Delta_0$$
- $$\mu = \sqrt{3(3+2)} = \sqrt{3(5)} = \sqrt{15}$$
- Q.  $[\text{Cu}(\text{NH}_3)_6]^+$
- $x+6(0)=1$   
 $x=1$
- $$\text{Cu}^{(29)} = d^9 s^2 \rightarrow d^{10} s^1$$
- $$\text{Cu}^+ \rightarrow d^{10} s^0$$
- $d^{10}$  system
- 
- $$\text{CFSE} =$$
- B.  $\Delta_0 = 21150 \text{ cm}^{-1} \rightarrow \text{'low' means weak ligands (high spin)}$   
 $E_p = 27750 \text{ cm}^{-1}$  energy
- 01-07-2022.
1.  $d^1$  in octahedral  $\therefore \text{CFSE} =$
  2. Cation exchange resin can be regenerated by dil. HCl or dil.  $\text{H}_2\text{SO}_4$
  3. Anion exchange resin can be regenerated by dil. NaOH.
  4. 1 ppm =  $0.07^\circ\text{Cl} = 0.1^\circ\text{Fr}$
  5. 1 part of  $\text{CaCl}_2 = 10^5$  part of water in  ${}^\circ\text{Fr}$ .
  6. SHE = Standard Hydrogen Electrode
  7. Reverse osmosis = Lower conc. to higher concentration.
  8. Nature of  $\text{O}_2$  according to MOT = paramagnetic.

9. Bond Order = Bonding electrons - Antibonding electrons

10. Spectrochemical Series



### Unit - I

1.  $N_2, O_2$  molecular orbital theory

2. CFSE calculation

3. Salient features of CFT

4. d orbital splitting in  $\Delta_o$  and  $\Delta_t$

### Unit - II

1. Ion Exchange Process

2. Reverse osmosis

3. EDTA problem —④

4. Treatment of <sup>river</sup> water to potable water.

### Unit - III

1. Problem on  $E_{cell}^\circ = E_R - E_L$

2. Problem on Nernst Equation

3. pH determination by Quinhydrone electrode.

4. pH by Glass electrode.

02-07-2022.

→ Quinhydrone Electrode pH value:

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1/QH_2}{[Q][H^+]^n}$$

where  $E^\circ$  is standard cell potential.

$$E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$

$$E = E^\circ - \frac{0.0591}{2} \log [H^+]^2$$

$$E = E^\circ - \frac{0.0591}{2} \log (H^+)$$

$$E = E^\circ - \frac{0.0591}{2} \times 2 \log (H^+)$$

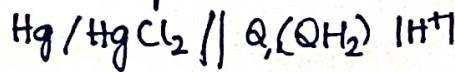
$$E^\circ = 0.699$$

$$\therefore E = 0.699 - 0.0591 \text{ pH}$$

$$pH = \frac{1}{2} (\lg H^+)$$

02-07-2022.

Combining with calomel electrode :- we get:



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

$$= (0.699 - 0.0591 \text{ pH}) - (0.2415)$$

$$E_{\text{cell}} = 0.4575 - 0.0591 \text{ pH}$$

$$0.0591 \text{ pH} = 0.4575 - E_{\text{cell}}$$

$$\text{pH} = \frac{0.4575 - E_{\text{cell}}}{0.0591} //$$

→ Glass Electrode pH value:

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

Glass || Calomel

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

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

Combining with calomel electrode, we get:-

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

$$E_{\text{cell}} = 0.2415 - (E^\circ + 0.0591 \text{ pH})$$

$$E_{\text{cell}} = 0.2415 - E_G^\circ - 0.0591 \text{ pH}$$

$$0.0591 \text{ pH} = 0.2415 - E_G^\circ - E_{\text{cell}}$$

$$\text{pH} = \frac{0.2415 - E_G^\circ - E_{\text{cell}}}{0.0591}$$

$$\text{pH} = \frac{0.2415 - 0.230 - E_{\text{cell}}}{0.0591}$$

$$\text{pH} = \frac{0.0115 - E_{\text{cell}}}{0.0591}$$

0.221  
0.230 v

2415  
2300  
115

## \* CORROSION

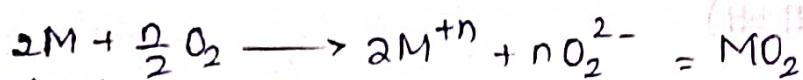
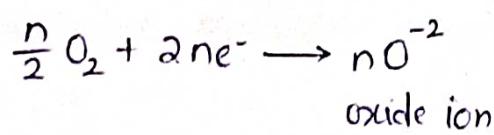
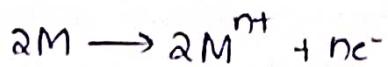
The process of deterioration, destruction and consequent loss of solid material metal through the unwanted chemical or electrochemical by its environment is called corrosion.

Two types:

I) Dry corrosion: This type of corrosion occurs mainly through the direct chemical reaction of the environment or atmospheric gases such as oxygen, halogen (i.e. chlorine), Hydrogen sulphide, nitrogen. The dry corrosion can be of three types:-

1) Oxidation corrosion: It is brought by direct oxidation of oxygen at low/high temperatures

usually in the absence of moisture.



### Mechanism:

Oxidation corrosion occurs first at surface of metal resulting metal oxide. The metal oxide scale forms a barrier, that tends to restrict the further oxidation. For oxidation to be continued, metal must diffuse outwards or oxygen must induce inwards. But the outward diffusion of the metal is much more rapid because metal ion is smaller than oxygen. It has higher mobility compared to oxygen.

Nature of the oxides formed on the surface plays an important part in oxidation corrosion.  $M + O_2 \rightarrow MO_2$ .

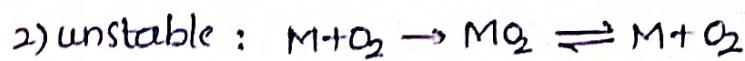
When oxidation starts, a thin layer of oxide forms on the metal surface and the nature of thin film of metal oxide is:-

i) stable: A stable layer is fine <sup>air</sup> granular structure and can adhere to the surface tightly to the parent metal/surface. Such adherence can stop the

07-07-2022.

penetration of oxygen.

Eg: (metals that form stable oxides) Al, Sn, Pb, Sr, Cu, Pt



3) volatile :

Molybdenum Oxide ( $MoO_3$ )

4) Porous :

$FeO$

### \* Pillingworth Bedworth Rule :

An oxide is protective ~~or~~ non-porous if the volume of oxide is greater than the volume of metal ~~per unit~~ from which it is formed.

On the other hand, if the volume of oxide is lesser than the volume of metal, then the metal surface is porous.

08-07-2022.

2) Corrosion by other gases :

The extent of corrosive effect depends mainly on the chemical affinity and the gases involved. The degree of attack depends on the formation of protective and non-protective film on the metal surface.

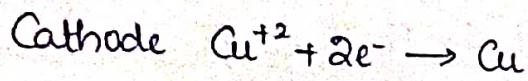
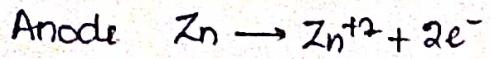
3) Liquid Metal Corrosion :

Liquid metal corrosion is due to chemical action of flowing liquid metal at high temperature on solid metal. Such corrosion occurs in devices used for nuclear power. The corrosion reaction involves either dissolution of solid metal by liquid metal (or) internal penetration of liquid metal into the solid metal.

### II) WET CORROSION : (or) ELECTROCHEMICAL CORROSION :

This type of corrosion occurs :

- 1) where a conducting liquid is in contact with the metal.
- 2) When two dissimilar metals are immersed or dipped partially in the solution. This corrosion occurs due to the existence of separate anodic or cathodic area, between which current flows through the conducting solution. In the anodic area, oxidation takes place. In the cathodic area, reduction takes place.



MECHANISM :

Electrochemical corrosion requires the flow of electrons

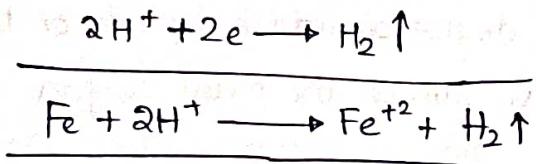
On the other hand, the cathode reaction consume this electron either by  
1) evolution of hydrogen ↑  
2) absorption of oxygen ↓

1) Evolution of hydrogen : Type Corrosion

Usually in acidic condition it takes place whenever the hydrogen comes out.

Consider metal like Fe, the anodic reaction is dissolution of iron with the liberation of electrons.  $\text{Fe} \rightarrow \text{Fe}^{+2} + 2e^-$ .

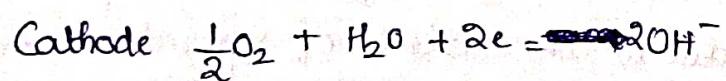
These electrons flow through the metal from anode to cathode where H ions (in acidic condition) are eliminated liberated as  $\text{H}_2$  gas.



2) Absorption of oxygen : Type Corrosion

In neutral condition of the electrolyte (like  $\text{NaCl}$ ) in the presence of atmospheric oxygen is a common example of this type of corrosion.

The surface of iron is usually coated with the thin film of iron oxide however, if this iron oxide ~~film~~ develops some cracks, anodic area behaviour on the surface while the well-metal part acts as cathode. It follows that the anodic area as small surface parts while nearly rest of the surface (metal) acts as cathode.



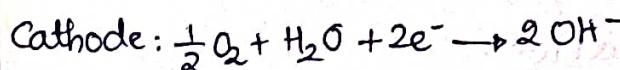
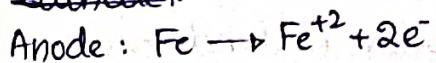
If  $\text{O}_2$  is enough



FORMULA OF RUST :  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$

## Waterline corrosion:

Cathode:



## \* Galvanic Series:

Mg                    natural environment

Mg alloy            anode for all below one

Zn

Al

Cd

Al alloys

Mild steel

CoSF / Fe

Pb

Sn

## \* Factors affecting corrosion rate:

- 1) Nature of Metal
- 2) Overvoltage
- 3) Relative anodic to cathodic area
- 4) Purity of Metal
- 5) Physical State of Metal
- 6) Nature of oxide film on Metal Surface
- 7) Purity Passive character of Metal
- 8) Solubility of corrosion product
- 9) Volatility of corrosion product ( $\text{MoO}_3$ )

## Nature of corroding environment:

- ① Temperature (corrosion increases)
- ② Humidity (high corrosion rate)
- ③ pH → Decrease in pH increases the corrosion rate.

## @ Cathodic Protection

The principle involved in this method is to force the metal to be protected and behave like cathode, thereby corrosion will not occur.

There are two types of cathodic protection:

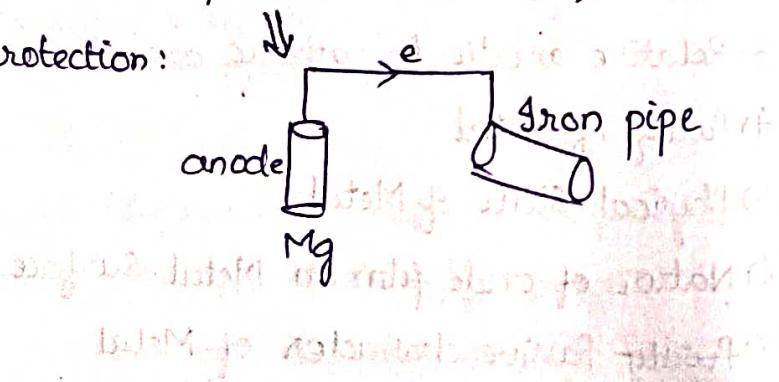
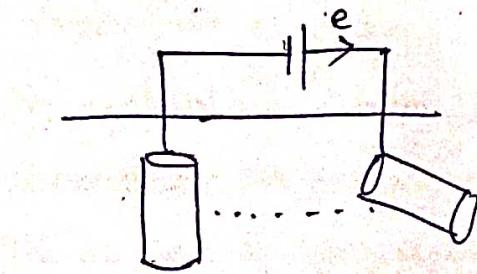
① Sacrificial Anodic Protection

② Impressed Current Cathodic Protection.

### ① Sacrificial Anodic Protection:

In this protection method, the metallic structure such as iron pipe is connected by a wire to a more anodic material, so that all the corrosion is concentrated on this active metal. The more active metal itself gets corroded slowly while the parent structure is protected. The more active metal used so employed is called Sacrificial Metal. The corroded sacrificial metal (anode block) can be replaced by fresh Mg block when consumed completely. The metals commonly employed are Mg, Zn, Al and their alloys. Important application of sacrificial anodic method include protection of buried pipeline, underground cables, ship-hulls, water tanks, etc.

### ② Impressed current cathodic protection:



In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. Usually, the impressed current is derived from direct current source from battery or rectifier with an insoluble anode like Graphite, high silica and scrap of iron. Usually, sufficient DC current is applied to insoluble anode buried in the soil.

## \* GALVANISATION:

Galvanizing is the process of coating iron or steel with a thin coat of zinc to prevent them from rusting. The process is carried out as follows:-  
 the iron or steel articles (sheet, plate, wire) is first cleaned by application, dil.  $H_2SO_4$ , for 15-20 minutes at  $60^\circ-90^\circ C$ . This treatment removes any scale or rust.

The article is then washed and dried. It is then immersed in the bath of molten zinc maintained  $430-425-430^\circ C$ . The surface of the bath is kept covered with a flux of  $NH_4Cl$  to prevent oxide formation. When the article is taken out, it is found to have been coated with a thin layer of zinc. It is then passed through a pair of hot rollers. This process removes any excess of zinc and produces a thin film of uniform thickness. Then it is annealed at temperature  $650^\circ C$  and finally cools down.

It is more likely to used for the protection of iron from atmospheric corrosion in the form of proofing sheets, etc.

It is pointed out here, zinc gets dissolved in acidic condition in forming highly toxic compound. Hence, galvanised utensil cannot be used for storing the food stuff, specially acidic ones (like pickles which are acidic in nature).

## \* TINNING:

Tinning is the coating of tin over the iron or steel articles.

The process consists: 1) treating surface steel sheet with dil. acid to remove any oxide layer.

After that it is passed through the bath of zinc chloride flux. The flux helps the molten metal to adhere and bond strongly with the metal sheet. The sheet passes through the type of molten Tin, and finally through a series of rollers.

From underneath, the surface of layer of palm oil. The palm oil protects the hot tin coated surface against the oxidation.

\* The rollers remove excess of Tin and produce a thin film of uniform thickness.

Uses: This possess considerable resistance against atmospheric corrosion. Moreover, because of non-toxic nature of the steel, Copper and brass sheet used for manufacturing for containing food stuffs.

28-07-2022 (Afternoon Session)

**Galvanising** & **Tinning**

i. A process of covering Fe or steel which thin coat of Zn. with thin layer of Sn(Tin).

2. Sacrificial Anodic Protection. 3. Due to the noble character of Sn.

3. This will keep protecting even if the zinc coating is punctured.

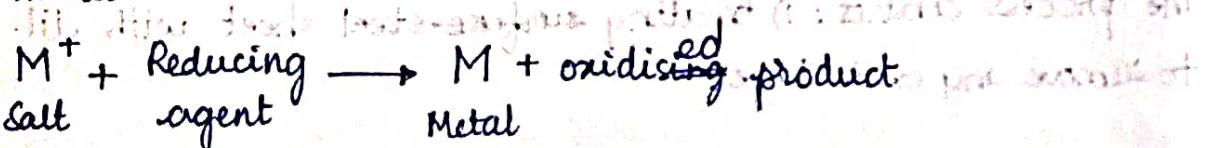
3. Tin coating can protect the underlying metal till the tin coating is perfect.

4. Galvanised containers can't be used for food storage.

4. This can be used for storage of food.

### ELECTROLESS PLATING:

Electroless plating is a technique of depositing noble metal from its salt solution on catalytically active surface of less noble metal.



The driving force is auto-catalytic redox reaction on pre-treated catalytic surface. Various aspects of the electroless plating are:

① preparation of the active surface of object to be plated.

This step is most important in this technique. This is achieved

by using one of the following methods:-

- 1) Etching, i.e. by acid treatment.
- 2) Electroplating a thin layer of the metal to be plated followed by heat treatment.
- 3) Treating with Stannous Chloride followed by dipping in Palladium Chloride ( $PdCl_2$ ) solution. This treatment produce a thin layer of palladium on treated surface. Usually, this is followed in the case of plastic and printed circuit boards.

## (2) Planting bath:

Planting bath is composed of "soluble salt of metal."

- 2) Reducing agent like formaldehyde.
- 3) complexing agent like tartarate, citrate, succinic acid.
- This improves the quality of deposit/coating.
- 4) Exalant like succinate, fluoride, etc. This ~~extends~~ enhances the planting rate.
- 5) Stabilizer like thiourea (or) cations of "lead (or) calcium" is added to prevent the decomposition of planting bath solution.
- b) Buffer like sodium acetate, sodium hydroxide + rochelle's salt added to control the pH of the bath.

## \* Advantages of Electroless Platings over Electro Plating:

1. No electrical energy is required.
2. Better throwing power.
3. Planting on the article made of insulator like plastic.
4. Electroless coated material better chemical and mechanical properties.

## \* Some Electroless Plating:

1. Electroless plating of Nickel
2. Pretreatment and activation of surface

**Advantages of Electroless Plating:**

44 | bewerkt, besty. d. d. Interv. mit der Kopie. Mit einer handschriftlichen  
Bemerkung: „Falsch“.

multicellular organisms with bounded, shield-shaped, external skin without cilia.

a. equal with a leading fastball with velocity (MPH) about

színi hagyománytól a régi plébániákban keltetik meg minden évben.

closed streets. Happy New Year! 12-3402.

and without it.

*Lutreola* is the plural of *buteo* and *luteus*

Was ist eigentlich ein Tropenprimitiv?

Lina. *Leucania stictis* (Hufnagel) still angles univittata. (3)

Während die anderen Tiere sich auf dem Boden aufhielten, saß der Löwe auf einer kleinen Erhebung.

*E. leucophaea* aborescens. Sunt etiam subarborei *E. leucophaea* et *E. leucophaea*

• *dark reddish*

*Brachys "mimulus (A) kneri"* sp. nov. (synonym of *B. mimulus* Schubert & Kuntze)

resten blev stod fritidsp. ja (samt højskole) ved formanden af  
Lundskolen i København, der var en af de 12 medlemmer.

the following + developed further either with regard to  
a) the morphology and

• And all the great heroes of history.

• *probabilis* *admodum* *non* *equivalent* *substantia* *in* *tempore*

• bantingat di pagoda lajukas di M-1

... among of animals. Method 2

• říční vodohospodářského úřadu v Brně, kde byl pořízen v roce 1992.

physiognomy. High forehead, slightly wrinkled. Noticeably slender.

W. H. G. - 1900

प्राचीन लिपि वाली शब्दों का अर्थ

10. विद्युति ज्ञानं तद्वा प्रविष्टं विद्युतिः

and the following have been adopted:

# UNIT-4: Reaction Mechanisms and the molecule of industrial application

Reactant + Reagent  $\rightarrow$  Intermediate  $\rightarrow$  Product  
(substrate).

Organic reaction can be of four types:-

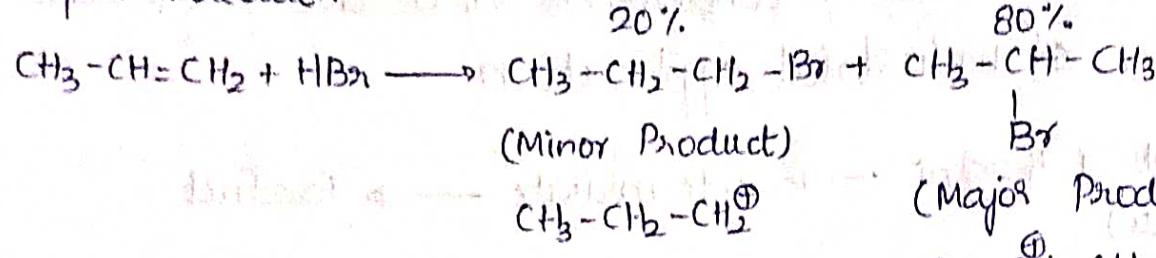
1. Substitution  $\xrightarrow{SN^1}$   
 $\xrightarrow{SN^2}$
2. Addition
3. Elimination  $\xrightarrow{E_1}$   
 $\xrightarrow{E_2}$
4. Re-arrangement

$$\text{rate} \propto [S]^1 [N\ddot{u}]^1$$

$$\text{Order of reaction} = 1+1 = 2$$

29-07-2022.

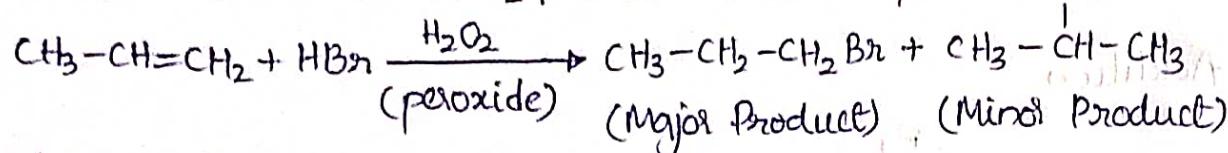
Propene molecule:



- This rule was proposed by Markonikov.

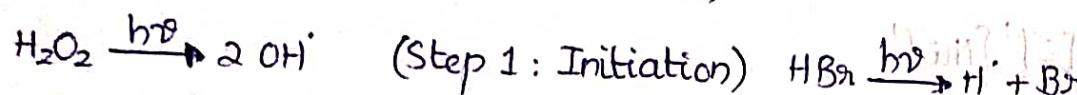
(more stable carbocation due to +I effect).

\* ANTI-MARKONIKOV RULE / PEROXIDE EFFECT / KHARA  $\xrightarrow{\text{H}_2\text{O}_2}$  SH EFFECT:

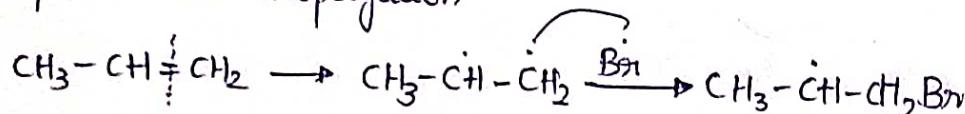


Addition of HBr to unsymmetrical alkene in presence of peroxide like Hydrogen Peroxide (or) Benzoyl Peroxide ( $\text{C}_6\text{H}_5\text{COO}_2$ ) takes place opposite to that of Markonikov Rule.

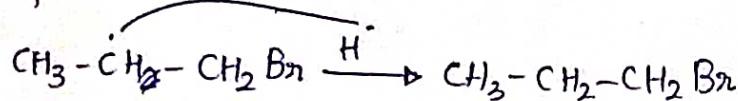
Mechanism: (free radical mechanism)



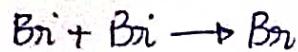
Step 2: Chain Propagation



Step 3:



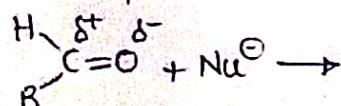
Step 4: Chain Termination



30-07-2022.

\* NUCLEOPHILIC ADDITION REACTION:

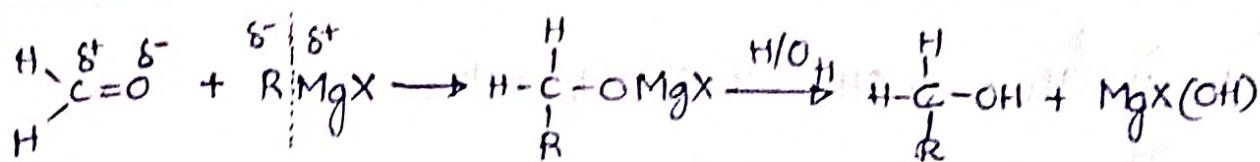
For example, reaction of carbonyl compound :-



Grignard Reagent =  $\text{RMgX}$  (Alkyl Magnesium Halide)

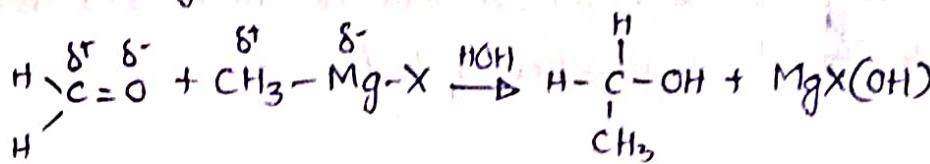
where  $\text{X} = \text{Br}, \text{I}$ .

30-07-2022.

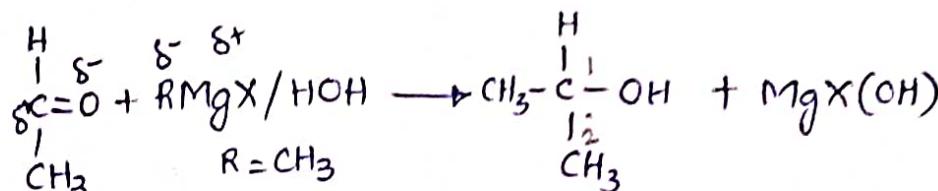


Formaldehyde

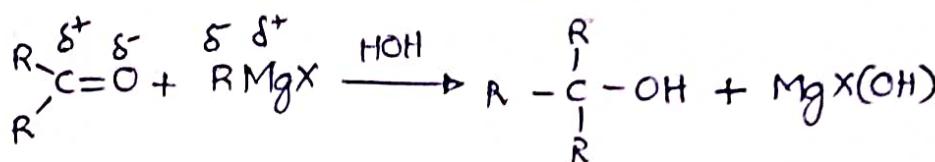
$1^\circ$  alcohol



Ethanol



$2^\circ$  alcohol

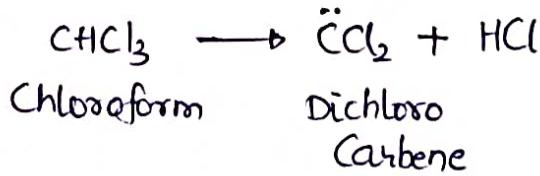


$3^\circ$  alcohol

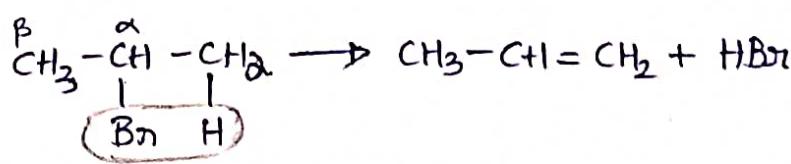
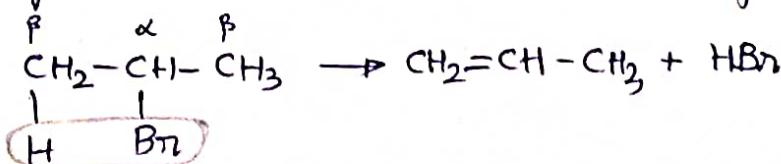
## \* ELIMINATION REACTION:

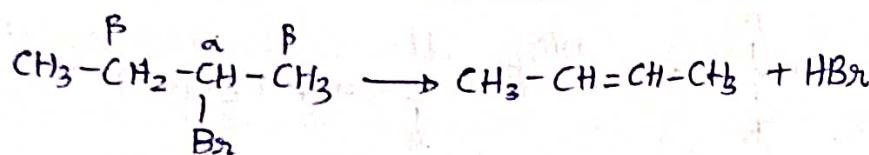
Elimination reaction is a reaction which involves removal of atom or group of atoms from the C-atom resulting in the formation of  $\pi$  bond between the C-atoms.

$\alpha$ -Elimination: When the two groups are eliminated from same C-atom, the process is known as  $\alpha$ -elimination. The reaction is rare.



$\beta$ -Elimination: When the two groups or atoms are removed from 2 adjacent C-atoms of the molecule, the process is known as  $\beta$ -Elimination.



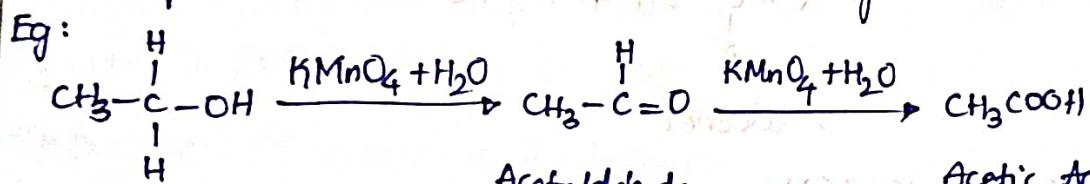


The Saytzeff Rule suggests that the hydrogen will be eliminated from that  $\beta$  C-atom which has lower number of hydrogens.

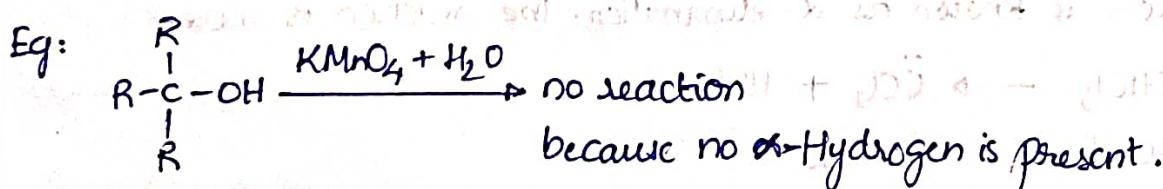
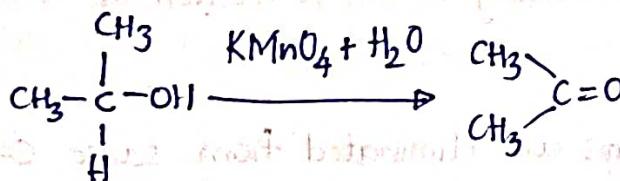
### Oxidation of Alcohols:

Alcohols can oxidise and the nature of products depends upon the type of alcohol and the condition of reaction. Most widely used oxidising agents are  $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$

Primary alcohols can be oxidised to aldehydes



Secondary alcohols



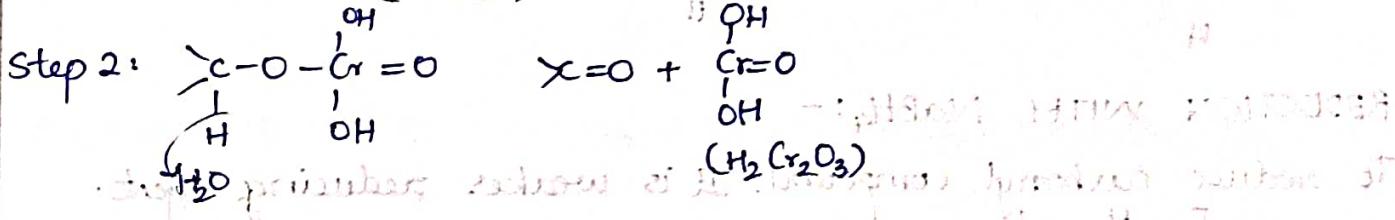
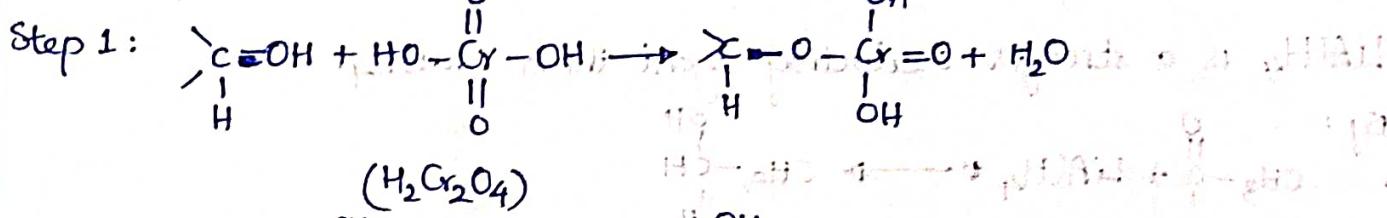
Chromic Acid :-

Oxidation involves chromium reagents such as Chromic Acid ( $\text{CrO}_3 + \text{H}_2\text{O}$ ) are simple to carry out and have been widely used. These reactions involve the formation of chromium ester.

01-08-2022.

CH<sub>3</sub>COOH → CH<sub>3</sub>-CO

Mechanism: ~~Reaction mechanism of Jones oxidation of alcohols~~



1° alcohol ~~ketones~~ ~~aldehydes~~

2° alcohol - ketones.

3° alcohol - ~~ketones~~ no reaction.

Oxidation by elimination of H<sub>2</sub>CrO<sub>3</sub>, a water molecule extracts ~~a~~ a proton from the carbon forming C= bond. The chromium ~~atom~~ is reduced as H<sub>2</sub>CrO<sub>3</sub> and eliminated.

Jones Reagent ~~is~~ known as Chromic ~~acid~~ acid + Sulphuric acid + acetone.

and is useful for oxidation of alcohols ~~which~~ which contain C=C or C≡C; allylic or benzylic compound.

(HOOC)<sub>n</sub> (CH<sub>2</sub>=CH<sub>2</sub>) : ~~Formation of ester~~

to many other with water (H<sub>2</sub>O) ~~compounds~~ addition of water

(alcohols) ~~methanol~~

with zinc in ~~methanol~~



nitrobenzene, benzene, anisole, ~~anisole~~ anisole, ~~anisole~~ anisole

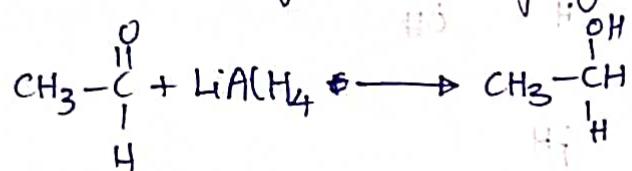
anisole, ~~anisole~~ anisole, ~~anisole~~ anisole, ~~anisole~~ anisole

04-08-2022.

## \* REDUCTION REACTION OF ALCOHOLS $\text{LiAlH}_4$ or $\text{NaBH}_4$

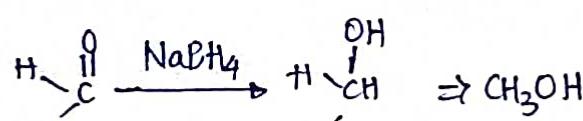
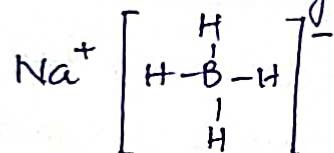
$\text{LiAlH}_4$  is a stronger reducing agent than  $\text{NaBH}_4$ .

Eq :

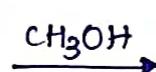
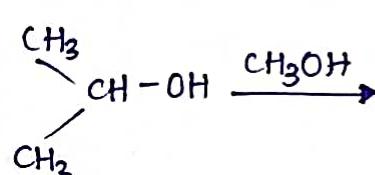
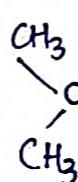
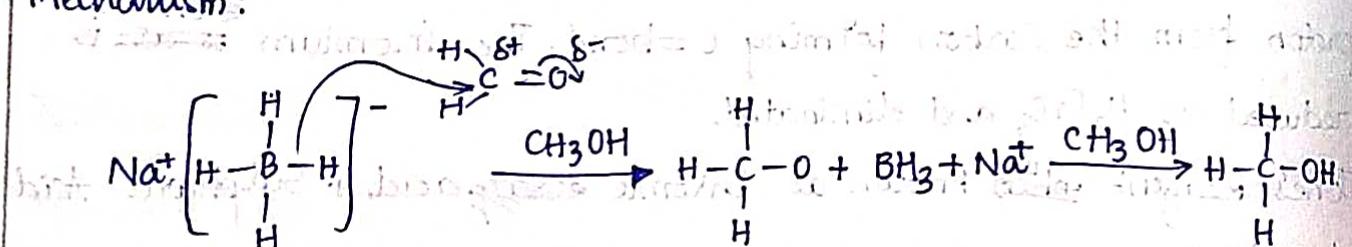


### REDUCTION WITH $\text{NaBH}_4$ :-

To reduce carbonyl compound. It is weaker reducing agent.



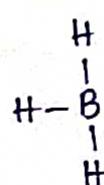
Mechanism:



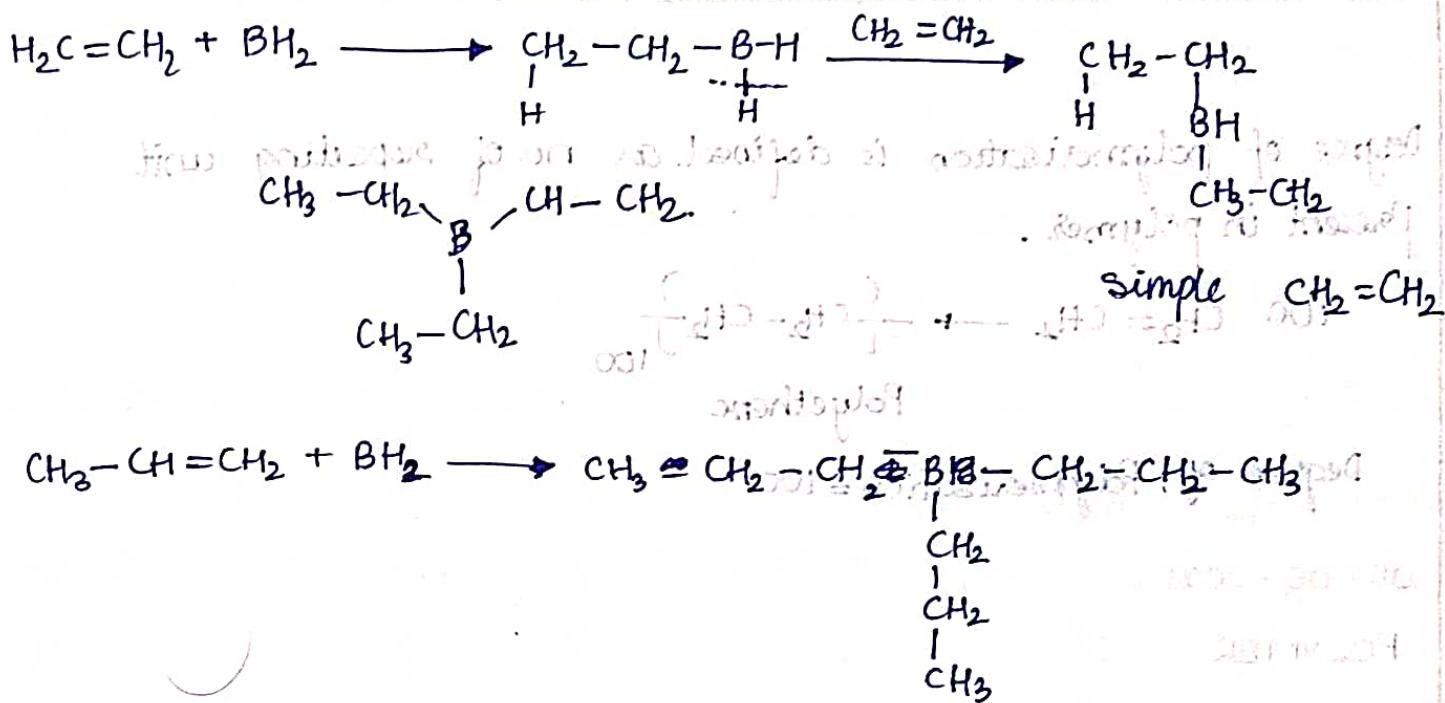
## \* HYDROBORATION OF OLEFINS: $(-\text{CH}_2=\text{CH}_2-)$ $(\text{HC}\equiv\text{CH})$

Borane is unstable compound ( $\text{BH}_3$ ) which exists in the form of diborane ( $\text{B}_2\text{H}_6$ ).

Borane is a Lewis Base.

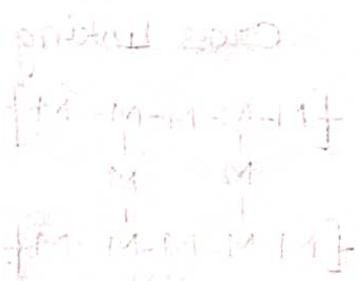


Addition of Borane to an alkene or alkyne is called hydroboration and the product is called alkyl borane.



Hydroboration reactions are carried out ~~not~~ in Ethers or Tetrahydrofuran (THF). The ~~extent~~ of hydroboration depends on no. of hydro~~oxygen~~ atoms present in borane and nature of olefins. If  $\text{BH}_3$  is used in hydrochlorination, the above three steps <sup>are</sup> followed.

### \* STRUCTURE, SYNTHESIS AND ~~APPLICATION~~ APPLICATION OF PARACETAMOL:



NAME: Acetaminophen

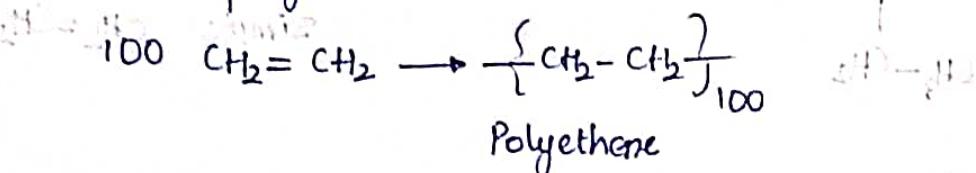
STRUCTURE:



STRUCTURE:

04-08-2022.

Degree of polymerisation is defined as no. of repeating unit present in polymer.



Degree of Polymerisation = 100

05-08-2022.

\* POLYMER

\* CLASSIFICATION OF POLYMER :

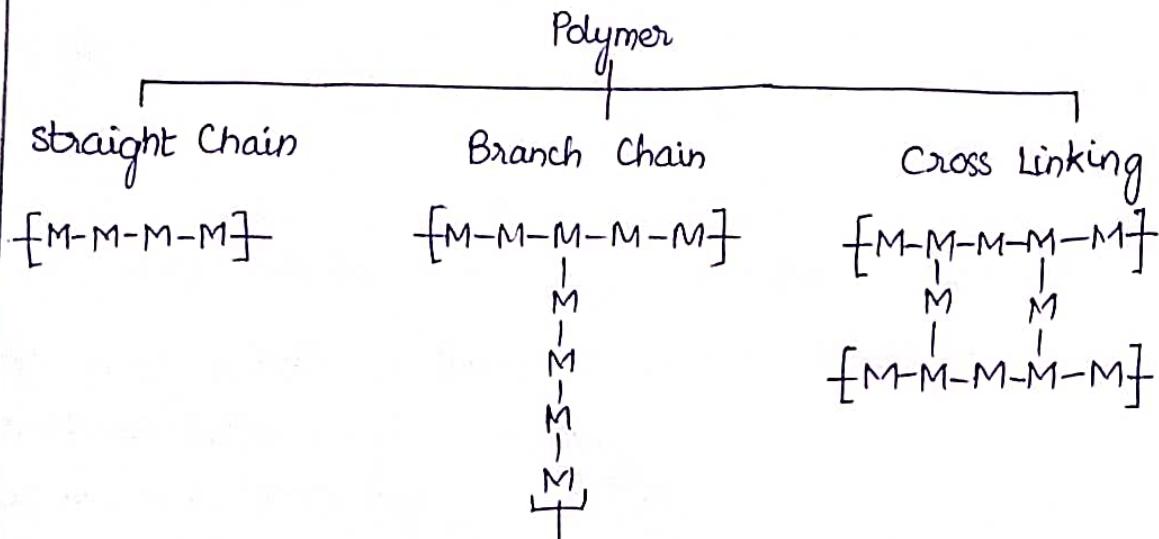
Polymer (straight chain)

Inorganic Polymer

Organic Polymer

Plastic      Rubber      Fibre

\* Classification of Polymer according to arrangement:



## \* TYPES OF POLYMERISATION:

### 1) Addition Polymerisation

1. Free radical polymerisation
2. Ionic polymerisation
3. Coordination polymerisation

### 2) Condensation Polymerisation

#### Addition Polymerisation

① It is a reaction that produces a polymer which is exact multiple of the monomer.

② Monomer contains double bond which is bifunctional.

③ The polymerisation takes place by self-condensation of the monomer, through the chain reaction.

④ In addition polymerisation, no byproducts are formed.

⑤ The polymer has the same chemical composition as the monomer.

⑥ The molecular weight of the polymer is sum of total molecular weight of the monomer.

⑦ The addition polymerisation takes place in three steps.

1. Initiation
2. Propagation
3. Termination

⑧ Exothermic and rapid process.

#### Condensation Polymerisation

① The reaction that produces polymer product which is not exact multiple of the monomer.

② The monomer contains functional group like  $\text{-OH}$ ,  $\text{-CHO}$ ,  $\text{-NH}$ .

③ The polymerisation takes place slowly step-wise via condensation reaction of the functional group.

④ In condensation polymerisation, a small byproduct is formed.

⑤ The polymer has not same chemical composition.

⑥

⑦ It is not a 3-step process. Directly, condensation process takes place.

⑧ Endothermic and slow process.

05-08-2022.

\* Free Radical Polymerisation involves three steps:

1. Initiation

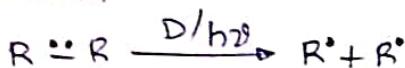
2. Propagation

3. Termination

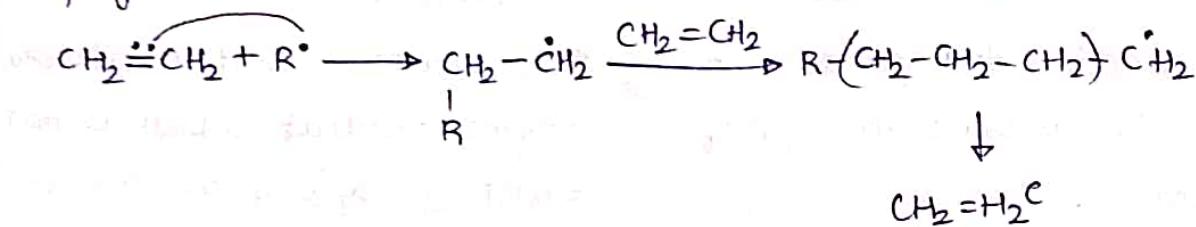
coupling reaction

disproportionation reaction

Initiation

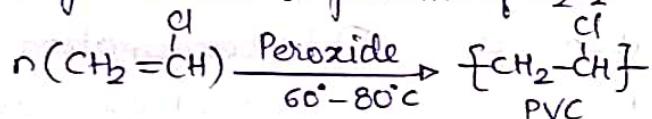


Propagation

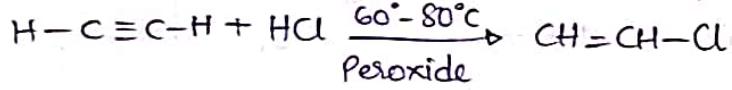


\* Preparation, Properties and application of vinyl chloride:

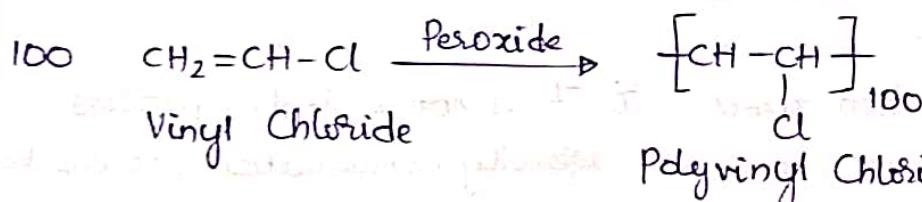
Polyvinyl chloride is produced by free radical chain polymerisation reaction of vinyl chloride in presence of  $H_2O_2$ .



Vinyl chloride can be prepared by preparing acetylene with hydrogen chloride



06-08-2022.



\* Properties of PVC:

1. PVC is a colourless, non-inflammable and chemically inert.
2. It has specific gravity around 1.33 and melting point  $148^\circ C$ .
3. Resistant to atmospheric conditions.
4. PVC is strong and brittle.
5. PVC is not stable to heat and UV radiation.

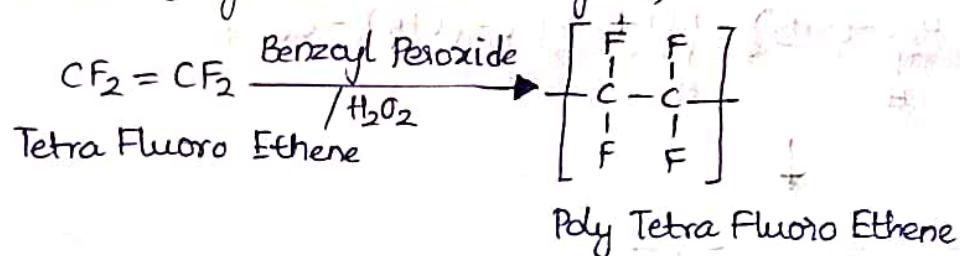
06-08-2022.

## 6. Plasticized PVC

### \* Engineering Applications :-

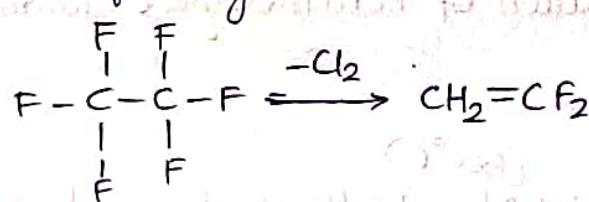
1. Plasticized PVC is used for electrical insulation, injection moulding articles.
2. It is used for making radio and telephone components, containers for storage and making building materials, aircrafts.
3. Unplasticized PVC is rigid and highly resistant to chemicals. It is used for making safety helmets, fridge components, tyres, cycle and motorcycle mud guards.

### \* TEFLON (Poly Tetra Fluoro Ethylene):



Common Name: Teflon

1. Teflon is obtained by free radical chain polymerisation of tetrafluoro ethene via ~~free~~ in presence of benzoyl peroxide or  $\text{H}_2\text{O}_2$ .
2. Tetra fluoro ethene is produced by dechlorination of syn dichloride in presence of catalyst.



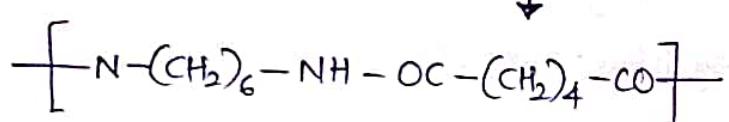
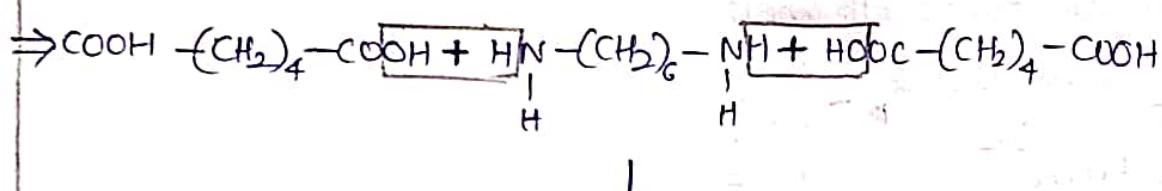
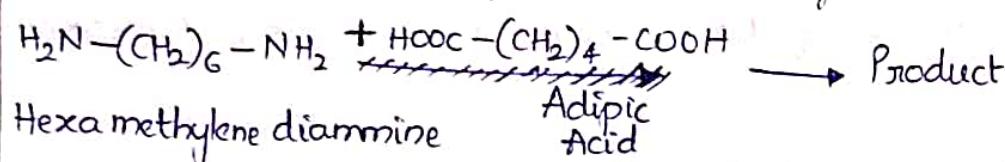
### \* Properties of Teflon:

1. Due to the presence of highly electronegative atom, teflon has got high melting point (above  $350^\circ\text{C}$ ).
2. Very high chemical resistance.
3. High Density. ( $2.12 \text{ g/cc}$ ).
4. It is very strong hard polymer that can be used in machinery for drilling and punching.
5. Teflon has very good insulator properties.
6. It possess abrasion.

★ Engineering Applications:

1. It is a very good insulating material for motors. It is used as cable and wire.
2. It is used for making gaskets, pump parts. Due to its extreme chemical resistance nature, it is used for making pipes for chemical transportation.
3. It is also used as coating material for non-sticky pans.

★ NYLON 6,6 : (Example of Condensation Polymerisation).



Nylon 6,6

1. Nylon belongs to polyamide class of synthetic polymers which have repeating amide groups.
2. Nylon 6,6 is produced by condensation of hexa methylene diamine and adipic acid.

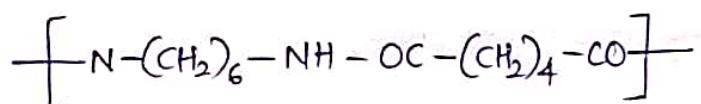
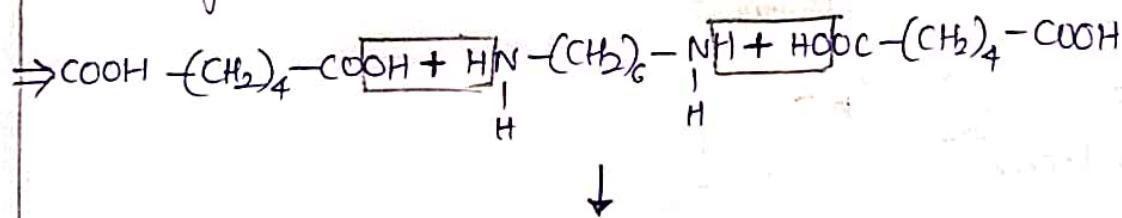
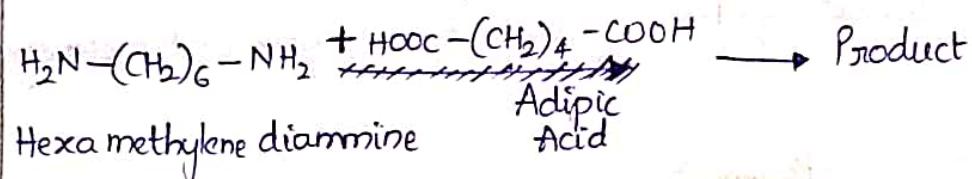
Properties :

1. Nylon 6,6 possess high melting point due to the hydrogen bonding b/w hydrogen of amide group and oxygen of carbonyl group.
2. Nylon 6,6 fiber has good strength. They are light and tough.
3. They absorb little moisture. Thus they are dry in nature. The fibers are flexible and return to original shape after use.
4. The fibers easily bend with ~~heat~~<sup>wool</sup> to

★ Engineering Applications:

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(500°C)

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4. The fibers easily bend with ~~wool~~ to

06-08-2022

## \* Engineering Applications :

- It is used for making socks and carpets .
- It is used for making

## UNIT - 5 : SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

Cosmic rays	X rays	UV rays	visible	near IR	micro waves	radio waves
-------------	--------	---------	---------	---------	-------------	-------------

→ increases

← Energy increases

Magnetic Resonance Imaging (MRI)

The study which deals with the interaction of electromagnetic waves (or) radiation with matter is called Spectroscopy.

$$E = \frac{hc}{\lambda} \quad \lambda \propto \frac{1}{\nu}$$

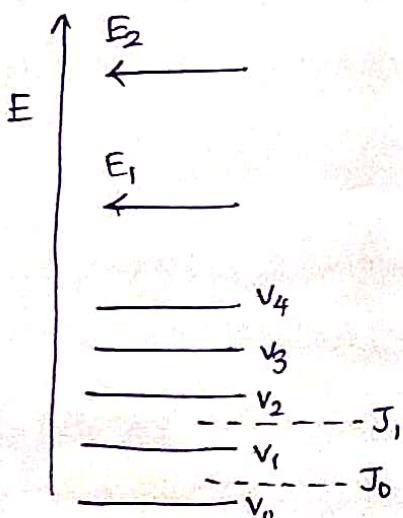
\* Beers-Lambert Law :-

$$A = \epsilon c l$$

absorpti  
vity      molar  
absorptivity      concentration  
                    of solution

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

incident beam of  
light  
Transmitted beam

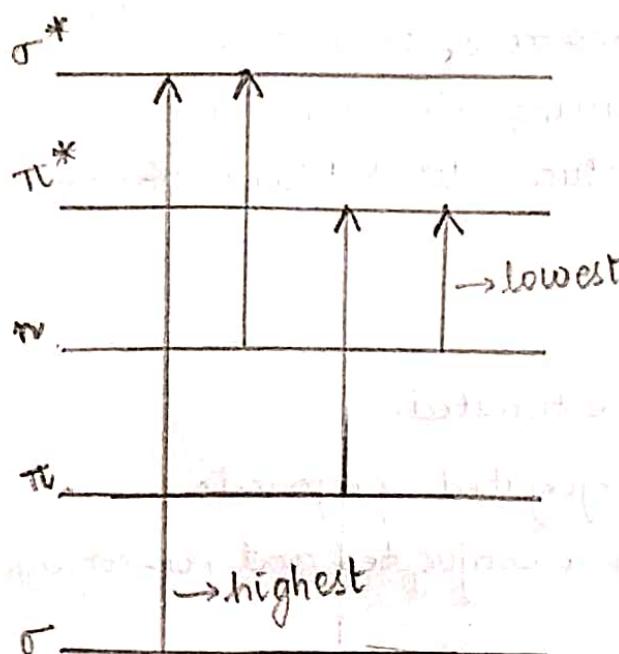


$$E_0 > E$$

$$\gamma_0 > \nu_1 = \text{Vibrational energies}$$

$$J_0 > J_1 = \text{Rotational energies}$$

## \* Types of Electronic Transition:-



- (1)  $\sigma \rightarrow \sigma^*$
- (2)  $\pi \rightarrow \pi^*$
- (3)  $n \rightarrow \pi^*$
- (4)  $n \rightarrow \sigma^*$

### (1) $\sigma \rightarrow \sigma^*$

The excitation between bonding  $\sigma$  & antibonding  $\sigma^*$  orbitals requires large energy corresponding to absorption in UV region.

Eg:  $\text{CH}_4$ , all alkanes, etc.

### (2) $\pi \rightarrow \pi^*$

This transition occurs in a compound that contains double, triple bond and even in aromatic compounds (=bond)

Eg, Ethylene ( $\text{CH}_2 = \text{CH}_2$ ) Absorption at 180 nm.

### (3) $n \rightarrow \pi^*$

Occurs in the molecule that must have non-bonding electrons in the atomic orbital.

Eg: Aldehydes and ketones, Absorption at 200 nm.

### (4) $n \rightarrow \sigma^*$

The excitation of an electron in an unshared pair bond to an antibonding  $\sigma^*$  orbital is called non-bonding  $\sigma^*$  condition.

Eg: Halogens, ~~Alkalis~~

## \* Application of UV-visible spectroscopy :-

### 1. Detection of functional group:

UV spectroscopy is used to detect the presence of chromophore.

Chromophore = group responsible for producing color in molecule.

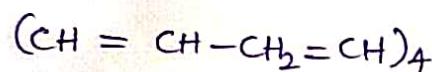
Auxochrome = the group that does not produce color but will intensify the color in the molecule.

### 2. Extent of conjugation:

In ~~pole~~-enes  $R-(CH=CH)-R$  can be estimated.

### 3. Distinction in conjugated and non-conjugated compound:

It is also used to distinguish between a conjugated and non-conjugated compound.



### 4. Identification of Unknown Compound:

### 5. Elucidation of structure with vitamins A and K:-

It is useful for the elucidation of the structure with  $K_1$  and  $K_2$  and also those of  $A_1$  and  $A_2$ .

$A_1$  absorbs 325 nm.

$A_2$  absorbs 351 nm.

due to the presence of additional ethylenic bond.

### 6. Determination of ~~con~~ conjugation of geometrical isomers:

→ cis-isomer and trans-isomer.

Eg: cis stilbene  $\lambda_{max} = 283$  nm

trans stilbene  $\lambda_{max} = 295.5$  nm

### 7. Determination of strength of H-bond of carbonyl compound:

In polar and non-polar ~~solvent~~ compounds, the strength of H-bond can be determined.

11-08-2022.

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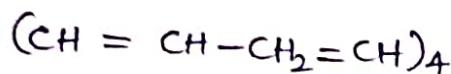
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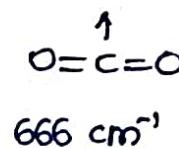
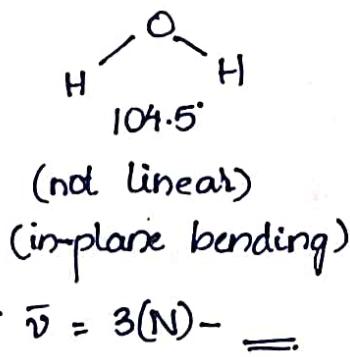
In polar and non-polar ~~solvent~~ compounds, the strength of H-bond can be determined.

\* Number of fundamental vibration:

- 1) Stretching vibration
- 2) Anti-symmetric stretching vibration
- 3) In-plane bending
- 4) Out-of-the-plane bending

• Homo bimolecular gases are IR inactive due to zero dipole moment.

• H<sub>2</sub>O molecule      • CO<sub>2</sub> molecule.



•  $\bar{v} = 3(N) - \underline{\underline{\quad}}$

\* NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY:

MRI - Magnetic Resonance Imaging.

Nuclei that have an odd number of proton or odd number of neutron or both (odd no. of proton and neutron) have property called spin that allowed them to study by NMR.

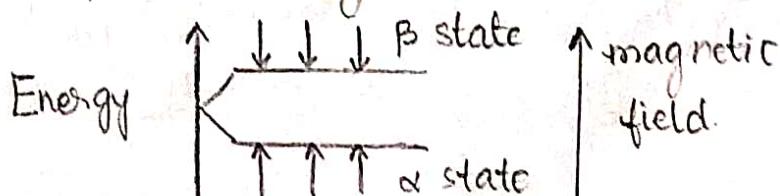
The NMR is based on <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>N, <sup>31</sup>P.

The nuclei such as <sup>12</sup>C, <sup>16</sup>O do not have spin. Therefore, cannot be studied by NMR.

$\alpha$  and  $\beta$  spin states:

Charge particle have magnetic moment and they behave like small bar magnet. In absence of an applied magnetic field, the magnetic moment of a nuclei are randomly oriented.

However, when placed in applied magnetic field, the magnetic moment of the particle is aligned.



18-08-2022.

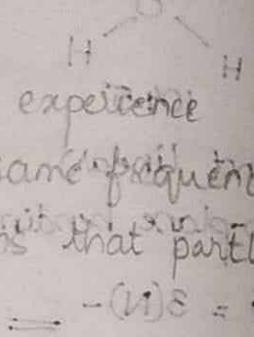
$$\Delta E = h\nu$$
$$= \frac{e\gamma}{2\pi} B_0$$

$\gamma$  = gyromagnetic ratio

$$H(\gamma) = 2.675 \times 10^8 \text{ T}$$

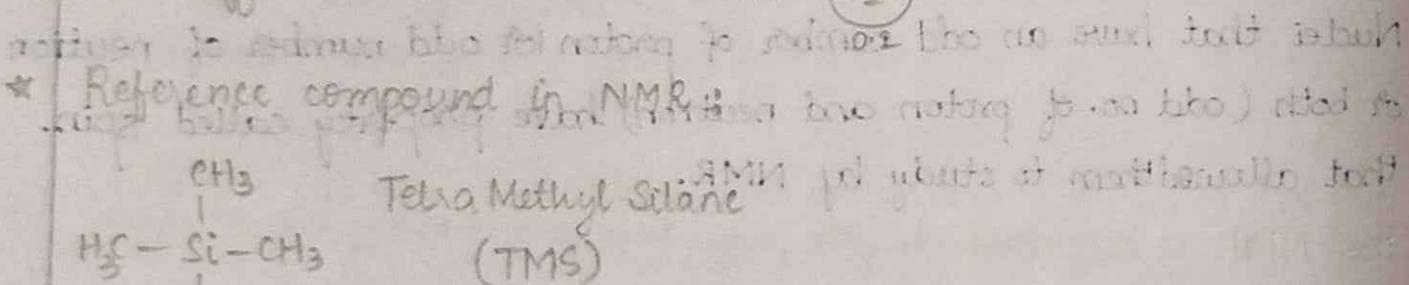
18-08-2022 (Afternoon Session)

- The frequency of the NMR signal depends on the strength of the magnetic field experienced by the nucleus.
- If all the molecule's hydrogen proton in the molecule experience same magnetic field effect, signal will come with same frequency.
- However a nucleus embedded in a cloud of electrons that partly shields the applied magnetic field.



:  $B_{\text{effective}} = B_{\text{applied}} - B_{\text{local magnetic field}}$

$$\text{Eq: } B_{\text{eff}} = 1.5 \text{ T} - 0.2 \text{ T} = 1.3 \text{ T} \quad 1.5 \text{ T} \rightarrow \text{H}_2\text{O}$$

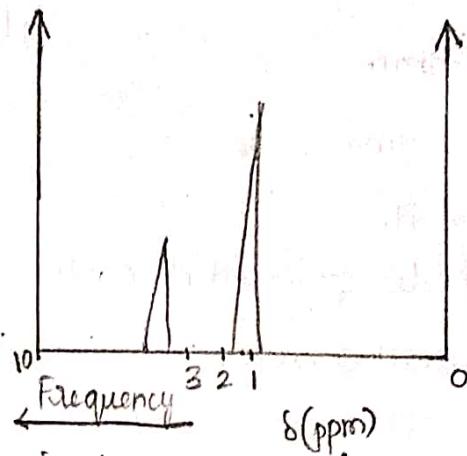


Q) Why we use TMS as reference compound?

Answer) The most commonly used reference compound for NMR is TMS because it is highly volatile (Boiling Point = 26.5°C)

• The methyl proton in TMS are in more electron-rich environment because silicon has less electronegative than carbon.

• Consequently, the signal from the methyl proton of the TMS is at lower frequencies than most of the other C.



### \* Chemical Shift:

- The chemical shift is a measure of how far the signal is from the signal of reference compound.
- The signal of TMS will always appear at  $\delta = 0$ .
- Date: 19-08-2022.
- Nuclei are NMR active that have odd no. of proton, odd no. of neutron or both.

### Tutorial (Unit 5)

Date: 26-08-2022.

#### Tutorial - 3

##### Important Topics

Date: 01-09-2022.

- $SN^1$  and  $SN^2$  Reactions
- Nuclear Magnetic Resonance
- Markownikoff and anti-Markownikoff Rule
  - ↳ Free Radical Polymerisation Reaction
  - ↳ Initiation, propagation, termination
  - ↳ Coupling
  - ↳ disproportionation
- Mechanism of reduction of carbonyl compound with  $NaBH_4$ ,  $LiAlH_4$ .
- Hydroboration
- Explain mechanism of addition of  $RMgX$  to carbonyl compound;
- Rate of corrosion increases in presence of  $O_2$ . Why?
- Sacrificial Anodic Protection
- Impressed Current Cathodic Protection.

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- Explain hot dipping method with diagram.
- waterline corrosion and galvanic corrosion
  - ↳ corrosion always takes place at anode.
  - ↳ corrosion will happen more at poorly oxygenated area.
- Define corrosion. Explain chemical corrosion.
- Pitting corrosion.

Q4

- Application of UV visible and IR (5 applications each)
- Principle of NMR (Any two applications) 3 marks.
- Bathochromic - Red shift i.e. shift towards wavelength shift
- Chromophore
- $\text{CO}_2$  has 4 theoretical modes of vibration  $3N-5 = 3 \times 3 - 5 = 4$ .
- How fingerprint region differ from functional group region?

\* Objective :-

- Galvanisation : coating of zinc to prevent corrosion.
- Degree of Polymerisation : No. of repeating units of the monomer.
- Carbocation : intermediate formed in  $E'$  and  $SN^{2+}$  reactions.
- Addition of HBr in olefins in presence of peroxide is
  - ✓ 1) electrophilic
  - 3) free radical
  - 2) nucleophilic
  - 4) None
- Monomers in Nylon 6,6 : Hexamethylene diamine and adipic acid.

. Forbidden electronic transition:

- ①  $\sigma \rightarrow \sigma^*$
- ②  $\pi \rightarrow \pi^*$
- ③  $\sigma \rightarrow \pi^*$
- ④ Both ① and ②

. Electronic transition takes place only in UV-visible range.

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- Addition reaction occurs in compound containing multiple bonds.
- Jones reagent:  $\text{CrO}_3 + \text{H}_2\text{O} + \text{H}_2\text{SO}_4$
- NMR & MRI full form = Nuclear Magnetic Resonance and Magnetic Resonance Imaging
- Aspirin  $\rightarrow$  2-acetoxy benzoic acid
- Paracetamol

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- UV-visible range  $\Rightarrow$  200 - 750 or 800 nm
- $\text{MoO}_2$  = Molybdenum Oxide undergoes waterline corrosion.
- Reducing agent gives electrons.

1. a) With help of neat diagram, explain the hot dipping of galvanisation. (3M)  
b) Explain galvanic corrosion and waterline corrosion. (2M)
2. a) Explain  $\text{S}\text{N}^2$  reaction. Why it undergoes Walden Inversion?  
b) Write 2 methods to terminate the polymerisation reaction.
3. a) 4 applications of UV visible spectroscopy  
b) Principle of NMR and write any two applications.
4. a) Define Corrosion. Explain the mechanism of dry corrosion.  
b) Write any 5 factors that affect corrosion rate.
5. a) Write the mechanism of reduction of carbonyl compound with  $\text{NaBH}_4$ .  
b) Explain the mechanism of free radical polymerisation.
6. a) What is order of reaction? Explain the mechanism of  $\text{S}\text{N}^1$  reaction with examples.  
b) Write the
7. a) Theoretically 4 fundamental modes for  $\text{CO}_2$ . Why 2 (practically)?  
b) Define chemical shift.