

WATER CHEMISTRY

Chemistry

20/9/18

- Characteristics of water:

- i) Colour
- ii) Taste & Odour
- iii) Turbidity & Sediments.
- iv) Microorganisms.
- v) Dissolved mineral matters. →
 - a) Hardness
 - b) Alkalinity
 - c) Total dissolved solids
 - d) Corrosion.
- vi) Dissolved Gases
- vii) Soluble silica
- viii) Oxidability.

ij) Colour : Yellowish / Greenish.

Purest water is colourless.

Inorganic elements (e.g; coloured ions Ex. iron, copper, etc..) impart colour.

Measured on Potassium chloro platinic scale. + few drops of cobalt chloride

iii) Turbidity:

✓ measured on silica scale.

Hint - turbidity produced by 1 mg/l of diatomaceous silica (Fuller's Earth)
settling & decantation

Filtration.

coagulation & filtration.

Settling, coagulation & filtration.

iv) Microorganism: MPN

v) Dissolved mineral matters:

a) Hardness: Property of existence of metal ions except alkali metal ions are/ is hardness of water.

Degree of Hardness: Sum of Caco₃ eq. of hardness constituents present per unit vol. of water sample.

Caco₃ eq. of hardness constituent = $\frac{\text{Amt. of hardness} \times 50}{\text{Eq. wt. of hardness.}}$

Units:

1. Milligram per litre (mg/L):

2. Parts per million (ppm):

$$1 \text{ mg/L} = 1 \text{ ppm.}$$

3. Degree French (°Fr.):

No. of parts of Caco₃ eq. of hardness present per 100000 (10⁵) parts of water sample.

$$1 \text{ mg/L} = 1 \text{ ppm} = 0.1 \text{ }^{\circ}\text{Fr.} = 0.07 \text{ }^{\circ}\text{Cl}$$

$$10 \text{ mg/L} = 10 \text{ ppm} = 1 \text{ }^{\circ}\text{Fr.} = 0.7 \text{ }^{\circ}\text{Cl}$$

$$14.3 \text{ mg/L} \quad 14.3 \text{ ppm} = 1.43 \text{ }^{\circ}\text{Fr.} = 1 \text{ }^{\circ}\text{Cl}$$

4. Degree Claude (°Cl):

No. of grains of Caco₃ eq. of hardness present per imperial gallon of water sample.

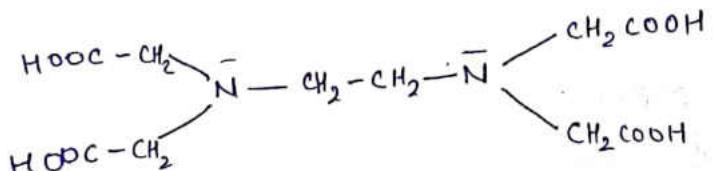
$$1 \text{ grain} = \frac{1}{7000} \text{ lbs}$$

$$1 \text{ gallon} = 10 \text{ lbs.}$$

Measurement:

1. Soap titration method:

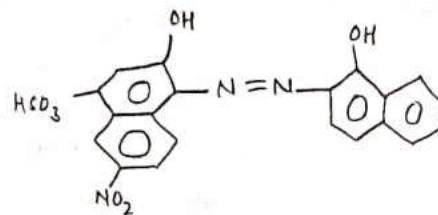
2. EDTA titration method:



EDTA(aq) is colourless.

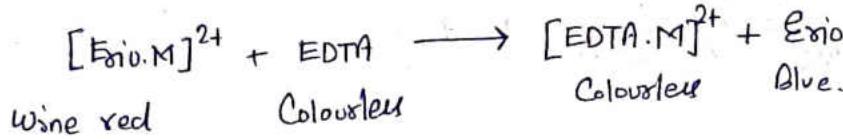
[EDTA · M]⁺⁺ is also ".

Eriochrome Black T



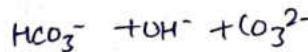
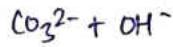
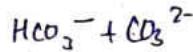
Eri (aq.) → Blue.

$[Eri \cdot M]^{2+} \rightarrow$ wine + red.



$$CaCO_3 \text{ eq. of hardness} = \frac{(Vol. \text{ of EDTA}) \times (\text{strength of EDTA}) \times 50 \times 1000}{\text{Volume of sample}} \\ = 40 \times \text{Vol. of EDTA}$$

b) Alkalinity :



Phenolphthalein

Colourless $\leftarrow \approx pH = 9.0 \rightarrow$ Pink

Methyl orange

Pink $\leftarrow \approx pH = 4.5 \rightarrow$ Orange / yellowish

$$\text{Amount of alkalinity in mg/L} = \frac{\text{Vol. of acid} \times \text{strength} \times 50 \times 1000}{\text{Vol. of sample (ml)}}$$

$P = 0 \quad [HCO_3^-] = M$

$P = \frac{1}{2} M \quad [CO_3^{2-}] = M (= 2P)$

$P = M \quad [OH^-] = M (= P)$

$P < \frac{1}{2} M \quad [CO_3^{2-}] = 2P \quad [HCO_3^-] = M - 2P$

$P > \frac{1}{2} M \quad [CO_3^{2-}] = 2(M - P) \quad [OH^-] = 2P - M$

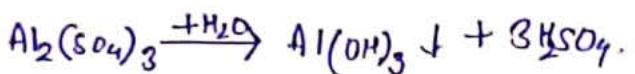
Sedimentation:

Factors:

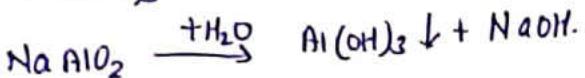
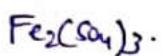
- ① Lateral flow velocity \rightarrow min.
- ② Sp. gr. of particles.
- ③ size of the particles.
- ④ Shape of the particles.
- ⑤ Temp of water.

viscosity $\propto \frac{1}{\text{relative density}}$.

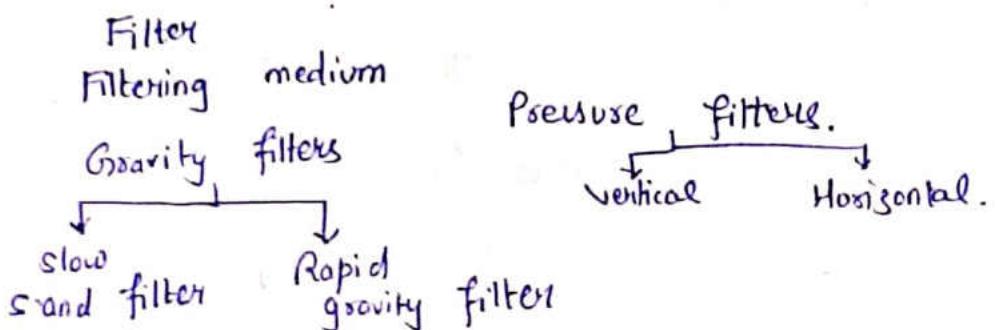
Coagulation or flocculation:



Alum



Filtration:



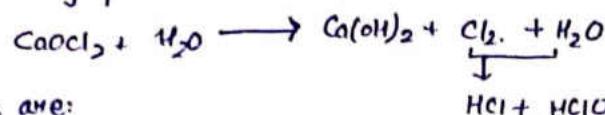
Disinfection / Sterilization:

Disinfectants are added to sterilize water in chemical process. Characteristics are:

- ① Should be able to kill the microorganisms.
- ② " " " " " microorganisms at normal temp.
- ③ Should be easily available.
- ④ Should be economic in use - cheap.
- ⑤ Should not leave any toxic effect after treatment.
- ⑥ Should be easy to monitor its concentration.
- ⑦ " " easily stable.

Procedures:

- ① Sterilization
- ② Bleaching powder. (CaOCl_2) ✓



- ③ HTH

- ④ Chloramines

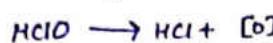
- ⑤ Chlorination.

- ⑥ Ozonation

- ⑦ UV radiation.

Theories are:

- ① Oxidation Theory:



$[\text{O}] + \text{microorganism} \rightarrow \text{microorganism killed.}$

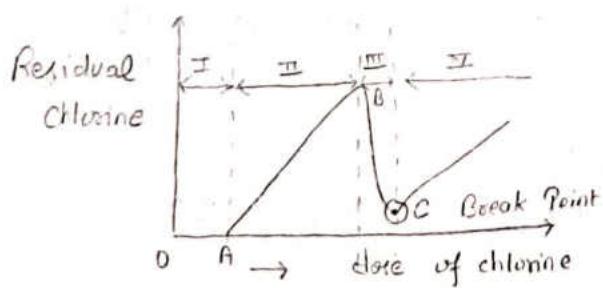
- ② Deactivation Theory: HClO deactivates enzymes.

Enzymes serve as food for cell growth of microorganisms.

In absence of proper food, microorganism dies out.

- ✓ Excess bleaching powder changes taste of water.
- ✓ Ca(OH)_2 and HCl after reaction form CaCl_2 . Amount of CaCl_2 is not too much but some amount of hardness is increased.
- ✓ To minimize hardness, HTH (CaOCl_2) can be used.
- ✓ But HTH isn't easily available, cost more and present in adequate amount.
- ✓ Chlorine is used mainly in chlorination. Chlorine can be used for many day because is present in elemental state. Small amounts are required unlike bleaching powder. Liquid chlorine is corrosive or toxic. It is too costly and availability is very low. It is inferior to bleaching powder. Even small excess amount of Cl_2 may lead to serious damage in quality of water.

Break point chlorination:



✓ OA, chlorine is unavailable, because it is used in oxidation of organic matter, killing of ~~and~~ sensitive microorganism, and oxidative/irradiative of residues.

✓ At C, all microorganism are killed. and after that there is slight increase because to take care of further contamination.

✓ Ozonisers are costlier. Ozonation of water is done to make water pure for medical purposes. Ozone is unstable if temp. is increased.

✓ Since microorganism are light, UV radiations kill the tissue of these organism. UV radiation is dangerous for people operating it. UV radiation operation is costlier also. It is physical one don't require any chemical composition.

- Softening:

✓ Hardness to non-hardness constituents.

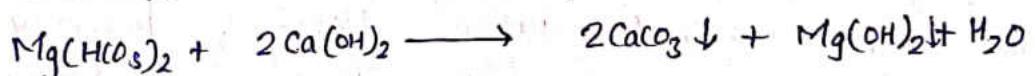
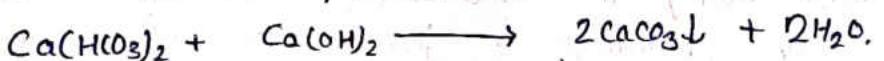
✓ Softening is done for industrial purposes.

✓ Three process are-

i) Lime-Soda process:

Principle: (I) Lime reacts with

a) all the temporary hardness.



b) permanent hardness except calcium permanent hardness.

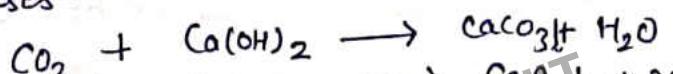
\Rightarrow Lime is itself an calcium espcl and therefore interaction not happen.



c) mineral acids

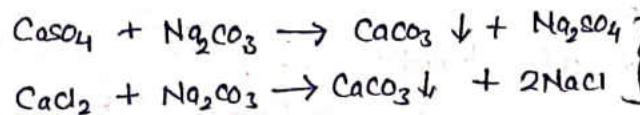


d) Gases-



(II) Soda reacts with

all the calcium permanent hardness



Sodium salts are
non-hardness causing
elements / cements

- ✓ Lime & soda should be added in calculated amount. Excess of these can contaminate water.

Calculation :

$$(I) \text{ Amount of lime required} = \frac{74}{100} [\text{CTH} + 2\text{MTH} + \text{MPH} + \text{Mineral acid} + \text{Gases} + \text{OH}^- - \text{NaAlO}_2] \times \frac{\text{Purity}}{\text{HCO}_3^-} \times 10^{-6} \times \frac{100}{\text{kg.}}$$

- ✓ Sodium aluminate on react with water forms hydroxyl ion. It is to be subtracted

$$(II) \text{ Amount of soda required} = \frac{106}{100} [\text{CPH} + \text{CPH introduced} (\text{MPH} + \text{Mineral acids} + \text{OH}^- + \text{CO}_3^{2-}) - \text{NaAlO}_2] \times \frac{\text{Purity}}{\text{HCO}_3^-} \times \frac{100}{\text{kg.}}$$

- ✓ Setup used for softening of water is called softener. These are:

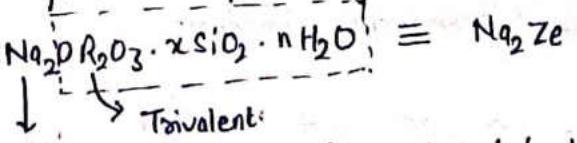
- | | | |
|-----------------------|---|---------------------------------|
| Gold processes | ① | / Batch Type |
| | ② | Conventional / Continuous type. |
| | ③ | Catalyst / Spyreactor type. |
| | ④ | Sludge / blanket type |
| | ⑤ | Hot L-S process. |

Solubility of CaCO_3 , Mg(OH)_2 etc. is very low in hot condition

Advantages: L-S process also eliminates microorganisms impurity. i.e.

Disadvantages: Large amount of precipitate is formed.

ii) Zeolite process / Permuntit process:



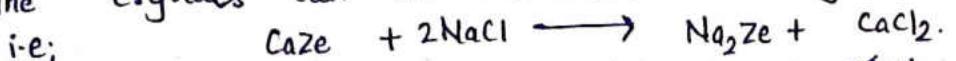
It reacts & get precipitated/replaced.

✓ This process removes both temporary & permanent hardness.



Regeneration:

✓ The crystals can be recovered back by passing NaCl solution.



Advantages:

✓ This process can be used periodically.

✓ Operational cost is negligible.

✓ Produces 0 hardness.

✓ Compact unit - easy to handle.

✓ Economic in use.

✓ can be automated.

✓ Automatically adjusts for incoming level of hardness.

✓ No sludge formation (sodium salts are soluble).

Limitations:

✓ Water should be non-turbid (no suspended impurity).

✓ Water should be free from mineral acids.

✓ Lead is not exchanged.

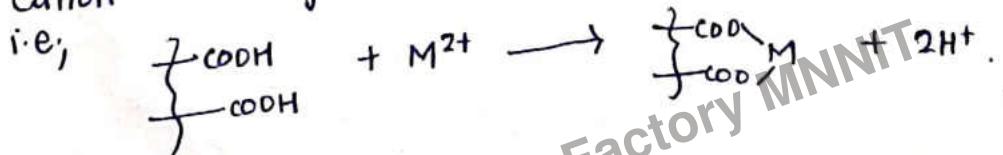
✓ Anions are not exchanged.

✓ Soluble salt content is more.

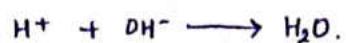
iii) Dimineralisation / Ionic Exchange process:

Two types-

i) cation exchange resins- have free $-\text{COOH}$, $-\text{SO}_3\text{H}$, oxalic groups.



iii) Anion exchange resin - have free $-OH$ (hydroxyl)

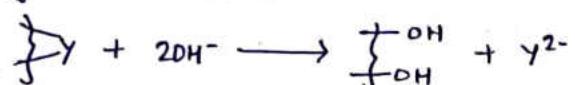


Regeneration:

① By dilute acid solution:



② By dilute alkali solution:



- Boiler Troubles:

Precipitation of impurities occurs at rapid rate since water is boiled in large scale.

As,

Ionic product of impurities $>$ Solubility product.

Problems-

1. Carry over
 - a) Priming.
 - b) Foaming.
2. Sledge and scale formation.
3. Caustic embrittlement.
4. Boiler corrosion.

i) Carry over:

Priming - formation of wet steam (water droplets in steam)

Foaming - formation of persistent bubbles.

Priming is because of -

- a) Higher water level.
- b) Large amount of dissolved solids (surface tension)
- c) High steam velocities.
- d) Sudden bailing.
- e) Improper boiler design.

- f) Sudden increase in rate of steam production.
- g) Formation of foam.

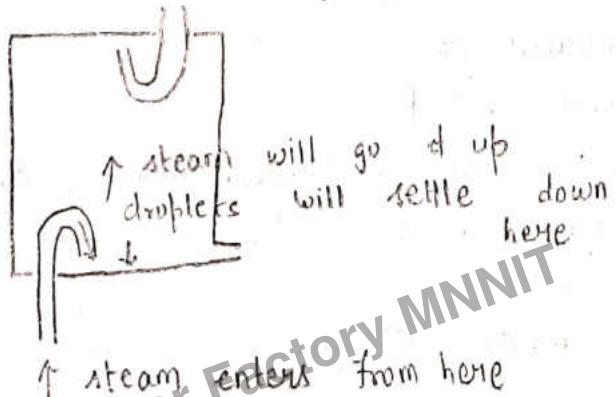
✓ Foam is due to presence of soaps, oils, greases, etc., which reduces surface tension and hence formation of persistent bubbles takes place.

✓ Carry over is undesirable due to

- ① Loss of heat (replacement of hot water by fresher water).
- ⇒ To reduce impurity it is replaced by fresh water.
- ② Water bubbles reduces superheat of steam.
- ⇒ Steam have more superheat and because of dissolution of bubbles in it or carry over it is lost.
- ⇒ During compression of engine, due to loss of superheat, condensation of steam takes place.
- ③ Passage of gritty matters.
- ⇒ Water droplets are associated with impurities.
- ④ Reduce the steam carrying capacity of tubes
- ⇒ due to blockage associated with gritty matters.
- ⑤ Incompressible water
- ⇒ Due to loss of superheat of steam (because of water droplets in it), mechanical advantage of heat is lost.
- ⑥ Foaming makes assessment of water level difficult.

✓ Priming can be avoided by -

- ① Fitting mechanical steam purifier.



- ② Avoiding rapid change in steam production rate.
- ③ Maintaining low water level.
- ④ Efficient filtration/ softening of feed water.
- ✓ Foaming can be avoided by -
- ① Removal of oil / soaps / waxes, etc. from feed water.
- ② Adding anti foaming agents Ex- Castor oil, etc;
- Sledge and Scale formation:
 - ↓
 - Loose slimy ppt. formed in boiler
 - If ppt. are sticky, then sledge is converted into scale.

Disadvantages of Sledge:

- ① Bad conductor of heat. Heat transfer will be hindered.
- ② Move to low water circulation area and hindered the examination of water since instruments are placed at that position.
- ③ If converted into scale, form thick layer.

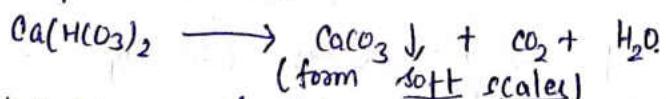
Treatment of Sledge:

Blow off / Blow down;

Replacing water (at a level or concⁿ of getting precipitation of impurities) with fresh water (so as to keep ionic product low and do not exceed solubility product).

Scale formation is due to -

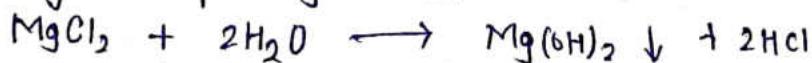
- ① Decomposition of bicarbonates.



- ② Precipitation of CaSO_4

CaSO_4 and other calcium salts are adherent and form hard scales.

- ③ Hydrolysis of Mg salts:



- ④ Formation of silicates: (form soft scale).

Silica reacts with metal to form metal silicates & form hard scales

Disadvantages of scale:

- i) Bad conductor of heat.
- Wastage of fuel.

thickness of scale	0.325	0.625	1.25	2.5
wastage of fuel	10%	15%	50%	100%

- ii) Boiler safety:

→ made up of metal. All the metals on strong heating become soft and chance of explosion may arise.

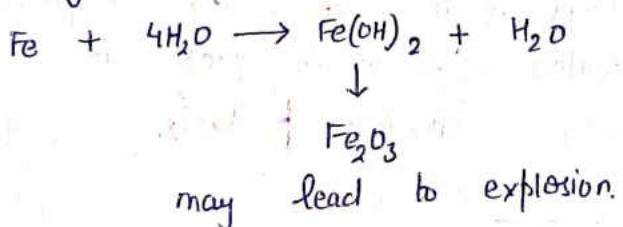
- iii) Decrease in efficiency of machines:

- Bad conductor, over heating causes in increase in rate of steam production which will effect the efficiency of machines.

- iv) Danger of explosion:

Due to scale formation, the temperature gap arises. Due to over heating, cracks are found in scales in which water enters through capillary action. The generation of steam at high rate in the cracks will increase pressure inside boiling-er and may result into explosion.

- v) Thinning of Boiler material:



Treatment of scale

Mechanical methods:

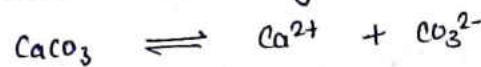
- i) Scrubbing with wire brushes / scrubbers. (usually for soft scales).
- ii) Hard scales can be removed by giving thermal shocks.

Chemical methods:

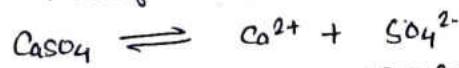
- i) Soft scales are removed by dil. acid solution.
- ii) Hard scales are removed by dil. EDTA solution. EDTA will form complex with metal ions.

Prevention

- i) Effective softening or filtering of water inside the boiler.
- ii) Reagents are added to convert hard scales into soft scales.
- Conditioning of water: Internal treatment to boiler water for conversion of hard scales to soft scales and then to sludges.
- iii) Carbonate conditioning:



$$K_{sp\text{ CaCO}_3} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$



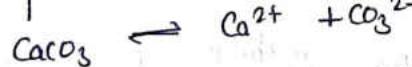
$$K_{sp\text{ CaSO}_4} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

Concentration of CO_3^{2-} is increased
the CO_3^{2-} inspite of SO_4^{2-} .

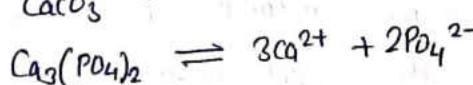
$$\frac{K_{sp\text{ CaCO}_3}}{K_{sp\text{ CaSO}_4}} = k = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}$$

$$k[\text{SO}_4^{2-}] = [\text{CO}_3^{2-}]$$

ii) Phosphate conditioning



$$K_{sp\text{ CaCO}_3} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$



$$K_{sp}^{\frac{1}{3}} \text{ Ca}_3(\text{PO}_4)_2 = [\text{Ca}^{2+}][\text{PO}_4^{3-}]^{\frac{2}{3}}$$

$$\frac{K_{sp}^{\frac{1}{3}} \text{ Ca}_3(\text{PO}_4)_2}{K_{sp\text{ CaCO}_3}} = k = \frac{[\text{Ca}^{2+}][\text{PO}_4^{3-}]^{\frac{2}{3}}}{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}$$

$$k[\text{CO}_3^{2-}] = [\text{PO}_4^{3-}]^{\frac{2}{3}}$$

iii) Electrical conditioning

iv) Radioactive conditioning

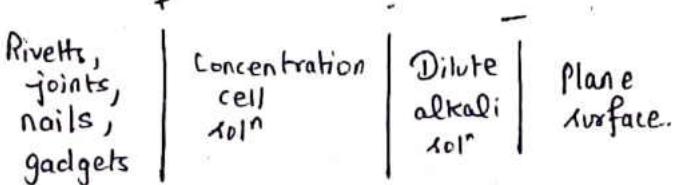
v) EDTA

vi) Calgon

vii) Kerosine

- Caustic Embrittlement:

- formation of concentration cell inside boilers.
- concentration of alkalies in the bends/gaps, etc. due to concentration of alkalies
- pH at these sites increases



Remedial 101^n

- ① Use of phosphate conditioning should be preferred.
- ② Careful adjustment of pH (near about 7)
- ③ Addition of Lignins, tannins, Na_2SO_4 , etc. enters into the gap.

Boiler corrosion:

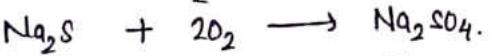
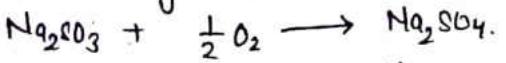
~~① Corrosion due to dissolved oxygen.~~

$$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + \text{Fe} \rightarrow \text{Fe(OH)}_2 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$$

(Rust)

Prevention:

- a) Adding reducing agent

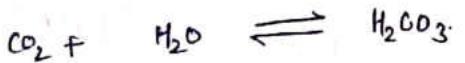


- b) Degasification.

- Temp. of water is increased to expel out ~~water~~ gases.

- c) Passing over selective steins.

② Corrosion due to dissolved CO_2 .

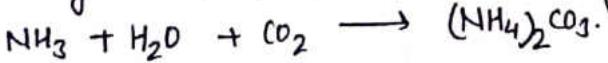


At high temp., H_2CO_3 causes corrosion despite of weak acid.



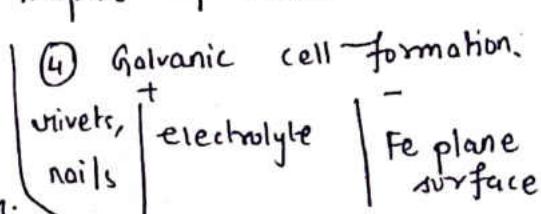
Prevention:

- a) Adding NH_3 .



- b) Degasification.

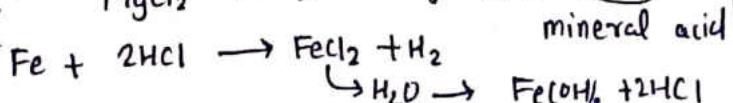
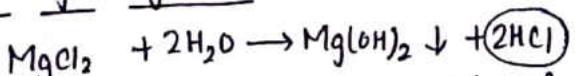
- c) By passing over selective steins.



Prevention:

Suspension rod or of zinc-sacrificed anode.

③ Hydrolysis of Mg salt:



Prevention:

Adding alkalinity calculated

from outside in amount.

Paper Factory MNNIT

Lubricants

Lubricants may be defined as a substance which reduces the friction when introduced between 2 sliding or moving surfaces and the phenomenon is known as lubrication.

- Functions:

- i) To Reduce friction.
- ii) To reduce wear & tear. & surface deformation.
- iii) Acts as a coolant to carry away heat (liquid lubricants & lubricating oil).
- iv) Reduces maintenance and running cost by preventing rusting and corrosion.

- Mechanisms:i) Hydrodynamic lubrication:

or Thick-film

or Fluid-film

Moving or sliding surfaces are separated from each other by a thick lubricant film and this type of lubrication is observed in light machines. (Ex- Sewing machine, Watches, Delicate scientific instruments).

Composition of lubricant: Hydrocarbon oil mixed with two additives.

a) Selected long chain polymers: As T ↑es, viscosity ↓es, these are added to minimise the change in viscosity of oil with increase in temperature.

b) Antioxidants (β -aminophenol): Hydrocarbon oil may have some unsaturated molecules & with increase in temp., these get oxidised and the formation of 'white gum' takes place. The 'white gum' disturbs the lubrication, that's why ' β -aminophenol' as an antioxidant is added to minimise the formation of 'white gum'. Phenol and its derivatives react with oxygen gives red-coloured

substance. Phenol also have greater affinity of oxygen at high temp.

ii) Boundary lubrication

or
Thin-film "

A thin layer of the lubricants is adsorbed on the surfaces which avoid direct surface to surface contact.

Composition of lubricant:

- Graphite or MoS_2 (in form of powder)
they are applied
- Mineral oil with small amount of fatty acids or fatty oils.
- Vegetable & animal oils and their soaps.

These lubricants work on the principle of adsorption.

iii) Extreme Pressure lubrication:

It is performed by extreme pressure additives in mineral oil where high temperature is reached due to very high speed of moving and/or sliding surfaces under pressure.

Composition of Lubricant: Extreme pressure additives in mineral oil

- Chlorinated Ester.
- Sulphurized oil.
- Tricretesyl phosphate.

Here, at high temp., these extreme pressure additives react with metal surface to form metal chlorides, sulphide and phosphide in the form of durable film. which can withstand high temp. due to their higher melting points.

Classifications:

3 categories are:

- i) Lubricating oils or Liquid lubricants
 - ii) Semi-Solid " or Greases
 - iii) Solid " (Ex- MoS_2 , Graphite etc.).

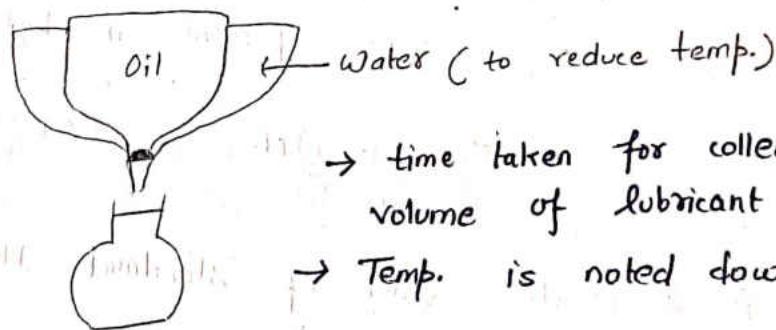
ij) Liquid Lubricants are classified in 3 categories-

- a) Vegetable & animal oil.
 - b) Mineral oil. (fractional distillation of 1 crude oil)
 - c) Blended oil.

- Testing properties of lubricating oil :

i) Viscosity: Viscosity differ in different oils because of C-C chain length and chain structure. Viscosity $\propto \frac{1}{\text{Temp.}}$

Glass viscometer is avoided in testing viscosity of lubricating oils. In this case, Redwood viscometer is used.



- i) Redwood 1 : outlet is smaller
ii) Redwood 2 : outlet is little bigger } working principle is same.
(used for higher viscous lubricant)

Viscosity index (VI): Rate at which the viscosity of an oil changes with temperature is measured by an empirical number known as VI.

Relatively small change in viscosity with temp. \Rightarrow HIGH VI
" large " " " " " " " \Rightarrow Low VI

Pennsylvania oil \rightarrow arbitrarily assigned a VI of 100
 Gulf oil \rightarrow " " "

$$\text{Viscosity Index (VI)} = \left(\frac{L-U}{L-H} \right) \times 100$$

L \rightarrow viscosity at 100°F of low VI standard (Gulf oil)
 H \rightarrow " " " high " " (Pennsylvania oil)
 U \rightarrow " " " unknown oil.

Ques: An oil sample under test has viscosity 564s at 100°F,
 , Gulf oil 774s at 100°F and that of Pennsylvania oil
 414s at 100°F. All the 3 oils show same viscosity value
 210°F. Calculate VI of unknown oil.

Soln

$$VI = \frac{774 - 564}{774 - 414} \times 100 = 58.33$$

ii) Saponification number: The number of milligram of KOH required
 to saponify the heavy material present in 1gm of oil.

$$SN = \frac{56.1 (\beta-S)N}{w}$$

56.1 \rightarrow equivalent weight of KOH.

B \rightarrow Titrate value of standard HCl for Blank
 Titrations. (in mL)

S \rightarrow " " " "
 " (")

" " " Sample

N = Normality of HCl

w = wt. of oil (in g)

Sample:
 w g of oil \rightarrow Excess known volume of alcoholic KOH, 80°C, 1 hr.
 to make oil soluble.

↓
Unreacted KOH titrated by standard HCl (5 ml)
conc is known

primary standard
↓
doesn't change with
time.

Blank:

wg of $H_2O \rightarrow$ same excess known
volume of alcoholic KOH,

80°C, 1 hr.

Ques: 1.6 gm of an oil was taken in a conical flask and excess alc. KOH was added and heated. The resultant solution consume 2.8 ml of 0.055 N HCl. 20.8 ml of same acid solution was required for blank titration.

Soln
$$56.1 \left(\frac{20.8 - 2.8}{1.6} \right) \times 0.55$$

Importance: All the vegetable & animal oils have known saponification number. Any deviation from these values with the experimental values indicates change of adulteration in given oil.

iii) Flash Point: Flash point of an oil is the lowest temperature at which oil gives vapour that will ignite for a moment when a small flame is brought near it.

Apparatus: A) Abel's apparatus

B) Pensky-Martin's apparatus (direct heating)
↳ used for oils having higher flash point.

Importance: It is used to indicate change of fire accidents in industries. Good lubricant should have flash point at least above the temperature at which it is used.

iv) Aniline Point: The minimum equilibrium solution temperature for equal volume of aniline and oil sample.

Lower aniline point of an oil indicates higher percentage of aromatic hydrocarbons. Aromatic hydrocarbons have tendency to dissolve natural & some synthetic rubber. So, higher percentage of aromatic hydrocarbon or lower aniline point of the oil has more chances of degradation of the oil when it comes in contact with Rubber packing or rubber sealing. Lubrication will not work properly.

Hence, low % of aromatic hydrocarbons or high aniline point of oil must be chosen.

Importance: To prevent or minimize the degradation of lubricating oil by Rubber sealing, Rubber packing, etc.

v) Steam Emulsion number (SEN): The time in which the water and oil emulsion separate out in different layers is called steam emulsion number. The quicker oil separates out, the lower SEN value & better the lubricating oil for most purposes.

Importance: To avoid corrosion of different surfaces.

- Greases: Semi-solid, obtained by combining lubricating oil with thickening agents (Thickeners)
↳ smaller quantity.

Thickening agents: ① Soap based. e.g., Soaps of Na^+ , K^+ , Ca^{2+} , etc.

② Non-soap based, e.g., Mica gel, Poly ureas, Graphite, Clays, etc.

improved
heat resistance
properties of greases.

Paper Factory MUNIT

Above certain temp., grease converts into liquid materials.

Preparation: Grease is prepared by 2 steps-

- ① Saponification of fat with alkaline is done to form soap.
- ② Hot lubricating oil is added to the ^{above} soap with constant mixing.

- Graphite:

Powdered form
or
Suspension in water or oil

weak attraction
(van der Waals force)



layered structure



Application:

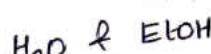
- 1) Internal combustion engine.
- 2) To produce "Graphite greases" → better heat resistance lubricant.
- 3) As lubricants in air compressors

- Phase equilibria:

Phase: Phase of substance is a form of matter i.e., uniform throughout in chemical composition & physical state.

Examples,

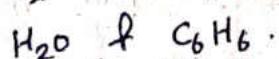
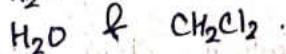
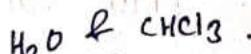
- i) Two completely miscible liquids: One phase.



On adding the NaCl on given solution, colourless solⁿ is formed. and on adding I₂, red colour is thoroughly formed.

NaCl is highly soluble in water & I₂ " " organic solvent producing red colour.

- ii) Two immiscible liquids: Two phases.



On adding I₂, lower part will become coloured (red) (CHCl₃ is denser than H₂O)

iii) Solute completely dissolved in a solvent : Unsaturated solution.
Glucose in H_2O \swarrow H-bonding and other attraction
that makes glucose dissolved in water.

\swarrow Unsaturation in the sense is, H_2O surrounds glucose molecules.

\swarrow One phase (Glucose solution phase)

iv) Solute completely dissolved in a solvent: Saturated solution.

\times on changing temp., nature of saturated solⁿ changes.

Glucose crystal is in equilibrium with glucose solⁿ:
after adding \searrow at saturation
in glucose solvent. point or after
that

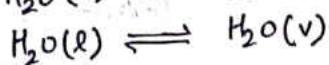
\swarrow Two phase is there

a) "Glucose solution" phase

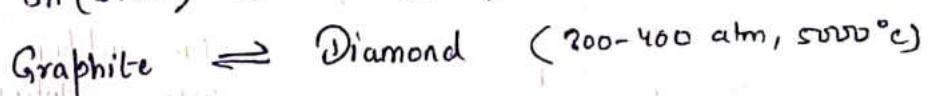
b) "Glucose solid" phase

v) Gas mixture: One phase (gas phase)

- Phase Transition:



Gases and their vapours are differentiated in side of critical temperature.



$\Delta G = -ve$ (Phase transition is possible to takes place).

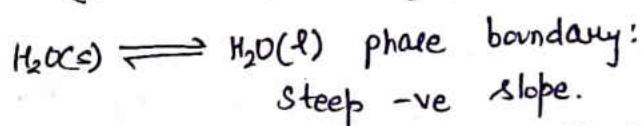
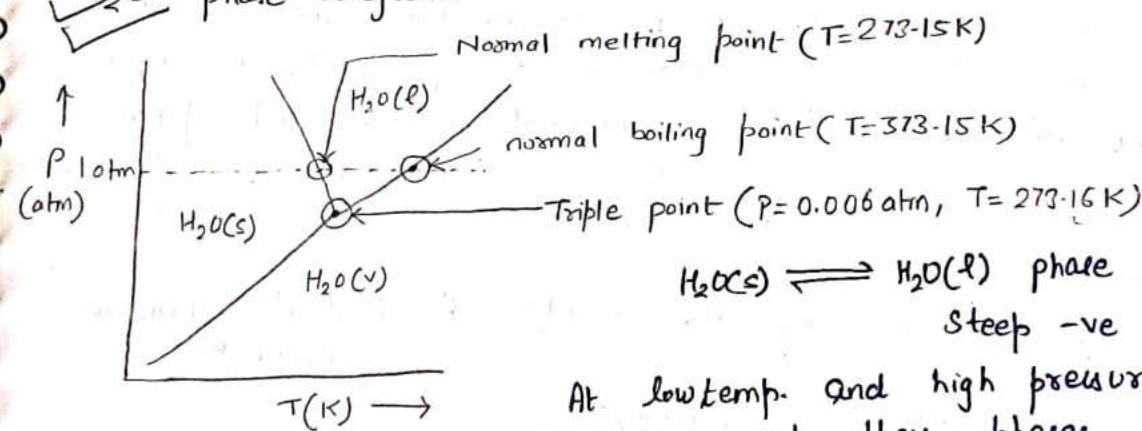
- Phase diagram & Phase Boundary:

\checkmark Diagram that shows the condition of temperature & pressure at which various phases of a substance are thermodynamically stable is known as phase diagram.

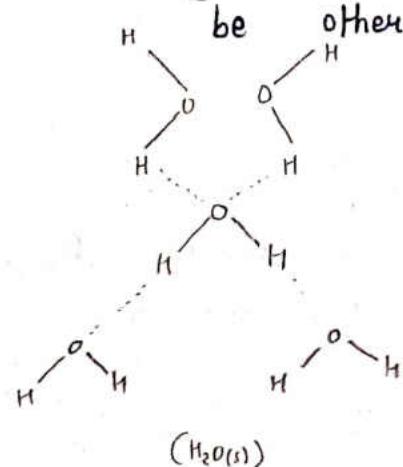
The boundaries between areas which show the values of pressure & temperature at which 2 phases are in equilibria are known as phase boundary.

- i) Boiling temp.: Temperature at which the vapour pressure of a liquid becomes equal to the external pressure or applied pressure. When external pressure is 1 atm, boiling temp. is called 'normal boiling point'.
- ii) Melting Temp.: Temperature at which liquid and solid phase of a substance coexist in equilibria at a specified external pressure. When external pressure is 1 atm, melting temp. is called 'normal melting point'.
- iii) Triple Point: Point on the point / phase diagram where 3 phases of a substance simultaneously coexist in equilibria. It is represented by a point where the phase boundaries are meeting.

H_2O phase diagram:



At low temp. and high pressure situation, we can get other phases of water all are in solid (in the form of $(\text{H}_2\text{O})_4$, $(\text{H}_2\text{O})_5$, $(\text{H}_2\text{O})_6$, etc; ...) and there may be other triple point existence.



Each water molecule is having 3-D structure, having 4 hydrogen bonds attached with other molecules. 2 are attached with lone pairs and rest 2 with bond pairs.

Phase Rule:

When equilibrium of phases is influenced by P , T and concentration then degrees of freedom,

$$F = C - P + 2 \quad \rightarrow \text{applicable in both reactive and unreactive system.}$$

C = no. of components.

P = no. of phases.

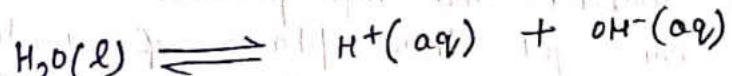
So, D.o.f. free. of equilib. system, the no. of variables required to specify its equilibria step

- only pressure
- " temp.
- Both pressure & temp.
- P and concentration.

Components: No. of components of a system are the smallest no. of independent chemical constituent taking part in equilibria by means of which the concentration of each phase can be expressed either directly or in terms of chemical equations.

No. of chemical compositions - No. of grouped chemical constituents.

Ex-



$$\text{No. of components } C = 3 - 2$$

In liquid phase,

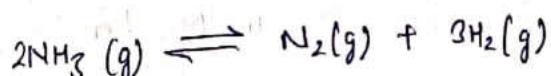
$$\textcircled{1} \quad K_{eq} = \frac{a_{H^+} \cdot a_{OH^-}}{a_{H_2O}}$$

$$\textcircled{2} \quad x_{H^+} = x_{OH^-}$$

$$D.O.F = 1 - 1 + 2$$

$$= 2$$

2 variables are required to specify liquid phase and that is pressure and temperature.



$$K_{eq} = \frac{a_{N_2} \cdot (a_{H_2})^3}{a_{NH_3}^2}$$

$$x_{N_2} = \frac{1}{3} x_{H_2}$$

$$C = 3 - 2 = 1$$

- Adsorption:

Factors affecting adsorption-

- Nature of adsorbent and its state of subdivision.
- Nature of adsorbate and its concentration.
- Temperature -

Types -

Physical adsorption

- Weak van der Waal force
- $\Delta H = -4 \text{ to } -40 \text{ kJ/mol}$

Chemical adsorption

- Strong selective chemical bonding.
- $\Delta H = -40 \text{ to } -800 \text{ kJ/mol}$.

- Freundlich adsorption isotherm:

✓ volume of gas adsorbed at pressure P

$$V = kP^\alpha \quad (0 < \alpha < 1)$$

k and α are const.

P is the pressure at equil. state, and $< P_1$

Solute from liquid solution on solid:
Ex- CH_3COOH and charcoal
2gm of solute adsorbed by 'm' gm of adsorbent with concn.

of solute 'c'

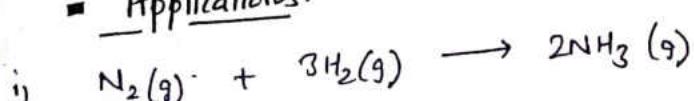
$$\frac{x}{m} = kc^\alpha \quad (0 < \alpha < 1).$$

k and α are const.
adsorption equilibrium concentration $< c_1$

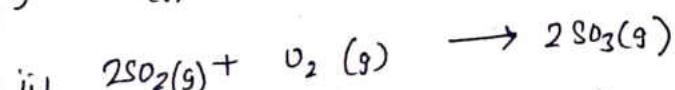
- Applications:

Surface

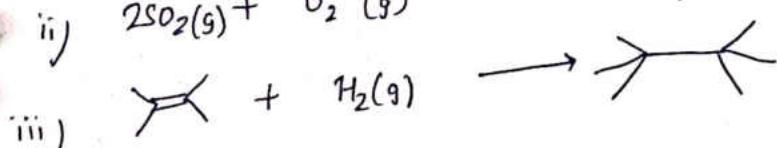
Fe



V_2O_5



Ni



POLYMERS

No. avg. Molecular weight, $\bar{M}_n = \frac{\sum_{i=1}^n n_i m_i}{\sum_{i=1}^n n_i}$

wt. avg. " " , $\bar{M}_w = \frac{\sum_{i=1}^n w_i m_i}{\sum_{i=1}^n w_i} = \frac{\sum_{i=1}^n n_i m_i^2}{\sum_{i=1}^n n_i m_i} \quad n = \frac{w}{m}$

$$\bar{M}_w \geq \bar{M}_n$$

$$\frac{\bar{M}_w}{\bar{M}_n} \geq 1$$

[Equal to 1 will exist when length of all chains are equal & uniform]

Viscosity avg. molecular weight, \bar{M}_v

$$\bar{M}_v = \left(\frac{\sum_{i=1}^n n_i m_i^\alpha}{\sum_{i=1}^n n_i m_i} \right)^{1/\alpha} \quad 0 < \alpha < 1$$

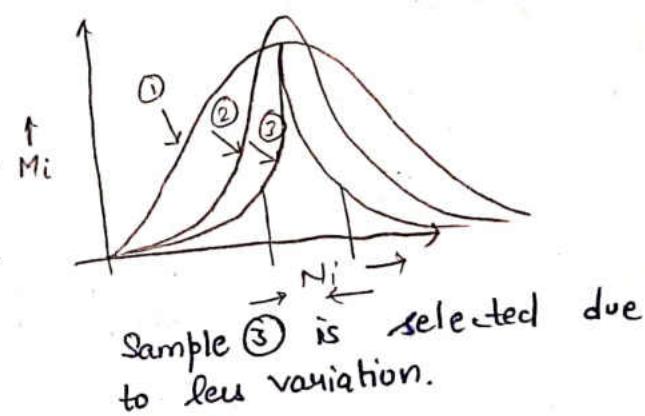
Sediment avg. molecular wt. \bar{M}_z

$$\bar{M}_z = \frac{\sum_{i=1}^n n_i m_i^3}{\sum_{i=1}^n n_i m_i^2}$$

$$\bar{M}_z > \bar{M}_w > \bar{M}_n > \bar{M}_v$$

$$[\eta] = k \bar{M}_v^\alpha$$

- ✓ Polymer a youngest member in materials family.
- ✓ " are macro molecules.
- ✓ " shows avg. property.
- ✓ Diff. types of molecular weight.
- ✓ Dispersity index & its significance
- ✓ MWD curves.



- Characteristics of Monomers

Eg:
 functionality, fav = $\frac{\sum n_i f_i}{\sum n_i} = \frac{2 \times 3 + 3 \times 2}{2+3} = 2.4$
 Maintain its stoichiometry.

- Degree of polymerisation: $\overline{DP} / \overline{DP}_n / n$

$$\overline{M_n} = M_0 \times \overline{DP}$$

- Extent of polymerisation:

- ✓ Extent of polymerisation value, p is always less than 1.
- ✓ Some are inactive

- Carother's Relation:

Case 1: $\frac{2}{fav} - \frac{2}{fav \cdot \overline{DP}} = p$

$$\boxed{\frac{2}{fav} \left[1 - \frac{1}{\overline{DP}} \right] = p}$$

$$\boxed{p < 1}$$

Case 2: when $fav = 2, p = 1 - \frac{1}{\overline{DP}}$

$$\overline{DP} = \frac{1}{1-p}$$

$$\frac{\overline{M_n}}{M_0} = \frac{1}{1-p}$$

$$\overline{M_n} - \overline{M_n}p = M_0$$

$$- \overline{M_n}p = M_0 - \overline{M_n}$$

$$p = \frac{\overline{M_n} - M_0}{\overline{M_n}}$$

$$\boxed{p = 1 - \frac{M_0}{\overline{M_n}}}$$

$$\boxed{\overline{M_n} = \frac{M_0}{1-p}}$$

$$\boxed{\overline{M_w} = \frac{M_0(1+p)}{(1-p)}}$$

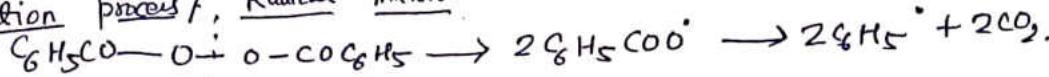
Case 3: $\overline{DP} \ggg$

$$\frac{2}{f_{av}} = P_c$$

✓ Highly cross linked structure is formed of bad quality.

- Chain polymerisation reacⁿ:

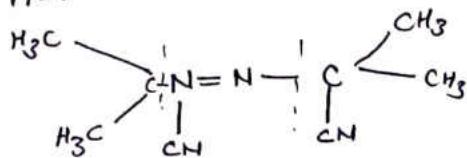
Initiation process / Radical initiat:



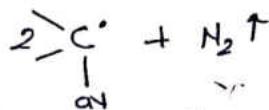
Non peroxide linkage initiators are also present.

Ex-

AIBN



Azo iso butyl nitroso do



→ It is very fast. → No loss of any atom.

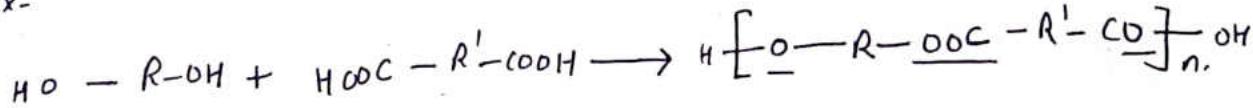
- Condensation polymerisation reacⁿ:

- Polycondensation reacⁿ.

- Step polymerisation reacⁿ

- Step growth polymerisation reacⁿ

Ex-



Total ester linkage ($2n-1$)

→ It occurs step wise & have slow rate.

→ Loss of atom takes place.

→ Reactant taken is excess will be present in both the ends of the chain.

→ $\gamma^0 \leq 1$

→ Degree of polymerisation, $\overline{DP} = \frac{1 + \gamma^0}{1 + \gamma^0 - 2\gamma^0 p}$

$$\overline{DP} = \frac{1}{1-p}$$

Paper Factory MNNIT

Effect of impurity on polymers:

$N_i = \%$ of impurity.

$N_o = \%$ of purity.

$$\overline{DP} = \frac{\frac{1+N_i}{N_o}}{(1-P) + \frac{N_i}{N_o}}$$

$$\frac{1 + \frac{2}{98}}{(0.02) + \frac{2}{98}} \times \frac{2}{100} \times 98 = \frac{196}{100}$$

$$\left(\frac{\frac{100}{98}}{0.02 \times 98 + 2} \right) \times \frac{100}{98} \approx 25X$$

$$\frac{1.96}{\frac{2.00}{3.96}}$$

Impurity drastically reduces degree of polymerization.

$$\overline{M_n} = M_o \times \overline{DP}$$

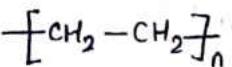
$$\overline{M_w} > \overline{M_n}$$

$$\overline{M_w} = \overline{M_n} \times (1+P)$$

$$\overline{M_v} = \frac{M_o}{(1-P)} \times (1+P)$$

Structure property relationship:

Polyethylene (PE)



Low density polyethylene , LDPE , High volume polyethylene (Highly branched)

High density polyethylene, HDPE , Low volume polyethylene. (High/Almost linear type)

Linear Low " " , LLDPE

High impact polyethylene , HIPE

High modulus " , HMPE

Ultra High Molecular Weight Polyethylene , UHMWPE

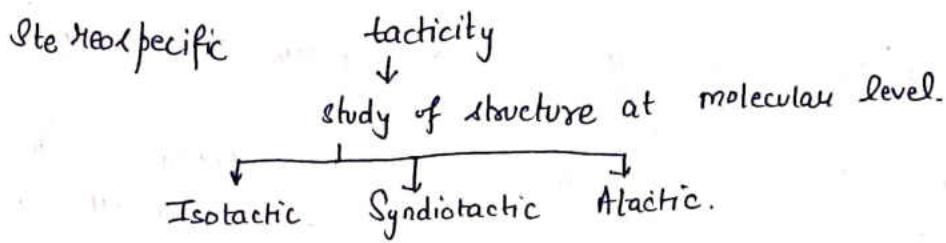
LDPE is good for membrane

HDPE is used for mechanical purposes.

Glass transition temp. (T_g) / Industrial used temp.

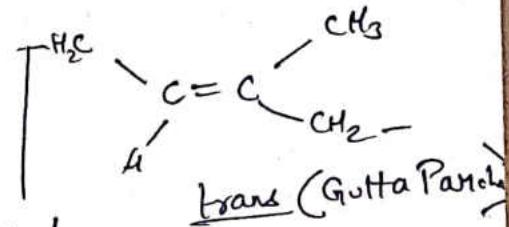
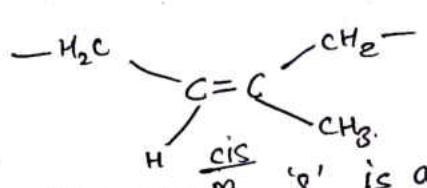
Ax (hard) (High glass transition temp).
 Al (weak)

At GTT, segmental movement occurs
& above that, viscous state is achieved



Rubber: a) Natural:

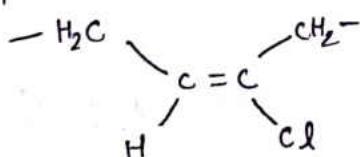
Isoprene structure:



- ✓ In vulcanisation, 82% max^m 's' is added
 - ✓ Max^m vulcanisation may make material brittle. (EBONITE) structure.
 - ✓ Cis form of isoprene is boat like structure
- trans form is having chair like structure
- 
- Material of less stress is selected.
 - In boat shape, stress is minimum and energy loss is minimum.

b) Synthetic:

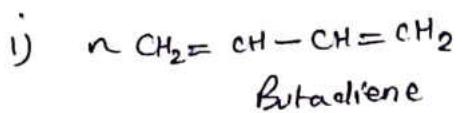
Neoprene structure



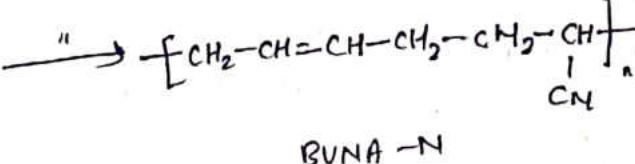
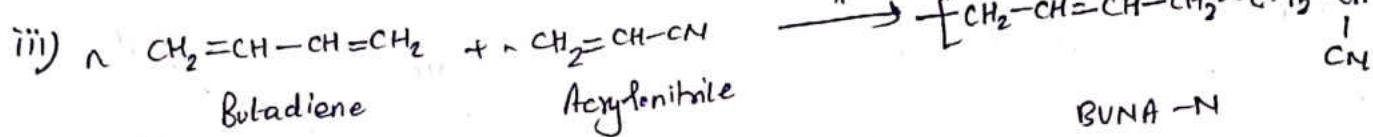
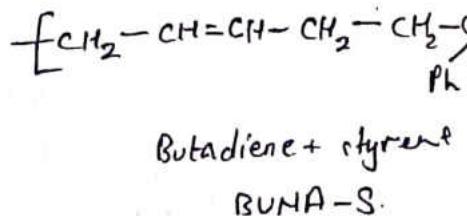
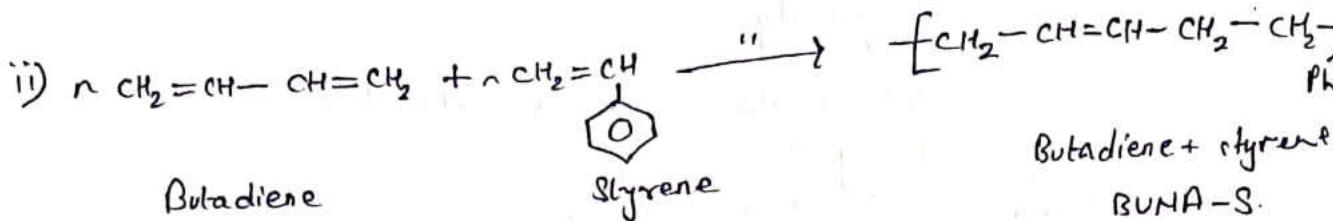
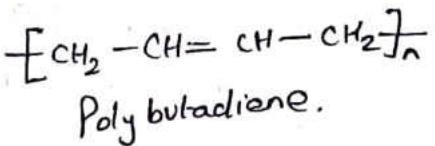
Copolymerisation types:
Random
Alternate
Block
AAABABBA
Graft

Copolymerisation:

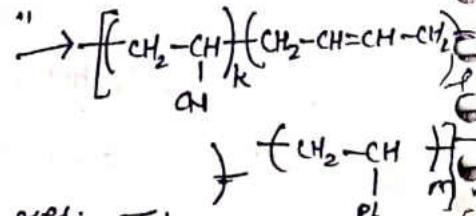
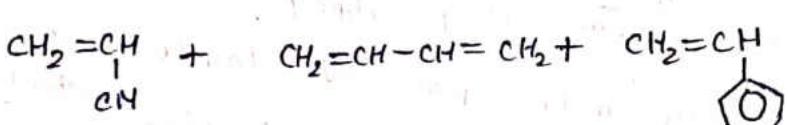
Ex:



polymerised



iv) ABS Rubber



✓ Polymerisation techniques for industrial purposes: Types are:

Bulk Polymerisation

Solution "

Suspension "

Emulsion "

Suspension and emulsion polymerisation are effective.

- Fibre/ Biodegradable / Biopolymers:

→ Spinning technique is used for production of fibres.

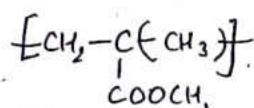
Wet spinning dry spinning } depending upon the surrounding material

↓ blow of inert air from lower side to remove solvent.

Pyrolysis: Combustion in absence of air in closed container. (11-12)
This method is costlier.

Mixing of Non-biodegradable with biodegradable polymers will restrict problems upto 50%.

PMMA \rightarrow Polymethyl methyl Acrylate.



- Viscometry avg. molecular weight, \bar{M}_v
 ~~\bar{M}_v of polymer~~ is determined by following —

Before that it was discussed diff. type of molecular weight of poly. like (\bar{M}_n , \bar{M}_w , \bar{M}_v , \bar{M}_z)

These were on the basis of number of polymer chain and its respective masses, Now using the viscosity value, \bar{M}_v can be determined

$$\eta = \frac{\pi \rho \mu^4}{8 l v}$$

ρ = Pressure exerted inside the viscometry advent.

μ = radius of capillary

l = length (upper to lower meniscus of viscometry)

v = Volume of soln taken, 10 ml.

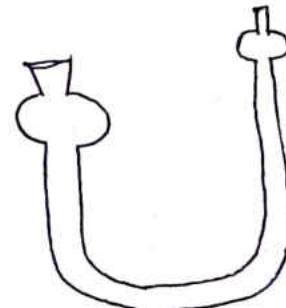
Here, P for solvent of solution is very marginal. so we take it same in all cases.

So, for solvent flow time, to
& solution " " , t

for relative viscosity, $\eta_{rel} = \frac{t}{t_0}$

Here, polymer solution we take very dilute from say 0.5% polymer solution (w/v)

Then, we find out



Specific viscosity $\eta_{sp} = \mu_{sol} - 1$

$$\boxed{\mu = 2}$$

Reduced / Relative " , $\mu_{red} = \mu_{sp}/c$ [conc of polymer soln]

Inherent viscosity, $\eta_{inh.} = \ln \frac{\mu_{red}}{2}$

Intrinsic viscosity $\eta_{int.}$ or $[\eta] = \lim_{c \rightarrow 0} \left(\frac{\mu_{sp}}{c} \right)$

$[\eta] \rightarrow$ it is also called a limiting viscosity.

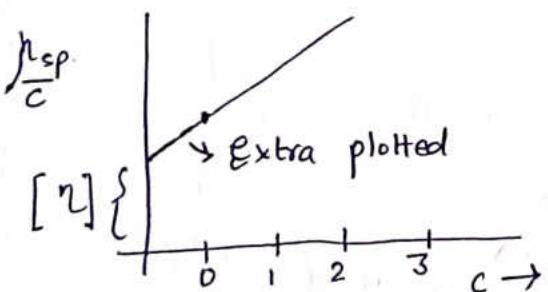
For infinitesmall dilute condition, we should measure the $(\frac{\eta_{sp}}{c})$

we take maximum 3 diff. concn of polymer soln. $C_1, C_2 \& C_3$.

then, measure

$$\left(\frac{\eta_{sp}}{c} \right) = K \bar{M}_v^\alpha$$

Mark eqn. & then plot.



So, $[\eta]$, K & α if known, we can find out \bar{M}_v
where, K & α are const.

α values lies b/w 0 & 1 $0 < \alpha < 1$

α depends on polymer nature of solvent

If we take log on both sides, of Mark eqn.

$$\log [\eta] = \alpha \log \bar{M}_v + \log K$$

It gives linear relation eqn.

On compⁿ $y = mx + c$

So, from slope we can find out \bar{M}_v and intercept
 $c = \log K$

Paper Factory MNNIT

Chemistry
Chemical Bonding

2/8/18

Types of bonding : ionic and covalent

Lattices and unit cell (cubic only)

Symmetry & symn. elements , their applications in lattices and molecules.

Valence Bond Theory.

Shapes and Geometries of simple molecules.

Hybridisation.

Molecular Orbital Theory.

Band Theory. for conductors , semiconductors & insulators

Impurities in semiconductors.

Defects in ionic solids.

✓ Although there is no sharp boundary between ionic & covalent bond. It is convenient to study them separately. before we can discuss lattices and molecules around us. The ionic bond model is simplest to assume that a solid like NaCl is made of cations and anions resulting in a 3-D lattice as evidenced by x-ray diffraction experiments. and the following observations:

1. They are soluble in polar solvents.

— Lattice: repetition of similar pts in space.

2. Have high melting points.

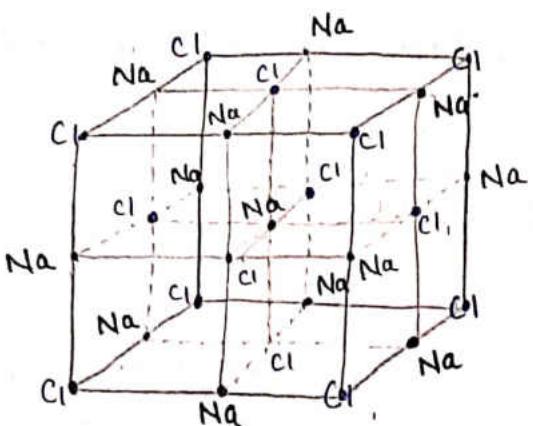
3. They conduct electricity in molten ^{state} and solutions. *

4. " are brittle in nature.

✓ In general , the conditions of ionic bond formation are one atom should have low ionisation energy , the other should have high electron affinity and the resulting lattice energy should be very high.

✓ X-ray shows that NaCl has a cubic lattice in which a cubic unit cell as shown in the figure exist in which the corners and face centers are occupied by

Cl atoms and edge center and body center are occupied by Na atoms.



NaCl crystallises (after being dissolved in ethanol) in octahedral-shaped crystals.

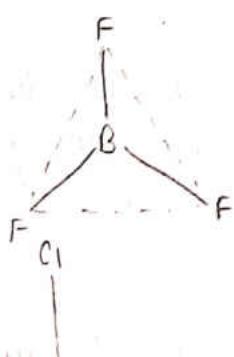
16/08/18

- Symmetry & Symmetry elements:

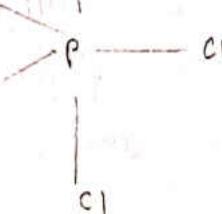
Symmetry: If a body can display more than one indistinguishable orientations after performing operations by any of the symmetry elements: axis of symmetry (line of symmetry), mirror plane of symmetry and point of symmetry (center of symmetry / center of inversion). then the body is said to have symmetry.

Every body contains C_1 axis which is given symbol E (identity elements). = Line of symmetry:

Ex- BF_3 .

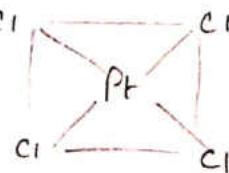


PCl_5



one C_3
three C_2

E

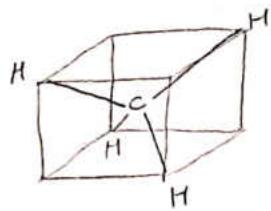


one C_4 .
four C_2 .

CH_4

One C_3
three C_2

Paper Factory MNNIT

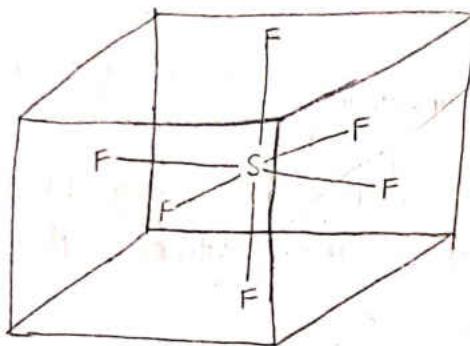


Three C_2 consider C at origin of x, y, z axis.

4 C_3 . E

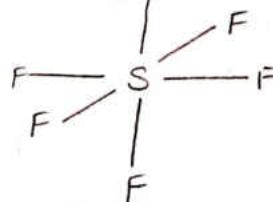
$C_3 \rightarrow$ triangle
$C_4 \rightarrow$ square
$C_2 \rightarrow$ lines.

SF_6



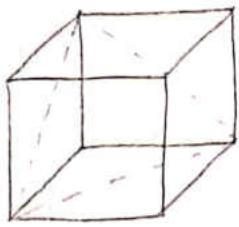
Three C_4

4. C_3 axis passes through opp. faces of octahedral.
FF, Six C_2 .

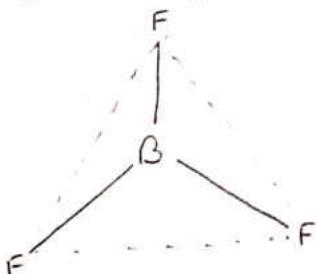


Three C_4

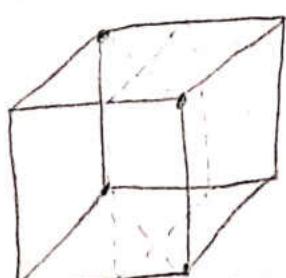
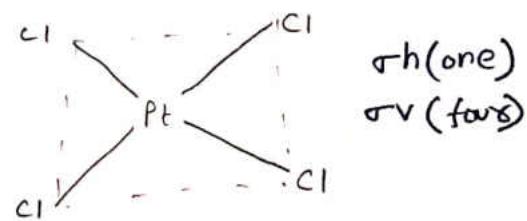
Four C_3
Six C_2



- Mirror plane of symmetry:
Symbol of mirror plane symmetry is σ

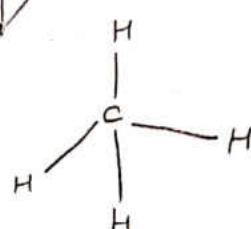


σ_h (one)
 σ_v (three)



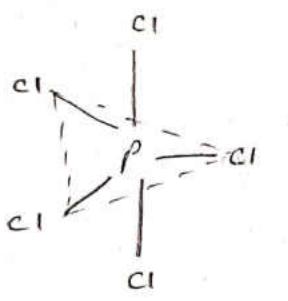
Rectangular plane (Plane in b/w two opp. faces)
(3)

Diagonal plane (Plane formed joining 2 opp. edges)
(6)

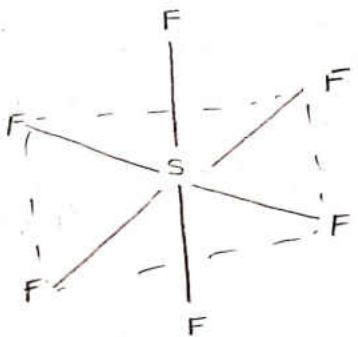


6 diagonal plane.

Paper Factory MNNIT



σ_h (one)
 σ_v (three)



σ_h (three)
 σ_d (six)
↳ dihedral
↳ bihexagonal.

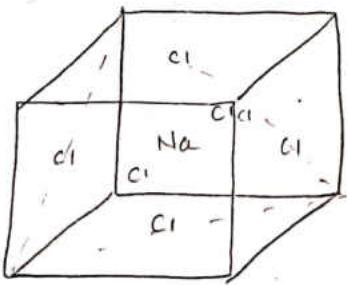
- Improper axis of symmetry:

$$S_n = C_n + \sigma_h$$

$S_2 = i$ (center of inversion) S_2 always counted in 1

Ques: In NaCl structure, if the atoms lie along 1 C_3 , 1 C_3 and 1 C_2 axis are removed from the lattice. then write the new formula of sodium chloride.

Soln



$1C_3$.
 $1C_4$.

1 Na⁺ and 2 Cl⁻
1 Na⁺ and 2 Cl⁻
1 Na⁺ and 2 Cl⁻

3

$6C_1$

$1C_3 \rightarrow$
 $1C_4$.

1 Na $\frac{2}{8} Cl$
1 Na $\frac{1}{2} \times 2 = 1 Cl$

$1C_2$

1 Na 1 Cl

1 Na $2 + \frac{1}{4} Cl$
2.25

3 Na 1.75 Cl

$$\begin{array}{r} 4.00 \\ - 2.25 \\ \hline 1.75 \end{array}$$

$$\frac{\frac{2}{1} + \frac{3}{4}}{8+3} = \frac{11}{4}$$

Na \cancel{Cl}
3 1.75

Hybridisation:

- ✓ Hybrid orbitals always make σ bond.
- ✓ They try to remain as far as possible from each other in 3-D space.
- ✓ The no. of hybrid orbitals formed is equal to the no. of atomic orbitals taking part in hybridisation.

hybridisation	No.	Geometry.
1p	2	—
1p ²	3	Y
1p ³	4	Y
clsp ²	4	X
1p ³ cl	5	X
1p ³ d ²	6	X
1p ³ d ³	7	X

Ques: On the basis of VBT, discuss shape & geometry of following

molecules
 SO_2 , SO_3 , H_2SO_4 , SO_4^{2-} , NH_3 , NH_4^+ , ClF_3 , HClO_4 , HClO_3 , HClO_2 ,
 HClO , XeF_2 , XeF_4 , XeF_6 , SF_4 , SF_6 .

i) HClO

$$\text{no. of hybrid orbitals of central atom} = \frac{1}{2}[V + M - C + A]$$

V = no. of valency e⁻ of cen. atom.

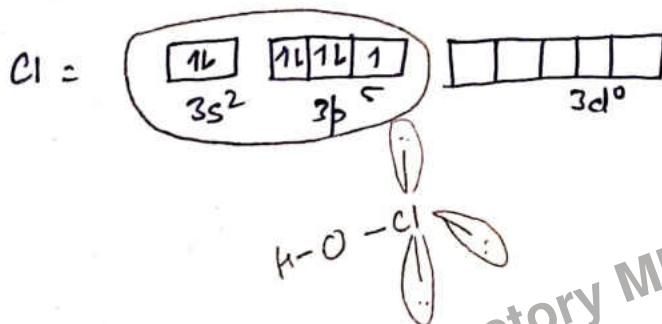
M = no. of monovalent atoms around central atom.

C = cationic charge (if any)

A = anionic " (")

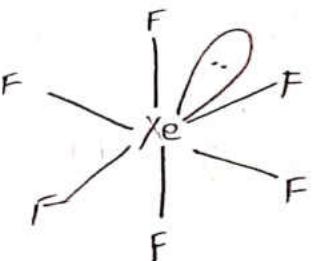
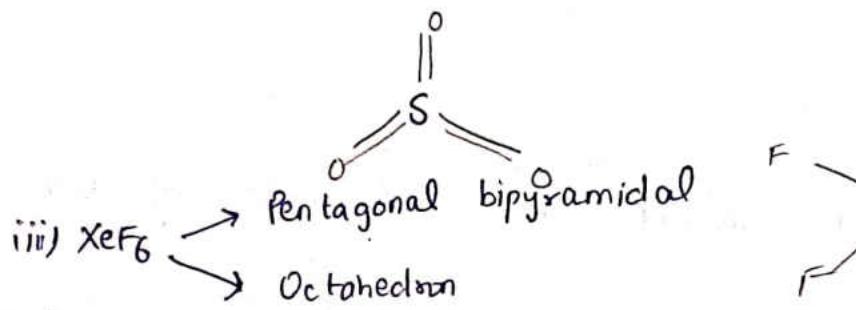
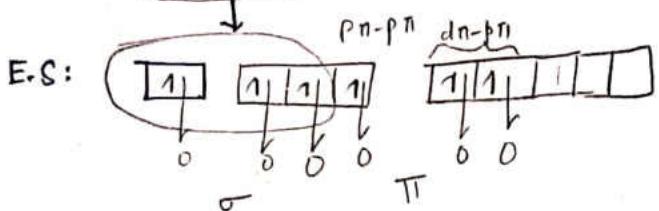
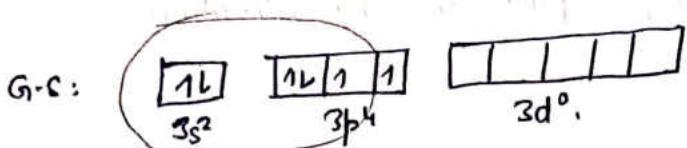
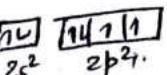
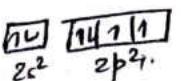
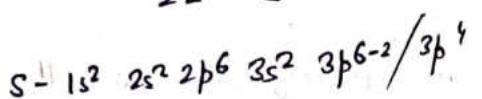
$$= \frac{1}{2}[7 + 1]$$

$$= 4 (\text{sp}^3)$$

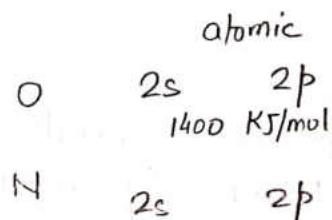
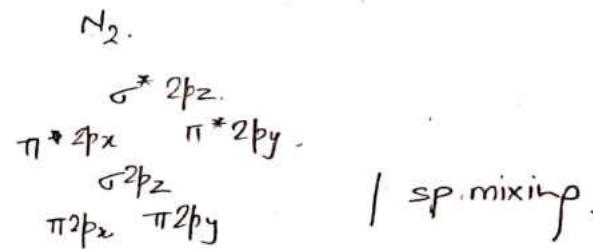
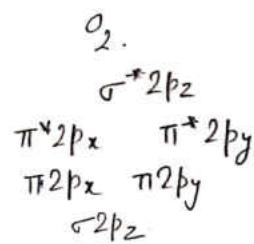


ii) SO_3 .

$$H = \frac{1}{2}[6-0] = 3 \cdot (s\beta^2)$$



- MOT (Molecular Orbital Theory):
 - Mulliken & Hund. form bonds unlike valence Bond Theory.
 - Overlapping results in formation of new orbitals called molecular orbitals.



In case of N, there is 400 KJ/mol repulsion in 2s & 2p orbitals due to low energy gap b/w 2s & 2p.

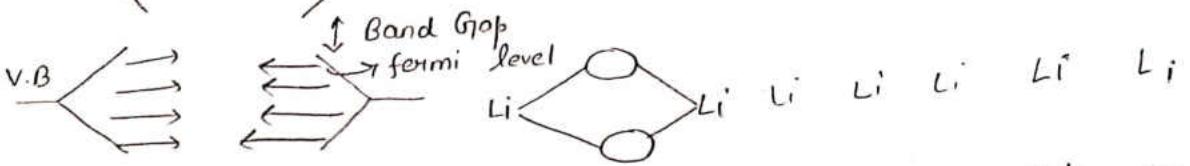
In such a case, energy distribution takes place, one orbital-energy gets lowered & as a result other orbital-energy gets higher value.

NO - I

$\begin{matrix} CO \\ CN \end{matrix} \rightarrow$ II

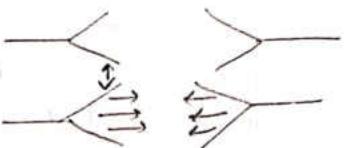
bond order calculated
stability of species

- Band Theory:
c.B closely spaced energy levels.

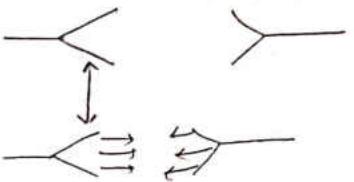


Based on amount of band gap, 3 substances are categorised,

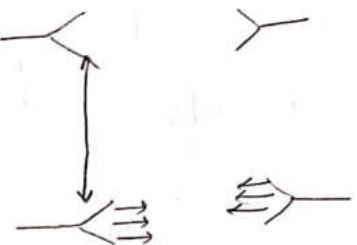
i) Conductors:



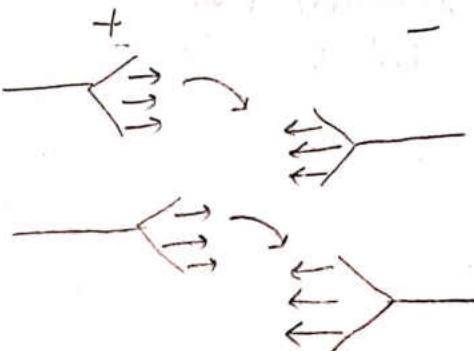
ii) Semiconductors:



iii) Insulators:



- Grey Sn on applying high pressure converts into conductor as white Sn. This wasn't explained by metallic bond theory.
- Thermal conduction can't be explained by band theory but can be explained by e⁻ sea model theory.
- Mechanism of conduction: and
- i) presence of holes in VB or presence of e⁻ in CB. acc^r to band theory



In conductors, after applying PD, VB & CB gets distorted acc^r to diag. and e⁻ in higher energy p.bands jump to lower energy p.bands. As e⁻ is increased in next p.band

Paper Factory MNMIT

energy gets increased and the process again starts to follow same pattern.

⇒ In case of insulators, there is no reason for e⁻s to jump to lower p. band because lower energy p. bands have no space to acquire extra e⁻s.

Attraction - energy gets lowered.

⇒ In case of semiconductors, a little heating or photoexcitation creates the situation.

⇒ Electrons in band having direction towards +ve electrode, due to attraction energy gets lowered.

⇒ In case of conductors bands are very close, so there is always holes in VB and electrons in CB.

The process of migration of e⁻ from higher to lower is continued till the external potential is maintained because the states from where electron move to the other level vacancy is created.

⇒ Top of valence band is Fermi level.

⇒ Electrical conduction is due to bands and thermal conduction is due electrons in σ or outermost orbital.

→ ~~n~~ n and p-type semiconductor:

n type

i) dope 15th group element in to 14th group element.

ii) Doping creates a new energy level which will have electrons.

The new energy level (impurity level) will lie close to conduction band.

iii) Electrons can now jump easily from impurity to CB

p type

i) dope 13th group element in to 14th group element.

ii) New energy level will lie close to valence band and be the new level is vacant.

iii) electrons jump from VB to vacant impurity and creates holes in VB.
Electric conduction takes place due to mechanism of conduction.

On applying ^{high} pressure, molecular density of semiconductor increases, band gap shrinks and hence transformation of semiconductor into conductor occurs.

Defects:

Defect is mainly due to environmental energy.

Two types in ionic solids—

- i) Stoichiometric $\xrightarrow{\text{Frenkel}}$ $\xrightarrow{\text{Schottky}}$
- ii) Non-stoichiometric.

Electrons trapped in crystal is F-center.

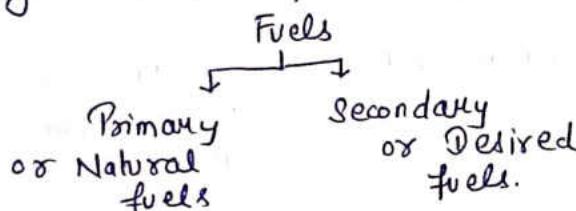
Chemistry

2/9/18

Chemistry of fuels & Combustion

1) Chemical fuels: These are substances which on proper burning give huge amount of heat economically. Energy is taken or stored from the sun by the photosynthesis or respiration process. Fuels have Carbon and Hydrogen as major components and N, O, & S, etc., as minor components. These are high energy contents (HEC).

- ✓ Major products are CO_2 and H_2O
- ✓ Fuels + $\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Heat}$
- ✓ Oxides of carbon, sulphur are stable.



- ✓ Secondary fuels are developed / found from natural fuels which have poor combustion rate and produce pollutant gases.
- ✓ Secondary fuels have good combustion rate and meet the cost as byproducts in their production.

- Characteristics of good fuel:

- ✓ Should have moderate ignition temp.
- ✓ " " negligible moisture content.
- ✓ " not have S, N, etc., polluting elements.
- ✓ " have moderate velocity of combustion
- ✓ " not have ashes.
- ✓ Mixed fuels ^{may} have high efficiency.
- ✓ Products of combustion shouldn't be hazardous to environment
- Calorific value: the amount of heat liberated when the unit mass of fuel is burned properly at normal / moderate velocity in presence of excess amount of atm. Oxygen

- Calorimeter:

Depending upon the type of fuels and their rate of combustion, calorimeter is of two types-

1. Bomb Calorimeter
2. Boy's Gas calorimeter.

✓ these devices condense back products to maintain room temp., so that rise of temp. can be measured.

✓ 2 types of calorific value-

- i) Higher calorific value (HCV) or (QCV) :- determined by calorimeter
- ii) Lower calorific value (LCV) or (NCV) :- value needed for work
(Latent heat can't be used for useful work)

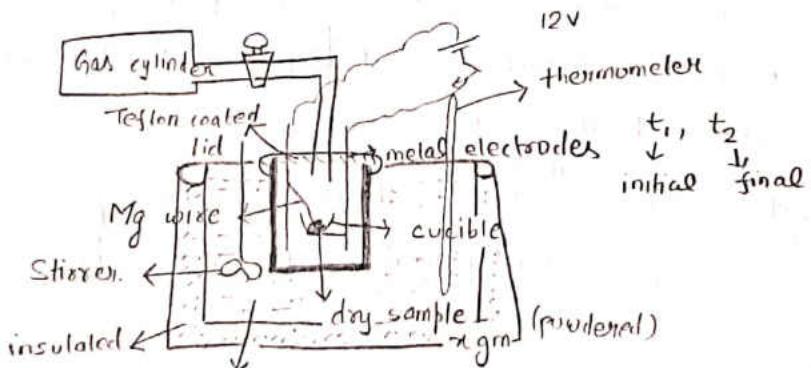
To determine LCV:

$$LCV = HCV - \text{Latent heat of steam}$$

$$= HCV - 0.09 \times H \times \frac{587}{1.07H} \text{ cal/mass.}$$

- Determination of HCV by bomb calorimeter:

✓ Bomb calorimeter determines the calorific value of solid & volatile liquids.



$W \text{ gm of water}$

$$HCV = \frac{(W + w)(t_2 - t_1)}{x} - (\text{fuel wire corr.} + \text{Acid conversion})$$

$\approx \text{water equivalent of calorimeter.}$

✓ 0.1 N HNO_3 is used to wash out ashes present in calorimeter.

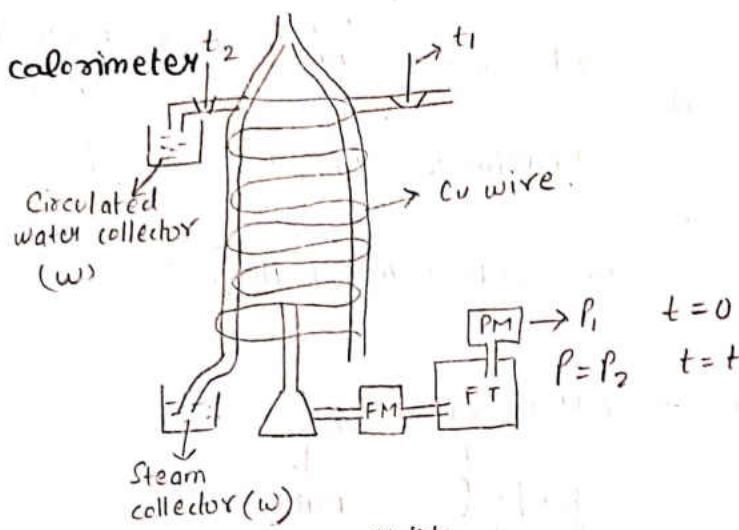
✓ Benzoic acid and naphthalene completely burn, and are

taken as ideal materials. These materials give ideal measurement.

Corrections -

- Fuse wire correction.
 - Heat loss "
 - Heat involved in conversion of $N \rightarrow NO_x$ & $S \rightarrow SO_x$
- ✓ Dickson method is used to determine ' t_c '.
- iv) Also, NO_x & SO_x react with steam to form HNO_3 and H_2SO_4 resp.
These reacn's are exothermic.

- Boy's Gas calorimeter



$$P = P_1 \quad t = 0 \\ P = P_2 \quad t = t$$

$$HCV = \frac{w(t_2 - t_1)}{V_t} \xrightarrow{\text{outlet temp.}} \text{inlet temp.}$$

Water collected during burning of gas in't Volume of gas burnt in time 't'

$$HCV = \frac{w(t_2 - t_1)}{V_t} \xrightarrow{\text{outlet temp.}} \text{inlet temp.}$$

Dulong's formula:

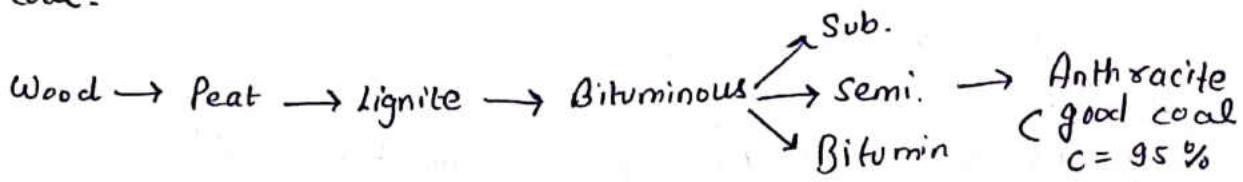
$$HCV \text{ of } C = 8080 \\ H = 34500 \\ S = 2240$$

Total hydrogen in the fuel.

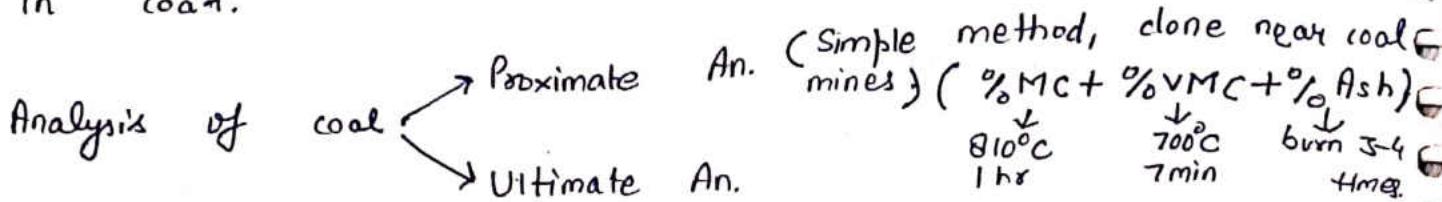
$$HCV = \frac{1}{100} [8080 C + 34500 \left(H - \frac{O}{8} \right) + 2240 S] \xrightarrow{\text{fixed hydrogen}} 6325 \text{ kJ/kg}$$

Solid fuel

i) Coal:



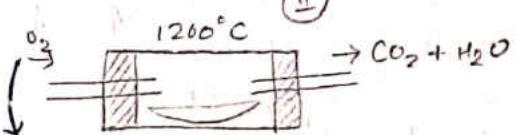
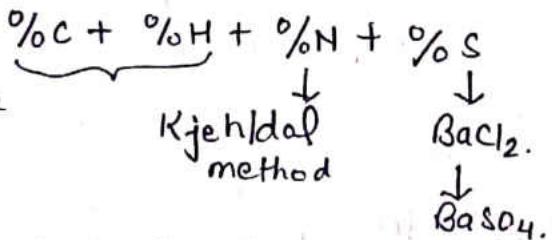
Anthracite can't be converted into coke because this type of coal has very less H content and for formation of coke, up to 14% of H is required in coal.



a) Proximate An. :

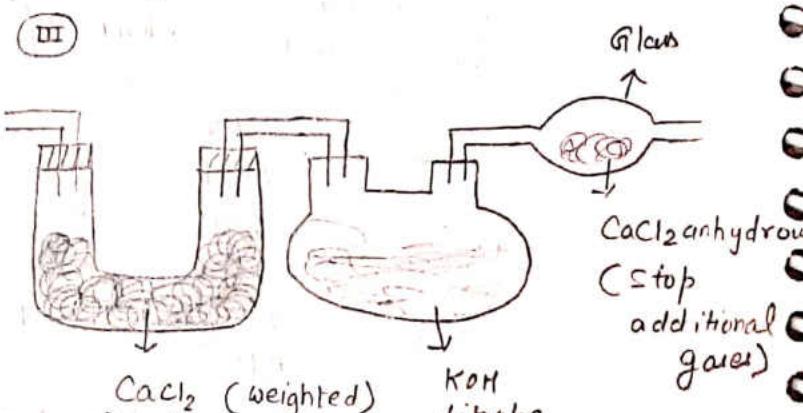
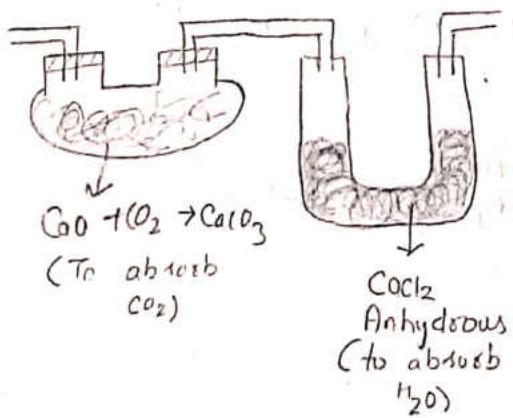
$$\%C = 100 - (MC + VMC + Ash)$$

b) Ultimate An. :



this oxygen mustn't contain any trace of moisture.

(I)



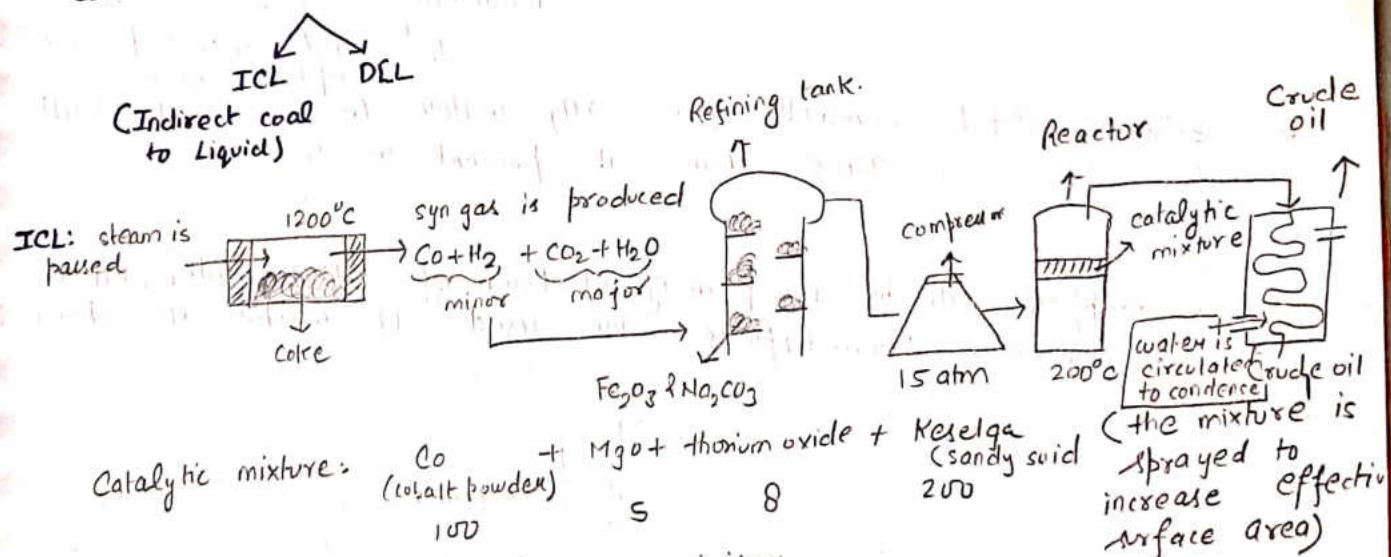
CaCl₂ (weighted)
Anhydrous
after the addition
of moisture, the
weight of tube ↑s
and hence we can
determine H₂O

- Carbonization of Coal:
High temp.
HTC LTC

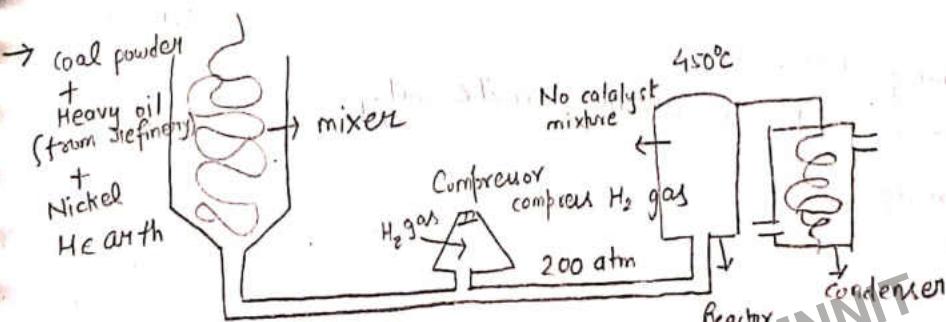
Coal having less S content & moisture b/w 10-14%. is suitable for formation of coke.

- ✓ Coal is burned upto 1000°C in limited supply of air.
- ✓ The process is carried out in Otto Halfmann reactor.
- ✓ By-products aren't wasted in this reactor.
- ✓ Good quality coke is produced in this process.
- ✓ Coal is burned upto $700^{\circ}\text{C} - 800^{\circ}\text{C}$.
- ✓ Process is carried out in Beehive reactor.
- ✓ By-products are wasted in this process.
- ✓ Bad quality coke is produced. Generally, domestic coke.

- Coal to Petroleum:



Crude oil so formed is very similar to crude oil obtain in crust but it is less viscous due to low molecular weight components.



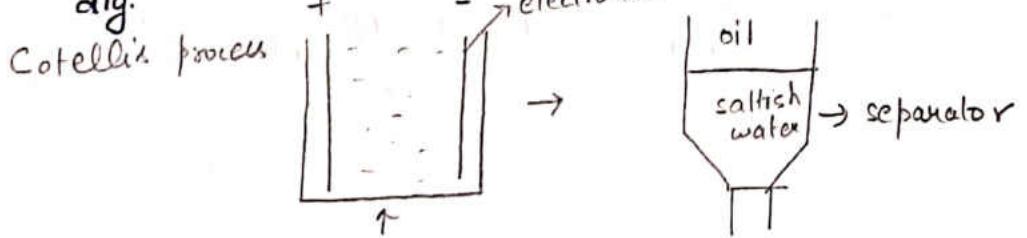
Reactions involved -

- i) $(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$ (alkanes)
- ii) $2nH_2 + nCO \rightarrow C_nH_{2n}$ (cycloalkanes) } 1 mole = main reacⁿ.
- iii) $2nH_2 + nCO \rightarrow C_nH_{2n-1}OH$ (alcohols)
- iv) $CO + H_2O \rightarrow CO_2 + H_2$ (water gas)
- v) $CO + CO \rightarrow CO_2 + C$
- vi) $YC + XM \rightarrow MC$ (Metals) (Metal carbide)

- Petroleum:

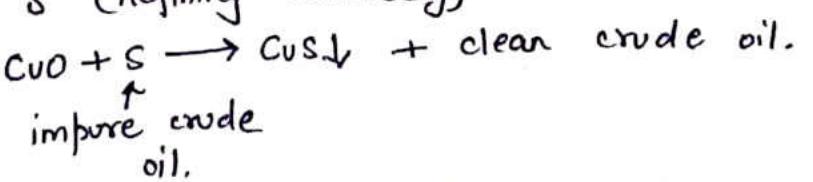
- ① Petroleum (rock oil) → are hydrocarbons
→ trapped in rocks.
→ 2 borewells are sucked (one in depth & one in moderate depth). to trap oil. extreme to exclude gases present in upper layer.
- ✓ extreme depth borewells use salty water to get oil. Salty water is less dense than oil present in rock.

- ② ✓ Oil trapped will be in form of emulsion of saltish water, oil & soil particles (negligible). Demulsifiers are used. It works as shown in dig.



This is used to destroy the layer of emulsion.

- ③ Removing of S (Refining basically)



④ fractional distillation

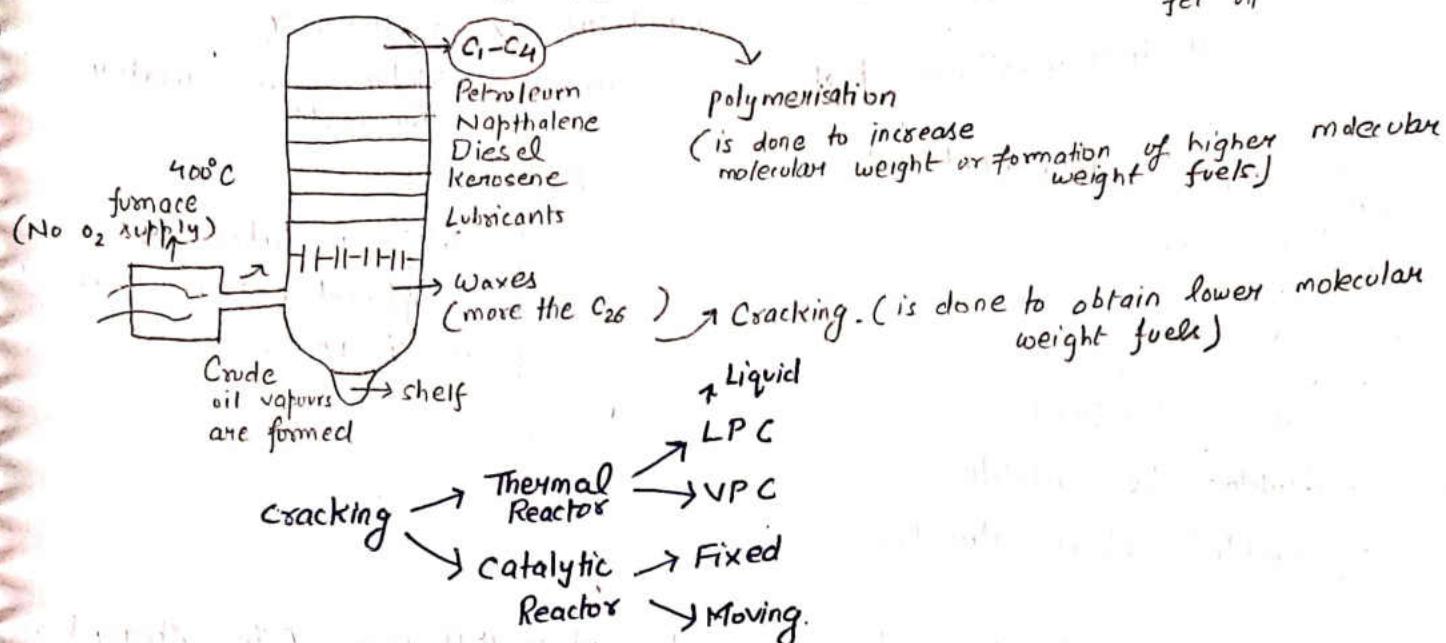
column height is diff for diff. crude oils (purity basically)

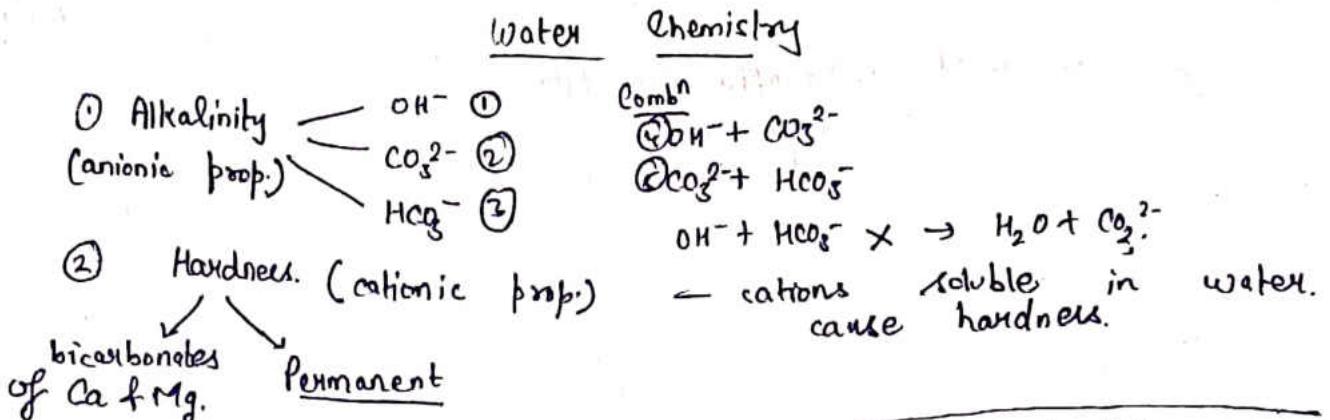
3 types are used - 1. Paraffin Base type

2. Asphaltic "

3. Mixed "

40% Gasoline, 20% Diesel, 6-7% jet oil





✓ treated not chemically but can be.

Primary Standard

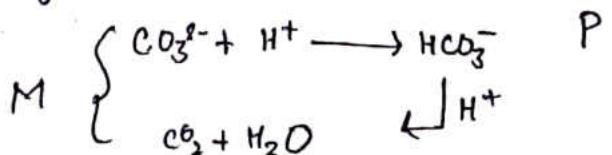
- shouldn't be volatile
- shouldn't absorb atm. O₂.

CaCO₃ is taken as standard. Its molecular wt is 100.

✓ Complete neutralisation doesn't give by phenolphthalein (for strong base)

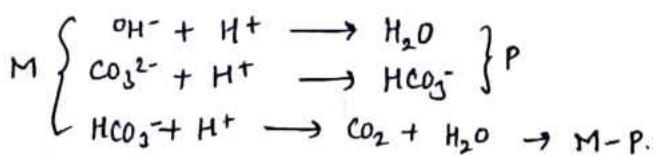
✓ In case of OH^- P = M

✓ " " " CO₃²⁻



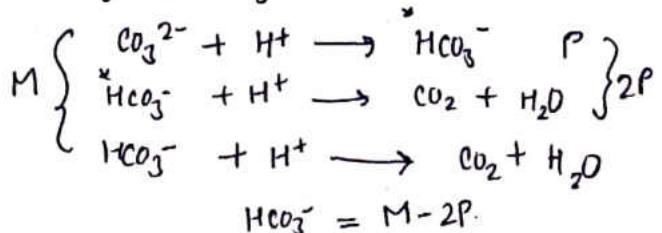
✓ In case of HCO₃⁻ $P = \frac{1}{2}M$ (not identified by phenolphthalein)

✓ OH⁻ & CO₃²⁻



$$\begin{aligned} \text{OH}^- &= M - 2(M-P) \\ &= 2P - M. \end{aligned}$$

✓ CO₃²⁻ & HCO₃⁻



Chemistry

Corrosion

- 1. Phenomenon
- 2. Theory & Mechanisms
- 3. Types of Corrosions
- 4. Factors affecting corrosion
- 5. Corrosion control or Prevention.

1. Phenomenon:

- ✓ Two things - metal and medium.
- ✓ Corrosion is surface phenomenon. It's not bulk reacⁿ.
- ✓ Heterogeneous reacⁿ ✓ 3 phases are involved. Electrochemical in nature.
- ✓ Corrosion depends on 3 things:-
 1. Rate of reaction
 2. Rate at which reactants & products diffuse away from each other.
 3. External factors (metal is medium)

3. Types of Corrosion:

10 common types of corrosion are:

i) General attack corrosion: (uniform attack corrosion): It is caused by a chemical or electrochemical reacⁿ that results in the deterioration of the entire exposed surface of the metal. It is considered as a safe form of corrosion due to the fact that it is predictable, manageable and often preventable.

ii) Localised corrosion: This targets one area of the metal structure. It is classified in 3 types-

a) Pitting: It is usually due to de-passivation of small area (leads to formation of a hole or cavity). This area becomes anodic, while part of remaining metal becomes

Electrochemical Series

Reaction (Oxidised form + ne⁻) → Reduced form

	$F_2(g) + 2e^-$	$2F^-$
	$Co^{3+} + e^-$	Co^{2+}
	$H_2O_2 + 2H^+ + 2e^-$	$2H_2O$
	$MnO_4^- + 8H^+ + 5e^-$	$Mn^{2+} + 4H_2O$
	$Au^{3+} + 3e^-$	$Au(s)$
	$Cl_2(g) + 2e^-$	$2Cl^-$
	$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$2Cr^{3+} + 7H_2O$
	$O_2(g) + 4H^+ + 4e^-$	$2H_2O$
	$MnO_2(s) + 4H^+ + 2e^-$	$Mn^{2+} + 2H_2O$
	$Br_2 + 2e^-$	$2Br^-$
	$NO_3^- + 4H^+ + 3e^-$	$NO(g) + 2H_2O$
	$2Hg^{2+} + 2e^-$	Hg_2^{2+}
	$Ag^+ + e^-$	$Ag(s)$
	$Fe^{3+} + e^-$	Fe^{2+}
	$O_2 + 2H^+ + 2e^-$	H_2O_2
	$I_2 + 2e^-$	$2I^-$
	$Cu^+ + e^-$	$2Cu(s)$
	$Cu^{2+} + 2e^-$	$Cu(s)$
	$AgCl + e^-$	$Ag(s) + Cl^-$
	$AgBr + e^-$	$Ag(s) + Br^-$
	$2H^+ + 2e^-$	$H_2(g)$
	$Pb^{2+} + 2e^-$	$Pb(s)$
	$Sn^{2+} + 2e^-$	$Sn(s)$
	$Ni^{2+} + 2e^-$	$Ni(s)$
	$Fe^{2+} + 2e^-$	$Fe(s)$
	$Cr^{3+} + 3e^-$	$Cr(s)$
	$Zn^{2+} + 2e^-$	$Zn(s)$
	$2H_2O + 2e^-$	$H_2 + 2OH^-(aq)$
	$Al^{3+} + 3e^- \rightarrow Al(s)$	-1.66
	$Mg^{2+} + 2e^- \rightarrow Mg(s)$	$+2.36$
	$Na^+ + e^- \rightarrow Na(s)$	-2.71
		→ $Ca^{2+} + 2e^- \rightarrow$
		$K^+ + e^- \rightarrow$
		$Li^+ + e^- \rightarrow$

Paper Factory MNM

cathodic, producing a localised galvanic reaction. It penetrates the metal and can lead to failure. It is often difficult to detect due to the fact that it is usually relatively small and may be covered by corrosion products.

- b) Crevice corrosion: It also occurs at specific location. It is associated with a stagnant micro-environment, like those found under gaskets, washers and clamps. Main reasons of this are acidic conditions and depletion of oxygen in a crevice.
- c) Filiform corrosion: Occurs under painted or plated surfaces when water breaches the coating. It spreads to cause structural weakness.

- iii) Galvanic corrosion: It occurs when 2 diff. metals are located together in a corrosive electrolyte. One metal becomes the anode and the other ^{the} cathode. The anode corrodes faster and the cathode deteriorates more slowly than it would otherwise.

Necessary conditions are:

- ✓ Electrochemically dissimilar metals must be present.
- ✓ Metals must be in electrical contact.
- ✓ Metals must be exposed to an electrolyte.

- iv) Environmental Cracking: Metals are affected from a combination of environmental conditions. Following types are
- ✓ Stress Corrosion Cracking (SCC)
 - ✓ Corrosion fatigue.
 - ✓ Hydrogen - induced cracking
 - ✓ Liquid metal embrittlement.

- v) Flow-Assisted Corrosion (FAC): It results when oxide layer (protective) on a metal surface is removed by wind or water.
- ✓ Erosion-assisted corrosion.

✓ Impingement.

✓ Cavitation.

vii) Intergranular corrosion: It is a chemical or electrochemical attack on the grain boundaries of a metal. It occurs due to impurities in the metal. Boundaries are more vulnerable than the bulk of the metal.

viii) De-Alloying: (Selective leaching): It is the selective corrosion of a specific element in an alloy. ex- de-alloying
→ de-zincification of unstabilized brass.

ix) Fretting corrosion: It occurs due to repeated wearing, weight or vibration on an uneven rough surface.

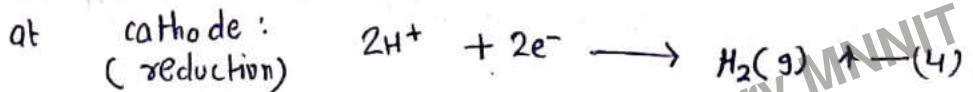
x) High-Temp. corrosion: Fuels used in gas turbines contain vanadium or sulphates can, during combustion, form comp. with a low melting point. These cpd's are very corrosive towards metal alloys normally resistant to high temp. and corrosion. It can also be caused by high temp. oxidation, sulfidation, and carbonization.

2. Theory & Mechanism:

✓ Moisture is necessary for corrosion.

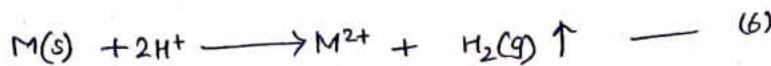
✓ Two types of mechanisms are derived -

i) By Hydrogen evolution: (when metal is immersed in dil. HCl)
Reactn: $M(s) + 2H_2O(l) \rightarrow M(OH)_2(s) + H_2(g) \quad (1)$



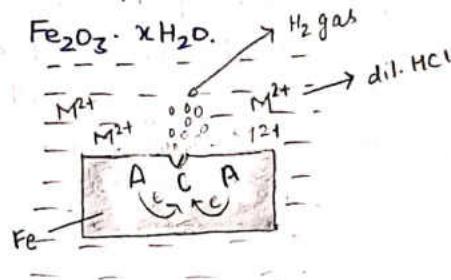
Paper Factory MNMIT

Overall,



In case of iron,

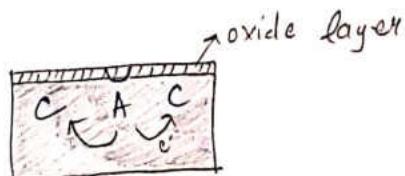
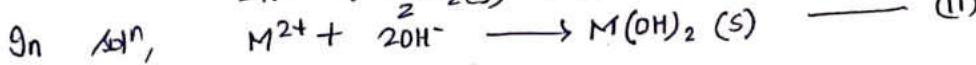
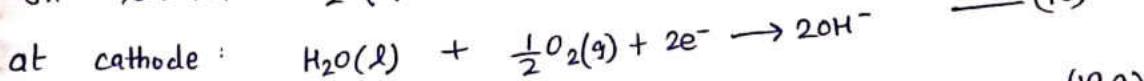
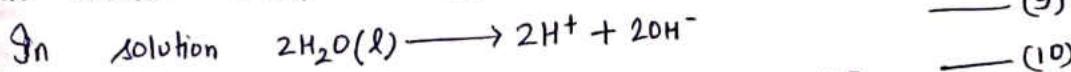
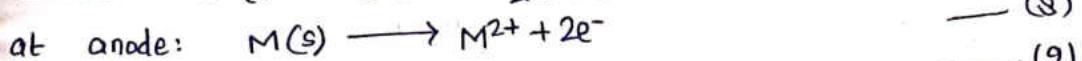
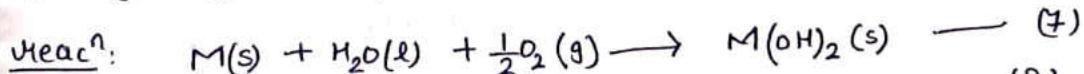
final product is



Factors

Anodic & Cathodic protection methods.

ii) By oxygen absorption:



3. a) Factors pertaining to Metal:

i) Position of metal in emf or galvanic series.

ii) Physical state of metal.

iii) Purity of metals.

iv) Surface characteristics.

v) Solubility of the salt of metal.

b) Factors pertaining to Medium:

i) influence of light.

ii) action of colloids.

iii) action of bacteria.

iv) Oxygen concentration.

- v) AC or DC Current.
vi) pH of the medium.
vii) temp., humidity, pollutants, SPMs
- diff. b/w emf & galvanic series.

a) i) Galvanic series → galvanic corrosion potential.

- ✓ reduction half reaction, H_2O production at O.I V states that below this every metal and alloy will oxidise.
- ✓ In this series, alloys are also included.

Pilling-Bedsworth rule:

- v) Solubility of salt is less, then it will restrict further corrosion at that place.
- ✓ Amphoteric metals corrode in basic medium.
- b) ii) colloids decrease the rate of corrosion.