

# Lubricants

IMP

→ Lubricants are those substances which can reduce frictional resistance bet<sup>n</sup> 2 moving <sup>their</sup> parts or sliding surface.

Ex:- Grease,  $\text{MoS}_2$ ,  $\text{C}_6\text{O}$ , teflon.

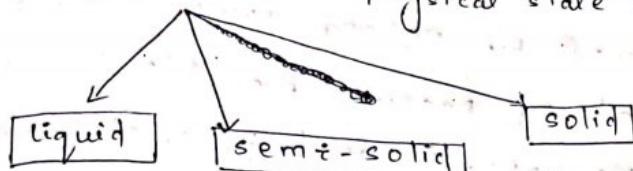
## Objectives of lubrication:-

Some of the objectives are:-

- To reduce the frictional resistance.
- To reduce wear and tear loss.
- To reduce noise.
- To reduce maintenance cost & running cost of machine.
- To prevent the machinery parts from corrosion.
- To reduce wastage of energy and thus increasing the efficiency of machine.
- It acts as coolant or cooling agent.
- It acts as heat transfer medium.
- It is used to restrict the entry of dust and moisture into the moving parts.
- It also acts as sealing agent or sealant.
- It is used to prevent leakage of gas or liquid from a container.
- It is used to transfer or dissolved the unwanted (foreign) particles.

## Classifications of lubricants:-

① On the basis of physical state of the lubricant.



Ex:- Vegetable  
or soyabean  
salt,

Animal oil,  
(lard & Tallow)

Mineral oil  
(HC oils)

Ex:- Grease  
(Na-based  
Ca-based  
Li-based)

Ex:- Cob,  
Graphite,  
 $\text{MoS}_2$ , Teflon tape,  
Talc.

② On the basis of application of the lubricant.

- Refrigeration oil
- Internal combustion oil
- Heat transfer oil
- IC engine oil
- cutting oil
- Transform oil

## Properties of Lubricating oil :-

Properties of lubricant should be properly understood, bcoz it helps us for selecting a suitable lubricant for a particular application.

(1) Viscosity :-  
It is the resistance offered by a fluid or liquid to its own flow. If viscosity is very

low, the wear and tear loss will be ~~less~~ more.

### 3) Kinematic viscosity:-

It is measured by noting down time of flow in second by passing oil flowing a specific volume of oil through a standard orifice from a fixed height under its own weight.

### ★. Viscosity index:-

It is a measure of rate of change of viscosity with change in temperature. For a good lubricating oil viscosity index would be high. (Min<sup>m</sup> change of viscosity with change in temp.).

One can increase the viscosity index of an oil by adding polymers & hydrocarbons. (High molecular weight like wax).

### (2) Acid value:-

No. of KOH required to neutralise acids obtained by hydrolysis of 1g of oil. For a good lubricating oil acid value should be less than 0.1.

### (3) Iodine value:- (I<sub>2</sub> value)

It is the no. of grams of iodine required to react with 100 gm. of oil.

For a good lubricating oil  $I_a$  value should be less than 50.

Drying oil  $\rightarrow I_a > 140 \rightarrow$  linseed oil

Semi-dryings  $\rightarrow 50-140 \rightarrow$  soyabean oil.

Non-drying  $\rightarrow < 50 \rightarrow$  coconut oil (castor oil)

$I_a$  value gives information about ~~to non-saturation~~

& unsaturation and volatility of oil.

#### (4) Flash point and fire point:-

It is measured using Kenneth's apparatus

Flash point: It is the lowest temp. in degree centigrade

at which an oil gives efficient inflammable vapour and gives a temporary flash of light when pilot flame is brought near to it.

#### Fire point:

It is the min temp. at which oil gives sufficient vapours and catch fire and burns at least for 5 seconds continuously when pilot flame is brought near to it.

$\rightarrow$  For a good lubricating oil, it should be much higher than working temperature.

It gives about Volatility of oil.

#### (5) Cloud point and pour point:-

These 2 parameters helps us to select a particular lubricant in a cold cond'.

- It is the temperature at which oil becomes cloudy upon pulling to lower temp. (Cloud point)
- It is the temp. at which an oil stops or ceases to flow when it is cooled. (Pour point)
- For a good lubricant thinner under cold condition it should be low.

#### (6) Thermal stability :-

It should be high in general, it shouldn't undergoes thermal decomposition during normal working temperature.

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#### (7) Carbon Residue:-

For a good lubricating oil carbon residue is as low as possible. It leads to wear & tear loss of the machinery part.

#### (8) Mechanical stability :-

For a good lubricating oil, mechanical stability should high, it should withstand high load during working.

#### (9) Steam emulsification Number:-

It is a time in second required to separate oil and water from an emulsion as separate layers at  $90^{\circ}\text{C}$ . In general, for a good lubricating oil, it should

have low steam emulsification no.  
For cutting oil high steam emulsification no. is needed.

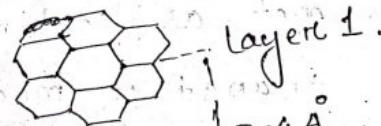
### Solid Lubricants:-

(Graphite, Mo<sub>2</sub>, Teflon tape, Mo<sub>2</sub>, Talc).

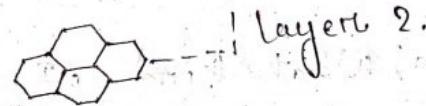
Q: Why graphite and Mo<sub>2</sub> acts as solid lubricants.

(i) Graphite:- It is layer st<sup>rc</sup>: the adjacent layers are separated by a distance of  $3.4 \text{ \AA}$ . The adjacent layers are held together by a weak vanderwells force of attraction. so, a shearing force is applied on it the adjacent layers slip past each other to reduced frictional resistance.

Q: Give reason that graphite can acts as lubricant even



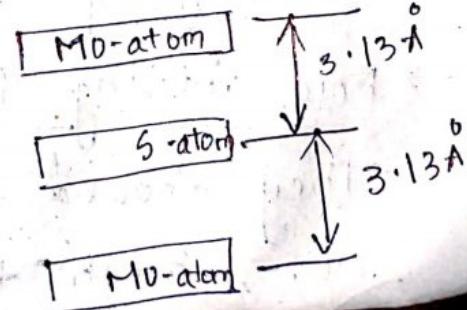
in the surface of moon.



A: It has very high viscosity index. It means there will be minimal change in viscosity with change in temp.

change in viscosity with change in temp.

(ii) Mo<sub>2</sub>:- It has sandwich st<sup>rc</sup>. (layer st<sup>rc</sup>). Hence a layer of sulphur atom lies bet<sup>n</sup> 2 layers of molecular atoms. Adjacent layers are separated by  $3.13 \text{ \AA}$  and help together by weak vanderwells force.



When a force is applied on its the adjacent layers slipped pass each other & reduced the frictional resistance bet<sup>n</sup> the two layers.

### Applications of Lubricants:-

For selecting a lubricant for a particular application we have to consider following 3 important points.

1. Working cond<sup>n</sup> of the machine.  
(Temperature, speed (low/high), load)
2. Various types of role to be it has to play.  
(Beside acting as lubricant, it has to act as coolant or to check medium or heat transfer medium).
3. Properties of lubricant.

(a) What kind of lubricant we have to use:-

→ Ic engine:-

We need a lubricant whose viscosity index is very high. Volatility should low, thermal stability should be high.

Generally, mineral oils with additive like graphite,  $\text{MoS}_2$ , chlorinated hydrocarbons

→ For cutting tools:-

They should have high steam emulsification no., high flash point & fire point,

adjacent  
reduced  
two

low volatility, high thermal stability.

ex:- Naphtha-based oil is used.

→ For delicate instrument :-

For scientific instruments, watches, showing machine etc.

All these instruments are subjected to low load and high speed.

Light oil or machine oil are generally used.

→ For refrigerators :- 04/12/19

Refrigerator works at very low temperature.

so, we have to choose a lubricant of low pour point and ~~cloud~~ point.

→ The Gears :-

They are subjected high pressure & load.

Lubricants, mechanical stability should be high. flash & fire point should be high. viscosity should be high. Mineral oil should be suspended with ~~not~~ graphite, fullerene,  $\text{MoS}_2$  etc.

→ In transformer :-

In this insulation is important and also the oil should acts as good heat transformer medium.

so, the lubricant with high dielectric constant, excellent heat transfer capacity

low pour point, high flash point, low

viscosity is required.

so, oils like paraffinic based oil, poly

aromatic hydrocarbon, polychlorinated

hydro-carbon etc.

### → Spindles in Textiles industry :-

Light oils i.e. low viscous oil basically machine oils are used of less oiliness and low volatility.

### Mechanism of lubrication :-

There are 3 types of mechanisms are there to express mechanism of lubrication.

#### ① Extreme pressure lubrication Mechanism.

(Machines are subjected to high pressure, high speed & high temp.) .

#### ② Thick film / fluid film / hydrodynamic lubrication mechanism (low load and high speed).

#### ③ thin film / boundary lubrication Mechanism ~~# mark~~ (high load and low speed).

Q:- What is lubricating oil. Discuss mechanism of extreme pressure lubrication.

→ When the two sliding surfaces under high pressure and speed, a local high temperature is attempt  $\rightarrow$  so, a liquid lubricant helps to stick <sup>to</sup> the inner side of 2 sliding surfaces and it may decompose and vapourise at high temp.  $\rightarrow$  so to meet this extreme cond<sup>n</sup> special additive to the lubricating

oil, these ~~parts~~ are known as extreme pressure additives. → These are organic compounds of Cl, P, S etc., tricresyl phosphate, chlorinated esters and chlorinated hydrocarbons.

- In this case 2 sliding surfaces are separated by a thin layer of lubricant of thickness less than ( $<$ )  $1000\text{ \AA}$ .
  - Under the application of high pressure & high speed, the additives in the lubricating oil react with metal (Fe) of the metallic surface to form metal chloride or metal sulphides or metal phosphide.
  - These have melting point is very high,  $> 650^\circ\text{C}$ , causes excellent metallical strength.
  - This is the reason why the lubricating oil with extreme pressure additives serviced as good lubricants under high temp., speed & cond<sup>n</sup> or pressure.
  - If some reason, lubricating film is broken then a new film is immediately formed to do the lubricating job.
- Characteristics :-
- Viscosity index should be high
  - Low volatility
  - Excellent Oilyness
  - High flash & fire point.

- excellent thermal and mechanical stability.
- low carbon residue.

### Application :-

- Generally this is applicable lubrication is complete mixture, crans, machining tools, railway track joints etc.

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### (2) Thick film lubrication mechanism :-

- In thick film lubrication, a thick layer of lubricant, thickness of lubrication is  $1000\text{ }\text{\AA}$ .
- A thick layer of lubricant is placed b/w two sliding surface.
- This mechanism is applicable where load and speed is high.
- Usually applicable in delicate instrument like lubrication of scientific instruments like microscope, spindles, watches etc.

For this type of lubrication, characteristic

- ↔ High oiliness
- ↔ Low pour point
- ↔ " Volatility
- ↔ " viscosity
- ↔ High flash point
- ↔ Good corrosion resistance.
- In this, oiliness plays an important role, because due to oiliness only it can stick to the inner side of the tool

sliding  
→ No U metals  
→ A h lubr  
→ If oth  
→ Us ve  
( h )

③

→ T

→

→

sliding surfaces.

→ No chemical reaction occurs bet<sup>n</sup> lubricating oil & metallic surfaces.

→ A hydro-dynamic pressure developed by the lubricating molecules.

→ If the 2 sliding surfaces apart from each other by a small distance.

→ Usually light oils (mineral oils blended with vegetable oils) are preferred for low load & high speed cond<sup>n</sup>.

### ③ thin film / boundary lubrication

→ This mechanism is applied when the load is high & there is low speed and usually works when the temperature is very low.

→ In this, two sliding surfaces are separated by a thin layer of lubricant (thickness of layer is less than 1000 Å)

→ For this characteristics;

→ The oil molecules should have long hydro-carbon chains.

→ Molecule should have polar groups to promote adsorption.

→ High viscosity index, good oiliness, low pour point, good corrosion resistance & heat resistance.

In general minerals oil suspended with Mo<sub>2</sub> graphite are preferred.

- In this lubrication, the lubricant is attached to the inner wall of metallic sliding part by physical & chemical process or both, it means that the oil molecules get adsorbed by physical adsorption or chemical adsorption up to a depth of 5-10 nm.
- The applied load is carried by the adsorb layer of lubricant.
- This mechanism occurs in gear box lubrication, rollers, tractors, piston rings in internal combustion (Ic) engines.

The three types of lubrication mechanism, differentiate.

Types of Mechanism	Thickness oil layers	Working condition	Types of oil uses	Uses/ Application
Thick film mechanism	$t \sim 1000\text{A}^{\circ}$ (thickness)	Low load & high speed no load normal temp.	light oils or HC oil or mineral + vegetable oil.	Delicate instruments
Thin film mechanism	$t < 1000\text{A}^{\circ}$	High load & low speed normal temp.	veg/mineral oil with graphite/ $\text{MoS}_2$ .	Gear Box, Rollers,
Extreme Pressure	$t = 10 - 1000\text{A}^{\circ}$	High load High speed High temp.	Mineral oil or veg oil with extreme pressure additives.	Raising track joints, concrete mixture aircraft.

molecule.

## - Nano-chemistry :-

- It is a branch of science deals with the study of synthesis of nano-materials characterization and application of nano-materials.
- What is nano-material ?  
Those materials whose length or diameter or thickness lies in the range of 1-100nm.
- In general, nano-materials possess many improve properties as compare to bulk-material.  
The main reason is that the nano-materials have very high surface area to volume ratio.

$$\frac{S.A}{\text{volume}} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$$

⇒  $r \downarrow \frac{S.A}{\text{volume}} \uparrow$   
(size)      volume

### Properties :-

1. Nano materials posses excellent adhesive property.
2. Posses excellent medicinal properties.
3. Heat transfer property.
4. Excellent catalytic property.
5. Improve mechanical property.
6. Posses excellent sensing property.

## Synthesis of Nano-materials :-

In general, two types of methods are adopted.

### ① Top-down Method :-

→ It is basically a size reduction method, in this approach, material is allowed to break into smaller particles ( $1-100\text{ nm}$ ) by some physical process like grinding, crushing, milling.

Ex:- High energy ball milling.

Limitations :-  $\text{Mm. } \text{---} \xrightarrow{\text{by milling}} \text{---} \rightarrow \text{O } (1-10\text{ nm})$

- (i) Contamination of products occurs.
- (ii) It introduces defects / imperfections in the materials.
- (iii) Very difficult to get uniform size particles.
- (iv) By this process huge amount of Nano. material synthesis isn't possible.
- (v) Very difficult to get very smaller particles ( $1-10\text{ nm}$ ) of range.

### ② Bottom-up Method:-

→ This method refers to build-up a material from the bottom (very small size) i.e; by addition of atom to atom, molecule to molecule or clusters to clusters addition.

Ex:- 1) Chemical Reduction method.

2) Hydro-thermal method.

3) Combustion - method.

4) Microwave synthesis

### 5) Sol-gel method. 6) Green synthesis

• Atom ( $0.1-0.5\text{ nm}$ )



○ ( $1-100\text{ nm}$ )

#### Advantages :-

- It develops particles free from defects, has the ability to produce particles of uniform size, shape and distribution.
- It develops particles of excellent purities, quantity and quality.
- Some of these are environmental friendly method, or microenvironment like microwave synthesis.

### \* Green synthesis of nano-material:-

- It is a bottom-up method, in which biological substances is used to synthesize nano-particle cost effective & environmental friendly.
- In this, no toxic chemical are used plant itself contain reducing agent & stabilizing agent.
- Various plants are used like extracts of neem, aloe vera, tulsi, papaya, leaves are used.

#### Advantages :-

- It doesn't
- It is a
- Least disp

#### Raw material

##### 1. Precursors

i)  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$

ii)  $\text{AgNO}_3$

iii)  $\text{Zn}(\text{NO}_3)_2$

iv)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

##### 2. Reducants

$\text{NH}_2\text{Ni}$

citric acid

$\text{NaBH}_4$

##### 3. Stabilizers

→ It pre-

→ It hel-

organic

##### ② Inorganic

##### ③ Organic

- Advantages:
- It doesn't produce toxic waste;
  - It is a low cost synthetic route.
  - Waste disposal cost is very less.

raw materials for synthesis of nano-materials:

1. Precursor Salt :-

- i)  $\text{HAuCl}_4$  /  $\text{AuCl}_3$  /  $\text{Au(OH)}_3$  → For synthesis of Au nano-material.
- ii)  $\text{AgNO}_3$  → Ag nano particles.
- iii)  $\text{Zn(NO}_3)_2$  → ZnO nano particles.
- iv)  $\text{CuSO}_4$  →  $\text{Cu}_2\text{O}$  nano-particles.

2. Reducing agent :-

$\text{NH}_2\text{NH}_2$       Plant extracts  
citric acid      (Poly phenols Alkaloids)

3. Stabilising Agent or Capping Agent :-
- It prevents agglomeration of particles.
  - It helps in stabilising the particles.

Organic  $\leftrightarrow$  ① Plant extract I  
(poly phenol)  
Inorganic  $\rightarrow$   $\text{NH}_2\text{C}_2\text{H}_4\text{OH} \rightarrow$  ethanol amine  
surfactant.

② Organic  $\rightarrow$  Polymers  
i)  $\text{CH}_2 + \text{CH}_2$  (PVA, PVP)  
ii)  $\text{CH}_2 = \text{CH}_2$  (PVC, PTFE)

## Synthesis of noble nano particles :-

(Au & Ag particles)

### A) For Ag particles :-

→ Silver nano-particles can be synthesize by taking the neem, aloverca, papaya extract etc. and  $\text{AgNO}_3$  soln of less concentration.

### Synthesis :-

#### 1. Preparation of precursors salt soln.

Take some amount of  $\text{AgNO}_3$  soln, and dissolved in a water (ion free or deionize water) to prepare 10 ml. of  $1\text{mM}$  ( $10^{-3}\text{M}$ ) soln.

#### 2. Preparation of plant extract.

Take 10 g. of neem leaves & boiled it with 100 ml. water for one hour. Now, filter the extract by passing through a  $0.45\text{-}\mu\text{m}$  membrane filter to get a clear extract soln.

#### 3. Development of silver nano particles :-

Take 5 ml. of plant extract in to a 50 ml. beaker. Then placed it on a hot magnetic stirrer maintain at about  $140^\circ\text{C}$ . After this add 1 ml of  $\text{AgNO}_3$  soln to it

dropwise using a micro-pipette. After hot stirring for about 1 min the colour of the soln suddenly changes to

greyish brown colour.

It shows that the silver nano-particles have been formed. Now, preserve it for characterization.

### 1. Characterization of nano-particles.

It can be characterized;

- (1) UV visible spectro-photometer
- (2) X-ray diffracto-meter
- (3) Scanning electron microscope (SEM)

→ UV visible spectro-photometric analysis:-

In the UV visible spectrum (absorbance against

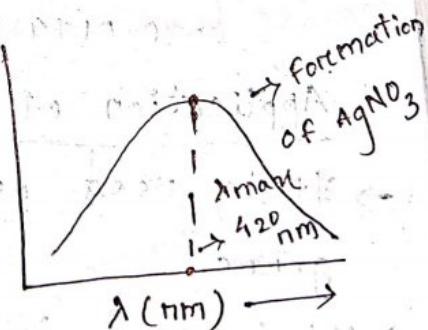
v/s wavelength field), a broad band appears near 420nm confirms formation of Ag nano-

particle.

This broad band is known as surface plasmon resonance (SPR) band. (This band arises due to collective oscillation of conduction band e<sup>-</sup> upon interaction of UV visible light. It is a temp. characteristic of nano-particle formation.

→ SEM :-

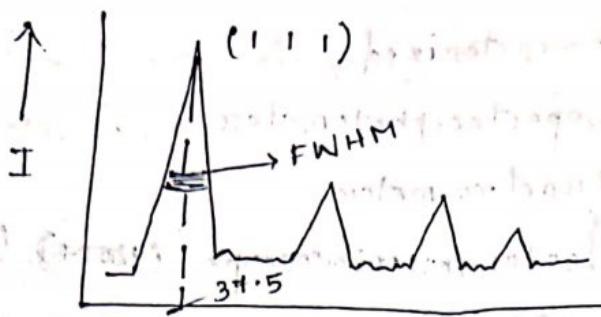
It gives information about shape, size and distribution of nano-particle.



→ X-ray diffraction pattern:

X-ray diffraction pattern is a plot of intensity of diffracted light against diffraction angle. Angle is  $2\theta$ . It gives information about the crystal type, crystallite size, etc.

In case of silver nano particles highly intense peak occurs at  $2\theta = 37.5^\circ$  correspond to (111), Plane of silver nano-particles.



Also we can calculate the crystallite size using Debye Scherrer eqn.

$$\text{crystallite size (nm)} = \frac{0.94\lambda}{B \cos \theta}$$

Where,  $\lambda$  = Wavelength of X ray =  $1.54 \text{ nm}$   
 $B$  = Full width and half maximum  
 of sub-peaks (in radian) (FWHM)  
 $\theta$  = diffraction angle

$$1^\circ = \frac{\pi}{180} \text{ radian}$$

$$= 0.0174 \text{ rad}$$

Application of silver nano-particles :-

- It is used as water treatment for killing germs.
- It is used in sensing application.
- Used in food packing.
- Used in cosmetics industry.
- Used in coatings.
- Used in textiles industry.
- Used in nano catalysts.

**B** For Au particles :-

### Synthesis

1. Preparation of plant extract:-

(same as Ag)

2. Preparation of precursors salt sol<sup>n</sup>:

Prepare 10 ml. of 100  $\mu$ M of HAuCl<sub>4</sub> by dissolving in calculated manner volume of ion free water.

3. Development of Au nano-particle:-

Take 5 ml. of extract sol<sup>n</sup> in a 50 ml. beaker & placed it on a hot magnetic stirrer at 60°C. Then add 1 ml of 100  $\mu$ M gold salt sol<sup>n</sup> dropped wisely. After stirring for about 2 min, colour changes to violet colour.

→ Formation of Au nano-particles

4. Characterization of nano-particles:-

→ UV visible analysis:-

In the UV visible spectrum, the SPR band appears near 520 nm, contains formation of nano-particles.

For rod shaped nano-particle, SPR band appears bet<sup>n</sup> 900-1100 nm.

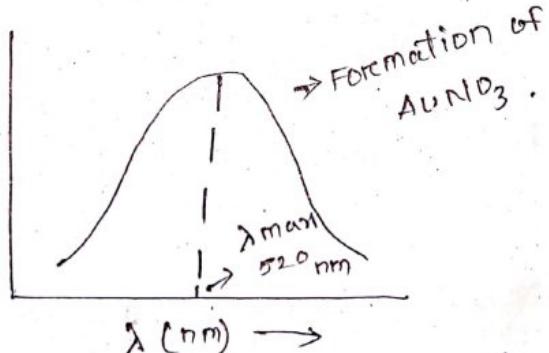
→ SEM:-

(Same as Ag)

→ X-ray pattern:-

It gives information about whether the nano-particles are

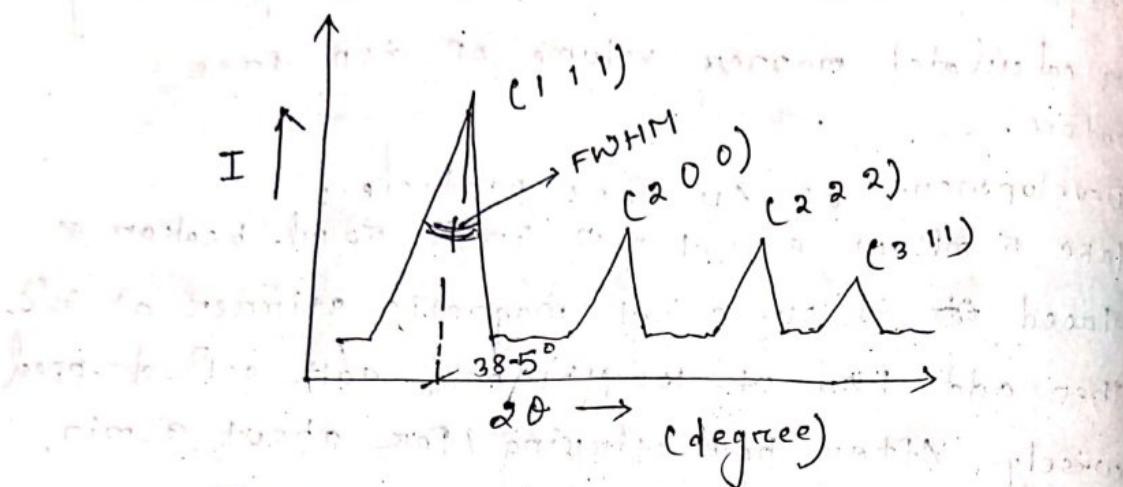
crystalline in nature, crystalline size and crystal lattice site.



From this pattern  $2\theta = 38.5^\circ$  corresponds to

(1 1 1) plane, confirms formation of  
Fcc nano-particles.

From this pattern we can calculate the  
crystallite size using Debye Scherrer eqn.



### Applications

- It is used in drug delivery.
- Used in photo-dynamic therapy.
- Used in bio-sensing as bio-sensor.
- Used in catalysis.
- Used in water treatment & cosmetics.

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# Synthesis characterization and application of Metal Oxide Nano Particles ( $ZnO$ & $Cu_2O$ ) :-

(i)  $ZnO$  :-

## ■ Synthesis of $ZnO$ nano-particles :-

Step-1 :-

- Preparation of aqueous plant extract.
- Take 10g of *habiscus* leaves in a 500 ml. beaker, add 200ml of deionised water into it. then boil it at  $100^{\circ}C$  by placing the beaker on a hot magnetic stirrer.

After 1 hour of heating cool the extract sol<sup>n</sup>.

Then pass the extract through a filter paper to get a clear sol<sup>n</sup>.

Store it for synthesis of nano-particles.

Step-2 :-

- Precursor salt (Preparation).
- Prepare 10 ml of 0.05 M  $Zn(NO_3)_2$  sol<sup>n</sup> by adding required amount of salt onto calculated volume of water.

Step-3 :-

## → Development of $ZnO$ nano-particles :-

Take 5 ml. of extract sol<sup>n</sup> in a 50 ml. of beaker.

Place it on a hot magnetic stirrer maintain at  $90^{\circ}C$ .

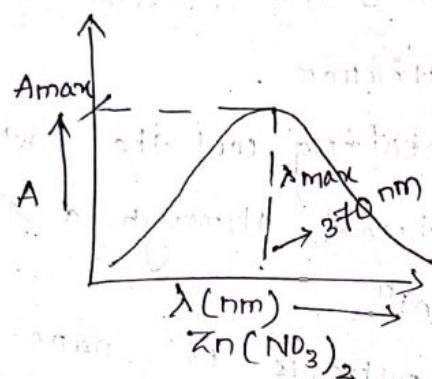
Now add 1 ml. of 0.05 M  $Zn(NO_3)_2$  sol<sup>n</sup>

into the beaker under hot stirring cond<sup>n</sup>. After hot stirring for about 10 mins white ppt. of ZnO are formed in it. The suspension is stored for its characterization.

### **[B] Characterization :-**

#### **(1) UV visible spectral analysis :-**

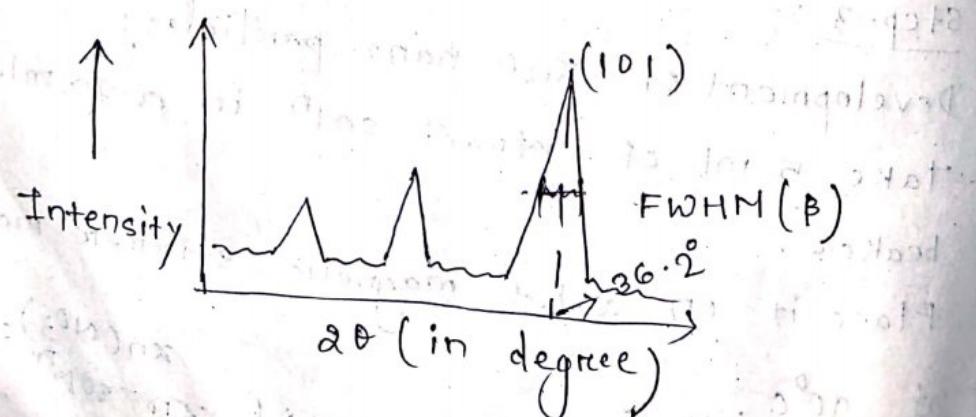
A broad absorption band found nearly 370 nm in the absorption spectrum, confirms formation of ZnO nano-particles of ZnO.



This is the SPR band of  $Zn(NO_3)_2$ .

#### **(2) XRD analysis :-**

From the XRD patterns we can find the crystal size, crystal lattice type whether the particles obtain amorphous or crystalline in nature.



From above XRD pattern we found that, highly intense peak at  $2\theta = 36.2^\circ$  corresponds to  $[1101]$  plane, suggests that ZnO has Wurtzite structure. The crystallite size can be determined in nm is

$$d(\text{nm}) = \frac{0.94\lambda}{B \cdot \cos \theta}$$

### (3) SEM analysis :-

SEM image gives information about shape, size and distribution of nano-particles.

### C Application :-

- It has excellent anti-bacterial & anti-fungal activities.
- It has gas sensing properties.
- It is used in coating industry.
- Acts as UV filtering agent.
- It is used in ceramic industry.
- Acts as corrosion inhibitor.
- Use in cosmetics.

### (ii) $\text{Cu}_2\text{O}$ :-

#### A Synthesis of $\text{Cu}_2\text{O}$ nano-particles :-

- Preparation of plant extract from leaves.
- Take 10g of orchid-leaves, in a 500 ml. beaker containing 200 ml. of water. Place it on a hot magnetic stirrer maintained at  $70^\circ\text{C}$ .

Now cool the extract soln and pass it through a filtering media to get a clear soln.

→ Preparation of precursor salt soln.

Prepare 10 ml of 0.5 M,  $\text{CuSO}_4$  soln.

→ Development of  $\text{Cu}_2\text{O}$  nano-particles:-

Take 5 ml of extract soln in a beaker & placed it in a magnetic stirrer maintained at about  $150^\circ\text{C}$ .

Now add  $\text{CuSO}_4$  soln into it dropwise.

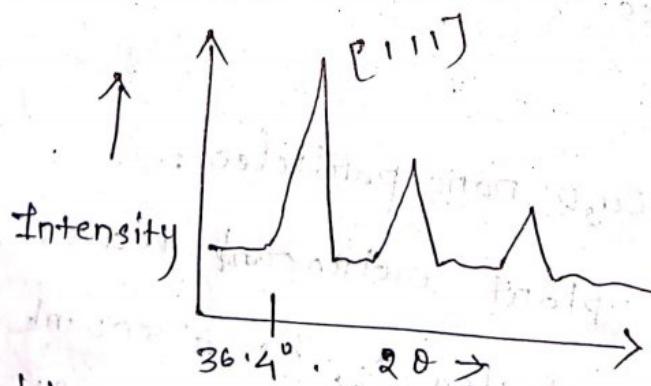
After some time of stirring (for 10 mins), blue colour changes to a reddish brown colour which suggest  $\text{Cu}_2\text{O}$  nano-particles.

### **[B] Characterization:-**

(1) UV visible spectral analysis :-

A broad SPR band appears near 470 nm in the spectrum confirms formation of  $\text{Cu}_2\text{O}$  nano-particles.

(2) XRD analysis :-



A highly intense peak obtained at  $2\theta = 36.4^\circ$  corresponds to  $[111]$  plane confirms cubic  $\text{Cu}_2\text{O}$  nano-particles.

### C Application:-

- Acts as an auto-catalyst.
- Acts as an anti-bacterial agent.
- It acts as anti-fouling agent.
- It is used in sensitive application.
- It acts as UV filtering agent.

## : Instrumental Techniques :-

31/10/19

(About Molecular Spectroscopy)

### Spectroscopy :-

- Branch of science deals with interaction of matter with electro-magnetic radiation.
- Spectroscopy concerns with investigation & measurement of spectrum obtained when matter interact with light.

### Molecular Spectroscopy :-

- It deals with study of interaction with study of molecules either with light or electro-magnetic radius.

#### Types :-

##### 1) Electronical Spectroscopy :- (UV-VIS Spectroscopy)

- It deals with the study of molecules & UV-visible visible light ( $200\text{nm} - 800\text{nm}$ ) by a molecule.
- Absorption of UV & visible light results in transition of  $e^-$  from ground state to excited state energy level. That's why it is otherwise known as electronic transition.

UV-visible spectrophotometer

##### 2) Vibrational Spectroscopy :-

- It deals with the study of interaction between molecular and IR light ( $800\text{nm} - 1\text{mm}$ )

→ Abs  
ν $\infty$   
3) R $\sigma$   
→ I $\tau$   
→ m  
→ e  
→ R $\sigma$

→ Absorption of IR light by molecule causes its vibration. (Infrared - IR).

3) Rotational Spectroscopy : (Microwave Spectroscopy).

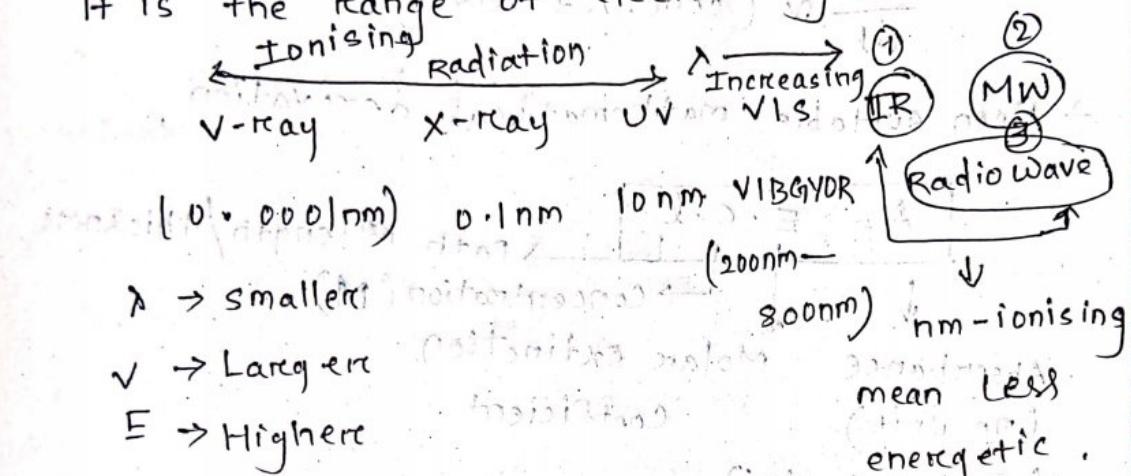
→ It deals with the study of molecule and microwave light.

→ Its wavelength ( $1\text{nm} - 30\text{cm}$ ).

→ Absorption of microwave light by a molecule results in rotation of a molecule.

Electromagnetic Spectrum :-

It is the range of electromagnetic radiations.



Interaction of light with matter :-

→ When a light of suitable frequency & wavelength is allowed to pass through a solid containing light absorbing substance, then small portion of light is absorbed by a molecule, small portion of light may be reflected at the interface and the rest will pass through simply.

## Light absorption law:-

(Beer-Lambert's law)

→ It states that when a mono-chromatic light is allowed to pass through a dil. soln of an absorbing medium, then the rate of decrease of intensity with the thickness of the absorbing medium is  $\propto$  to intensity of light as well as conc. of absorbing medium.

$$\frac{-dI}{dl} \propto (\text{conc.} \times \text{Intensity})$$

→ Upon suitable mathematical derivation,

$$A = E \cdot C \cdot l$$

↓              ↓              ↓  
 Absorbance    Concentration (M)    Path length/thickness  
 (no unit)       Molare extinction coefficient

Absorbance → A measure of extent of light absorption by an absorbing substance/molecule.

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

$I_0$  → Intensity of light before passing through the soln.

$I_t$  → Intensity of light after passing through the soln.

## Molar extinction Coefficient (E) :-

- It is a measure of strength of electronic transition
- It gives information about intensity of absorption band.

→ Unit ;

$$E = \frac{A}{C \cdot l} = \frac{1}{M \cdot cm} = M^{-1} \cdot cm^{-1}$$

## Transmittance (T)

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

(no unit)

The ratio of light after passing through soln to before passing through soln.

Relation between A and T :-

$$A = \log_{10} \frac{I_0}{I_t} = -\log \left( \frac{I_t}{I_0} \right) = -\log T$$

$$A = -\log T$$

$$\log T = -A$$

$$T = 10^{-A}$$

∴ (T) :-

$$T \times 100$$

By taking log both sides of ∴ T = T × 100

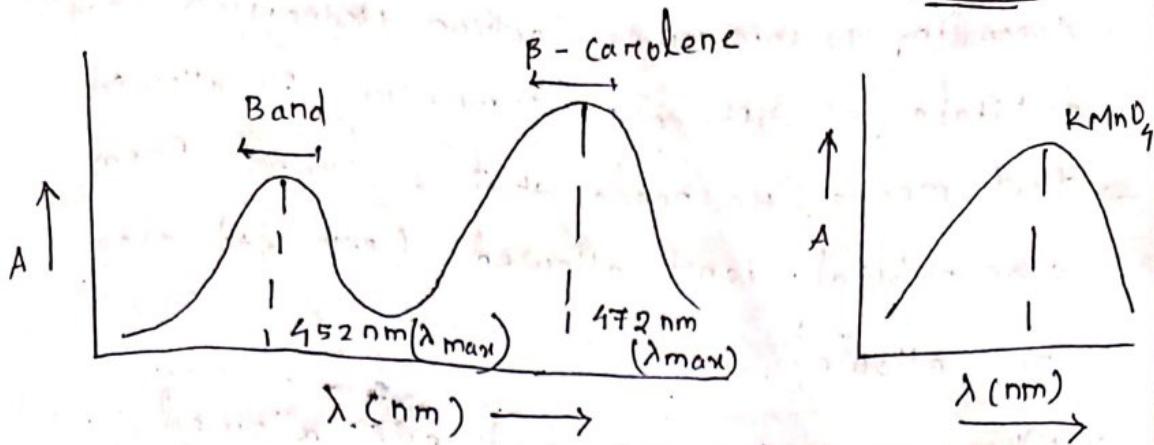
$$\Rightarrow \log (\% T) = \log (T \times 100)$$

$$= \log T + \log 100$$

$$= \log T + 2$$

$$\log \% T = -A + 2$$

$$A = 2 - \log (\% T)$$



Q "What is absorption band. Mention 2 imp parameters used to describe."

①  $\lambda_{\max}$  → Gives info. about the pos<sup>n</sup> of the band.

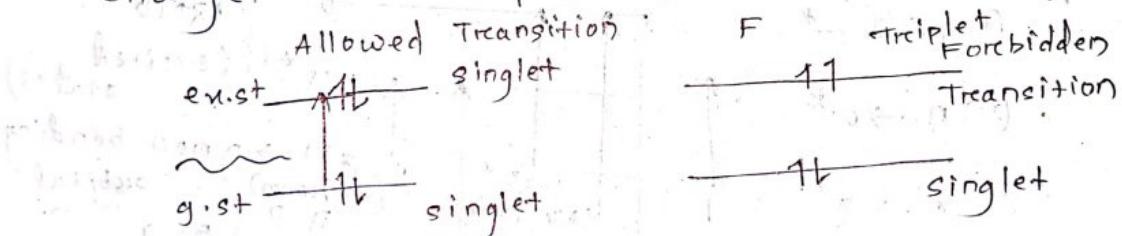
②  $\epsilon_{\max}$  → Gives info. about the height or intensity of the band height & intensity.

### Selection Rule:-

→ The restriction imposed on electronic transitions is known as selection rule.

#### ① Spin Rule:-

According to this rule electron transition can occurs bet<sup>n</sup> 2 energy levels without change in its spin. (Retention of spin)



$$\Delta S = 0$$

$S$  = spin multiplicity.

② Symmetry Rule :- (orbital rule)  
 According to this rule, electron transition bet' orbitals of different symmetry is allowed.  
 → that means its needs that  $e^-$  trans' from  $s \rightarrow s$  orbital isn't allowed. ( $P \rightarrow P$ ,  $d \rightarrow d$  also not allowed).  
 → Whence as  $P \rightarrow s$  &  $s \rightarrow P$ ,  $P \rightarrow d$  are allowed.

$$\Delta l = 0 \quad S \rightarrow S$$

$$\Delta l = \pm 1 \quad S \rightarrow P \quad (\text{allowed})$$

Whence  $\Delta l = 0$ , not allowed.

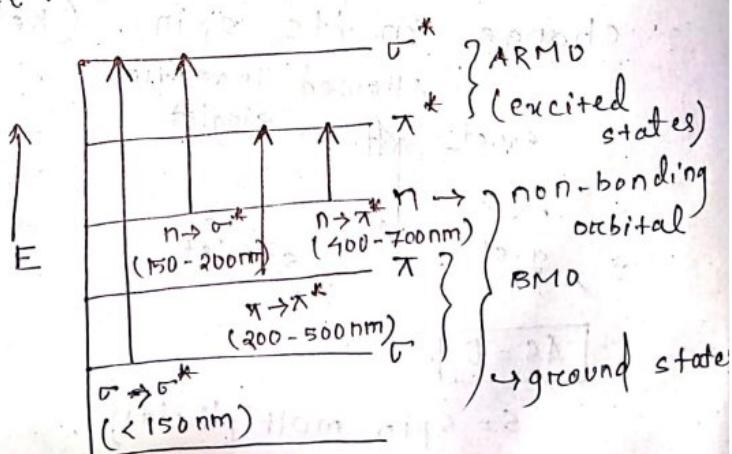
### Electronic transition in molecules:-

When a UV & visible light of suitable energy is absorbed by molecule, then trans' of  $e^-$  will occurs from the ground state molecular orbital ( $\sigma, \pi, n$ ) to excited state molecular orbital ( $\sigma^*, \pi^*$ ).

In general, 4 types of  $e^-$  trans' are found,

in a molecule.

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



①  $\sigma \rightarrow \sigma^*$

→ It can occurs by absorption of highly energetic light. (less than 150 nm)  $\rightarrow \lambda < 150$  nm.

→ this trans<sup>n</sup> can occur in molecule having  $\sigma$ -bond.

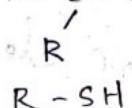
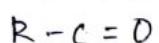
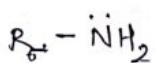
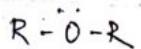
Ex:- alkanes (methane, ethane, ...)

②  $n \rightarrow \sigma^*$

→ this trans<sup>n</sup> can occur by absorption of light of wavelength. ( $150 > \lambda > 200$ )

→ this trans<sup>n</sup> will occur in a molecule having  $\sigma$  bond & non-bonding  $e^-$ .

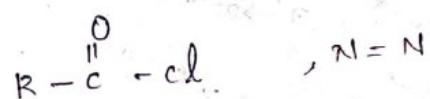
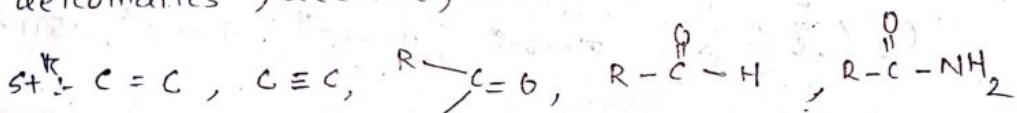
Ex:- Halogen compounds



③  $\pi \rightarrow \pi^*$

→ this trans<sup>n</sup> can occur by absorbing light of wavelength ( $200 > \lambda > 500$  nm).

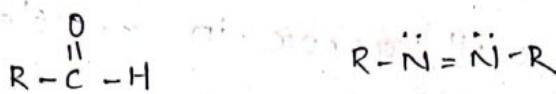
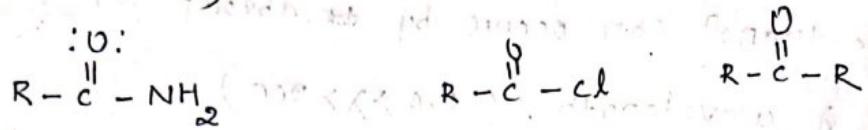
→ this trans<sup>n</sup> found in alkene, alkynes, aromatics, acetone, amide.



①  $n \rightarrow \pi^*$

→ This transition will occur by absorption of lowest amount of energy i.e; required light of wave length (400-700nm).

→ This transition will be exhibited by the molecule of non-bonding  $e^-$  and  $\pi e^-$ .



From the above  $e^-$  trans<sup>n</sup> diagram it is

find that

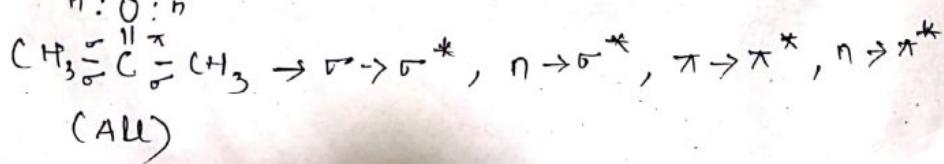
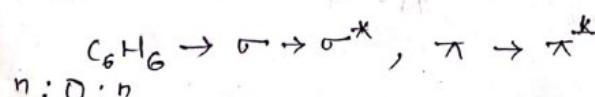
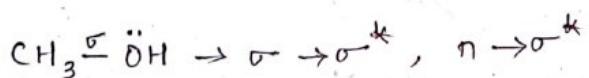
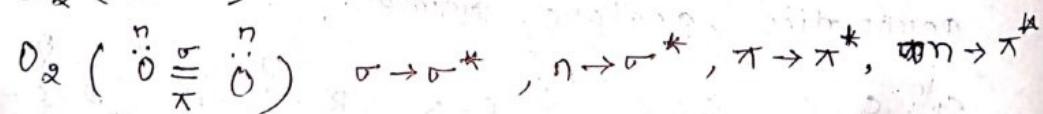
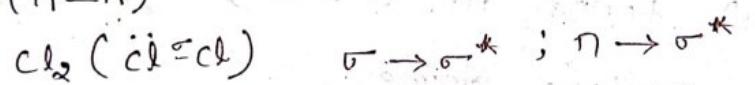
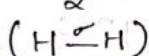
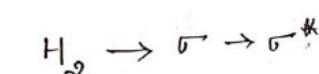
$$\Delta E_{\sigma \rightarrow \sigma^*} > \Delta E_{n \rightarrow \sigma^*} > \Delta E_{\pi \rightarrow \pi^*} > \Delta E_{h \rightarrow \pi^*}$$

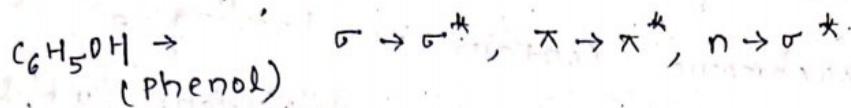
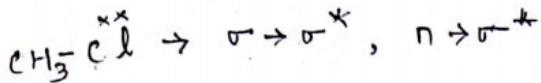
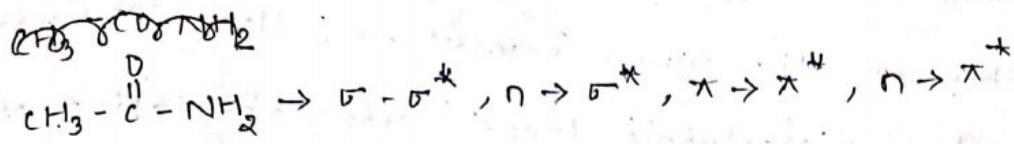
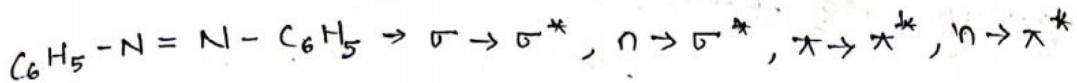
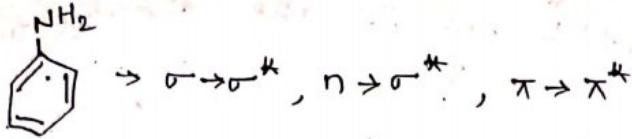
The energy spacing  $\rightarrow \Delta E$

Q:- What is selection rule?

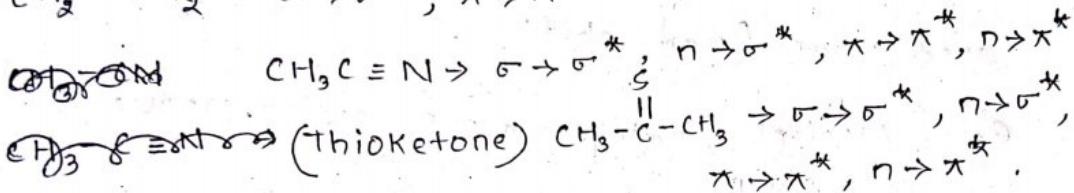
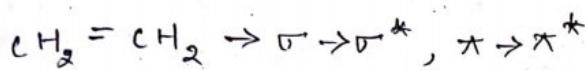
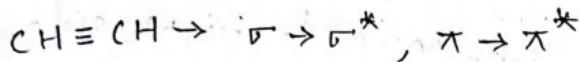
Briefly discuss various types of electronic trans<sup>n</sup> occur in a molecule.

Possible electronic transition in some molecules:





Cyclohexane



### Chromophore & Auxochrome :-

Chromophore:-

→ It is derived from a greek words "chromo" (Colour) and "phores" (impartive / generative).

→ Any molecule or part of a molecule, which has the ability to undergoes electronic transition upon absorption of UV light.

Example:-  $C=C$  (Alkene group).

$C \equiv C$  (Alkyne group)

$C_6H_5$  (Phenyl group)

$-NO_2$  (Nitro group)

$N=N$  (Azo group)

aldehyde, cyanide, ketone.

In toluene () , which one is the chromophoric group. <sup>Ans:-</sup> ~~NO<sub>2</sub>~~ phenyl.

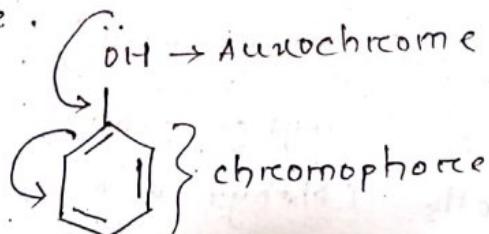
### Auxochrome :-

- They are the colour intensifiers. Alone they can't undergo electronic transn upon absorption of UV visible light.
- All auxochrome contain non-bonding  $e^-$ . Any functional group or substituent, which attached to the chromophore causes a shift in the absorption band, to shift towards longer wavelength i.e; towards right side or red side (red shift).

Ex:- Alcohol, halogen group, amino group, group also alcoxy (-OR group).

### Reason behind red shift :-

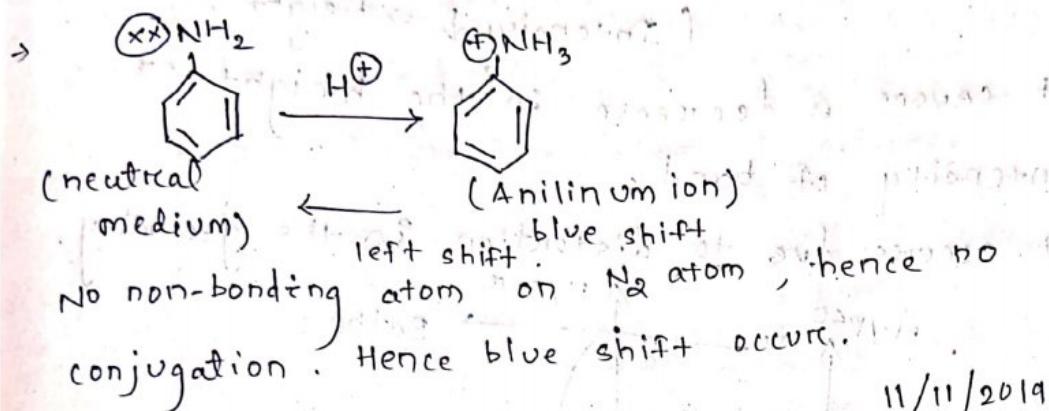
- Non-bonding  $e^-$  of auxochrome helps in extending conjugation of a chromophore (conjugation effect)
- this happens due to interaction bet<sup>n</sup> non-bonding  $e^-$  of auxochrome &  $\pi-e^-$  of chromophore.



Q:- Benzene gives an absorption band at 255 nm, whereas aniline gives an absorption band at 280 nm.

» Aniline is an azo group helps in conjugate, hence red shift.

Q:- Aniline absorbs at 280 nm in an neutral medium, whereas its blue shift occurs in an acidic medium.



11/11/2019

Shifting of absorption band:  
There are 4 types of shifts can occur with an absorption band.

(1) Bathochromic shift (Red shift) ( $\lambda_{\text{max}} \uparrow$ )  
→ It causes shifting of absorption band towards the right side i.e. towards red side (higher wavelength side).

→ It happens due to addition of an bathochromic agent or due to change in polarity of solvent.

(2) Hypsochromic shift (Blue shift) ( $\lambda_{\text{max}} \downarrow$ )  
→ It causes shifting of absorption band towards the left side i.e; blue side towards lower wavelength side.

→ It happens due to removal of an ~~autochro~~  
or due to change in polarity of solvent.

(3) Hyperchromic shift :- ( $\epsilon_{max} \uparrow$ )  $\Rightarrow$

(Intensity  $\uparrow$  or height  $\uparrow$ )

→ It causes an increase in the height or  
intensity of band.

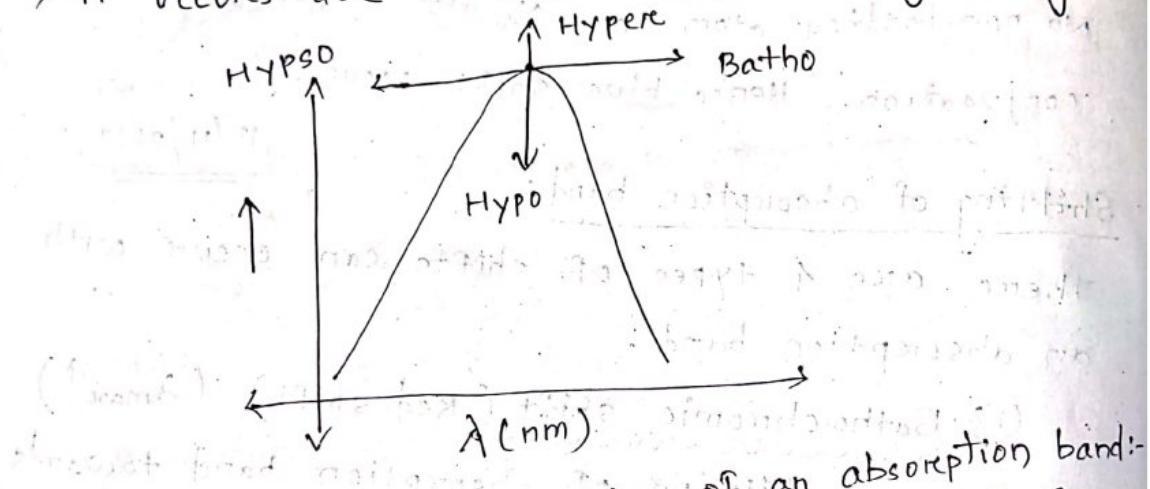
→ It happens due to addition of an ~~autochro~~

(4) Hypochromic shift :- ( $\epsilon_{max} \downarrow$ )

(Intensity  $\downarrow$   $\Rightarrow$  Height  $\downarrow$ )

→ It causes a decrease in the height or  
intensity of band.

→ It occurs due to distortion in the geometry.



Factors affecting shifting of an absorption band:-  
~~autochro~~ (-OH, -X, -OR)

(1) Presence of an ~~autochro~~

(2) Conjugation present:-

→ When a single and double bond present alter-  
natively in a compound, then the compound is  
said to be conjugated compound.

→ Conjugation in a compound reduces the  
energy gap bet<sup>n</sup> ground state and excited  
level, thus  $\lambda$  increases, red shift occur.

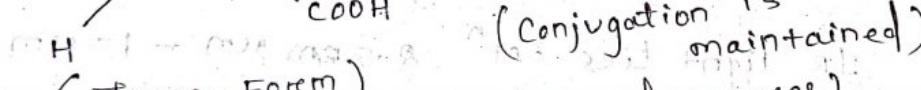
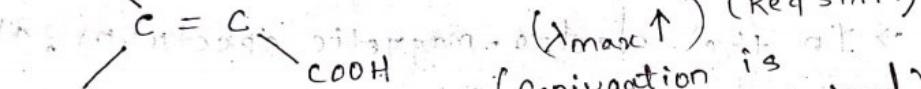
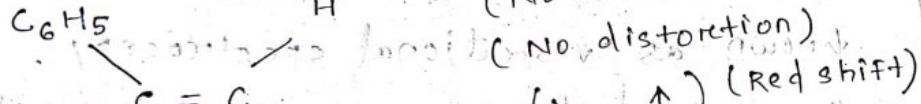
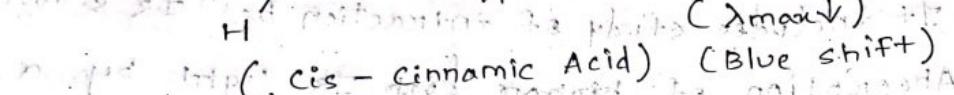
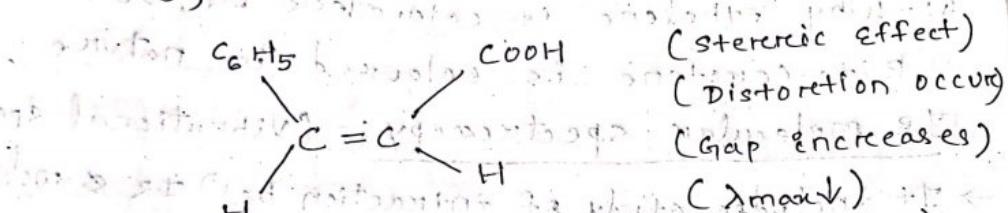
(3) Steric Effect :- (Steric hindrance)

(Bulky group effect)

→ Between cis isomer & trans isomer, trans isomer absorbs UV visible light at higher wavelength.

→ In case of cis isomer due to presence of 2 bulky group on the same side of  $\text{C}=\text{C}$ , steric repulsion occurs.

And this results in distortion on the geometry of the molecule, this causes removal of conjugation effect. Hence the energy gap between two energy levels increases,  $\lambda$  decreases.



Q:- Give reason that trans-form UV visible light at higher wavelength than cis-Form.

### Applications of UV visible spectroscopy

→ We can check purity of a compound.

→ We can differentiate betw cis & trans-form.

→ " " conjugated compound.  
non-conjugated

- We can find out the conc. of a coloured substance
- We can study kinetics of a chemical reaction & molecular mass of a compound.

Q:- Give reason that why Beta-carotene, Ann carot. and lycopine is coloured in nature.

- In both compound II double bonds are present. It means they are highly conjugated compounds.
- But we know that addition of one double bond to a system shifts the absorption band 40-45 nm towards right.

Q:- Why ethylene is colourless, but Beta-carotene is coloured in nature.

IR molecular spectroscopy :- (Vibrational spectroscopy)

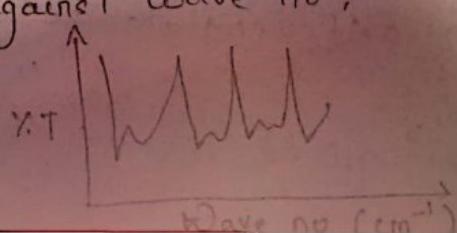
- It includes study of interaction bet<sup>n</sup> IR & molecule.
- Absorption of infrared light by a molecule causes its vibration. It is also known as vibrational spectroscopy.

→ In the electro-magnetic spectrum, the  $\lambda$  of IR light lies bet<sup>n</sup>  $2.5 \text{ mm } \mu\text{m} - 15 \mu\text{m}$ .

→ In terms of wave no.  $\gamma$ , the IR light varies bet<sup>n</sup>  $1,000 \text{ cm}^{-1} - 667 \text{ cm}^{-1}$ .

Vibration Spectrum :- (IR spectrum)

- It is a  $\gamma$ . transmittance ( $\gamma$ .t) against wave no. or absorbance against wave no.



## Principles :-

When an IR light of a suitable wavelength is absorbed by a molecule, then trans<sup>n</sup> of molecule occurs from the ground state vibrational level to the excited state vibrational level.

An IR light will be absorbed by those molecule for which there will be change in dipole moment, with change in bond distance, during vibration.

It means change in dipole moment to change in bond distance is  $\neq 0$ .

Change in dipole moment

Change in bond distance

so, accordingly we can classify molecules into two categories :-

i) IR active  $\rightarrow \frac{d\mu}{dr} \neq 0$  (All polar molecules)  
 $(\text{H}_2\text{O}, \text{CO}, \text{CN}, \text{NO})$

ii) IR inactive  $\rightarrow \frac{d\mu}{dr} = 0$  (Non polar molecules)  
 $(\text{H}_2, \text{Cl}_2, \text{O}_2, \text{CH}_4, \text{Cl}_4)$

Types of molecular vibration :-

When an IR light is absorbed by molecule its energy increases and results in two types of fundamental vibration.

1) stretching vibrations :-

In it the bond distance bet<sup>n</sup> two atoms either increases or decreases.

Hence there is no change in bond angle.

It is up 2 types.

### 1. Symmetrical stretching

→ Net dipole moment = 0 D

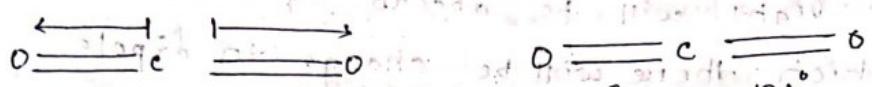
$$\mu = q \cdot d$$

### 2. Asymmetrical stretching

→ Net dipole moment =

some +ve value

$$\Rightarrow \frac{d\mu}{d\bar{\nu}} = 0 \text{ (IR inactive)} \rightarrow \frac{d\mu}{d\bar{\nu}} \neq 0 \text{ (IR active)}$$



$\neq 180^\circ$ ,  $\neq 180^\circ$   
Symmetric伸展

Q: Give reasons that, Asymmetric stretching is IR active.

Q: Asymmetric stretching found at higher wave no. than symmetric stretching. Give reason.

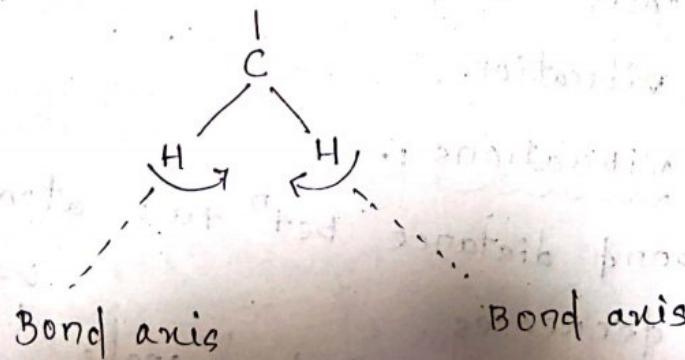
→ For an asymmetric stretching to occur more amount of energy is required than symmetric stretching.

→ We know that,  $E = hc\bar{\nu}$  i.e. ( $E \propto \bar{\nu}$ )

→ Hence, it requires more energy, it will occur at higher wave no.

### 2) Bending vibration :-

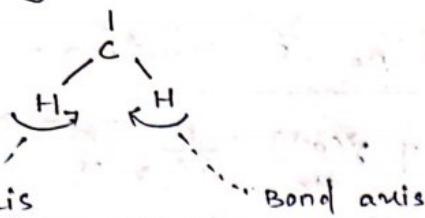
→ In this, bond angle changes with respect to the bond axis.



## Types of bending vibration :-

(4 types)

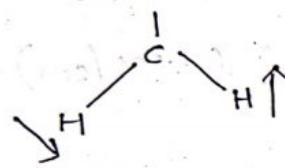
### (1) Scissoring vibration :-



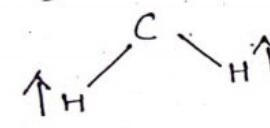
### (2) Rocking vibration :-



### (3) Twisting :-



### (4) Wagging :-



→ There are more no. of bending vibration than stretching vibration.

Q: stretching vib<sup>n</sup> occurs at higher wave no. than bending vib<sup>n</sup>. Why?

→ We know that it is easy to bend a string than to stretch. That means bending requires less energy than stretching. Thus, less energy means low wave no.  
Hence it happens like this.

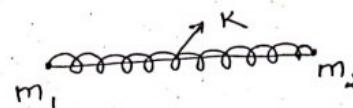
\* For bending vibration to occur, the molecule must contain three atoms. For a diatomic molecule, only symmetric stretching occurs but no bending occurs.

Frequency and wave no. of vibration :-

$$\text{Vibrational frequency } \gamma (\text{s}^{-1}) = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Where  $k$  = force constant & it is a measure of bond strength. (Unit -  $\text{kg m/s}^2$ ,  $\text{N/m}$ ,  $\text{dyne/cm}$ )

$$\mu = \text{Reduced mass} = \frac{m_1 m_2}{m_1 + m_2}$$



From the above, we know that  $\gamma \uparrow$  when  $k \uparrow$   $\mu \downarrow$

$$k = 4\pi^2 \gamma^2 \mu \quad \text{unit (N/m), (dyne/cm).}$$

Wave no. ( $\bar{\nu}$ ):-

$$\bar{\nu} (\text{cm}^{-1}) = \frac{\gamma}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$k = 4\pi^2 c^2 \bar{\nu}^{-2} \mu$$

Q: Calculate the reduced mass of HF molecule.

Given that  $m_H = 1.008 \text{ u}$ ,  $m_F = 19 \text{ u}$

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

$$= \left( \frac{1.008 \times 19}{1.008 + 19} \right)$$

$$= 0.9572 \text{ u} \quad \therefore \text{But we know that;}$$

$$= 0.9572 \times 1.66 \times 10^{-24} \text{ kg}$$

$$= 1.588 \times 10^{-24} \text{ gm}$$

1 u or 1 amu

$$= 1.667 \times 10^{-24} \text{ g}$$

$$= 1.667 \times 10^{-24} \text{ kg}$$

Q: calculate the vibrational frequency and wave no. of CH stretching vibration.

Take  $m_c = 12 \text{ u}$

$m_H = 1 \text{ u}$

$$K = 5 \times 10^5 \text{ dyne/cm} (\text{gm/s}^2)$$

$$\mu = \left( \frac{12 \times 1}{12 + 1} \right) = \frac{12}{13} \text{ u} = \frac{12}{13} \times 1.66 \times 10^{-24} \text{ g} = 1.476 \times 10^{-24} \text{ g}$$

$$\text{i) } \gamma = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} = \frac{1}{2 \times 3.14} \sqrt{\frac{5 \times 10^5}{1.476 \times 10^{-24}}} = 9.3 \times 10^{13} \text{ s}^{-1} (\text{Hz})$$

$$\overline{\gamma} = \frac{\gamma}{c} = \frac{9.3 \times 10^{13} \text{ s}^{-1}}{3 \times 10^{10} \text{ cm/s}} = 3100 \text{ cm}^{-1}$$

Ans

14/11/19

Force constant (K) :-

$$K = 4\pi^2 \gamma^2 \mu \text{ (If frequency given)} \Rightarrow \gamma = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

$$K = 4\pi^2 \nu^{-2} c^2 \mu \text{ (If wave no. is given)} \Rightarrow \nu = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

Q: Vibrational frequency of CO molecule is  $5.9 \times 10^{13} \text{ Hz}$ .

$$\gamma = 5.9 \times 10^{13} \text{ Hz}$$

$m_c = 12 \text{ u}$  and  $m_o = 16 \text{ u}$

$$\text{Ans: } \mu_{CO} = \frac{m_1 m_2}{m_1 + m_2} = \frac{12 \times 16}{28} = \frac{48}{7} = 6.89 \text{ u.}$$

$$= 6.89 \times 10^{-24} \times 1.66 \text{ g}$$

$$= 11.48 \times 10^{-24} \text{ g}$$

$$K = 4 \times (3.14)^2 \times 11.48 \times 10^{-24} \text{ g} \times (5.9 \times 10^{13} \text{ s}^{-1})^2$$

$$= 1569 \times 10^3 \text{ g/s}^2$$

$$= 1569 \text{ kg/s}^2$$

Q: Wave no. of He<sub>2</sub> molecule  $\overline{\gamma} = 2890 \text{ cm}^{-1}$

Calculate the force constant of the molecule

by taking  $m_H = 1 \text{ u}$  and  $m_{\text{Cl}} = 35.5 \text{ u}$ .

Ans :-  $\mu = \frac{m_1 m_2}{m_1 + m_2} = \left( \frac{1 \times 35.5}{1 + 35.5} \right) \times 1.66 \times 10^{-24} \text{ g}$   
 $= 1.614 \times 10^{-24} \text{ g}$

$$K = 4 \times (3.14)^2 \times (2890 \text{ cm}^{-1})^2 \times (3 \times 10^{10} \text{ cm/s})^2 \times 1.614 \times 10^{-24} \text{ g}$$
  
 $= 448625 \text{ g/s}^2$

### Vibrational frequency and isotopic substitution.

$$\gamma \propto \mu$$

$$\gamma = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

$$\Rightarrow \gamma \downarrow \mu \uparrow$$

Q:- In  $\text{CHCl}_3$ ,  $\text{C-H}_{\text{str}}$  vibration occurs at  $3000 \text{ cm}^{-1}$ . Then calculate the wave no. of  $\text{C-D}_{\text{str}}$  vibration in  $\text{CDCl}_3$ . (Take  $m_c = 12 \text{ u}$ ,  $m_H = 1 \text{ u}$ ,  $m_D = 2 \text{ u}$ )

$$\overline{\gamma}_{\text{C-H}_{\text{str}}} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu_{\text{C-H}}}} \quad \text{--- (1)}$$

$$\overline{\gamma}_{\text{C-D}_{\text{str}}} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu_{\text{C-D}}}} \quad \text{--- (2)}$$

Now, (2)/(1)  $\frac{\overline{\gamma}_{\text{C-D}}}{\overline{\gamma}_{\text{C-H}}} = \sqrt{\frac{\mu_{\text{C-H}}}{\mu_{\text{C-D}}}}$

$$\mu_{\text{C-H}} = \frac{12 \times 1}{13} = 0.92 \text{ u}$$

$$\mu_{\text{C-D}} = \frac{12 \times 2}{13+2} = \frac{24}{14} = 1.71 \text{ u}$$

$$\frac{\overline{\gamma}_{\text{C-D}}}{\overline{\gamma}_{\text{C-H}}} = \sqrt{\frac{\mu_{\text{C-H}}}{\mu_{\text{C-D}}}} = \sqrt{\frac{0.92}{1.71}}$$

$$\Rightarrow \bar{\nu}_{\text{C-H}} = \bar{\nu}_{\text{CH}} \times \sqrt{\frac{0.92}{0.71}} = 3000 \times \sqrt{\frac{0.92}{0.71}} = 2190 \text{ cm}^{-1}$$

Vibrational energy :-

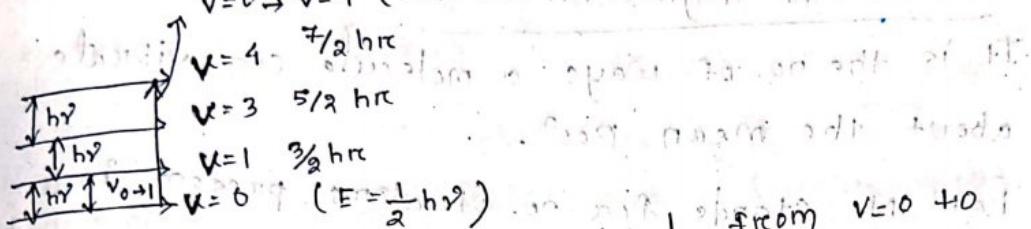
$$E_{\text{vib}} = \left( v + \frac{1}{2} \right) h\nu$$

$v$  = Vibrational quantum no. = 0, 1, 2, 3, 4, ...

$$E_{\text{vib}} = \frac{1}{2} h\nu$$

(Ground state  $\rightarrow v=0$ , Zero point energy (ZPE)).

$v=0 \rightarrow v=1$  (not allowed)



Now, For transition of molecule

$$v=1 \rightarrow v=2, \Delta E_{1 \rightarrow 2} = \frac{3}{2} h\nu - \frac{1}{2} h\nu = h\nu$$

$$\Delta E_{1 \rightarrow 2} = h\nu = \Delta E_{2 \rightarrow 3} = \Delta E_{3 \rightarrow 4}$$

All the vibrational energy level are equispaced

by an amount  $h\nu$ .

selection rule for vibrational spectroscopy:-

$$\Delta v = \pm 1, \text{ where } v = \text{vib. quantum no.}$$

Change  $\pm 1$  is allowed.

Q:- What is finger print region?

$\Rightarrow$  In the IR spectrum  $1500 \text{ cm}^{-1} - 500 \text{ cm}^{-1}$  is known

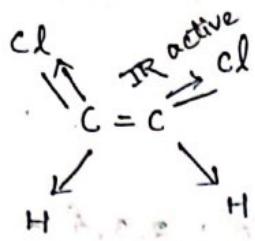
as finger print region.

$\Rightarrow$  Only bending vibration are found in this region.

$\Rightarrow$  This region is used to distinguish between

two organic molecules.

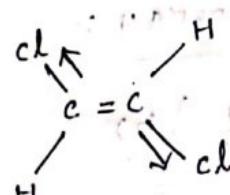
Q. Cis-form is IR active, whereas trans-form is IR inactive. Give reason.



cis form

Net,  $\mu > 0$

IR active.



trans form

Net  $\mu = 0$

IR-inactive

### Vibrational degree of freedom :-

It is the no. of ways a molecule can vibrate about the mean pos<sup>n</sup>.

Let N stands for no. of atoms present in a molecule.

(i) For a linear molecule no. of vibrational

$$\text{degree of freedom} = \boxed{3N - 5}$$

$\left\{ \begin{array}{l} \text{CO}_2, \text{CS}_2, \text{OCS}, \\ \text{HCl}, \text{HF}, \text{CO}, \text{NO} \end{array} \right\}$

$$\text{For CO}_2, N=3, 3 \times 3 - 5 = \boxed{4}$$

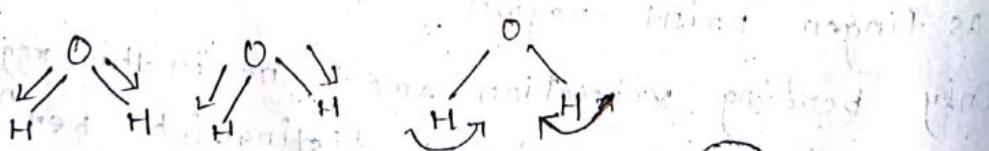
$$\text{For HCl, } N=2, 3 \times 2 - 5 = \boxed{1}$$

$$\text{For C}_2\text{H}_2, \text{CN}, N=4, 3 \times 4 - 5 = \boxed{7}$$

(ii) For Non-linear molecule no. of vibrational

$$\text{degree of freedom} = \boxed{3N - 6}$$

$$\text{For H}_2\text{O, } N=3, 3 \times 3 - 6 = \boxed{3}$$



$$\text{For C}_6\text{H}_6, N=12, 3 \times 12 - 6 = \boxed{30}$$

$$\text{For CHCl}_3, N=5, 3 \times 5 - 6 = \boxed{9}$$

## Applications of vibrational spectroscopy:-

- Detection of functional group.
- , It helps in finding the molecular structure of a compound.
- , Detection of purity of the compound.
- , Distinguish bet<sup>n</sup> cis & trans isomers.
- , We can find the force const.
- , We can study the isotopic substitution.
- , We can study interaction bet<sup>n</sup> solute and solvent molecule or molecule.

Q: A molecule is vibrating with a frequency of  $9 \times 10^{13} \text{ s}^{-1}$ . Then find out spacing bet<sup>n</sup> vibrational energy level, zero point energy, vibrational energy of the molecule for the 1st excited state.

Ans :-

$$\Delta E_{\text{vib}} = h\nu = 6.626 \times 10^{-34} \text{ Js} \times 9 \times 10^{13} \text{ s}^{-1}$$

$$= 59.63 \times 10^{-21} \text{ J}$$

$$E_{\text{vib}} = \frac{3}{2} h\nu = 1.5 \times 59.63 \times 10^{-21} \text{ J}$$

$$= 88.5 \times 10^{-21} \text{ J. (For 1st excited state)}$$

$$ZPE = \frac{1}{2} h\nu = \frac{1}{2} \times 59.63 \times 10^{-21} \text{ J}$$

$$= 29.81 \times 10^{-21} \text{ J}$$

## Rotational or Microwave Spectroscopy:-

It deals with study of interaction bet<sup>n</sup> molecule and micro-waves/light.

$$\text{wave no}(\bar{\nu}) = 1 - 100 \text{ cm}^{-1}$$

## Microwave active & inactive molecule :-

- All molecules can't absorb microwave light & undergoes rotation.
- Only molecules having permanent dipole moment (all polar molecules) can absorb microwave length. These are called microwave active light. ex:-  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{CHCl}_3$ ,  $\text{HX}$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{CH}_3\text{CN}$ ,  $(\text{CH}_3)_2\text{C}=\text{O}$ .
- All non-polar molecules (dipole moment = 0) are microwave inactive.

e.g.;  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CCl}_4$ ,  $\text{PCl}_5$ ,  $\text{BF}_3$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{SF}_6$ .

## Basic Principle:-

- When microwave light is absorbed by molecule, then "trans" of molecule occurs from ground state rotational energy level ( $J=0$ ) to excited ( $J \rightarrow$  Rotational quantum no.) by obeying the selection rule i.e.,  $\Delta J = \pm 1$

## Rotational Energy :- (In J)

$$\textcircled{1} \quad E_{\text{rot}} = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$= B J(J+1)$$

$$\text{Where; } B = \frac{h^2}{8\pi^2 I} = \frac{h^2}{8\pi^2 \mu r^2} \Rightarrow B \propto \frac{1}{\mu}$$

$J \rightarrow$  Rotational quantum no.

$I \rightarrow$  Moment of inertia

$$I = \mu r^2, \text{ where, } \mu = \text{Reduced mass} = \frac{m_1 m_2}{m_1 + m_2}$$

$r = \text{Bond length (A}^\circ/\text{nm})$

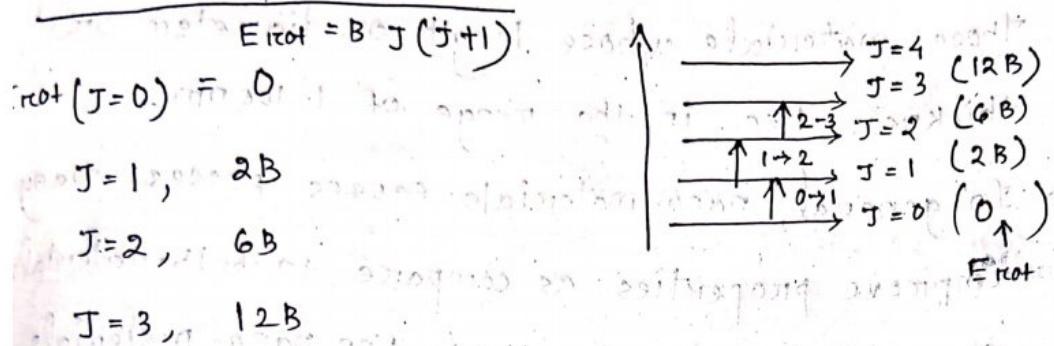
$$\textcircled{2} \quad E_{\text{rot}} = \frac{\hbar}{8\pi^2 I c} J(J+1)$$

$$= B J(J+1), \quad B = \frac{\hbar}{8\pi^2 I c} \text{ (cm}^{-1}\text{)}$$

$c \rightarrow$  velocity of light.

As, mass increases rotational energy decreases.

Rotational Energy level :-



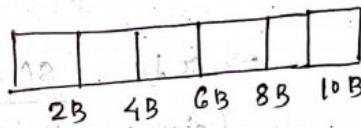
→ Rotational molecule of ground state is  $J=0$ .  
And for 1st rotational excited state is  $J=2B$ .

Rotational Transitions and Rotational Spectrum:-

$$\Delta E_{\text{rot}}_{0 \rightarrow 1} = 2B - 0 = 2B$$

$$\Delta E_{\text{rot}}_{1 \rightarrow 2} = 6B - 2B = 4B$$

$$\Delta E_{\text{rot}}_{2 \rightarrow 3} = 12B - 6B = 6B$$



In the line spectrum, all the lines are equispaced

by  $2B$ : Application :-

- Bond length ( $r$ ) between two atoms in a molecule, we can find.
- We can study the effect of isotopic substitution in a molecule.

- We can detect the symmetry of a molecule
- We can find out dipole moment ( $\mu$ ) of a molecule.

Ques

# Water Treatment:- Module-1

→ The process by which the undesirable impurities from the water and make it fit or suitable for domestic or industrial application, is known as water treatment.

## Types of impurities:-

Impurities are may be:

(1) Suspended impurities (clay & silica( $\text{SiO}_2$ ))

— Particle size greater than 1000 nm.

(2) Colloidal impurities (Fine form of clay or silicate particles)

— Particle size 1-1000 nm.

(3) Dissolved impurities (Dissolved salts of  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Mn}^{+2}$  etc....)

— Particle size less than 1 nm.

(4) Micro-organisms (Bacteria, fungal, algae).

— Dissolved  $\text{O}_2$  &  $\text{CO}_2$ .

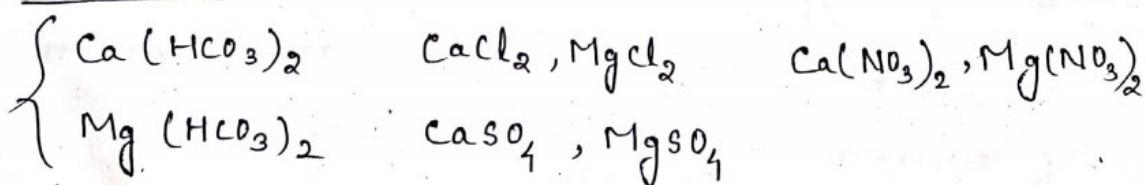
Q:- What is hardness?

→ Hardness can be defined as soap consuming capacity.

→ It is a characteristics of water by which it prevents foaming or lathering.

→ Hardness of water is due to presence of dissolve salt of Ca, Mg and some heavy metals like Al, Fe & Mn.

→ Salts are:-



Bicarbonates, chloride, sulphate & nitrate of Ca & Mg.

→ other salts are :-  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{MnSO}_4$

Real.  $\text{C}_{17}\text{H}_{35}\text{COONa}$  Hard water  
(Soap)  $\text{Ca}^{2+}$  +  $\text{H}_2\text{O}$  from natural salt  
(Sodium stearate) (soda) ↓  
↓ precipitate to soap

$(\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca} + 2\text{NaCl}$  precipitate to soap  
(calcium stearate) white ppt.

H.W. will be no precipitate formed (e)  
(soft water)

$\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  to form barium sulphate (precipitate to soap)  
 $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  to form precipitate to soap

(soda, soap, salt, alkali) precipitate to soap  
precipitate to soap

precipitate to soap

precipitate to soap

$\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$

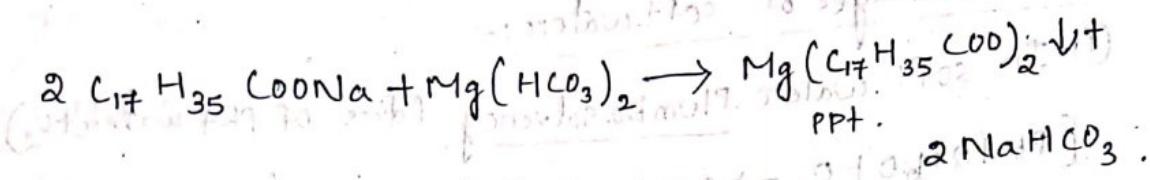
slight soln

$\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$

$\text{Ba}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$ ,  
B14 & 20 to start with  
stability, should be addressed

Q: Why do hardwaters consumes so much soap?

We know that,

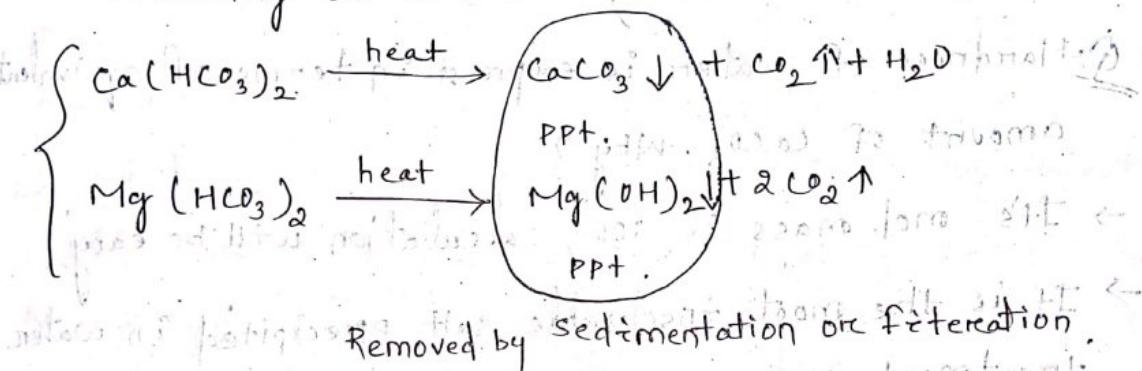
$$2 \text{C}_{17}\text{H}_{35}\text{COONa} + \text{Ca}(\text{HCO}_3)_2 \rightarrow \text{Ca(C}_{17}\text{H}_{35}\text{COO})_2 \downarrow + 2\text{NaHCO}_3$$


### Types of hardness:-

#### (1) Temporary hardness:-

→ Constituent like  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$ , if present in water are called temporary hardness.

→ Because, these constituent on hitting or boiling, they gives ppt. and they will settled down (sedimentation), or filtering or combination of both.



#### (2) Permanent hardness:-

→ Constituents are  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ;  $\text{MgSO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ , etc.

→ It can't be removed by boiling or hitting process.

But can be removed by softening process, like

lime soda process, zeolite & Resin process.

(Polymeric membrane)

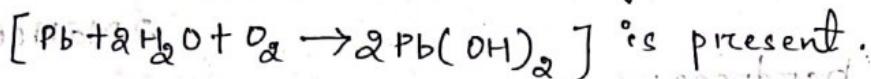
### (3) Total hardness :-

Temporary hardness + Permanent hardness

Q: Diff. bet<sup>n</sup> soft water / hared water

Disadvantages of soft water:-

① In soft water Plumbo solvency (diss. of Pb + Water to  $Pb(OH)_2$ )



\* This process doesn't happen in hared water, bcoz

Pb reacts  $Ca(HCO_3)_2$ ,  $Mg(HCO_3)_2$  to form  $PbCO_3$  ppt.

which gets coated over the inner wall of ~~coated~~ water pipe.

Q: How to express hardness of water?

(Degree of hardness)

Q: Hardness of water is expressed in terms of equivalent

amount of  $CaCO_3$ . Why?

→ It's mol. mass is 100, calculation will be easy.

→ It is the most insoluble salt precipitated in water treatment process.

④ Non-hardness constituent :-

These constituent doesn't impact hardness to water.

Ex:-  $Na_2SO_4$ ,  $K_2SO_4$ , NaCl,  $NaCO_3$ ,  $NaAlO_2$ ,  
 $KOH$ ,  $NaOH$ ,  $Fe_2O_3$ ,  $SiO_2$  --- etc.

Degree of hardness:-

$CaCO_3$  equivalent hardness =  $\frac{\text{Strength of } (mg/L)}{\text{hardness causing salt}} \times \frac{100}{(\text{mol. mass of } CaCO_3)}$

$\times \frac{\text{Mol. mass of hardness causing salt}}{n \text{ factors}}$

### n-factors :-

All Ca & Mg salts  $\rightarrow$  2

$\text{FeSO}_4$   $\rightarrow$  2

$\text{Al}_2(\text{SO}_4)_3 \rightarrow 2 \times 3 = 6$

$\text{Na}(\text{AlO}_2) \rightarrow 1$

$\text{NaHCO}_3 \rightarrow 1$

### Atomic mass :-

Ca = 40

Mg = 24

Na = 23

O = 16

H = 1

S = 32

N = 14

Al = 27

Q. Find out the hardness of H<sub>2</sub>O as  $\text{CaCO}_3$  equivalent

(if the hard H<sub>2</sub>O contains 16.2 mg of  $\text{Ca}(\text{HCO}_3)_2$ )

Ans :-  $\text{Ca}(\text{HCO}_3)_2 = 162$  (mol. mass)

$$162 = 40 + 1 + 12 + 48 \times 2$$

$$\text{Equivalent of hardness} = 162 \times \left( \frac{100}{2 \times \frac{162}{10}} \right) = 100 \text{ mg/L}$$

Q. Find out the hardness of a hard water sample

containing 950 mg/l of  $\text{MgSO}_4$ ?

Ans :-  $\text{MgSO}_4 = 24 + 32 + (4 \times 16) = 120$  (mol. mass)

$$\text{Equivalent of hardness} = 120 \times \left( \frac{100}{2 \times \frac{120}{10}} \right) = 100 \text{ mg/L}$$

$$950 \times \frac{100}{2 \times \frac{120}{10}} = \frac{9500}{12} = 791.66 \text{ mg/L}$$

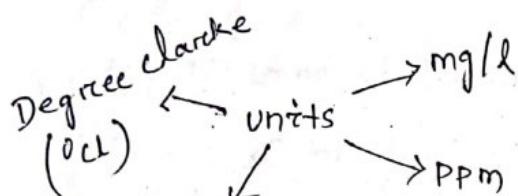
Q: A water contains 3420 mg/l of  $\text{Al}_2(\text{SO}_4)_3$ . Find the hardness as  $\text{CaCO}_3$  equivalent?

$$\begin{array}{l} \text{Al}_2(\text{SO}_4)_3 = 312 \\ \downarrow \quad \downarrow \\ 27 \times 2 = 54 \quad (32+64) \times 3 \end{array}$$

Now, ~~3420 mg/l~~

$$\left[ \frac{3420 \text{ (mg/l)} \times 100}{54 \times \frac{312(114)}{63}} \right] = 3000 \text{ mg/l.}$$

Units of hardness :-



Degreee French ( $^{\circ}\text{Fr}_n$ )

① PPM :- one part of  $\text{CaCO}_3$  eq. hardness per million parts of water.

② mg/l :- One gram of  $\text{CaCO}_3$  eq. hardness per litre of water.

③ Degreee french :- One part of degreee french of  $\text{CaCO}_3$  eq. hardness per  $10^5$  parts of water.

④ Degreee clarke :- One part of degreee clarke of  $\text{CaCO}_3$  eq. hardness per 40,000 parts of water.

$$\frac{10^6 \text{ ppm}}{10^6} = \frac{10^5 {}^\circ\text{FRC}}{10^6} = \frac{70,000 {}^\circ\text{cl}}{10^6}$$

$$\Rightarrow 1 \text{ ppm} = 0.1 {}^\circ\text{FRC} = 0.07 {}^\circ\text{cl} = 1 \text{ mg/L}$$

Q:- 1 ppm = 1 mg/l (why?)

$$1 \text{ mg} \rightarrow 1 \text{ L}$$

$$\approx 1000 \text{ gm}$$

$$\approx 1000 \times 1000 \text{ mg}$$

$$\approx 10^6 \text{ mg.}$$

Q:- Write some adv. & disadv. of hardwaters?

adv:- ① calcium is required for strengthening of bone & teeth.

② No. Plumbo solvency in water.

19/08/19

A sample of water ion analysis found to contain the following impurities :-

	mg/L	Molar mass	n-factor	CaCO <sub>3</sub> eq.
Ca(HCO <sub>3</sub> ) <sub>2</sub>	16.2	162	2	$\frac{162 \times 100}{(2 \times 162)} = 100$
CaSO <sub>4</sub>	13.6	136	2	$\frac{13.6 \times 100}{(2 \times 136)} = 10$
Ca(NO <sub>3</sub> ) <sub>2</sub>	16.4	164	2	$\frac{16.4 \times 100}{(2 \times 164)} = 10$
Mg(NO <sub>3</sub> ) <sub>2</sub>	11.8	148	2	$\frac{11.8 \times 100}{(2 \times 148)} = 10$
CaCl <sub>2</sub>	11.1	111	2	$\frac{11.1 \times 100}{(2 \times 111)} = 10$
Na <sub>2</sub> SO <sub>4</sub> (Non-hardness)	2.0 ppm	2.0	—	—

Q:- Find out temporary hardness, permanent hardness and total hardness as CaCO<sub>3</sub> equivalent in all the four units.

For, Temporary hardness = 100 mg/L

$$= 100 \text{ PPM}$$

$$= 10$$

$$\begin{aligned} & 100 \text{ mg/L. (Temp)} \\ & = 10 \text{ mg/L (Temp)} \\ & = 10 \text{ mg/L (Per)} \\ & = 10 \text{ mg/L (P)} \\ & = 10 \text{ mg/L (P)} \end{aligned}$$

Q:- Ass. A wat

in mg

Mg (H)

Mg Cl<sub>2</sub>

Mg SO<sub>4</sub>

NaCl

NaH

Find H<sub>2</sub>O

fr end

eq.

$$= 100 \text{ mg/L. (Temp.)}$$

$$= 10 \text{ mg/L (Temporary) (Permanent)}$$

$$= 10 \text{ mg/L (Temp.) (Permanent)}$$

$$= 10 \text{ mg/L (Permanent) (Permanent)}$$

$$= 10 \text{ mg/L (Permanent)}$$

Ans.

Q: A water sample contains the following impurities in mg/L unit.

$$\text{Mg}(\text{HCO}_3)_2 = \frac{\text{mg/L}}{25}$$

$$\text{Mg Cl}_2 = 10$$

$$\text{Mg SO}_4 = 15$$

$$\text{NaCl} = 10$$

$$\text{NaHCO}_3 = 5$$

Find out the total hardness in  $\text{CaCO}_3$  eq. in degree french & degree clarke units.

Q:- A water sample contains 100 ppm of  $Mg(HCO_3)_2$  and 200 ppm of  $Ca(HCO_3)_2$  and 150 ppm of  $Na(HCO_3)$ , what will the hardness of water after boiling the water for 20 mins.

Ans:- 0.

Q:- A water sample contains 25 mg/l of  $Mg(HCO_3)_2$  and 95 mg/l of  $MgCl_2$ . Find the hardness of water at  $CaCO_3$  eq. after boiling. the water.

Ans:- 100 mg/l

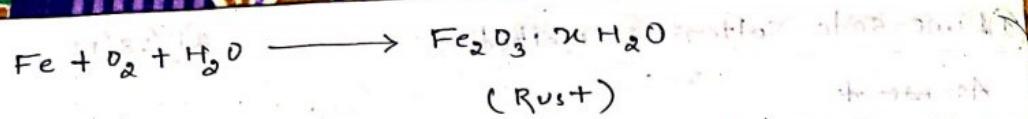
### Boiling Boilers for with hard water:

→ When hard water is used for boiler operation the following problems will occurs in it.

- ① Corrosion of boiler due to alkaline constituent present in hard water.
- ② Formation of scales & sludges.

### Characteristics of a boiler feed water:-

- Water should be soft.
- Water should be free from alkaline constituent.
- Water should be free from acidic constituent.
- Water should be free from dissolved  $O_2$  &  $CO_2$ .



Q: What are the various causes of boiler corrosion?

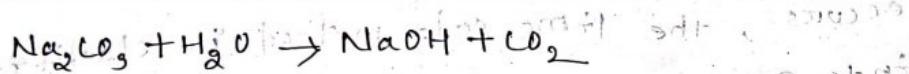
① Hardness of water.

② Presence of acidic and alkaline constituents.

Alkalinity of water & its limitations:-

→ It is the measure of water to neutralise acidic constituent.

→ Alkalinity in water is due to the presence of



→ Limitation:-

It causes corrosion of water.

Softening methods:-

→ The process by which hard water can be converted into soft water or degree of hardness can be reduced, is known as softening of water.

Various softening methods are:-

① Lime soda softening methods.

② Ion exchange softening.

Zeolite softening

Ion-exchange Resin.

## ① Lime-soda softening method:-

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As we know hardness  
→ The principle is to convert the soluble constituent  $(Ca(HCO_3)_2, CaCl_2, Mg(SO_4)_2)$  into insoluble substances by addition of calculated amount of lime  $(Ca(OH)_2)$  & soda  $(Na_2CO_3)$  and then removing those insoluble masses  $(CaCO_3, Mg(OH)_2)$  by sedimentation (settling) & filtration.

→ This method is basically based on precipitation reaction fact about of nature in pH

→ Depending upon the temp. at which softening occurs, the lime-soda method is classified into 2 types.

① Cold lime-soda method

② Hot lime-soda method

### Cold lime-soda method:-

→ This softening method performs at room temp.

→ In this method, calculated amount of lime and soda is added to the hard water.

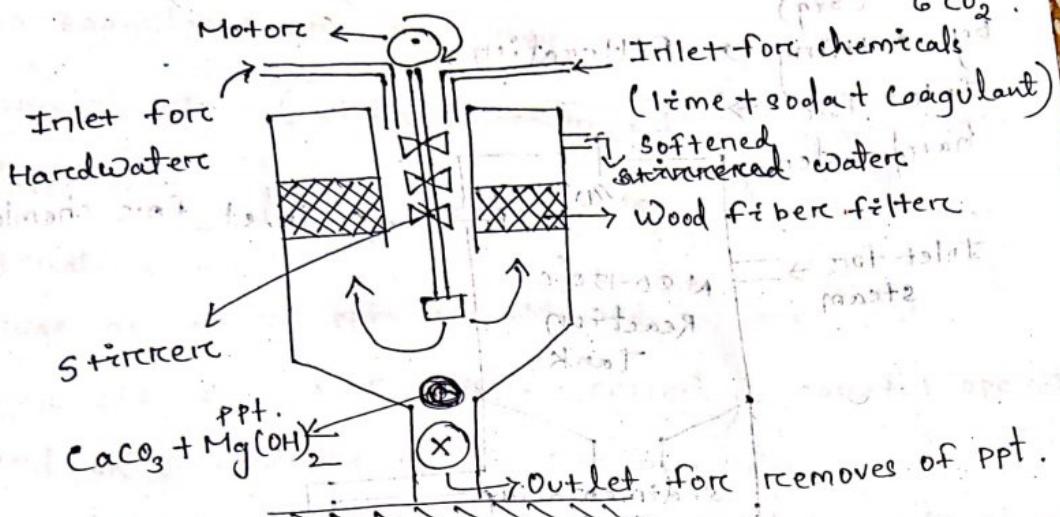
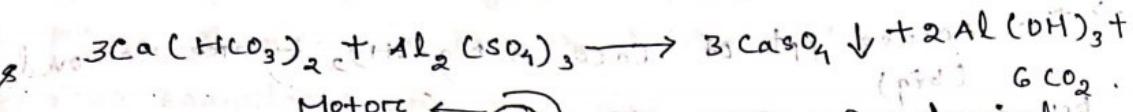
→ Mixing betw. hard water and those two chemicals are done using a stirrer driven by motor.

→ After mixing for some times it forms fine precipitates of  $CaCO_3$  &  $Mg(OH)_2$ .

→ These fine precipitated takes more time to settle down. they even pass through the filter paper.

→ So, in order to avoid this, chemicals like Potas Alum ( $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ ),  $FeSO_4$ ,  $Al_2(SO_4)_3$ ,

$\text{NaAlO}_2$  are added along with lime soda in order to convert fine ppt. in to coarse ppt.  
 → Later the coarse ppt. can be removed by sedimentation & filtration process.



### Limitations:-

- More chemicals are required.
- Softening rate is low.
- Dissolved gases like  $\text{O}_2, \text{CO}_2$  can't be removed.
- Pathogenic bacteria aren't killed.
- Softened water has residual hardness of 50-60 ppm.

Q:- What is coagulant and its uses?

Ans:- Some chemicals

Ans:- Some chemicals like  $\text{FeSO}_4, \text{Al}_2(\text{SO}_4)_3, \text{NaAlO}_2$ , which are added to convert fine particles

to coarse particles called as "coagulant".

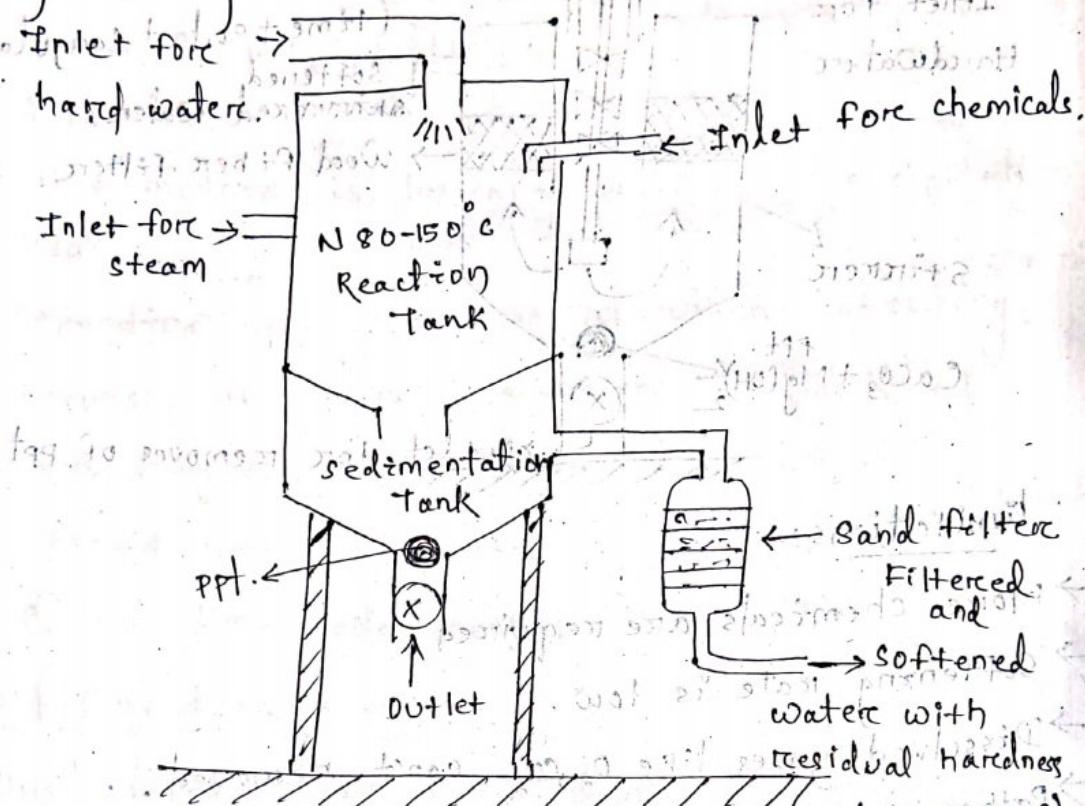
Q:- What is why coagulant is added to the lime soda softener?

→ To precipitate fine particles

## Hot Soda Softening Method:

→ In this method calculated amount of lime and soda is added to the water maintained at  $80-150^{\circ}\text{C}$  by passing superheated steam in to the softener.

→ The coarse ppt. of  $\text{CaCO}_3$  &  $\text{Mg(OH)}_2$  is removed by settling & filtration.



(Continuous hot lime soda softener.)

→ The above softener consists of 3 main parts:-

① A reaction tank, where reaction occurs.

② A sedimentation tank, where settling of ppt. occurs.

③ A sand filter retains any fine ppt., which can't be settling down in the settling tank.

Q:- What are the advantages of hot lime soda process over cold lime soda process?

Ans Adv. of hot lime soda process are:-

→ Softening capacity is higher.

- Less time is required.
- Dissolved gases can be removed.
- Pathogenic bacteria like E. coli can be killed.
- Filtration capacity is higher.
- Less chemical is required for softening.
- No coagulants are required.

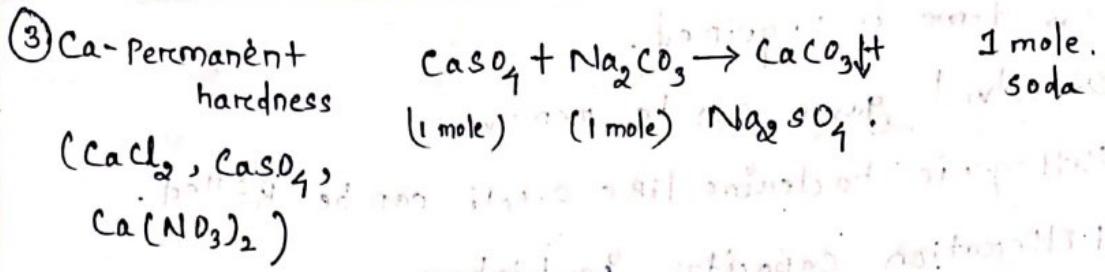
### Limitations:- (lime soda softening process) 22/08/19

- Water soften by this process is not fit for the operation.
- Huge amount of ppt are obtained.
- For efficient & economical softening, careful operation and skill supervision is essential.

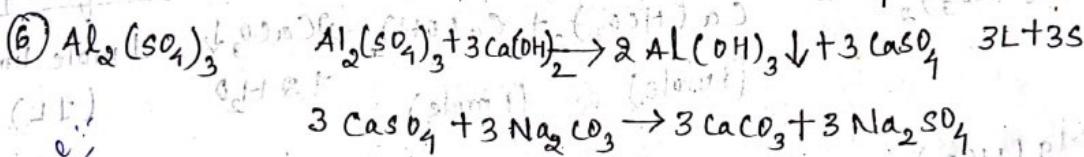
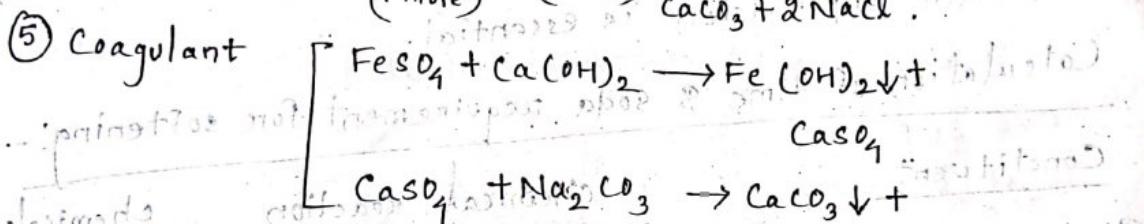
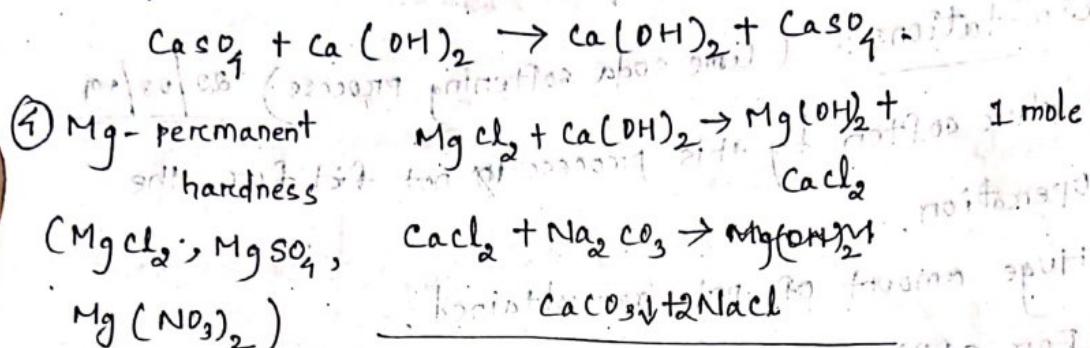
### Calculation of lime & soda requirement for softening:-

Constituent	Chemical reaction	chemicals required
① $\text{Ca}(\text{HCO}_3)_2$	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	1 mole lime (1 mole) (1 mole) (1 L)
② $\text{Mg}(\text{HCO}_3)_2$	$\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{Ca}(\text{HCO}_3)_2 + 2\text{H}_2\text{O}$	2 mole lime (1 mole) (2 mole) (2 L)

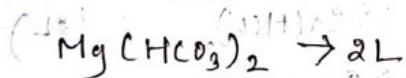
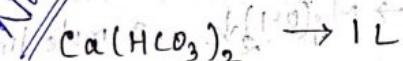
Q: Give explanation that 1 mole of  $\text{Ca}(\text{HCO}_3)_2$  requires 1 mole of lime, whereas 1 mole of  $\text{Mg}(\text{HCO}_3)_2$  needs 2 mole of lime.



Q: Give reason that Ca-permanent hardness don't require lime.

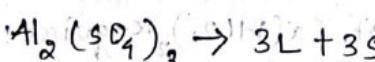
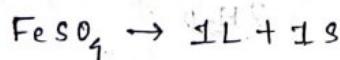


Note

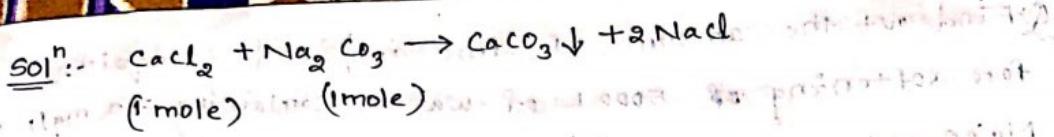


Ca-permanent hardness  $\rightarrow 1\text{S}$

Mg-permanent hardness  $\rightarrow 1\text{L} + 1\text{S}$



Q: Find out amount of lime & soda required for softening of 1000 L of hard water containing  $22.2 \text{ mg/L}$  of  $\text{CaCl}_2$ .



(1 mole) (1 mole)

1 mole of  $\text{CaCl}_2$  = 1 mole of  $\text{Na}_2\text{CO}_3$

111 g of  $\text{CaCl}_2$  =  $46 + 12 + 48 = 106$  g of  $\text{Na}_2\text{CO}_3$

22.2 mg/l of  $\text{CaCl}_2$  =  $\left( \frac{106}{111} \times 22.2 \text{ mg/l} \right)$

⇒ softening of 1L of hard water require  $\left( \frac{106}{111} \times 22.2 \right)$  mg of  $\text{Na}_2\text{CO}_3$ .

softening of 1mL of hard water require =

$$= \frac{106}{111} \times 22.2 \times 1000$$

$$= 21200 \text{ mg}$$

$$= 21.2 \text{ g}$$

Lime require = 0 g

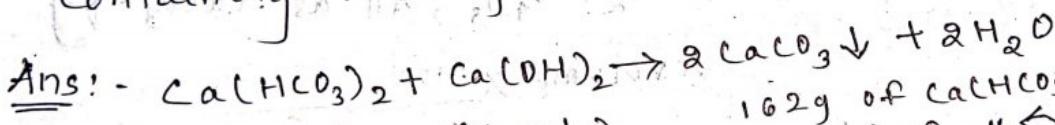
Hence, soda require =  $\frac{106}{100} \times (\text{CaCl}_2 \text{ as } \text{CaCO}_3 \text{ eqv.}) \times$

volume of water  
to be soften.

Q: Calculate the amount of lime & soda require

for softening of 5000 Litres of hard water

containing 16.2 mg/l of  $\text{Ca}(\text{HCO}_3)_2$ .



(1 mole) (1 mole)

16.2 g of  $\text{Ca}(\text{HCO}_3)_2$  = 74 g of lime.

16.2 mg/L of  $\text{Ca}(\text{HCO}_3)_2$  =  $\frac{74}{162} \times 10^3$  mg/L of  $\text{Ca}(\text{OH})_2$

softening of 1L of hard water require  
~~16.2 mg/l~~ →  $\left( \frac{74}{162} \times 16.2 \right)$  mg/L  $\text{Ca}(\text{OH})_2$

5000 L →  $\left( \frac{74}{162} \times 16.2 \times 5000 \right)$  mg/L of lime.

$$\rightarrow \frac{74}{162} \times 16.2 \times 5000 = 3700 \text{ mg}$$

$$= 37 \text{ g of lime.}$$

Soda required = 0 g.

Q: Find out the amount of lime and soda required for softening of 5000 L of water containing 72 mg/L of  $MgSO_4$ .

Ans :-  $MgSO_4 \text{ is } 1L + 1S \quad 72 \times \frac{100}{2 \times \frac{100}{100}} = \frac{7200}{180} = 60 \text{ mg/L}$

Lime required =  $\frac{74}{100} (\text{MgSO}_4 \text{ as } CaCO_3 \text{ eq.}) \times \text{Volume}$   
=  $\frac{74}{100} (60) \times 5000$   
= 222000 mg  
= 222 gm.

Soda required =  $\frac{106}{100} (\text{MgSO}_4 \text{ as } CaCO_3 \text{ eq.}) \times \text{Volume}$   
=  $\frac{106}{100} (60) \times 5000$

= 318000 mg  
= 318 gm.

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(1) Lime required =  $\frac{74}{100} (Ca(HCO_3)_2 + 2 \times Mg(HCO_3)_2 + Mg \text{ permanent hardness} + FeSO_4 + (MgCl_2, MgSO_4, Mg(NO_3)_2 + 3 \times Al_2(SO_4)_3; \text{ All as } CaCO_3 \text{ eq.})$

2 Soda required =  $\frac{106}{100} (\text{Ca permanent hardness} + Mg \text{ permanent hardness} + FeSO_4 + 3 \times Al_2(SO_4)_3) \text{ All as } CaCO_3 \text{ eq.} \times \text{Volume} \times \frac{100}{100}$

Soda required =  $\frac{106}{100} (\text{Ca permanent hardness} + Mg \text{ permanent hardness} + FeSO_4 + 3 \times Al_2(SO_4)_3) \text{ All as } CaCO_3 \text{ eq.} \times \text{Volume} \times \frac{100}{100}$

% purity of soda.

PO = basis of calculation

Q: Calculate the amount of lime and soda required for softening of 50,000 l. of hard water containing 144 mg/l,  $Mg(HCO_3)_2$ , 25 mg/l,  $Ca(HCO_3)_2$ , 95 mg/l  $MgCl_2$ , 111 mg/l,  $CaCl_2$  & 15 mg/l  $Na_2SO_4$ .

Ans :-	constituent	strength	chemical needed	Molar mass	$caco_3$ eq.
①	$Mg(HCO_3)_2$	144	2 L	146	$\frac{144 \times 100}{2 \times 146} = 98.6$
②	$Ca(HCO_3)_2$	25	1 L	162	$\frac{25 \times 100}{2 \times 162} = 15.4$
③	$CaCl_2$	111	1 L	111	$\frac{111 \times 100}{2 \times 111} = 100$
④	$MgCl_2$	95	1 L + 1 S	95	$\frac{95 \times 100}{2 \times 95} = 100$

$$\text{lime required} = \frac{74}{100} (Ca(HCO_3)_2 + 2 \times Mg(HCO_3)_2 + MgCl_2) \text{ All as } caco_3 \text{ eqv.}$$

$$(Mg) \times 1000 \times \frac{100}{\text{Purity}} \times \text{volume} \times \frac{100}{100}$$

$$= \frac{74}{100} [15.4 + (2 \times 98.6) + 100] \times 50,000 \times \frac{100}{100}$$

$$= 11566200 \text{ mg} = 11566.2 \text{ g} = 11.5662 \text{ k.g.}$$

$$\text{soda required} = \frac{106}{100} (CaCl_2 + MgCl_2 \text{ as } caco_3) \times \text{volume} \times \frac{100}{100 \text{ purity}}$$

$$= \frac{106}{100} [100 + 100] \times 50,000 \times \frac{100}{100}$$

$$= 10600000 \text{ mg} = 10600 \text{ g} = 10.6 \text{ kg.}$$

Q: On analysis of a hard water sample it is found that the water contains 25 mg/L  $Mg(HCO_3)_2$ , 15 mg/L  $MgCl_2$ , 10 mg/L  $Ca(HCO_3)_2$  and 10 mg/L  $CaCl_2$ .

80 mg/L  $\text{CaSO}_4$  and 300 mg/L  $\text{SiO}_2$ . Calculate amount of lime (98% purity) and soda (97% purity) for softening of 30 Litres of hard water.

Soln:	Constituent	Strength	Chemical required	Molar mass	$\text{CaCO}_3$ eq.
	$\text{Mg}(\text{HCO}_3)_2$	25	2L	196	$\frac{25 \times 100}{2 \times 196} = 17.12$
	$\text{MgCl}_2$	15 L	1L + 1S	95	$\frac{15 \times 100}{2 \times 95} = 15.78$
	$\text{CaSO}_4$	20	1S	136	$\frac{20 \times 100}{2 \times 136} = 14.70$

$$\text{lime required} = \frac{74}{100} [2 \times \text{Mg}(\text{HCO}_3)_2 + \text{MgCl}_2; \text{as eq. } \text{CaCO}_3] \times$$

$$= \frac{74}{100} \left[ (2 \times 17.12) + 15.78 \right] \times 30,000 \times \frac{100}{98}$$

$$= 1133106.122 \text{ mg}$$

$$= 1.133 \text{ kg.}$$

$$\text{soda required} = \frac{106}{100} [\text{MgCl}_2 + \text{CaSO}_4; \text{as eq. } \text{CaCO}_3] \times$$

$$= \frac{106}{100} \left[ 15.76 + 14.7 \right] \times 30,000 \times \frac{100}{97}$$

$$= 999241.2371 \text{ mg}$$

$$= 0.9992 \text{ kg.}$$

Q:- A hard water sample contain 75 ppm of  $\text{Ca}(\text{HCO}_3)_2$ , require, 30 ppm of  $\text{Ca}(\text{NO}_3)_2$ , 30 ppm of  $\text{Mg}(\text{SO}_4)_2$  and 100 ppm of  $\text{Na}(\text{NO}_3)_2$ . calculate

amount of lime and soda required for softening  
of  $10^6$  L of water.

Q.: On analysis of hard water sample, it is found  
that the water contains 25 mg/L  $Mg(HCO_3)_2$ ,  
15 mg/L of  $MgCl_2$ , 20 mg/L  $CaSO_4$  and 300 mg/L  
Soda. Calculate amount of lime (98% purity) and  
soda (97% purity) for softening of 30,000 L  
of hard water. Find out the total cost of  
chemicals required to soften 30,000 L of hard water  
if the cost of lime is ₹100/kg and cost of soda  
is ₹150/kg.

Ans:- Lime required = 1.133 kg

$$\text{Cost of lime} = 1.133 \times 100 = ₹ 133/-$$

$$\text{Soda required} = 0.9992 \text{ kg}$$

$$\text{Cost of soda} = 0.9992 \times 100 = ₹ 99/-$$

$$\begin{aligned}\text{Total cost of chemicals} &= ₹ (133 + 99) / - \\ &= ₹ 232 / - (\text{approx})\end{aligned}$$

## Q. Zeolite Softening Method

28/08/19

Q: Why zeolite is used for softening?

→ Zeolite is an inorganic porous material, its chemical formula is like  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ ,  
 $[x=2-10, y=2-6]$  it is hydrated sodium aluminosilicate.

→ Zeolite has the ability to exchange reversibly, its sodium ( $\text{Na}^+$ ) ion for hardness causing ion ( $\text{Ca}^{2+}, \text{Mg}^{2+}$ ) of hard water.

→ It is of 2 types: ex:- Synthetic  $\rightarrow$  More porous  $\rightarrow$  Higher ion exchange capacity  
Natural  $\rightarrow$  Relatively less porous  
Lesser ion exchange

Q: Why synthetic zeolite is more preferable?

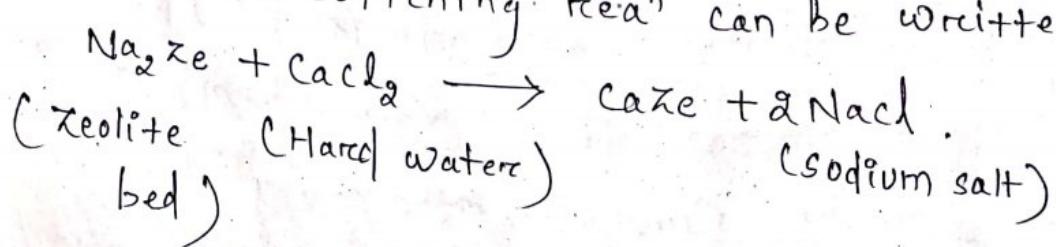
Ans: → More porous material  
→ Higher ion exchange capacity.

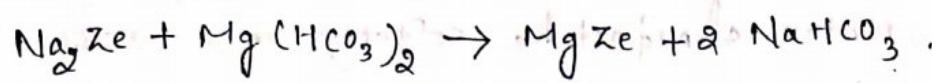
Zeolite softening method :-

→ When hard water ( $\text{Ca}^{2+}, \text{Mg}^{2+}$ ) is passed through a bed of layers of zeolite, then  $\text{Ca}^{2+}, \text{Mg}^{2+}$  ions of hard water will be block by the zeolite or the outgoing water will contain sodium ( $\text{Na}^+$ ) salt.

→ Let, the zeolite will be represented by  $\text{Na}_2\text{Ze}$ .

Then the softening reaction can be written by;

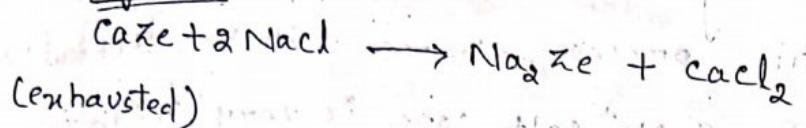




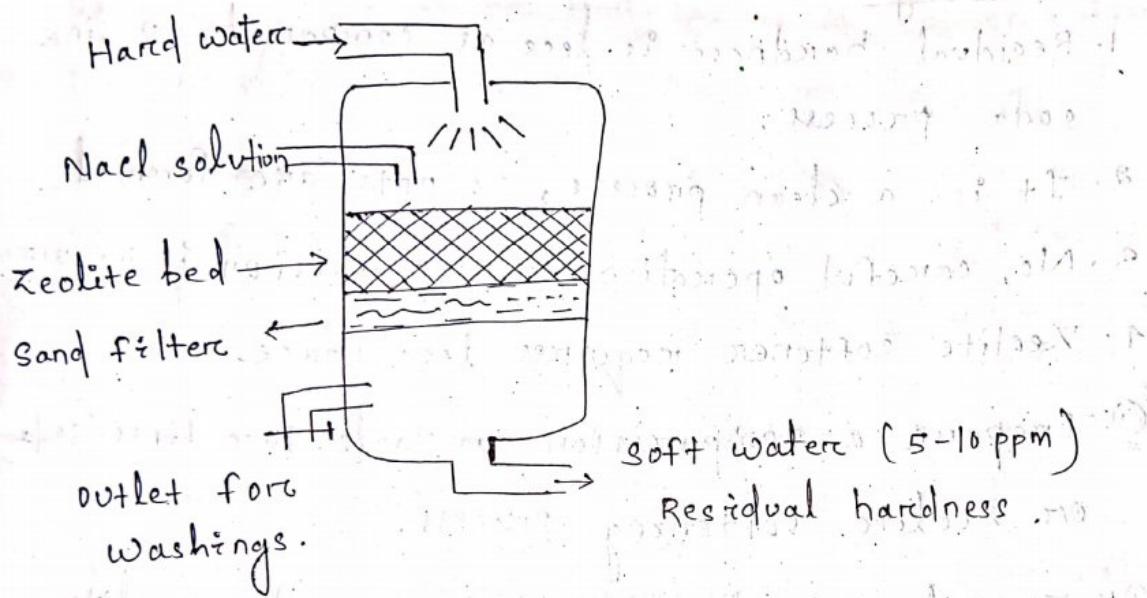
→ After sometime of softening the zeolite needs regeneration process because it has no Na<sup>+</sup> ion attach to it.

→ The regeneration can be done by spraying NaCl soln. or Brine soln. to the exhausted zeolite.

Regeneration:-



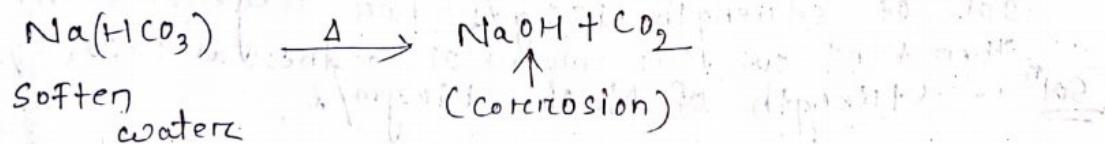
zeolite. Zeolite softener:-



Limitations:-

1. As the residual hardness bet<sup>n</sup> 5-10 PPM, not fit for boiler operation.

for boiler operation :-



2. If only cation exchanger. (Basic ex.)

3. Turbid water don't soften by this process.  
Coz; it blocks the pores. so, filtration will be stopped.

4. Acidic water shouldn't be soften, because it dissolves the zeolite.
5. The <sup>hot</sup> water shouldn't be soften as it dissolves the zeolite.
6. Dissolve gases can't be removed by this process.
7. Pathogenic bacteria aren't killed.
8. Water containing  $\text{Ca}^{+2}$ ,  $\text{Mn}^{+2}$  shouldn't be soften by this process; there will be difficulty in regeneration.
9. Nat salt conc. is very high in the soften water.

- Advantages:-
1. Residual hardness is less as compared to lime-soda process.
  2. It is a clean process, no ppt's are formed.
  3. No, careful operation or supervision is required.
  4. Zeolite softener requires less space.

Q:- Prepare a comparison table for lime-soda or zeolite softening process.

Q:- 50,000 l of hard water are softened by zeolite softener. An exhausted zeolite (A zeolite having 0 softening capacity) requires 150 l of NaCl sol<sup>n</sup> of strength 150 gm/l for regeneration. Then find out the amount of hardness as  $\text{CaCO}_3$  eq.  
Sol<sup>n</sup> :- Strength of NaCl = 150 gm/l.

$\Rightarrow$  1 L of NaCl sol<sup>n</sup> contains = 150 g of NaCl.

$$\begin{aligned}
 150 \text{ L} " " " " &= 150 \times 150 = 22,500 \text{ g} \\
 &= 22500 \times 10^3 \text{ mg of NaCl} \\
 &= (22500 \times 10^3) \times \frac{100}{\frac{2 \times 58.5}{100}}
 \end{aligned}$$

$$= 19230769.23 \text{ mg}$$

$$\cong 1.923 \times 10^7 \text{ mg as } \text{CaCO}_3 \text{ eq.}$$

Now, 50,000 L of hard water contains  $1.923 \times 10^7$  mg of hardness

$$1 \text{ L of water} = \frac{1.923 \times 10^7}{50,000}$$

$$= 384.61 \text{ mg/L or}$$

Q. An exhausted zeolite softener was regenerated by passing 150 L of NaCl sol<sup>n</sup> of strength 100 g/L. Find the total volume of water that can be softened by the water that can be a softener if hardness of water is 500 ppm as  $\text{CaCO}_3$  eq.

Sol<sup>n</sup>: - Strength of NaCl = 100 g/L

$\Rightarrow 1 \text{ L of NaCl sol}^n \text{ contains } = 100 \text{ g of NaCl}$

$$\Rightarrow 150 \text{ L of " " } = (15000 \times 10^3) \times \left( \frac{100}{2 \times 50.5} \right)$$

Given that,  $\cong 1.28 \times 10^7 \text{ mg as } \text{CaCO}_3 \text{ eq.}$

hardness = 500 ppm = 500 mg/L

$\Rightarrow 500 \text{ mg of hardness constituent in } 1 \text{ L of water.}$

$$1.28 \times 10^7 \text{ mg " " " } = \frac{1}{500} \times 1.28 \times 10^7$$

$$= 25641 \text{ L.}$$

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### Zeolite Softening

1. Residual hardness is less.  $\rightarrow$  Residual hardness is more.
2. Salt conc. is higher.  $\rightarrow$  Relatively less Nat. salt conc. & (sodium salt)
3. Pathogenic bacteria are  $\rightarrow$  In hot lime soda softening process, pathogenic bacteria are killed.
4. Dissolved gases can't remove.  $\rightarrow$  Dissolved gases can remove.
5. No ppt., a clean process.  $\rightarrow$  ppt. occurs.
6. Less space requires.  $\rightarrow$  More space requires.
7. Turbid & acidic water  $\rightarrow$  No, such limitations. Should be avoided.
8.  $Mn^{2+}$  and  $Fe^{2+}$  can't be removed  $\rightarrow$  No, such limitations.
9. Hot water can't be used.  $\rightarrow$  No, such limitations.
10. Regeneration of zeolite  $\rightarrow$  Regeneration isn't required.

### Lime Soda softening

- (3) Res.  $\rightarrow$  It is  
 $\rightarrow$  In + ion  
 $\rightarrow$  Ther. mic  
 $\rightarrow$  Resi.

(1)

(2)

### (3) Resin Softening Method :-

- It is also an ion exchange process.
- In this process, thermosetting resins are used as ion exchangers.
- Thermosetting resins are cross-linked polymer with micropore structure.

→ Resins used for softening are of 2 types:-

(1) Cation exchange Resin :- This resin has got the ability to exchange its cation ( $x^+$ ) reversibly for cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ) of hard water.

→ To act as cation exchanger, acidic functional groups like  $-COOH$ ,  $-OH$ ,  $-COO^-$ ,  $-SO_3H$  are attached to the resin.

(2) Anion exchange Resin :- It will exchange reversibly its anion ( $OH^-$ ) for anion present in the hard water.

→ To behave as anion exchanger basic functional groups like  $-NH_2$  as hydroxide, are attached to the thermo-setting resin.

Working process :- After suitable conditions

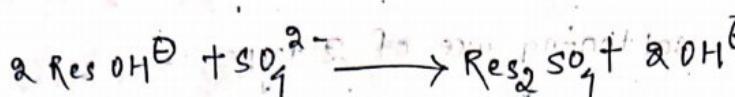
→ this softening method consists up to two ion exchangers and two regenerating tanks.

→ When hard water is passed through a cation exchange resin the  $Ca^{2+}$ ,  $Mg^{2+}$  ions are written by and its ion along with outgoing water.

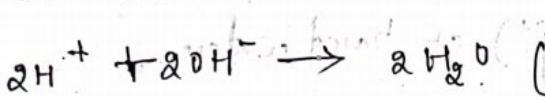


(Hard  
water)

Now, this outgoing water will be passed through an ion exchange region. So, that anions of hard water



→ the  $\text{H}^+$  ion exchange by cation exchanger and the  $\text{OH}^-$  " " " anion "



This is the reason why this is otherwise known as deionisation & demineralisation process.

### Regeneration process:

After softening for regeneration time, we loose

are exhausted. Regeneration solution is avoided if a

so their regeneration is required.

The exhausted cation exchanger can be regenerated

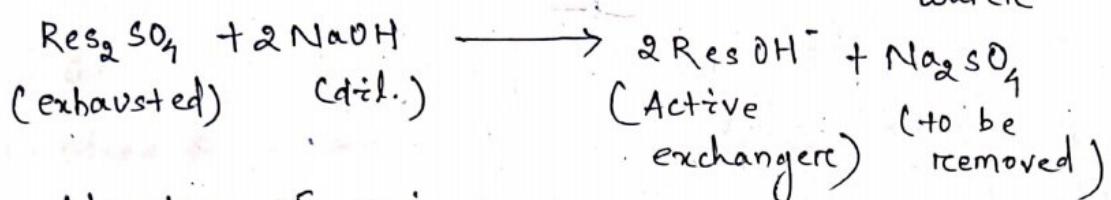
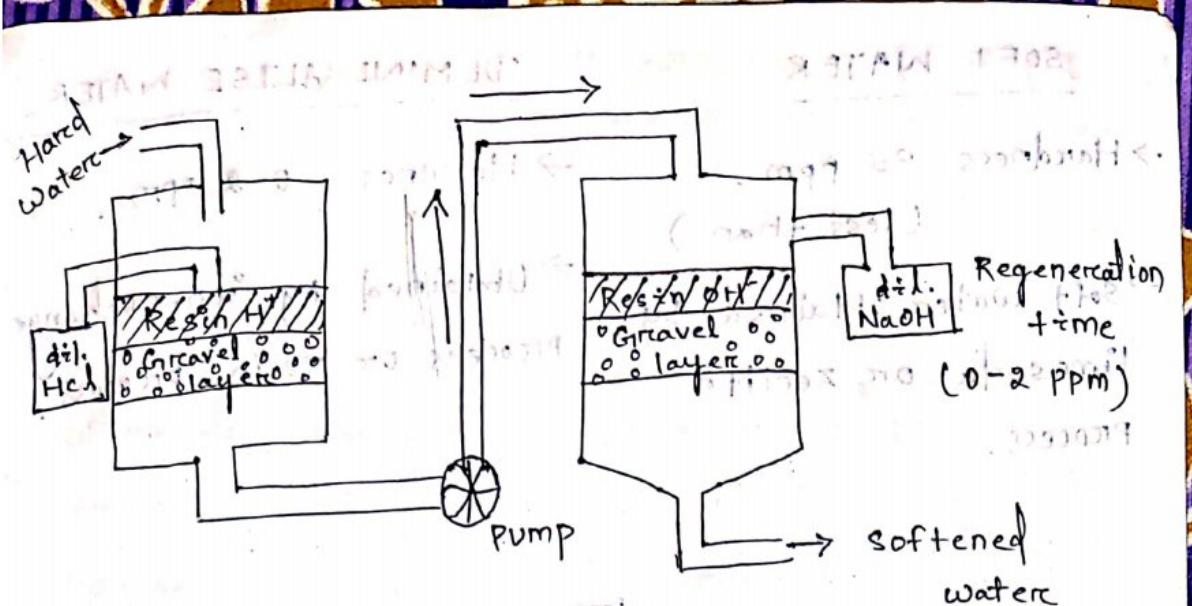
washing it with dil.  $\text{HCl}$ .

$\text{Res}_2 \text{Ca} + 2\text{HCl}$

(Exhausted) - dil.

The exhausted anion exchanger can be regenerated

washing it with  $\text{Na}_2\text{SO}_4$ . So, we work with



Advantages of resin process:-

04/09/19

- Residual hardness lie bet<sup>n</sup> 0-2 ppm. So, water is fit for boiler operation.
- Rate of softening & softening capacity is very high.
- Hot water & acidic water, alkaline water can be softened.

Limitations:-

- Problems with turbid water. It can't be softened.
- It is a costly process.
- Ion free water not fit for drinking.

Q:- Diff. bet<sup>n</sup> soft water & demineralise water.

## SOFT WATER

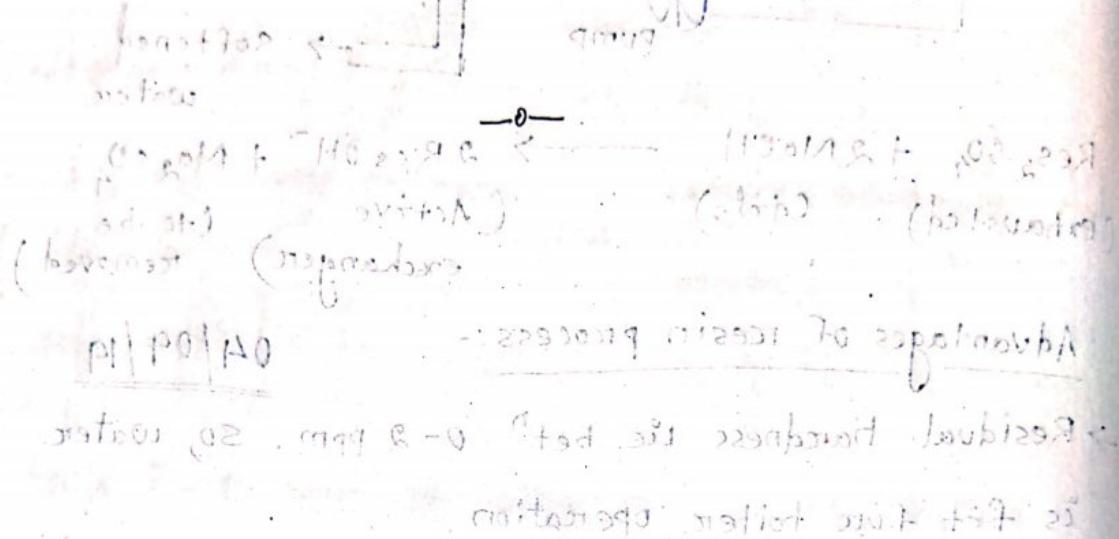
→ Hardness 85 ppm.  
(less than)

→ Soft water obtained by  
Limesoda or zeolite  
process.

## DEMINERALISE WATER

→ Hardness 0-2 ppm.

→ Obtained by ion-exchange  
process or resin process



## Module-2

# CORROSION SCIENCE

Q:- What is corrosion?

→ A process that gradual loss of metal from its surface due to unwanted chemical or electro-chemical reaction of metals with its environment.

examples :-

① Rusting of iron

② Grey layer on the surface of copper vessel.

③ Black layer of silver articles (Tarnishing)

Limitations :- (Disadvantages)

→ Loss of useful properties of metal.

→ Results in loss in efficiencies of machinery.

→ Contamination of product occurs.

→ Contamination of drinking water.

→ Leakage of toxic liquids or gases.

→ Non-predictable failures of machinery, that may leads to loss of life.

Types of corrosion :-

It is 2 types :-

① Chemical or dry corrosion

→ It occurs in dry atmosphere or non-aqueous environment.

→ It occurs when metallic exposed to dry atmosphere containing gases like  $O_2$ ,  $Cl_2$ ,  $H_2S$ , etc.

or non-aqueous liquids. Ex:- Oxidation corrosion.

## ② Electro-chemical/Wet corrosion [S - Type]

- It occurs in ~~wet~~ wet atmosphere containing moisture and proceeds via electro-chemical reaction.
- Ex:- Rusting of iron.
- Q:- Diff. bet<sup>n</sup> dry & wet corrosion :-

### chemical or dry corrosion

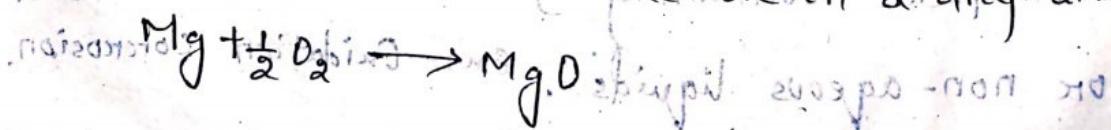
- Occurs in dry atmosphere. → Occurs in wet atmosphere.
- Proceeds via direct attack. → Proceeds via formation of electro-chemical cell.

### electro-chemical/Wet corrosion

- Dry corrosion is a slow process.
- Only occurs in heterogenous process.
- It is uniform in nature. → It is non-uniform.
- Ex:-
- Oxidation corrosion. → Rusting of iron.

## ★ DRY OR CHEMICAL CORROSION

- Oxidation corrosion is a dry corrosion.
- It occurs when a metal (Fe, Cu, Zn, Al, Na, K, Hg...) is exposed to oxygen ( $O_2$ ) atmosphere in absence of moisture or in a dry atmosphere.



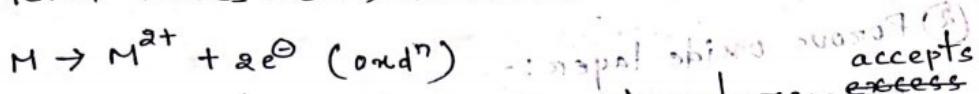
## Mechanism of oxidation corrosion

Let's take the formation of metal oxides ( $MO_x$ )

by react betw metal & oxygen gas

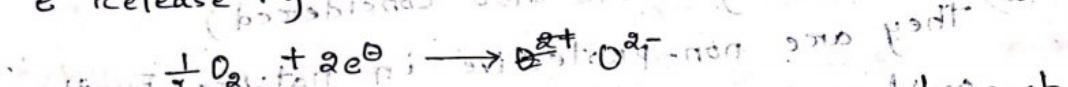
The various steps involved are :-

1. Metal loses electrons to form metal ions.



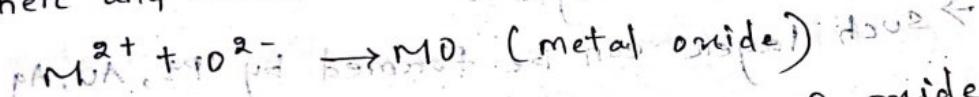
2. The oxygen present in the atmosphere accepts excess

$e^-$  release by metals to form oxides.



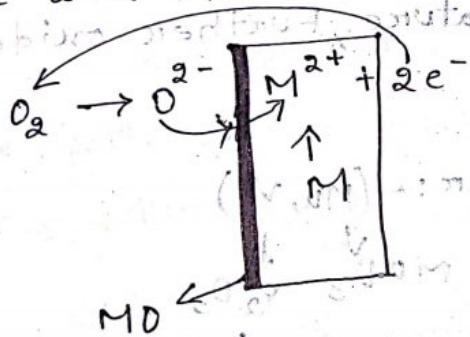
3. Now,  $M^{2+}$  ions and  $O^{2-}$  ions move towards each

other and form metal oxide at the surface.



4. As the time passes, the thickness of oxide

layer will increase.



5. the nature of oxide layer formed on the surface will decide whether further oxidation will take place or not.

05/09/2019

Nature of metal oxides

→ When a metal is exposed to oxygen atmosphere a thin layer of oxide is formed on his

surface.

→ Nature of oxide may be of following types:-

① Non-porous or stable oxide layer :-

→ Metals like Cu, Al, Cr forms non-porous or stable layers. Copper & Iron form these layers.

→ So, they are protective in nature. No further oxidation / corrosion will occur.

Q:- Give  
Ans:-  
Cr.

② Porous oxide layer:-

→ Fe, Al, Ca, Mg etc. forms porous layer.

(Na, Ca, Mg etc. also considered)

→ They are non-protective in nature. Further oxidation / corrosion will occur.

atm  
Circ  
OR WI  
all  
→ WI  
or  
→ By  
Pm  
sharic  
Pz  
→ Ac

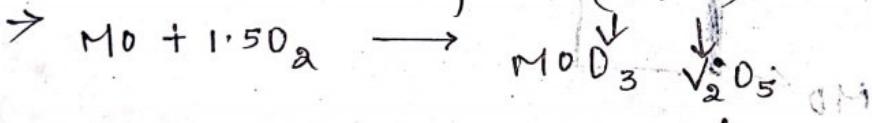
③ Unstable oxide layer:-

→ such layers can be formed by Pt, Au, Ag etc.

so  $\text{Pt} + \text{O}_2 \rightleftharpoons (\text{PtO}_2) (\text{Au}_2\text{O}_2) (\text{Ag}_2\text{O})$

→ It is safe in nature. Further oxidation will occur.

④ Volatile oxide layer:- (Mo, V)



→ Rapid oxidation / corrosion will occur.

Q:- What do you mean by protective oxide layer?

Ans:- Non-porous or stable oxide layer is known as protective oxide layer.

Q:- Which class of oxide layer favours oxidation?

→ Porous & volatile oxide layers.

Q: Give reason that stainless steel maintains its resistance or shining for a long period of time?

→ As we know, that steel is an alloy of Fe, Al, Cr, etc. (so, when it expose to oxygen &

atmosphere, it forms protective oxide layer)

( $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  to prevent oxidation corrosion)

OR white rusting of Fe will be avoided by alloying with Cr & Al. Give explanation.

→ We know that Fe forms a porous oxide layer on exposure to oxygen, helps oxidation corrosion.

→ By allowing it with Al, Cr, it will form a protective oxide layer to prevent oxidation

corrosion.

Pilling-Bedworth Rule (PBR) for corrosion

→ According to this rule, smaller is the specific volume ratio

specific volume ratio =  $\frac{\text{Vol. of metal oxide}}{\text{Vol. of oxide}}$

In this case oxide layer is porous in nature.

In this case oxide layer is porous in nature, as greater is the rate of oxidation corrosion, as oxide layer is porous in nature.

Significance: - this rule helps us to knowing whether the oxide layer is protective

or non-protective in nature.

→ If specific volume is greater than 1, but

less than 2, then oxide layer is non-

porous and protective ( $\text{Cu}, \text{Al}, \text{Cr}$ ).

- If specific volume ratio is less than 1 it is porous and non-protective in nature (Na/K/Ce)
- If specific volume ratio is greater than 1 it is also non-protective (Fe)

### ★ Electro-chemical Corrosion / Wet Corrosion:

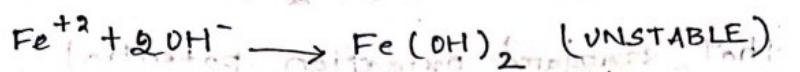
- It is a wet corrosion occurs when a metal will expose to humid atmosphere & proceeds with formation of electrochemical cell.
- It involves:
  - Formation of separate anodic & cathodic regions on two parts, b/w which corrosion current can pass through electrolyte.
  - Generation of metal ions by loss of  $e^-$  at anode.
  - Formation of ions like  $\text{OH}^-$  by accepting  $e^-$  at cathodic region or cathode.
  - Diffusion of two oppositely charged ions takes place to form corrosion product near cathode.

Let's take the example of rusting of iron in an alkaline or neutral atmosphere.

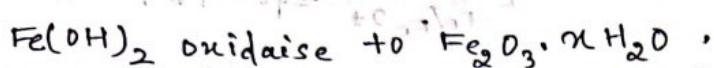
#### Mechanism of rusting of Iron:

- When Fe is exposed to a humid environment Fe lose  $e^-$  to form  $\text{Fe}^{2+}$  ion by oxidation process.
- Anode (Oxid<sup>n</sup>):  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$
- $\text{H}_2\text{O}$  &  $\text{O}_2$  in the environment consume  $e^-$  to form  $\text{OH}^-$  ions. cathode (Red<sup>n</sup>):  $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^-$

3. The two oppositely charged ions ( $\text{Fe}^{+2}$ ,  $\text{OH}^-$ ) move towards each other to form Ferricous hydroxide.



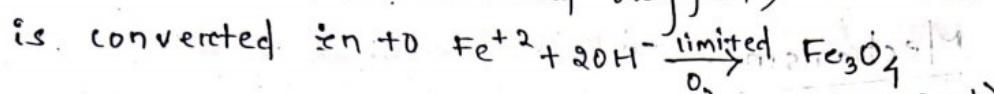
i) In presence of excess or sufficient oxygen,



(Brown rust) - Hematite.

(Non-magnetic in nature)

ii) In presence of limited oxygen,  $\text{Fe}(\text{OH})_2$



(Black Rust)

(Magnetic)

Factors affecting the rate of rusting of iron :-

i) conc. of  $\text{O}_2$  in the atmosphere :-

rate of rusting  $\propto$  conc. of  $\text{O}_2$  in the atmosphere.

ii) % humidity in the environment :-

(Directly proportional).

iii) the rust itself.

The rust itself acts as a barrier to further oxidation of iron.

iv) When iron is connected to less active metal like copper (Cu).

Some typical electro-chemical corrosion :-

1. Galvanic corrosion :-

→ It is an wet corrosion / electro-chemical corrosion.

→ It occurs when 2 different metals are connected

and exposed to a corrosive environment.

→ Hence, the metal with low standard red<sup>n</sup> potential

or high standard oxid<sup>n</sup> potential acts as anode

and suffers from corrosion.

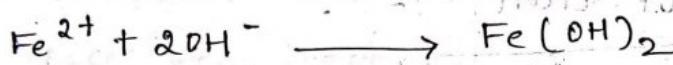
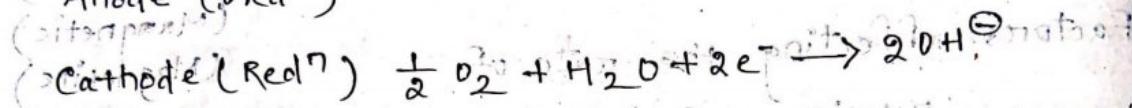
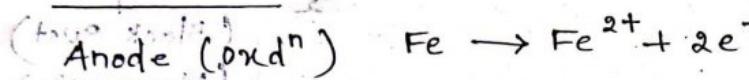
ex:- Fe & Cu are connected and exposed to a humid environment ( $O_2 + H_2O$ ).

→ We know that standard oxidation potential of Fe is  $+0.46\text{ V}$ .  $E^\circ_{Fe/Fe^{2+}} = +0.46\text{ V}$  and standard reduction potential of Cu is  $E^\circ_{Cu/Cu^{+2}} = -0.32\text{ V}$ .

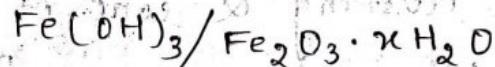
Therefore, Fe acts as anode.

Cu acts as cathode.

### Mechanism



↓ Further oxidation



Rust

→ Galvanic corrosion is otherwise known as bimetallic or differential corrosion.

### Control of galvanic corrosion

→ By providing an insulating layer / coating between 2 layers.

→ Anodic area  $>$  cathodic area.

→ Try to avoid galvanic coupling.

Q: What is galvanic corrosion? Discuss its mechanism with a suitable example.

How to control it?

Fact  
① Diff  
Lo  
b

②

③

## Factors affecting galvanic corrosion:-

- ① Difference in standard potential of two metals:-  
Larger the difference of standard potential greater be the galvanic corrosion.

- ② Size of anode :-

If  $\frac{\text{cathodic Area}}{\text{Anodic Area}} < 1 \Rightarrow$  less corrosion

$> 1 \Rightarrow$  Intense/fast corrosion

- ③ % humidity :-

% humidity  $\propto$  rate of corrosion

## 2. Differential aeration corrosion:

(O<sub>2</sub> conc. cell corrosion)

$\rightarrow$  It is a conc. cell corrosion.

$\rightarrow$  It is of 2 types :-

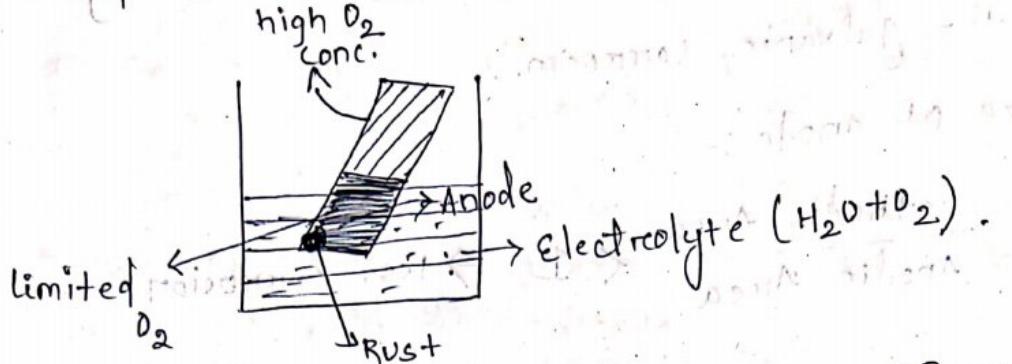
① Electrolyte conc. cell corrosion :- It occurs when the metal surface is exposed to an electrolyte of different conc.

② Differential aeration corrosion :- It occurs when the metal surface is exposed to different air or oxygen conc.

$\rightarrow$  In this case, metallic part which is exposed to limited oxygen acts an anode & suffers from corrosion.

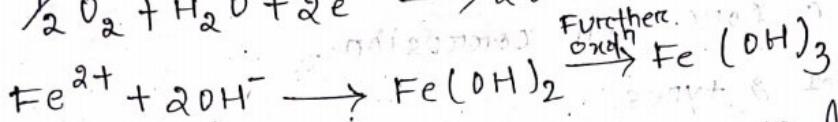
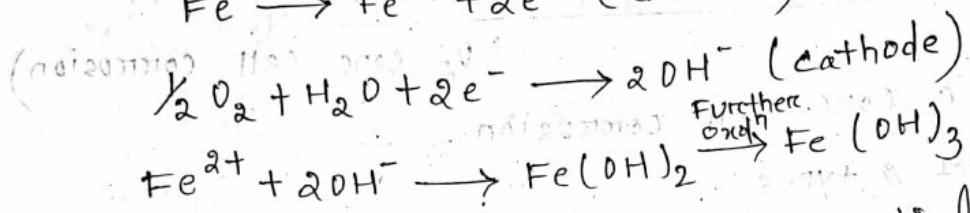
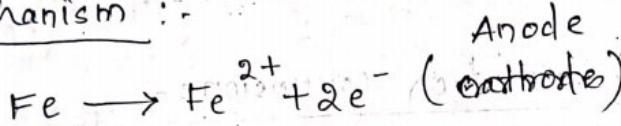
$\rightarrow$  Let's consider that, an iron metal is partially dipped in an electrolyte & rest part of iron metal exposed to atmosphere.

→ In this case metallic part dipped in the electrolyte is exposed to less oxygen as compare to metallic part exposed to atmosphere.



→ So, dipped part acts as an anode & suffers from corrosion.

### Mechanism :-



Some typical examples of differential aeration corrosion are:

① Waterline Corrosion

② Pit Corrosion

③ Soil Corrosion

① Waterline Corrosion:-

→ It is a diff. aeration corrosion.

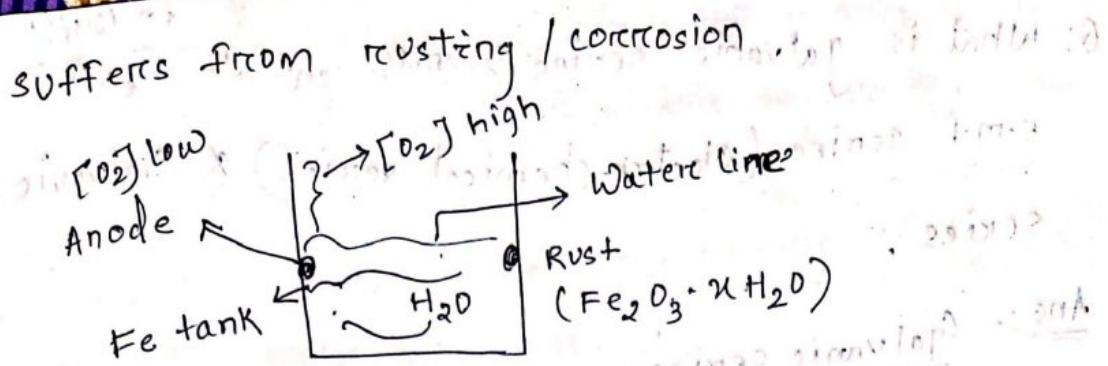
→ Corrosion of metal occurs just below the water line, when a iron tank is

half filled with water.

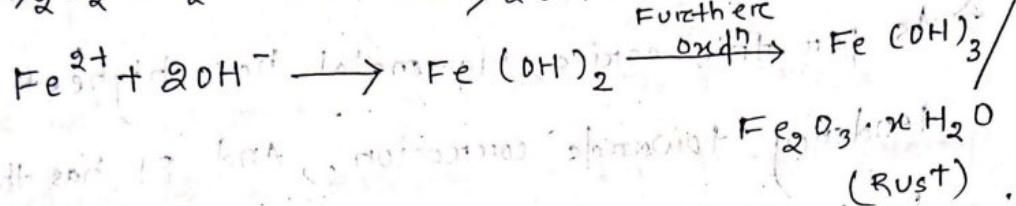
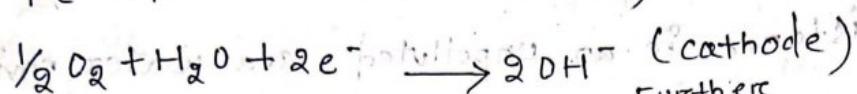
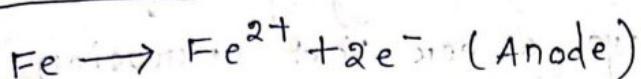
→ In this case, the metallic part

below the water line is exposed to

limited O<sub>2</sub>, so, it acts as an anode &



Mechanism:-



Q:- How much rust (Fe<sub>2</sub>O<sub>3</sub> · 3H<sub>2</sub>O) of that composition will be formed when 100 kg of iron is completely rusted away?

Soln :- Fe<sub>2</sub>O<sub>3</sub> · 3H<sub>2</sub>O - Molecular formula of rust. (Given)

Hence atomic mass of Fe  $\rightarrow$  56

Now, molecular mass of rust  $\rightarrow (2 \times 56) + (3 \times 16) + 3(18) = 214$

2 × 56 g of iron given rust  $\rightarrow$  214 g.

(112 g)

$$1 g \rightarrow \frac{214}{112} g$$

$$100 \text{ kg} \rightarrow \left( \frac{214}{112} \times 100 \right) \text{ kg} = 191.07 \text{ kg rust}$$

Q:- How much rust Fe<sub>2</sub>O<sub>3</sub> · nH<sub>2</sub>O will be formed when 150 kg of Fe is completely rusted?

2018-19 session 3rd term 3rd semester

Topic 10: Electrochemistry and its applications

Q:- What is galvanic series? Differentiate between Galvanic e.m.f series (Electro-chemical series) & Galvanic series.

Ans :- Galvanic series :-

→ It is obtained by arranging sequentially metals & alloys as per that corrosion resistance is an unpolluted sea water environment.

→ As per this series, Mg metal has highest tendency towards corrosion, and Pt has the least tendency towards corrosion.

→ This series predicts the relative tendencies of various metals & alloys towards corrosion.

↳ Galvanic Series

① It is obtained by arranging standard reduction potential in the increasing order for various metals & non-metals.

② It includes metals & non-metals.

③ No place for alloys.

④ Pos<sup>n</sup> of metals & non-metals are constant.

⑤ Gives information about relative displacement tendency.

① It is obtained by arranging metals & alloys sequentially.

② It consists of metals & alloys.

③ No place for non-metals.

④ Pos<sup>n</sup> changes by changing the environment of metals.

⑤ Gives information about corrosion tendency.

## Factors affecting Corrosion:-

- We know that, corrosion occurs due to interaction bet'n metal & environment.
- So, nature of metal and the nature of environment affect the rate of corrosion.
- Here nature of metal means its posn in the galvanic series, size of the anode, nature of oxide formed on its surface, purity of metals, particle size of metal, solubility of corrosion products, volatility of corrosion products.

(Nature of environment includes temp, humidity, pH of the electrolyte, presence of suspended particles in the atmosphere.)

### ① Nature of metal affecting rate of corrosion:-

- Posn of metal in galvanic series.
- In general active metals act as anodes.
- Rate of corrosion can be studied from its posn, larger is the diff. posn greater will be the rate of corrosion.

### ② Anodic size :-

- If size of anode is much smaller than size of cathode, intense corrosion will occur.

### ③ Nature of oxide formed on its surface:-

- For a protective oxide film, it should be non-porous in nature.

Ex:- Aluminium oxide.

### ④ Purity of metal:-

- Corrosion occurs at a ~~rate~~ rapid in case of impure metal, than pure metal.

BlO<sub>2</sub> impurity in metal makes it heterogeneous  
so, it leads to formation of electro-chemical  
cell & corrosion then leads to corrosion.

Q:- (Give reason that impure Zn suffers from  
rapid corrosion, than pure Zn).

⑤ Particle size :-  
→ We know that surface area increases as  
particle size decreases.

→ So, as particle size decreases, rate of reaction  
increases.

⑥ Solubility of corrosion product :-  
→ If the corrosion product get dissolves in the  
electrolyte, rapid corrosion will occur.  
→ If it insoluble in nature, it get coated  
over the metal & resist corrosion.

Q:- (Rapid corrosion occurs, when Fe is dipped  
in H<sub>2</sub>SO<sub>4</sub>, whereas, least corrosion occurs  
when Pb is dipped in H<sub>2</sub>SO<sub>4</sub>)

Hint:- PbSO<sub>4</sub> insoluble in nature, whereas as FeSO<sub>4</sub> is  
soluble, It get absorbed.

⑦ Volatility of corrosion product :-  
→ If corrosion product like MoO<sub>3</sub>, is volatile  
in nature, then rapid corrosion is occur.

⑧ Passive nature of metals :-

⑨ Passivity :- It is the phenomenon by which a  
metal achieve its higher corrosion resistance  
than expected, in its pos in the electro-chemical series.

is known as passivity. 16/09/2019

### Nature of environment affecting rate of corrosion:

① Temperature :- As temp. of environment increases the rate of reac? & diffusion increases, hence rate of corrosion increases.

② pH of medium / Electrolyte :- Rate of corrosion is

greater in acidic medium ( $\text{pH} < 7$ ) than in alkaline ( $\text{pH} > 7$ ) or neutral medium ( $\text{pH} = 7$ ).

③ Humidity (%) :- % humidity increases, rate of corrosion increases (directly proportional)

④ Presence of impurities in the atmosphere :- Presence of impurities like  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{CO}_2$ , etc. and fumes of  $\text{HCl}$  &  $\text{H}_2\text{SO}_4$  in the atmosphere of industrial area make the environment acidic. So, rate of corrosion is more than in domestic area.

⑤ Presence of suspended particles :- Presence of suspended like  $\text{NaCl}$ , activated charcoal,  $(\text{NH}_4\text{NO}_2)_4$  &  $(\text{NH}_4)_2\text{SO}_4$  absorb moisture from the atmosphere & act as strong electrolyte. Thus, assist in electrochemical corrosion.

Q:- Sn (Tin) undergoes <sup>rapid</sup> corrosion in presence of  $\text{Cl}$  gas, whereas  $\text{Ag}$  resists. Give reason.

Ans :- Sn reacts with  $\text{Cl}_2$  to form  $\text{SnCl}_4$  (A volatile mass)  
 $(\text{Sn} + 2\text{Cl}_2 \rightarrow \text{SnCl}_4)$

So, it undergoes rapid corrosion, whereas Ag forms a protective layer on its surface as  $(\text{Ag} + \frac{1}{2}\text{Cl}_2 \rightarrow \text{AgCl})$

Q :- Corrosion of iron occurs rapidly in saline water than in ordinary water. Explain.

Ans :- In saline water presence of  $\text{NaCl}$ , makes it more conductive & acts as excellent electrolyte relative to ordinary electrolyte. So, it favours corrosion.

Although Al lies above Fe in electrochemical series, Fe undergoes corrosion.

Q :- Al lies above Fe in electrochemical series, yet Fe undergoes corrosion. Give reason.

Ans :- When Al expose to  $\text{O}_2$  from  $\text{Al}_2\text{O}_3$  forms protective layer on their surface, whereas Fe forms porous layer on its surface.

Q :- Nut & bolt should be of same metal.

Give reason.

Ans :- Otherwise galvanic corrosion will occur.

Q :- Why does part of an iron nail inside the wooden st<sup>n</sup> (wood) undergoes corrosion to oxygen?

Ans :- Bcoz, part of the nail inside the wood is exposed to relatively less  $\text{O}_2$  & acts as anode. Hence corrosion will occur.

due to diff. aeration corrosion conc. cell.

Q:- A piece of pure Zn and impure Zn placed in a salt sol<sup>n</sup>, which will corrode faster?

Ans :- Impure Zn will corrode faster due to electro-chemical corrosion.

Q:- Corrosion of water filled steel or iron tank occurs below the waterline. Give reason.

Ans :- Due to diff. aeration corrosion.

Q:- Why an iron bar (sheet) shouldn't be connected to Cu.

Ans :- Otherwise galvanic corrosion will occur.

Q:- Iron corrodes under a drop of sol<sup>n</sup>. Give reason.

Ans :- Bcoz that part below the drop is exposed (metallic)

to limited O<sub>2</sub>. so, it will act as an anode & suffers from diff. aeration corrosion.

Q:- Wire mesh corrodes faster than the corners. Give reason.

A:- Corners or joint area are less exposed to O<sub>2</sub>. And acts as anode & suffers from diff. aeration corrosion.

Q:- Small anodic area results in intense corrosion. Give reasons.

Ans :- Intense corrosion occurs if cathodic area is greater than anodic area, then cathode will demand huge no. of e<sup>-</sup> from the smaller anode.

This huge demand of  $e^-$  can only be fulfilled when the rate of rush of  $e^-$  will be very fast in anode, this means rapid. So intense corrosion will occur.

Q:- A cu equipment shouldn't posses a small steel or iron board. (Same ↑)

Ans Q:- A pure Fe metallic rod, have emerged vertically in water starts corroding at the bottom. Give reason.

Ans:- The metallic part emerged in water is less excess to limited amount of  $O_2$  and that part acts as anode & due to diff. aeration corrosion.

Q:- The rate of metallic corrosion increases with increase in temp. Give reasons?

Q:- Al isn't attacked by conc.  $HNO_3$ . Why?

Q:- Pb resists dissolution with conc.  $H_2SO_4$  whereas Fe suffers rapid corrosion.

Ans:- Forms protective layer ( $PbSO_4$ ) which acts as barrier.

Q:- Presence of  $SO_2$  &  $CO_2$  in atmosphere assists corrosion. Why?

Ans :- Such gases make the environment acidic

& it acts as strong electrolyte.

Q:- Why is deposition of sand & dirty particles on the metal surface for a long period is undesirable?

Ans:- The metallic part just below the sand or dirty particle is exposed to limited amount of  $O_2$ . So, it acts as small anode & suffers from rapid or intense diff. aeration corrosion.

18/09/19

### Control of rate of corrosion:-

Various corrosion preventing methods are:-

- ① By use of pure metal → Because impurity in metal assists in formation of electro-chemical cell.
- ② By alloying → (A modification in the nature of metal) Rate of corrosion can be minimized by alloying with Al, Cr etc.
- ③ By proper design→
  - Contact of two different metals should be avoided.
  - If different metals are connected, then the area of anode should be much greater than area of cathode.
  - If 2 metals have to be connected, then they should be closer to each other in a galvanic or electrochemical series.
  - By putting an insulating layer betw 2 metals
  - In any earth structural design, sharp corners and recesses should be avoided.

## ① By modification of environment :-

→ If corrosion is due to diss.  $O_2$ , this can be

prevented, by its removal of  $O_2$  adding  
Hydrazine ( $N_2H_4$ ).

→ If corrosion is due to humidity, it can be  
controlled by using de-humidify agent.

↓  
(silica gel/  
activated charcoal)

→ If corrosion is due to acidic masses,  
then it can be controlled by neutralising  
it with equal amount of base.

## 5) By metallic coating :- (Zn, Sn coating)

(Protective)

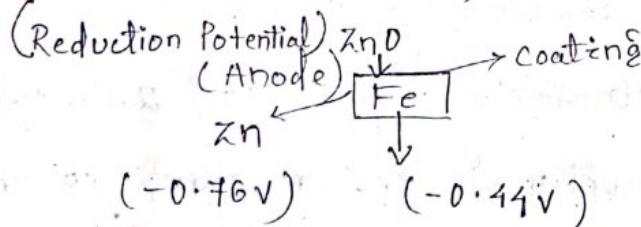
→ It is of 2 types. (i) Anodic metal coating  
(ii) Cathodic metal coating.

### (i) Anodic metal coating

\* In this method, which is to be protected  
from corrosion that metal is coated by a  
more active metal (anodic metal).

Ex:- Coating of Zn metal on the surface  
of Fe. (Zn & Mg are used as anodic coating  
w.r.t Fe)

→ The process of coating of Zn on the  
surface of Fe, is called galvanisation.



→ Hence Zn acts as anode and its standard  
reduction potential is less than Fe.

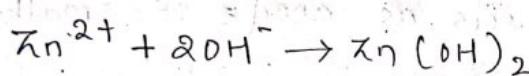
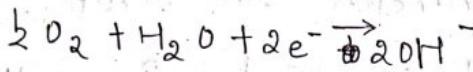
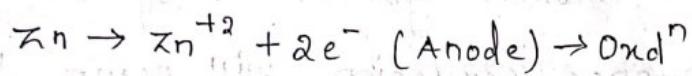
\* In case of galvanization iron, the base metal(Fe) is protected from corrosion by following 2 ways.

- 1) When it expose to atmosphere Zn provides a protective oxide layer on the surface of iron.

- 2) By sacrificial protection method.

Let's consider that a small portion of Oxide layer has pilled up or punctured or destroy. Then in this case the more anodic metal Zn will act as anode and suffers from corrosion.

→ Hence,  $ZnO$

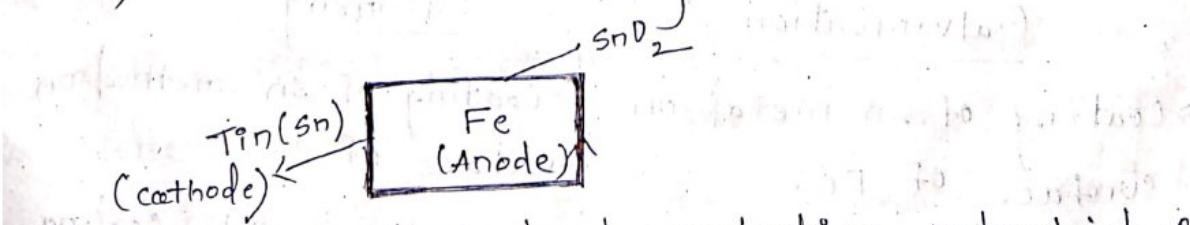


(Corrosion product)

(ii) Cathodizing metal coating: - 19/09/19

\* In this method, the metal which is protected from corrosion to be coated by a less active metal than it. (Ni & Sn acts as cathodizing metal coating w.r.t Fe)

Ex:- Coating a layer of Sn on the surface of Fe, is known as Tinning process.



→ We know that standard reduction potential of Fe is  $-0.44\text{ V}$ , whereas that of Zn is  $-0.14\text{ V}$ . (higher reduction potential.)

So, in this case Fe acts as an anode and Sn acts as an anode.

When a Sn coated Fe container is exposed to atmosphere, then a protective oxide layer of Sn; Stannic Oxide ( $\text{SnO}_2$ ) developed on the surface of Fe.

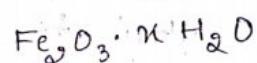
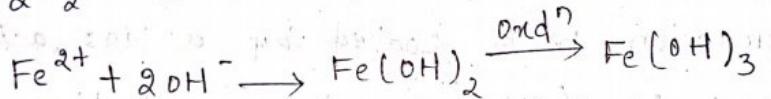
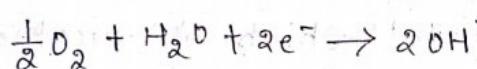
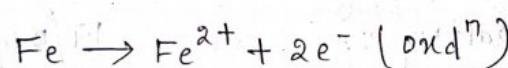
→ Tinning process is a single protection method.

Protected the underlining Fe by forming

Protective oxide on its surface.

→ If due to some reason, the protective oxide layer is broken got pilled up or broken, then intense corrosion will occur, because the underlining Fe acts as anode of smaller in size.

→ The intense corrosion proceeds as follow:-



(Rust)

Q: Distinguish bet<sup>n</sup> galvanisation & tinning.

Galvanisation

Tinning

→ Coating of Zn metal on surface of Fe. → Coating of Sn method on surface of Fe.

→ Anodic metal coating. → Cathodic metal coating

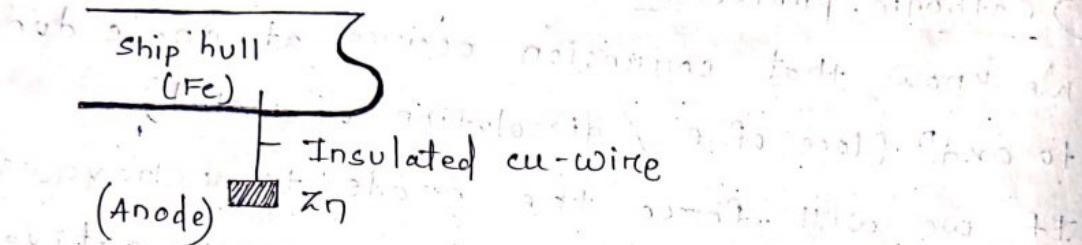
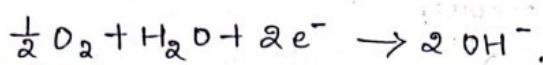
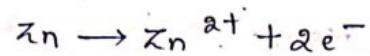
→ Protect Fe by double protection method. (always) → Protect Fe by single protection.

1. Forming an oxide layer.
2. Sacrificially.  
→ Galvanized iron (GI pipes) → Tin coated Fe containers  
containers isn't suitable are saved to store food  
food for storing items. Other items.  
wise food poisoning occurs.  
(Toxic to human being)

#### ⑥ Cathodic protection :-

- We know that corrosion occurs at anode due to oxd<sup>n</sup> (loss of e<sup>-</sup> / dissolution of metal).
- If we will force the anode to behave as cathode by connecting it to a more active metal then, the metal which we want to protect from corrosion behave as cathode.
- This method is known as cathodic protection. It is also known as electro-chemical protection method.
- Sacrificial anodic protection method :- (example)
- \* It is a cathodic protection method, in which the metallic st<sup>n</sup> which is to be protected from corrosion to be connected by a wire (cu wire) to a more anodic metal like Mg, Zn etc.
- \* So that, the corrosion will occurs as more active metal, metallic st<sup>n</sup> can be protected.
- \* Hence the more active metal Mg, Zn wire is known as sacrificial anodic protection method.
- \* This method is used to prevent corrosion

or to control corrosion of underground pipelines, cables, various marine structures, water tanks, ship hulls.



### ⑦ Use of inhibition:-

Inhibitors:- These are the chemical substances added to the environment or electrolyte to reduce the rate of either anodic / cathodic reaction. It is of two types:-

i) Anodic inhibitors  $\rightarrow$  Substances like chromates, molybdates, phosphates, silicates of transition metals are used to sub-process the rate of anodic reaction.

ii) Cathodic inhibitors  $\rightarrow$  Substances like amines, metal soaps, thiourea are added to cathodic reaction.

Q:1) Fe undergoes oxidation faster than Al even though ironic plate below Al in the electrochemical series. Give reason.

Ans :- When Fe & Al exposed to  $O_2$ , Fe forms a porous oxide layer on its surface whereas Al forms a non-porous (protective) oxide layer on its surface.

Q:2) Why a Cu equipment shouldn't possess a small steel iron bolt?

Ans :- Bcoz, it will undergoes galvanic corrosion (bi-metallic corrosion / differential aeration corrosion). As, hence a small iron steel bolt will acts as anode.

Q:3) Rusting of Fe is quicker in saline  $H_2O$  than in normal  $H_2O$ .

Ans :- Saline  $H_2O$  is more conductive and will act as good electrolyte.

Q:4) Why a Zn plate should be fixed to the lower part of the ship hull?

Ans :- Hence Zn plate will protect the Fe, in the ship hull acts as sacrificial anode.

Q:5) A pure metal rod have emerged vertically in  $H_2O$  and starts corroding in water at the bottom.

Ans ! - Corrosion will occur at bottom part bcoz it is expose to less amount of  $O_2$  so it acts as anode.

Q:6) Corrosion of water filled steel or Fe iron occurs below the water line.

Ans:- Differential aeration corrosion.

Q:7) Fe corrodes faster under the drop of a salt soln.

Ans:- Metallic part just below the salt is exposed to less amount of  $O_2$ . So, it acts as small anode & suffers from intains diff. aeration corrosion.

Q:8) Presence of gases like  $SO_2$ ,  $CO_2$  in the atmosphere assists electro-chemical corrosion. Give reasons.

Ans:- Bcoz, these gases react with  $H_2O$  to make the environment acidic enhancing assisting electro-chemical corrosion.

Q:9) Al isn't attacked by even conc.  $HNO_3$ . Give reason?

Ans: Bcoz, it forms a protective oxide layer, when it reacts with  $HNO_3$  (a strong oxidising agent).

Q:10) Sn undergoes severe corrosion in presence of  $Cl_2$  gas whereas Ag resists it. Give reason.

Ans:-  $Sn + 2Cl \rightarrow SnCl_4$  (Volatile nature)

$Ag + 2Cl \rightarrow AgCl$  (protective layer)

Q:11) Why does part of an iron nail inside a wood undergoes corrosion. Why?

Ans:- Part inside the wood acts as anode & suffers from diff. aeration corrosion.

Q: 12) Wire mesh corrodes faster at the joints or corners. Give reasons?

Ans :- Because, these areas are less amount of oxygen acts as anode & undergoes corrosion.

Q: 13) Small anodic area or large cathodic area results in intense corrosion. Explain it.

Ans :- As the cathodic area  $>$  anodic area, then the bigger cathode will demand a large no. of  $e^-$  to the anode. ( $e^-$  supplier) This demand of  $e^-$  by the cathode can be fulfil the rate of loss of  $e^-$  by the small anode will be very high. This means the small anode will suffer from rapid corrosion.

Q: 14) Why any deposition of dirty particles on the surface of metal for a long period is unwanted?

Ans :- It is unwanted, bcoz rapid corrosion (diff.) aeration corrosion will occur on the surface of metal and it will lead to pit.

L.R.:-

Mechanism of dry / wet corrosion

Diff. aeration corrosion

Metallic coating

Waterline corrosion

Cathodic protection

Nature of metal

Sacrificial anodic protection method

Temporary / permanent hardness

Total hardness (With numericals)

limesoda / zeolite softening process

Resin process

Q:-15) Find out the amount of lime and soda required for softening of 5000 L of hard water containing 11.1 mg/L  $\text{CaCl}_2$ , 16.2 mg/L  $\text{Ca}(\text{HCO}_3)_2$  and 100 mg/L  $\text{Na}_2\text{SO}_4$ .

Constituent	Chemical needed	Strength (mg/L)	Molar mass
$\text{CaCl}_2$		11.1	111
$\text{Ca}(\text{HCO}_3)_2$		16.2	162
$\text{Na}_2\text{SO}_4$			

$$\text{CaCO}_3 \text{ eq. wt.} = \frac{100}{2} = 50 \text{ mg/L}$$

$$\text{lime required} = \frac{11.1 \times 5000 \times 100}{111} = 5000 \text{ mg/L}$$

$$\text{soda required} = \frac{16.2 \times 5000 \times 100}{162} = 5000 \text{ mg/L}$$

Lime required :-

$$\frac{74}{100} \times 10 \times 5000 \times \frac{100}{100} = 37000 \text{ mg} = 37 \text{ g}$$

Soda required :-

$$\frac{106}{100} \times 10 \times 5000 \times \frac{1}{100} = 53000 \text{ mg} = 53 \text{ g}$$

26/09/2019

$$\rightarrow \text{Higher calorific value} = \text{LCV} + 0.09 \times \gamma \cdot H \times 587 \\ (\text{HCV})$$

Q:- Under what cond<sup>n</sup> HCV = LCV?

If  $\gamma \cdot H$  in the fuel is 0, then  $\text{HCV} = \text{LCV} + 0$

$$\rightarrow \underbrace{\text{kcal/kg, cal/g}}_{\text{Solid fuel}} \Rightarrow \text{HCV} = \text{LCV}.$$

Q:- 10 kg of a coal liberates 10,000 kcal of heat upon complete combustion. Find its calorific value.

$$\text{Ans}:- 10 \text{ kg} \rightarrow 10,000 \text{ kcal}$$

$$1 \text{ kg} \rightarrow \frac{10,000}{10} \text{ kcal} \\ = 1000 \text{ kcal}$$

Q:- 100 m<sup>3</sup> of LPG gas upon complete combustion has liberated 50,000 kcal of heat. Find its calorific value.

$$\text{Ans}:- 100 \text{ m}^3 \rightarrow 50,000 \text{ kcal}$$

$$1 \text{ m}^3 \rightarrow \frac{50,000}{100} \\ = 500 \text{ kcal.}$$

\* Calorific value is nothing, it total quantity of heat liberated by burning of 1 kg of fuel (1 m<sup>3</sup>)

Characteristics of a good fuel :-

1 → The calorific value is high.

2 → It should have moderate ignition temp.

ignition temp.:- It is the min<sup>m</sup> amount of temp., which must be supplied to the fuel. So, that after this, it can burn smoothly without further supply of external heat.

- Low ignition temp. has chances of fire hazards.  
→ Very high " " means much more time required to burn it.

3) Product of combustion shouldn't be harmful.

That means shouldn't form products like  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$  etc.

4) It shouldn't contain elements like  $\text{N}_2$  and should form less amount of ash.

5) Low cost

6) Easy to transport.

7) Low storage cost.

8) Shouldn't undergo spontaneous combustion.

9) Should undergoes control combustion process.

10) Rate of combustion must be moderate.

11) Should have very less amount of moisture content.

Calculation of HCV & LCV:-

→ It can be find out experimentally using a Bomb Calorimeter.

→ theoretically it can be calculated using the following formula:

$$\text{HCV} = \frac{1}{100} \left[ 8080 \times \gamma \cdot C + 34500 \left( \gamma \cdot H_o - \frac{\gamma \cdot O}{8} \right) + 2240 \times \gamma \cdot S \right] \quad (\text{Dulong's formula})$$

<u>Constituent</u>	<u>C</u>	<u>H</u>	<u>S</u>
HCV (kcal/kg)	8080	34500	2240

$$LCV = HCV - 0.09 \times \%H \times 587.$$

Q:- calculate HCV or GCV and LCV or NCV of a coal sample, having following composition by weight %.

Ans :- C = 82%

H = 8%

O = 5%

S = 2.5%

N = 2.5%

$$\text{So, } HCV = \frac{1}{100} \left[ 8080 \times \%C + 34500 \left( \frac{\%H}{8} \right) + 2240 \times \%S \right]$$

$$= \frac{1}{100} \left[ (8080 \times 82) + 34500 \left( 8 \cdot \frac{5}{8} \right) + 2240 \times 2.5 \right]$$

$$= 88925.97 \text{ Kcal/kg}$$

$$LCV = HCV - 0.09 \times \%H \times 587$$

$$( \text{kcal/kg} ) = 9225.97 - ( 0.09 \times 8 \times 587 )$$

$$= 8803.33 \text{ Kcal/kg}$$

Q:- A sample of coal was found to have the following composition by weight :-

$$C = 75\% \quad S = 0\%$$

$$H = 5.2\%$$

$$O = 12.1\%$$

$$N = 3.2\%$$

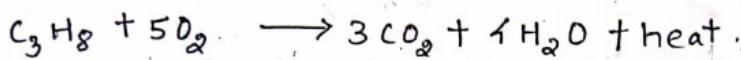
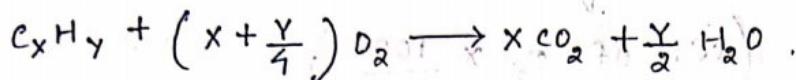
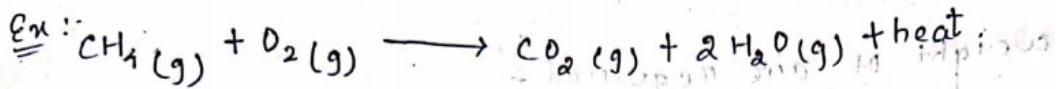
$$\text{Ash} = 4.5\%$$

$$\text{Ans!} \quad \left\{ \begin{array}{l} HCV = 7332 \text{ Kcal/kg} \\ LCV = 7057 \text{ Kcal/kg} \end{array} \right.$$

## Combustion and its calculations:-

What is combustion?

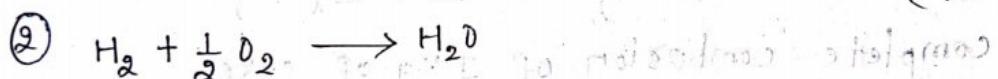
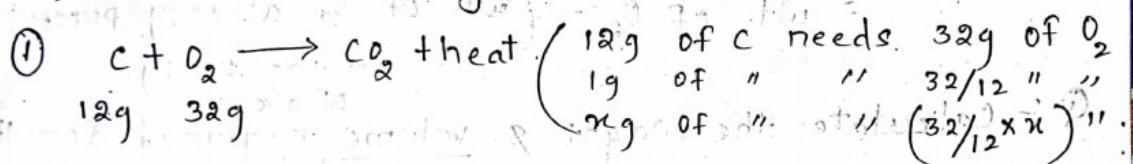
→ It is an exo-thermic chemical reac<sup>n</sup>, results in generation of huge amount of heat energy along with useful for domestic & industrial operations.



Combustion calculation for solid fuel:-

→ For solid fuels, the data would be given in the form of % of element (like %C, %H, %S, %O---etc).

→ C, H & S can undergo combustion calculation.



$$2g = 16g$$

$$1g = \frac{16}{2} g$$

$$y g = \left(\frac{16}{2} \times y\right) g$$



$$32g = 32g \text{ of O}_2$$

$$1g = \frac{32}{32} g \text{ of O}_2$$

$$z g = \left(\frac{32}{32} \times z\right) g = z \text{ gm of O}_2$$

→ N<sub>2</sub> is } non-combustible.

→ Ash

→ Moisture

Weight of O<sub>2</sub> required :-

Weight of O<sub>2</sub> required =

$$\left[ \left( \frac{32}{12} \times \text{wt. of Carbon} \right) + \left( \frac{16}{2} \times \text{wt. of H} \right) + \left( \frac{32}{32} \times \text{wt. of S} \right) \right]$$

Weight of air required :-

Weight of air required =

$$\left( \text{wt. of O}_2 \times \frac{100}{23} \right)$$

\* If O<sub>2</sub> is already present in the fuel, then amount of O<sub>2</sub> required for the combustion of solid fuel will be less.

Net wt. of O<sub>2</sub> needed

$$= \text{wt. of O}_2 - (\text{wt. of O}_2 \text{ already present in the fuel})$$

Q:- Calculate the weight & volume required for the complete combustion of 1 Kg of coke.

Ans:- Hence we will assume that,



$$12g \rightarrow 32g$$

$$1g \rightarrow \frac{32}{12} g$$

$$\frac{1000g}{12} \rightarrow \frac{32}{12} \times 1000$$

$$1Kg \rightarrow \frac{32}{12} \times 1Kg$$

$$= 2.666 \text{ kg of O}_2$$

$$\text{Weight of air required} = \text{wt. of O}_2 \times \frac{100}{23}$$

$$= 2.666 \times \frac{100}{23}$$

$$= 11.59 \text{ Kg.}$$

Average molecular mass of air = 77% of N<sub>2</sub> + 23% O<sub>2</sub>

$$= \frac{77 \times 28 + 23 \times 32}{100}$$

$$= 28.92 \text{ g. (Molar mass)}$$

We know that,

28.92 g of air at 0°C (STP) occupies 22.4 Ltr of gas

$$1 \text{ g} \quad " \quad " \quad " = \frac{22.4}{28.92} \text{ of gas}$$

$$11.59 \text{ kg} \quad " \quad " \quad " = \frac{22.4}{28.92} \times (11.59 \times 10^3 \text{ g})$$

Q:- A solid fuel have the following % of composition.

C = 72%, H = 5%, N = 6%, Moisture, Ash.

Calculate the weight of air required for complete combustion of 100 kg of this fuel.

Soln :- 100 kg of fuel containing 72 kg 'C'.

$$\text{Wt. of O}_2 \text{ required} = \left[ \left( \frac{32}{12} \times 72 \right) + \left( \frac{16}{2} \times 5 \right) \right]$$

$$= 232 \text{ kg.}$$

$$\text{Wt. of Air} = \text{Wt. of O}_2 \times \frac{100}{25}$$

$$= 232 \times \frac{100}{25}$$

$$= 928.8 \text{ kg.}$$

Q:- The % composition of coal sample is 'C' = 80%,

H = 4%, O = 3%, N = 3%, S = 2%, ash = 5%,

moisture = 3%. Calculate the total amount of heat required for complete combustion of 1 kg of coal.

Soln :- 1 kg of coal sample contains = 800 g of C  
 (1000 g)  $\therefore$  weight of H =  $\frac{16}{12} \times 800 = 40$  g of H  
 $\therefore$  weight of O =  $\frac{32}{12} \times 800 = 20$  g of O  
 $\therefore$  weight of S = 20 g of S.

Net weight of O<sub>2</sub> required

$$= \left[ \left( \frac{32}{12} \times 800 \right) + \left( \frac{16}{2} \times 40 \right) + \left( \frac{32}{32} \times 20 \right) \right] - \text{wt. of O}_2 \text{ in the fuel}$$

$$= 2473 - 30 \text{ g}$$

$$= 2443 \text{ g}$$

Weight of air required;

$$2443 \times \frac{100}{23} = 10623.78 \text{ gm.}$$

H.W Find out volume of air required

$$\text{Volume of air} = \frac{22.4}{28.92} (10623.78 \times 10^3)$$

$$= 8227101 \text{ L. Ans } \underline{16/10/2019}$$

Q Write a solid sample have the following

composition :- C = 70%, H = 7%, N = 6%, S = 3%.

Ash = 8%, Moist = 6%. Calculate the actual weight of air required for the complete combustion of 1 kg of fuel. If 50% excess air was used for combustion.

Soln :- 1 kg of fuel contains

1 kg (1000 g)

X C = 700 g. X Ash = 80 g

X H = 70 g X Moisture = 60 g

X N = 60 g

X S = 30 g

Net weight of Oxygen Required;

$$\begin{aligned} &= \left[ \left( \frac{32}{12} \times 700 \right) + \left( \frac{16}{8} \times 70 \right) + \left( \frac{32}{32} \times 30 \right) \right] - 0 \\ &= (1866.6 + 560 + 30) \\ &= 2456.6 \text{ gm.} \end{aligned}$$

$$\text{Weight of air} = \left( 2456 \times \frac{100}{23} \right) = 10681 \text{ gm.}$$

If 50% excess air was used, then actual weight of air =  $\left( 10681 \times \frac{150}{100} \right) = 16021 \text{ gm.}$

Combustion calculation of gaseous fuel:

Gaseous fuel contains the following constituents,

like  $\text{CH}_4, \text{H}_2, \text{CO}, \text{CO}_2, \text{N}_2, \text{O}_2$ .

( $\text{CH}_4$  or any hydrocarbons are combustable)

$\text{H}_2, \text{CO}$  combustable.

$\text{CO}_2$  → stable, non-combustable.

$\text{N}_2$  → endothermic process, non-combustable.

$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$  ⇒ 1 v. of  $\text{CH}_4$  needed  
1 vol. (g) 1 vol. (g) 2 v. of  $\text{O}_2$

$(\text{C}_x\text{H}_y + (\text{x} + \frac{\text{y}}{4})\text{O}_2 \rightarrow \text{xCO}_2 + \frac{\text{y}}{2}\text{H}_2\text{O}$  ⇒  $\text{xCO}_2 + \frac{\text{y}}{2}\text{H}_2\text{O}$  needed

$\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O} \Rightarrow 1 \text{ v. of } \text{C}_3\text{H}_8 \text{ needed}$   
1 vol. 5 vol. 5 v. of  $\text{O}_2$

$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \Rightarrow 1 \text{ v. of } \text{H}_2 \text{ needed } \frac{1}{2} \text{ v.}$   
1 vol.  $\frac{1}{2}$  vol. of  $\text{O}_2$

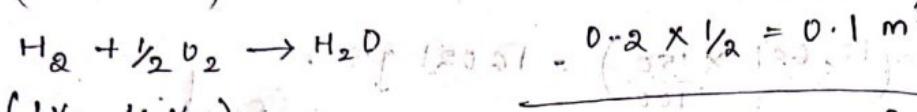
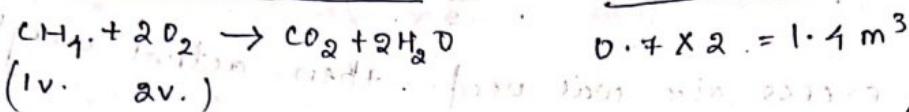
$\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \Rightarrow 1 \text{ v. of CO needed}$   
1 vol.  $\frac{1}{2}$  vol.  $\frac{1}{2}$  v. of  $\text{O}_2$

A gaseous fuel has the following composition

Q. by volume %.  $\text{CH}_4 = 70\%$ ,  $\text{H}_2 = 20\%$ ,  $\text{N}_2 = 10\%$ . calculate vol. of air required for complete combustion of  $1\text{m}^3$  of this gaseous fuel.

<u>Soln :-</u>	<u>constituents</u>	<u>gm / 1 m<sup>3</sup> gas</u>
$\text{CH}_4 = 70\%$	$\text{CH}_4$	$70 \times 0.7 \text{ gm} = 49 \text{ gm}$
$\text{H}_2 = 20\%$	$\text{H}_2$	$20 \times 0.2 \text{ gm} = 4 \text{ gm}$
$\text{N}_2 = 10\%$	$\text{N}_2$	$10 \times 0.1 \text{ gm} = 1 \text{ gm}$

Combustion Reaction      Vol. of O<sub>2</sub> Required



Total O<sub>2</sub> =  $1.1 + 0.1 = 1.2 \text{ m}^3$  of O<sub>2</sub>

$\times$  proportion of O<sub>2</sub> in air =  $\frac{21}{29}$

∴ Vol. of air required =

$$1 \text{ m}^3 = 10^3 \text{ L}$$

$$= \left( 1.2 \text{ m}^3 \times \frac{100}{21} \right) = 5.714 \text{ m}^3$$

(In vol. air O<sub>2</sub> present in air = 21%).

Wet. of air needed =

As we know,

22.4 L air weighs  $\rightarrow 28.92 \text{ g}$

1 L air weighs  $\rightarrow \frac{28.92}{22.4}$ .

Q:- A gaseous fuel contains following composition

by volume %. CH<sub>4</sub> = 60%, H<sub>2</sub> = 10%, N<sub>2</sub> = 10%

O<sub>2</sub> = 20%. If 50% excess air was used for combustion of this fuel, then find out

actual vol. of air was supplied to burn

1 m<sup>3</sup> of this fuel.

<u>Soln :-</u> <u>Constituents</u>	<u>y.</u>	<u>gm 1m<sup>3</sup> gas</u>	<u>Combustion Reac<sup>n</sup></u>
CH <sub>4</sub>	60%	0.6 m <sup>3</sup>	CH <sub>4</sub> + 2O <sub>2</sub> → CO <sub>2</sub> + 2H <sub>2</sub> O
H <sub>2</sub>	10%	0.1 m <sup>3</sup>	H <sub>2</sub> + 1/2 O <sub>2</sub> → H <sub>2</sub> O
N <sub>2</sub>	10%	0.1 m <sup>3</sup>	X
O <sub>2</sub>	20%	0.2 m <sup>3</sup>	X

Vol. of O<sub>2</sub> Reqd;

$$CH_4 \rightarrow 0.6 \times 2 = 1.2 m^3$$

$$H_2 \rightarrow 0.1 \times 1/2 = 0.05 m^3$$

$$Vol. of O_2 = 1.25 m^3$$

$$Net \ vol. \ of O_2 = 1.25 - (vol. \ of \ O_2 \ in \ the \ fuel)$$

$$= 1.25 - 0.2 = 1.05 m^3$$

If 50% excess air was used, then vol. of air used, =  $5 \times \frac{150}{100} = 7.5 m^3$ .

Assg.

Q:- A gaseous fuel contain following constituent

by following constituent: C<sub>3</sub>H<sub>8</sub> = 19.0%,

H<sub>2</sub> = 10%, CO = 20%, O<sub>2</sub> = 20%, N<sub>2</sub> = 10%.

Find out vol. & wt. of air required for the complete combustion of 1000 L of this gas.

Solid fuel :-

→ Solid fuels are of 2 types.

1. Natural (coal or wood)

2. Synthetic or man-made (charcoal, coke, candle)

→ Coal is a fossil fuel.

Fossil fuels are natural ones and also non-

-renewable, can be obtained by the application

of high temperature and pressure to fossilize

remains of plants and animals by anaerobic

bacterial decomposition very deep under the

Earth's crust!

Advantages & Disadvantages of solid fuel:-Advantages :-

→ It has moderate ignition temp.

→ Relatively of low cost. → easy to transport.

Disadvantages :-

→ Relatively of low calorific value.

→ Non-combustible matter content is high.

→ Not use in internal combustion engines.

→ causes lots of air pollution.

→ Combustion process can't be controlled easily.

Types of coal :-

It is up 3 types.

1. Lignites - Lowest Rank coal (%C = 60-70)

C.V = 6500-7,000 Kcal/kg.

2. Bituminous  $\rightarrow$  Common coal, ( $\% C = 80 - 90\%$ )

$$C.V = 7500 - 8,000 \text{ kcal/kg}$$

3. Anthracite  $\rightarrow$  Highest Rank Coal ( $\% C = 92 - 99\%$ )

$$C.V = 8500 - 8800 \text{ kcal/kg}$$

Characteristics of a good quality of coal :-

$\rightarrow$  Non-combustible matter content should be low.

$\rightarrow$  Moisture content should be low.

$\rightarrow$  calorific value should be high.

$\rightarrow$  sulphur content is as low as possible.

$\rightarrow$  Calorific intensity (Max<sup>m</sup> temp reached by

suitable burning in coal sample) should be high.

$\rightarrow$  It should have the good coking quality.

(conversion of coal to coke)

LQ  
Gmark  
Analysis of Coal :-

$\rightarrow$  It is performed to know the quality of a coal.

$\rightarrow$  There are 2 types of coal analysis.

1. Proximate Analysis

2. Ultimate Analysis

1. Proximate Analysis :-

(What is proximate analysis & its importance)

$\rightarrow$  It is an approximate analysis of coal, which

finds % of moisture content, % of volatile

matter content, % ash content and % of

fixed C content of a fuel sample.

fixed C content of a fuel sample.

### % of moisture matter :-

→ Take 1g of coal sample. Place it inside an electrical oven, maintain in  $110^{\circ}\text{C}$  and to be kept for  $7-10^{\circ}\text{C}$ .

→ Now, find out the weight loss.

Let the weight of coal sample after the removal of moisture content be;

$$\% \text{ moisture} = \left( \frac{\text{wt. loss due to removal of moisture}}{\text{Total wt. of coal}} \times 100 \right)$$

$$\text{wt. before} = \frac{1 - 0.9}{1} \times 100 \\ = 10\%$$

### % volatile matter :-

→ After the removal of moisture the sample to be kept in an electrical furnace maintain at  $750^{\circ}\text{C}$  and to be kept for 20 mins.

→ Take out the sample, cool it & weigh.

Let the weight be 0.71g. Report the weight loss.

$$\% \text{ volatile matter} = \left( \frac{\text{wt. loss due to removal of volatile matter}}{\text{Total wt. of coal (1g)}} \times 100 \right)$$

$$\text{wt. loss} = \frac{0.9 - 0.7}{1} \times 100 = 20\%$$

### % ash :-

→ After the removal of moisture & volatile matter, sample to be kept in an electrical furnace maintain at  $900^{\circ}\text{C}$ , fore the time till complete combustion occurs.

→ then take out the sample, cool it at room temp and report it.

$$\% \text{ Ash} = \left( \frac{\text{wt. of Ash}}{\text{Total wt. of coal (g)}} \times 100 \right)$$
$$= \frac{0.1}{1} \times 100 = 10\%$$

% fixed carbon :-

$$\% \text{ fixed C} = 100 - \% (\text{moisture + volatile matter + ash})$$
$$= 100 - (10 + 20 + 10)\%$$
$$= 100\% - 40\%$$
$$= 60\%$$

Importance of proximate analysis :-

- In general for a good quality of coal sample, % fixed carbon should be high because higher is its %, higher will its calorific value.
- Moisture content should be as low as possible because as % of moisture content increases, lower will be the calorific value.
- Volatile matter content should be as low as possible, because % of volatile matter increases, % C of fixed carbon decreases and hence calorific value decreases.
- Ash content should be as low as possible, as it is non-combustible in nature. As % of ash increases fixed carbon content decreases.

## \* Ultimate Analysis :-

→ It is the most accurate method of analysis of coal, which helps us to know about the elemental composition of the sample and about the non-combustible matter content.

→ In this analysis, we can find out:

- (1) % of Carbon content
- (2) % of H content
- (3) % of N content
- (4) % of S "
- (5) % of O "
- (6) % of ash "

→ In this analysis, % of fixed carbon is given by

$$\% \text{ C} = 100 - \% \text{ of } (\text{C} + \text{H} + \text{N} + \text{S} + \text{Ash})$$

Significance :-

1. % C content - Higher is the % C, higher is the calorific value.

For a good coal sample % C should be high.  
2. % H content - It should be high, because it gives high calorific value.

3. % N content - As higher the % of N, lower the calorific value.

4. % S content - It should be low. Otherwise volatile matter content will be high & also it leads to harmful combustion products.

5. % of O content - In general higher % of O  $\Rightarrow$  large % of moisture in the fuel.

6. % of ash content - % ash produced by burning of fuel as low as possible coz it is as combustible as nature.

### Gaseous Fuel :-

Two types of gaseous fuel.

1. Natural gas

2. Man-made gas (Water gas, LPG, coal gas, bio-gas etc.)

Advantages: High calorific value relative to solid fuel.

→ High calorific value relative to solid fuel.

→ Thermal efficiency is high.

→ Easily transferable and cost is low.

→ Internal combustion fuel and engine.

→ Internal combustion possible without pollution.

→ Complete combustion possible without pollution.

or a little pollution.

→ If incomplete burning occurs without

forming ash.

→ They burn without smoke with very very

little smoke.

→ Combustion process can be controlled.

→ Ignition temp. is low.

Disadvantages: More hazardous.

→ Chances of fire hazard.

→ storage cost is high.

→ costly than solid fuel.

Write some gaseous fuel.

(1) LPG :-

→ LPG can be obtained as bi-product by the fractional distillation of petroleum.

Or it can be obtained by cracking of heavy oils.

→ Calorific value of LPG is  $\approx 27,800 \text{ Kcal/m}^3$ .

→ Chemical composition :-

Butane, Isobutane, Butene; Propane, Ethane etc.

→ Domestic & industrial heating and as internal combustion.

(2) CNG :-

→ It is obtained by an-aerobic bacterial decomposition.

→ Anaerobic bacterial decomposition includes animals & plants parts under favourable cond'n very deep under the earth crust.

→  $12,000 - 14,000 \text{ Kcal/m}^3$  - calorific value.

(Methane (60% + 0%) along with some % of ethane, CO,  $\text{CO}_2$  etc.)

→ It is used in IC engine fuel, and manufacture of carbon black (a filler) in rubber industry.

(3) Nat.

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- (3) Water gas :- mixture of combustible gases.
- It is obtained from coal or coke.
  - It consists up large % of combustible gases  $\{CO + H_2\}$  and relatively less % of non-combustible gases like  $CO_2$  and  $N_2$ .
  - calorific value is  $2800 \text{ Kcal/m}^3$ .
  - Avg composition :-  $H = 51\%$ ,  $CO = 41\%$ ,  $CO_2$  and  $4\% N_2$ .
  - Uses :- Heating purpose (In laboratory). People are used in furnace for heating. It is used for providing reducing atmosphere. It is also used for manufacturing of methanol.
- $$(CO + H_2) + H_2O \rightarrow CH_3OH \text{ (Methanol)}$$
- Water gas is nothing but air heated with coal (It is a source).
- Water gas is otherwise known as Blue gas.
- Water gas - synthesis of methanol (Synthesis gas)

- (4) Producer gas :- gaseous fuel obtained from the solid fuel coal or coke.
- It is a secondary gaseous fuel.
  - It mainly consists up non-combustible gases like  $N_2$  &  $CO_2$  and combustible gases like

- It contains large % of non-combustible gases.
- The avg composition  $N_2 \rightarrow 52-55\%$ .
- $CO_2 \rightarrow 22-30\%$ .
- $H \rightarrow 10-12\%$ .
- $CO \rightarrow 3\%$ .
- The calorific value is  $1300 \text{ kcal/m}^3$ .
- Uses :- Heating purpose.  
For as reducing agent.

#### (5) Liquid Fuel :-

- They are of 2 types :
  - Natural (primary) - Petroleum
  - Artificial (secondary) - Petrol, Diesel, Kerosene
- Advantages :-
- Calorific value is higher than solid fuel.
- Used in internal combustion engine.
- Easy to transport through pipe line.
- Complete combustion without formation of ash or dust.
- Disadvantages :-
- Chances of fire hazard due to its ignition temperature.
- Storage and transportation cost is high.
- Storage loss is occurs.
- Cost is relatively higher than the solid fuel.

### i) Petroleum:-

- It is otherwise known as crude oil or rock oil.
- It is a coloured viscous oil, found deep under the earth's crust.
- It mainly consists of hydro-carbon like cyclo-alkanes, aromatic compound, straight chain & branch chain hydro-carbon.

### Refining the Petroleum:-

- As petroleum is a mixture of various hydro-carbons.
- It can be converted into many useful fractions or products like petrol, diesel, kerosene, petroleum ethers by fractional distillation.
- The refining process consists of following 3 steps:-
  - 1) Removal of water droplets from petroleum.
  - 2) Removal of sulphur compounds from petroleum.
  - 3) Fractional distillation (Evaporation + Condensation)

### Assignment:-

What do you mean by refining.

Discuss refining of petroleum by drawing schematic diagram of fractionating column.

### Important fractionating product:-

#### 1) Petrol or Gasoline

→ Boiling point range  $40 - 120^{\circ}\text{C}$ .

→ The C-chain  $C_5 - C_{10}$ , (Pentane to decane).

→ Calorific value  $11250 \text{ Kcal/kg}$ .

2) Kerosene :-

- Boiling point range  $180^{\circ}\text{C} - 250^{\circ}\text{C}$  & index of refraction  $n_{D}^{20} = 1.51 - 1.56$ .
- Carbon chain length  $C_{10} - C_{16}$  (alkanes)
- Calorific value 11,100 kcal/kg.

3) Diesel :-

- Boiling point range  $250^{\circ}\text{C} - 320^{\circ}\text{C}$ .
- $C_{15} - C_{18}$ . (C-chain length)
- Calorific Value 11,000 kcal/kg.

A. Knocking :-

- It is a metallic sound generated during internal combustion engine due to spontaneous ignition of the last portion of fuel-air mixture in the cylinder.

→ Knocking occurs when compression ratio reaches its critical value in internal combustion engine.

Compression Ratio =  $\frac{\text{Vol. of cylinder}}{\text{Vol. of air mixture at the end of suction stroke}}$

Disadvantages:-  
→ At the end of compression stroke.

- Knocking → Efficiency decreases.
- It damages the cylinders also.

Anti-knocking substance :-

→ Materials like tetra-ethyl lead (TEL).

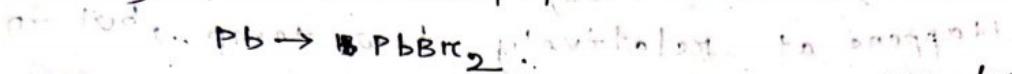
$(C_2H_5)_4Pb$ , When added to petrol it prevents Knocking. So, it is an anti-knocking substance.

> In the internal combustion engine TEL, converted in to Pb and deposit there.

Deposition of Pb reduces the life of the engine.

so, in order to avoid this ethylene-di-bromide is added to petrol along with TEL.

so, that the Pb can form Lead bromide ( $PbBr_2$ ) a volatile mass, which can be easily escape through the silencer pipe.



24/10/19

1. Why small amount of ethylene di-bromide should be added along with TEL to petrol.

2. Mention the various factors affecting knocking?

i) Design of the engine.

ii) Running conditions.

iii) Chemical structure of hydro-carbon in the fuel.

Tendency towards Knocking of n-Alkanes >

mono-substituted alkanes > cyclo alkane > Alkanes >

Poly substituted Alkanes > Aromatics.

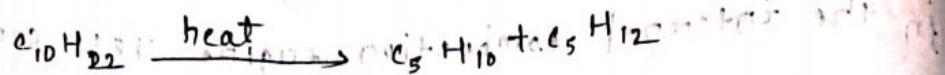
→ A good quality of petrol should contain less amount of alkanes and large % of aromatics.

\* Cracking :-

→ It is a process of decomposition of high molecular weight hydro-carbons of high

boiling point to low molecular weight of

hydro carbon of low boiling point.



174°C      ~40°C; bp. 39°C

(B.P.)

(i) Thermal cracking :-

Occurs by at high temp. and high pressure  
in absence of catalyst.

(ii) Catalytic cracking :-

Happens at relatively low temp., but in  
(400-450°C)

presence of Pt/Rh,  $Al_2O_3$  ( $Al_2O_3 \cdot 3SiO_2$ )

Uses of Cracking :-

→ We can prepare LPG from heavy oil.

→ We can synthesize synthetic petrol.

Q:- What are the advantages of catalytic

cracking over thermal cracking?

(1) High yield of petrol.

(2) Better quality of petrol.

(Petrol has high anti-knocking resistance  
due to presence of aromatic  
poly-substituted alkanes).

(3) Obtained petrol contain very less sulphur  
contain

(4) It also contain very less amount of  
olefins, means less % of gum forming

substance are present.

### Octane No. :-

→ It is a parameter used to know quality no. of petrol.

<u>Petrol fuel</u>	<u>Octane No.</u>	<u>Characteristics</u>
(n-heptane)	0	Knocks severely
(Iso-octane)	100	Knocking resistance
2,2,4-trimethyl Petane)		is very high.

→ Octane no. is the % of iso-octane present in the mixture of iso-octane and n-heptane, which have the same knocking characteristics as the petrol fuel.

→ For e.g.; if the % of iso-octane in the mixture is 90 the Octane no. is 90.

### Cetane No. :-

→ Used to know the quality of diesel fuel.

<u>Diesel fuel</u>	<u>Cetane No.</u>	<u>Characteristics</u>
Methyl Napthalene	0	Knocks severely
hexadecane (Cetane)	100	Knocking resistance is very high.

→ % of hexadecane or cetane present in the mixture of hexadecane & methyl Napthalene which has the same knocking characteristics as the diesel fuel.

DIC alkenes > branched alkenes  
→ It should, A good quality of diesel contain a large amount of n-alkanes and less % of aromatics.

## - ENERGY SCIENCE

### Battery :-

→ A device which converts chemical energy to electrical energy.  
→ Battery ~~are~~ consists of large no. of electrochemical cells connected in series.

### Types of battery :-

(1) Primary battery / Primary cell :-  
→ It is non-rechargeable i.e; the cell reaction is non-reversible.

Ex:- Zn-graphite cell.

(2) Secondary battery :-

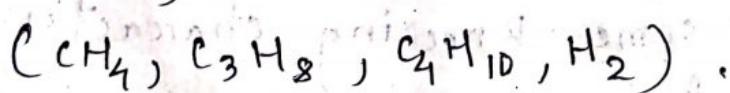
→ Rechargeable battery.

→ Lead storage battery.

Lip iron cell.

(3) Fuel cell / Flow battery :-

→ In this case, chemical energy of fuel, directly converted to electrical energy,



→ A storage cell and  
→ When discharged  
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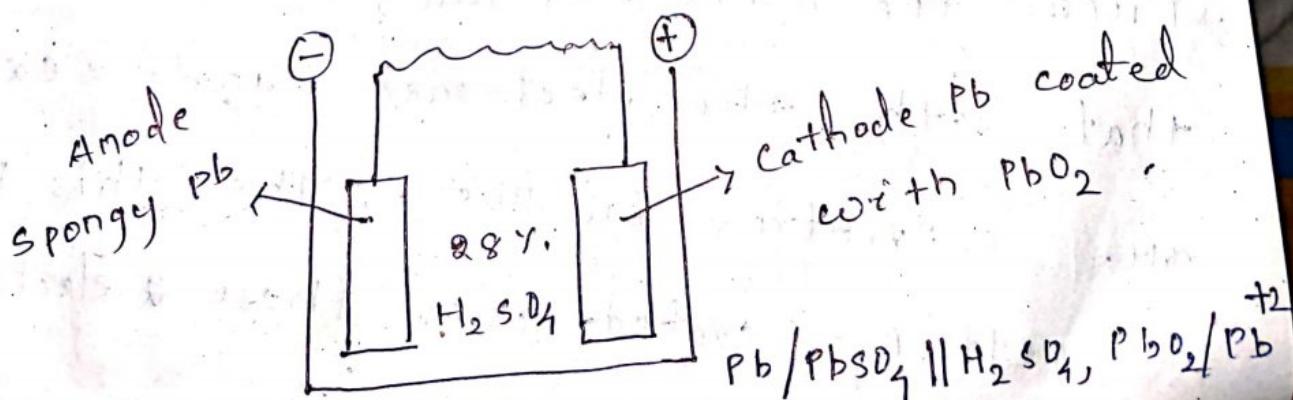
## Lead Acid storage cell :-

28/10/19

- It is a secondary or rechargeable cell.
- A storage cell acts both as electro-chemical cell and electrolytic cell.
- When it acts as electro-chemical cell during discharging chemical energy of the cell is converted to electrical energy.
- But, when it acts as electrolytic cell, during charging electrical energy converts into chemical energy.

### Working & Construction:-

- In general, this battery consists up at least 6 nos. of electro-chemical cells (2V) connected in series.
- In this cell, porous & spongy Pb acts as anode (-ve electrode) and Pb coated with  $\text{PbO}_2$  acts as cathode (+ve electrode).
- 28%  $\text{H}_2\text{SO}_4$  acts as electrolyte.
- All the electrodes are connected and kept deeped in this electrolyte.
- 1 such electro-chemical cell looks like this:-



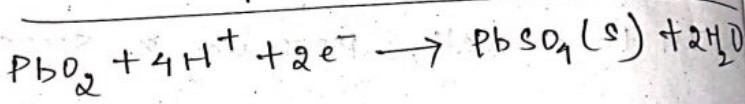
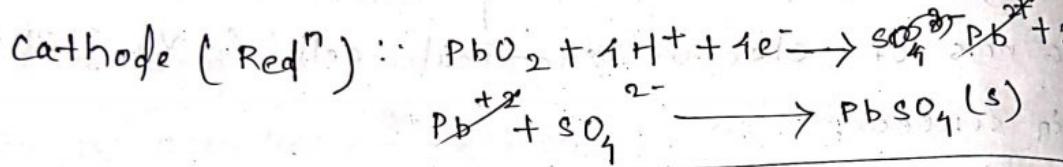
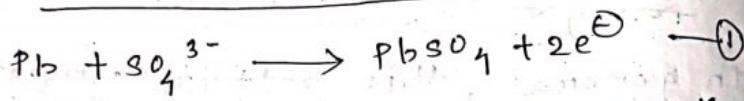
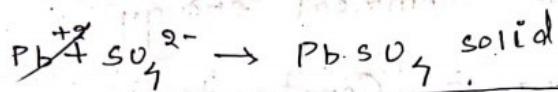
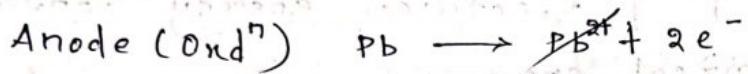
## Working :-

During working following a process occurs in battery :- (1) Discharging (2) charging.

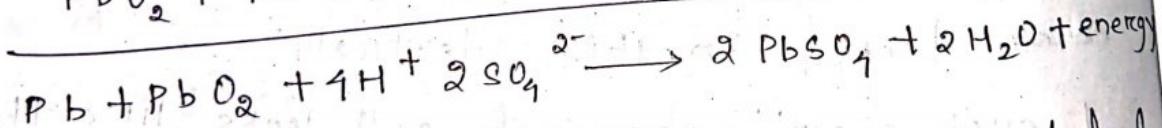
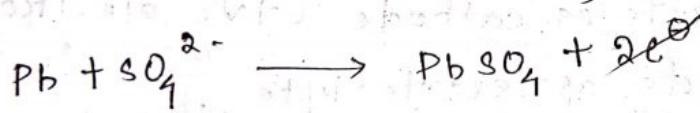
### (1) Discharging :-

During discharging chemical energy converts to electrical energy.

#### Reac<sup>n</sup> :-



Net cell reaction during discharging:-



From the above cell reac<sup>n</sup>, it is concluded

that both the electrodes (anode & cathode) are converting in  $PbSO_4$ . Then this  $PbSO_4$  is getting coated over those 2 electrolytes.

$H_2SO_4$  is con means that it will not s

### (2) Charging :-

→ During char to chemic

→ Reac<sup>n</sup> :- sc energy is that the

→ In this c-charging

→ And the treak over

#### ② Reac<sup>n</sup> :-

Anode :-

cathode :-

so, Net :-

$PbSO_4$

limit

→ Over

$H_2O$  to  $H_2$

$H_2$

$\text{H}_2\text{SO}_4$  is converting into water, this means that conc. of  $\text{H}_2\text{SO}_4$  is decreasing.

→ This is the reason why after sometimes it will not supply electrical energy.

### (a) Charging :-

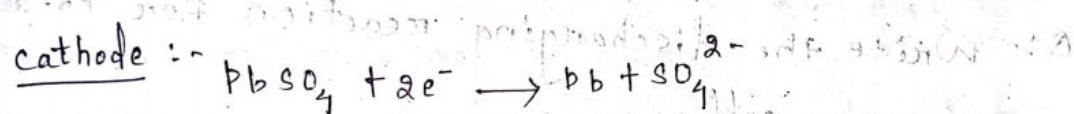
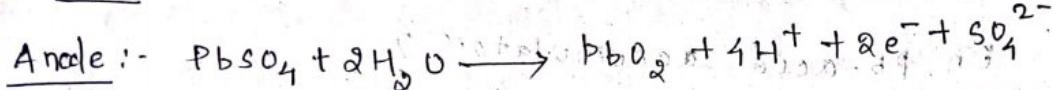
→ During charging, electrical energy is converted to chemical energy.

→ Reason: In SO, during charging, electrical energy is supplied to the battery so that the cell react can be reversed.

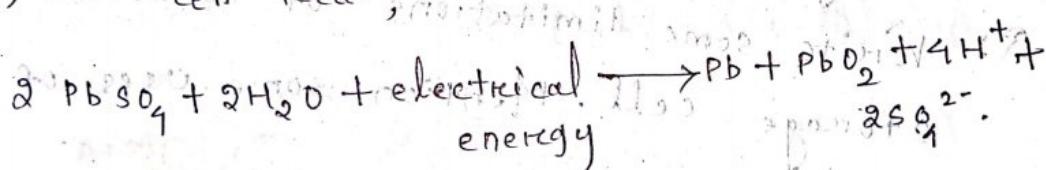
→ In this case, the anode react during discharging will be the cathodic react in a reverse way.

→ And the cathodic react will be the anodic react in a different way.

### (b) Reactions :-



So, Net cell react;



### Limitations :-

→ Overcharging causes electrolysis of water to  $\text{H}_2\text{O} + \text{O}_2$ .

This results in increasing the conc. of  $\text{H}_2\text{SO}_4$ .

- It may damage the electrode both Pb and  $PbO_2$ .
- Overcharging may leads to explosion of battery.
- Lead is toxic, not environmental friendly.
- The O/P voltage decreases by decreasing temperature, because due to this viscosity increases. Movement or mobility of ion decreases.

Uses: - 30/10/19

It is used in various vehicles like truck, bus etc. as battery.

Q:- What is a storage cell with accumulators?

Q:- Which anode, cathode & electrolyte used in Pb-acid accumulators?

Q:- Write the discharging reaction for Pb-acid storage cell.

Q:- Write some limitations of Pb-acid storage cell. Mention some uses of it.

Q:- What is a storage cell? Write the discharging & charging of Pb-acid cell.

Mention some of its usage and limitations.

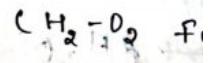
Q:- Discuss conc cell. (diagram)  
Q:- Fuel cell.

### Fuel Cell

→ It is a device which converts chemical energy ( $O_2$ ) to electrical energy.

Reaction: -  $2H_2 + O_2 \rightarrow 2H_2O$

Construction



Construction

→ It consists of two electrodes doped with ions.

→ One electrode is the anode & the other is the cathode.

→  $\Delta G^\circ = -25\% \text{ KJ}$

→ This is the principle of the elec.

Anode

$H_2$ -gas inlet

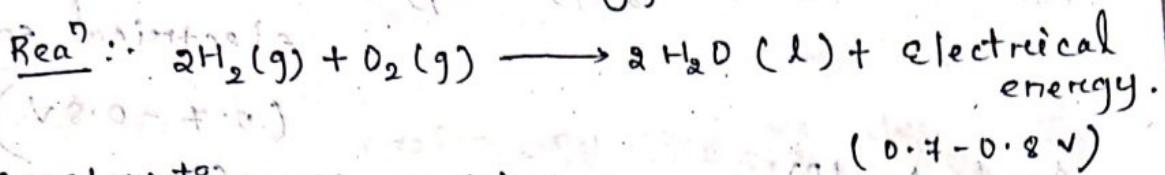
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Q:- Discuss const<sup>n</sup> & working of pb - acid storage cell. (diagram)

Q:- Fuel cell : -

Fuel Cell :-

→ It is a device which converts directly convert the chemical energy of fuel & oxidiser ( $O_2$ ) to electrical energy.



Construction & working :-

( $H_2-O_2$  fuel cell)

Construction :- (Alkaline hydrogen fuel cell)

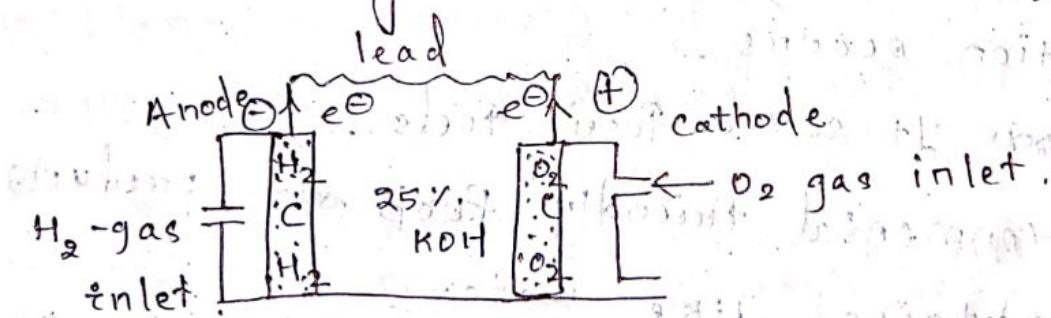
→ It consists up two porous graphite electrodes

dipped with palladium/iridium catalysts. (Pd/Rh)

→ One electrode will acts as anode (-ve electrode) the other one electrode acts as cathode. (+ve electrode)

→ 25% KOH acts as electrolyte.

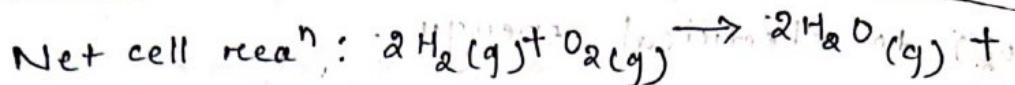
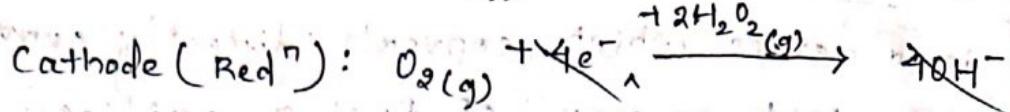
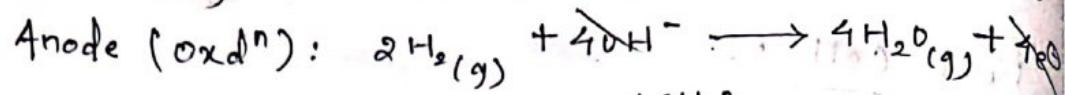
→ this two electrodes are set immersed in the electrolyte. (Bacon's cell)



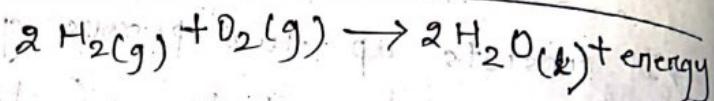
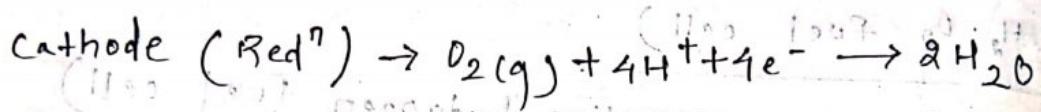
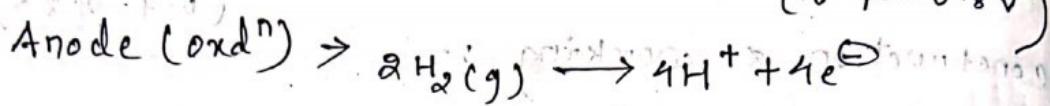
The fuel ( $H_2$ ) cylinder is kept behind anode.

Working :-

When  $H_2$  &  $O_2$  gas bubbled in to the cell, the following chemical gases reaction occurs.



$$(0.7 - 0.8V)$$



Advantages :-

→ It has higher % of efficiency which we can reach up to 90% of efficiency.

→ Fuel cell generators are noiseless.

→ Also almost no vibrationless and less pollution occurs.

→ By this it saves fossil fuels.

→ Environmental friendly products like water are obtained.

→ Charging is not required but it needs fill when both the fuel cells are working.

## Limitations :-

- Relatively costly process
- Not portable.
- Space requirement is more.
- Very difficult to get pure  $H_2$  &  $O_2$ .
- Finding suitable catalyst, which can't be poisoned easily is a difficult task.

## Uses :-

- Used in space crafts, military vehicles and sub-marine.

## Photo Voltaic cell or Solar cell :- (P.V cell)

- It is a device, which directly converts light energy into electrical energy.
- Some of the P.V. materials are crystalline Si, Cadmium Telluride ( $CdTe$ ),  $GaAs$ , derivatives of fullerenes ( $C_{60}$ ), polymeric paste material.

## Lithium ion battery (secondary cell) :-

- Rechargeable battery.
- Like other electrochemical cell, it consists up an anode a cathode (lithium cobalt oxide-  $LiCoO_2$ ), electrolyte (dimethyl carbonate  $[(CH_3)_2CO_3]$ )