

NAME Rukhsana Wajahath ROLL NO. 06

STANDARD SUBJECT chemistry

SCHOOL / COLLEGE CELL NO.

INDEX

Weekly Schedule for the Subject

Subject

<i>Day</i>	<i>Mon</i>	<i>Tue</i>	<i>Wed</i>	<i>Thu</i>	<i>Fri</i>	<i>Sat</i>
<i>Period</i>				13 9x		

21/12/20

UNIT-II

Water chemistry

* Water is the most important element required by Human beings.

A majority of human body 60% to 70% comprises of water. Moreover it is widely used in industries such as: paper industry, textile industry, cooling Boiler feed, laundries, chemical industry.

Sources of water:

- 1) Rain water: It is the purest form of natural water. However due to the suspended particles and other gases present in atmosphere it gets polluted.
- 2) River water: Rivers are formed by rain and during its flow over the surface of land it dissolves the minerals of soil.
- 3) Lake water: It contains constant chemical composition. The mineral but high quantity of organic matter.
- 4) sea water: It is the most impure form of natural water containing high amount of salt.

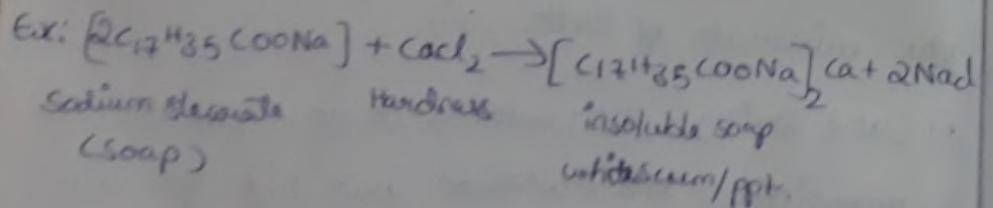
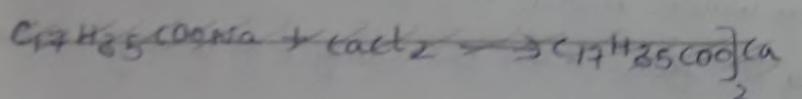
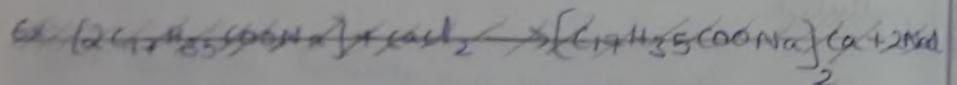
5) Underground water: It contains more of dissolved salt and is of high organic purity.

Hardness of water:

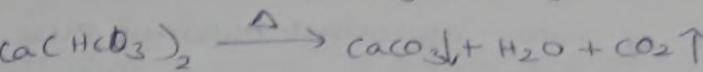
The water which does not produce lather with soap is called hard water.

The hardness of water is caused due to the presence of dissolved salts of calcium, magnesium and other heavy metals.

When hard water is treated with soap it does not produce lather but instead forms a white scum/ppt due to the formation of insoluble soap of Ca and Mg.



It can be destroyed by boiling.



2) Permanent Hardness: [Non-carbonate hardness]

It is caused due to the presence of chlorides and sulphates of Ca, Mg and other heavy metals.

It cannot be removed by boiling.

Therefore, it requires only chemical treatment to remove permanent hardness.

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

→ Units of Hardness:

The concentration of hardness is expressed in terms of equivalent amount of CaCO_3 as the molecular weight of $\text{CaCO}_3 = 100$ and the equivalent weight of $\text{CaCO}_3 = 50$.

moreover, it is the insoluble salt that can be precipitated in water treatment.

Types of Hardness:

1) Temporary hardness: [carbonate hardness]

It is caused due to the presence of dissolved bicarbonates of Ca, Mg and other heavy metals.

1) Part per million: (ppm) It is the number of parts of CaCO_3 equivalent hardness present in 10^6 parts of water.

2) milligram per litre: (mg/L) It is the number of milligrams of CaCO_3 equivalent hardness present in one litre of water.

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

3) Degree Clark: ($^{\circ}\text{Cl}$) It is the number of parts of CaCO_3 equivalent hardness present in 70,000 (gallon) parts of water.

$$1 \text{ ppm} = 0.07 \text{ }^{\circ}\text{Cl}$$

4) Degree French: ($^{\circ}\text{Fr}$) It is the number of parts of CaCO_3 equivalent hardness present in 10^5 parts of water.

$$1 \text{ ppm} = 0.1 \text{ }^{\circ}\text{Fr}$$

5) Milli equivalent per litre: (meq/L) It is the number of milli equivalence of CaCO_3 hardness present in 1 litre of water.

$$1 \text{ ppm} = 0.02 \text{ meq/L}$$

Relation b/w the units of hardness is:

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1 \text{ Fr} = 0.07 \text{ }^{\circ}\text{Cl} = 0.02 \text{ meq/L}$$

*Numericals:

① calculate the hardness caused by 168 mg/L of magnesium carbonate (MgCO_3) salt.

$$\begin{aligned} \text{Sol: Hardness} &= \frac{\text{amt of given salt}}{\text{mol. wt.}} \times 100 \\ &= 168 \times \frac{100}{84} \\ &= 200 \text{ mg/L} \\ &= 200 \text{ ppm.} \end{aligned}$$

② calculate the hardness present in a water sample containing 13.6 mg/L of CaSO_4 and 7.3 mg/L of $\text{Mg}(\text{HCO}_3)_2$.

$$\begin{aligned} \text{Sol: Temporary hardness caused by } \text{Mg}(\text{HCO}_3)_2 \\ \text{Mg}(\text{HCO}_3) &= 7.3 \times \frac{100}{146} = 5 \text{ mg/L} \\ &= 5 \text{ ppm} \end{aligned}$$

permanent hardness is caused due to

$$\text{CaSO}_4 = 13.6 \times \frac{100}{136} = 10 \text{ mg/L} = 10 \text{ ppm}$$

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

$$= 5 + 10 = 15 \text{ ppm}$$

③ calculate the total hardness of 1000 litre of a sample of water containing 16.2 mg/L of $\text{Ca}(\text{HCO}_3)_2$, 11.1 mg/L of CaCl_2 , 60mg/L of MgSO_4 and 19 mg/L of MgCl_2

Sol: Temporary hardness is caused by

$$\text{Ca}(\text{HCO}_3)_2 = 16.2 \times \frac{100}{162} = 10 \text{ mg/L}$$

$$= 10 \text{ ppm}$$

permanent hardness is caused by to

CaCl_2 ,	MgSO_4 ,	MgCl_2
$= \frac{11.1 \times 100}{111}$	$= \frac{60 \times 100}{120}$	$= \frac{19 \times 100}{95}$
$= 10 \text{ mg/L}$	$= 50 \text{ mg/L}$	$= 20 \text{ mg/L}$
$= 10 \text{ ppm}$	$= 50 \text{ ppm}$	$= 20 \text{ ppm}$

$$\begin{aligned}\text{Total hardness} &= \text{Temporary hardness} + \text{permanent hardness} \\ &= 10 + 10 + 50 + 20 \\ &= 90 \text{ ppm}\end{aligned}$$

for 1 litre hardness = 90 ppm

$$\therefore \text{for 1000 litres hardness} = \frac{90 \times 1000}{1000}$$

$$= 90,000 \text{ ppm}$$

④ 1 litre of water from an underground reservoir in Tirupati town in A.P showed the following analysis for contents:

$$\begin{aligned}\text{Mg}(\text{HCO}_3)_2 &= 42 \text{ mg}, \quad \text{Ca}(\text{HCO}_3)_2 = 146 \text{ mg}, \\ \text{CaCl}_2 &= 71 \text{ mg}, \quad \text{NaOH} = 40 \text{ mg}, \quad \text{MgSO}_4 = 48 \text{ mg}, \\ \text{organic impurities} &= 100 \text{ mg}\end{aligned}$$

calculate temporary & permanent hardness of the sample of 10,000 lit. of water.

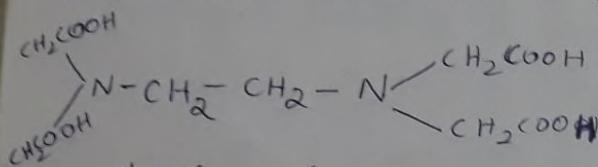
Sol:

* Determination of hardness by EDTA method : ^(Imp)

The hardness of water is usually measured as concentration of Ca^{+2} and Mg^{+2} ions only.

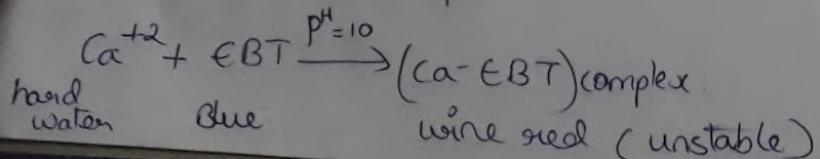
Its determination by EDTA involves complexometric titrations.

EDTA is ethylene diamine tetra acetic acid which is available as its disodium salt obtained in high purity state and can be used as standard solution. The EDTA solution is a valuable titrant because the reagent combines with metal ions in 1:1 ratio.

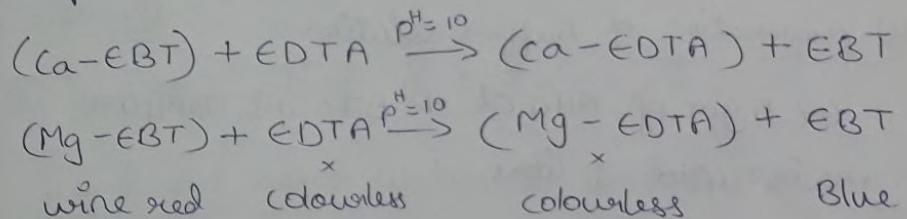


Structure of EDTA

In order to determine the equivalence point, triphenylmethane black-T (EBT) indicator is used. EBT is blue in colour and forms the ~~weak~~^{weak} unstable wine red complexes with Ca^{+2} and Mg^{+2} metal ions. As EBT functions in $\text{pH}=10$ the hard water to which it is added is buffered by using $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$.



During the course of titration against EDTA solution first the free Ca^{+2} and Mg^{+2} ions combine with EDTA to give stable colourless (M-EDTA) complex (where M is Ca or Mg). After all the free ions are consumed the next drop of EDTA displays EBT from (M-EBT) complex. There by releasing free EBT. Hence at the end point the colour changes from wine-red to blue. The order of stability of complexes $\text{Ca-EDTA} > \text{Mg-EDTA} > \text{Mg-EBT}$



This gives total hardness present in water.

To estimate permanent hardness, the temporary hardness is removed by boiling. The ~~stock~~ solution is filtered to remove the precipitate and then titrated with EDTA.

Temporary hardness is calculated by subtracting permanent hardness from total hardness.

* Preparation of solutions:

1) Preparation of standard hard water -

1gm of CaCO_3 + HCl made up to 1L with distilled water.

2) Preparation of EDTA solution -

4gm of EDTA Crystals made upto 1L

3) Preparation of indicator -

0.5gm of EBT in 100 ml alcohol

4) Preparation of buffer solution -

67.5 gm of NH_4Cl + 570 ml NH_4OH
made upto 1 litre.

* Procedure:

1) Standardization of EDTA (V_1 , ml)

20ml of standard hard water + Buffer +
2-3 drops of EBT titrate against EDTA
wine-red \rightarrow blue

2) Determination of total hardness (V_2 , ml)

20ml of sample water + buffer + 2-3 drops
of EBT titrate against EDTA
wine-red \rightarrow blue

③ Determination of permanent hardness (V_3 , ml)

100ml of sample water is boiled to $\frac{1}{4}$ th its original volume to remove temporary hardness. It is then filtered to remove the ppt and the filtrate is made upto 100ml with distilled water.

20ml of boiled water + buffer + 2-3 drops EBT

titrate against EDTA till wine-red \rightarrow blue.

* Calculations:

① Standardization of EDTA (V_1 , ml)

20ml std hard water = V_1 , ml EDTA

$20 \times 1 \text{ mg CaCO}_3 = V_1 \text{ ml EDTA}$

$\frac{20 \times 1 \text{ mg CaCO}_3}{V_1} = 1 \text{ ml EDTA}$

$$1 \text{ ml EDTA} = \frac{20}{V_1} \text{ mg CaCO}_3$$

② Determination of total hardness (V_2 , ml)

20ml sample water = V_2 , ml EDTA

$= V_2 \times \frac{20}{V_1} \text{ mg CaCO}_3$

$$\text{for 1 litre (1000 ml)} = 1000 \times \frac{V_2 \times 20}{V_1} \times \frac{1}{20}$$

$$= 1000 \times \frac{V_2}{V_1} \text{ mg/L}$$

$$\therefore \text{Total hardness} = 1000 \times \frac{V_2}{V_1} \text{ ppm}$$

③ determination of permanent hardness (mg/ml)

$$20 \text{ ml boiled water} = V_3 \text{ ml EDTA}$$

$$= \frac{V_3}{V_1} \times \frac{20}{20} \text{ mg CaCO}_3$$

$$\text{for 1 litre (1000 ml)} = 1000 \times V_3 \times \frac{20}{V_1} \times \frac{1}{20}$$

$$= 1000 \times \frac{V_3}{V_1} \text{ mg/L}$$

$$\therefore \text{permanent hardness} = 1000 \times \frac{V_3}{V_1} \text{ ppm}$$

④ determination of temporary hardness

$$\begin{aligned}\text{Temporary Hardness} &= \text{Total hardness} - \text{permanent Hardness} \\ &= 1000 \times \frac{V_2}{V_1} - 1000 \times \frac{V_3}{V_1} \\ &= 1000 \times \frac{(V_2 - V_3)}{V_1} \text{ ppm}\end{aligned}$$

$$\therefore \text{Temporary hardness} = 1000 \times \frac{(V_2 - V_3)}{V_1} \text{ ppm.}$$

* Numericals:

- ① A standard hard water contains 15 gm of CaCO_3 in 1 litre of water. 20 ml of this solution required 25 ml of EDTA during titration. 100 ml of sample water required 18 ml of EDTA solution. The sample water after boiling and cooling and filtering required 12 ml of EDTA. Estimate the types of hardness present?

sd:⇒ Standardization of EDTA :

$$\begin{aligned}25 \text{ ml of EDTA} - 20 \text{ ml std. hard water} \\ = 20 \times 15 \text{ mg CaCO}_3 \quad 15 \text{ g} \rightarrow 12 \\ ? \rightarrow 1 \text{ ml} \\ = 300 \text{ mg CaCO}_3\end{aligned}$$

$$1 \text{ ml EDTA} = \frac{300}{25} = 12 \text{ mg CaCO}_3$$

⇒ Total hardness ??

$$\begin{aligned}100 \text{ ml sample} &= 18 \text{ ml EDTA} \\ &= 18 \times 12 \text{ mg CaCO}_3 \\ &= 216 \text{ mg CaCO}_3\end{aligned}$$

$$\begin{aligned}\text{for 1 litre sample water} &= \frac{216}{100} \times 1000 \\ &= 2160 \text{ mg CaCO}_3 \\ &= 2160 \text{ mg/L}\end{aligned}$$

$$\therefore \text{Total hardness} = 2160 \text{ ppm.}$$

Permanent hardness:

$$\begin{aligned}100 \text{ ml of boiled water} &= 12 \text{ ml EDTA} \\ &= 12 \times 12 \text{ mg CaCO}_3 \\ &= 144 \text{ mg CaCO}_3\end{aligned}$$

$$\begin{aligned}\text{for 1 litre boiled water} &= \frac{144}{100} \times 1000 \\ &= 1440 \text{ mg/L}\end{aligned}$$

$$\therefore \text{permanent hardness} = 1440 \text{ ppm.}$$

Temporary hardness:

Total hardness - ~~permanent~~ permanent hardness

$$= 2160 - 1440$$

$$= 720 \text{ ppm.}$$

$$\therefore \text{Temporary hardness} = 720 \text{ ppm.}$$

② 50 ml of standard hard water contains 1 mg of CaCO_3 per ml. It consumes 25 ml of EDTA. 50 ml of sample water consumes 25 ml of same EDTA solution using EBT indicator. Calculate the total hardness present in sample water?

Sol: Standardization of EDTA:

$$\begin{aligned}25 \text{ ml of EDTA} &= 50 \text{ ml std. hard water} \\ &= 50 \times 1 \text{ mg CaCO}_3 \\ &= 50 \text{ mg CaCO}_3\end{aligned}$$

$$1 \text{ ml EDTA} = \frac{50 \times 1}{25} = 2 \text{ mg}$$

$$1 \text{ ml EDTA} = 2 \text{ mg CaCO}_3$$

Total hardness:

$$\begin{aligned}50 \text{ ml sample water} &= 25 \text{ ml EDTA} \\ &= 25 \times 2 \text{ mg CaCO}_3 \\ &= 50 \text{ mg CaCO}_3\end{aligned}$$

$$\text{for 1 litre (1000 ml)} = \frac{50 \times 1000}{50} = 1000 \text{ mg/L}$$

$$\text{Total hardness} = 1000 \text{ ppm}$$

③ 250 ml of hard water required 17 ml of 0.025 M EDTA solution calculate the total hardness in the water sample given

$$\text{Sol: } \frac{M_{\text{sample}}}{M_{\text{water}}} = \frac{M_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{sample}} \times V_{\text{water}}}$$

$$= \frac{0.025 \times 17}{250} = 0.0017 \text{ M}$$

$$\text{wt of } \text{CaCO}_3 \text{ eq} = M \times \text{mol. wt}$$

$$= 0.0017 \times 100$$

$$= 0.17 \text{ gm/L}$$

$$= 0.17 \times 1000 \text{ mg/L}$$

$$= 170 \text{ mg/L}$$

$$1 \text{ g} = 1000 \text{ mg}$$

→ Total hardness:

$$\therefore \text{Total hardness} = 170 \text{ ppm}$$

④ 250 ml of hard water was boiled, filtered and made upto the mark ~~with~~ with distilled water. It required 3 ml of $\frac{N}{50}$ EDTA solution. Estimate the type of hardness present?

$$\text{Sol: } \frac{N_{\text{boiled}}}{N_{\text{water}}} = \frac{N_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{Boiled}} \times V_{\text{water}}}$$

$$\frac{N}{50} = \frac{1}{50} N$$

$$= \frac{0.02 \times 3}{250} = 0.00024 \text{ N}$$

$$\frac{1}{50} = 0.02$$

$$\frac{N}{50} = \frac{1}{50} N$$

$$\text{wt of } \text{CaCO}_3 \text{ eq} = N \times \text{eq. wt}$$

$$= 0.00024 \times 50$$

$$= 0.012 \text{ gm/L}$$

$$= 0.012 \times 1000 \text{ mg/L}$$

$$= 12 \text{ mg/L}$$

$$1 \text{ g} = 1000 \text{ mg}$$

$$\therefore \text{permanent hardness} = 12 \text{ ppm}.$$

* Alkalinity of water:

Alkalinity is the measure of ability of water to neutralise the acids. It is defined as the total content of those substances which cause an increase in hydroxide concentration upon dissociation / due to hydrolysis.

The Alkalinity of water is caused due to presence of

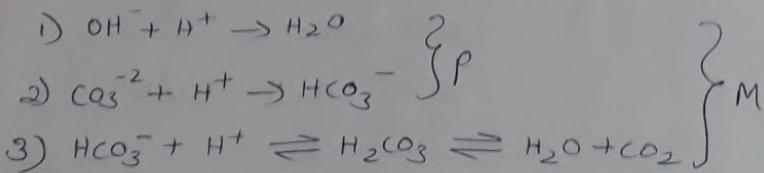
① caustic alkalinity - OH^- , CO_3^{2-} ions

② Bicarbonate alkalinity - HCO_3^- ions

③ But all the three ions can never exists together because



The alkalinity in water is estimated by titrating against a standard acid using phenolphthalein and methyl orange as indicators. Based on the following reactions,



The titration against the standard acid upto [P] end point marks completion of reactions ① & ② that is complete neutralization of OH^- ions and half of CO_3^{2-} whereas

titrations upto [M] end point corresponds to completion of reactions ① ② ③ that is complete neutralization of OH^- , HCO_3^- , CO_3^{2-}

Procedure:

100 ml of sample water is taken in a ~~conical~~ conical flask and 2-3 drops of phenolphthalein indicator is ~~not~~ added. It is titrated against $\frac{N}{50}$ HCl or H_2SO_4 solution till the pink colour disappears (V_1 ml). Then to the same solution methyl orange indicator is added and the titrations are continued till the colour changes

to red (V_2 ml).

* Calculations:

① Carbonates (CO_3^{2-})

$$N_{\text{CO}_3^{2-}} = \frac{N_{\text{HCl}} \times V_{\text{HCl}}}{V_{\text{CO}_3^{2-}}}$$

$$\text{wt of } \text{CO}_3^{2-} = N \times \text{eq. wt.}$$

$$\begin{aligned} \text{wt of } \text{CaCO}_3 \text{ eq.} &= \text{wt of } \text{CO}_3^{2-} \times \frac{50}{30} \\ &= a \text{ gm/L} \\ &= a \text{ gm/L} \times 1000 \\ &= y \text{ mg/L} \\ &= y \text{ ppm.} \end{aligned}$$

② Bicarbonates (HCO_3^-)

$$N_{\text{HCO}_3^-} = \frac{N_{\text{HCl}} \times V_{\text{HCl}}}{V_{\text{HCO}_3^-}}$$

$$\text{wt of } \text{HCO}_3^- = N \times \text{eq. wt.}$$

$$\begin{aligned} \text{wt of } \text{CaCO}_3 \text{ eq.} &= \text{wt of } \text{HCO}_3^- \times \frac{50}{61} \\ &= a \text{ gm/L} \\ &= a \text{ gm/L} \times 1000 \end{aligned}$$

$$= b \text{ mg/L}$$

$$= b \text{ ppm.}$$

③ Hydroxides (OH^-)

$$N_{\text{OH}^-} = \frac{N_{\text{HCl}} \times V_{\text{HCl}}}{V_{\text{OH}^-}}$$

$$\text{wt of } \text{OH}^- = N \times \text{eq. wt}$$

$$\text{wt of } \text{CaCO}_3 \text{ eq.} = \text{wt of } \text{OH}^- \times \frac{50}{17}$$

$$= m \text{ gm/L}$$

$$= m \text{ gm/L} \times 1000$$

$$= n \text{ mg/L}$$

$$= n \text{ ppm.}$$

* Results of titrations:

S.No	-	OH^-	CO_3^{2-}	HCO_3^-
(i)	$p=0$	0	0	M
(ii)	$p=M$	$p \text{ or } M$	0	0
(iii)	$p=\frac{1}{2}M$	0	$2p$	0
(iv)	$p > \frac{1}{2}M$	$M-2(M-p)$ $= 2p-M$	$2(M-p)$	0
(v)	$p < \frac{1}{2}M$	0	$2p$	$M-2p$

1) When $p=0$ Alkalinity is only due to HCO_3^- ions.

2) When $p=M$ Alkalinity is only due to OH^- ions.

3) When $p=\frac{1}{2}M$ then only CO_3^{2-} ions are present as Half of CO_3^{2-} neutralization is with Phenolphthalein and complete neutralization is with methyl orange. Therefore, Alkalinity due to $\text{CO}_3^{2-} = 2p$

4) When $p < \frac{1}{2}M$, both CO_3^{2-} & HCO_3^- ions are present. Alkalinity due to CO_3^{2-} is $2p$ and alkalinity due to HCO_3^- is $(M-2p)$.

5) When $p > \frac{1}{2}M$ then OH^- and CO_3^{2-} ions are present alkalinity due to CO_3^{2-} is $2(M-p)$ & alkalinity due to OH^- is $2p-M$.

→ (Numericals)

* Numericals:

① 50 ml of sample water required 5 ml of $\frac{N}{50}$ HCl using methyl orange indicator but did not give any colour with phenolphthalein. Estimate the alkalinity present?

Sol: As $p=0$ alkalinity is due to HCO_3^- ions.

$$\text{NHCO}_3^- = \frac{\text{NHCL} \times \text{VHCL}}{\text{VHCO}_3^-} = \frac{0.02 \times 5}{50} = 0.002$$

$$\text{wt of } \text{HCO}_3^- = \text{NHCO}_3^- \times \text{eq. wt}$$

$$= 0.002 \times 61 = 0.122$$

$$\text{wt of } \text{CaCO}_3 \text{ eq.} = \text{wt of } \text{HCO}_3^- \times \frac{50}{61}$$

$$= \frac{0.122 \times 60}{61} = 0.1 \text{ gm/L}$$

$$= 0.1 \text{ gm/L} \times 100$$

$$= 100 \text{ mg/L}$$

Alkalinity due to $\text{HCO}_3^- = 100 \text{ ppm.}$

② 100 ml of sample water required 4 ml of $\frac{N}{50}$ HCl solution, upto [P] end was required for further titration upto [M] end point. determine the type of alkalinity.

Sol: $P = 4 \text{ mL}$

$$M = 16 + 4 = 20 \text{ mL}$$

$$P = \frac{1}{2} M$$

$$\text{here } P < \frac{1}{2} M$$

As $P < \frac{1}{2} M$ alkalinity is due to HCO_3^- and $\text{CO}_3^{2-} = 2P = 2 \times 4 = 8 \text{ mL}$

$$M - 2P = 20 - 8 \text{ mL} = 12 \text{ mL}$$

$$\text{NCO}_3^{2-} = \frac{\text{NHCL} \times \text{VHCL}}{\text{VCO}_3^-} = \frac{0.02 \times 8}{100} = 0.0016$$

$$\text{wt of } \text{CO}_3^{2-} = \text{NCO}_3^{2-} \times \text{eq. wt} = 0.0016 \times 30 \\ = 0.048$$

$$\text{wt of } \text{CaCO}_3 = \text{wt of } \text{CO}_3^{2-} \times \frac{50}{30}$$

$$= 0.048 \times \frac{50}{30} = 0.08 \text{ gm/L} \times \frac{1000}{1000}$$

$$= 80 \text{ mg/L}$$

$$= 80 \text{ ppm.}$$

$$\text{NHCO}_3^- = \frac{\text{N HCl} \times V_{\text{HCl}}}{V_{\text{HCO}_3^-}} = \frac{0.02 \times 12}{100}$$

$$= 0.0024$$

$$\text{wt of HCO}_3^- = \text{NHCO}_3^- \times \text{eq. wt}$$

$$= 0.0024 \times 61$$

$$= 0.1464$$

$$\text{wt of CaCO}_3 \text{ eq} = \text{wt of HCO}_3^- \times \frac{50}{61}$$

$$= 0.1464 \times \frac{50}{61}$$

$$= 0.12 \text{ gm/L} \times 1000$$

$$= 120 \text{ mg/L}$$

$$= 120 \text{ ppm}$$

Alkalinity due to $\text{CO}_3^{2-} = 80 \text{ ppm}$

Alkalinity due to $\text{HCO}_3^- = 120 \text{ ppm}$.

Total Alkalinity = 200 ppm.

③ 200 mL of water sample on titration with $\frac{N}{50} \text{ H}_2\text{SO}_4$ using phenolphthalein required 10 mL of the acid. Another lot of 200 mL sample also required 10 mL of acid to obtain methyl orange end point to determine the type of alkalinity.

As $p = M$ alkalinity is only

$$p = M = 10 \text{ mL}$$

$$\text{OH}^- = p = M$$

$$\text{NOH}^- = \frac{\text{NH}_2\text{SO}_4 \times V_{\text{H}_2\text{SO}_4}}{V_{\text{OH}^-}} = \frac{0.02 \times 10}{200}$$

$$= 0.001$$

$$\text{wt. of OH}^- = \text{NOH}^- \times \text{eq. wt}$$

$$= 0.001 \times 17$$

$$= 0.017$$

$$\text{wt. of CaCO}_3 \text{ eq} = \text{wt of OH}^- \times \frac{50}{17} = 0.017 \times \frac{50}{17}$$

$$= 0.05 \text{ gm/L} \times \frac{1000}{1000}$$

$$= 50 \text{ mg/L}$$

Alkalinity due to $\text{OH}^- = 50 \text{ ppm}$.

④ 500 ml of sample water on titration with N/50 H_2SO_4 gave a titr. value of 29 ml upto [P] end point and the sample on titration with the same acid gave a titr. value of 58 ml upto [M] end point.

$$\text{Sol: } p = 29 \text{ ml}$$

$$M = 2(p) = 58 \text{ ml.}$$

$$p = \frac{1}{2} M. \text{ Alkalinity is only due to } CO_3^{2-} \text{ ions.}$$

$$= 2p = 2 \times 29 \text{ ml}$$

$$= 58 \text{ ml.}$$

$$N_{CO_3^{2-}} = \frac{N_{HCl} \times V_{HCl}}{V_{CO_3^{2-}}} = \frac{0.02 \times 58}{500} = 0.00232$$

$$\text{wt of } CO_3^{2-} = N_{CO_3^{2-}} \times \text{eq. wt}$$

$$= 0.00232 \times 30 = 0.0696$$

$$\text{wt of } CaCO_3 \text{ eq} = \text{wt of } CO_3^{2-} \times \frac{50}{30}$$

$$= 0.0696 \times \frac{50}{30}$$

$$= 0.116 \text{ gm/L} \times 1000$$

$$= 116 \text{ mg/L}$$

$$\text{Alkalinity due to } CO_3^{2-} = 116 \text{ ppm}$$

⑤ A sample of water was alkaline to phenolphthalein and methyl orange. 100ml of this water sample and another 20ml for complete neutralization upto [M] end point. Determine the type and extent of alkalinity. As $p > \frac{1}{2} M$. alkalinity is due to

$$\textcircled{1} OH^- \text{ ions} = 2p - M = 2 \times 30 - 50 = 10 \text{ ml}$$

$$\textcircled{2} CO_3^{2-} \text{ ions} = 2(M - p) = 2(50 - 30) = 40 \text{ ml.}$$

$$\text{Sol: } N_{CO_3^{2-}} = \frac{N_{HCl} \times V_{HCl}}{V_{CO_3^{2-}}} = \frac{0.02 \times 40}{100}$$

$$= 0.008$$

$$\text{wt of } CO_3^{2-} = N_{CO_3^{2-}} \times \text{eq. wt}$$

$$= 0.008 \times 30$$

$$= 0.24$$

$$\text{wt of } CaCO_3 = \text{wt of } CO_3^{2-} \times \frac{50}{30}$$

$$= 0.24 \times \frac{50}{30} = 0.4$$

$$= 0.4 \text{ gm/L}$$

$$= 0.4 \text{ gm/L} \times 1000$$

$$= 400 \text{ mg/L}$$

$$\text{Alkalinity due to } CO_3^{2-} = 400 \text{ ppm.}$$

$$\text{NOH}^- = \frac{N_{\text{HCl}} \times V_{\text{HCl}}}{\text{NOH}^-} = \frac{0.02 \times 10}{100} \\ = 0.002$$

$$\text{wt of OH}^- = \text{NOH}^- \text{ eq. wt} = 0.002 \times 17 \\ = 0.034$$

$$\text{wt of CaCO}_3 \text{ eq. wt} = \text{wt of OH}^- \times \frac{50}{17} \\ = 0.034 \times 50/17 \\ = 0.1 \text{ gm/L} \\ = 0.1 \times 1000 \text{ mg/L} \\ = 100 \text{ mg/L}$$

Alkalinity is due to $\text{OH}^- = 100 \text{ ppm}$

$$\text{Total Alkalinity} = 400 \text{ ppm} + 100 \text{ ppm} \\ = 500 \text{ ppm}$$

* Ion exchange method : (demineralization)

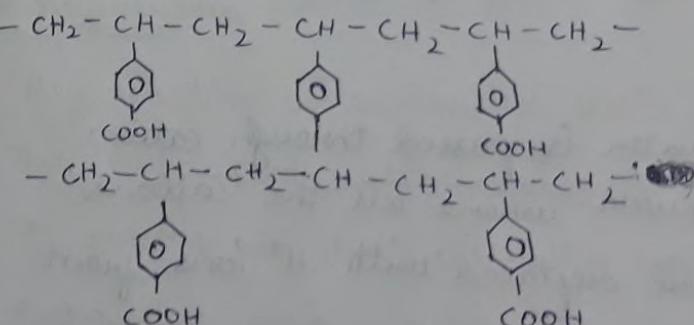
In this process water is passed through two cylinders containing cation exchange resin and anion exchange resin where H^+ ions replace the cations (Mg^{+2} , Ca^{+2}) and OH^- ions replace the anions (HCO_3^{-2} , Cl^{-} , $\text{SO}_4^{=2}$,

respectively which are responsible for causing hardness in water. So the water softens by this method has 0 ppm hardness and it is as good as distilled water when the resins get used up they are ~~set~~ to be exhausted and are regenerated by Acid / Alkali treatment.

* cation-exchange resin (CR-H)

These are insoluble cross-linked porous polymeric materials containing replaceable H^+ ions.

Eg: styrene divinyl benzene co-polymer substituted with acidic groups like $-\text{COOH}$, $-\text{SO}_3\text{H}$ etc..

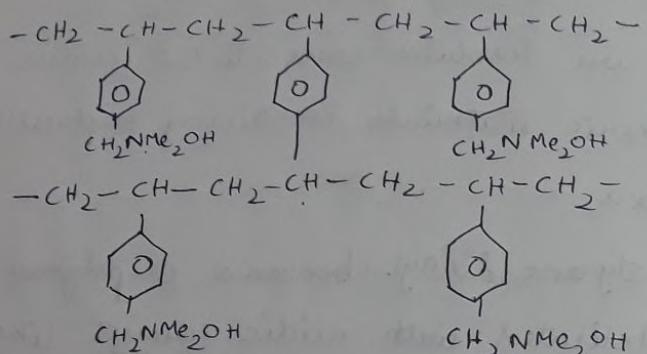


cation exchange resin

* Anion-exchange resin : (R-OH)

These are insoluble cross linked porous polymeric materials containing replaceable OH⁻ ions.

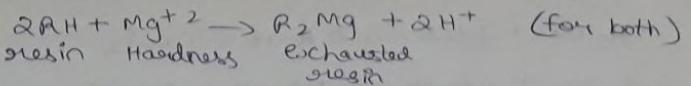
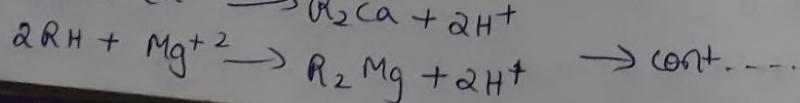
Ex: styrene divinyl benzene co-polymer substituted with amino groups (or) quaternary ammonium (or) phosphonium groups



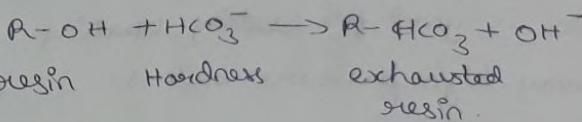
Anion exchange resin

* process:

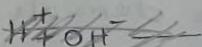
1) The hard water is passed through cation exchange column where all the cations Ca²⁺, Mg²⁺ are replaced with H⁺ ions from the resin and equivalent amount of H⁺ is released from this column.



2) When water is passed through anion exchange column where all the anions Cl⁻, SO₄²⁻, HCO₃⁻ are removed and equivalent amount of OH⁻ ions are released from this column.



3) The H⁺ and OH⁻ ions released from cation and anion exchange columns combine to produce water.

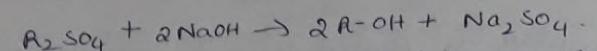
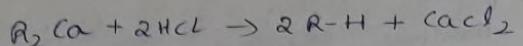


Regeneration:

(Regeneration of exhausted resin)

The exhausted cation resin is regenerated by passing dil HCl / dil H₂SO₄ whereas exhausted anion exchange resin is regenerated by using - dil NaOH.

The columns are then washed and the washings passed to sink (or) drain



exhausted
resin

regenerated
resin

washings
(waste)
sink/drain.

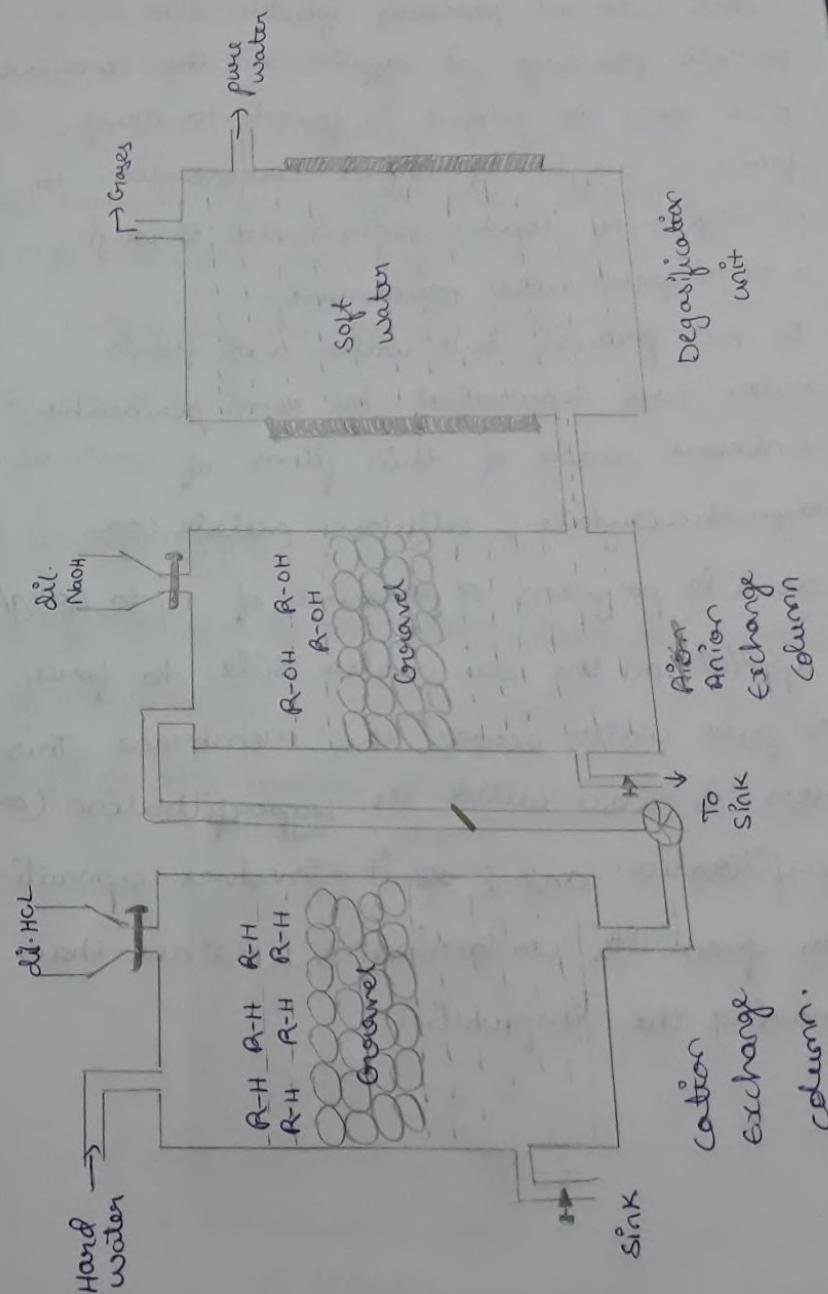
* Advantages:

- 1) Highly acidic / alkaline water can be softened.
- 2) The process is good for treating water for very high pressure boilers.
- 3) Mixed bed ionisers with only one cylinder are also available.

* Disadvantages:

- 1) costly equipments and expensive chemicals are required.
- 2) low turbidity water must be used.
- 3) temporary hardness must be removed before treating water by this method.

* Diagram:



* Reverse osmosis: (Desalination)

when external pressure greater than osmotic pressure is applied on the concnetrated side then the solvent is forced to move from a region of higher concentration to a region of lower concentration through a semi permeable membrane.

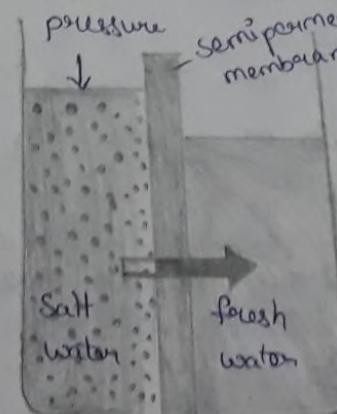
In RO process salt water and fresh water are separated by semi permeable membrane made of thin films of polymethacrylate, cellulose acetate (or), polyamide polymers. A pressure of 15 to 40 kg/cm² is applied on the sea water side to force the pure water across the membrane. This process is also called as Hyperfiltration (or) Superfiltration and it involves separating water from its contaminants rather than removing the impurities.

⇒ Advantages:

- 1) Simple and reliable process.
- 2) Low capital cost and low operating cost
- 3) Life time of membrane is quite high.
- 4) Removes ionic, non-ionic, colloidal and high molecular wt. organic matter.
- 5) extremely low energy consumption
- 6) Membranes can be replaced within short duration.

⇒ Disadvantages:

- 1) Efficiency of the plant depends on maintenance of membranes.
- 2) pH of the water should be around 4



OSMOSIS

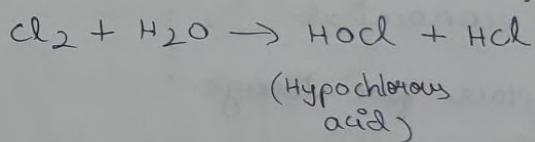
* specifications of potable water: (Drinking or municipal water)

- 1) colourless odourless and pleasant to taste.
- 2) should be free from suspended particles and dissolved impurities.
- 3) should be non-corrosive in nature.
- 4) should be free from disease producing microorganisms and pathogens and objectionable dissolved gas like H_2S .
- 5) pH should be in the range of 6.5 to 8.5.
- 6) Alkalinity should not be more than 200 ppm.
- 7) Should not be turbid.
- 8) Total dissolved solids (TDS) should be less than 500 ppm.
- 9) Toxic minerals such as - Pb, As, Cr should not be present.
- 10) Should be free from health hazards and sanitary defects.

* Disinfection: The process of destroying or killing pathogens (disease producing microorganisms) and making the water safe for use is called as disinfection or sterilization.

ex: chlorination, ozonation, U.V Radiation.

* Disinfection by chlorine: chlorine is the most common disinfectant used in the form of gas/solution (or) bleaching powder. chlorine when added to water forms hypochlorous acid which is a powerful disinfectant and germicide



Germs + HOCl \rightarrow Germs are killed.

HOCl reacts with the bacterial enzymes and inactivates them which are very much essential for the growth and metabolic processes thus leading to the death of micro-organisms.

Cl_2 is a more effective disinfectant at lower pH of (5-6.5) (5-6.5)

* factors affecting efficiency of chlorination:

- 1) Time of contact - The death rate of micro-organisms is maximum to start with and it goes on decreasing with time.
- 2) Temperature of water - With increase in temperature the number of pathogens decreases.
- 3) pH of water - At lower pH of 5 to 6.5 less contact time is required for disinfection.

* Advantages of chlorination:

1) effective and economical

2) requires less place for storage

3) Stable and does not deteriorate on standing.

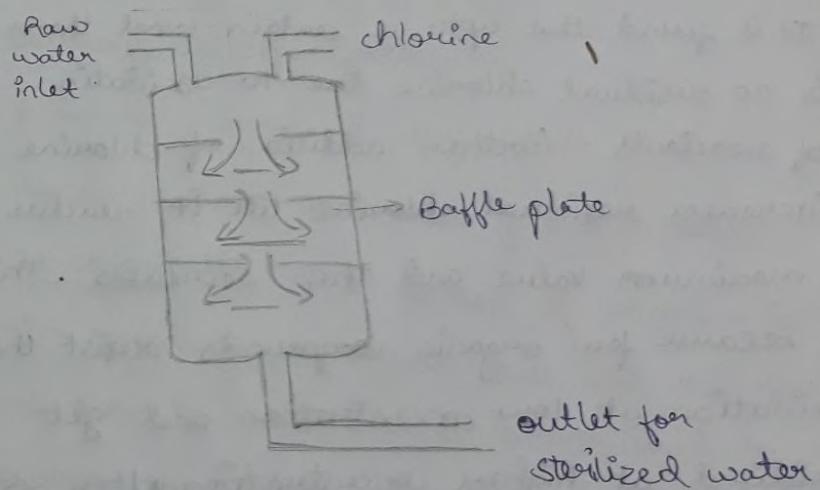
4) Most ideal disinfectant.

5) leaves no salt impurities.

No sludge is formed.

* Disadvantages:

- 1) Excess chlorine produces an unpleasant taste and odour.
- 2) All this irritation on mucous membrane.
- 3) free chlorine in treated water should not exceed 0.1-0.2 ppm.
- 4) Requires effective dechlorination.



CHLORINATOR

* Break point chlorination:

The chlorination of water to such an extent which not only destroys the living ~~the~~ organisms but also other impurities like organic matter, reducing substances, free ammonia etc. is called as break point chlorination.

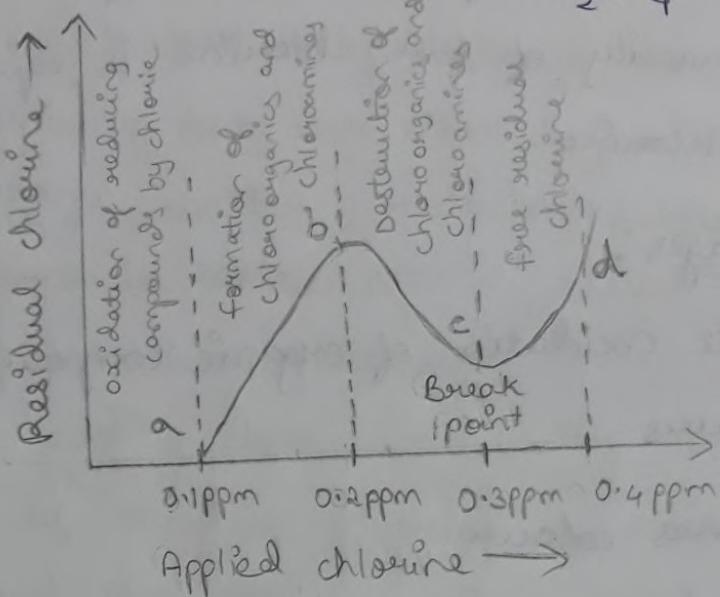
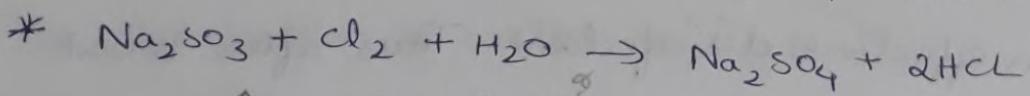
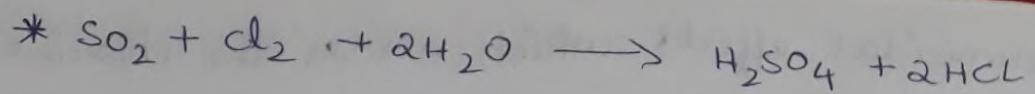
After adding chlorine to water the quantity of residual chlorine is estimated. It is found that upto a certain level there is no residual chlorine due to oxidation of reactants. Further addition of chlorine increases residual chlorine till it reaches a maximum value and then decreases. This is because few organic compounds resist the oxidation at low concentration and get oxidised at higher concentration after sometime when all the organic matter is oxidised there is an increase in the level of residual chlorine. This point is called as break point after this point free residual chlorine increases in water and produces

germical effects which makes the chlorine an effective disinfectant. Thus after break point quantity of free chlorine is equal to added chlorine.

* Advantages:

- 1) complete oxidation of organic compounds and NH_3 occurs.
- 2) Removes colour
- 3) Destroys all the pathogens
- 4) Prevents growth of any weeds in water.
- 5) Removes odour and taste from water.

⇒ De-chlorination: The excess of chlorine in water produces unpleasant taste and colour. Thus ~~the~~ de-chlorination is required to remove the excess chlorine, bad colour and decomposed products. De-chlorination is carried out by passing water through molecular carbon bed (or) by adding activated carbon (or) by passing SO_2 gas (or) sodium thiosulphate.



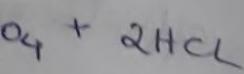
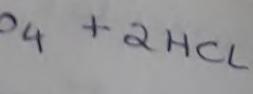
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* Defined
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UNIT - V

Green chemistry

*Definition : Green chemistry is the design of chemical products or processes that reduces or eliminate the use and generation of hazardous substance.

Green chemistry is the use of chemistry for pollution prevention by environmentally conscious designs of chemical products and processes that reduce or eliminate the use of or generate the hazardous substances.

Eg: Natural gas, Bio gas, fuel cells, lithium anion battery, wind energy, solar energy, Hydroelectric energy, use of geothermal power, Tidal power etc.

*principles of green chemistry:

There are 12 principles of green chemistry developed by paul Anastas and John Warner.

1) Prevention: It is better to prevent waste than to treat or clean up waste after it has been created.

- 2) Atom economy: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- 3) Less Hazardous chemical synthesis: Whenever practicable synthetic methods should be designed to one and generate substances that posses little or no toxicity to human health and the environment.
- 4) Designing safer chemical: chemical products should be designed to affect their desired function while minimizing their ~~actual~~ toxicity.
- 5) Safer solvents and auxiliaries: The use of auxiliary substances (such as solvents, separation agents, etc.) atoms should be made necessary whenever possible and innocuous when used.
- 6) Design for energy efficiency: Energy requirement of chemical processes should be recognised for their environmental and economical impacts and should be minimized if possible synthetic methods so should be conducted at ambient temperature and pressure.
- 7) Use of renewable feed stocks: A raw material or feed stock should be renewable rather than depleting whenever technically and economically practicable.
- 8) Reduce - Derivatives: Unnecessary derivatization (use of blocking groups) should be minimized or avoided if possible, because such steps requires additional reagents and can generate waste.
- 9) Catalysis: catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- 10) Design for degradation: chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not

persist in the environment

i) Real-time analysis for pollution prevention:

Analytical methodologies need to be further developed to allow for the real time, in process monitoring and control prior to the formation of hazardous substances.

ii) Inherently safer chemistry for accident prevention:

Substance and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and ~~other~~ fires.

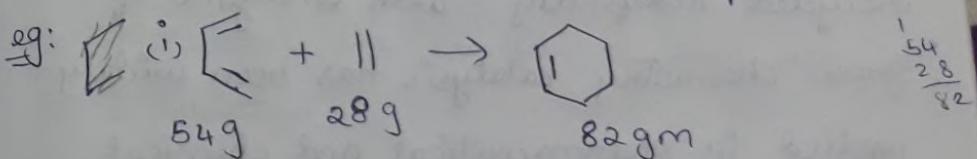
* Atom economy: Atom economy is a method of determining the efficiency with which raw materials - reactants (or) feed stock are used regardless of the percentage yield obtained in the reaction. The atoms that are not directly involved in formation of products are wasted atom. The measure of atom economy suggests to find a way

of making the same product with the waste of fewer reactant atoms.

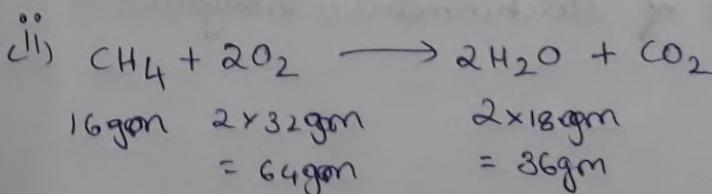
* Definition: Atom economy is the mass (%) percentage of reactants used in the final product, divided by the total mass of reactants which gives a numerical measure of atom economy.

$$\text{Atom economy} = \frac{\text{fw of atoms utilized}}{\text{fw of all reactant}} \times 100$$

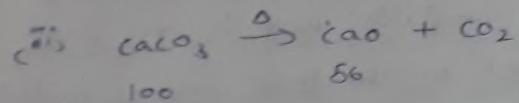
The atom economy concept is a useful tool available for designing reactions with minimum wastage. The term atom efficiency signifies that as many as reactants reacting atoms possible should end up in useful products.



$$\text{Atom economy} = \frac{82}{54+28} = 100\%.$$



$$\text{Atom economy} = \frac{36}{16+64} = \frac{36}{80} \times 100 \\ = 45\%$$



$$\text{Atom economy} = \frac{56}{100} \times 100 = 56\%$$

* Catalysis: A catalyst is defined as a substance that changes the velocity of a reaction without itself being changed in the process. It lowers the activation energy of the reaction but in doing so it is not consumed. Thus catalyst can be used in small amounts and can be recycled indefinitely. With emergence of green chemistry catalysis has been widely applied in pharmaceutical and chemical industry with the main aim of minimizing the enormous amount of waste generated by the use of stoichiometric inorganic reagents.

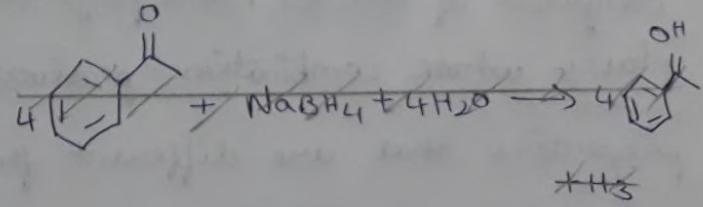
Catalysis

catalysts are specific in their action and effective at catalysing highly selective processes with complex substrates. Catalyst can be enzymatic in their actions. Enzymes are the most efficient and common catalyst found in nature.

A good catalyst should possess following qualities.

- 1) It plays a vital role in environmentally friendly synthesis of new/existing chemicals
- 2) It produces lesser byproducts, co-products and other waste products addressing the benefits of atom economy.
- 3) It minimizes the hazards
- 4) It reduces the number of steps required in a reaction.

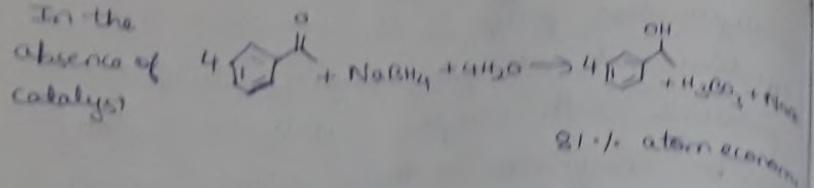
~~Q17~~ In the absence of catalyst



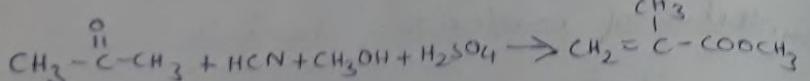
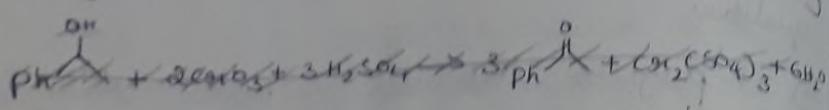
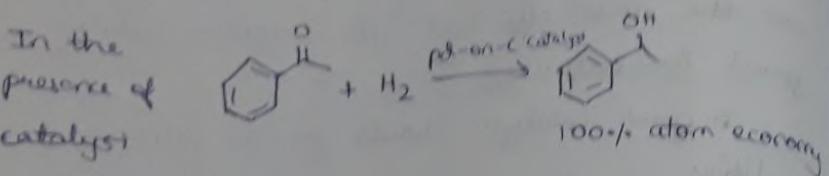
Q9:

Production of Benzophenone

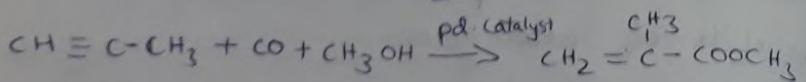
In the absence of catalyst



In the presence of catalyst



$$\text{Atom economy} = \frac{100}{215} \times 100 = 46.5\%$$



$$\text{Atom economy} = \frac{100}{100} \times 100 = 100\%$$

* Composite material: A materials system composed of two or more physically distinct phases whose combination produces aggregate properties that are different from those of its constituents.

(Ans)

Two or more chemically distinct materials which when combined have improved properties over the individual materials. composites could be natural or synthetic.

* Properties of composites (Advantages)

- 1) They have high specific strength.
- 2) They do not use these strength even at high temperatures.
- 3) They are hard and tough.
- 4) They have good impact resistance and thermal shock resistance.
- 5) They possess high low specific gravity and low cost.
- 6) They have better creep and fatigue strength.
- 7) They possess high corrosion and oxidation resistance compared to metals.
- 8) They have desirable coefficient of thermal expansion.
- 9) Conductivity and electrical conductivity are low and can be controlled.

10) They can withstand extreme temperature conditions.

* Examples:

1) wood - (cellulose fibres and lignin)

2) Bone - (collagen and apatite)

3) Rain coat, insulating tape, composite brick, reinforced concrete.

* constituent of composite:

composites in general consists of two phases

1) Matrix

2) Dispersed phase

⇒ Matrix: It is the main constituent of composite. It is the continuous body which encloses the composite and gives it the bulk form. It is the bonding material which adheres to the reinforcing material depending on the type of matrix composites are classified as PMC, MMC, CMC

* functions of a matrix:

→ Holds the fibres together.

→ protects the fibres from environment.

→ Distributes the loads evenly between fibres so that all fibres are subjected to the same amount of strain.

→ Enhances transverse properties of a laminate.

→ Improves impact and fracture resistance of a component.

→ Cavity inter lamina shear.

* Desired properties of a matrix:

→ Reduced moisture absorption.

→ low shrinkage

→ low coefficient of thermal expansion.

→ Strength at elevated temperature (depending on application).

→ Low temperature capability (depending on application).

→ Excellent chemical resistance (depending on application).

⇒ Dispersed phase: It is the structural constituent that determines the internal structure of the composite. It may be fibre, particle, whisker or flakes.

1) fibres: fibres are long and thin filament of any polymer, metal or ceramic having high length to diameter ratio, high tensile strength and high stiffness.

e.g: glass fibres, carbon fibres, Boron fibres, aramid fibres, ceramic fibres etc...

2) particles/particulates: These are small pieces of hard solid materials which can be metallic or non-metallic. They are randomly distributed in the matrix. They increase the surface hardness, strength and performance at elevated temperatures reduced shrinkage and friction and modify thermal and electrical conductivity.

e.g: concrete, cement etc...

3) flakes: These are thin solids having two dimensional geometry and can be packed more efficiently than fibres and particulates spherical particulates they impart equal strength in ~~the~~ a plane compared to fibres (reinforces unidirectionally)

e.g: mica flakes - used in electrical and thermal insulating applications.

4) whiskers: These are thin, strong filaments or fibres of several millimetres in length and several micron in thickness. They have high degree of crystallinity, high elastic modulus and higher strength. But their use in composites is limited due to their high cost and difficulty in use.

e.g: graphite, silicon, carbide, sapphire, aluminium oxide etc...

* Classification of composites:

1) On the basis of types of matrix composites are classified as

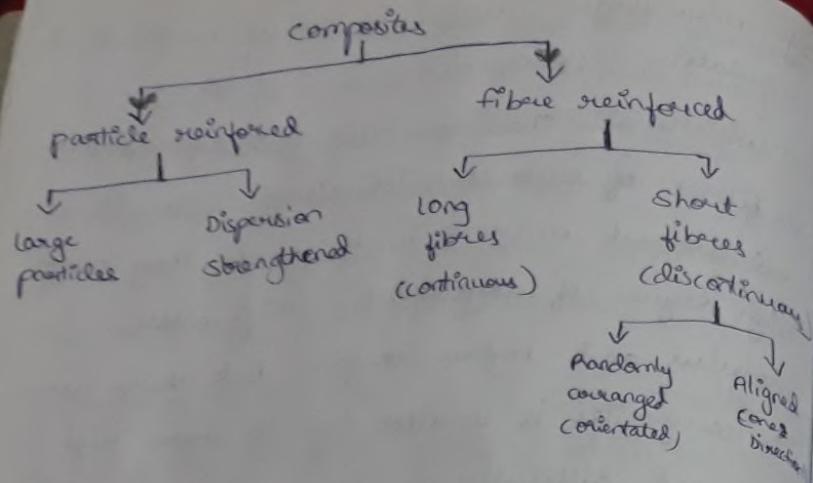
PMC - Polymer matrix composites.

MMC - Metal matrix composite.

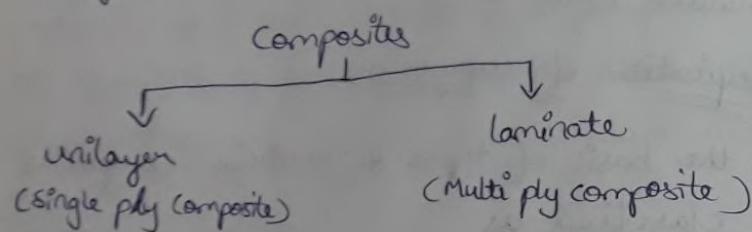
CMC - Ceramic matrix composite.

2) On the basis of type of reinforcement are classified as





3) on the basis of ply / lamina / layers are classified as



* Matrix based composites:

① Polymer matrix composite: (PMC)

low cost, light weight, tough, ~~corrosive~~, and corrosion resistant but have low strength, stiffness and thermal stability

e.g.: Glass, carbon fibres dispersed in thermoset polymer matrix.

② Metal matrix composite: (MMC)

Ductile, Thermal shock resistant, easy to process, Higher operating temperatures, creep resistance but costly

e.g.: Al, Ti, Cu, steel, Mg are used as matrix.

③ Ceramic matrix composite: (CMC)

Thermally stable, High stiffness, High melting point and good resistance to oxidation but brittle with low tensile strength and low shock resistance.

e.g.: Zirconia particles in Al_2O_3 matrix

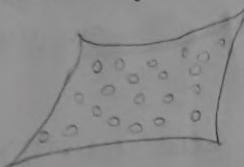
* Particle reinforced composite:

Reinforcement material is in form of large or small particles suspended in matrix. It is called particulate composite.

④ Large particle composite: The particles should be small and evenly distributed throughout the matrix the shape may be square, triangular (or) round but ~~in~~ the dimension

of all sizes are usually equally. The particulate ~~face~~ phase is harder and stiffer than the matrix.

e.g.: Automobile tyres, cement, concrete



② Dispersion strengthened composites: Very small particles of 10 to 100 nm are used as reinforcing material. The dispersed phase - may be metallic or non metallic such composites retain strength even at elevated temperatures ~~for~~ at longer periods. The matrix bears the major part of applied load.

e.g.: High temperature strength of Ni alloy is enhanced by adding thorium (ThO_3) particles.

* Fibre reinforced composites: These composites involves three components: a filament, a fibre, polymer matrix and a bonding agent.

FRC posses - high specific strength, high specific modulus, high stiffness, low overall density, high yield strength, fracture strength and good mechanical properties. The matrix and the fibre reinforcements should be chemically compatible with no undesirable reaction between them. The fibres should be stable at room temperature and retain there strength at higher temperatures.

e.g.: Glass FRC - used in automobile ~~petrol~~ parts, storage tanks, plastic pipes, floorings and underground petrol storage tanks.

* carbon FRC - used in aircraft wings and body fishing rods, turbine plates, sports material

* aramid FRC - used in automobile brakes and ~~clutches~~, ropes, cables, marine industry, bullet proof fabrics

* Alumina / carbon FRC - used in automobile industry and turbine engines.

continuous

long fibres -



continuous FRC

aligned.



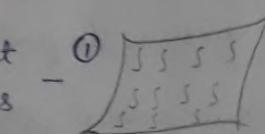
0° - 90°

orientation

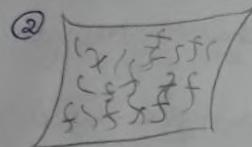


Multidirectional
orientation

short
fibres -



discontinuous FRC
aligned



Randomly
orientated

* Structural composites: (Layered composites)

These composites consists of both homogenous material and composite material bonded together in layers. Layered composites have high strength but possess low shear strength.

① Laminar composite: unilayer/single ply

In laminar composites two dimensional layers of two different materials are

stacked and glued together such that the orientation of high strength direction varies with each successive layer. The individual unidirectional laminae piles are oriented in such a way that the resultant structural component has desired mechanical and physical properties in different direction.

e.g: modern ski, plywood, plastic based laminates.



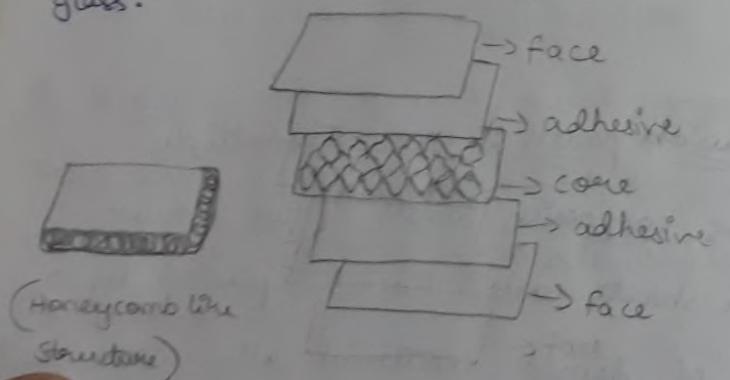
② Sandwich panels: Laminated/multiply.

These composites consists of two stronger outer sheets called faces separated by a layer of densed material called core.

The three layers are joined together by an adhesive. The core material is of honey comb structure with lower strength and stiffness which resists deformation at

right angles to provide rigidity as thickness of core increases, stiffness also increases. The face material bears most of the load and stress. Core materials used are synthetic rubbers and foamed polymers. Face materials are FRP, plywood, titanium, steel and aluminium alloys.

e.g.: Sandwich panels are used in roofs, walls, floors, aircraft for wings, ~~fuselage~~ fuselage and tailplane skins, safety glass.



* Applications of composite material:

- 1) In automobile industry and transportation industry (e.g. steel & aluminium body)
- 2) Marine applications like shafts, hulls, spans (for racing boats)
- 3) Aeronautical application like components of rockets, aircrafts (business and military) missiles etc.
- 4) Communication antennae, electronic circuit boards (e.g. PCB, bread board)
- 5) Safety equipment like ballistic protection and air bags of cars.

* Biodiesel: Biodiesel is mono alkyl ester of long chain fatty acid which is made from transesterification of vegetable oil and animal fats.

* Sources of biodiesel: A variety of oils both edible and non-edible are used for production of bio-diesel.

e.g.: palm oil, sunflower oil, olive oil,
soya bean oil etc...

animal fats includes - chicken fat, fish oil
omega 3-fatty acid.
certain plant species from which biodiesel
can be extracted include - Jatropha curcas,
pangamica pinnata, Azadirachta indica,
~~Madhuca~~ Madhuca indica

* Properties of bio-diesel:

- 1) Bio-diesel is light yellow to dark brown
coloured liquid.
 - 2) It is non-miscible with water.
 - 3) High boiling point and low vapour pressure.
 - 4) Low density of 0.88 gm/cc.
 - 5) Higher flash point than petro diesel.
 - 6) Viscosity is similar to petro diesel.
 - 7) Biodegradable, non-toxic, produces
lesser ~~harmful~~ emissions.
 - 8) Higher cetane ratings.
 - 9) Its calorific value is ~~325~~ 37.27 MJ/L.
 - 10) Ecofriendly and sulphur free emissions.
 - 11) Can be easily blended with petro diesel.
- * Advantages of bio-diesel: (Significance / Importance)
- 1) can be blended with petro diesel and used
in diesel engines. In India 20% blend is
used.
 - 2) Reduces CO and CO₂ emissions.
 - 3) completes the CO₂ cycle.
 - 4) contains lesser aromatic hydrocarbons.
 - 5) Higher cetane number improves performance
and efficiency.
 - 6) Sulphur free and clean burning fuel.
 - 7) Increases the engine efficiency and no
engine modification is required.
 - 8) Biodegradable, Renewable fuel, Non-toxic
and ecofriendly.
 - 9) It reduces particulate emissions.
 - 10) It works as a lubricant for diesel engines.

itself which increases the life of engine.

i) It possess flash point greater than 150°C

ii) The process of extraction is simple as it involves only two steps

- * extracting the oil from sources

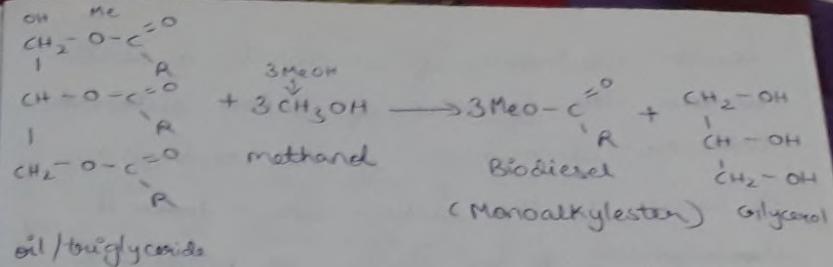
- * Esterification of oil.

Transesterification

* Transesterification: Bio-diesel is prepared by transesterification of oil (Triglyceride) with an alcohol. The reaction involves methanol with triglyceride in 3:1 ratio in presence of basic catalyst which gives a monoalkyl ester - Biodiesel and by product - glycerol.

The catalyst used can be acidic, basic or enzymatic but usually alkali catalyzed reactions are faster.

Glycerol are used in pharmaceutical industry.



* Carbon neutrality: carbon neutral, or having a net zero carbon footprint, refers to achieving net zero carbon emissions by balancing a measured amount of carbon released with an equivalent amount sequestered or offset, or buying enough carbon credits to make up the difference.

Carbon neutral status is achieved by balancing CO₂ released with renewable sources of energy. Carbon offsetting is done by paying others to remove CO₂ by planting trees or funding carbon projects or by buying carbon credit etc...

carbon neutrality of bio diesel is zero because the amount of carbon released into the atmosphere on its combustion is same as the carbon taken from the atmosphere & by plants. As biodiesel releases the same amount of CO_2 that the plants absorb therefore there is no negative impact on the carbon cycle.

solids

* polymers
polymers
are high
together
molecules

e.g.: plastic

* fund

in a

for

mus

bon

is

stop

me

d is zero
on released
combustion
from the
biodiesel
of CO_2 that
there is
carbon cycle.

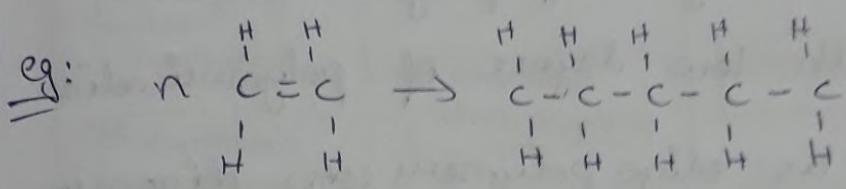
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UNIT - III

Engineering materials

* polymers: (Definition)

polymers or micro molecules are giant molecules or high molecular weight which are built together by linking large no. of small molecules known as monomers.



ethene

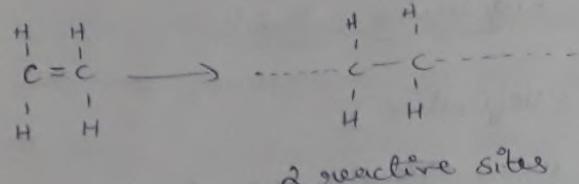
(monomer)

Polyethene

(polymer)

* functionality: The number of bonding sites in a monomer is called as functionality. For a substance to behave as monomer it must have at least two reactive sites or bonding sites (bifunctional). If the monomer is ~~bifunctional~~ bifunctional it produces linear or straight chain polymers whereas. If the monomer is trifunctional it forms

Cross linked 3D network polymer



* Degree of polymerisation: The no. of repeating units in a polymeric chain is known as degree of polymerisation.

Polymers with low degree of polymerisation are known as oligo polymers (or) oligomers with molecular weight ranging from 500-5000 units. The polymers with high degree of polymerisation are known as High polymers with molecular weight ranging from 10,000 - 2,00,000.

Note: The basic requirement for a substance to behave as monomer.

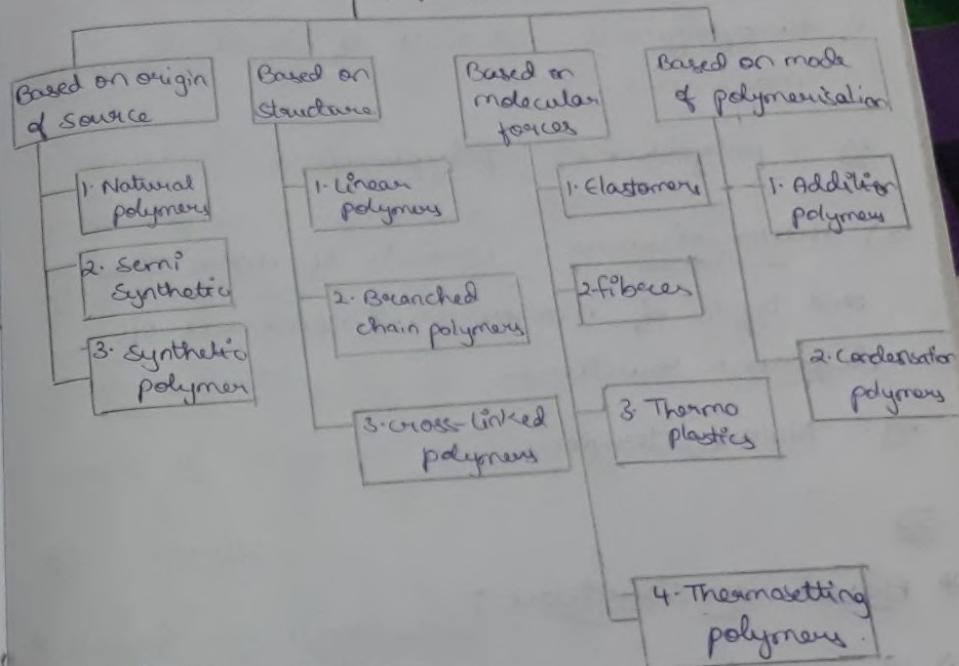
a) presence of double / triple bond
(or)

presence of unsaturation

b) presence of polar groups.

* Classification of polymers:

Classification of polymers



* Based on source:

1) Natural polymer - These are found in nature or these polymers are isolated from natural materials

e.g: starch, protein, cellulose etc....

2) Synthetic polymer - These are man made polymers or these are synthesized from.

low molecular weight compounds.

e.g.: polythene, pvc, polystyrene.

* Based on monomers:

1) Homopolymers - consists of identical monomers.

e.g.: polyethene, polypropylene

2) Heteropolymers - consists of more than one type of monomer / monomeric of different structures

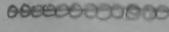
e.g.: Nylon, Terylene



* Based on structure:

1) Linear polymer - These are straight chain polymers

e.g.: Nylon, polyethene



Linear

2) Branched polymer - The polymeric chain has several branches

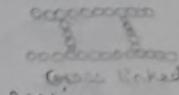
e.g.: Glycogen



Branched

3) Cross-linked polymers: Several cross-linking b/w the polymeric chain gives rise to 3D network

e.g.: Bakelite, urea formaldehyde resin.



* Based on main chain:

1) Homo chain polymer - The main chain is made of same species of atom

e.g.: polyethylene



2) Hetero chain polymer - The main chain is made of different species of atom

e.g.: Terylene



* Based on application:

1) plastics - High polymeric material which can be molded into various shapes and possess the property of plasticity. They are further divided into thermosetting and thermoplastics.

e.g.: pvc, polyethene, Bakelite etc...

2) fibres : These are natural long chain polymers with high tensile strength, rigidity, stiffness and are characterised by high melting point.

e.g.: Nylon 6:6, Kevlar

3) elastomer : These are high polymers with characteristic elasticity as the molecules are arranged in form of spring shaped chains (or) zig-zag pattern.

e.g.: Natural rubber, Silicone rubber, Buna-S rubber, ~~Silastic~~ Butyl rubber.

* Thermo plastic and Thermo setting resins:

Thermo plastic resins are formed by addition polymerisation. They possess long chain linear structure and can be softened on heating and harden on cooling. The repeated heating and cooling process does not alter the chemical nature as the change is only physical.

Thermosetting resins are formed by condensation polymerisation and possess three dimensional structure. Once these resins solidify they cannot be softened again on heating. Thus there are permanent setting resins.

Q1:

Thermoplastic

- formed by addition on chain polymerisation.
- Generally long chain linear polymers.
- They readily soften on heating.
- They melt on heating.
- They can be softened reshaped and reused hence possess scrap value.
- Weak, soft and less brittle.

- They cannot withstand high temperatures.

- Plasticity is directly prop to temp.

Thermosetting

- formed by condensation or step polymerisation.
- They have three dimensional network structure.
- do not soften on heating.
- They get charred on prolonged heating.
- They cannot be reshaped and reused, hence no scrap value.
- Hard, strong and more brittle.
- They can withstand higher temperature.
- Plasticity unaffected by change in temp.

→ soluble in some organic solvents.

e.g.: polyethene, polystyrene, PVC

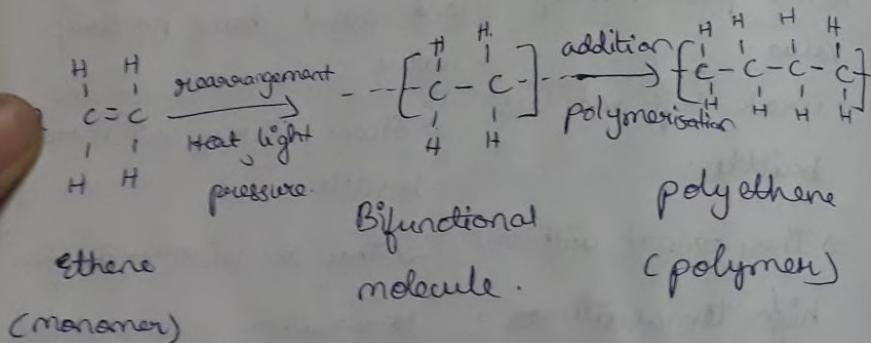
→ Insoluble in all types of solvents.

→ Bakelite, urea formaldehyde resin, epoxy resin.

⇒ Types of polymerisation:

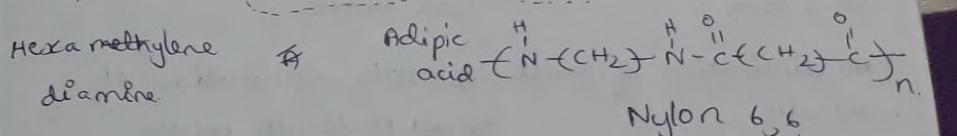
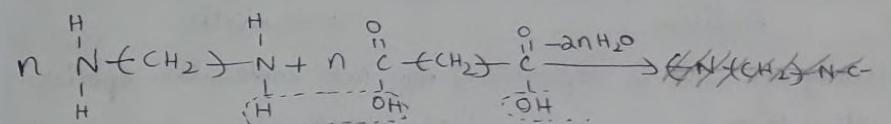
i) Addition or chain polymerisation:

In addition polymerisation the product formed is an exact multiple of original monomeric unit. The monomer contains double or triple bond which by inter molecular rearrangement makes the molecule bifunctional forming a homo chain polymer. The monomer adds one at a time to the polymer and no other by product is formed.

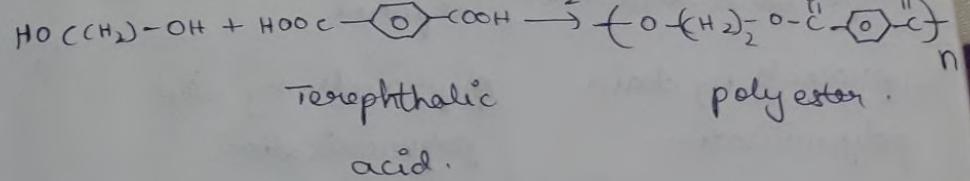


ii) condensation polymerisation (Step polymerisation)

It is the polymerisation reaction obtained between monomers containing polar groups with the elimination of small molecules like H_2O , HCl , etc... along with the product. The polymerisation proceeds by step wise mechanism and the rate of reaction is slow.

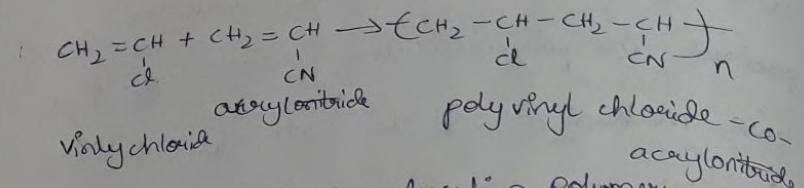
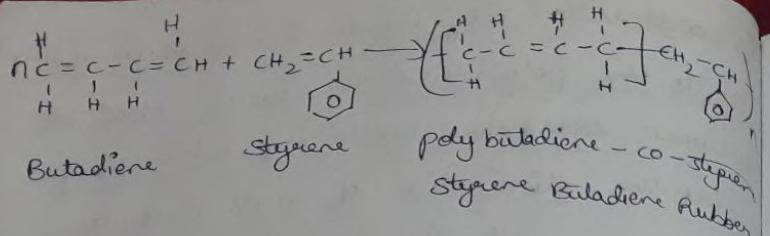


Terephthalic acid.



iii) Co-polymerisation: It is a joint polymerisation of two or more different monomer species

to give high mol wt. compounds known as co-polymers.



* Differences b/w Addition & condensation polymers

Addition	condensation
1) only one unit is repeated at a time	1) Any two molecular species can react.
2) No elimination of small molecules.	2) Mostly elimination of small molecules occur.
3) presence of double or triple bond required.	3) presence of polar groups required.
4) proceeds by chain polymerisation.	4) proceeds by step polymerisation
5) Rate of reaction is fast.	5) Slow rate of reaction
6) Mechanism includes free radical carbonium ion and carbonium ion.	6) only condensation reaction occurs.

- 2) catalyst used are Lewis acids and bases are used.
- 3) Homochain polymers are formed.
- 4) Mostly thermoplastics are formed.
- 5) eg: polyethylene, polystyrene, polypropylene, pvc
- 6) mostly mineral acids and bases are used.
- 7) Heterochain polymers are formed.
- 8) mostly thermosetting polymers formed.
- 9) eg: Bakelite, Nylon, urea formaldehyde resin etc...

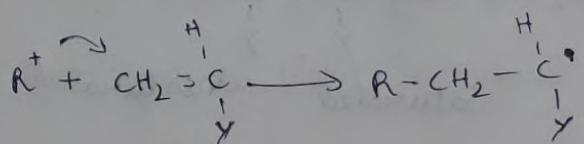
* Free radical mechanism of addition polymerisation:

① Initiation step:

In this step free radicals are formed by homolytic fission of an initiator which reacts with monomeric molecules to form chain initiating species.



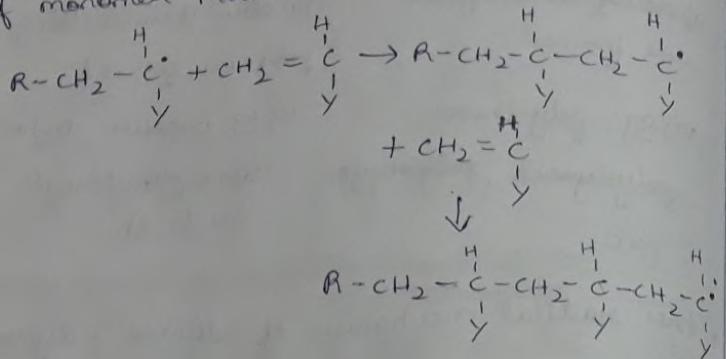
Initiation free radicals.



chain initiating species.

② propagation step:

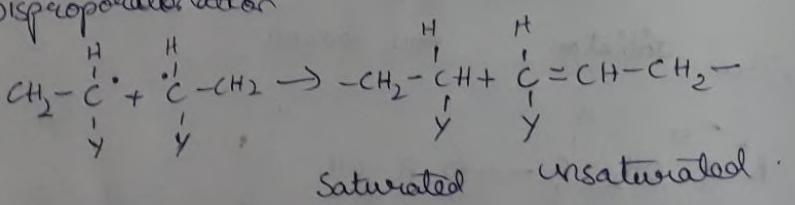
The chain initiating species continues to grow by successive additions of large number of monomer molecules.



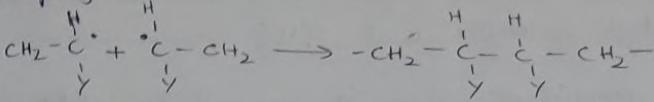
③ Termination step:

The propagation step gets terminated at some point either by ~~over~~ coupling or by disproportionation. Once the propagation steps, the polymer is called as dead polymer.

Disproportionation

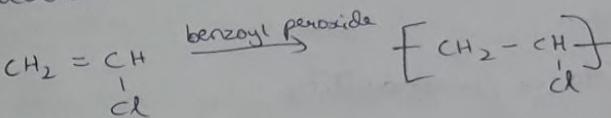


coupling



* polyvinyl chloride: (PVC) - plastics

preparation - PVC is prepared by heating a water emulsion of vinyl chloride in presence of a benzoyl peroxide as catalyst in an autoclave.



Vinyl chloride

PVC (polyvinyl chloride)

properties -

- 1) PVC is colourless, odourless and non-inflammable
- 2) Its softening point is 148°C .
- 3) chemically inert thermoplastic
- 4) Tougher and stronger than polyethene
- 5) Resistant to light inorganic acids and bases
- 6) Stiff and hard polymer.
- 7) Excellent oil resistance and resistance to weathering.

③ Superior chemical resistance but soluble in ethyl chloride and PHF.

* Note: plasticized PVC is soften by adding plasticisers such as dibutyl phthalate or tricresyl phosphate or ~~softly~~ diethyl phthalate to rigid PVC.

- It is a good insulator.
- Compared to leather it has greater abrasion resistance.
- Flex resistance/washability.
- Water proof in nature.

* uses:

Plasticized PVC is used for

- Making dining table mats.
- Rain coats.
- Garden hose.
- Table cloth..
- Curtains.
- Tool handles.
- Toys and gadgets.
- Chemical containers
- Conveyer belts.

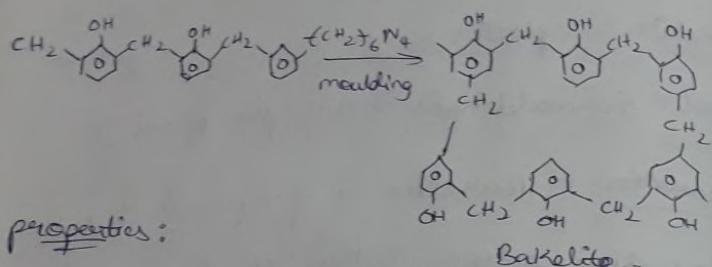
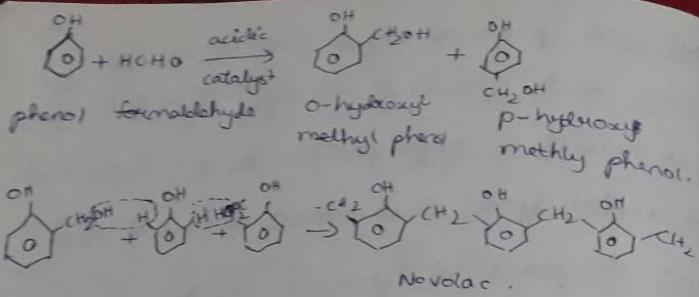
Unplasticized PVC or Rigid PVC is used for

- Making sheets for tank linings, light fittings, safety helmets, refrigerator frame, tyre cycle and motorcycle mudguards as rods and tubes in place of ferrous metals.

* Bakelite: (plastics)

(phenol-formaldehyde resin/ phenoplast)

Preparation - Bakelite is prepared by condensation polymerisation of phenol with formaldehyde in presence of an acidic catalyst, the thermocet bakelite is produced. Initially in the first step, ortho and para hydroxy methyl phenol are formed which react to produce a linear polymer Novolac. During moulding step, hexamethylene tetramine is added to convert soluble and fusible Novolac into hard and infusible solid on cross linked structures called as bakelite.



* properties:

- 1) It is rigid, hard, scratch resistant, impermeable, water resistant insoluble solvent.
 - 2) Resistant to non-oxidising agents - acids, salts, inorganic solvents.
 - 3) easily attacked by alkalis.
 - 4) possess excellent ~~isotom~~ insulating character.

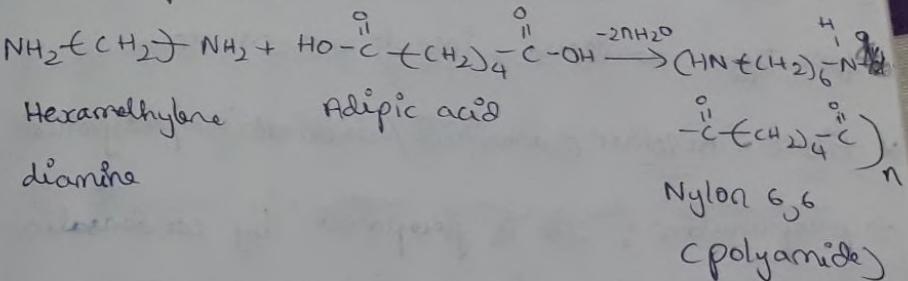
* uses:

- ① electrical parts - switches, plugs, switch boards, heater handles.

- 2) for making moulded articles like telephone parts, cabinets for TV.
- 3) It is used as H exchanger resin in water softening process.
- 4) used in paints and varnishes.
- 5) used for making bearing in propeller shafts for paper industry and rolling mills.

* fibres: Nylon 6,6 (polyamide)

→ Preparation: It is prepared by condensation reaction between hexamethylene diamine and adipic acid.



* properties:

- It is light, horny and possess high M.p = 265°C
 - High tensile strength and abrasion resistance
 - Insoluble in all types of solvents.
 - Thermoplastic in nature.

- Absorbs little moisture, therefore drip dry in nature.
- very flexible and crystalline in nature.
- on mixing with wood, the strength and adhesion resistance increases.

* use:

i) used as fibre in making socks, carpet, garments etc.

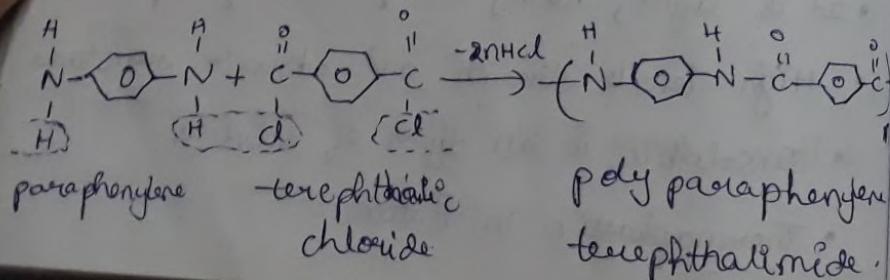
ii) used in making filaments for ropes, bristle for tooth brush, tyre cord etc.

iii) used in oil filters.

iv) used in transmission belts, ribbons for type writers, insect screens etc.

* fibre = Kevlar (aramid / aromatic polyamide)

→ preparation: It is prepared by condensation polymerisation of paraphenylen with terephthalic chloride.



→ properties:

- light weight, high tensile strength and high modulus.
- low thermal expansion hence thermally stable.
- abrasive and impact resistant.
- used as protective layer of graphite laminate.

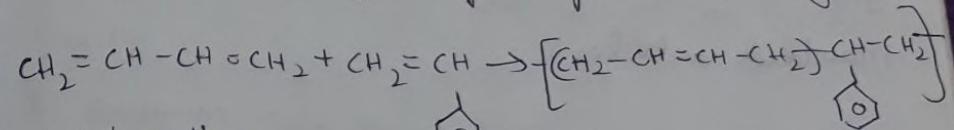
→ use:

- used in light weight boat hulls, race cars, bullet proof jackets and puncture resistant tyres, aircraft parts, cables and conveyor belts.

* elastomer: (SBR - S)

→ preparation: It is prepared by co-polymerisation of butadiene (75%) and styrene (25%).

In presence of ~~perox~~ persulphate catalyst



1,3 butadiene



Styrene

poly butadiene
-co-styrene

SBR (Styrene butadiene rubber)

→ Properties:

- Resembles natural rubber in processing characteristic.
- Possess high abrasion resistance and load bearing capacity.
- Gets oxidised in presence of small amounts of ozone.
- can be ~~vulcanized~~ vulcanized similar to natural rubber using sulphur.

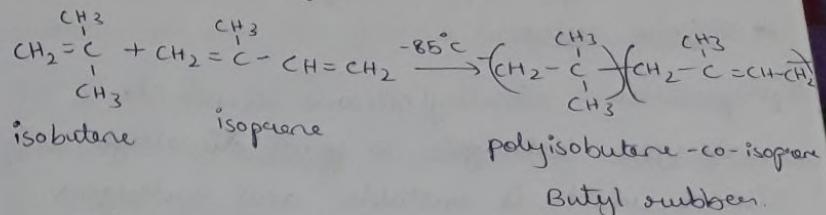
→ uses:

- Mainly used in manufacture of motor tyres.
- Also used for wires and cable insulation, footwear components, floor tiles, shoe soles, waterproof fabrics, carpet backing, gaskets, tank lining and other house moulded articles.

* Butyl rubber:

→ Preparation: By co-polymerisation of isobutene with small amounts of isoprene at a low temperature of -85°C in presence of

BF_3 ~~ether~~ as catalyst



* Properties:

- 1) It is cheaper than other synthetic rubbers.
- 2) It is impermeable to air and other gases.
- 3) excellent resistance to heat, abrasion, chemicals - HCl , H_2SO_4 , HNO_3 and polar solvents that is alcohol and ketones.
- 4) High resistance to ozone.
- 5) Good electrical insulation properties.
- 6) Soluble in hydrocarbon solvents like benzene.
- 7) can be vulcanized but cannot be hardened much.
- 8) Becomes soft on oxidative degradation.

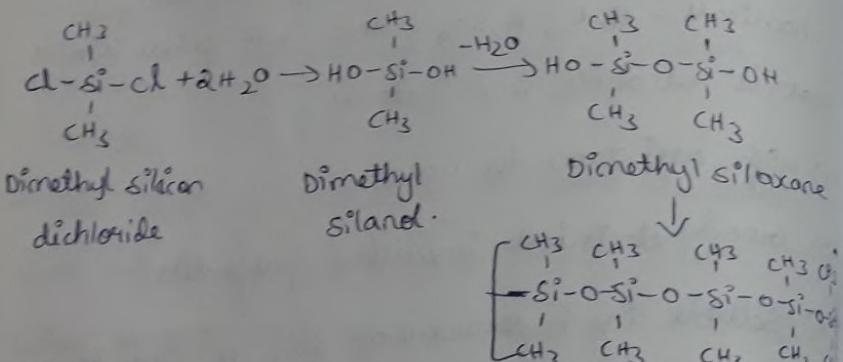
→ uses:

for making cycle and automobile tubes, hoses, automobile parts, conveyor belts for food, Tank lining for storing acids,

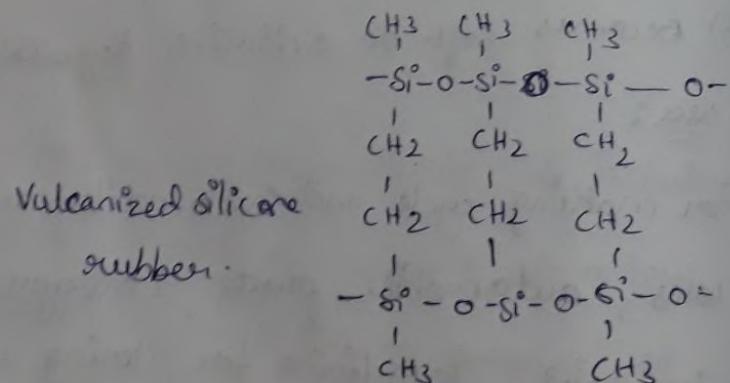
insulation for high voltage wires / cables.

* Silicone rubber:

⇒ preparation: Dimethyl silicone dichloride undergoes hydrolysis to form dimethyl silanol which is unstable and undergoes condensation to give dimethyl siloxane. The polymerisation of dimethyl siloxane produces silicone rubber which can be vulcanized in presence of organic peroxides.



Silicone rubber
peroxide ↓ Vulcanisation



⇒ properties:

- 1) stable and remain flexible in temperature range of $90-250^\circ\text{C}$.
- 2) Resistant to sunlight, weathering, boiling water, dil acids / bases
- 3) unaffected by ozone and oxygen
- 4) At high temperature decomposes to give silica.



⇒ uses: used in manufacture of tyres for fighter aircrafts, search lights, aircraft engine, wire and cable insulation. In preparing lubricants, paints and coatings, used as adhesive, for making artificial heart valves, transfusion tubes and in plastic surgery, packaging material, tubes and gaskets.

* conducting polymers: A polymer that can conduct electricity is called as conducting polymer. These polymers exhibit the property of conduction due to the presence of extensive conjugation in the backbone. i.e. presence of alternate π -bonds. The p-orbitals of adjacent carbon atoms overlap to form π -bonding molecular orbitals (BMO) and π^* -antibonding molecular orbitals ($ABMO$). These molecular orbitals spread over the entire length of polymer chain. The BMO are similar to valence band in metals and $ABMO$ similar to the conduction band. When a potential is applied electrons get excited from valence bond to conduction band and as they become mobile they conduct electricity.

* Types of conductivity

* Classification of conducting polymers:

conducting polymers are broadly classified into two types

- ① Intrinsically conducting polymers
- ② Extrinsically conducting polymers.

→ Intrinsically conducting polymers: These polymers have extensive conjugation in the backbone. They are further divided into 2 types

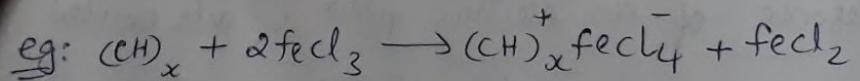
① Undoped conducting polymers: These polymers contain conjugated πe^- which increase their conductivity. The overlapping of conjugated πe^- over the entire ~~the~~ backbone.

Result in formation of valence band as well as conduction band which extend over the entire polymer molecule. The bands are separated by a significant band gap. In presence of an electric field e^- gets excited and become mobile in the conduction band.

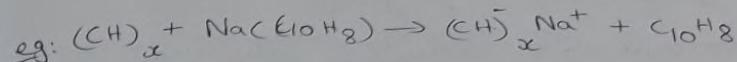
e.g.: polyacetylene, polypyrrole, polyaniline etc...

* Doped conducting polymers: These polymers have Tr^- in their backbone and their conductivities are increased by doping. Here Doping means creating a positive or negative charge on the polymer backbone either by oxidation or reduction. Oxidation gives rise to p-doping and reduction gives rise to n-doping. Doping increases the surface ~~conducting~~ conduction of polymer. Doping is carried out by exposing a polymer to a doping agent in either gaseous or solution phase.

* p-doping: Is generally done with Lewis acids which extract an e^- from the polymer due to which it gets oxidised and acquires +ve charge



* n-doping: The polymer is treated with Lewis bases which reduces the polymer as a result of which it acquires -ve charge



→ Extrinsically conducting polymers: In these polymers conductor is due to the presence of ~~some~~ externally added substance. They are of 2 types:

① Conductive element filled polymers: The polymer does not conduct electricity itself. Fillers like carbon black, metallic fibers and metallic oxides are added to the polymer after which they conduct electricity.

eg: ① carbon black filled polypropylene

② Blended conducting polymers: These are obtained by adding or blending a conventional polymer with a conductive polymer such polymers possess better physical, mechanical and chemical properties.

and can be easily processed.

e.g: polyaniline + polystyrene

polyaniline + polyethylene oxide.

③ co-ordination conducting polymers:

(Inorganic polymer)

It is a charge transfer complex containing polymer obtained by combining a metal atom with a polyderlate ligand. Although the degree of polymerisation is small yet they exhibit corrosion characteristics.

* polyacetylene:

Polyacetylene is a simplest organic ~~polymer~~

~~isotropic~~ intrinsic conducting polymer

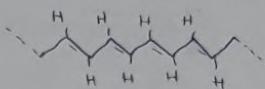
repeating unit $-C_2H_2-$. It exists as a flat molecule with bond angle of 120° .

It contains long ~~radii~~ with bond angle

of chain of carbon atoms with alternate single and double bonds. Polyacetylene

exists in cis and trans form where trans polyacetylene is thermodynamically

more stable than cis form



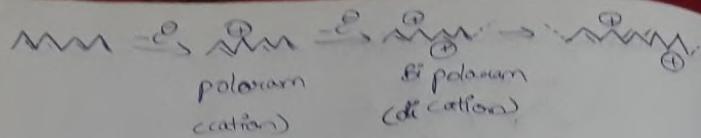
Trans poly acetylene

* Mechanism of conduction in polyacetylene: Polyacetylene is a weak semiconductor-type polymer but when it is doped its conductivity increases a million times making it a good conductor like metals.

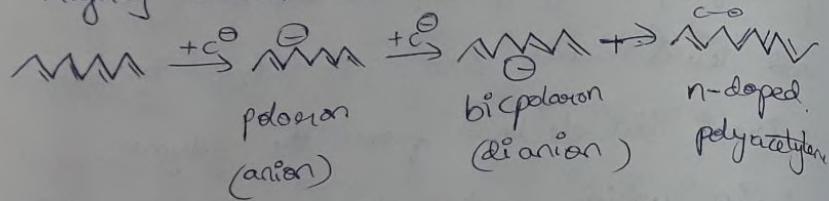
* p-doping: When polyacetylene is subjected to p-doping using p-dopants like halogens and Lewis acids (BF_3 , I_2 , Cl_2). They extract an electron from the polymer chain which makes the chain ~~cation~~ cation and the acceptor as anion.

p-doped polyacetylene retains its conductivity even after exposure to air for several days.





* n-doping: for ~~for~~ n-doping, Lewis bases and Alkali metals (Li , Na , K) are used when n-dopants are added -ve charge is created on polymer backbone as it becomes anionic and the donor becomes cationic. The doping increases the conductivity but n-doped polyacetylene are highly sensitive to air and moisture.



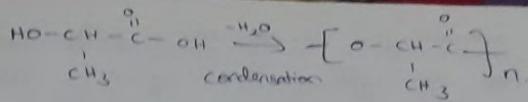
* Application of conducting polymers:

- 1) Making rechargeable batteries which are button sized, light in weight and long lasting.
- 2) Making membrane in ion exchange resins.
- 3) Used for designing artificial muscles, artificial nerves and brain cells.
- 4) Used in making analytical ~~sens~~ sensors for pH , heat, O_2 etc ...
- 5) controlled release of drugs in cancer treatment.
- 6) photo conducting polymers are used in graphic display
- 7) Ink for pointing circuits.
- 8) used in battery fuel and cell technology.
- 9) used in solar cells, diodes and transistors.
- 10) Electromagnetic screening materials.
- 11) wirings in aircraft and aerospace components.

* Bio-degradable polymers: Bio-degradation means the enzymatically promoted breakdown of a polymer caused by micro organisms such as bacteria, fungi, algae etc. The extent to which a polymer degrade into small fragments is called as degree of bio-degradation.

* Polylactic acid (PLA)

PLA is a thermo plastic polyester made from lactic acid which is a natural molecule widely used in food preserving and flavouring agents. Lactic acid can be synthesized from microbial fermentation of sugars from potato, starch, corn, sugar and other dairy products. This lactic acid undergoes fermentation and condensation to form ~~the~~ polylactic acid.



Lactic acid

Polylactic acid

* Properties:

- 1) PLA can be processed into fibre and films like other thermoplastics.
- 2) Water sensitive and degrade slowly by hydrolysis. ~~Brittle in nature~~
- 3) Brittle in nature.
- 4) Bio-degradable non-toxic and eco-friendly.
- 5) Melting temp can be increased from 40-50°C and heat deflection temp can be increased from -60°C to 190°C by blending it with poly D-lactide (PDLA).

* Advantages:

- 1) Lactic acid is the raw material for production of ~~bio~~ biodegradable lactide polymers.

② possess advantages over other polymers due to its strength, thermoplastic nature, biocompatibility and availability from renewable source.

③ Biodegradable blends are prepared from PLA mixed with other polymers which improves the biodegradability.

* Degradation of PLA:

PLA degrades quickly to CO_2 & H_2O (CO_2 , CH_4 and H_2O) under high temp and high humidity by ~~hydrolysis~~ undergoing hydrolysis followed by bacterial attack on the fragmented residue. The high molecular weight polymer is hydrolysed to low molecular weight oligomers.

* Application of PLA:

- 1) packaging materials, paper coatings and disposable articles.
- 2) used in biomedical application like ~~stents~~ stent, dialysis and drug delivery devices.
- 3) Medical implants in form of anchors, screws, plates, pins, rods, mesh as (It breaks inside the body in 6 months to 2 years).
- 4) can be manufactured in form of fibers, disposable garments and diapers, upholstery and other hygiene products.

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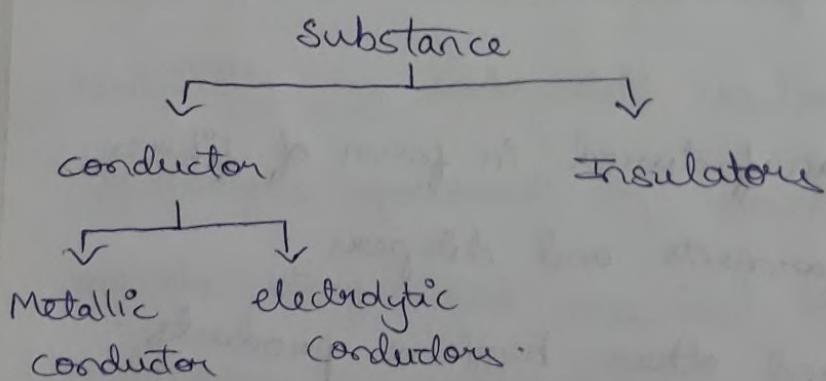
UNIT - I

Electrochemistry

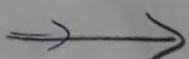
* Definition: It is the branch of chemistry which deals with the study of chemical reactions brought about by electrical energy.

It is the study of processes involved in interconversion of electrical energy and chemical energy.

* Types of conductors:



* Differences b/w metallic and electrolytic conductors:



Mechanism of electrical conduction

- * Electrolytic conduction: Electrolysis is the process of decomposition of an electrolyte by passage of electric current. An electrolytic cell consists of an electrolytic solution in which two electrodes are immersed, which are connected to the terminals of a battery such that anode is connected to the positive terminal and cathode to the negative terminal.

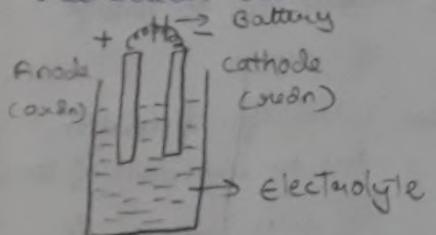
Metallic conduction

- 1. Passage of electricity is due to flow of electrons.
- 2. No chemical decomposition of the substance
- 3. No transfer of matter.
- 4. With increase in temperature conductance decreases.
- 5. Transfer of matter due to movement of ions.
- 6. With increase in temperature conductance also increases.

Electrolytic conduction

- 1. It is due to movement of ions towards oppositely charged electrodes.
- 2. Chemical decomposition occurs due to passage of current.

Anions with ' $-ve$ ' charge migrate to anode and cations with ' $+ve$ ' charge migrate to cathode. Therefore, at anode oxidation takes place (loss of e^-) and at cathode reduction occurs. (gain of e^-)



Electrolytic cell.

* Galvanic cell (or) electrochemical cell

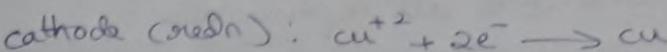
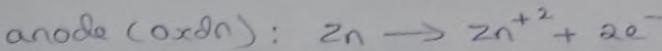
An Electrochemical cell converts chemical energy to electrical energy i.e., The electric current is generated by a spontaneous redox reaction.

Eg: Daniel cell: It is a typical voltaic cell which consists of zinc rod as anode.

Placed in zinc sulphate soln. and copper rod as cathode placed in copper sulphate soln. The two electrodes are joined together by a wire to galvanometer and a salt bridge is introduced

to connect the two solutions. The flow of electrons is from anode to cathode. But the flow of current is from cathode to anode.

* All reactions:



* Cell diagram:



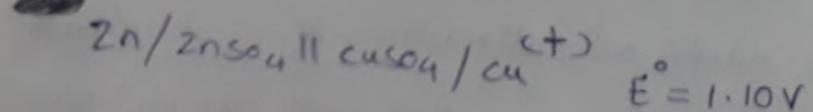
Galvanic cell

* Cell EMF: The flow of current through the circuit is determined by the push of e^- at anode and attraction of e^- at cathode. This the driving force that sends the electron through circuit and is called as cell potential (or) electromotive force (emf) which is measured as cell voltage in volts.

$$\begin{aligned}
 \text{cell} &= E_{\text{cathode}} - E_{\text{anode}} \\
 &= E_{\text{Cu}} - E_{\text{Zn}} \\
 &= +0.34 - (-0.76) \\
 &= +0.34 + 0.76 \\
 &= +1.10\text{V}
 \end{aligned}$$

* Cell notation (or) Cell representation:

Cell notation is the symbolic representation of an electrochemical cell. A single vertical line represents phase boundary between the metal electrode and the electrolyte solution. A double vertical line represents the salt bridge. The anodic half cell is written on the left and the cathodic half cell on the right. The value of ~~emf~~ emf of a cell is written to the cathodic right side.



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

* Salt bridge: It is an inverted U-shaped tube open at both the ends containing salts like $\text{KCl}/\text{NH}_4\text{NO}_3$ in agar-agar gel.

* functions of salt bridge:

- 1) connects the two solution in a galvanic cell and prevents intermixing of solution.
- 2) prevents the accumulation of charges around the electrodes.
- 3) Allows the flow of anions from the $\text{Cu}^{(+)}$ cathodic solution to anionic solution.
- 4) It maintains the electro neutrality of the solution and completes the circuit.

* Differences between electrolytic and galvanic cell:

Galvanic cell	Electrolytic cell
1. Spontaneous redox reactions occur.	1. Non-spontaneous redox redox reaction.
2. Electrical energy is generated by redox reaction.	2. Electrical energy brings about the chemical reaction.
3. Chemical energy is converted to electrical energy.	3. Electrical energy is converted to chemical energy.

4. Anode is positive electrode and cathode is the electrode.

5. Half cells are connected by a salt bridge.

6. Application lies in batteries.

4. Anode is the electrode and cathode is -ve electrode.

5. electrodes are kept in the same electrolytic solution.

6. Application lies in electroplating and purification of Cu

* Electrode potential: The electrode potential is the tendency of an electrode to lose (or gain electrons when in contact with its own ion in solution). The elements having tendency to lose electrons and get oxidised are set to possess oxidation potential and the one's having tendency to gain electrons and get reduced possessed reduction potential.

i) Standard electrode potential: (E°)

It is the potential developed at electrode-electrolyte interface when a metal electrode is in contact with its soluble

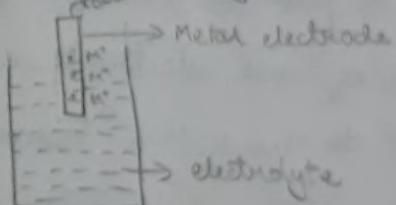
salt solution (i.e., electrolyte) having one molar concentration. At 25°C (or) 298K temp.

If gaseous substance like H_2 , Cl_2 , O_2 etc... are involved then they act at one atmospheric pressure.

(ii) Single electrode potential: (CE)

It is the potential developed at electrode-electrolyte interface when the concentration of electrolyte is other than one molar, pressure of gas

other than one atmosphere and the temperature may (or) may not be 25°C .



Single electrode.

* (iii) Standard reduction potential: (SRP)

The potential developed at the electrode-electrolyte interface when a metal electrode gains electrons and gets reduced when in contact with its soluble salt solution having one molar concentration at 25°C (or) 298K temperature. And if gases are involved

they act at one atmospheric pressure.

* Determination of electrode potential:

The absolute value of single electrode potential can never be measured because either oxidation nor reduction can take place independently. However, it is possible to measure the potential difference between two electrodes. By combining them to form a complete cell with the help of a potentiometer. By fixing the potential of one electrode as zero. It is possible to assign a numerical value to the other electrode. Thus, electrode potential can be measured with respect to a reference electrode. For this purpose standard ~~standard~~ hydrogen electrode (SHE) is used. As $E^{\circ}_{\text{SHE}} = 0.0V$ The half cell potential of other electrodes would be the total E_{cell} measured on the potentiometer.

If these measurements are carried out under standard conditions. Then it is called standard electrode potential.

* All single standard electrode potentials are referred to as potentials on hydrogen scale.

* Electrochemical Series: The series in which the reduction potentials of various electrodes have been arranged in increasing order downwards. with hydrogen electrode taken as zero volts is termed as electrochemical series. The electrodes lie above hydrogen have $-E^{\circ}$ values. And the ~~other~~ ones lie below hydrogen have $+E^{\circ}$ values. All the electrode potentials are referred to as potentials on hydrogen scale.

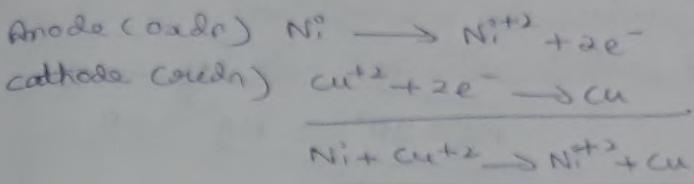
* Applications of electrochemical series:

- 1) The elements lie above hydrogen higher up in the series with -SRP values act as strong ~~strong~~ reducing agents.

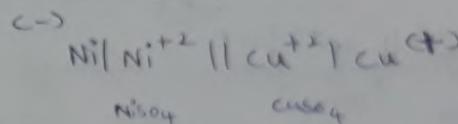
- 2) The species higher up in the series with lower SRP acts as anode.
 3) The elements above hydrogen can easily displace hydrogen from acids to release hydrogen gas.
 4) Electrochemical series can be used to predict the spontaneity of any redox reaction.
 5) The series helps to decide anodic (oxy)
~~cathodic~~ cathodic codings to prevent corrosion
- | <u>Element</u> | <u>E_{SRP}° (Volts)</u> |
|----------------|---|
| Li | -3.04 |
| K | -2.9 |
| Ca | -2.8 |
| Na | -2.71 |
| Mg | -2.37 |
| Al | -1.66 |
| Zn | -0.26 |
| Fe | -0.44 |
| H ₂ | 0.0 |
| Cu | +0.34 |
| Ag | +0.798 |
- Noble

(i) Write cell notation, cell reaction and cell EMF using Cu and Ni
 $E^{\circ}_{Cu^{+2}/Cu} = +0.34V, E^{\circ}_{Ni^{+2}/Ni} = -0.24V$
 higher SRP, cathode lower SRP, anode

* Cell reactions:



* Cell Notation:



* Cell EMF:

$$E_{cell} = E_{cathode} - E_{anode}$$

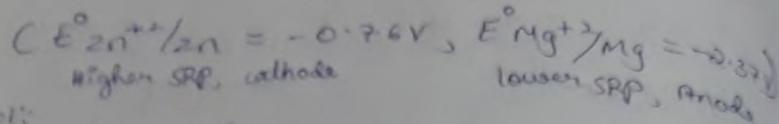
$$= E_{Cu} - E_{Ni^{\circ}}$$

$$= +0.34 - (-0.24)$$

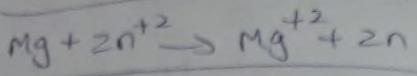
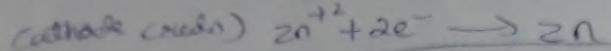
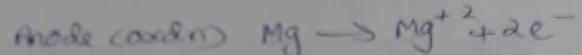
$$= +0.34 + 0.24$$

$$= +0.58 V.$$

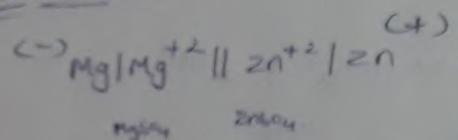
Q) Write cell reaction, cell notation and cell EMF using Zn and Mg.



Sol:
* cell reactions:



* cell notation:



* cell EMF:

$$E_{\text{cell}} = \text{E}_\text{cathode} - \text{E}_\text{anode}$$

$$= E_{Zn} - E_{Mg}$$

$$= -0.76 - (-0.37)$$

$$= -0.76 + 0.37$$

$$= +1.61V$$

* Nernst equation: The Nernst equation gives relation between cell reaction and cell EMF. It helps to study the variation of electrode potential with concentration of metal ions in solution. Nernst equation establishes relationship between single electrode potential and standard electrode potential.

for a general chemical reaction,



Nernst equation is derived from ~~Nernst's~~ van't Hoff's isotherm

$$\Delta G_i = \Delta G_i^\circ + RT \ln Q \dots \textcircled{1}$$

where ΔG_i = change in gibbs free energy

ΔG_i° = change in std. gibbs free energy.

R = gas constant $8.314 \text{ J/K mol}^{\circ}$

T = Temperature in Kelvin

$$\ln Q = \ln K_{\text{eq}} = \frac{[P]}{[R]} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$\Delta G_1 = -nFE$ and $\Delta G_1^\circ = -nFE^\circ$
Substituting ΔG_1 and ΔG_1° for eq ①

$$\Delta G_1 = \Delta G_1^\circ + RT \ln K_{eq}$$

$$-nFE = -nFE^\circ + RT \ln K_{eq}$$

Dividing throughout by $-nF$

$$\frac{-nFE}{-nF} = \frac{-nFE^\circ}{-nF} + \frac{RT \ln K_{eq}}{-nF}$$

$$E = E^\circ - \frac{RT \ln K_{eq}}{nF}$$

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{cell} = E_{cell}^\circ - \frac{2.303 \frac{RT}{nF} \log}{\frac{[C]^c [D]^d}{[A]^a [B]^b}}$$

Basic nearest equation.

where

E = single electrode potential

E° = standard electrode potential

F = faraday (96,500 C)

n = no. of e^- transfer

Substituting $R = 8.314 \text{ J}$ and $F = 96,500 \text{ C}$ at 25°C i.e. 298 K

$$E_{cell} = E_{cell}^\circ - \frac{0.0591}{n} \cdot \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

at 298K
at 25°C
only.

Anode (oxdn) $\rightarrow M \rightarrow M^{+n} + ne^-$

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

concentration for metal $\rightarrow 1$,
gas \rightarrow standard pressure
 $[M] = 1$

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

* cathode: (Redn) $M^{+n} + ne^- \rightarrow M$

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

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

* Daniel cell: $Zn + Cu^{+2} \rightleftharpoons Zn^{+2} + Cu$ $n=2$

$$E_{cell} = E_{cell}^\circ - \frac{0.0591}{n} \cdot \log \frac{[Zn^{+2}][Cu]}{[Zn][Cu^{+2}]}$$

$w, Zn = 1$

$$= E_{cell}^\circ - \frac{0.0591}{n} \cdot \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

* Applications of Nernst equation:

- 1) used to study the effect of electrolyte concentration on electrode potential.
- 2) used to calculate the single electrode potential of a half cell.
- 3) used to for calculation of cell potential under non-standard conditions.
- 4) The pH of a solution can be calculated from nernst equation using

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

- 5) It is possible to determine the unknown concentration of one of the species in a cell. If E_{cell}° and the concentration of other species is known.
- 6) It is used to find the valency of an ion or the number of electrons involved in a reaction.
- 7) It gives equations for potentiometric and pH metric experiments

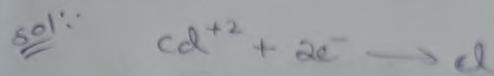
* for a spontaneous process $\Delta G < 0$ and $\Delta E > 0$ ~~at equilibrium~~

At equilibrium $\Delta G = 0$ $\Delta E = 0$

* for a Non-spontaneous process $\Delta G > 0$ and $\Delta E < 0$.

① calculate ΔG° for standard cadmium cell at 298K if $E^{\circ}_{\text{cadmium}} = +1.02 \text{ V}$

$$E_{\text{Cd}^{+2}/\text{Cd}}^{\circ} = +1.02 \text{ V}$$

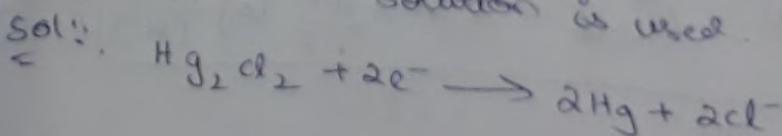


$$\Delta G^{\circ} = -nFE^{\circ}$$

$$= -2 \times 96500 \times 1.02$$

$$= -196860 \text{ J/mol}$$

② calculate the electrode potential for calomel electrode at 298K if $E_{\text{SCE}}^{\circ} = 0.280 \text{ V}$ and 0.1M KCl solution is used.



$$E_{\text{SCE}} = E_{\text{SCE}}^{\circ} - \frac{0.0591}{n} \log[\text{Cl}^-]^2$$

$$= 0.280 - \frac{0.0591}{2} \log[0.1]^2$$

$$= 0.280 - \frac{0.0591}{2} \times 2 \log 0.1$$

$$= +0.8391 \text{ V}$$

$$E_{\text{cell}} = +0.8391 \text{ V}$$

Q calculate the single electrode potentials of copper at 25°C if $E_{\text{Cu}^{+2}/\text{Cu}}^{\circ} = +0.34$, and 0.01 M CuSO_4 solution is taken

$$\begin{aligned} \text{SOL: } E_{\text{Cu}^{+2}/\text{Cu}} &= E_{\text{Cu}^{+2}/\text{Cu}}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[\text{Cu}^{+2}]} \\ &= +0.34 - \frac{0.0591}{2} \log \frac{1}{0.01} \\ &= 0.8609 \text{ V.} \end{aligned}$$

Q calculate the EMF of Daniell cell if the ratio of concentration of Zn^{+2} : Cu^{+2} = 0.1 At 30°C if $E_{\text{cell}} = 1.10 \text{ V}$

$$\text{SOL: } E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log \left(\frac{[\text{P}]}{[\text{R}]} \right) \left(\frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]} \right)^2$$

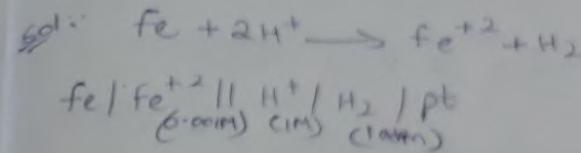


$$\begin{aligned} &= 1.10 - \frac{2.303 \times 8.314 \times 303}{96,500 \times 2} \times \log (0.01) \\ &= 1.130 \text{ V.} \end{aligned}$$

$$= 1.10 - \frac{2.303 \times 8.314 \times 303}{96,500 \times 2} \times \log (0.01)$$

$$= 1.130 \text{ V.}$$

Q calculate the EMF of the following cell at 25°C If $E_{\text{Fe}^{+2}/\text{Fe}}^{\circ} = -0.44 \text{ V}$ and $E_{\text{H}^{+}/\text{H}_2}^{\circ} = 0.0 \text{ V}$



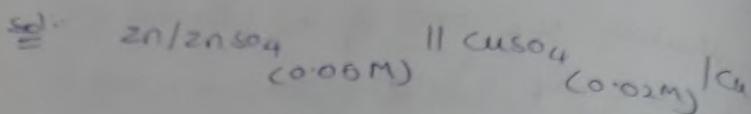
$$E_{\text{cell}} = E_{\text{C}} - E_{\text{A}}$$

$$\begin{aligned} &= E_{\text{H}^{+}/\text{H}_2}^{\circ} - E_{\text{Fe}^{+2}/\text{Fe}}^{\circ} = 0 - (-0.44) \\ &= +0.44 \text{ V.} \end{aligned}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Fe}^{+2}]}{[\text{H}^{+}]^2}$$

$$\begin{aligned} &= 0.44 - \frac{0.0591}{2} \log \frac{0.001}{(1)^2} \\ &= 0.5286 \text{ V.} \end{aligned}$$

Q) calculate the EMF of the following cell at 25°C if $E_{Zn^{+2}/Zn}^{\circ} = -0.76\text{ V}$
and $E_{Cu^{+2}/Cu}^{\circ} = +0.34\text{ V}$



$$E_{\text{cell}} = E_{\text{c}}^{\circ} - E_{\text{n}}^{\circ} = E_{\text{Cu}}^{\circ} - E_{\text{Zn}}^{\circ}$$

$$= +0.34 - (-0.76)$$

$$= +1.10\text{ V}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]}$$

$$= +1.10 - \frac{0.0591}{2} \log \frac{[0.05]}{[0.02]}$$

$$= 1.0882\text{ V.}$$

* Reference electrodes: It is an electrode of STD potential with which we can compare the potential of other electrodes. Its reaction does not change the EMF of the cell.

→ reference electrodes are broadly classified into 2 types

(a) primary reference electrode: [SHE]

is a primary reference electrode which is used for measurement of all potentials, the potential of SHE is taken as 0° at all temp. but it is quite difficult to set up Hydrogen electrode at 1 atm pressure with [1M] HCl concentration. Also it cannot be used in solutions containing redox systems. It gets poisoned by mercury, arsenic and oxidising agents like $\text{Fe}^{+3}/\text{MnO}_4^-$ / $\text{Cr}_2\text{O}_7^{2-}$ etc. Hence it cannot be used in solutions containing these ions.

(b) secondary Reference electrode: To overcome the difficulties encountered by SHE secondary reference electrode like calomel electrode/glass/quinhydrone electrodes are used.



* Reversible and irreversible cell: A cell is said to be reversible if it satisfies the three conditions when connected to an external source of EMF acting in the opposite direction. If any one of the conditions is not satisfied then it is called as an irreversible cell.

- i) If $E_{\text{ext}} > E_{\text{cell}}$ then current flows from the external source and reactions occur in the cell.
- ii) If $E_{\text{ext}} < E_{\text{cell}}$ then current flows from the cell and reactions occur in the reverse direction.
- iii) If $E_{\text{ext}} = E_{\text{cell}}$ then no current flows in the circuit and no chemical reaction takes place.

* Types of Reversible electrodes:

Metal - metal ion electrode.

e.g: Daniell electrode.

2) Metal - metal ⁱⁿsoluble electrode.
e.g: calomel electrode.

3) Gas ion electrode.

e.g: Hydrogen electrode.

4) Redox electrode.

e.g: quinhydrone.

5) Ion selective electrode.

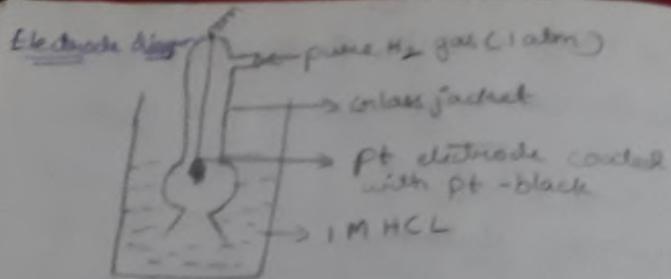
e.g: iodine electrode.

6) Metal amalgam electrode.

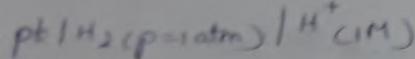
~~7)~~

* standard hydrogen electrode: (gas-ion electrode)

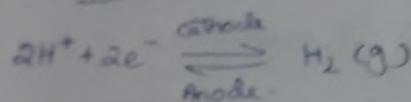
SHE consists of platinum electrode coated with pt black. immersed in 1M HCl solution. At 25°C which is welded in a glass jacket having a side tube for entry of H_2 gas. The H_2 gas is bubbled at (1 atm) pressure through the glass ~~jacket~~ jacket over the platinum electrode which passes into the solution.



Electrode representation:



Electrode reaction:



Electrode EMF:

$$\text{At std condition } E_{2H^+/H_2}^\circ = 0.0V$$

Non std. condition

$$E_{2H^+/H_2} = E_{2H^+/H_2}^\circ - \frac{0.0591}{n} \log \frac{[H_2]}{[H^+]^2}$$

$$= 0 - \frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$

$$= 0 + \frac{0.0591}{2} \cdot 2 \log [H^+]$$

$$= 0.0591 \cdot \log [H^+]$$

$$\boxed{E_{2H^+/H_2} = -0.0591 \rho_H}$$

* The electrode is sensitive to H^+ ions.

* Saturated calomel electrode: (SCE)

[Metal-metal insoluble salt electrode]

~~SCE~~ calomel electrode consists of Hg and $Hg_2Cl_2 + Hg$ paste in contact with KCl solution and pt wire for electrical contact.

Electrode diagram:



calomel electrode consists of a tube in which a pt wire is dipped into a mercury layer placed at the bottom covered with the paste of $Hg_2Cl_2 + Hg$ (calomel paste) which is in contact with KCl solution. The potential of the calomel electrode depends on the concentration of KCl used.



(i) saturated calomel electrode - sat. KCl is used - $E_{SCE}^{\circ} = 0.242V$

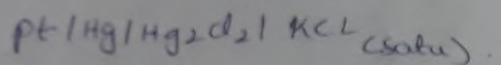
(ii) for normal calomel electrode - 1M KCl solution is used.

$$E_{NCE}^{\circ} = 0.282V$$

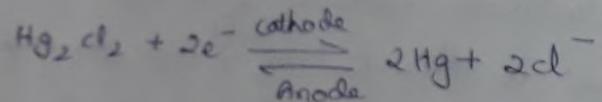
(iii) for decinormal calomel electrode - 0.1M KCl solution is used.

$$E_{DNCE}^{\circ} = 0.336V$$

Electrode representation:



Electrode reaction:



Electrode EMF:

$$E_{SCE} = E_{SCE}^{\circ} - \frac{0.0591}{n} \log \frac{[Hg]^2 [Cl^-]}{[Hg_2Cl_2]}$$

$$= 0.242 - \frac{0.0591}{2} \log [Cl^-]^2$$

$$= 0.242 - \frac{0.0591}{2} \cdot 2 \log [Cl^-]$$

$$E_{SCE} = 0.242 - 0.0591 \log [Cl^-]$$

* electrode is reversible to Cl^- ions.

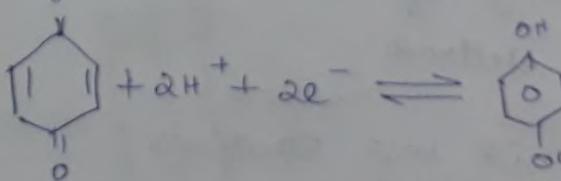
* Advantages:

- 1) simple to construct.
- 2) free from surface sensitivity.
- 3) Results are stable over a long period of time even if temperature changes.

Quinhydrone electrode: (redox electrode)

quinhydrone is 1:1 molar / equimolar mixture of quinone and hydroquinone which exist in equilibrium in presence of H^+ ions.

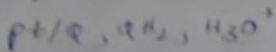
The electrode consists of Pt electrode dipped in acid test solution which is saturated with quinhydrone. The $E_{Q/QH_2}^{\circ} = 0.6996$



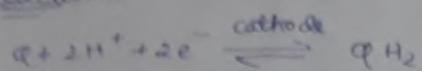
Quinone.

Hydroquinone

Electrode representation:



electrode reaction:



electrode EMF:

$$\begin{aligned} E_{\text{H}_2/\text{H}_2} - E^{\circ}_{\text{H}_2/\text{H}_2} &= \frac{0.0591}{2} \log \frac{[\text{H}_2]}{[\text{H}]^2} \\ &= 0.6996 - 0.0591 \log \frac{1}{[\text{H}]^2} \end{aligned}$$

$$E_{\text{H}_2/\text{H}_2} = 0.6996 - 0.0591/\text{pH}$$

The electrode is reversible to H^+ ions i.e. potential depends on pH of soln.

Advantages of quinhydrone:

i) Simple to set up.

ii) Reversibility eqn is achieved faster than hydrogen electrode.

iii) Best for acid base titrations.

iv) Can be used in presence of ions of many metals.

* Disadvantages:

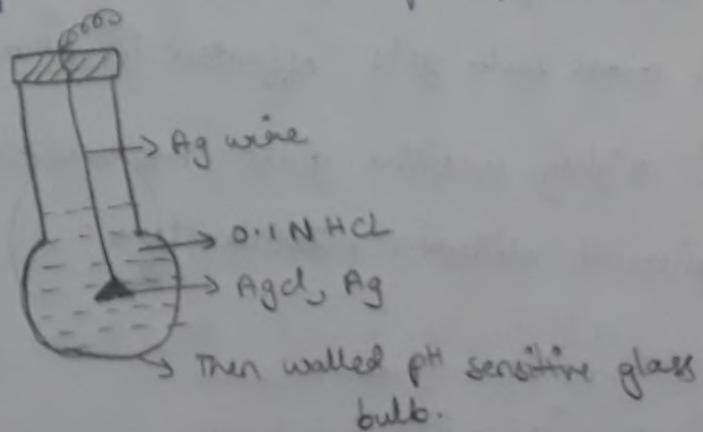
i) At high pH emf value fluctuates.

ii) Cannot be used in solutions containing redox system.

iii) Works well in solutions with pH less than 8.

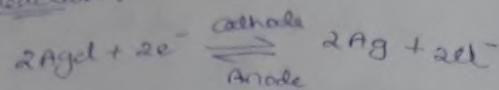
* Glass electrode: (Ion-selective electrode)

It consists of thin walled pH sensitive glass bulb at the lower end containing AgCl coated Ag electrode (on pt wire) dipped in 0.1N HCl solution. When this electrode is placed in a test soln. potential develops across a glass membrane due to the pH changes inside and outside the membrane which helps to measure the pH of solution.



Electrode representation: oxals/HCl ($\text{Ca}_2\text{O}_4\text{NO}_2$) / Ag/Ag^+

Electrode reaction:



Electrode EMF:

$$E_{\text{Cf}} = E_{\text{Cf}}^\circ - 0.0591 \text{ pH}$$

Advantages:

- i) Simple and easy to use.
- ii) eqn is rapidly achieved.
- iii) accurate results.
- iv) Not easily poisoned.
- v) can be used in turbid coloured and colored solutions.

Disadvantages:

- i) glass bulb gets effected in pH above 12.
- ii) slightly sensitive glass membrane requires spherical electrodes potentiometry.



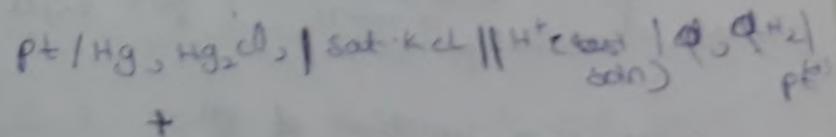
Determination of pH of a solution using quinhydrone electrode
(potentiometer acid-base titrations)

reference electrode: (ANODE) - SCE acts as anode. It consists of Hg metal covered with $\text{Hg}_2\text{Cl}_2 + \text{Hg}$ paste in contact with saturated KCl solution and a pt wire for electrical contact $E_{\text{SCE}}^\circ = 0.242 \text{ V}$.

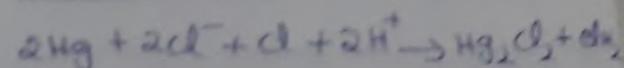
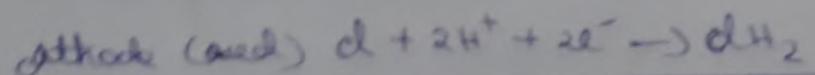
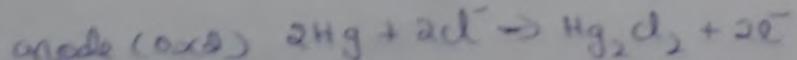
2) Indicator electrode: (cathode) quinhydrone is used as cathode. It is 1:1 equimolar mixture of quinone and hydroquinone.

$$E_{\text{Q/H}_2}^\circ = 0.6996 \text{ V}$$

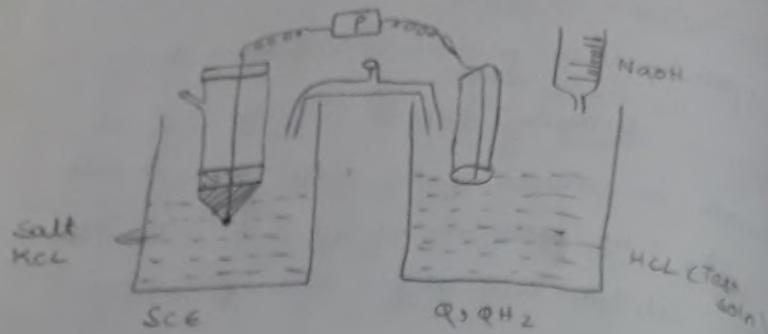
3) All notation:



4) All reactions:



Cell diagram:



$$\begin{aligned} \text{Cell EMF: } E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{Q_3 QH_2} - E_{\text{SCE}} \\ &= (0.6996 - 0.0591 \text{ pH}) - 0.242 \end{aligned}$$

$$E_{\text{cell}} = 0.458 - 0.0591 \text{ pH}$$

$$\boxed{\text{pH} = \frac{0.458 - E_{\text{cell}}}{0.0591}}$$

pH ↑ $E_{\text{cell}} \downarrow$

E_{cell} is a function of pH.

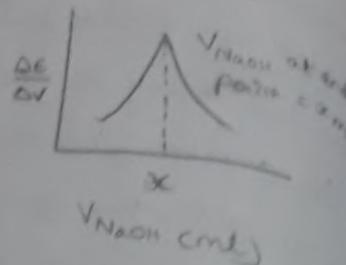
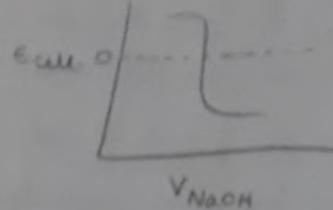


titration

* Titration: The H^+ test soln. is taken in a beaker and a few ml of quinhydrone is added. pt electrode is dipped into the soln. The base NaOH is taken in the burette and in another beaker SCE is placed in sat KCl soln. The two half cells are connected by a salt bridge and the electrodes are connected to the terminals of the potentiometer. Initial EMF is noted before adding NaOH soln. As NaOH is added from the burette the EMF values gradually decrease but near the end point, sudden decrease in EMF occurs to the extent that the values change from +ve to -ve

This titration gives approximate V_{NaOH} required. To find the exact end point the titration is repeated by adding NaOH in 0.1 ml intervals in the vicinity of end point

Graphs:



2) The potential of Ag/AgCl electrode with respect to SCE is -0.022 V . Find the value of standard reduction potential of Ag/AgCl electrode.

$$\text{Sol: } E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E^{\circ}_{\text{Ag/AgCl}} - E^{\circ}_{\text{SCE}}$$

$$-0.022 = E^{\circ}_{\text{Ag/AgCl}} - 0.242$$

$$E^{\circ}_{\text{Ag/AgCl}} = +0.220\text{ V}$$

3) The EMF of a cell is 0.8089 V when SCE and quinhydrone are used to construct the cell. calculate the pH of the test solution. Also calculate the pH if the EMF is 0 .

~~$$\text{Sol: } \frac{pH}{0.458} = \frac{0.8089}{0.2640}$$~~

$$pH = \frac{0.458 - E_{\text{cell}}}{0.0891}$$

$$= \frac{0.458 - 0.3089}{0.0891}$$

$$= 2.62$$

$$\text{pH} = \frac{0.458 - 0.2640}{0.0891} = 3.28$$

~~$$\frac{14.496(0.0891)(0.2640)}{28.28} < 0.242$$~~

At $E_{cell} = 0$ then

$$pH = \frac{0.458 - 0}{0.0591} = 7.74$$

Sub-unit: BATTERIES

A battery is a device which transforms chemical energy into electrical energy. Depending on their recharging capacity, batteries are classified into primary, secondary and flow batteries.

i) primary battery: These are non-rechargeable cells which are meant for single use i.e., They are to be discarded after use.

It works only as a galvanic cell because the cell reactions are irreversible and electrical energy is obtained at the expense of chemical reaction. The battery becomes ~~dead~~ dead when the reactants get completely converted to products. These cells cannot be recharged.

e.g.: Dry cell



iii) secondary batteries / storage cells

These are rechargeable and meant for multi-cycle use. It behaves as electrolytic cell (charging) and as galvanic cell (discharging). The cell reactions can be reversed by external application of current in opposite direction. Secondary batteries can be used through a number of cycles of charging and discharging till the capacity is lost due to leakage *

(or) short circuit

* e.g.: ~~lead~~ Pb-acid battery ($Pb-H_2SO_4$)

Ni-Cd battery

Li-ion battery

iii) flow batteries: (fuel cells)

It is an electrochemical cell that converts the chemical energy of fuel and oxidant into electricity.

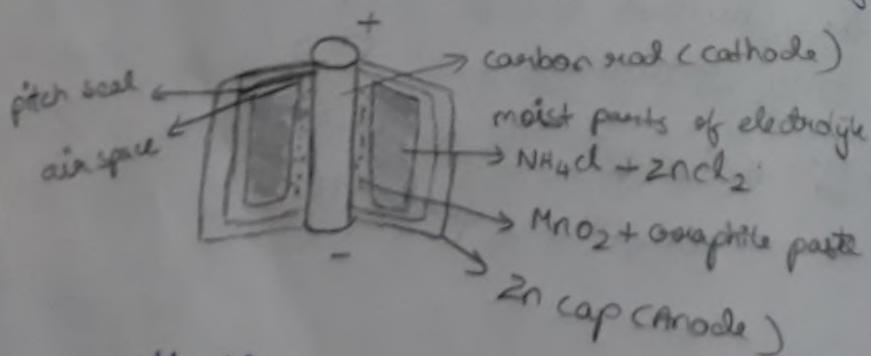
* e.g. ~~lead~~ H_2-O_2 fuel cell

CH_3OH-O_2 fuel cell.

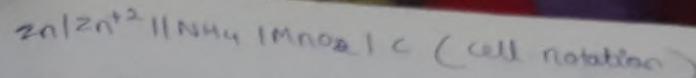
* Dry cell: (zinc-carbon battery) Leclanche

The dry cell is a primary battery which consists of zinc anode and carbon cathode. The outer container is made of zinc sheet as anode and a graphite rod with a metal cap acts as cathode.

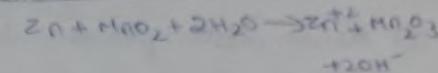
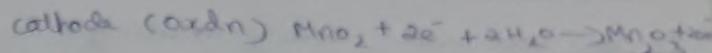
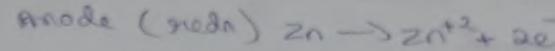
The cathode is surrounded by thick moist paste of MnO_2 + graphite. The outer layer consists of a paste of $\text{NH}_4\text{Cl} + \text{ZnCl}_2$ as electrolyte. To the electrolyte starch or methyl cellulose is added to make a thick paste so that the battery becomes stable against discharging. The entire set up is packed in polyethylene or card board material and a plastic coating is given to prevent any leakage from the battery.



All diagram



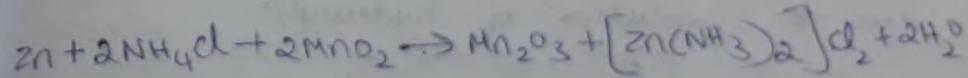
* all reactions:



secondary reactions: The OH^- ions produced at the electrode react with NH_4Cl to give ammonia which disrupts the flow of current. This is prevented by reacting NH_3 with ZnCl_2 to form a complex.



* overall reaction:



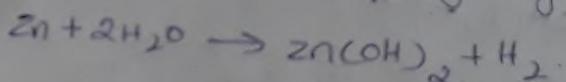
It is called as dry cell due to the absence of any mobile liquid.

* Advantages:

- 1) Maintains better voltage as current is withdrawn.
- 2) Low cost and readily availing.
- 3) Reasonable power density and ~~heat~~ reliable performance.
- 4) Gives Voltage of 1.5V
- 5) Zn does not readily dissolve in basic medium.

* Disadvantages:

- 1) Not suitable for high voltage applications.
- 2) Not rechargeable.
- 3) optimum temperature range is 20 to 40°C
- 4) ~~cell~~ self discharging takes place due to evolution of hydrogen.

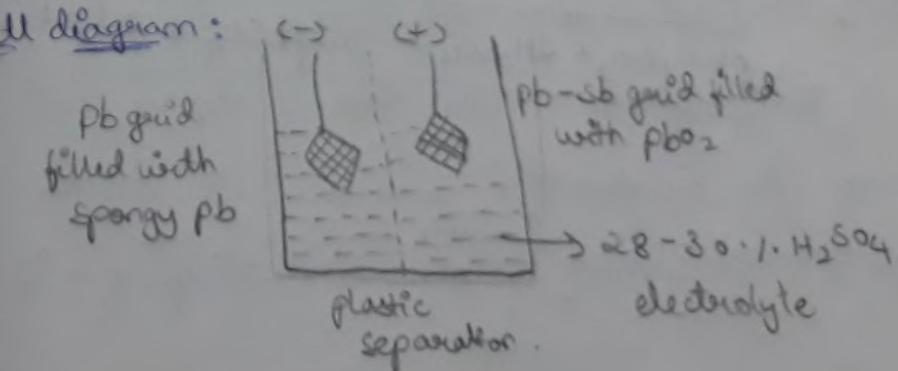


The cell runs down slowly even when not ~~used~~ in use.

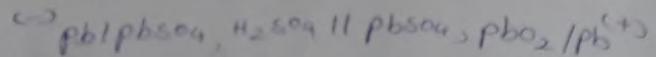
* Uses: used in calculators, portable electric and electronic devices, computers, watches, photographic equipments, Transistors, torches etc....

* Pb-acid battery: (secondary storage cell)
The Pb-acid battery is so called because the electrolyte is an acid and the electrode are lead plates. The anode is lead grid filled with spongy lead. while cathode is Pb-Sb grid filled with PbO_2 . And an inert porous material separates the two electrodes. The electrolyte is 28-30% H_2SO_4 (specific gravity = 1.2). The battery consists of 3 to 6 such cells joined together in series enclosed in side an ebonite case. Each cell gives the voltage of 2volts and 6 such cells can generate 12volts.

Cell diagram:



1. Cell action:

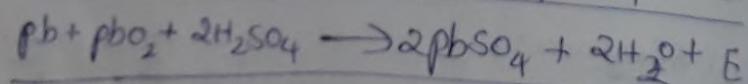
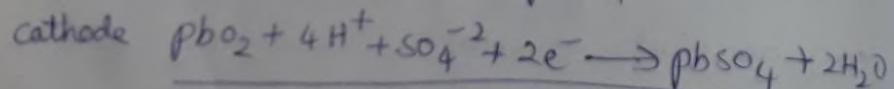
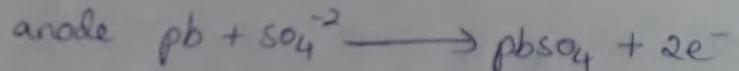


The EMF of the cell depends on the concentration of H_2SO_4 used. During discharge the density of the battery decreases from 1.2 g/c.c to 1g/c.c indicating the weakening of the battery.

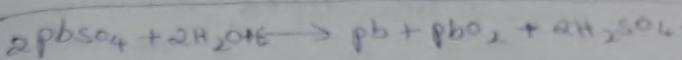
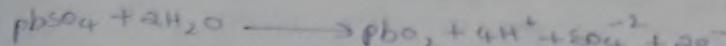
when the concentration of H_2SO_4 decreases to 5%,

battery is recharged by connecting it ~~to~~ to external source of EMF. During discharging the battery acts as an galvanic cell and during charging acts as an electrolytic cell.

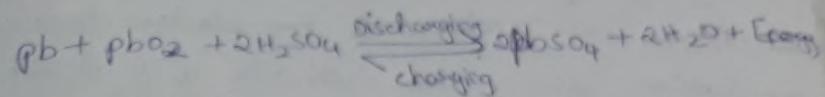
Discharging: (Galvanic cell)



Charging: (Electrolytic cell)



* Net reaction:



* uses: It is used in automobiles, ups, trains, electric vehicles, submarines, mines, hospitals, labs etc.

* Li-ion battery: The cell reactions in Li-ion battery involves the migration of Li-ions between the positive and negative electrode. There are no chemical changes at the electrodes (or) in the electrolyte concentration. In Li-ion batteries

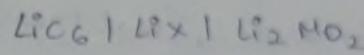
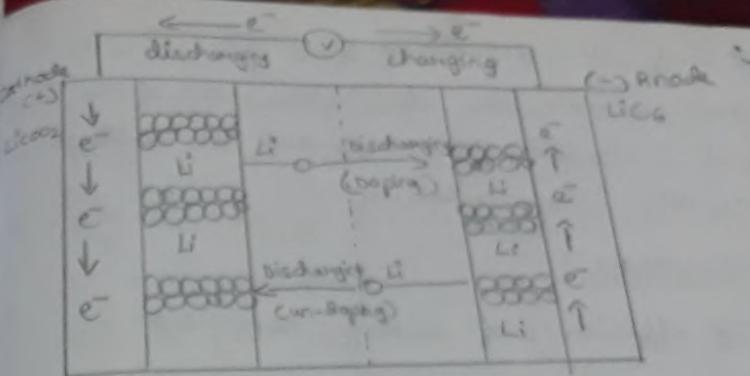
The anode is ~~not~~ carbon (or) graphite in which Li-ions are intercalated to form Li-graphite intercalated compound. (Li-GIC)

The cathode comprises of lithium metal oxide complexes like LiCoO_2 , LiMn_2 , LiNiO_2 . The electrolyte is complex lithium salt in solvents like LiPF_6 . A micro porous membrane acts as a separator between the anode and cathode. During charging of lithium ion battery, the Li^+ -ions are extracted by electrochemical oxidation from the cathode and doped by electrochemical reduction into Li_xMO_2 .

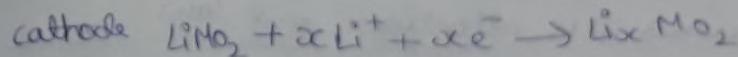
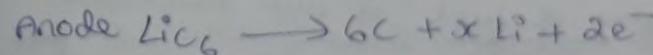
* cell notation:
 carbon anode | during discharging Li^+ -ions are extracted from anode by oxidation and inserted into cathode by reduction \rightarrow cell voltage = 3.6 - 3.7 V.

* Uses: widely used in mobile phones, laptops, video cameras, electric vehicles etc....

* cell diagram:



* cell reaction:



* Fuel cell: A fuel cell is a galvanic cell that converts the chemical energy of fuel (CH_3OH , H_2 , CH_4) and an oxidant (O_2/air) into electricity.

→ Advantages:

- 1) High efficiency of energy conversion.
- 2) silent operation therefore, no noise pollution.
- 3) free from vibration, heat transfer and thermal pollution.
- 4) waste products are harmless and eco-friendly.
- 5) Recharging of fuel is not required.
- 6) Requires less attention and low maintenance cost.
- 7) saves fossil fuels.

→ Disadvantages:

- 1) Initial cost is very high.
- 2) fuel in form of gases and oxygen needs to be stored in tanks under pressure.

3) power output is moderate.

4) for appreciable ~~less~~ voltage a battery of fuel cell must be available.

* Methanol-oxygen fuel cell: ($\text{CH}_3\text{OH}-\text{O}_2$)

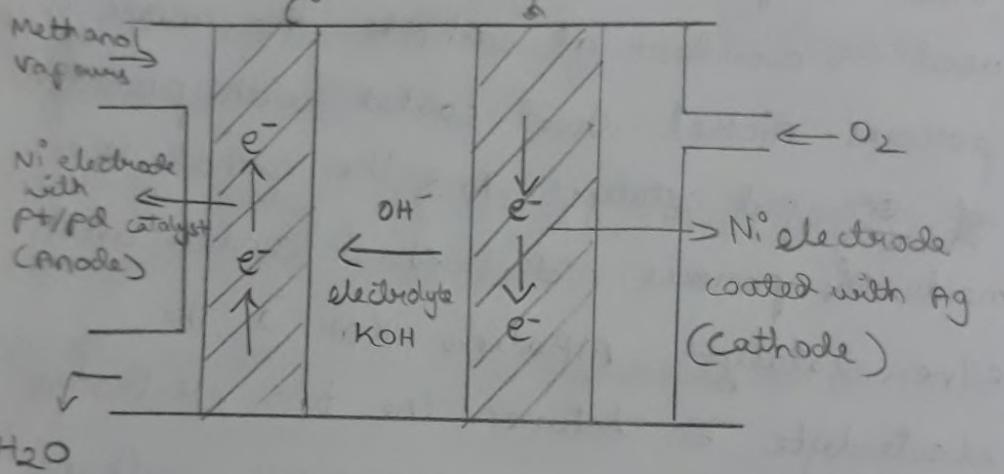
In $\text{CH}_3\text{OH}-\text{O}_2$ fuel cell. The methanol is used as fuel at anode and oxygen is used as oxidant at cathode. The anode is porous nickel sheet coated with platinum or pd catalyst and the cathode is made of porous nickel sheet coated with silver catalyst. Alkaline KOH is the electrolyte. In between the two electrodes for continuous supply of electricity methanol vapours are passed through anode and oxygen through cathode.

* Uses: (Applications)

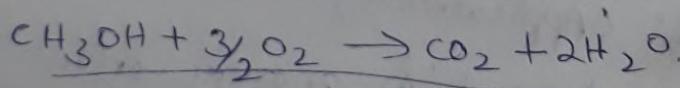
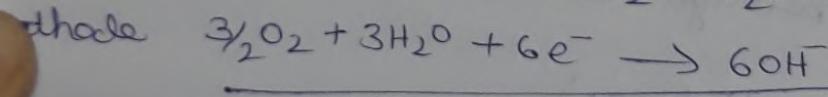
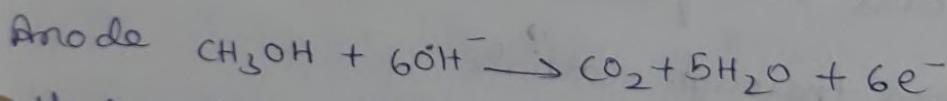
- 1) can store high energy content in small space.
- 2) produces limited power with high efficiency.

- 3) produces low toxic effluents.
- 4) used in military equipments as battery charger.
- 5) Also used as an energy source in space vehicles, submarines etc. . . .

cell diagram: electric current.



cell reaction:



UNIT II : WATER CHEMISTRY

07/12/21

SUB-UNIT : CORROSION

* Corrosion: The process of destruction of metallic surface due to chemical or electrochemical attack by the humid atmosphere or polluted environment is called as corrosion.

Corrosion is an oxidation process starting at the surface of the metals which decreases the strength of metals.

* Causes of corrosion:

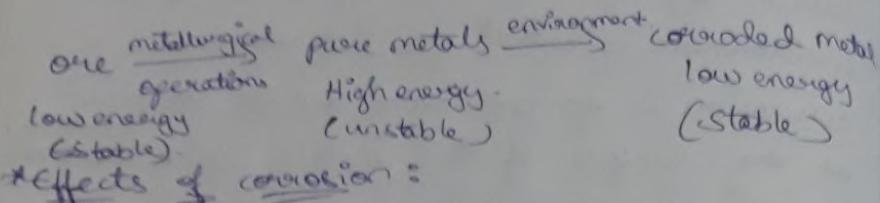
1) During oxidation of metals free energy of the system decreases i.e. $\Delta G^\circ = -ve$ therefore, metal is more stable in combined state than in free state.

2) Metals exists as ~~these~~ combined state as ones in nature which is thermodynamically stable with low energy.

3) To ~~extract pure metal more energy is required~~

3) To extract pure metals from one more energy is required. After metallurgical operations pure metals are obtained but

due to their high energy they are thermodynamically unstable and preferred to return back to combine state by interacting with the environment which leads to corrosion of metals.



* Effects of corrosion:

- 1) Loss of useful properties of metals and thus loss of efficiency.
- 2) Decrease in rate of production as replacing corroded equipments is time consuming.
- 3) Increase in maintenance and production cost
- 4) Contamination of products.

* Rusting of iron in moist air makes the metal useless.

- (ii) In sea water rusting of ships is a major problem.

* corrosion of metallic structure decreases the ductile nature resulting in cracks.

- * Type of corrosion: There are two types of corrosion. ~~Dry & wet corrosion~~
- 1) Dry or chemical corrosion.
 - 2) wet or electrochemical corrosion.

* Dry (or) chemical corrosion: In this type of corrosion metal directly comes in contact with environmental gases like O_2 , Cl_2 , SO_2 , CO_2 , N_2 etc. (or) Anhydrous inorganic liquids, acids / bases vapours resulting in chemical reaction between the two.

There are three types of dry corrosion:

- 1) Oxidation corrosion.
- 2) Corrosion by other gases.
- 3) Liquid metal corrosion.

* Oxidation corrosion: It takes place by direct action of oxygen ~~on~~ on metal surface at lower temperature or higher

temperature in the absence of moisture to give metal oxide. The extent of corrosion depends upon the nature of oxide layer formed on the metal surface

(a) stable oxide layer: It is continuous, adherent and covers the entire surface of metal. Hence it is very protective in nature and does not allow further attack of corrosion.

* Eg: Aluminium, lead, chromium etc.

(b) unstable oxide layer: It is formed in case of metals like platinum, silver, gold etc... where the oxide layer generates back To give the metal and oxygen. Hence such metals do not undergo corrosion.

(c) volatile oxide layer: The oxide layer formed ~~it~~ does not stay on the metallic surface as it is volatile. The metal is subjected to further attack of corrosion.

(d) porous (or) non-protective layer: In case of metals like Fe, alkali and alkaline earth metals the oxide layer is non-continuous, non-adherent, porous and does not cover the entire surface of metals. Hence the metal ~~is~~ is exposed to further attack of corrosion leading to severe corrosion.

The ~~PBR~~ PBR (pilling bedworth ratio) decides the protective nature of oxide layer. If $PBR \geq 1$ then the oxide layer is protective and If $PBR \leq 1$ then it is non-protective.

$$PBR = \frac{\text{Vol. of corrosion product}}{\text{Vol. of metal consumed}}$$

(e) corrosion by other gases: It takes place by direct action of gases like Cl_2 , SO_2 , SO_3 , etc.... on the metal. The degree of attack depends on the formation of protective (or) non-protective film formed on the surface of metal.

If protective non-porous film is formed then the extent of corrosion decreases.

* e.g.: AgCl film on Ag.

If porous non-protective film is formed then the degree of attack increases.

* e.g.: SnCl₄ layer on Sn.

3) Liquid metal corrosion: In this type of corrosion, a liquid metal flowing at a very high temperature attacks on the solid metal due to which it gets dissolved. Also liquid metal can penetrate into solid metal thereby leading to corrosion of the solid metal.

* e.g.: Nuclear plants

* wet on electrochemical corrosion: This type of corrosion takes place when a conducting liquid is in contact with metal surface (or) when there is heterogeneity on the metallic surface.

When two dissimilar metals are in contact with an electrolyte they form anodic and cathodic areas and current flows through the conducting medium to form a galvanic cell. At anodic area, oxidation occurs and due to the loss of electrons, the metal undergoes corrosion. Whereas, the cathodic area is uncorroded.

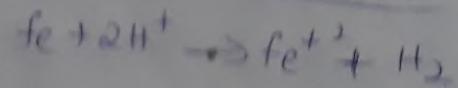
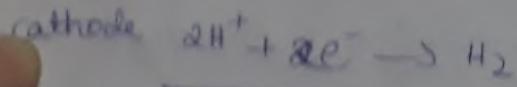
* Mechanism of wet corrosion:

In wet corrosion the current flows from anode to cathode at anode oxidation takes place liberating e⁻ whereas at cathode the e⁻ are consumed either by evolution of hydrogen or by absorption of O₂ depending on the nature of corrosive environment.



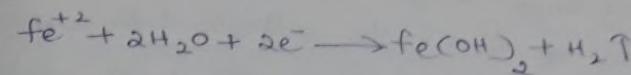
(i) corrosion in acidic medium:

(Evolution of H_2): In industrial areas polluting gases like SO_2 , SO_3 , CO_2 , oxides of Nitrogen etc. are present which dissolve in moisture to form acidic solution. When such a solution comes in contact with a sheet of iron it forms acidic medium around the metal when the oxide layer form on the surface of metal develops cracks or pores it leads to formation of anodic and cathodic areas resulting in the following reactions

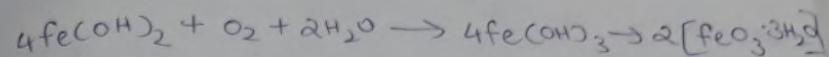


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* secondary reactions:



If enough oxygen is present.

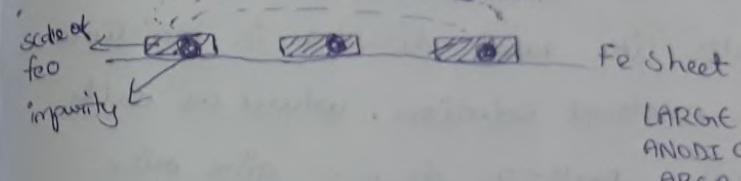


unstable. Rust yellow ochre

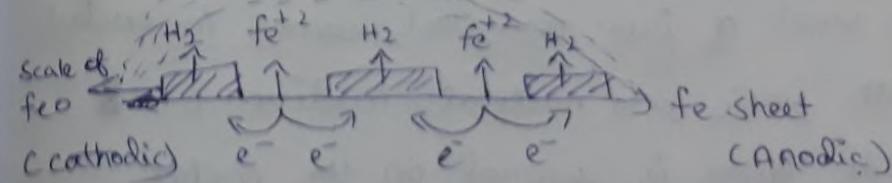
If oxygen is limited black crust Fe_3O_4 is formed.

* Corrosion in acidic medium (Evolution of H_2)

Acidic medium



Acidic medium



Corrosion in acidic medium is not very serious but it is generalised.

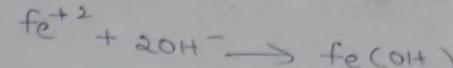
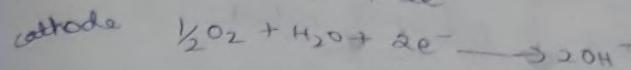
This is so because the anodic area

is very large compared to cathodic area. The evolution of H_2 at the cathode sets up polarization phenomenon and as the solubility of Fe^{+2} exceeds its saturation limit the formation of Fe^{+2} decreases. Thus due to these two factors after some time the corrosion of the metal stops.

* Corrosion in basic (or) neutral medium: (Absorption of oxygen.)

When salts like $NaCl$ dissolve in moisture it gives neutral solution. whereas salts like Na_2CO_3 , $NaHCO_3$ etc... give rise to basic (or) Alkaline medium. When a sheet of iron (or) steel comes in contact with basic (or) neutral medium. An oxide layer is formed on the metal surface. If the oxide layer develops cracks then an electric chemical cell is formed with small anodic areas and large cathodic areas.

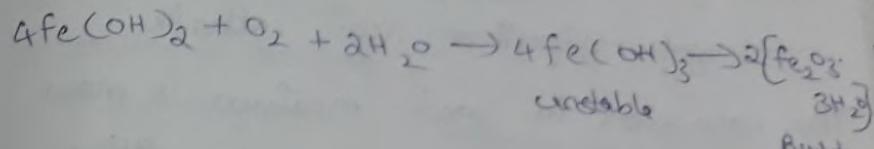
* Primary reaction:



primary corrosion product.

* Secondary reaction:

If enough oxygen is present.

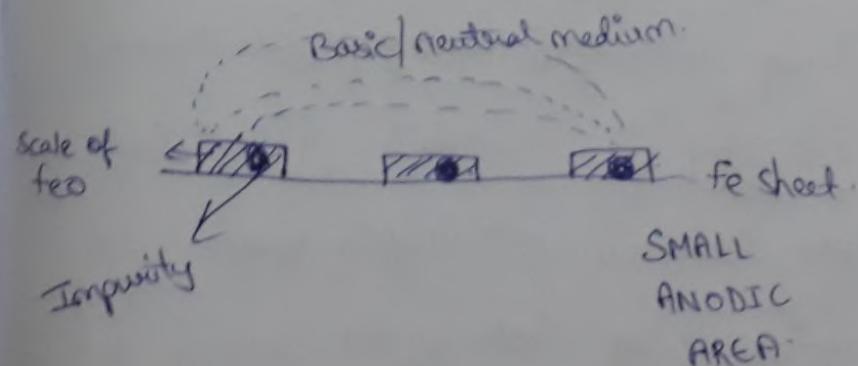


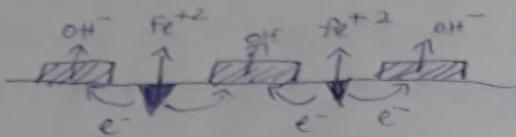
Rust.
Yellow
rust.

If oxygen is limited black crust Fe_3O_4 is formed.

Corrosion in basic/ neutral medium:

(Absorption of O_2)





The Fe^{+2} formed at anode and OH^- formed at cathode combine near the cathode because smaller Fe^{+2} ions can diffuse more rapidly thus corrosion takes place at anode whereas the rust gets deposited near cathode.

The corrosion in basic medium is more severe (or) localized leading to pitting corrosion.

* Differences between dry and wet corrosion:

→ [Next page]

Dry/chemical	wet/electrochemical
1. corrosion occurs in absence of moisture	1. Requires moisture (electrolyte as conducting medium)
2. It involves direct chemical attack on the metal surface	2. It involves formation of electrochemical or galvanic cell.
3. slow process	3. rapid process
4. corrosion products are formed at the site of corrosion.	4. corrosion occurs at anode but corrosion product deposits at cathode.
5. Uniform corrosion	5. Non-uniform corrosion.
6. occurs on homogeneous or heterogeneous surfaces	6. occurs only on heterogeneous metal surface.

* Differential aeration corrosion:

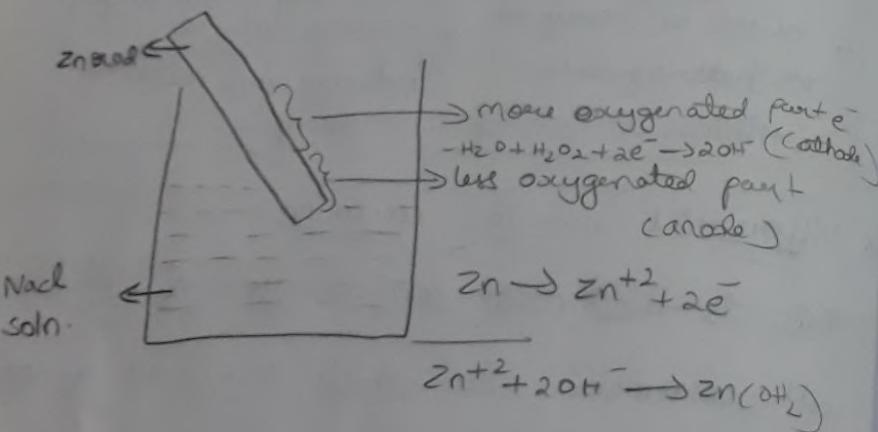
This is the most common type of concentration cell corrosion, in which one part of the metal is exposed to different air concentration from the other part resulting in difference of potential b/w the differently aerated areas.

The more oxygenated part (highly

aerated area) becomes cathode while the less oxygenated part (poorly aerated area) becomes acts as anode

The corrosion occurs at anode which is poorly aerated.

e.g.: zinc metal partially dipped in NaCl soln. undergoes corrosion just below the water line which is less oxygenated due to which Zn gets dissolved at the anodic areas.



E.g.) Metal rod dipped in a soln

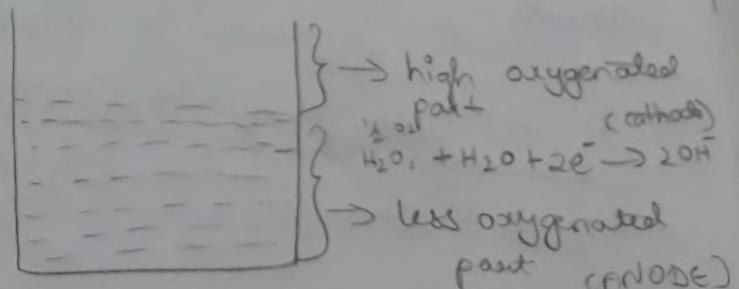
2) ship sailing in water

3) A nail hammered in a wooden block where head acts as cathode & stem (tail) acts as anode.

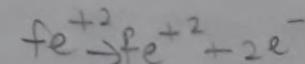
Q) water line corrosion: The water stored in steel tanks (as water tankers have maximum amount of corrosion just below the water line. The area of tank above the water level is more aerated area & acts as cathode which is unaffected by corrosion

The area below the water level is poorly aerated and acts as anode which undergoes corrosion

Q) Waterline corrosion is commonly found in marine engineering. It is accelerated when aquatic plants stick to the sides of ships also the drinking water stored in iron tanks will have water line corrosion.



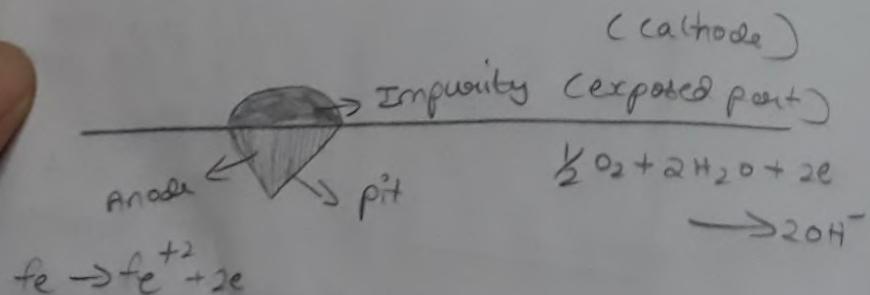
Net reaction:



② pitting corrosion: It is a localised corrosion which forms pits or cavities in corrosion. It is caused due to breaking or cracking of protective film on the metal surface. The break down can be due to roughness, scratches, non-uniform stress, or chemical action. The pits (or) cavities formed, small anodic areas and the other exposed part forms large cathodic area. This leads to severe corrosion.

The presence of impurities like sand, dust, scales, also leads to pitting corrosion.

The parts of metal below the impurity acts as anode and the other area as cathode.



* Factors influencing rate of corrosion:

① Nature of metal:

② position of metal in ^{alloy} ~~in~~ galvanic series:

when two metals (or) alloys are in electrical contact in presence of an electrolyte then the more active metal higher up in series will act as anode & undergoes corrosion. Thus, greater the difference b/w the metals faster is the rate of corrosion.

③ Relative areas of anode & cathode:

when 2 dissimilar metals are in contact then the corrosion on the anodic part is directly proportional to the ratio of areas of cathodic part and anodic part. In case of small anodic areas corrosion is more

severe, rapid & localised because the great demand for electrons by the

large cathodic area can be fulfilled by a smaller anode by undergoing continuous rapid corrosion.

③ Purity of metals: The impurity in a metal leads to heterogeneity forming small electrochemical cell at the exposed part of metal which causes anodic areas to undergo corrosion. pure metals are less corroded than impure metals.

④ Nature of surface oxide film: If the corrosion product is soluble or volatile, then corrosion proceeds at fastest rate until all the metal is consumed. If corrosion product is insoluble, continues & adherent then it covers the metal surface & acts as a physical barrier thereby decreasing further rate of corrosion.

If corrosion products is discontinuous or porous then corrosion will be severe.

→ metals like aluminium, chromium, Mg, Ni are passive and exhibit higher corrosion resistance due to thin protective oxide film formed on the surface which posses self healing nature when broken or exposed to environment.

II Nature of Environment:

① Temperature: With increase in temp of environment the rate of corrosion increases.

② Humidity: The corrosion of metal is rapid in humid atmosphere because atmospheric gases dissolve in moisture to produce an electrolyte which sets up an electrochemical cell. Also, sometimes the oxide layer absorbs moisture which leads to electrochemical corrosion.

(ii) effect of pH: The acidic medium is more corrosive than basic / neutral medium; i.e. lower the pH, greater is the rate of corrosion. The corrosion of metals attacked by lower pH can be reduced by increasing the pH of the attacking environment.

* corrosion control methods - cathodic protection:
The principle involved in the cathodic protection is to force the metal to be protected to behave as cathode as a result of which corrosion does not take place. This protection can be achieved by connecting the base metal to external source of energy which may be a metal generator or a rectifier.

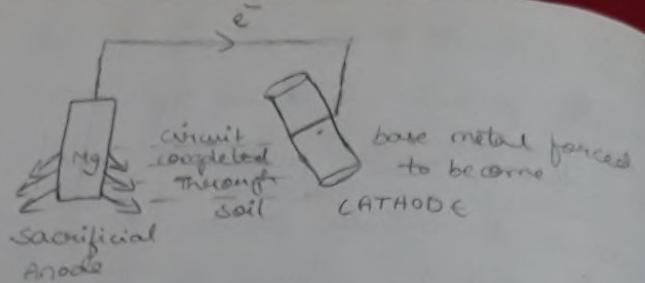
* cathodic protection:

cathodic protection is of two types:
(i) sacrificial anodic protection: In this method the metallic structure to be protected is connected by a wire ~~tap~~ to a more anodic metal so that all the corrosion takes place at the anode. The parent structure thus becomes cathodic and is protected whereas, the more active metal gets corroded. As the more active metal sacrifices itself to protect the base metal it is termed as sacrificial anode which is replaced after it gets consumed.

The usually used metals for sacrificial anode are: Mg, Zn, Al and their alloys.

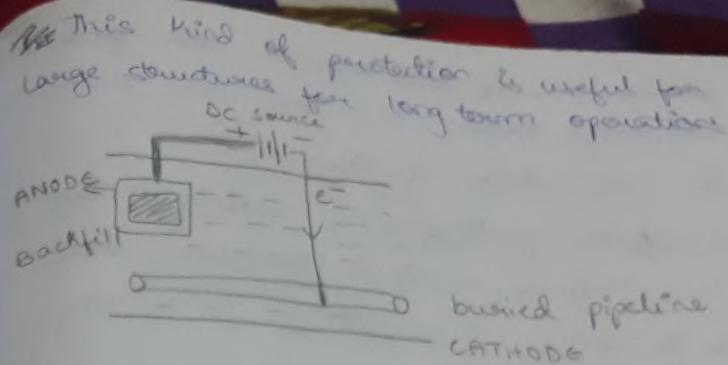
* Applications:

* used for protection of buried ~~pipelines~~ pipelines, underground coffee cables, ~~orange~~ ship hulls, water-tank etc..



2) Impressed current cathodic protection:

In this method an impressed current is applied in the opposite direction to nullify the corrosion current and convert the corroded metal to cathode. The impressed current is derived from a DC source connected to an insoluble anode (graphite or platinum). The anode is usually placed in a backfill (gypsum) so as to increase the electrical contact with the surrounding soil. The external source produces current in the direction reverse to the corrosion current such that the parent structure is forced to behave as cathode and is protected.



* Applications: used to protect water tanks, buried oil pipelines and water pipelines, condensers, transmission lines, towers, laid-up ships etc

* Surface coatings: (Metallic coatings)
coating provides a physical barrier between the base metals and its environment and protects the metal from corrosion when the base metal is coated with another metal it is called as metallic coating. The metallic coating is of two types

1) Anodic coating: The coating metal has lower S.R.P than the base metal due to

which it itself gets corroded and protects the base metal

② Galvanization of steel

③ Cathodic coating: The coating metal has higher corrosion resistance due to its noble character as it is less reactive.

④ Tinning

* Hot dipping by galvanization: Hot dipping is a common method of coating in which metals with low melting point such as Pb, Zn, Al. are coated on metals with high melting point such as iron, steel and copper. The process consists of dipping the base metal in a bath containing molten coating metal covered with a flux. The most widely used hot dipping method is galvanization

Galvanization: Galvanization is a process of coating iron with zinc to prevent it from rusting. The steps involved are:

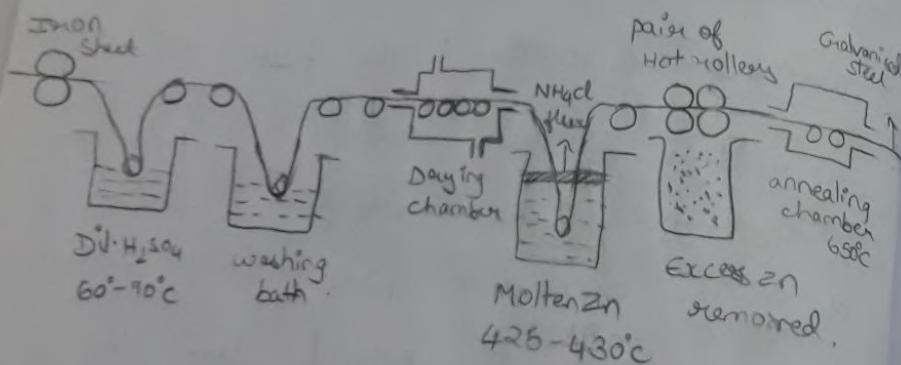
1) Acid pickling: The base metal is cleaned with water and organic solvents to remove oil, grease and other impurities. It is then treated with dil. H_2SO_4 soln. ~~for 15 to 20 mins at 60°-90°C~~ To remove scales of oxides, rust or impurities.

2) Washing and coating: The base metal or article is then washed with water and ~~then~~ dried. It is dipped in hot bath of molten zinc at 425-430°C covered with a layer of NH_4Cl flux. The flux prevents oxidation of molten zinc and acts as a binder for proper ~~adhesive~~ adhesion of zinc on the surface.

③ Rolling: The coated article is then passed through ^{Hot} rollers to remove excess of zinc so that thin film of uniform thickness is achieved.

④ Annealing: The zinc coated article is annealed at 650°C in an annealing chamber and finally cooled down.

* uses: used in coating of wires, pipes, nails, bolts, screws, Tubes, roof sheets etc...



* Note: Galvanized ~~steel~~ utensils cannot be used for preparing or storing food because zinc dissolves in dilute acids to form highly toxic or poisonous compounds.

UNIT - IV chemical fuels

* Definition: The term fuel includes all combustible ~~substances~~ substances that combine with oxygen from the atmosphere and undergoes combustion to produce large amount of heat along with the products which can be used for ~~for~~ domestic and industrial purposes



chemical fuels are substances which on exothermic reactions with oxygen during combustion liberate Heat and end product.

* classification of chemical fuels:

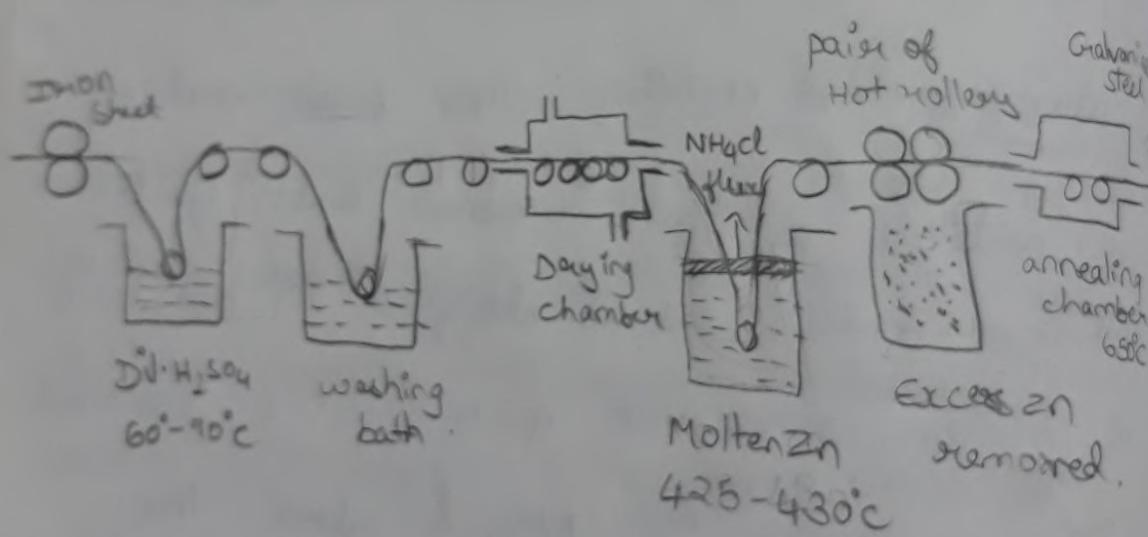
The chemical fuel may be solid, liquid or gaseous either naturally found or artificially prepared



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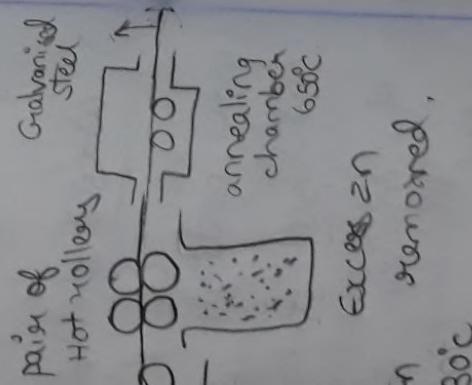
icle is then
to remove excess
of uniform

13/21

UNIT - IV chemical fuels

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and article is
in annealing
old drossed.
wires, pipes,
roofs, roof sheets



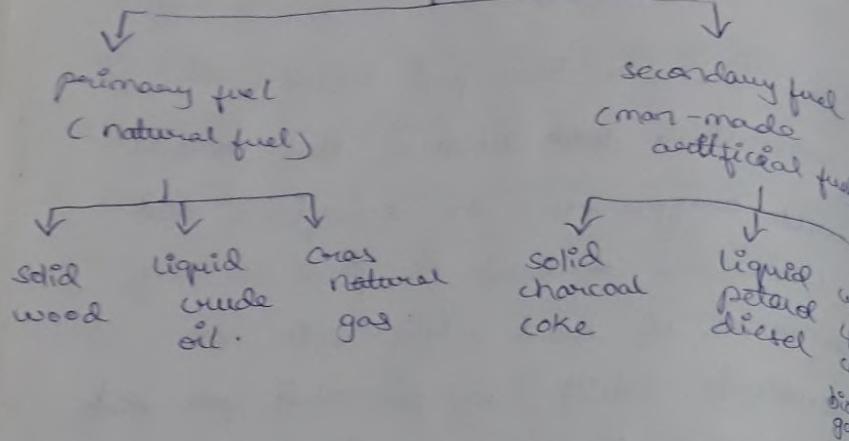
at 300°C

* classification of chemical fuels:

The chemical fuels may be solid, liquid or gaseous either naturally found or artificially prepared



Based on occurrence



* Requirements of good fuel: ~~A good fuel must possess high calorific value.~~

- 1) A good fuel must possess high calorific value.
- 2) fuels should possess low moisture content.
- 3) An ideal fuel must have moderate ignition temperature.
- 4) A good fuel ~~must possess~~ should possess low non-combustible matter.
- 5) fuels should have moderate rate of combustion for continuous supply of heat.

- 6) A good fuel should be readily available, easy to transport & store and of low cost.
- 7) fuels must not produce harmful gases and toxic substances which pollute the environment.
- 8) fuel should burn in air with efficiency without much smoke.
- 9) combustion of fuel must be easy to start and stop i.e controllable combustion.

* comparison b/w solid, liquid and gaseous fuel:

I) Solid fuels:

* Advantages:

- 1) easy to transport.
- 2) convenient to store without risk of explosion.
- 3) Low cost of production
- 4) possess moderate ignition temperature.

* Disadvantages:

- 1) High ash content
- 2) Low thermal efficiency.
- 3) Burns with clinker formation.

- 4) High cost of Handling.
- 5) Low calorific value compared to liquid fuels.
- 6) Requires large excess of air for complete combustion.
- 7) cannot be used in IC engines.
(Internal combustion engines).

II) Liquid fuel:

* Advantages:

- 1) possess high calorific value than solid fuels.
- 2) Burns without forming ash or cinders.
- 3) Easy ~~to~~ to transport through pipelines.
- 4) can be stored without any loss.
- 5) clean in use and economic in labour.
- 6) The flame produced can easily be controlled by adjusting the supply.
- 7) Requires less furnace space for combustion.
- 8) Requires less excess of air for complete combustion.

1) can be used in IC engines

Disadvantages:

- 1) costlier than solid fuels.
- 2) requires costly storage tanks.
- 3) possess greater risk of fire hazards.
- 4) special burners and spraying apparatus required.
- 5) produces bad ~~odour~~ odour.
- 6) choking of sprayers is a major drawback.

III) Gaseous fuel:

* Advantages:

- 1) easy to transport through pipelines.
- 2) possess high heat content and produces higher temperatures.
- 3) easily controllable combustion.
- 4) clean in use and eco friendly.
- 5) Burns without heat loss.
- 6) possess high calorific value.
- 7) Requires very less excess of air Supply.

- 3) free from solid and liquid impurities
- 9) can be used in IC engines.

* Diseadvantages:

- 1) very large storage tanks are required
- 2) higher risks of fire hazards.
- 3) costly as compared to solid and liquid fuels.

* Calorific value: calorific value is the amount of heat liberated from complete combustion of unit mass or unit volume of fuel in air or oxygen. units are cal/gm (or) Kcal/kg (or) Kcal/m³

* Higher calorific value or Gross calorific value: (HCV (or) GCV)
The total amount of heat liberated when a unit mass (or) unit volume of the fuel has been completely burned and the products of combustion are cooled to room temperature is termed as HCV (or) GCV

⇒ Lower calorific value (or) Net calorific value: (LCV (or) NCV) The net heat produced when a unit mass (or) unit volume of fuel is completely burned and the products of combustion are not cooled to room temperature but are allowed to escape into the atmosphere.

$$HCV = GCV - 0.09H \times 587 \text{ cal/g.}$$

~~Net calorific value~~

* Theoretical calculations of calorific value by duulong formula:

The calorific value of a fuel can be estimated from duulong formula where

HCV of hydrogen = 34500, carbon = 8080
sulphur = 2240.

* The duulong formula for calculating HCV and NCV is

$$HCV = \frac{1}{100} [8080C + 34500(H - \frac{S}{8}) + 2240S]$$

$$LCV = HCV - 0.09H \times 587 \text{ cal/gm}$$

① calculate the HCV and LCV for a sample of coal. Having the following composition. C=82.1%, H=3.1%, S=1.1%, N=0.8%, O=3.9% and ash=9.1%.

$$\begin{aligned} \text{Sol: } HCV &= \frac{1}{100} [8080C + 34500(H - \frac{O}{8}) + 2240S] \\ &\quad \text{cal/gm} \\ &= \frac{1}{100} [8080 \times 82 + 34500(3.1 - \frac{3.9}{8}) + 2240 \times 1.1] \\ &= 7551.55 \text{ cal/gm} \end{aligned}$$

$$\begin{aligned} LCV &= HCV - 0.09H \times 587 \\ &= 7551.55 - 0.09 \times 3.1 \times 587 \\ &= 7387.7 \text{ cal/gm} \end{aligned}$$

② calculate the LCV of a fuel if it contains 6.5% Hydrogen and GCV of fuel is 3500 Kcal/kg.

$$\begin{aligned} \text{Sol: } LCV &= GCV - 0.09H \times 587 \\ &= 3500 - 0.09(6.5) \times 587 \\ &= 3156.6 \text{ Kcal/kg.} \end{aligned}$$

③ calculate the HCV and LCV of a fuel having C=80.1%, H=7.1%, O=3.1%, S=2.51%, ash=4.4%, N=2.1%.

$$\begin{aligned} \text{Sol: } HCV &= \frac{1}{100} [8080C + 34500(H - \frac{O}{8}) + 2240S] \\ &= \frac{1}{100} [8080 \times 80 + 34500(7 - \frac{3.1}{8}) + 2240 \times 2.51] \\ &= 8828.02 \text{ Kcal/kg} \end{aligned}$$

$$\begin{aligned} LCV &= HCV - 0.09H \times 587 \\ &= 8828.02 - 0.09 \times 7 \times 587 \\ &= 8458.20 \text{ Kcal/kg.} \end{aligned}$$

* Combustion: Combustion is an exothermic chemical reaction accompanied by development of heat and light at rapid rate which increases the temperature considerably.

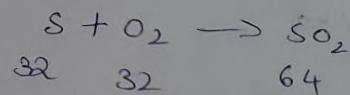
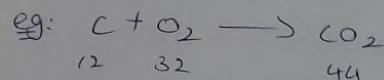
* Ignition temperature of fuel: It is the minimum temperature at which the substance ignites and burns without further

addition of heat externally. The fuel must be pre heated to ignition temperature for proper combustion of the fuel.

e.g.: coal is pre heated by adding kerosene paper (or) wood.

* Combustion calculations:

1) Substances combine in definite proportions which are determined by their molecular mass.



2) composition of air

a) By volume = ~~$\frac{100}{21}$~~ $\frac{100}{21}$ (or) 4.76 vol of air provides 1 volume of O_2 for combustion by

b) By weight = $\frac{100}{23}$ (or) 4.35 wt of air provides unit weight of O_2 for combustion

3) 1 gm mole of any gas at STP occupies 22.4 L.

e.g.: 32 gm of oxygen occupies 22.4 L at STP.
1) The molecular mass of air is 28.94 gm/mol.

2) The theoretical amount of oxygen required for complete combustion of 1 kg of solid (or) liquid fuel is given by the formula

$$\frac{32}{12} C + 8 \left[H - \frac{O}{8} \right] + S$$

3) The amount of air required for combustion of 1 kg of fuel is given by the formula

$$\frac{100}{23} \times \left[\frac{\frac{32}{12} C + 8 \left[H - \frac{O}{8} \right] + S}{100} \right]$$

* Ranking in coal: Rank is a calculative measure of carbon content in coal. It is defined as the degree or extent of moderation. The soft coal has low percentage of carbon and are termed as the low rank coals whereas the hard coals have high percentage of carbons and are termed as high rank coal.

wood \rightarrow peat \rightarrow lignite \rightarrow bituminous coal
 Sol. 50% 67% 67% 80% \rightarrow Anthracite
 93%.

% C	\rightarrow low rank	\rightarrow low rank	\rightarrow low rank	\rightarrow High rank	\rightarrow High rank
CFC	4000-4500	4115-4600	6500-7100	8000-8500	86500-8700

Q) calculate the weight and volume of air required for complete combustion of 1 kg of carbon.

$$\text{Sol: wt. of air} = \frac{100}{23} \times \frac{32}{12} \text{ C.}$$

$$= \frac{100}{23} \times \frac{32}{12} \times 1 = 11.39 \text{ kg air}$$

$$\text{wt. of air} = 28.94 \text{ g air} \rightarrow 22.4 \text{ lit}$$

$$11.39 \text{ kg} \times 1000 \text{ air} \rightarrow ?$$

$$\frac{11.39 \times 1000 \times 22.4}{28.94} = 2970 \text{ lit air}$$

Q) calculate the weight and volume of air required for complete combustion of 3 kg of carbon. Calculate the volume in m³.

$$\text{Sol: wt. of air} = \frac{100}{23} \times \frac{32}{12} \text{ C.}$$

$$= \frac{100}{23} \times \frac{32}{12} \times 3 = 34.78 \text{ kg air}$$

$$\text{Vol. of air} = 28.94 \text{ g air} \rightarrow 22.4 \text{ lit}$$

$$34.78 \times 1000 \text{ air} \rightarrow ?$$

$$= \frac{34.78 \times 1000 \times 22.4}{28.94} = 26920.2 \text{ lit air}$$

$$= 26.920 \text{ m}^3 \text{ air}$$

Q) Calculate the weight of air required for combustion of a fuel having the following combustion.

$$C = 80\%, H = 4\%, O = 8\%, N = 3\%, S = 2\%$$

$$\text{ash} = 5\%, \text{ moisture} = 3\%$$

calculate if 60% excess air is supplied.

$$\text{Sol: wt. of air} = \frac{100}{23} \times \frac{32}{12} C + 8 \left[\frac{H - O}{8} \right] + S$$

$$= \frac{100}{23} \times \frac{32}{12} \times 80 + 8 \left[\frac{4 - 8}{8} \right] + 2$$

$$= \frac{100}{23} \times 2.443 = 10.62 \text{ kg air}$$

$$\text{for } 60\% \text{ excess } 10.62 \times \frac{160}{100} = 16.9 \text{ kg air}$$

Q) A sample of fuel has $C = 72\%, H = 3\%, O = 4\%$, $N = 2\%, S = 9\%, \text{ ash} = 8\%, \text{ moisture} = 6\%$. calculate the quantity of air required for 5 kg of the fuel.

$$\text{Sol: wt. of air} = \frac{100}{23} \times \text{wt. of oxygen}$$

$$\text{wt. of air} = \frac{100}{23} \times \frac{32}{12} \times 72 + 8 \left[\frac{3 - 4}{8} \right] + 3$$

$$= \frac{100}{23} \times 2.31 = 10.04 \text{ kg air}$$

$$\text{for } 5 \text{ kg fuel} = 10.04 \times 5 = 50.2 \text{ kg air}$$

Q) A coal sample was found to have $C = 78\%, H = 5.2\%, O = 12.1\%, \text{ ash} = 4.5\%$.

Calculate the weight of air required for complete combustion of 1 kg of coal sample also calculate if 40% excess air is supplied calculate the GCV and NCV of the fuel.

$$\text{Sol: wt. of air} = \frac{100}{23} \times \frac{32}{12} \times C + 8 \left[\frac{H - O}{8} \right] + S$$

$$= \frac{100}{23} \times \frac{32}{12} \times 75 + 8 \left[5.2 - \frac{12.1}{8} \right]$$

$$= 9.978 \text{ kg air}$$

for 40% excess air

$$9.978 \times \frac{140}{100} = 13.969 \text{ kg air}$$

$$\text{GCV} = \frac{1}{100} \left[8080 C + 34500 (H - \frac{1}{8}) + 22.405 \right] \text{ cal/gm}$$

$$= \frac{1}{100} \left[8080 \times 75 + 34500 (5.2 - \frac{12.1}{8}) \right]$$

$$= 7332.18 \text{ cal/gm.}$$

$$\text{NCV} = \text{GCV} - 0.094 \times 587 \text{ cal/gm}$$

$$= 7332.18 - 0.094 \times 5.2 \text{ Spt}$$

$$= 7057.46 \text{ cal/gm.}$$

* Analysis of coal: In order to assess the quality of coal it is subjected to proximate and ultimate analysis.

① proximate analysis include determination of moisture volatile matter ash and fixed carbon content. It gives information about practical utility of coal.

② ultimate analysis include determination of carbon hydrogen nitrogen sulphur present in coal. This data is useful for industrial purposes.

proximate analysis of coal:

① Moisture: Known weight of finely powdered coal is taken in the silicon crucible and heated in electric hot air when at $105^{\circ}-110^{\circ}\text{C}$ for 1 hour the crucible then it is removed after cooling in a desirable its weight is noted. The process of heating cooling and weare is separated till constant weight is obtained the loss in weight is reported as percentage of moisture.

$$\% \text{ moisture} = \frac{\text{loss in weight}}{\text{no. of coal}} \times 100.$$

Significance: The presence of moisture content in coal increase the cost and transports changes it lower the calorific value and garrishes furnace high rank coal should contains 5 to 10% moisture.

② Volatile matter: The sample left in the crucible is covered with a lead and placed in electric muffled furnace at $250 \pm 20^\circ\text{C}$ for 7 min the crucible is then removed and cooled in desiccator and weight is noted the loss in weight is reported as percentage of volatile matter.

$$\% \text{ volatile matter} = \frac{\text{loss in weight}}{\text{wt. of coal}} \times 100$$

Significance: The non-combustible matter present in fuel doesn't act through calorific value hence it is undesirable coal containing high volatile matter burns with long flame high smoke

and low calorific value also the volume of furnace required is large. ~~Supply of air leads to pollution and reduces life span~~

③ Ash content: The sample left in the crucible is heated without the bend in presence of air or oxygen at 700 to 750°C for $\frac{1}{2}$ hour in electric muffled the weight ~~is repeated~~ it is of the residue occupied after the coal is noted the process of heating cooling and weight is repeated if constant weight is obtained.

$$\% \text{ ash} = \frac{\text{wt. of ash formed}}{\text{wt. of coal}} \times 100$$

Significance: Ash is non combustible nuclear matter left behind after burning the coal it reduces the calorific value and decreases the efficiency of coal it increases the transporting and handling and storing cost and additional cost is cost in

ash disposal the presence of ash destroy the furnace walls obstructs the supply of air leads to pollution and matatizing carbony.

④ fixed carbon: It is obtained by deducting the sum total moisture volatile matter and ash from hundred

$$\% \text{ fixed C} = 100 - \% \text{ C} (\text{M+VM+A})$$

Significance: High carbon content means high calorific value indicating better quality of coal it helps in designing the furnace and the slope of fire box.

Ultimate analysis of coal:

① carbon and hydrogen an known quantity of coal is burned in a current of dry oxygen with carbon and hydrogen get oxidised to CO_2 and H_2O these products are passed through two bulbs in a one bulb anhydrous CaCl_2 taken which observes H_2O and in the other

bulb KOH is taken which obscures CO_2 the weight of CaCl_2 and KOH are then determined the increase in weight of each bulb

separate represents the weight of H_2O formed while the increase in state KOH represents the weight CO_2 is formed.

$$\% \text{ C} = \frac{\text{increase in wt. of KOH} \times 12}{\text{wt. of coal sample} \times 44} \times 100$$

$$\% \text{ H} = \frac{\text{increase in wt of } \text{CaCl}_2}{\text{wt. of coal sample}} \times \frac{2}{18} \times 100$$

Significance: The measure combustible content of coal is current hydrogen is usually associated with volatile matter the available hydrogen contribute towards the calorific value of fuel greater the percentage of carbon and hydrogen better is quality of coal and higher is its

calorific value Higher percentage of carbon reduces the size of combustion

chlorides required.

- (2) Nitrogen: one gram of powdered coal is taken in Kjeldahl's flask and treated with concentrated H_2SO_4 along with $K_2S_2O_8$ and excess water clear solution is obtained it is liberates with NH_3 which is distilled over and absorbed in a known ~~volume~~ of point one M H_2SO_4 solution (p.) then unreacted acid is determined by back titration with point one N. NaOH the amount of acid neutralized by liberated ammonia then the coal sample is determined.

$$\% \text{ N} = \frac{\text{wt. of N}}{\text{wt. of coal sample}} \times 100$$

$$\% \text{ N} = \frac{0.4(CV_1 - V_2)}{\text{wt. of coal sample}} \times 1.4$$

Significance: It is an inert in combustible gas in presence of which is undesirable a good quality coal should have

very little nitrogen called nitrogen in fuel get converted to various oxides of nitrogen certain reacts with ozone resulting in depletion in ozone layer.

- (3) Sulphur: A known calorific weight is burned in calorific meter in a current of oxygen by which sulphur is oxidized to Sulphur the ash from bomb calorimeter is exhausted for dil. H_2SO_4 and treated with $BaCl_2$ solution precipitate with Sulphate.

$$\% \text{ S} = \frac{\text{wt. of Barium obtained}}{\text{wt. of coal}} \times \frac{32}{233} \times 100$$

Significance: Sulphur is the undesirable constituent present in coal. It increase the calorific value the SO_2 and SO_3 gas is produced pollute the environment and contribute to acid rain the coal is containing 65 to 70% where one

unsuitable for used in metallurgy and in iron industry.

④ oxygen: The percentage of oxygen is directly obtained by deducting the sum of $\% \text{O} = 100 - \% (\text{C} + \text{H} + \text{N} + \text{S})$

Significance: oxygen is usually present in combine form with hydrogen high oxygen content coal have high moisture content low cv and low cooling power thus a good quality coal should have low oxygen content.

Q) 2.5gm of coal was take in a splea crucible and heated for 1 hour for 110°C giving and residue of 2.4 gm was obtained to crucible was covered with lead and heated for 7 minutes at 960°C . The crucible was then heated without the lead until constant weight of 0.232 gms was obtained calculate % results -

$$\% \text{ moisture} = \frac{w_1 - w_2}{\text{wt}} \times 100 = \frac{2.5 - 2.425}{2.5} \times 100 \\ = 3.1\%$$

$$\% \text{ volatile matter} = \frac{w_2 - w_3}{\text{wt of coal}} \times 100 = \frac{2.425 - 1.32}{2.5} \times 100 \\ = 36.2\%$$

$$\% \text{ ash} = \frac{\text{wt of ash formed}}{\text{wt of coal}} \times 100 = \frac{0.232}{2.5} \times 100 \\ = 9.28\%$$

$$\% \text{ fixed carbon} = 100 - (\text{M} + \text{V} + \text{A}) \\ = 100 - (3 + 36.2 + 9.28) \\ = 51.52\%$$

Q) 3.12gm of coal taken in Kyeldhal's flask give NH_3 gas which was obtained in 50ml of 0.1N H_2SO_4 the excess acid required 12.5ml of 0.1N NaOH for neutralization determine % results -

$$\% \text{ N} = \frac{0.1(V_1 - V_2)}{\text{wt of coal}} \times 1.4 \\ = 0.1 \frac{(50 - 12.5)}{3.12} \times 1.4 = 1.68\%$$

Q) 0.1 gm of sample coal was heated in a bomb calorific meter and the ash formed was treated with BaCl₂ which gave a ppt of 0.01 gm BaSO₄ calculate percentage results ultimate analysis.

$$\text{Sol: } \therefore S = \frac{\text{wt. of CaSO}_4}{\text{wt. of coal}} \times \frac{32}{233} \times 100 \\ = \frac{0.01}{0.1} \times \frac{32}{233} \times 100 \\ = 1.37\%$$

* Liquid fuels: The crude oil & petrol is a major source of liquid fuels. Petroleum is usually found below the earth surface floating upon a layer of brine and has a layer of natural gas on top of it.

Petroleum is drilled from the earth crust and sent to refill it

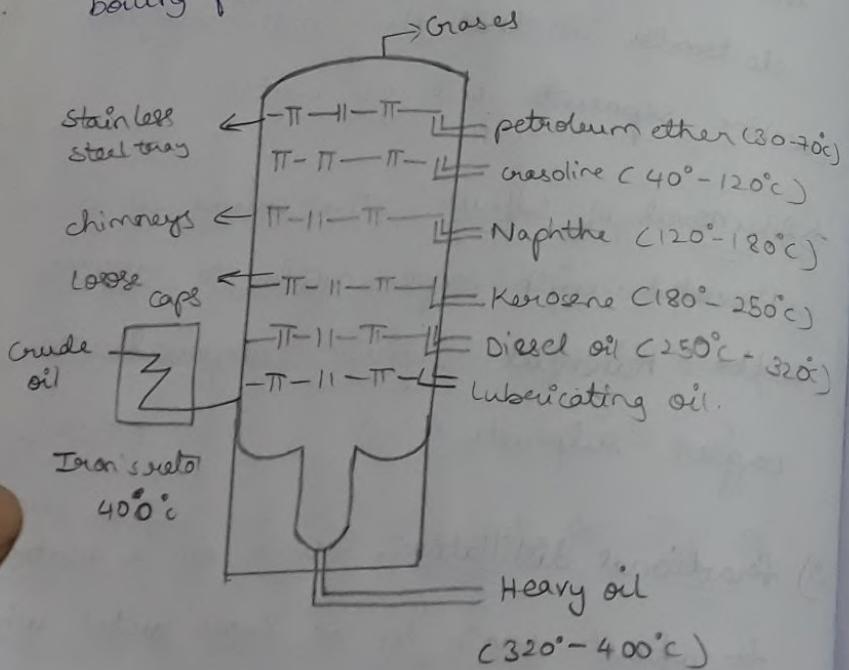
* Refining of crude oil: The crude oil is separated into various fractions by fractional distillation this process is called as refining of crude oil.

1) Cotterall's process: The water from crude oil is separated by cotterall's process here the crude oil is float b/w highly charged electrodes so that the water droplets combine separate out as water.

2) Removal of sulphur: The crude oil is treated with copper oxide to remove the harmful sulphur compounds as copper sulphate.

3) Fractional distillation: crude oil is heated to about 400°C in an iron retort where all the volatile constituents are evaporated the hot vapours are then passed through a tall tower known as fractionating column. The column

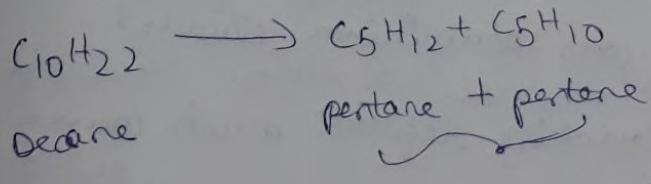
consists of a no. of horizontal stainless steel trays provided with individual chimneys which are covered with loose caps. As the vapour moves up, fractional condensation takes place at different heights of the column. The higher boiling fractions condensed first while the lower boiling fractions condense later.



Major fractions obtained from fractional distillation

	Gasoline	Kerosene oil	Diesel oil
composition	Mixture of hydrocarbons from C_5H_{12} - C_8H_{18}	Mixture of hydrocarbons from $C_{10}H_{22}$ - $C_{16}H_{24}$	Mixture of hydrocarbons from $C_{15}H_{32}$ - $C_{18}H_{38}$
temp	obtained b/w $40^{\circ}-120^{\circ}C$	obtained b/w $180^{\circ}-120^{\circ}C$	obtained b/w $250^{\circ}-320^{\circ}C$
calorific	11,280	11,100	11,000
uses	used as fuel in IC engine in aeroplanes and also at automobiles	used as fuel in stores, jet engine fuel and furnacing oil gas	used as fuel in diesel engine.

* Cracking: It is defined as decomposition of high molecular weight hydrocarbon of high boiling point into simpler low molecular wt. hydrocarbons of low boiling point.

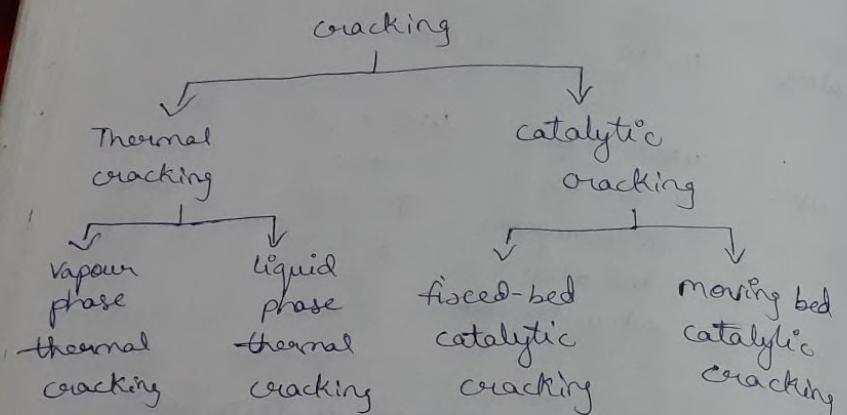


$$B.P = 174^{\circ}C$$

$$B.P = 36 - 50^{\circ}C$$

Significance / Importance: Cracking helps to overcome the shortage of gasoline. Also the petrol obtained by cracking has better characteristics than straight run petrol.

Types of cracking:



* Moving bed catalytic cracking: Catalytic cracking involves decomposition of higher mol. weight hydrocarbons into lower molecular wt. hydrocarbons by using a suitable catalyst such as alumina (or) aluminium silicate.

Catalytic cracking requires much lower temp and pressure when compared to

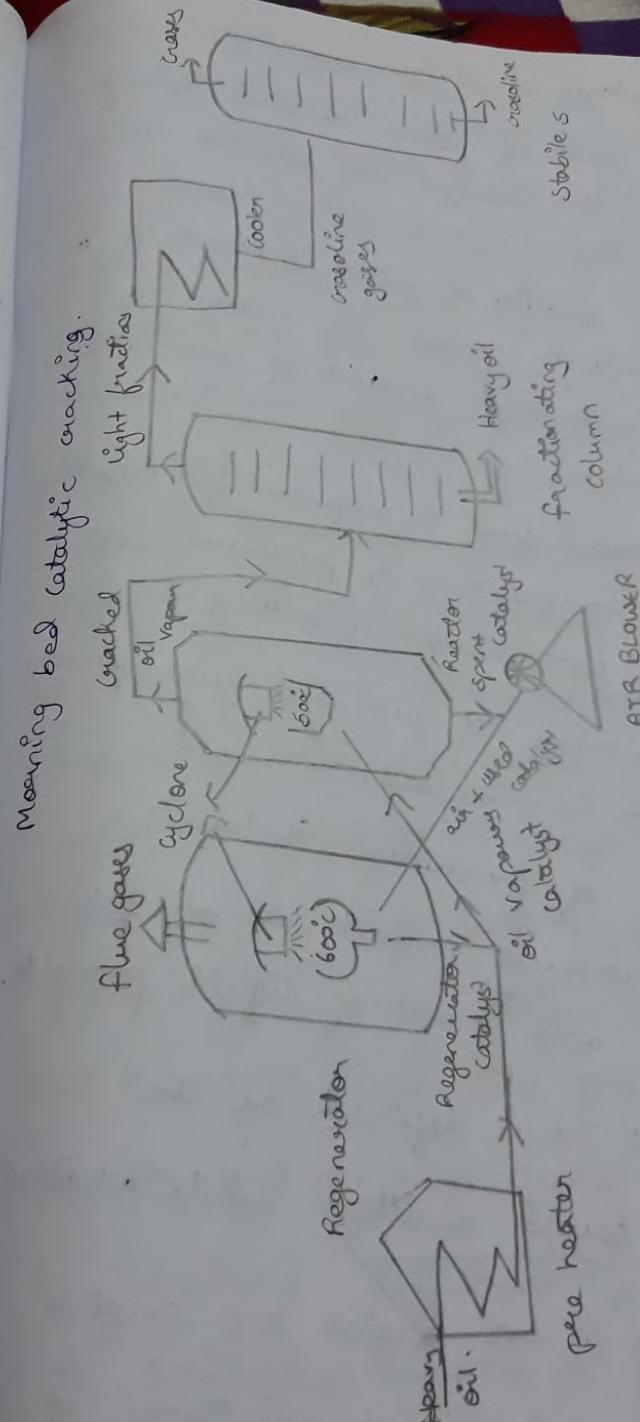
Thermal cracking:

In moving bed catalytic cracking the feed oil is first heated in a pre heating coil. Heated oil vapours mixed along with very finely powdered hot catalyst are passed into the reactor which is maintained at 500°C . Due to high temp of catalyst (600°C) the cracking of heavy oil starts even before entering into the reactor. The cracked oil vapours are then passed through fractionating column through the internal cyclone fixed at top of the reactor which allows only cracked oil vapours to pass and retains the catalyst in the reactor itself.

In the fractionating column the heavy oil is separated and the vapours are then passed through the cooler where gasoline condenses along with other gases.

This is then sent to a stabilizer where the dissolved gases are removed & pure gasoline is recovered. The cyclone in the reactor removes the catalyst which settles at the bottom & is fixed by air blast to the regenerator maintained at 600°C . In the regenerator the cyclone releases fine fuel gases & the regenerated catalyst is mixed with the first incoming oil vapours.

→ (Diagram)



* Advantages of catalyst cracking:

- 1) The yield of petrol obtained is high because the catalyst are selective in their action.
 - 2) Better quality of petrol is obtained as the products contain less amount of sulphur and high amount of aromatic hydrocarbons.
 - 3) No external fuel is required for cracking.
 - 4) A much lower temp & pressure are sufficient for catalytic cracking.
 - 5) The percentage of gum and gum forming compounds is very low.
 - 6) The cost of production is low.
 - 7) The products contain less of gas and coke and more of liquid products.
- * Knocking: It is defined as the rattling sound emitted while accelerating the engine in an engine IC engine (Internal combustion) a mixture of

gasoline vapour & air is used as fuel after initiation of combustion reaction by an electric spark in the cylinder. The flame should spread smoothly through the gaseous mixture due to which the expanding gas moves the piston down. sometimes due to compression the air + fuel mixture gets heated to a temp. greater than the ignition temperature which leads to auto ignition even before sparking. This produces knocking. It can also be caused due to multiple flame fronts within the cylinder instead of a single flame.

These flames collide with explosive force producing a sharp metallic ringing or knocking noise. The pre ignition of the fuel + air mixture also leads to knocking. In some cases the rate of oxidation becomes so great that

the last portion of fuel + air mixture gets self ignited instantaneous producing explosive violence known as knocking which results in loss of efficiency

* Disadvantages of Knocking: Knocking results in decrease power output and mechanical damage due to overheating of IC engine parts.

Prolonged knocking leads to loss in efficiency.

* factors affecting Knocking:

- 1) Design of engine.
- 2) Running conditions.
- 3) Chemical structure of fuel i.e aromatic hydrocarbons have higher anti-knocking properties than paraffins and alkenes.

Alkanes > Mono substituted alkanes > Cyclic alkanes > Alkenes > Poly substituted alkenes > Aromatic hydrocarbons

* Octane number: The percentage of iso octane in mixture of n-heptane + iso octane which has the same knocking characteristics as gasoline sample under the same set of conditions is known as octane number

Eg: Gasoline with ON = 90 has same knocking characteristics as mixture of 90% iso octane + 10% n-heptane.

* Antiknock agents: Are added to enhance the octane no.

Eg: TEL, Diethyl telluride, benzene
(Tetraethyl lead)

* Unleaded petrol: The petrol whose octane no. is increased without adding lead compounds is called as unleaded petrol octane boosters like.

MTBE (methyl tertiary butyl ether)

ETBE (ethyl tertiary butyl ether)

Methanol, ethanol etc.

Knocking in diesel engine: The combustion of fuel in diesel engine is not instantaneous. The interval b/w the start of fuel injection & its ignition is called as ignition delay. The ignition delay is due to time taken for vapourisation of individual droplets & raising of vapour to its ignition temp.

When ignition delay is long it leads to fuel accumulation in the engine even before ignition. In such case, when ignited, an explosion occurs due to increased temp & pressure which results in diesel knock. It is better to have fuels with short ignition delay which should be long enough for compression stroke to be completed.

Cetane: The percentage of n-hexa decrease in a mixture of 2-methyl naphthalene + n-hexa decane which has some ignition characteristics as the diesel sample under the same set of conditions is known as cetane no.

Eg: A sample with CN = 40 performs with same efficiency as a mixture of 40% n-hexadecane + 60% 2-methyl naphthalene.

→ Differences b/w octane no. of cetane no.

Octane No.	Cetane No.
1) % of isooctane + n-heptane.	1) % of hexadecane in a mixture of hexadecane + 2-methyl naphthalene.
2) ON is used to assess the quality of gasoline or other IC engine fuels.	2) CN is used to find suitability of diesel fuel.
3) ON can be enhanced by adding TEL, benzene, MTBE etc.	3) CN is increased by adding alkyl nitriles.

4. st. chain hydrocarbons have low CN.

4. ST. chain' hydrocarbons have high CN

⇒ LPG - liquefied petroleum gas (gas)
bottled gas (gas) Refinery gas:

LPG is obtained as byproduct during
the cracking of heavy oil or from
natural gas.

LPG is dehydrated (removed moisture)
desulphurised & traces of mercaptans &
(organic sulphides) are added to give
warning of gas leakage)

$$CV = 27800 \text{ Kcal/m}^3$$

It's calorific value $CV = 27800 \text{ Kcal/m}^3$.

composition of LPG: It mainly consists of
hydrocarbons which can exist as gas
under atmospheric pressure and also
can be readily liquefied under high
pressure. Mainly includes n-butane
along with iso-butane, butylene
(or) propane.

* Advantages:

- 1) Higher efficiency in heating rate.
- 2) easy & clean to use - handle and store.
- 3) well designed burners ensure complete combustion.
- 4) produces no smoke, therefore ecofriendly.
- 5) portable in cylinders even to remote places
- 6) posses less health hazards.
- 7) requires less maintenance.
- 8) compared to gasoline it easily mixes with air, cheaper & knock resistance.

* uses:

- 1) widely used as domestic & industrial fuel.
- 2) used as source for petro chemicals.
- 3) can be used as direct motor fuel.
- 4) used in IC engines.

→ CNG - (Compressed natural gas)

CNG is natural gas compressed to high pressure of 1000 atm.

It's calorific value varies b/w 12000 - 14000 Kcal/m³

composition: Mainly consists of methane

CH₄ 80 - 90 %

Ethane 4 - 5 %

Propane 1.7 - 2 %

Oxygen 0.5 - 0.6 %

C₄ and higher 0.7 - 0.8 %

C₆ and higher 0.2 - 0.3 %

CO₂ + N₂ 3 - 9 %

* Advantages:

- 1) low cost and high efficiency.
- 2) complete and homogenous combustion.
- 3) undergoes clean burning therefore ecofriendly.
- 4) produces very less particulate emission

and unburned hydrocarbons.

g) where released in air, mixes haphazardly than petrol & diesel.

* compared to LPG, CNG is much safer fuel as it ignites at higher temp, low operating cost & conversion of gasoline automobiles to CNG automobiles is very easy.

* uses:

- 1) used as domestic fuel for heating, cooking etc.
- 2) Also used in Automobiles.