I. Short Answer Type Questions

Prob.1 *Explain scale and sludge formation.* [R.T.U. 2018]

OR

Differentiate between sludge and scale?

Sol. When the precipitate formed is soft, slimy and loose, known as sludge and is hard and firmly adhering on the inner walls of boilers, known as scale.

Prob.2 *Essential parameter of potable water.* [R.T.U. 2017]

Sol. The essential parameters of potable water include color, odor, pH, total dissolved solids, hardness, alkalinity, elemental compounds such as iron, manganese, sulphate, nitrate, chloride, fluoride, arsenic, chromium, copper, cyanide, lead, mercury, zinc and coliform bacteria.

Prob.3 *Calgon conditioning of boiler.* [R.T.U. 2017]

OR

Write short note on Calgon conditioning. [R.T.U. 2011]

Sol. Calgon conditioning : When calgon [Sodium meta-hexa phosphate $Na_2[Na_4(PO_3)_6]$ is added to boiler water, it prevents the scale and sludge formation by forming soluble complex compounds with $CaSO_4$.

$$Na_2\left[Na_4(PO_3)_6\right] \rightleftharpoons 2Na^+ + \left[Na_4P_6O_{18}\right]^{-2}$$

$$2CaSO_4 + \left[Na_4P_6O_{18}\right]^{-2} \rightarrow \left[Ca_2P_6O_{18}\right]^{-2} + 2Na_2SO_4$$

Prob.4 *What do you understand by hardness of water?*

Sol. The characteristic property of water which prevents the lathering of soap, due to presence of certain salts of calcium and magnesium and other heavy metals (like Al^{3+}, Fe^{3+} and Mn^{2+}) dissolved in water.

Prob.5 ***What do you mean by boiler corrosion?***

Sol. The "decay" or "disintegration" of boiler material either by a chemical or electrochemical reaction with its environment is known as "**Boiler Corrosion**".

Prob.6 ***Give the causes of priming.***

Sol. Priming caused by (i) the presence of large amounts of dissolved solids (ii) very high water level (iii) high steam velocity (iv) improper designing of boiler (v) sudden increase in steam production rate which leads to sudden boiling.

Prob.7 ***What do you mean by sedimentation?***

Sol. The process of allowing water to stand undisturbed in big tanks for some time in order to facilitate the settling down of the coarse suspended particles due to the force of gravity is called sedimentation.

Prob.8 ***What is break point chlorination?***

Sol. "Chlorination of water to such an extent that not only living organism but also other organic impurities in water are destroyed is called break point chlorination."

II. Long Answer Type Questions

Prob.1 ***Discuss the treatment of ground water to be used for domestic purposes.*** **[R.T.U. 2018]**

Sol. Treatment of Water for Municipal Supply (Purification of Water)

The table list the types of impurities and the process to be employed for removing them.

S.No.	Process used for Removal	Impurities
1.	Screening	Floating material such as leaves and twinges.
2.	Sedimentation	Suspended impurities such as sand, clay
3.	Filtration	Colloidal impurities and large organism
4.	Disinfection	Pathogenic bacteria

1. Screening : It is a process of removing floating materials like leaves and twigs etc. from water. Raw water is passed through screens having holes, when the floating matter is retained by them and water is allowed to pass.

2. Sedimentation : The process of allowing water to stand undisturbed in big tanks for some time in order to facilitate the settling down of the coarse suspended particles due to the force of gravity is called sedimentation.

3. Filtration : This is the process of removal of coarse impurities (e.g coagulated colloidal material, suspended matter etc.) and some of micro–organisms by passing water through a porous material consisting of a bed of fine sand and other granular materials. The porous material used for filtration is called a filter.

The filters used for water treatment are of two types (i) gravity type filters, and (ii) pressure type filters. The gravity type filters can further classified as slow sand filter and rapid sand filters. The water for municipal supply is usually filtered by gravity sand filter.

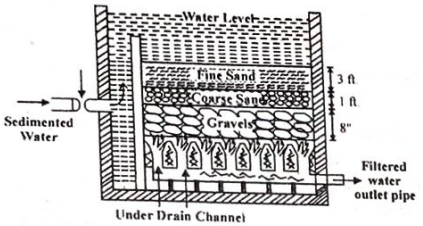


Fig. : Sand Filter

4. Sterilization (Disinfection) of Water : The filtered water still contains small amounts of pathogenic (disease producing) bacterias which must be removed or destroyed if the water has to be used for drinking or municipal purposes.

The process of destroying/killing of pathogenic bacterias and other micro-organisms from water to make it safe for use is known as disinfection and the chemicals used for this purpose are called disinfectants. Disinfection does not ensure total destruction of all living organisms. On the other hand, sterilization means complete destruction of all living organisms which is possible by boiling the water over a period of time.

Characteristics of an Ideal Disinfectant

(i) It should kill the pathogens quickly at room temperature.

(ii) It should be inexpensive.

(iii) It should not be toxic to human.

(iv) It should provide protection against any contamination in water during conveyance or storage

Prob.2 ***What is softening of water? Explain the softening of water by Zeolite method with diagram and chemical reaction.*** **[R.T.U. 2018]**

OR

Describe zeolite method of water softening with its limitations. **[R.T.U. 2017]**

Sol. Softening of Water : The process of removing the hardness causing salts from water is called softening of water. Hard water is unsuitable for industries as well as for domestic purposes. Therefore, it is necessary to remove the hardnesss of water before using in various industries, boilers etc. The softening of hard water can be done by :

(i) Removal of hardness causing salts of calcium and magnesium.

(ii) Conversion of these salts into soluble sodium salts.

(iii) Combination of the above methods.

The hardness causing salts can be removed mainly by three methods.

(i) Lime-Soda Method (ii) Zeolite Method and (iii) Ion-exchange Methods.

Zeolite or Permute Method : The name zeolite is derived from two Greek words (zein + lethos) which means **'boiling stone'.** The name was first used by Cronstedt (a Swedish geologist in 1756) to a certain group of naturally occurring minerals so that released their **'water of hydration'** in the form of **steam**. This is a sodium aluminium orthosilicate or sodium zeolite : $Na_2O.Al_2O_3.xSiO_2.yH_2O$, where x = 2 to 10 and y = 2 to 6 (which can be expressed as Na_2Z, where Z is the insoluble radical frame work). Therefore, zeolites are naturally occurring hydrated sodium alumino silicate minerals which are capable of exchanging reversibly its sodium ion with the hardness producing ions such as Ca^{2+}, Mg^{2+}.

Zeolites are of two types

(i) Natural Zeolites are non-porous, amorphous and are derived from green sands by washing, heating and treating with NaOH. e.g.

Natrolite : $Na_2O.Al_2O_3.4SiO_2.2H_2O$;

Thomsonite : $Na_2O, Al_2O, Al_2O_3.3SiO_2.2H_2O$

Laumontite : $CaO.Al_2O_3.4SiO_2.4H_2O$

(ii) Synthetic Zeolites are porous and possess a gel structure. They are usually prepared by heating together china clay, feldspar and soda ash. Synthetic zeolites possess higher exchange capacity per unit weight as compared to natural zeolites.

1. Structure

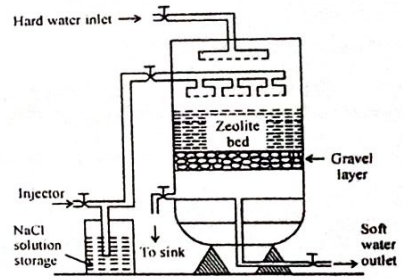


Fig. 1 : Permute Process for Softening of Hard Water

2. Process

This process removes both temporary and permanent hardness. Zeolite can be represented as Na_2Z, where Z is the insoluble radical framework. The zeolite (Permutit) is loosely packed over a layer of coarse sand in a tank (see fig.) . Hard water is allowed to percolate through a bed of active granular Na_2Z. The Ca^{2+} and Mg^{2+} ions present in hard water get replaced by the sodium ions of zeolite. The various reactions that take place are as follows–

$$Ca(HCO_3)_2 + Na_2Z \longrightarrow CaZ + 2NaHCO_3$$

$$Mg(HCO_3)_2 + Na_2Z \longrightarrow MgZ + 2NaHCO_3$$

$$CaSO_4 + Na_2Z \longrightarrow CaZ + Na_2SO_4$$

$$MgSO_4 + Na_2Z \longrightarrow MgZ + Na_2SO_4$$

$$CaCl_2 + Na_2Z \longrightarrow CaZ + 2\,NaCl$$

$$MgCl_2 + Na_2Z \longrightarrow MgZ + 2\,NaCl$$

$$Fe(HCO_3)_2 + Na_2Z \longrightarrow FeZ + 2\,NaHCO_3$$

$$Mn(HCO_3)_2 + Na_2Z \longrightarrow MnZ + 2\,NaHCO_3$$

Hardness Zeolite

This sodium salts formed in the above reactions remain dissolved in the softened water and do not cause any hardness.

Regeneration of the Zeolite

When the process is continued for, the zeolite is completely converted into calcium and magnesium zeolites and gets exhausted. Now the supply of hard water is stopped and zeolite regenerated by treatment for some hours with 10% solution of NaCl.

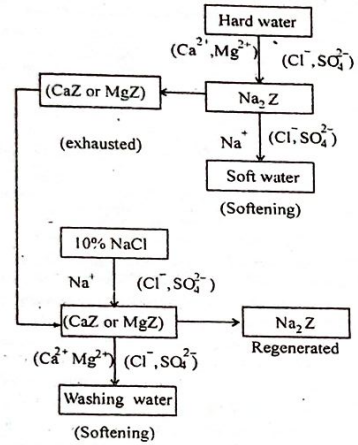


Fig. 2 : Scheme for Softening of Water by Zeolite Process

When the sodium salt of zeolite is formed.

$$CaZ + 2NaCl \rightleftharpoons Na_2Z + CaCl_2$$

$$MgZ + 2\,NaCl \rightleftharpoons Na_2Z + MgCl_2$$

After this treatment, the packing is washed with water to remove the chloride of Ca^{2+} and Mg^{2+} formed in the regeneration process. The washings are led to drain and in the regenerated zeolite is used again for the softening process.

Soft water obtained by this method is used for laundry purpose and can not be used for boiler purpose because it may cause caustic embrittlement.

Note : The amount of NaCl used for regeneration of exhausted zeolite and the hardness of water may be calculated using following formula

$$\text{Hardness of water (Mg/L)} = \frac{50 \times W \times V_2 \times 10^3}{58.5 \times V_1}$$

Where :

W = Amount of NaCl present per litre in gms.

V_2 = Total volume of NaCl used for regeneration in litre

V_1 = Total volume of water softened in litres.

Limitations of the Process

1. The water containing turbidity and suspended impurities can not be treated by this method because turbidity clogs the pores of the zeolite bed.
2. Anions are not removed by this method. Wat containing HCO_3^- gets converted to $NaHCO_3$.

$$NaHCO_3 \longrightarrow NaOH + CO_2$$

Such ion is not suitable for boiler which cau corrosion of boilers. Since NaOH may lead caustic embrittlement.

3. If water contains large quantities of Mn^{2+} and Fe ions as these ions convert sodium zeolite into the respective zeolite which are difficult to l regenerated.
4. Water containing mineral acids, destroy the sodiu zeolite and hence they must be neutralized wi Na_2CO_3 in advance, before feeding the water in the zeolite bed.
5. The softened water obtained by this proce contains several dissolved salts. Such water is n fit for boiler use.
6. Hot water should not be used as the zeolite ten to dissolve in it.

Advantages of the Process

1. The hardness is almost completely removed a water of about 10 ppm hardness is produced.
2. The equipment used is compact and does not occu much space.
3. No impurities are precipitated, so there is no risk formation of sludge in treated water.
4. For maintenance as well as operations, less skill needed.
5. It is quite clean and rapid process which requir less time for softening.
6. The process automatically adjusts itself to wat of different hardness.

Disadvantages of the Process

1. Treated water contains more sodium salts.
2. Turbid water cannot be treated satisfactorily.
3. The process only replaces Ca^{2+} and Mg^{2+} by N ions but not all other ions which are harmful boilers.
4. All acidic anions (like CO_3^{2-} and HCO_3^-) leaves $NaHCO_3$ decomposes producing CO_2 which results in corrosion and Na_2CO_3 hydrolys to NaOH, which results in caustic embrittlemen

Prob.3 *A sample of water having the following analysis :*

$Mg(HCO_3)_2$ = 73 mg/L

$Ca(HCO_3)_2$ = 162 mg/L

$CaSO_4$ = 136 mg/L

$CaCl_2$ = 111 mg/L

$MgCl_2$ = 95 mg/L

$NaCl$ = 58.5 mg/L

Calculate the temporary, permanent and total hardness of water in terms of Clark degree.

[R.T.U. 2018]

Sol.

Constituents	Amount mg/L [A]	Multiplication Factor [M]	$CaCO_3$ Equivalent = [A] × [M]
$Mg(HCO_3)_2$	73	$\frac{100}{146}$	$73 \times \frac{100}{146} = 50$ mg/L
$Ca(HCO_3)_2$	162	$\frac{100}{162}$	$162 \times \frac{100}{162} = 100$ mg/L
$CaSO_4$	136	$\frac{100}{136}$	$136 \times \frac{100}{136} = 100$ mg/L
$CaCl_2$	111	$\frac{100}{111}$	$111 \times \frac{100}{111} = 100$ mg/L
NaCl	58.5	Doesn't cause any hardness	–

Temporary hardness is due to bicarbonates of calcium and magnesium.

Temporary hardness = 50 + 100 = 150 mg/L

= 150 × 0.07 °Cl

[∵ 1 mg/L = 0.07 °Cl]

= 10.5 °Cl

Permanent hardness is due to chloride and sulphate of calcium and magnesium

Permanent hardness = 100 + 100 + 100 = 300 mg/L

= 300 × 0.07 °Cl

= 21 °Cl **Ans.**

Total hardness of water = 10.5 + 21 = 31.5 °Cl **Ans.**

Prob.4 *Calculate the requirement of Lime and Soda for softening 10^5 litres of water.*

Analysis of water is as follows :

HCO_3^- = 396.5 mg/Lit; Mg^{+2} = 42 mg/Lit

Ca^{++} = 90 mg/Lit; H^+ = 1.5 mg/Lit

$FeSO_4.7H_2O$ = 14 mg/Lit

The purity of Lime is 91% and that of Soda is 97.2%.

[R.T.U. 2017]

Sol. Conversion into $CaCO_3$ equivalents

Constituents	Amount	Multiplication Factor	$CaCO_3$ equivalent
HCO_3^-	396.5 ppm	100/122	396.5×100/122 = 325 ppm
Mg^{2+}	42 ppm	100/24	42×100/24 = 175 ppm
Ca^{2+}	90 ppm	100/40	90×100/40 = 225 ppm
$FeSO_4.7H_2O$	14 ppm	100/278	14×100/278 = 5 ppm
H^+	1.5 ppm	100/2	1.5×100/2 = 75 ppm

Lime Requirement

$$= \frac{\text{Mol. weight of } Ca(OH)_2}{100} \times \left[\begin{matrix}\text{CaCO}_3\text{ equivalent of } Mg^{2+} \\ +HCO_3^- + FeSO_4.7H_2O + H^+\end{matrix}\right]$$

$$\times \frac{91}{100}(\text{purity of lime}) \times \text{Volume of water}$$

$$= \frac{74}{100} \times [175 + 325 + 5 + 75] \times \frac{91}{100} \times \frac{10^5}{1000\,(\text{in grams})}$$

= 39057.2 g = 39.0572 kg

Soda Requirement

$$= \frac{\text{Mol. weight of } Na_2CO_3}{100} \times \left[\begin{matrix}\text{CaCO}_3\text{ equivalent of } Ca^{2+} + \\ Mg^{2+} + FeSO_4.7H_2O + H^+ - \\ HCO_3^-\end{matrix}\right]$$

$$\times \frac{97.2}{100}(\text{purity of soda}) \times \text{Volume of water}$$

$$= \frac{106}{100} \times [175 + 225 + 5 + 75 - 325] \times \frac{97.2}{100} \times \frac{10^5}{1000\,(\text{in grams})}$$

= 15969.96 g = 15.96996 kg

Prob.5 *Discuss preventive measures to minimize the problem of scale formation in boilers.* **[R.T.U. 2017]**

Sol. Prevention of Scale Formation

Blow-Down Operation : The blow-down operation is done to prevent higher concentration of undesirable substance in boiler water. This removes a portion of the concentrated water

(v) Sodium Aluminate ($NaAlO_2$) Conditioning

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3\downarrow$$

[Gelatinous ppt]

NaOH reacts with $MgCl_2$, precipitates Mg^{2+} as $Mg(OH)_2$

$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2\downarrow + 2NaCl$$

$Mg(OH)_2$ and $Al(OH)_3$ are flocculent precipitates and they entrap finely suspended and colloidal impurities along with silica. Now these precipitates can be removed by blow down operation.

(vi) Radioactive Conditioning : The energy radiations emitted by radioactive salts placed inside the boiler water at a certain points. These salts prevent scale formation.

(vii) Electrical Conditioning : This is done by sealed glass bulbs, containing mercury (Hg) connected to a battery and the bulbs kept rotating are placed in the raw boiler water. Mercury bulbs emits electrical discharges when water boils which controls scale forming particle to stick together to form sludge.

(viii) Complexometric Method : Scale formation can also be prevented by adding a solution of EDTA (1.5% alkaline, pH = 8.5) to boiler feed water. EDTA reacts with scale forming cations to form stable and soluble complex.

Prob.6 *(a) Explain break point chlorination with diagram and also write it's advantages. –*

(b) Define degree of hardness. A standard hard water solution contain 30 g $CaCO_3$ per litre 30 ml. of this required 25 ml. of EDTA solution on titration 30 ml. of water sample required 20 ml. of EDTA solution. The sample after boiling required 15 ml. EDTA solution. Calculate temporary, permanent and total hardness of water sample. [R.T.U. 2016]

Sol.(a) Break Point Chlorination Curve : It may be defined as the chlorination of water to such an extent that not only living organism but also other organic impurities in water are destroyed.

When chlorine is added to water, it is used for different reactions like oxidation of oxidizable substance, chlorination of organic substance, destructive oxidation of organic substances and disinfection of pathogens.

Initially all the chlorine added is consumed and there is no free chlorine. This is due to complete oxidation of oxidizable substances. As the applied chlorine increases, there is steady increase in amount of residual chlorine. This stage corresponds to formation of chloro-organic compounds and chloramines when the dose of chlorine increase, destruction of chloro organic and chloramines take place.

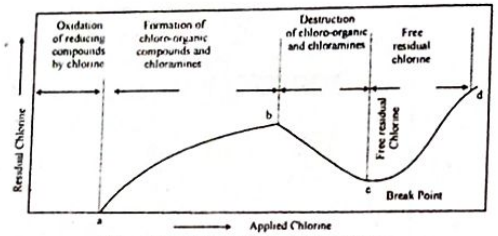


Fig. : Break Point Chlorination Curve

Addition of chlorine in such dosages is known as break point or free residual chlorination. The breakpoint chlorination ensure complete destruction of organic compounds, which gives color, unpleasant odour and bad taste. In addition to it a complete destruction of disease producing micro–organisms is also ensured.

Advantages

(1) It oxidizes complete organic matters, dissolved ammonia and other reducing particles.
(2) It removes color (which is due to the presence of organic compounds).
(3) It destroys (~ 100%) all the bacterias.
(4) It removes bad odour and bad taste.

Sol.(b) Degree of Hardness : The degree of hardness of water is conveniently expressed in terms of equivalent amount of $CaCO_3$. Although hardness of water is never present in the form of calcium carbonate because it is insoluble in water and hardness is actually caused by bicarbonates, chlorides and sulphates of calcium and magnesium.

Given 1 litre of Standard Hard water contain 30 g $CaCO_3$

1 ml of Standard Hard water contains 30 mg $CaCO_3$

Now 25 ml of EDTA
= 30 ml of Standard Hard Water
= 30 × 30
= 900 mg of $CaCO_3$
⇒ 1 ml of EDTA

$$= \frac{900}{25} \text{ mg of } CaCO_3 \text{ equivalent hardness}$$

= 36 mg of $CaCO_3$ equivalent hardness

(1) Calculation of Total Hardness of water
30 ml of sample water
= 20 ml of EDTA
= 20 × 36
= 720 mg of $CaCO_3$ eq. hardness
∴ 1 litre of sample water
= 7200 mg of $CaCO_3$ eq. hardness
Total hardness of water
= 7200 ppm

(2) Calculation of Permanent Hardness
30 ml of boiled water
= 15 ml of EDTA
= 15 × 36
= 540 mg of $CaCO_3$ eq. hardness
1 litre of boiled water
= 5400 mg of $CaCO_3$ eq. hardness
Hence Permanent hardness of water
= 5400 ppm

(3) Calculation of Temporary Hardness
= Total Hardness – Permanent Hardness
= 7200 – 5400 = 1800

Prob.7 *(a) What is the basic principle of complexometric titration, also give chemical reaction?*

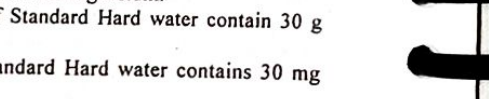
(b) What do you understand by sedimentation process?

(c) Calculate temporary, permanent hardness and total hardness present in hard water sample from following data obtained in soap titration method when 40 ml. of water is titrated with Soap solution

(i) Lather factor = 0.8 ml. soap solution
(ii) Total hardness = 14.6 ml. soap solution
(iii) Permanent hardness = 7.5 ml. soap solution
(iv) Standard hardwater (SHW) = (250 mg/L $CaCO_3$) = 30.8 ml soap solution. [R.T.U. 2016]

Sol.(a) Basic Principle of Complexometric Titration: Hardness of water can be determined by EDTA (complexometric) method.

EDTA (ethylene diamine tetra acetic acid) is an extraordinary strong complexing agent.



As, it is not very soluble in water and hence EDTA in the form of its disodium salt is normally used in all complexometric titrations.

This acts as a tetra/hexa dentate ligand and attaches itself with metal ions (through O or N atoms) to give very stable, soluble and colorless complexes. Since hardness of water is due to Ca^{2+} and Mg^{2+} mainly, their presence can be conventionally determined by titrating a water sample against standard solution of Na_2H_2Y using a suitable ion indicator to note the end point.

When hard water is titrated against EDTA then EDTA or its sodium salts form stable complex ions with calcium (Ca^{2+}) or magnesium (Mg^{2+}) ions in water.

$$\begin{bmatrix} Ca^{2+} \\ Mg^{2+} \end{bmatrix} + EDTA \rightarrow \begin{bmatrix} Ca^{2+} \\ Mg^{2+} \end{bmatrix} EDTA \text{ Complex.}$$

The titration is carried out in presence of indicator, Erichrome black–T. The indicator when added in small amount

1 litre of Permanent hardness $= 2.233 \times \frac{1000}{40}$

$= 55.833$ mg $CaCO_3$ eq.

Permanent hardness = 55.833 mg of $CaCO_3$ eq./l

or 55.833 mg/L

Hence temporary hardness = Total hardness – Permanent Hardness

$= 115 - 55.833$

$= 59.167$ mg/L

Prob.8 ***(a) Calculate the amount of lime and soda needed for softening 1,00,000 litres of water containing HCl = 8.3 mg/L, $Al_2(SO_4)_3$ = 36.2 mg/L, $MgCl_2$ = 11.5 mg/L, NaCl = 29.30 mg/L. Purity of lime is 90% and that of soda is 98%. 10% chemicals are to be used excess in order to complete the reaction quickly.***

(b) Describe carry over and caustic embrittlement. How can they be prevented? [R.T.U. 2016]

Sol.(a) Conversion into $CaCO_3$ Equivalent :

S. No.	Substance	Amount of substance	Multiplication Factor	Equivalent of $CaCO_3$
1.	HCl	8.3 mg/L	$\frac{100}{73}$	$\frac{100}{73} \times 8.3 = 11.36$
2.	$Al_2(SO_4)_3$	36.2 mg/L	$\frac{100}{114}$	$\frac{100}{114} \times 36.2 = 31.75$
3.	$MgCl_2$	11.5 mg/L	$\frac{100}{95}$	$\frac{100}{95} \times 11.5 = 12.10$

Note : NaCl does not cause hardness

Volume of water = 100000 litre

Lime Requirement :

$$= \frac{74}{100}[11.36 + 31.75 + 12.10] \text{ mg/L}$$

$= 40.85$ mg/L

Lime required of given quality (*i.e.* 90%) with 10% excess

$$= 40.85 \times \frac{100}{90} \times \frac{110}{100}$$

$= 49.42$ mg/L

100000 litres of water required

$$= 49.42 \text{ mg/l} \times 100000 \times \frac{1 \text{ kg}}{10^6 \text{ mg}}$$

$= 4.942$ kg of lime

Soda Requirement :

$$= \frac{106}{100}[11.36 + 31.75 + 12.10] \text{ mg/L}$$

$$= \frac{106}{100}[55.21] \text{ mg/L}$$

$= 58.52$ mg/L

Soda required of given quality *i.e.* 98% purity with 10% excess

$$= 58.52 \times \frac{100}{98} \times \frac{110}{100} = 70.80 \text{ mg/L}$$

Soda required for 100000 litre of water

$$\Rightarrow 70.80 \text{ mg/L} \times 100000 \text{ litre} \times \frac{1 \text{ kg}}{10^6 \text{ mg}}$$

$\Rightarrow$ 7.080 kg of soda.

Sol.(b) Carry over : The phenomenon of carrying of water along with impurities by steam is called "carry over". This is mainly due to priming and foaming. Priming and foaming usually occur together. They are objectionable because-

(i) Dissolved salts or suspended solids in water carried by the wet steam to superheater and turbine, blades, where they get deposited as water evaporates. This deposit decreases the efficiency of boiler.

(ii) Dissolved salts may enter the parts of other machinery, thereby decreasing their life.

(iii) The maintenance of the boiler pressure becomes difficult because of improper judgement of actual height of water.

Prevention :

(i) The prime means of preventing carryover is to have good mechanical steam separation devices.

(ii) For low/medium pressure fire tube boiler where steam purity is not stringent, gravity separation its normally satisfactory.

(iii) As steam pressure rises the difference in density reduces making gravity separation less effective.

(iv) Carryover can never be eliminated completely.

(v) The primary consideration in the selection of boiler and its operating is the amount of carryover that can be tolerated.

Caustic Embrittlement : This is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. It is a form of corrosion caused by high concentration of sodium hydroxide in boiler water. It is most likely to occur in boilers operating at high pressures, where NaOH is produced in the boiler by the hydrolysis of some residual Na_2CO_3 obtained from water softening process like lime soda.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

The formation of NaOH makes the boiler water caustic. This caustic water penetrates into the minute hair cracks present in the inner side of boiler by capillary action. When

the water evaporates and the concentration of dissolved NaOH increases progressively which attacks the surrounding area, thereby dissolving the iron of boiler as **sodium ferrate**.

$$Fe + 2NaOH \longrightarrow \underset{\text{Sodium ferrate}}{Na_2FeO_2} + H_2O\uparrow$$

$$3Na_2FeO_2 + 4H_2O \longrightarrow 6NaOH + Fe_3O_4 + H_2\uparrow$$

$$6Na_2FeO_2 + 6H_2O + O_2 \longrightarrow 12NaOH + 2Fe_3O_4$$

This causes the formation of irregular inter-angular cracks on the boiler metal particularly at place of high local stress like bend, joints, rivets etc. Caustic embrittlement is a case of stress corrosion and is a localized electrochemical phenomenon. The concentration cell set up during this phenomenon can be expressed as shown–

Iron at the point of high local stress e.g. rivets, bends, joints.	Concentrated NaOH(aq) solution	Dilute NaOH(aq) solution	Iron at plane surface

with the iron surrounded by dilute NaOH at plane surface acting as the cathode, while the iron surrounded by conc. NaOH acting as the anode. The iron in the anodic part gets dissolved or corroded.

Prevention of Caustic Embrittlement

(i) The water to be used in boilers should be softened by sodium phosphate instead of sodium carbonate.

(ii) The tannin or lignin should be added to the boiler water which blocks the minute crakes and thus preventing the infiltration of NaOH.

(iii) It can be prevented by the addition of sodium sulphate which also block the hair cracks, thereby preventing infiltration of caustic soda solution in these. Generally the concentrations of Na_2SO_4: NaOH are maintained at 1 : 1, 2 : 1, or 3 : 1 for operating pressure of 10, 20 and greater than 20 atmospheres respectively to check caustic embrittlement in boilers. However, use of a very high concentration of Na_2SO_4 may lead to the formation of $CaSO_4$ scales. Then Na_3PO_4 should be used. Na_3PO_4 is an effective conditioning agent and also is over 300 times than Na_2SO_4 in suppressing embrittlement.

(iv) The excess of alkali in boiler feed water should be neutralized.

(v) The use of a excess of sodium carbonate should be avoided in lime-soda process in boiler feed water treatment.

(vi) The pH of the boiler feed water should be carefully adjusted to 8-9.

Prob.9 ***(a) Write short notes on Permutit method. Compare the lime-soda, Zeolite and Ion-exchange method.***

(b) A sample analysis gave the following results - H_2SO_4 = 198 mg/L, $CaSO_4$ = 274 mg/L, $MgSO_4$ = 28 mg/L and NaCl = 28 mg/L water is to be supplied to the town of the population of one lakh only. The daily consumption of water is 60 litre per head. Calculate the cost of lime and soda required for the softening the hardwater for town for the month May 2004. If the cost is Rs. 10/- per kg and soda is Rs. 8/- per kg. [R.T.U. 2016]

Sol.(a) Permutit Method : *Refer to Long Answer Prob.2.*

Comparison among Lime-soda, Zeolite and Ion-exchange method :

S. No.	Lime-Soda Process	Zeolite Process	Ion Exchange Process
1.	Treated water contains 10–15 ppm residual hardness.	Treated water contains residual hardness of 0–15 ppm.	Treated water contains residual hardness of 0–12 ppm.
2.	Operating expenses are high.	Operating expenses are low.	Operating expenses are high.
3.	Low capital cost process.	Cost of material plant is high.	Cost of material plant is highest.
4.	Acidic water can be treated.	Acidic water cannot be treated.	Resins are very inert. Acidic water is well treated.
5.	Raw water can have suspended impurities.	Water must be free from suspended impurities.	Water should be free from suspended impurities.
6.	Coagulation filtration removal of sludge is required.	No removal and disposal is required.	Not required.
7.	Hardness of water must be know.. in advance.	Not required.	Not required.
8.	Treated water contains lesser amount of dissolved solids.	Treated water contains more dissoived solids.	No dissolved solids.
9.	Plant occupies more space.	Plant occupies less space.	Plant occupies less space.
Demerits	Disposal of large amount of sludge formation during process	Do not remove CO_2. Treated water contain more Na^+ salts	Replace only ions not HCO^-_3, CO_3^{-2} etc.
Merits	Economic process.	Automatic process easy and cheap.	Can be used for acidic and alkaline water.

Sol.(b) Given data :

H_2SO_4 = 198 mg/L

$CaSO_4$ = 274 mg/L

$MgSO_4$ = 28 mg/L

NaCl = 28 mg/L

Population = 1 lakh

Daily consumption = 60 litre per head

No. of days = 31

Cost of lime = Rs. 10/- kg.

Cost of soda = Rs. 8/- kg.

Total volume of water consumed in 31 days;

V = 100000 × 60 × 31

= 186,000,000 L

S. No.	Substance	Amount of Substance	Multiplication Factor	$CaCO_3$ Equivalent
1.	H_2SO_4	198 mg/L	–	–
2.	$CaSO_4$	274 mg/L	100/136	201.47 ppm
3.	$MgSO_4$	28 mg/L	100/120	23.33 ppm
4.	NaCl	28 mg/L	–	–

H_2SO_4 and NaCl doesn't cause hardness.

Lime Requirement :

$$= \frac{74}{100}[Mg\,SO_4]\,mg/L \times \text{Vol. of water}$$

$$= \frac{74}{100}[23.33] \times 186,000,000$$

$$= 3,211.1412\,kg$$

Soda Requirement :

$$= \frac{106}{100}[CaSO_4 + MgSO_4]\,mg/L \times \text{Vol. of water}$$

$$= \frac{106}{100}[201.47 + 23.33] \times 186,000,000$$

$$= 44,321.568\,kg$$

Softening Cost :

= Cost of Lime + Cost of Soda

= (3,211.1412 × 10) + (44,321.568 × 8)

= 386,683.956

= 386,684 Rs.

Prob.10 ***Explain temporary and permanent hardness of water. Discuss various chemical methods of disinfection of water.*** [R.T.U. 2015, 2012; R.U. 2000]

OR

Explain EDTA method for determination of hardness of water. [R.T.U. 2015]

OR

Explain temporary and permanent hardness of water. [R.T.U. 2014]

OR

What is hardness of water? Explain hardness determination by EDTA method. [R.T.U. 2013]

OR

What is hardness of water? What do you understand by temporary and permanent hardness?

[R.T.U. 2011, 2010]

Sol. Hardness of Water : Hardness in water is that characteristic which "prevents the lathering of soap". This is due to presence in water of certain salts of calcium, magnesium and other heavy metals dissolved in it. Hardness of water is of two types :

(1) Temporary (Bicarbonate type) hardness.

(2) Permanent (Non–carbonate type) hardness.

1. Temporary Hardness (Carbonate Hardness): The temporary hardness of water is due to the soluble bicarbonates of calcium and magnesium. When water is boiled, the bicarbonate ions present in it are decomposed to carbonate and carbon dioxide.

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2\downarrow + 2CO_2\uparrow$$

The Ca^{2+} and Mg^{2+} ions readily combine with the carbonate ions to form insoluble $CaCO_3$ and $MgCO_3$. So the temporary hardness can be largely removed by easy means like boiling etc.

2. Permanent Hardness (Non-carbonate Hardness): It is due to dissolved chlorides, sulphates and nitrates of calcium and magnesium. The difference of total hardness and temporary hardness is also called non–carbonates hardness. The hardness caused due to the presence of chlorides and sulphates of Ca, Mg, Fe and other heavy metals, cannot be removed by boiling. Hardness of water is objectionable for following reasons :

(a) Large amount of soap is wasted to get the desired results in laundry industry, since soap has no cleaning action unless all the Ca, Mg or heavy metal ions are precipitated.

(b) In industries, these salts of water during course of circulation get deposited at different parts of boilers as scales, damaging the system by corrosion, heat resistance, choking etc.

EDTA : *Refer to Long Answer Prob.7(a).*

Various steps involved in this method are :

(1) Standardization of EDTA solution.

(2) Determination of total hardness of water.

(3) Determination of permanent hardness of water.

Calculation

50 ml of standard hard water = V_1 ml of EDTA

∴ 50 × 1mg of $CaCO_3$ = V_1 ml of EDTA

$\therefore$ 1 m*l* of EDTA = $\frac{50}{V_1}$ mg of $CaCO_3$ eq.

Now 50 m*l* of given hard water = V_2 m*l* of EDTA

$\frac{V_2 \times 50}{V_1}$ mg of $CaCO_3$ eq.

$\therefore$ 1 L of given hard water = $\frac{1000V_2}{V_1}$ mg of $CaCO_3$ eq.

$\therefore$ Total hardness = $1000\frac{V_2}{V_1}$ mg/*l* or ppm.

Now 50 m*l* of boiled water = V_3 m*l* of EDTA

$= \frac{V_3 \times 50}{V_1}$ mg of $CaCO_3$ eq.

1000 m*l* of boiled water = $\frac{1000V_3}{V_1}$ mg of $CaCO_3$ eq.

Permanent hardness = $\frac{1000V_3}{V_1}$ ppm

Temporary hardness = (Total – Permanent) hardness

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

Chemical Methods of Disinfection of Water

The disinfection of water can be carried out by the following methods :

(1) Chlorination Method : Chlorine is the most commonly used disinfectant. It may be added directly as gas or in form of concentrated solution in water. Correct dose and sufficient time of contact should be ensured for effective disinfection.

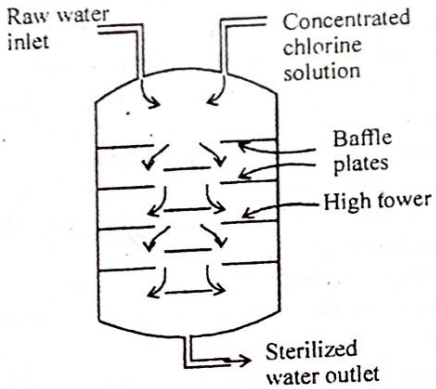


Fig. 1 : Chlorinator

$$H_2O + Cl_2 \xrightarrow[10-15\,min]{2-3\,ppm} HOCl + HCl$$

$HOCl \rightarrow$ Bacterias are killed

Apparatus used for disinfection by chlorine is known as chlorinator. It is a large tower containing number of baffle plates. From its top raw water and chlorine solution are introduced. These get thoroughly mixed during their passage through the tower. Disinfected water is taken out from the outlet at bottom of chlorinator.

(2) By Bleaching Powder Method : Chlorine may be added in the form of bleaching powder. The chemical reaction of bleaching powder in water is given below :

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \rightarrow HCl + HOCl \text{ (unstable hypochlorous acid)}$$

$$HOCl \rightarrow HCl + [O] \text{ (nascent oxygen)}$$

The nascent oxygen destroys pathogens by oxidation.

(3) Ozonization Method : The ozone is highly unstable, harmless gas and an excellent disinfectant. It breakdown liberating nascent oxygen and kills pathogens.

$$O_3 \rightarrow O_2 + [O] \text{ (nascent oxygen)}$$

Disinfection of water by ozone is carried out in ozone sterilizer which is having separate inlets and outlets of water. Separate inlet for ozone is also provided. During the treatment, ozone is manufactured and bubbled through water contained in sterilizer. The sterilized water is removed from top through the outlet.

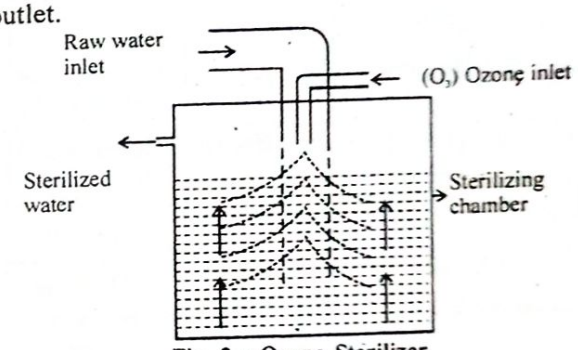


Fig. 2 : Ozone Sterilizer

(4) Boiling Method : Water becomes free from disease causing bacteria if water is boiled for 10–15 minutes at 60° to 70°C.

(5) Chloramine ($ClNH_2$) Method : It is an excellent bactericidal.

$$ClNH_2 + H_2O \rightarrow HOCl + NH_3 \text{ (disinfectant)}$$

$$HOCl \rightarrow HCl + [O] \text{(nascent oxygen)}$$

Prob.11 ***What are the requirements of drinking water? How is turbid water clarified on a large scale? Explain the principle involved.*** **[R.T.U. 2015]**

OR

What are the characteristics of drinking water. Explain various steps involved in removing suspended impurities from the water. **[R.T.U. 2014]**

OR

What is municipal water? Describe all the steps involved in getting municipal grade potable water. **[R.T.U. 2013]**

Prob.12 ***Describe lime-soda process for water softening. Give the chemical reaction involved during the softening.*** **[R.T.U. 2015]**

OR

Write short note on Reactions involved in Lime-soda method. **[R.T.U. 2014]**

OR

Describe the continuous hot lime-soda method for softening hard water. Also give the chemical reactions involved in lime-soda process.

[R.T.U. 2012, (II sem.) 2009, 2008]

OR

Describe the continuous lime soda process of softening hard water. Compare between continuous cold and hot lime – soda process.

Sol. Continuous Lime-Soda Process : The basic principle of this method is to convert all the soluble hardness causing constituents into insoluble precipitates by appropriate chemical reactions.

In this process, a suspension of calcium hydroxide (lime) and sodium carbonate (soda) is added to water in calculated quantities based on the concentration of impurities.

Reactions Involved in Treatment

(a) $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$

(b) $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$

$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCO_3$

(c) $Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+$

(d) $Mg^{2+} + Ca(OH)_2 \rightarrow Ca^{2+} + Mg(OH)_2$

$Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+$

(e) $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$

(f) $2H^+ + Ca(OH)_2 \rightarrow Ca^{2+} + 2H_2O$

$Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+$

(g) $2HCO_3^- + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O + CO_3^{2-}$

(h) $Fe^{2+} + Ca(OH)_2 \rightarrow Ca^{2+} + Fe(OH)_2$

$Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + H_2O$

(i) $Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 3CaSO_4 + 2Al(OH)_3$

$3CaSO_4 + 3Na_2CO_3 \rightarrow 3Na_2SO_4 + 3CaCO_3$

Since 100 parts of $CaCO_3$ are equivalent to 74 parts of $Ca(OH)_2$, the lime required for removing hardness is

$$\textbf{Lime Required} = \frac{74}{100}[\text{Temp.}Ca^{2+} + 2\times \text{Temp.}Mg^{2+} + \text{Perm.}Mg^{2+} + Fe^{2+} + Al^{3+} + CO_2 + H^+ (HCl \text{ or } H_2SO_4) + HCO_3^- - Na^{3+}AlO_2]$$

Soda Required

$$= \frac{106}{100}[\text{Perm.}(Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+}) + H^+ - HCO_3^-]$$

Advantages of Lime-Soda Process

1. Less amount of coagulants are required.
2. The pH of soft water is higher which prevents corrosion of the distribution pipes.
3. Amount of impurities such as iron and manganese are also decreased.
4. Water produced after treatment is of alkaline nature. Amount of micro organism are reduced.
5. It is very economical method.

Disadvantages of Lime-Soda Process

1. This process cannot be used for domestic purpose because it is difficult to find amount of lime-soda required.
2. It is not suitable for laundry industry, where $CaCO_3$ may end up on the clothing.
3. Skilled and careful supervision is required for efficient and economical operation.
4. It creates the problem of disposal of sludge.
5. The hardness of water is not completely removed.

Comparison between Cold and Hot Lime-Soda Process

S.No.	Cold Lime-Soda Process	Hot Lime-Soda Process
1.	Reactions are slow	Reactions are fast and complete
2.	Filtration is slow.	Filtration is fast.
3.	Less efficient.	Very efficient.
4.	Softening capacity is low.	Softening capacity is high.
5.	Use of coagulant is necessary.	No coagulants are required.
6.	Requirement of lime consumption is as per stochiometry.	Less quantity of lime is required as temporary hardness is removed by boiling.
7.	Steam is not used.	Steam is used, which increases fuel consumption.
8.	Residual hardness of soft water produced is 50–60 ppm.	Residual hardness of soft water produced is 15–30 ppm.

Prob.13 ***A sample of water on analysis has been found to contain the following impurities in ppm.***

$Ca(HCO_3)_2 = 48.5$

$Mg(HCO_3)_2 = 29.2$

$MgCl_2 = 3.5$

$MgSO_4 = 4.8$

$CaCl_2 = 33.3$

$CaSO_4 = 54.4$

Calculate the quantity of lime and soda required for softening of one million litres of water. **[R.T.U. 2015]**

Sol.

Constituents	Quantity (W)	Equivalent wt.(E)	Hardness in terms of $CaCO_3$ Equivalent = $\frac{W\times 50}{E}$
$Ca(HCO_3)_2$	48.5 ppm	81	$48.5\times\frac{50}{81} = 29.94$ ppm
$Mg(HCO_3)_2$	29.2 ppm	73	$29.2\times\frac{50}{73} = 20$ ppm
$MgCl_2$	3.5 ppm	47.5	$3.5\times\frac{50}{47.5} = 3.68$ ppm
$MgSO_4$	4.8 ppm	60	$4.8\times\frac{50}{60} = 4$ ppm
$CaCl_2$	33.3 ppm	55.5	$33.3\times\frac{50}{55.5} = 30$ ppm
$CaSO_4$	54.4 ppm	68	$54.4\times\frac{50}{68} = 40$ ppm

$$\textbf{Lime required} = \frac{74}{100}[Ca(HCO_3)_2 + 2Mg(HCO_3)_2 + MgCl_2 + MgSO_4 \text{ as } CaCO_3 \text{ eq.}] \times \text{Volume of Water}$$

$$= \frac{74}{100}[29.94 + 2(20) + 3.68 + 4] \times 10^6$$

$$= \frac{74}{100}[77.62] \times 10^6 \text{ mg}$$

$$= 57.4 \times 10^6 \text{ mg}$$

$$= 57.4 \text{ kg}$$

$$\textbf{Soda required} = \frac{106}{100}[MgCl_2 + MgSO_4 + CaCl_2 + CaSO_4 \text{ as } CaCO_3 \text{ eq.}] \times \text{Volume of water}$$

$$= \frac{106}{100}[3.68 + 4 + 30 + 40] \times 10^6 \text{ mg}$$

$$= \frac{106}{100} \times 77.68 \times 10^6 = 82.34 \times 10^6 \text{ mg}$$

$$= 82.34 \text{ kg}$$

Prob.19 ***Explain Demineralization process of water softening with diagram.*** **[R.T.U. 2014]**

OR

Write short note on the Deionization method of softening. **[R.T.U. 2013]**

Sol. Ion Exchange Process (Demineralization or Deionization)

The substances capable of exchange of ions with the electrolyte solution are called ion exchangers. The process of ion exchange is the property of an ion exchangers to exchange an ion in its structure with an ion in solution that is brought in contact with it.

Since all the cations and anions are completely removed in this process, so it is known as '**complete deionization**'. Ion exchangers are organic cross, linked, insoluble, high molecular weight, polymers with a porous structure, and the '**functional groups**' attached to the chains are responsible for the ion-exchange properties. The ion exchanger or ion exchange resins may be classified as :

Cation Exchangers : Resins containing acidic functional groups like (–COOH, – SO_3H etc.) are capable of exchanging their H^+ ions with other cations which comes in their contact; and hence they are termed as cation exchangers e.g. styrene divinyl benzene copolymers which on sulphonation, or carboxylation acquire capability to exchange their hydrogen ions with other cations in water.

They can be represented as R^-H^+ where R^- represents the insoluble polymer matrix.

The exchange reactions are

$$2R^-H^+ + Mg^{2+} \rightarrow R_2Mg + 2H^+$$

$$2R^-H^+ + Ca^{2+} \rightarrow R_2Ca + 2H^+$$

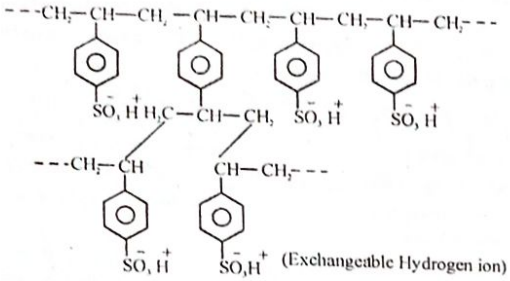


Fig. 1 : Cation Exchanger (Sulphonate form)

Amberlite IR – 120; and Dovex – 50 are commercially available cation exchange resins.

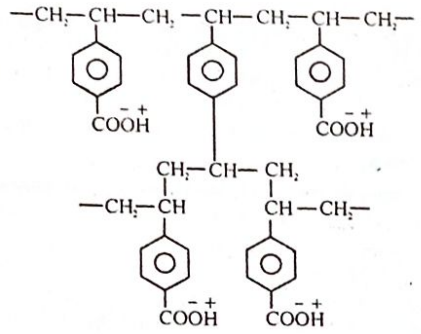


Fig. 2 : Cation Exchanger (Carboxylate form)

Anion Exchangers : Resin containing basic functional group like amino or quaternary ammonium ($-N^+R_3$) or quaternary phosphonium or hydroxides or hydrochloride are capable of exchanging their anion with other anions in water and therefore are known as anion exchangers e.g. styrene divinyl benzene or amine formaldehyde copolymers. These after treatment with dilute NaOH solution, become capable to exchange their OH^- anions with other anions present in water.

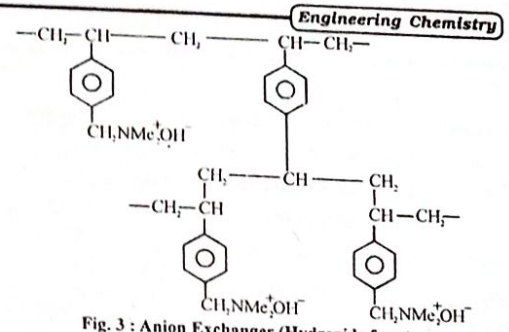


Fig. 3 : Anion Exchanger (Hydroxide form)

They can be simply represented as R^+OH^- where R^+ represents the insoluble organic matrix.

The exchange reactions are

$$2R^+OH^- + SO_4^{2-} \rightarrow R_2SO_4 + 2OH^-$$

$$R^+OH^- + Cl^- \rightarrow RCl + OH^-$$

$$2R^+OH^- + CO_3^{2-} \rightarrow R_2CO_3 + 2OH^-$$

Amberlite 400 and Dovex–3 are commercially available anion exchangers.

Process : The apparatus used for softening hard water by this method consists of two containers, one containing cation exchange resin and the other anion exchange resin over a bed of gravel.

Hard water is first passed through the cation exchange resin. The cations present in hard water get exchanged with H^+ ions of the resin.

$$Ca^{++} + 2R^- - H^+ \rightarrow R_2Ca + 2H^+$$

or

$$Mg^{++} + 2R^- - H^+ \rightarrow R_2Mg + 2H^+$$

The water coming out of the first container thus contains free ions in acidic in nature. It is now passed through the anion exchange resin. This resin exchanges the anions with OH^- ions.

$$R^+ - OH^- + Cl^- \rightarrow RCl + OH^-$$

$$2R^+ - OH^- + SO_4^{2-} \rightarrow R_2SO_4 + 2OH^-$$

(Anion exchanger) (In hard water)

The OH^- ions thus formed combine with free H^+ ions to form H_2O molecules.

$$H^+ + OH^- \rightarrow H_2O$$

Thus, the water coming out from the second container is neither acidic nor basic and is free from all cations and anions that were present in hard water. It is known as deionized or demineralized water.

Regeneration : The continuous use of resins exhaust them after some time. Therefore, they must be regenerated. The exhausted cation exchanger column is regenerated by passing a solution of moderately conc. HCl or H_2SO_4 solution through it.

$$R_2Ca + 2H^+ \rightarrow 2RH^+ + Ca^{2+} \text{(washing)}$$

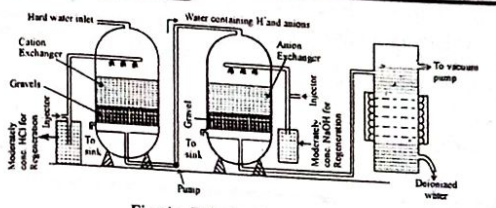


Fig. 4 : Deionization of Water

It is followed by washing with distilled water and the washings containing Ca^{2+}, Mg^{2+}, Cl^- or SO_4^{2-} are drained out.

The exhausted anion exchanger column is regenerated by passing a solution of moderately conc. NaOH solution through it.

$$R_2SO_4^{2-} + NaOH \rightarrow 2R - OH^- + SO_4^{2-} \text{ (washing)}$$

$$R - Cl^- + NaOH \rightarrow R - OH + Cl^-$$

Again, the column is washed with deionized water and the washings containing Na^+ and SO_4^{2-} or Cl^- ions are drained out.

Prob.20 ***Write short note on Priming and Foaming.***

[R.T.U. 2014, 12, 11 (I Sem.), 09, 08]

Sol. Priming and Foaming : When a boiler produces steam rapidly, some particles of the liquid water are carried along with the steam. This process of "Water–Steam" formation is called Priming. Priming is caused by

(a) The presence of large amount of dissolved solids
(b) High steam velocities
(c) Sudden boiling
(d) Improper boiling design and
(e) Sudden increase in steam production rate.

Foaming is the production of persistent foam or bubbles in boilers, which do not break easily. Foaming is due to presence of substances like oil.

Priming and foaming usually occur together. They are objectionable because

(a) Dissolved salts in boiler water are carried by the wet steam to super – heater and turbine blades, where they get deposited as water evaporates. This water reduces their efficiency.
(b) Dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery.
(c) Actual height of the water column cannot be judged properly, thereby making the maintenance of the boiler pressure becomes difficult.

Prob.21 *Write a short note on scale and sludge formation.*

[R.T.U. 2014, 11]

OR

Describe scale and sludge formation in boilers. How are they removed? Discuss in detail.

[R.T.U. 2012, Raj. Univ. 2004]

Sol. Boilers are used for steam generation. When hard water is evaporated, progressively the concentration of dissolved salt is increased.

When their saturation points are reached, the dissolved salts of calcium and magnesium along with other soluble impurities are precipitated on the inner walls of boilers and in due course of time adhere to the metal surface in the form of scales and sludges.

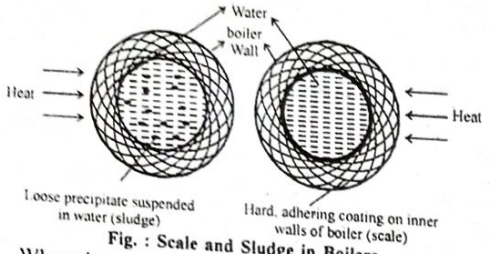


Fig. : Scale and Sludge in Boilers

When the precipitate formed is soft, slimy and loose, known as sludge and is hard and firmly adhering on the inner walls of boilers known as scale.

The sludges are generally formed by the substance, which have greater solubility in hot water than cold water. So, sludges are formed in colder parts of boilers.

Theories of Scale Formation: *Refer to Long Answer Prob.15.*

Theories of Sludge Formation

(a) Decrease in Solubility : Certain impurities in water decreases solubility with increase of temperature, so such impurities separates out from water at a higher temperature e.g. In $CaSO_4$ solubility decreases with increase of temperature.

(b) Hydrolysis of Salts : The soluble magnesium salts are hydrolyzed under high temperature conditions to give soft $Mg(OH)_2$ scale.

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 \downarrow + 2HCl \uparrow$$

(c) Chemical Decomposition : The decomposition of bicarbonates of calcium and magnesium takes place to give rise two carbonates $CaCO_3$ and $MgCO_3$ respectively.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \rightarrow MgCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$MgCO_3$ may further decompose near boiling point of water to give $Mg(OH)_2$

$$MgCO_3 + H_2O \rightarrow Mg(OH)_2 \downarrow + CO_2 \uparrow$$

These salts precipitate and deposits inside the boiler as scale and sludge.

(d) Formation of Silicates : If small amount of SiO_2 is present in boiler feed water it give rise to formation of $CaSiO_3$ and $MgSiO_3$, adhere very firmly to inner walls of boiler.

Removal of Scales and Sludges

1. If they are loosely bound to inner surface of the boiler, can be removed with the help of scrape or wire brush or wood.
2. If they strongly adhere to walls and are hard, can be removed by dissolving them by adding certain chemicals like
   (a) 5–10% HCl solution.
   (b) EDTA solution.
3. **Blow down operations :** In continuous blow down, a definite concentration of substance in boiler water is maintained. Intermittent blow down is aimed at removing sludge from a boiler water. Thus blow down operation is attempted to keep salt concentration at a specific level and to control sludge in the boiler.

Prob.22 *(a) What is softening of water? Describe softening of water by zeolite method with diagram.*

[R.T.U. 2013]

OR

Write short note on zeolite method. [R.T.U. 2012]

(b) The hardness of 5000L of water sample was removed by zeolite softner. Zeolite softner requires 100L of NaCl solution containing 10,000mg/L of NaCl for regeneration. Determine the hardness of sample water.

[R.T.U. 2013]

Sol. (a) Softening of Water : *Refer to Long Answer Prob.2(a).*

Sol. (b) Hardness (mg/*l*) $= \dfrac{m \times v_2 \times 50}{v_1 \times 58.5}$

m = Concentration of NaCl = 10,000 mg/*l*

v_2 = Volume of NaCl required for regeneration = 100 L

v_1 = Volume of hard water to be soften = 5000 L

$$\text{Hardness (mg/}l\text{)} = \frac{10000 \times 100 \times 50}{5000 \times 58.5}$$

$$= 170.94 \text{ mg/}l$$

PREVIOUS YEARS QUESTIONS

I. SHORT ANSWER TYPE QUESTIONS

Prob.1 *What is meant by the term cracking?* [R.T.U. 2018]

Sol. Cracking : Cracking is a process by which the larger molecules are broken down into smaller molecules giving more useful lighter fractions.

Cracking consists of conversion of C–H and C–C bonds of high molecular weight hydrocarbons into more usable low boiling hydrocarbons of lower molecular weight.

$$C_{10}H_{22} \rightarrow C_5H_{12} + C_5H_{10}$$

$$C_8H_{18} \rightarrow C_5H_{12} + C_3H_6$$

Prob.2 ***Arrange n-octance, naphthalene, iso-octane in increasing order of their knocking tendency.*** **[R.T.U. 2018]**

Sol. Naphthalene < Iso-octane < n-octane

Prob.3 ***What are Net Calorific Value (NCV) and a Gross Calorific Value (GCV) of fuel?*** [R.T.U. 2017]

Sol. Higher Calorific Value (HCV) : It is defined as the total amount of heat generated when a unit quantity of fuel is completely burnt and the products of combustion are cooled down to room temperature.

The fuel when containing hydrogen is burnt, the hydrogen present undergoes combustion and will be converted into steam. As the products of combustion are cooled to room temperature, the steam gets condensed into water and latent heat is evolved. Thus, the latent heat of condensation of steam so liberated is included in the gross calorific value.

Lower Calorific Value (LCV) : During combustion of the fuel, water vapour escapes as such along with hot combustion by-product gases and thus, are not condensed. Hence, a lesser amount of heat is available. This is called lower or net calorific value and may be defined as the amount of heat liberated when one unit mass of fuel is burnt completely and hot combustion products are allowed to escape.

Thus, LCV = HCV – latent heat of water vapour formed.

Since, 1 part by mass of hydrogen gives 9 parts by mass of water, the equation becomes :

LCV = HCV – (mass of H_2 in fuel × 9 × latent heat of steam)

Prob.4 ***What is meant by calorific value of a fuel?***

Sol. Calorific value of a fuel is defined as **"The total quantity of heat liberated, by the complete combustion of one unit mass (or volume) of fuel."**

Prob.5 ***Give any two characteristics of a good fuel.***

Sol. 1. High Calorific Value : The fuel should have a high calorific value, i.e. high heat content. Since the amount of heat liberated and temperature attained depends upon the calorific value of fuel.

2. Low Moisture Content : The fuel should have low moisture content, because moisture content of the fuel reduces the heating value.

Prob.6 ***What do you understand by "octane number" of a fuel?***

Sol. The octane number of a fuel is the percentage of volume of iso–octane in a mixture of iso–octane and n–haptane which having the similar knocking characteristics of fuel as under test in standard condition.

Prob.7 ***Give the uses of oil gas.***

Sol. Oil gas used to improve the calorific value of water gas and the mixture of the two gases is called carburetted water gas. Oil gas is used as laboratory gas.

Prob.8 ***Calculate the gross and net calorific value of a coal sample having the following composition : C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and ash = 4.4%.***

Sol. $$GCV = \frac{1}{100}\left[8,080C + 34,500\left(H - \frac{O}{8}\right) + 2,240S\right] \text{K Cal/kg}$$

$$= \frac{1}{100}\left[8,080 \times 80 + 34,500\left(7 - \frac{3}{8}\right) + 2,240 \times 3.5\right] \text{K Cal/kg}$$

GCV = 8828.025 KCal/kg

NCV = GCV – 0.09H × 587 K Cal/kg

= [8828.025 – 0.09 × 7 × 587]K Cal/kg

= 8458.215 K Cal/kg.

II. Long Answer Type Questions

Prob.1 ***How gross calorific value of a solid fuel is determined by Bomb Calorimeter.*** [R.T.U. 2018]

Sol. Determination of Calorific Value by Bomb Calorimeter : The calorific value of solids and non-volatile liquid fuels is determined by Bomb-Calorimeter.

Construction : It consists of following parts :

(i) *Steel bomb* : It is strong cylindrical container made up of stainless steel. It is provided with gas tight screw cap or lid. The lid is provided with two holes for electrodes and one for oxygen inlet valve.

A small ring is fitted to one of the electrode which acts as a support for silica crucible.

(ii) Bomb is placed in *copper calorimeter* containing a known amount of water. It is provided with an *electrical stirrer* and *Backmann's thermometer.*

(iii) Copper calorimeter is surrounded by the air jacket and *water jacket* to prevent any loss of heat due to radiation.

(iv) *Crucible* made up of nickel, or fused silica which contains the fuel. The crucible is placed inside the ring attached to one of the electrodes.

Working : A known amount of given fuel is taken in silica crucible supported over the ring. A piece of fine magnesium wire is tightly stretched across the electrodes touching fuel sample.

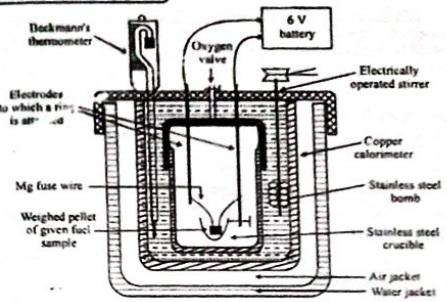


Fig. : Bomb Calorimeter

The bomb is placed inside calorimeter which contains known amount of water. After through stirring, initial temperature of water is noted with help of thermometer. The electrodes are connected to 6 volt battery and circuit is completed. Fuel burns with evolution of heat. Heat produced is transferred to water which raises the temperature of water. Maximum temperature is recorded. Time taken to cool the water in calorimeter from maximum temperature to room temperature is also noted.

Calculations : Let weight of the fuel sample taken = x gm

Weight of water taken in calorimeter = W gm

Higher calorific value = L cals/gm

Water equivalent of calorimeter, stirrer, thermometer etc. = w gm

Initial temperature = t_1°C

Final temperature = t_2°C

Heat liberated by burning of fuels = xL

Heat absorbed by water and apparatus = $(W+w)(t_2 - t_1)$

Since, Heat liberated = Heat absorbed

$xL = (W+w)(t_2 - t_1)$

$L\ (HCV) = (W+w)(t_2 - t_1)/x$

H = Percentage of hydrogen in fuel then, mass of water produced from one gm of fuel

$$= \frac{9H}{100} g = 0.09g$$

∴ Heat taken by water to form steam

= 0.09 H × latent heat of steam (587 cal/g)

LCV = HCV – Latent heat of water formed

= {L (HCV) – 0.09H × 587} calories/gm

For more accurate results, corrections have to be incorporated in above equation.

(i) **Fuse wire correction :** The heat produced, as measured above, the heat given out by ignition of fuse wire used.

(ii) **Acid correction :** Under high pressure and temperature, nitrogen and sulphur present in fuel oxidized to sulphuric acid and nitric acid.

(iii) **Cooling correction :** Rate of cooling and actual time taken is added to rise in temperature.

$$\therefore (HCV) = \frac{(W + w)(t_2 - t_1 + \text{cooling correction}) - (\text{Acid} + \text{fuse wire correction})}{\text{Mass of fuel}(x)}$$

Prob.2 ***What is water gas and its composition? How it is prepared on industrial scale? Explain its uses.*** [R.T.U. 2018]

Sol. Water Gas : Water gas is also called blue gas because it burns with blue flame. Water gas is a mixture of carbonmonoxide and hydrogen (50% along with small amount of non-combustible gases such as carbon dioxide and nitrogen. The equipment used for production of water gas is identical to that used in production of producer gas. The difference lies in the operation. This consists two operation cycles i.e., alternatively air blowing and steam blowing.

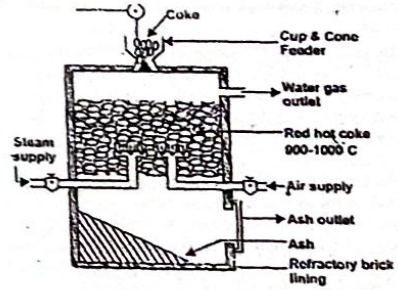


Fig.

Reactions involved : When steam (H_2O) reacts with red hot coke at about 1000°C, the following reactions take place

$C + H_2O \rightarrow CO + H_2$ — 29 kcal (endothermic)

$C + 2H_2O \rightarrow CO_2 + 2H_2$ — 19 kcal (endothermic)

As both above reactions are endothermic, the fuel bed (Coal/Coke) cools down.

The above endothermic reactions cause a fall in temperature of coal bed. In order to raise the temperature, steam supply is withdrawn and in its place only air is introduced. The following exothermic reactions take place. The outgoing gases generated in this cycle are -

$C + O_2 \rightarrow CO_2 + 94$ kcal

$2C + O_2 \rightarrow 2CO + 53$ kcal

A mixture of CO_2 and N_2 cannot be used as fuel but there is a rise in temperature to about 1000°C. It is properly maintained by alternatively sending steam and air. Average composition of water gas is CO = 41%, H_2 = 51%, CO_2 = 4% and N_2 = 4% and it has calorific value of about 2,800 kcal/m^3. It is enriched with some gaseous hydrocarbon. This is so called Carburetted water gas contains CO = 25%, H_2 = 35%, hydrocarbons = 35%, N_2 = 5% and CO_2 = 5%.

Uses of Water Gas :

(i) Water gas is used to remove the carbon monoxide from full cell application.
(ii) It reacts with producer gas and produces fuel gas.
(iii) It is used to gain pure hydrogen for synthesis of Ammonia.
(iv) This gas is also used in Fischer-Tropsch process to convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons.

Prob.3 ***Calculate the weight of air needed for complete combustion of 5.0 kg of a coal cantaining 80% carbon, 15% hydrogen and rest is oxygen.*** [R.T.U. 2018]

Sol. We have

Constituents	Weight in 1kg of coal (kg)	Combustion Reaction	Weight of O_2 (in kg)
C	0.80	$C + O_2 \rightarrow CO_2$	$0.80 \times \frac{32}{12} = 2.13$
H	0.15	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$0.15 \times \frac{16}{2} = 1.2$
O	0.05	–	–
			Total O_2 = 3.33 O_2 in Tuel = 0.05 Net O2 = 3.28

Total weight of air needed for complete combustion of 5 kg of coal

$$= \frac{5 \times 3.28 \times 100}{23}$$

$$= 71.3 \text{ kg}$$

Ans.

Prob.4 ***(a) What is carbonization of coal? Explain Beehive coke oven method of coal carbonization.***

(b) Explain the composition and uses of coal gas. [R.T.U. 2017]

Sol.(a) Carbonization of Coal : When coal is heated strongly in absence of air, it looses volatile matter and gets converted into lustrous, dense, strong, porous and coherent mass known as coke. This process of converting coal into coke is called carbonization. The coal having a tendency to get softness, well and fuse together during combustion, can be converted into cokes. Bituminous coal can be converted into coke. This process of carbonization is also called **destructive distillation**. The quality and yields of various products depends mainly on (i) rank and type of coal carbonised, (ii) temperature of carbonization and (iii) duration of carbonization. Carbonization is used to produce metallurgical coke, smokeless fuel for domestic purpose, and gas making.

The useful liquids produced are benzole, oilsand tar, where as gaseous by product is coal gas.

Steps in Carbonization Process :

Bituminous coals —(slow heating)→ Moisture and some gases are eliminated

↓ Δ 260°C-270°C (approximately)

Decomposition of coal followed by evolution of gases and tarry vapours ←(350°C, Δ)— H_2O, H_2S, low molecular weight alkanes and alkenes are formed

↓ Δ 400°C

Coking coals are formed, becomes soft and plastic —(700°C, Δ)→ Hydrogen is eliminated →

—(800°C, Δ)→ Plastic mass forms a foam like mass with evolution of gases —(At still high temperature)→ Coke is formed by solidification of foam like mass

Beehive's Oven Method : This is the earliest and cheapest method for the manufacturing of metallurgical coke.

Construction : The Beehive's oven is a dome shaped structure made of bricks. This is about 4m wide and 2.5 m high and having a capacity of about 8-10 tonnes of coal. It has two openings, one at the top for the charging of coal and the other at the side through which the coke formed is removed. This side opening also act as inlet for air supply and when desired.

Process : The coal is charged through the top opening and evenly levelled to form about 0.6-0.75 m thick layer. Some air is supplied in from the side opening and the coal is ignited. Volatile matter eliminates or burns through the partially closed side door. Combustion is allowed to proceed in a gradually diminishing supply of air, so that slow carbonization from the top layer to the bottom layer takes place. The complete carbonization takes about 3-4 days. The hard metallurgical coke formed is quenched with water and taken out from the discharge side opening. The yield of coke is about 60-80% of the coal charged and average about 5-6 tonnes of coke per oven.

After the process is over, the oven is hot enough to continue the next operation with a fresh charge and several such type of ovens can be worked in series to minimize wastage of heat. The by-products are non recoverable in this method.

Limitations

(i) Yield of coke is lower due to partial combustion.
(ii) Lack of flexibility of operation.
(iii) No recovery of by-products which are useful chemicals takes place.

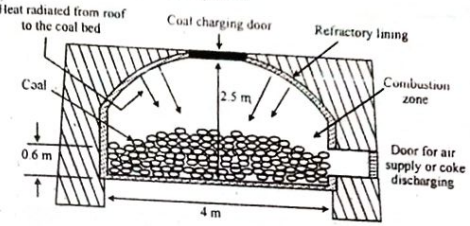


Fig. : Beehive's coke oven

Sol.(b) Coal gas : Coal gas is a colorless gas having a characteristic odor. It is lighter than air and slightly soluble in water. It burns with long smoky flame. Its calorific value is about 4,900 kcal/m^3. Its average composition is constituent H_2

Constituent	H_2	CH_4	CO	N_2	C_2H_4	C_2H_2	CO_2	Rest
Percentage	47	32	7	4	3	2	1	4

Applications

The important applications of coal gas are :

(i) As a fuel.
(ii) Domestic and commercial illumination.
(iii) In metallurgical operations for providing reducing atmosphere.

Prob.5 ***Calculate the gross and net calorific value of a coal sample having the following composition :***

C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and ash = 4.4%

[Gross CV in kcal/kg, C = 8,080; H = 34,500; S= 2240]. [R.T.U. 2011, Raj. Univ. (Back) 2008]

OR

Calculate the gross and net calorific values of a coal sample having the following composition :

C = 80 %; H = 07%; O = 03%; S = 3.5%; N = 2.1% and ash = 4.4% [R.T.U. 2017]

Sol. Gross Calorific Value (GCV)

$$= \frac{1}{100}\left[8080 \times C + 34500\left[H - \frac{O}{8}\right] + 2240 \times S\right] \text{ kcal/kg}$$

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left[7 - \frac{3}{8}\right] + 2240 \times 3.5\right] \text{ kcal/kg}$$

$$= \frac{1}{100}[646400 + 228562.5 + 7840] \text{ kcal/kg}$$

$$= 8828.025 \text{ kcal/kg.}$$

Net calorific value = GCV – 0.09H × 587 kcal/kg

= 8828.025 – 0.09 × 7 × 587 kcal/kg

= 8458.215 kcal/kg

Prob.6 ***What is carbonization of coal? Describe Otto-Hoffmann's By-product oven method of coke manufacturing.*** [R.T.U. Dec. 2016]

Sol. Carbonization or Manufacturing of Coke : *Refer to Long Answer Prob.4(a).*

Otto–Hoffmann's By-Product Coke Oven Method : This method has advantage that the by-products like coal gas, NH_3, benzoyl oil, tar etc. are recovered and heating is done externally by coal gas evolved during the process itself or by producer gas.

Principle : The heating is done on the basis of **regenerative principle of heat economy**, *i.e.* utilization of the waste flue gases for heating of checker works of bricks.

Construction : The by-product coke oven consists of a number of narrow silica chambers. Each chamber is about 10–12 meter long, 3–4 meter high and 0.40–0.45m wide which erected side by side with vertical flues in between them to form a sort of battery. Each chamber has a hole at the top to introduce the charge, a gas take off (for the removal of volatile matter) and a refractory lined cast iron door at each end for coke discharge. A single oven can hold about 16 to 24 tonnes of coal.

Working : Finely powdered coal is entered through the charging hole at the top of the chambers which are then tightly closed at both ends to cut off the supply of air. After then by burning producer gas or coal gas, the coke ovens are heated 1200°C and normally employing a **regenerative principle** to achieve as economical heating as possible.

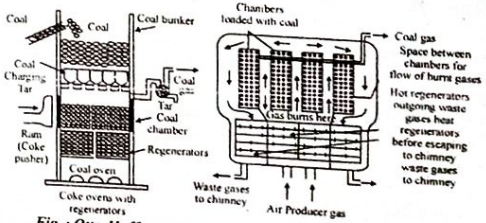


Fig. : Otto-Hoffman's by-product coke oven with regenerators

the help of a water seal. A pipe from the hydraulic main leads to the gas holder. This pipe has a testing tap.

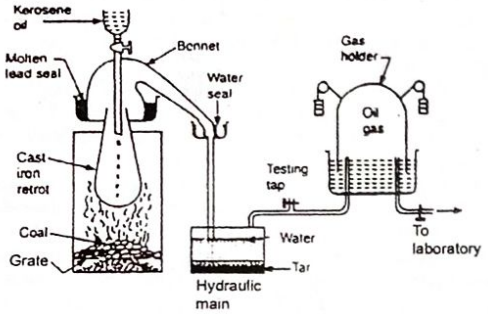


Fig. : Manufacturing of oil gas

The retort is heated to red hot and a stream of kerosene oil is allowed to fall on the bottom of red hot retort. As it comes in contact with red hot surface of the retort, the kerosene oil decomposes into number of lower hydrocarbon gases like CH_4, C_2H_6, C_2H_4 etc. A tarry material of volatile nature is also produced. The resulting gaseous mixture passes out through the bonnet over to a hydraulic main (a tank containing water). Here tar gets condensed. Then at the testing tap, from where the samples of gas can be taken for testing.

The proper cracking of oil is estimated from the color of the gas. A good oil gas should have a golden color. Finally the gas stored over water in gas holders. Yield of the gas is about 40 to 50%. Oil gas is conveyed to laboratory through pipes from the gas holders whenever required.

Application

Oil gas is used to improve the calorific value of water gas and the mixture of the two gases is called **carburetted water gas.** Oil gas is also used as laboratory gas.

Prob.8 ***What is cracking of fuel? Describe with diagram moving-bed catalytic cracking of petroleum.*** *[R.T.U. Dec. 2016]*

Sol. Cracking : *Refer to Q.1 (Short Answer)*

Important cracking processes developed so far are (a) thermal cracking, (b) catalytic cracking.

(a) Thermal cracking : When heavy petroleum oil is heated above the decomposition temperature, the molecules are broken and rearranged to give smaller molecules of the paraffin and olefin series and some hydrogen.

$$R.CH_2.CH_2.CH_2R' \rightarrow R.CH.CH_2 + CH_3R'$$

Thermal cracking can be carried out either in (i) liquid phase (ii) vapour phase.

(b) Catalytic cracking : When cracking is carried out in the presence of suitable catalysts, it is known as catalytic cracking.

Moving-bed (Fludised-bed) Catalytic Cracking : In this process the solid catalyst is very finely powdered to a fluid from that it behaves almost like a fluid (liquid) and can be transported in the gas stream. Figure represents a typical appratus.

The heavy oil vapours are mixed with the fine catalyst and forced to a large reactor at 500°C. Here the vapours and catalyst mixture forms a floating and moving bed. The cracking starts to produce smaller molecules in vapour form and some carbon. The carbon gets deposited over the catalyst particles, due to which they become heavy and settle down. The heavy catalyst particles are then sent to a regenerator, where they are heated to 600°C to burn off the carbon. These active catalyst particles now are brought back to the reactor along with the fresh oil vapours.

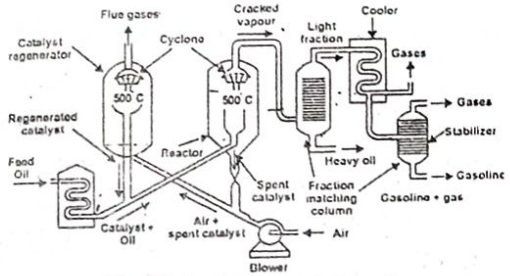


Fig. : Moving-bed type catalytic cracking

The vapours formed in the reactor are passed through a centrifugal separator called cyclone, which does not allow to pass through catalyst particles but allow to pass the vapours to the fractionating column. Here heavy fractions get condensed to oil while light vapours are allowed to pass through the coolers. In the cooler, they get condensed to liquid gasoline along with same dissolved gases. This gasoline is finally passed through stabilizer, where dissolved gases are removed and more petrol is collected.

Prob.9 ***Write short note on any two of the following.***
(a) Characteristics of good fuel. *[R.T.U. Dec. 2016]*
(b) Refining of petroleum *[R.T.U. Dec. 2016, 15, 13]*
(c) Pulverized coal and its advantages *[R.T.U. Dec. 2016]*

Sol.(a) Characteristics of good fuel :

1. **High calorific value (Heating value) :** Since the amount of heat liberated and temperature attained depends upon calorific value, calorific value of fuel should be high.
2. **Ignition temperature :** In order to have active combustion, the fuel should be heated to a sufficient temperature. The minimum temperature at which active combustion of the fuel takes place when the firing is at once started, is called as ignition temperature. High ignition temperature causes difficulties in combustion of fuel, a large amount of heat energy is required, but safe during transportation and storage. Low ignition temperature is dangerous for transportation and storage, it may cause fire hazard. Hence, an ideal fuel should have moderate ignition temperature.
3. **Low Ash or non-combustible matter :** As non-combustible or ash content reduces the heating value, increase the cost of storage and disposal, besides it causes major enviornmental problem. The non-combustible matter increases the cost of fuel.
4. **Low moisture content :** The presence of moisture will reduce the heating value. It has to be dried before use. Moisture content should be as low as possible. The coal may contain moisture in two forms, i.e. free and inherent moisture. Free moisture is that which wets the coal and it can be removed on exposure to air. Inherent moisture is that which is locked in the pores of coal and is not visible. Air dried and even freshly mined coal appearing dry may contain inherent water. It can be removed by heating.
5. **The combustion product should not be harmful:** Fuel should be such that a safe and clean combustion is ensured. Too much smoke and obnoxious odours are not desirable. The fuel on combustion should not liberate harmful, dangerous products which can cause harm to living organism and environment. The harmful gases are such as SO_2, CO, H_2S, PH_3 etc.
6. **Moderate velocity of combustion :** The velocity of combustion should be moderate. If it is slow, the required high temperature may not be attained, whereas in case of high, major part of heat energy will be radiated to atmosphere.
7. **Easy to Store and Transport :** It should be safe, convenient and economical for storage and transport. It is costlier for gasesous fuel in comparison to solid and liquid fuel.
8. **Low cost :** The fuel should be cheap and readily available.

Sol.(b) Refining of Crude Petroleum : Petroleum coming out from ground is dark colored, thick liquid and mixture of various hydrocarbons containing a lot of impurities (sand, brine etc.). It is therefore separated into a number of useful fractions by fractional distillation.

"The process of separation of crude oil into various fractions by *fractional distillation* and desired specific products obtained from these fractions by removing objectionable impurities is known as *refining of petroleum* and the plants set up for this purpose are called *oil refineries.*"

The process of refining involves the following steps :

(i) **Removal of Water by Cottrell's Process :** Crude oil coming out from the earth crust is an emulsion of oil and brine (salt water). The crude oil is allowed to flow between two highly charged electrodes where colloidal water droplets coalesce to form large drops and separates out from the oil.

(ii) **Removal of Sulphur Compounds :** The crude oil is allowed to be treated with copper oxide, where sulphur is converted into insoluble copper sulphide which may be removed by filtration.
They exhibit bad odor and color, cause corrosion of metal parts of ICE and lowers the response to the anti-knocking agent.

(iii) **Fractional Distillation :** The crude oil is heated first in an iron retort at about 400°C. The most of oil is evaporated (except asphalt or coke).

The hot vapors are then passed into the long fractionating column. Fractionating column is a long cylindrical tower containing a series of horizontal stainless steel trays at short distances. Each tray is provided with small chimney which are covered with loose cap called bubble tower. As the vapors go high, they become cooler and condense. The higher boiling fraction (300°C) condenses first at the bottom while lower boiling fractions will condense later near the top of the tower. The outlets in tower are provided in the side of the column to withdraw a number of fractions. Various fractions are collected at intermediate points, depending upon their boiling points. High boiling fractions, getting collected at the bottom, can be further subjected to cracking to get more useful low boiling fractions.

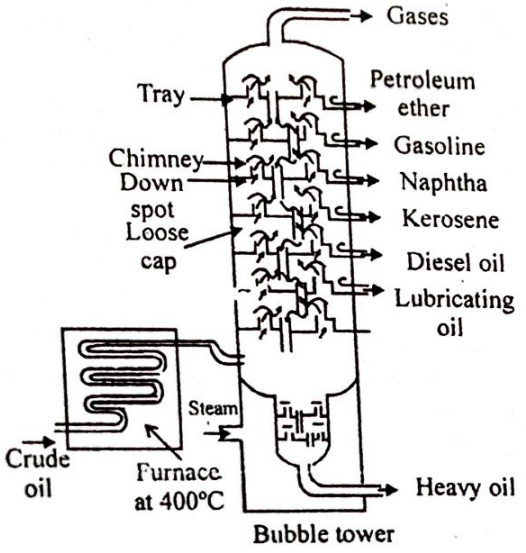


Fig.: Fractional distillation of crude petroleum

Sol.(c) Pulverized Coal : The combustion rate of coal with oxygen of air is slow due to less area of contact between them. The rate of combustion can be increased by either (i) increasing the amount of air which results in waste of heat as heat is carried away by excess of air or (ii) finely powdering or pulverizing the coal which results in increased area of contact between coal and oxygen. Pulverized coal can be transported by means of screw conveyor or stream of air, and thus, transportation is quite comparable with that of liquid or gaseous fuel.

The chief advantages associated with the use of pulverized coals are :

(i) Complete combustion is obtained with less excess of air and reduces wastage of heat. Higher temperature, and higher thermal efficiency are achieved.

(ii) Rate of combustion can be controlled easily as in case of liquid or gaseous fuels.

(iii) Heating of the furnace can be stopped or started at any time, and thus, resulting in saving of fuel.

(iv) Low grade coals having high ash content can be economically used. This is particularly important for Indian coals (most coals contain high ash).

(v) Overall operation costs including labour are low.

Prob.10 ***Describe the determination of calorific value of gaseous fuel by Junker's Calorimeter.*** ***[R.T.U. Dec. 2016]***

Sol. Determination of Calorific Value By Junker's Calorimeter : The Junker's calorimeter is used to determine the calorific value of gaseous fuels. It involves the following main parts in its construction.

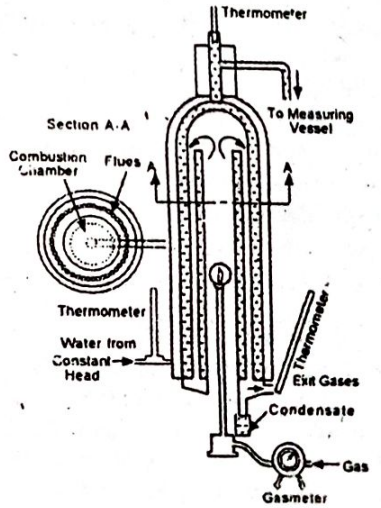


Fig. : Junker's Gas Calorimeter

(1) Bunsen Burner : There is a gas burner which is clamped at the bottom and can be easily pulled out of the combustion chamber or pushed up into it during the performance of experiment. This special type of burner is called Bunsen Burner.

(iv) Temperature of outlet water = 36 °C
(v) Weight of steam condensed = 0.030 kg.
Calculate the higher and lower calorific value at STP. Take latent heat of vaporization of water as 580 K cal/kg.
[R.T.U. Dec. 2016]

Sol. Given :

$V = 0.1\ m^3$ at STP
$W = 26\ kg$
$T_1 = 26°C$
$T_2 = 36\ °C$
$m = 0.030\ kg$

We know that,

$$HCV = \frac{W(T_2 - T_1)}{V}$$

$$= \frac{26(36-26)}{0.1}$$

$$= 2600\ kcal/m^3$$

$$LCV = HCV - \left(\frac{m}{V}\right) \times 580$$

$$= 2600 - \left(\frac{0.030}{0.1}\right) \times 580$$

$$= 2600 - 174$$

$$= 2426\ kcal/m^3$$

Prob.12 *Write short notes on the Ultimate analysis of coal.*
[R.T.U.Dec. 2016]

Sol. Ultimate Analysis of Coal : It includes determination of percentage of carbon, hydrogen, sulphur and nitrogen.

(a) Determination of Carbon and Hydrogen : About 1-2 gm accurately weighted coal sample is burnt in a current of oxygen in a combustion apparatus. As a result C and H of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and $CaCl_2$ tubes of known weight.

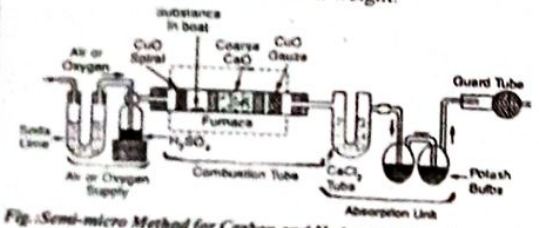


Fig. :Semi-micro Method for Carbon and Hydrogen Determination

The increase in weight of KOH and $CaCl_2$ gives the amount of CO_2 and H_2O formed as result of combustion. We can calculate the percentage of carbon and hydrogen.

$$C + O_2 \rightarrow CO_2;$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$
$$CaCl_2 + 7H_2O \rightarrow CaCl_2.7H_2O$$

$$\% \text{ of } C = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of coal sample taken} \times 44}$$

$$\% \text{ of } H = \frac{\text{Increase in weight of } CaCl_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample taken} \times 18}$$

(b) Determination of Nitrogen : To estimate the percentage of nitrogen, a known quantity of powdered and dry coal sample is taken in kjeldahl's flask and heated with conc. H_2SO_4 along with $CuSO_4$ in the presence of K_2SO_4 as catalyst. Thus, clear solution is obtained (i.e. when whole nitrogen is converted into ammonium sulphate). It is treated with excess of NaOH to when liberate ammonia.

$$N_2 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

The NH_3, thus, liberated is distilled over and absorbed in a known volume (V_1) of standard H_2SO_4 solution $\frac{N}{10}$. The volume of unused H_2SO_4 is then determined by titrating against with standard $\frac{N}{10}$ NaOH solution.

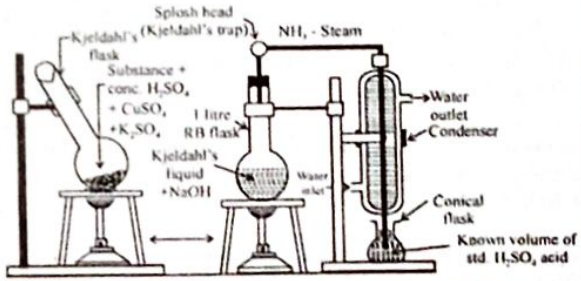


Fig. : Estimation of Nitrogen by Kjeldahl's Method

The percentage of nitrogen in the coal can be determined by knowing the volume of acid consumed by liberated ammonia.

Calculation:

Let, the weight of coal sample taken = w g
Volume of standard acid Solution of normality

$$\frac{N}{10} = V \text{ ml}$$

Volume of the standard alkali solution of normality N/10 required for titration of excess acid (unused acid) = v ml

Because acid and alkalies neutralize in equivalent amounts.

So, the volume of acid solution of normality (N/10) left unused = v ml

Volume of acid solution of normality N/10 used for neutralizing

$$NH_3 = (V - v)\text{ ml} = x \text{ ml}$$

x ml of N/10 acid solution = x ml of (N/10) NH_3 solution
1000 ml of 1N NH_3 solution = 17 g of NH_3 =14 g of Nitrogen

$$x \text{ ml of } N_1 \text{"}NH_3\text{"} = \frac{14}{1000} \times x \times N_1 \text{ g of Nitrogen}$$

$$\% \text{ of Nitrogen} = \frac{14}{1000} \times x \times N_1 \times \frac{100}{w}$$

$$\% \text{ of Nitrogen} = \frac{\text{Volume of acid consumed} \times \text{Normality} \times 1.4}{\text{Weight of the sample}}$$

$$= \frac{1.4 \times N_1 \times x}{w}$$

(c) Determination of Sulphur : A known amount of coal sample is burnt completely in bomb calorimeter in a current of oxygen by which sulphur present in coal is converted into sulphate. The ash obtained from the oxygen bomb calorimeter is extracted with dil. HCl. The acid extract is then treated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$\% \text{ of } S = \frac{\text{Weight of } BaSO_4 \text{ obtained} \times 32 \times 100}{\text{Weight of coal sample taken in bomb} \times 233}$$

(d) Ash determination is carried out as in proximate analysis.

(e) Oxygen : The total sum of the percentage of carbon, hydrogen, nitrogen, sulphur and ash content subtracted from 100, gives the percentage of oxygen.

% of oxygen= 100 – % of (C + H + S + N + ash)

Prob.13 ***Determine the theoretical weight of air required for the complete combustion of fuel having C= 75%, H = 8% and O = 3% percentage composition. Assuming that 50% excess air is to be used, calculate the weight of air supplied.*** *[R.T.U. Dec. 2016]*

Sol. We have:

Constituents	Wt. in 1 kg of coal (kg)	Combustion Reaction	Wt. of O_2 (in kg)
C	0.75	$C + O_2 \rightarrow CO_2$	$0.75 \times \frac{32}{12} = 2$
H	0.08	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.08 \times \frac{16}{2} = 0.64$
O	0.03	–	–
Ash	0.14	–	–
			Total O_2 = 2.64
			O_2 in fuel =0.03
			Net O_2 = 2.61

(i) Beehive's Oven Method : *Refer to Long Answer Prob.4(a).*

(ii) Otto–Hoffmann's By-Product Coke Oven Method : *Refer to Long Answer Prob.6.*

Prob.16 ***Write short note on Reforming.*** ***[R.T.U. 2012]***

OR

What is reforming? Explain various reforming process of gasoline. ***[R.T.U. Jan. 2016]***

Sol. Reforming : Reforming is a process involving modification of the structure of molecules by the action of heat, pressure and a catalyst (usually platinum (pt)) to give high octane petrol and petrol chemicals feed stock. This is carried out to convert "*straight chain hydrocarbon with a low octane number to branch chain or cyclic compounds with high octane number. This process also known as upgradation of gasoline.*" The anti-knock characteristics of gasoline can be improved by reforming.

By reforming process,

(i) Paraffins are converted to isoparaffins.

(ii) Paraffins are converted to naphthalenes.

(iii) Naphthalenes are converted to aromatics.

$$C_7H_{16} + \text{Catalyst} \longrightarrow \underset{\text{Toluene}}{C_7H_8} + \underset{\text{Hydrogen}}{4H_2}$$

$$\underset{\text{Cyclohexane}}{C_6H_{12}} \longrightarrow \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Hydrogen}}{3H_2} \uparrow$$

Reforming is carried out either thermally or by the presence of catalyst (catalytically).

Thermal Reforming

This process involves heating the straight run gasoline in a reactor at 500–600 °C under a pressure of 85 atmosphere in the absence of a catalyst. The conditions are well controlled to prevent the formation of gas at the expense of gasoline. The degree of reforming is controlled by quenching (cooling) the product vapors by a cold oil spray. The reformed products are then fractionated to remove residual gases (stabilizing). During thermal reforming some cracking also occurs to yield alkanes and alkenes. These may undergo dehydrogenation followed by cyclization to give naphthalenes.

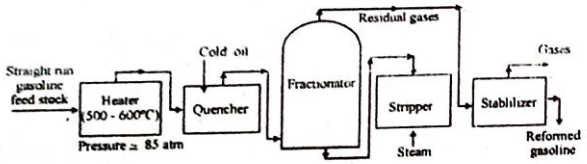


Fig. 1 : Thermal reforming of straight run gasoline

Conversion of n-alkanes to branched chain alkanes also takes place during this process.

Catalytic Reforming

This process produces a product having better fuel characteristics at lower pressure as compared to thermal reforming. Catalytic reforming is done in the presence of a catalyst (Platinum supported on alumina) at 460–530°C and 35–50 atmospheric pressure by using either a fixed–bed or moving (fluidized) bed process. This process using Pt as catalyst is also known as *platforming* and reformed or stabilized gasoline is also known as *Plat-formates*.

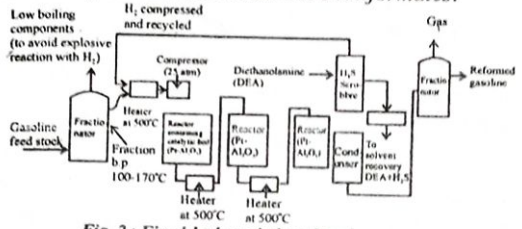
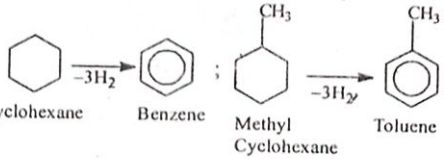


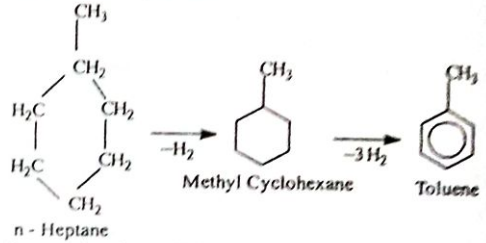
Fig. 2 : Fixed-bed catalytic reforming process

A few of reforming reactions are given below. These are dehydrogenation, dehydrocyclization, Isomerization and Hydro-cracking reactions.

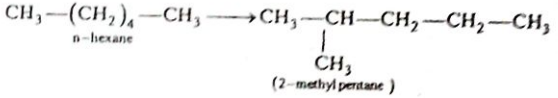
(1) Dehydrogenation : Cyclic alkanes undergo dehydrogenation to form aromatic compounds.



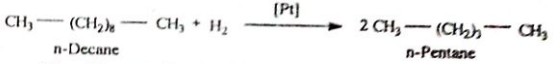
(2) Dehydrocyclization : n-alkanes become cyclic alkanes, which undergo dehydrogenation and form aromatic compounds.



(3) Isomerization : This is used for the conversion of a straight chain compound into a branched hydrocarbon.



(4) Hydro–cracking : n-paraffins are mixed with hydrogen and passed over a hot catalyst. Hydrocracking takes place resulting in higher hydrocarbons.



The liberated hydrogen can be used to hydrogenate alkane, to remove sulphur in feed stock oil or to promote cracking of larger molecules.

Prob.17 ***A gas used in an internal combustion engine had, 40% of H_2, 30% of CH_4, 17% of CO, 5% of N_2, 3% of C_3H_8 and 5% of C_2H_2. Find the volume of air needed for combustion of gas. If air supplied is 45% excess, find the volume analysis of dry products.*** ***[R.T.U. Jan. 2016]***

Sol.

Constituents	Volume in $1m^3$ of gas	Combustion Reaction	O_2 required (in m^3)	Volume of dry gas (in m^3)
H_2	0.40	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$0.40 \times \frac{1}{2} = 0.2$	—
CH_4	0.30	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$0.30 \times 2 = 0.6$	$CO_2 = 0.30 \times 1 = 0.30$
CO	0.17	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	$0.17 \times \frac{1}{2} = 0.085$	$CO_2 = 0.17 \times 1 = 0.17$
N_2	0.05	—	—	$N_2 = 0.05$
C_3H_8	0.03	$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	$0.03 \times 5 = 0.15$	$CO_2 = 0.03 \times 3 = 0.09$
C_2H_2	0.05	$C_2H_2 + \frac{5}{2}O_2 \rightarrow 2CO_2 + H_2O$	$0.05 \times \frac{5}{2} = 0.125$	$CO_2 = 0.05 \times 2 = 0.1$
Total			1.16	0.71

O_2 required = 1.16 m^3

Therefore, Air required $= 1.16 \times \frac{100}{21} = 5.52 m^3$

Excess air required $= 5.52 \times \frac{45}{100} = 2.484\ m^3$

Volume of O_2 in excess air $= \frac{2.484 \times 21}{100} = 0.52164\ m^3$

Total air supplied = 5.52 + 2.484 = 8.004 m^3

N_2 from air $= \frac{8.004 \times 79}{100} = 6.323\ m^3$

CO_2 in combustion products = 0.30 + 0.17 + 0.09 + 0.1 = 0.66 m^3

O_2 in combustion products = 0.5216 m^3

Total N_2 = 6.323 + 0.05 = 6.373 m^3

Total volume of dry combustion products

$O_2(0.5216) + N_2(6.373) + CO_2(0.66) = 7.5547\ m^3$

Therefore, volume percentage analysis of dry products will be as following :

$$CO_2 = \frac{0.66 \times 100}{7.5547} = 8.733\%$$

$$N_2 = \frac{6.373 \times 100}{7.5547} = 84.35\%$$

and $$O_2 = \frac{0.5216 \times 100}{7.5547} = 6.9045\%$$

Prob. 8 ***What is proximate analysis of coal? Explain the steps involved in proximate analysis of coal.*** *[R.T.U.2014]*

OR

Write short note on Elemental analysis of fuel. *[R.T.U. Jan. 2016]*

OR

Write note on proximate analysis of coal and its significance. *[R.T.U. 2015]*

OR

What is the proximate and ultimate analysis of coal? How carbon, hydrogen, sulphur and nitrogen are estimated? *[R.T.U.2013]*

OR

What is ultimate and proximate analysis of coal? Discuss their significance. How are ultimate and proximate analysis done? *[R.T.U.2012, 2011]*

OR

Describe methods of proximate analysis of coal. What is the significance of proximate analysis? *[R.T.U. 2010, 2009, 2007; Raj.Univ. 2005, 2003, 2002, 2001]*

Sol. Analysis of Coal : The composition of fuels varies widely and hence it is necessary to analyze and interpret the results. These tell us about fuel so that it can be selected for proper industrial use, price fixation and commercial classification.

The quality of a coal is ascertained by the following two types of analysis :

1. Proximate Analysis
2. Ultimate Analysis

Proximate analysis gives valuable information about the practical utility of coal. Proximate analysis is comparatively cheaper and simpler as against ultimate analysis which is very tedious and the costs of the equipments required are very high.

However, two types of analysis are complimentary and give necessary data to decide about the quality of coal.

(i) Proximate Analysis : It is empirical but important analysis dealing with determination of moisture contents, volatile matter, ash content and fixed carbon.

(a) Determination of Moisture Content : A known quantity of coal sample is heated at 105-110° C in crucible. Then cooled in desiccator, the loss in weight represents the moisture content.

$$\% \text{ of mixture} = \frac{x - y}{x} \times 100$$

where, x = weight of sample

y = weight of sample after drying,

x – y = weight loss on drying.

(b) Determination of Ash Content : A weighted sample is heated to 800° C in electric furnace for 1 hour. Then cooled in desiccator. The residue is weighted as ash.

$$\% \text{ of ash} = \frac{\text{weight of ash left}}{\text{weight of coal sample taken}} \times 100$$

(c) Determination of Volatile Matter : A weighted sample of coal is heated in crucible for 7 minutes at 950° C. Crucible is cooled rapidly to prevent any oxidation. The loss of weight is reported as volatile matter.

$$\% \text{ of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal sample taken}} \times 100$$

(d) Determination of Fixed Carbon

% of fixed carbon =100 – (% moisture + % volatile matter + % ash).

(ii) Ultimate Analysis of Coal and Coke : *Refer to Long Answer Prob.9.*

Significance of Proximate Analysis : It helps us to determine the quality of coal. The following factors are taken into consideration, for selection of coal for various use.

1. **Calorific Value :** The coal with high calorific value is preferred.
2. **Moisture Content :** Coal with low moisture is preferred. Moisture in coal reduces the heating value of coal.
3. **Ash Content :** The coal with low ash contents is preferred. It does not take part in combustion and lowers the heating value of coal.

Prob.23 ***The ultimate analysis of a coal sample gives the following data : C = 84.5%, N = 0.5%, H = 6%, O = 8.4%, and S = 1%. Calculate the high and low calorific values by using Dulong's formula.*** ***[R.T.U. 2015]***

Sol. C = 84.5%, N = 0.5%, H = 6%, O = 8.4%, and S = 1%

According to Dulong's Formula

Higher calorific value of

C = 8080 cal/gm = 8080 kcal/ kg

Higher calorific value of

H = 34500 cal/gm = 34500 kcal/kg

Higher calorific value of

S = 2240 cal/gm = 2240 kcal/kg

Higher calorific value

$$HCV = \frac{1}{100}\left[8080 \times C + 34500\left(H - \frac{O}{8}\right) + 2240\ S\right] kcal/kg$$

$$= \frac{1}{100}\left[8080 \times 84.5 + 34500\left(6 - \frac{8.4}{8}\right) + 2240 \times 1\right] kcal/kg$$

$$= \frac{1}{100}\left[682760 + 34500(4.95) + 2240\right] kcal/kg$$

$$= \frac{1}{100}\left[682760 + 170775 + 2240\right] kcal/kg$$

$$= 8557.75 \text{ kcal/kg}$$

Low calorific value

$$LCV = [HCV - 0.09H \times 587] kcal/kg$$

$$= [8557.75 - 0.09(6) \times 587]$$

$$= 8240.77 \text{ kcal/kg}$$

(b) The following data were obtained in a Junker's gas calorimeter experiment :

Volume of gas burnt = 0.1 m^3 at STP
Weight of water heated = 25 kg
Temperature of inlet water = 20°C
Temeprature of outlet water = 33°C
Weight of steam condensed = 0.025 kg
Calculate the higher and lower calorific value. Take the latent heat of steam as 580 kcal/kg.

[R.T.U. 2013, I Sem.2008]

Sol.(a) $$HCV=\frac{(W_1+W_2)(T_2-T_1)\times S}{m}\ kJ/kg$$

$$=\frac{(250+150)(29.1-27.3)\times 4.187}{0.72}\ kJ/kg$$

$$=4187\ kJ/kg$$

Sol.(b) Given

$V=0.1\ m^3$
$W=25\ kg$
$T_1=20°C$
$T_2=33°C$
$m=0.025\ kg$

$$HCV=\frac{W(T_2-T_1)}{V}$$

$$=\frac{25(33-20)}{0.1}=3250\ k\ cal/m^3$$

$$LCV=HCV-\left(\frac{m}{V}\right)\times 580$$

$$=3250-\left(\frac{0.025}{0.1}\right)\times 580$$

$$=3105\ k\ cal/m^3$$

Prob.32 *(a) Define and classify fuels. Describe and give important characteristics of good metallurgical coke and Hoffmann process of manufacturing coke.*

(b) What is Knocking in an IC engine? How it is related to the structure of constituent hydrocarbons? Define Octane number. *[R.T.U. 2012]*

Sol.(a) Fuels are naturally occurring or manufactured combustible organic substances which act as a source of heat. Any source of heat energy is called as fuel. The fuel includes all combustible substances that combine with oxygen from the atmosphere with the evolution of large amount of heat which can be used economically for domestic and industrial purposes.

Therefore, the term 'fuel' may be defined as ***"any fissionable chemical material or any reactant which gives energy in the form of heat that can be used for producing powder"***. In other words ***"Fuel is a combustible substance containing carbon as main constituent, which is capable of releasing large amount of heat (or energy)"***. For example : coal, wood, charcoal, petrol, diesel, oil gas, producer gas, kerosene, liquified petroleum gas, CNG etc.

Classification of Fuels : The fuels are classified according to :

1. Occurrence
2. State of Aggregation

Classification of Fuels According to Occurrence

According to occurrence, fuels are classified as :

(i) **Primary or Natural Fuel :** These are found in nature e.g. wood, peat, petroleum, natural gas etc.

(ii) **Secondary or Artificial Fuel :** Those which are derived from the primary fuels e.g. coke, charcoal, petrol, kerosene, diesel, coal gas, oil gas, producer gas, blast furnace gas etc.

Classification of Fuels According to State of Aggregation

According to state of aggregation, fuels are classified as (i) Solid (ii) Liquid (iii) Gaseous, which may be primary or secondary fuel.

Table : Classification of Fuels

S. No.	Occurrence	State of Aggregation		
		Solid Fuel	Liquid Fuel	Gaseous Fuel
1.	Primary or natural fuel	Wood, Peat, Lignite, Bituminous, Anthracite, Dung Coal	Crude petroleum oil	Natural gas
2.	Secondary fuel	Coke, Charcoal, Petroleum etc.	Kerosene, Diesel, Petrol, Synthetic gasoline, Coaltar, L.P.G.	Coal gas, Producer gas, Water gas, Oil gas, Biogas, Blast furnace gas, Coke oven gas etc.

Important Characteristics of Good Metallurgical Coke : It must have following characteristics–

(i) **Purity :** The percentage of ash, moisture, S and P contents should be as low as possible.

(ii) **Porosity :** Higher the porosity, larger will be the surface area, meaning complete combustion.

(iii) **Size :** Size of coke should be uniform.

(iv) **Strength :** The coke should be quite compact, hard strong to withstand dropping abrasion as well as the presence of the over burden.

(v) **Calorific Value :** Coke should have high CV.

(vi) **Reactivity :** The coke used for water gas manufacture must be reactive to steam.

(vii) **Combustibility :** Coke should burn easily.

Metallurgical Coke (Hard coke) Manufactured by Otto–Hoffmann's By-Product Coke Oven Method : *Refer to Long Answer Prob.6.*

Sol.(b) Knocking : When low quality of fuel used in internal combustion engine which does not run smoothly and the rate of oxidation in internal combustion engine becomes so great that the last portion of the fuel-air mixture gets ignited instantaneously, producing an explosive violence known as **'Knocking'**.

Relation between Chemical Structure and Knocking: The chemical structure of the gasoline hydrocarbons has a close relation with knocking properties :

(i) Knocking tendency decreases with increase in the compactness of the molecules, double bonds and cyclic structures. So, olefins of the same carbon chain lengths has better antiknock properties (Less knocking) than the corresponding paraffins.

(ii) In normal paraffins, the knocking increases with increase in the length of the carbon chain. For example, the tendency to knock in straight chain paraffins the order is :

n-heptane > n-hexane > n-pentane > n-butane

(iii) Branched chain hydrocarbons have better anti-knock properties (less knocking) than straight chain paraffins. Thus the order of knocking tendency of different isomers of heptane is :

n-heptane > 2-methyl hexane > 2,2-dimethyle pentane

(iv) Aromatic hydrocarbons like benzene and toluene have very high anti-knocking tendency (very low knocking tendency).

In general knocking tendency decreases in the following order :

Straight chain paraffins > Branched chain paraffins > Olefins > Cycloparaffins > Aromatics

So, knocking has been found to be maximum in fuels containing straight chain paraffins (which increases with increasing carbon chain) and minimum in fuels containing aromatics and branched chain hydrocarbons. Knocking tendency decreases with the increase in the number of C = C and rings.

Hence, fuels containing straight chain paraffins are worst, while those containing aromatic and branched chain hydrocarbons are best.

Octane Number : *Refer to Long Answer Prob.28.*

Prob.33 *(a) What are the important gaseous fuels? Describe the manufacturing of coal gas. What are the advantages of gaseous fuels over other kinds of fuels?*

(b) Write short note on Gaseous fuels. *[R.T.U. 2012, 2007]*

CORROSION AND ITS CONTROL 3

CHAPTER IN A NUTSHELL

❑ **Corrosion**

Corrosion is the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings.

❑ **Causes of Corrosion**

Metals exist in nature in the form of oxides, sulphides, sulphates and carbonates, etc. These chemically combined states of metal known as 'ore' has low energy and is thus thermodynamically stable state of metal. A considerable amount of energy is required for the extraction of the metal. Therefore, the extracted metal (in the isolated form) has higher energy and thus it is thermodynamically unstable state. Thus it is the natural tendency of metal to go back to the thermodynamically stable state (ore of metal). During this course mostly oxides are formed.

Ore of metal (Thermodynamically stable state) —Metallurgical process, +Energy or (Reduction)→ Pure metal (Thermodynamically unstable state) —Oxidation or ←Corrosion→ Corroded metal + Release of energy

❑ **Consequences of Corrosion**

The main consequences of corrosion are :

1. Plant shut down due to failure.
2. Increase in maintenance and production cost.
3. Contamination or loss of product.
4. Loss of useful properties of metal and thus loss of efficiency.
5. Decrease in production rate because efficiency is less.
6. Replacement of corroded equipment is time consuming.
7. 25% of annual world production of iron is wasted due to corrosion.

From the above discussion it becomes clear that study of corrosion and its prevention is essential to both the engineers and metallurgists.

PREVIOUS YEARS QUESTIONS

I. SHORT ANSWER TYPE QUESTIONS

Prob.1 ***Water line corrosion.*** *[R.T.U. 2017]*

Sol. Water Line Corrosion : When water is stored in a metallic tank, it is observed that the metal below the waterline gets corroded. It is because the water below the waterline is poorly oxygenated and acts as an anode. The metal above the waterline is highly oxygenated and acts as a cathode. Hence corrosion of metal below the waterline takes place.

Prob.2 ***Define corrosion.***

Sol. The process by which the metals have a tendency to go back to their combined state is known as Corrosion. The corrosion is thus exactly the reverse of extraction of metals.

Prob.3 ***What is wet corrosion?***

Sol. The corrosion involving the flow of electrons from a particular part of the metal surface called *anodic area* and some other part called *cathodic area* through a conducting solution is called *electrochemical* or *wet corrosion.*

Prob.4 ***What do you understand by "electrochemical series?"***

Sol. A series which involves an arrangement of various electrodes in the increasing order of their standard reduction potentials or decreasing order of standard oxidation potentials on hydrogen scale, is called "electrochemical series".

Prob.5 ***What is meant by the term passivity (Passivation)?***

Sol. Passivation is the phenomenon by which a metal or alloy exhibits a much higher corrosion resistance due to the formation of a highly protective, very thin (about 0.0004 mm thick) and quite invisible film on the surface. This film is insoluble, non-porous and of such a 'self healing nature' that when broken, it will repair itself on re-exposure to oxidizing conditions.

Prob.6 ***What do you understand by galvanizing?***

Sol. Galvanizing : The process of coating of layer of zinc on steel is called galvanizing. Since Zn is anodic with respect to Fe, Zn undergoes corrosion and the specimen is saved.

Prob.7 ***What is pitting corrosion?***

Sol. Pitting corrosion is a *localized accelerated attack* at some place on the metal surface, pitting corrosion thus results in the formation of pinholes, pits as well as cavities in the metal, and these irregularities may penetrate deep into the metal causing destruction of pipes and tubes.

Prob.8 ***What is calorizing?***

Sol. Calorizing : The base metal is heated with a powder mixture of Al and Al_2O_3, together with a trace of ammonium chloride as a flux in a drum at a temperature of 840°C – 930°C for 4-6 hours. Calorized steel is used for making furnace parts.

Prob.9 ***What is chromizing?***

Sol. Chromizing : The base metal is heated with a powdered mixture of 55% chromium and 45% alumina at a temperature of 1300°C – 1400°C for 3 to 4 hours in a closed drum. The used of aluming is to prevent the coalescence of chromium particles.

II. LONG ANSWER TYPE QUESTIONS

Prob.1 ***Explain the importance of "timing" in corrosion control.*** *[R.T.U. 2018]*

Note : Read 'timing' as tinning.

Sol. Cathodic Metal Coating (Tinning) : The process of uniform coating of tin on iron is called tinning. Although tin is cathodic with respect to Fe, still this method is superior. This is because tin is a time tested metal, and is non-toxic.

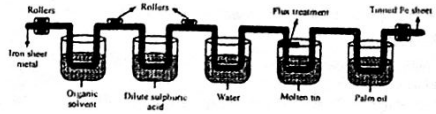


Fig. 2 : Tinning of Steel Sheet

Tinning involves the following steps.

1.Degreasing: The base metal is first washing with benzene or toluence to remove greasy oil material.

2. Pickling: After then, the base metal is pickled (washing) with sulphuric acid to remove surface impurities (oxide layer).

3. Flux treatment: Then it is dipped in $NH_4Cl/SnCl_2$ flux and dried. The flux helps the molten metal to adhere to the metal sheet.

4. Hot dipping : Then, the base metal dipped in molten tin followed by dipping in palm oil. The palm oil protect the hot tin-coated surface against oxidation.

Excess of tin removed by rolling and form a thin film of uniform thickness on the steel sheet.

Applications

1. Copper sheets coated with tin are used for making utensils and household equipments.
2. Variety of food stuff like meat, fish, fruits are preserved in tinned cans which last for years.
3. Various type of body food like milk powder are preserved in tinned cans.
4. Edible oils, butter, cheese, medicines are preserved in tinning cans.

Prob.2 ***Why iron pipe is galvanized?*** *[R.T.U. 2018]*

Sol. Iron is the most commonly used construction metal due to its low cost and easy availability. It can be protected from corrosion by covering its surface with metallic coatings. The process of coating a layer of zinc on iron is called galvanizing. Zinc is anodic in nature with respect to iron. Hence, coating of zinc on iron is anodic, because its electrode potentials is lower than that of the iron which is base metal here. Zinc acts when anode is attacked, leaving the underlying cathodic metal (iron) unattached, even if it is exposed when pores, breaks or discontinuities occur in such an anodic coating. Iron is not corroded, till all the coating metal (Zn) is consumed. This is the reason why iron pipe is galvanized.

Prob.3(a) Explain theory of wet electrochemical corrosion of metals.

(b) Discuss various methods for the prevention of corrosion. **[R.T.U. 2017]**

Sol.(a) Wet or Electrochemical Theory : The corrosion involving the flow of electrons from a particular part of the metal surface called *anodic area* and some other part called *cathodic area* through a conducting solution is called *electrochemical* or *wet corrosion*.

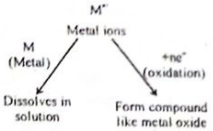
This type of corrosion occurs under the following conditions–

(i) When conducting liquid with varying amount of oxygen is in contact with a metal.

(ii) When two dissimilar metals or alloys are in contact with each other in the presence of an aqueous solution or moisture.

According to this theory, the corrosion of a metal in aqueous solution may be thought of as a two step process, *i.e.*, oxidation and reduction. This type of corrosion exists, due to separate anodic and cathodic areas between which current flows through the conducting medium and corrosion cell is formed.

Oxidation reaction takes place at anodic area, so anodic metal is destroyed by assuming combined state (like metal oxides) or dissolving state. Hence, corrosion always occurs at anodic areas.



Whereas, at cathodic area, reduction takes place, consuming the electrons involved in the oxidation (Anodic) reaction, with the evolution of hydrogen or absorption of oxygen, depending upon the nature of corrosive environment.

Thus, corrosion takes place as a result of local action, which involves

(i) presence of a conducting medium

(ii) the formation of separate anodic and cathodic areas in contact with each other

(iii) corrosion of anodic parts only and

(iv) formation of corrosion product somewhere between electrodes.

Example of corrosion is rusting of iron.

The popular examples of absorption of oxygen type corrosion is, rusting of iron in neutral aqueous solution of NaCl in the presence of oxygen.

The surface of iron is covered with a film of oxide. However, if this iron oxide film develops some cracks, anodic areas are developed on the surface of iron metal. These anodic areas are small surface part and almost whole of the rest metal surface forms large cathodic part.

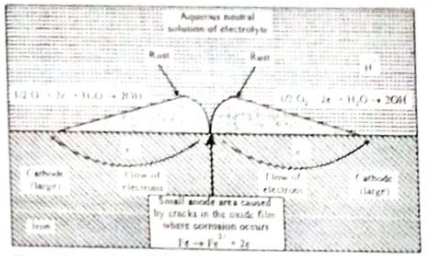


Fig. : Mechanism of Wet Corrosion by Oxygen Absorption

At the anodic areas, iron dissolves as Fe^{2+} ions with the liberation of electrons (oxidation).

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \text{(At Anode, Oxidation)}$$

The liberated electrons flow from anodic to cathodic areas through the iron metal, where electrons are taken up by the dissolved oxygen as

$$H_2O + O_2 + 2e^- \longrightarrow 2OH^- \text{ (At Cathode, Reduction)}$$

The Fe^{2+} ions formed at anode as well as OH^- ions formed at cathode and combine to form a compound $Fe(OH)_2$, which is soft brown rust.

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

In presence of excess oxygen, $Fe(OH)_2$ is oxidized to $Fe(OH)_3$.

$$4Fe(OH)_2 + 2H_2O + O_2 \longrightarrow 4Fe(OH)_3 \downarrow$$

This product, known as yellow rust has the actual composition as $Fe_2O_3.3H_2O$.

If the supply of oxygen is limited then the corrosion product is Fe_3O_4, (the black anhydrous magnetite) *i.e.* Ferrosoferric oxide is formed.

$$6Fe(OH)_2 + O_2 \longrightarrow (Fe_2O_3.FeO)_2.6H_2O$$

The net corrosion reaction due to rusting of iron is :

$$4Fe + 3O_2 + 6H_2O \longrightarrow \underset{\text{Rust}}{2(Fe_2O_3.3H_2O)}$$

Note : As we know that Fe^{2+} ion is smaller in size than OH^- ion, the Fe^{2+} ions will diffuse more rapidly than OH^- ions, hence corrosion takes place at the anode, but rust is deposited at or near the cathode.

Sol.(b) Corrosion Control (Protection against Corrosion) :

1. Using Pure Metal

The corrosion-resistance of a given metal may be improved by increasing its purity. Purification of metals like Al, Mg, etc., provides a coherent and impervious protective oxide film on their surfaces, when exposed to environment. However, corrosion-resistance of a purified metal depends on the nature of corrosive environment. For example, the corrosion resistance of Al depends on its oxide film formation, which is highly protective only on the high purity metal. So, impurities in a metal cause heterogeneity, which decreases corrosion resistance of the metal.

2. Proper Designing

The design of the material should be such that "corrosion even if it occurs is uniform and does not result in intense and localized corrosion". Some important design principles are :

(i) If two dissimilar metals in contact have to be used, they should be as close as possible to each other in the electrochemical series.

(ii) The anodic metal should not be painted or coated, when in contact with a dissimilar cathodic metal, because any break in coating would lead to rapid localized corrosion.

(iii) When two dissimilar metals are to be in contact, the anodic material should have as large area as possible; whereas the cathodic metal should have as much smaller area as possible.

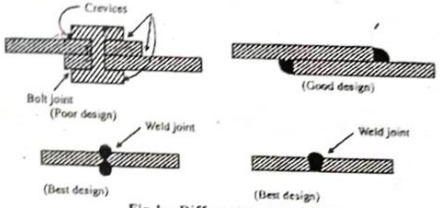


Fig.1 : Different types of joints

(iv) Prevent the occurrence of hetrogeneties, both in the metal and in the corrosive environment. Thus, a proper design should avoid the presence of crevices between adjacent parts of the structure, even in the case of the same metal, since crevices permit concentration differences. Bolts and rivets are, therefore undesirable for this reason and these should preferably be replaced by a butt-weld.

(v) Avoid the contact of dissimilar metals in the presence of a corroding solution.

If this principle is not followed, then corrosion is localized on the more active metal (in the immediate vicinity of contact). While the less active metal remains protected.

(vi) Whenever the direct joining of dissimilar metals, is unavoidable, an insulting fitting may be applied in-between them to avoid direct metal-metal electrical contact.

(vii) Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas.

(viii) It is desirable that the design allows for adequate cleaning and flushing of the critical parts (i.e., susceptible to dirt, deposition etc.) of the equipment.

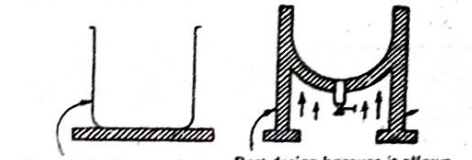


Fig. 2 : Prevention of corrosion by design

Sharp corners and recesses should be avoided because they favour the formation of stagnant areas and accumulation of solids, etc.

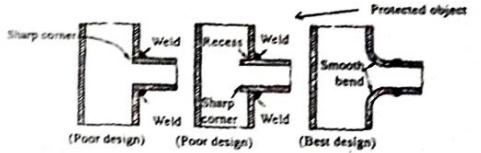


Fig. 3 : Prevention of corrosion by design

3. Cathodic Protection : The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur. There are two types of cathodic protections

(i) Impressed Current Cathodic Protection : In this method, an impressed current is applied in opposite direction to nullify the corrosion current and concert the corroding metal from anode to cathode.

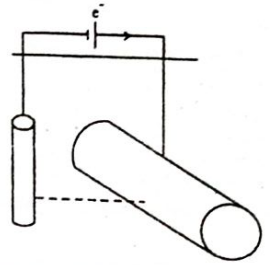


Fig. 1 : Electrons are supplied from an external cell so that the object itself becomes cathodic and is not oxidized

The object to be protected is made cathode by connecting it to negative terminal of DC source. This type of cathodic protection has been applied to open water- box coolers, water-tanks, buried oil or water pipes, condensers, transmission line towers, marine pipes, laid-up ships, etc. This kind of protection technique is, particularly, useful for large structures for long-term operations.

(ii) Sacrificial Anodic Protection Method: In this protection method, the metallic structure (to be protected) is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly, while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys. Important applications of sacrificial anodic method include protection of buried pipelines, underground cables, marine structures, water-tanks, etc.

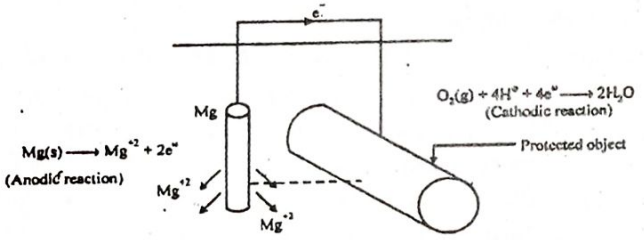


Fig. 2 : An anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object

4. Application of Metallic Coatings

The coating of one metal over the other is the most important method of protection from corrosion. Such protective layers may be produced on the surface by more corrosion resistant metal (such as Ni, Cr, Zn and Sn) by the process of electroplating, hot dipping, vapourising etc.

(i) Metals such as Au, Ag, W, Pt etc. (noble metals) are used for electroplating on the desired metal. When a noble metal is electroplated, it projects the base metal by virtue of its noble character. Tin plating and nickel plating are the most common examples. The electroplating of zinc is known as cold galvanizing. In electroplating, the object to be plated is made the cathode. The electrolyte is a salt of the metal to be deposited. The anode may be of the metal to be deposited or it may be an inert electrode (such as graphite). The anode (that of the metal to be deposited) dissolves to coat the metal in the solution. Au, Ag, Cr, Ni, Cu, Zn, Sn etc. can be electroplated.

(ii) Vapourising: Some metals can also be used as surface layers (deposition) by allowing their vapours to strike metallic surfaces with which they undergo alloying. Zn and Al are examples of this category. The deposition of Zn by this process is known as dry galvanizing and deposition of aluminium is called calourising.

(iii) Hot Dipping: It involves coating metals with films of metals having low melting points like Zn, Sn, Pb etc. This process involves dipping the cleaned metal in the both of molten metals. The liquid metal forms an alloy with the solid metal and as a result, a coating is formed on the surface. Tin plated iron and zinc plated iron (galvanizing) are the examples of 'Hot dipping process'.

The tin coating of iron does not allow iron to have a direct interaction with moisture and air and hence no rusting takes place. In Zn coating of iron, even when the protective coating is broken, iron is still resistant to corrosion (or rusting) because Zn is above iron in electrochemical series (so, Zn is more reactive than Fe).

A cheaper coating called 'terneplate' is produced by dipping iron in a molten alloy containing 20% Sn (tin) and 80% Pb (lead).

(iv) Metal Spraying: It is only used when hot dipping is not possible. This method is also utilized for huge structures such as bridges or industrial plants etc.

In scoop process, molten metal (Zn, Al, Cu etc.) are sprayed on the cold surface to be coated from spraying pistol and this adheres strongly but does not actually penetrate.

(v) Cementation : In this method, the metal to be deposited forms an alloy with the surface of the metal on which deposition occurs. The articles to be coated are packed in powdered coating metal in a drum which can be rotated and heated at a temperature slightly below the melting point of the more fusible metal.

Prob.4 ***What is corrosion? Discuss the mechanism of electrochemical corrosion.*** ***[R.T.U. 2016]***

Sol. Corrosion is the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings. One of the most widely accepted definition is that **"Corrosion is the slow but spontaneous deterioration of metals (except gold and platinum) by chemical or electrochemical reaction with its environment".**

Examples

(1) Formation of a layer of reddish brown scale of $Fe_2O_3.2H_2O$ on the surface of iron, also known as *"rusting of iron"*.

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$$

$$2Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_2O_3.2H_2O$$

(2) Formation of green layer of basic carbonate, $CuCO + Cu(OH)_2$ on the surface of copper when exposed to moist air containing CO_2.

(3) Reaction of Cl_2 gas with Mg or Sn.

Wet or Electrochemical Theory : *Refer to Long Answer Prob.3(a).*

Prob.7 ***Write short notes on the following :***

(a) Galvanic corrosion.

(b) Stress corrosion.

(c) Pitting corrosion ***[R.T.U. 2014]***

Sol.(a) Galvanic Corrosion : When two dissimilar metals like Zn and Cu are electrically connected and are exposed to an electrolyte, the metal higher in the electrochemical series with more negative electrode potential form anode and undergoes corrosion. Zn, which is higher in electrochemical series forms the anode and is attacked and gets dissolved, while Cu which is lower in electrochemical series, acts as the cathode. Since corrosion is due to the set up of a galvanic cell it is called **'galvanic corrosion'.** Galvanic corrosion is also known as *Differential Metal Corrosion* (DMC).

Mechanism : When Zn is in electrical contact with copper and is immersed in a corrosive environment, zinc metal, being higher up in the electrochemical series, acts as the anode and gets corroded, as shown in fig., whereas, the copper metal which is lower down in the series (+ve reduction potential) behaves as the cathode of the dissimilar metals. The tendency of a metal to corrode in a galvanic cell is determined by its position in the "galvanic series" of metals and alloys. As a result of this, corrosion current is flow from the anodic area (Zn) to the cathodic area (Cu) by the driving force which is due to the potential difference between the two.

Corrosion of zinc is given as follows :

At the anodic area,

$Zn \rightarrow Zn^{+2} + 2e^-$ (Oxidation and Corrosion)

At the cathodic area,

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{(Reduction and Protection)}$$

Overall reaction is the formation of $Zn(OH)_2$.

$$Zn + \frac{1}{2}O_2 + H_2O \rightarrow Zn(OH)_2$$

(i) **Corrosion by Hydrogen Evolution :** In acidic medium corrosion of zinc occurs with the formation of zinc salt and evolution of H_2.

$$Zn + HCl \rightarrow ZnCl_2 + H_2$$

(ii) **By Oxygen Absorption :** In neutral medium, the cathodic reaction gives OH^- ions which react with zinc ions forming its hydroxide as given above.

In a galvanic corrosion cell of the type explain about Zn gets corroded while Cu is protected.

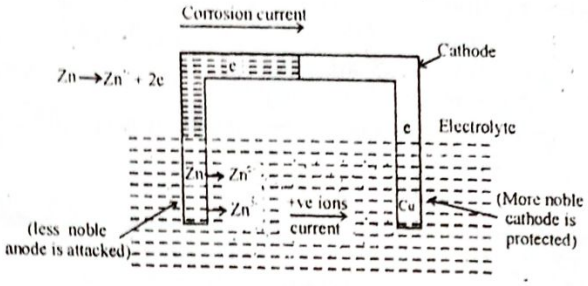


Fig. : Galvanic Corrosion

Sol. (b) Stress Corrosion : Stress corrosion or stress cracking is the type of corrosion which in common is fabricated articles of some alloys like high zinc brasses and nickel brasses are destroyed by this corrosion and such corrosion is due to the presence of stresses caused by heavy working like rolling, drawing, insufficient annealing etc.

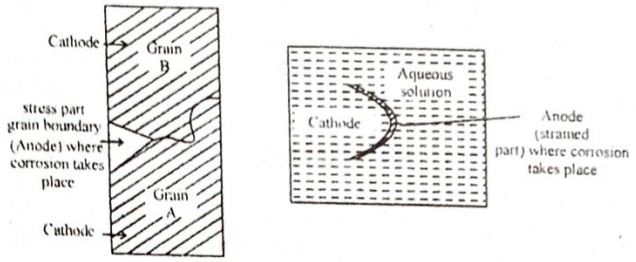


Fig. : Stress Corrosion

This type of corrosion is the combined effect of **static tensile stresses** and the corrosive environment on an alloy and is uncommon in case of pure metals. Stress corrosion is probably due to localized electrochemical corrosion occurring along narrow paths forming local anodic and cathodic areas on the metal surface. Presence of stress produces strains, which develops localized zones of higher electrode potential. These become very chemically reactive and they are attacked even by a mild corrosive environment, resulting in the formation of a crack.

Stress corrosion is characterized by a highly localized attack that takes place when the overall corrosion is almost negligible. Stress corrosion agents are highly specific and selective. For example,

(i) Mild steel is stress corroded by caustic alkalies and nitrate solution

(ii) Brass is stress corroded by ammonia

(iii) Stainless steel is stress corroded by chloride solutions.

Sol. (c) Pitting Corrosion : Pitting corrosion is a *localized accelerated attack* at some place on the metal surface, pitting corrosion thus results in the formation of pinholes, pits as well as cavities in the metal, and these irregularities may penetrate deep into the metal causing destruction of pipes and tubes.

Pitting corrosion may be due to the following important reasons–

(a) External environment is not homogeneous.

(b) Metal surfaces are not homogeneous.

(c) Films are not perfectly uniform.

(d) Environment is not uniform with respect to concentration.

(e) Crystallography directions are not equal in the reactivity.

(f) Scratches or cut edges sliding under load.

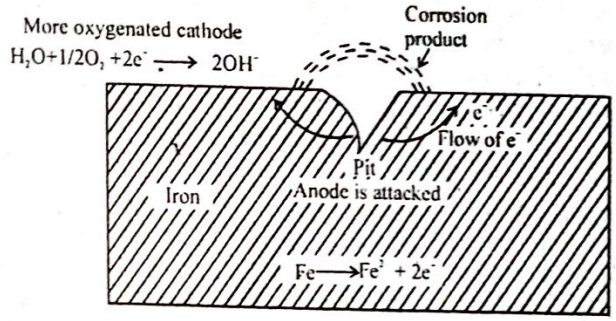


Fig. : Pitting Corrosion at the Surface of Iron

Pitting is generally caused as a result of breakdown of cracking of the protective film on a metal at specific point and pitting is neither uniform nor has a constant rate. As result of pitting, small anodic and large cathodic areas are developed and once a pit is formed, the rate of corrosion will be increased. Pitting occurs mostly in chloride solution containing a depolarizer (oxygen or oxidizing salt).

Prob.8 ***What is corrosion? Explain the mechanism of wet electrochemical corrosion and its prevention.*** ***[R.T.U. 20***

OR

Explain "rusting of iron" with the help electrochemical theory of corrosion. ***[R.T.U. 20.***

Sol. Corrosion : *Refer to Long Answer Prob.4.*

Mechanism of Wet Electrochemical Corrosion : *Refer Long Answer Prob.3(a).*

Prevention : *Refer to Long Answer Prob.3(b).*

Prob.9 ***Write short note on dry corrosion and pilli bedsworth's rule.*** ***[R.T.U. 20***

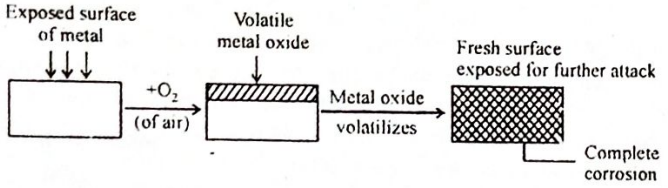


Fig. 4 : Volatile Oxide Layer

(iv) **Porous** : When metal oxide layer has pores or cracks, the atmospheric O_2 penetrates the metal through these pores or cracks. Corrosion continues till the entire metal is converted into its oxides, e.g. Li, K, Na, Mg etc. form porous oxides.

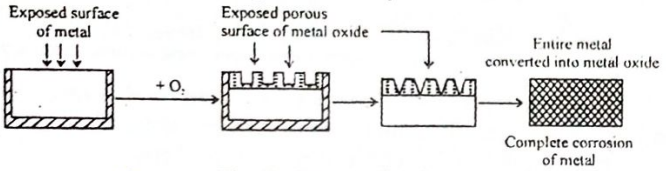


Fig. 5 : Porous Oxide Layer

Pilling–Bedworth Rule : Protective and non-protective nature of oxide layer mainly depends on the 'Pilling-Bedworth Rule'. According to this rule, an oxide is protective or non -porous, if the volume of the metal oxide is at least as great as the volume of the metal from which it is formed. On the other hand, oxide layer is non–protective or porous, if the volume of the metal oxide is less than the volume of the metal from which it is formed, because it cannot prevent the diffusion or access of oxygen to the fresh metal surface below.

Pilling–Bedworth Ratio : The ratio of the volume of the metal oxide formed to the volume of the metal consumed. This is called as Pilling-Bedworth ratio.

$$\text{Ratio} = \frac{\text{Volume of the metal oxide formed}}{\text{Volume of the metal consumed}}$$

Thus, Li, Na, K etc. and Mg, Ca, Sr etc. form porous oxides of volume less than the volume of metals and promotes corrosion continuously non–stop.

On the other hand, metal like Al forms oxides of volume higher than the volume of metal. Due to the absence of any pores in the oxide film, the rate of corrosion rapidly decreases to zero.

(b) Corrosion by Anhydrous Liquid

This corrosion occurs when the anhydrous liquid attacks directly on the surface metals. Anhydrous liquids are of three types–

(i) **Inorganic Liquid** : At ordinary temperature, HF, Br_2 etc. directly attack the metal surface and cause such type of corrosion.

(ii) **Organic Corrosion** : Phenols, picric acid etc. attack directly to metal surface and cause such type of corrosion even at room temperature.

(iii) **Liquid Metals** : When liquid metal is allowed to flow over solid metal at high temperature, corrosion occurs, and is known as **liquid metal corrosion.** It leads to weakening to solid metal.

(c) Corrosion by Other Gases

This occurs when dry gases like H_2, Cl_2, F_2, CO_2, SO_2, H_2S etc. directly attack the surface of the metal or alloy which depends mainly on the chemical affinity between the metal and gas. But the degree of attack depends on the formation of protective and non protective layers on the metal surface.

For example,

(i) $2Ag + Cl_2 \longrightarrow 2AgCl$

AgCl film being protective and thus protects the metal from further attack of chlorine on silver.

(ii) $Sn + 2Cl_2 \longrightarrow SnCl_4$

$SnCl_4$ film being volatile and hence Sn undergoes excessive corrosion.

Dry corrosion depends upon the following conditions.

(i) **Chemical Affinity** : More the affinity existing between metals and environment, corrosion will be more and vice–versa. Highly reactive metals such as Na, K, Ca corrode rapidly even at room temperature. But even at high temperature, noble metals are not corroded.

(ii) **Temperature** : Higher the temperature, greater is corrosion.

(iii) **Corrosion Product** : More volatile and porous corrosion product increases the rate of corrosion. Stable corrosion product decreases the rate of corrosion.

The soluble or volatile products of corrosion get readily removed from the metal surface and fresh metal area exposes for further chemical attack.

Prob.10 ***(a) What is atmospheric corrosion? Why metals like Cu, Sn, Pb, Al etc are corroded slowly as compared to Na, Ca, Mg, Fe etc?***

(b) What is electrode potential? Explain mechanism of corrosion by galvanic cell action. ***[R.T.U. 2012]***

FLASH AND FIRE POINT

Flash point of an oil is the lowest temperature at which the combustible liquid gives-off sufficient vapors that spontaneously ignite for a moment when a small flame is brought near the vapor of lubricating oil.

Fire Point of oil is the lowest temperature at where the vapors of an oil began to produce a continuous flame.

CLOUD AND POUR POINT

When the temperature is lowered upto a particular point, the oil becomes cloudy in appearance. This temperature is called **cloud point.**

When temperature is lowered upto a certain temperature, the oil ceases to flow or pour or becomes semisolid. This temperature is known as **pour point.**

FRICTION

When two surfaces come in contact, simple laws of friction are followed with exceptions.

The friction generated, thus, can hamper the system in three ways:

(i) **Energy Loss :** Work done is far less as compared to power supplied to a unit.

(ii) **Heat Generation :** Friction give rise to heat which may cause deformation of shape and seizure of surfaces.

(iii) **Material Loss :** Moving parts either break or deformed.

LUBRICANTS

(i) Any substance introduced between moving or sliding surfaces to reduce friction in order to avoid or reduce the wear and tear is known as **lubricant.**

(ii) The process of reducing friction between two sliding or moving bodies by the introduction of lubricant is known as **lubrication.**

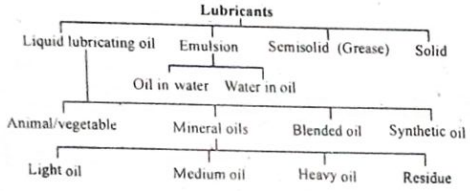
FUNCTIONS OF LUBRICANT

1. Prevents direct metal to metal contact, hence reduce wear and tear and surface deformation.
2. Prevents loss of energy so efficiency is increased.
3. It prevents seizure of machines.
4. Act as coolant in engines.
5. Act as seal around piston ring to prevent loss of pressure or scaling.
6. Remove contaminated products.
7. Absorb shocks between bearing and other engine parts.
8. Reduces maintenance cost of machines.

MECHANISM OF LUBRICATION (TYPES OF LUBRICATION)

1. Fluid film or hydrodynamic lubrication (Thick film).
2. Boundary lubrication (Thin–film lubrication).
3. Extreme pressure lubrication.

CLASSIFICATION OF LUBRICANTS



PREVIOUS YEARS QUESTIONS

I. SHORT ANSWER TYPE QUESTIONS

Prob.1 ***Write the name and composition of Portland cement.*** *[R.T.U. 2018]*

Sol. Composition of Portland Cement :

Oxides	Abbreviated form	Percent Limit
Lime (CaO)	C	60-67
Silica $(SiO)_2$	S	17-25
Alumina (Al_2O_3)	A	3-8
Iron Oxide (Fe_2O_3)	F	0.5-6
Magnesia (MgO)	—	0.1-4
Sulphur trioxide (SO_3)	—	1-2
Soda and Potash $(Na_2O + K_2O)$	—	0.5-1.3

Prob.2 ***Define the term lubricant and mention their important functions.*** *[R.T.U. 2018]*

Sol. Lubricants : The metal to metal frictional resistance can be minimized by using certain suitable substances which form a thin layer in between the moving parts, which keep them apart such substance are called lubricants.

Any substance introduced between moving or sliding surfaces to reduce the friction in order to avoid or reduce the wear and tear is known as lubricant.

Functions of Lubricants :

(1) The foremost important function of a lubricant is to reduce friction.

(2) It reduces wear and tear and surface deformation.

(3) It acts as a coolant and carries away the destructive heat produced due to friction.

(4) It acts as a seal around piston ring, ICE and cylinder wall, thereby preventing the leakage of gases under high pressure from the cylinder as also scaling of bearing against the entry of dirt.

(5) It reduces expansion of metals by frictional heat.

(6) It reduces unsmooth relative motion of the moving sliding parts.

(7) It reduces maintenance and running cost of the machine.

(8) It absorbs shocks between bearing and other engine parts thereby reducing noise.

(9) It also carries away contaminated products. Later, they can be removed from the system by oil draining or by oil purification system.

Prob.3 ***Importance of annealing of glass.*** *[R.T.U. 2017]*

Sol. Importance of Annealing

(i) Making the entire glass item uniformly hot and holding that temperature steady long enough to remove all stress caused from the manufacturing process.

(ii) Annealing cycle also include cooling down slow enough so as do not allow too much stress to build back up.

Prob.4 ***Industrial significance of viscosity measurement.*** *[R.T.U. 2017]*

Sol. Significance of Viscosity Measurement :

1. Viscosity of lubricating oil determines its performance under operating conditions.
2. If the viscosity of liquid is too low, the fluid lubricant film cannot be maintained between the moving surfaces, as a result of which excessive wear may take place.
3. If the viscosity of the lubricating oil is too high, excessive friction will take place.

Prob.5 ***Define cement.***

Sol. Any substance which have adhesive and cohesive properties and capable of bonding materials like bricks, stones, building block etc is called cement. The main constituents of cement are of various aluminates and silicates of calcium.

Prob.6 ***How cement can be classified? Explain in brief.***

Sol. Cement can be classified in two types :

(1) Hydraulic Cements : These are most widely used and capable of setting and hardening under water, Examples – portland cement.

(2) Non-hydraulic Cements : These are the cementing material which harden in air. It cannot be used under water.

Example - Ordinary Cement

Prob.7 ***What do you understand by "portland cement"?***

Sol. Portland cement is the most important reliable cementing material is also known as **"magic powder".** It consists primarily of compounds of lime, alumina, silica and iron. It forms a paste when mixed with water. This paste subsequently hardens and binds the aggregates (crushed rock, sand, gravel etc.) together to form a hard durable mass called concrete.

Prob.8 ***Define refractories.***

Sol. Refractories are those material that can withstand at extremely high temperature without softening, melting or deformation in shape. Refractory retain their chemical and physical identity at elevated temperature.

Prob.9 ***Give the properties of refractories.***

Sol. (i) Refractoriness
(ii) Thermal Expansion and Construction
(iii) Strength or Refractoriness Under Load (RUL)
(iv) Porosity
(v) Thermal Spalling
(vi) Corrosion and Erosion Resistance
(vii) Chemical Inertness
(viii) Thermal Conductivity
(ix) Electrical Conductivity
(x) Heat Capacity
(xi) Dimensional Stability
(xii) Permeability
(xiii) Texture

Prob.10 ***What is meant by fire clay bricks?***

Sol. Fire clays are hydrated aluminium silicates having the general composition, $Al_2O_3.2SiO_2.2H_2O$ with impurities of sand and gravel, alkalies oxide, sulphate and sulphide, silicates and carbonates of Ca and Mg, small quantity of TiO_2. These raw materials are used for making the fire clay refractory.

Prob.11 ***Give any two uses of fire clay refractories.***

Sol. 1. The fire clay refractories are used for linings of blast furnace, reverberatory furnaces, stoves, open hearths in the steel plants.

2. These are also widely used in foundries, lime, continuous ceramic pottery and metallurgical kilns, glass, brass and copper furnaces.

Prob.12 ***Define glass.***

Sol. Glass is a super cooled liquid consisting of a mixture of silicates. Physically, glass may be defined as a amorphous hard, rigid, transparent or translucent, brittle, super cooled liquid, non crystalline substance having no definite melting point and appropriate high viscosity to prevent crystallization.

Chemically, glass may be defined as a fused mixture of silicates of alkali and alkaline earth compounds and other glass constituents like CaO, MgO, SnO_2, barium oxide and lead oxide.

Prob.13 ***Give the advantages of optical fibres.***

Sol.
1. Have low signal attenuation.
2. Have very large information transmission capacity.
3. Have small size, lighter in weight and low cost transmission.
4. Fibre is much more reliable and ease of maintenance.
5. Communication is more confidential and private and no cross–talk in optical fibres.
6. Have very wide bandwidth.

Prob.14 ***What do you understand by optical fibres?***

Sol. Optical fibres are extremely fine-pipes, hair thin diameter made from high purity and low dispersion glass which can be used as wave guide for telecommunication by transmission of high frequency pulses of light without decrease in intensity. It is made up of high purity glass core (Ga–doped) having a higher refractive index and cover in a equally high quality cladding (fused silica) of lower refractive index.

Prob.15 ***Write down any two functions of lubricants.***

Sol. (i) The first and foremost function of a lubricant is to reduce friction.

(ii) It prevents the direct contact between rubbing surfaces, hence it reduces wear and tear and surface deformation. Thus, it reduces the maintenance and running cost of the machine.

Prob.16 ***Give the qualities of a good liquid lubricant.***

Sol. A good liquid lubricant must possess:

(i) Low vapour pressure or high boiling point
(ii) Adequate viscosity for particular service conditions
(iii) Low freezing point
(iv) High oxidation resistance and heat stability
(v) Non corrosive properties
(vi) Resistance to decomposition at higher and elevated temperatures.

Prob.17 ***What do you understand by "SAE number"?***

Sol. The efficiency and viscosity of these oils at various temperatures is provided by an index known as **"SAE number"** given in accordance with norms of **Society of Automobile Engineers (SAE).**

Prob.18 ***An oil sample under test has a viscosity same as that of standard gulf oil (low viscosity standard) and Pennsylvanian oil (high Viscosity Index standard) at 210°F. Their viscosities at 100° F are 61 sec, 758 sec and 420 sec respectively. Calculate Viscosity Index of the same oil.***

Sol. L = 758 sec, H = 420 sec, and U = 61 sec

$$\text{So viscosity index of given sample} = \frac{L-U}{L-H}\times 100$$

$$= \frac{758-61}{758-420}\times 100$$

V.I. = 206.2

Prob.19 ***Define flash point and fire point.***

Sol. Flash point is the lowest temperature at which the lubricating oil gives off enough vapours that is ignited for a moment, when a test flame is brought near it. The fire point is the lowest temperature at which the vapours of the lubricating oil burn continuously for at least 5 seconds when a test flame is brought near it.

Prob.20 ***What do you understand by "cloud point"?***

Sol. The particular temperature at which lubricating oil becomes cloudy or hazy in appearance, is called its "cloud point"

Prob.21 ***What do you mean by "SEN number"?***

Sol. The time in second in which oil and water emulsion separate out in distinct layers is called "steam emulsion number (SEN)' or 'demulsification number'. A good lubricant possesses low steam emulsion number.

Prob.22 ***What is meant by "saponification number"?***

Sol. Saponification Number or value of an oil is the number of mg of KOH required to saponify fatty material present in 1g of the oil.

3. Polar groups to promote wetting and spreading over the metallic surfaces at high pressure.
4. Active atoms or groups which can form chemical bonds with the metals or other surfaces.
5 High viscosity index.
6. Heat and oxidation resistance.
7. Good oiliness.

Following are the lubricants used for boundary lubrication:

(i) Solid lubricants, greases and mineral oils : These are thermally stable but possess poor oiliness which is improved by adding small amount of fatty acids or fatty oils.

(ii) Vegetable and animal oil and their soaps : They possess oiliness but poor stability because they decompose at high temperature. They are also used as additives to improve oiliness of mineral oils.

(iii) Graphite and molybdenum disulphide either alone or as stable suspensions : They can bear compression as well as high temperature and posses low internal friction.

Prob.2 ***Describe with a neat diagram how Portland Cement is manufactured by wet process. Explain chemical reaction involved in the process.*** *[R.T.U. 2018]*

Sol. Wet Process : It is quite common and is universally employed for manufacturing of portland cement.

Following are the steps involved in manufacturing of cement :

(i) Crushing : Raw materials are grinded in ball mills and passed to tube mill conveyed through means of screw driver. The material is mixed with 30-40% water before grinding.

(ii) Mixing of Raw Materials : The muddy mixture thus formed is known as slurry, which is generally stored in big tanks. This slurry contains about 38 to 40 percent water. The slurry is then pumped into the rotary kiln where it is burnt.

(iii) Burning : Actual chemical changes take place in rotary kiln. The rotary kiln is perfectly tined with refractory bricks to avoid any thermal loss.

The kiln is slightly inclined downwards towards the exit end. It can be rotated at desired speed as it is mounted on rollers. The material is introduced in the rotary kiln from the upper end. As the kiln rotates, the material passes slowly from the upper to lower end at a rate controlled by slope and speed of rotations of the kiln. Heating of kiln is done by burning of pulverized coal which is introduced through special burners. Temperature maintained is 1400–1500° C. As the material passes through the kiln, its temperature is raised to the point of clinkering temperature where the actual chemical reactions take place.

In fact, there are different zones in the rotary kiln viz.

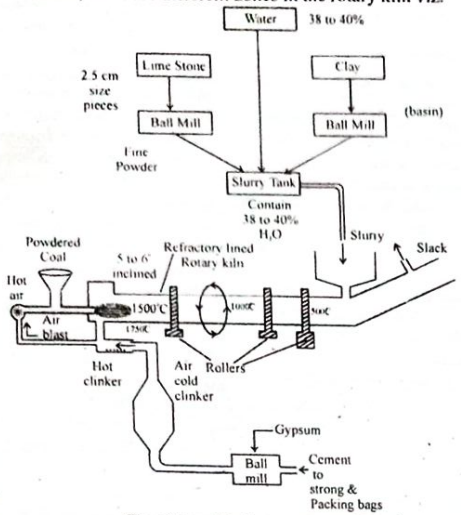


Fig. : Rotary kiln for cement manufacturing

(a) Drying Zone : This is the upper one fourth part of rotary kiln, here the temperature is moderate (100–500°C). This zone is known as drying zone, because in this zone; water is driven out of the slurry by means of hot gases.

(b) Preheating Zone: Temperature in this zone varies from 500 to 700°C where clay decomposes.

(c) Calcination Zone : Its temperature is about 1000° C and it is the middle portions of the kiln. Here, organic matter burns away. Calcium carbonate decomposes into calcium oxide and carbon dioxide which escapes.

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

(d) Burning or Clinker Zone : It is the hottest and bottom portion of the rotary kiln. In this part, temperature is about 1400° C–1500° C. In this zone, mixture melts and forms little rounded pasty masses about the size of peas which are called clinks. The clinkers produced is greenish or black in color, the clinks formed are falls out from this lower end of the kiln. The main reactions takes place are following :

$$CaCO_3 \rightarrow CaO + CO_2$$
$$2CaO + SiO_2 \rightarrow 2CaO.SiO_2$$
$$3CaO + SiO_2 \rightarrow 3CaOSiO_2$$
$$3CaO + Al_2O_3 \rightarrow 3CaO.Al_2O_3$$
$$4CaO + Fe_2O_3 + Al_2O_3 \rightarrow 4CaO \cdot Fe_2O_3 \cdot Al_2O_3$$

(e) Cooling of Clinkers : Clinkers formed as pellets are very hot to handle; so, they are allowed to cool very carefully at moderate rate. The cooling of clinkers is done by air quenching cooling system in which atmospheric air sucked through a suction pump and hot clinkers are allowed to pass through the air, as a result, clinkers are cooled but the sucked air becomes hot and in further passed to the pulverized coal to increase its temperature for its efficient burning. In cooling, cave is to be taken to cool them at moderate rate because if cooling is fast then the clinkers are converted with glass balls and with slow cooling rate then desired β form is converted into γ form and in both the cases, these will no binding behaviour in the clinkers.

(f) Grinding : After cooling, the clinkers are grounded to a fine powder in ball mills, according to the class of the product. Finely ground clinkers set very quickly by absorption of moisture from the atmosphere. Therefore, a small quantity (2-3%) of gypsum is added which acts as retarder to prevent quick setting of the cement.

Gypsum retards the dissolution of C_3A by forming tricalcium sulphoaluminate ($3CaO.Al_2O_3$. x $CasO_4.2H_2O$) which is insoluble.

$$3CaO.Al_2O_3 + xCaSO_4.2H_2O \rightarrow 3CaO.Al_2O_3.xCaSO_4.2H_2O$$

C_3A — gypsum — Tricalcium sulpho-aluminate (Insoluble)

Formation of insoluble product prevent too early further reactions of setting and hardening. This mixture of ground clinkers and gypsum powder is known as portland cement, which is now ready for packing.

(g) Packing : The ground fine powder of cement is stored in silos from which packed by automatic machines into 50 kg bag.

Role of Gypsum in Portland Cement : Gypsum is added during grinding of cement. Gypsum is used as a retarder for setting, otherwise cement when mixed with water will set quickly during grinding.

Gypsum is good fire-resistant material having good insulating properties and thus retards fine damage to wooden and steel framing.

Prob.3 ***Classify various types of glass and write short notes on :***

(a) Borosilicate glass
(b) Alumino silicate glass
(c) Optical glass *[R.T.U. 2018]*

Sol. (a) Glasses are classified as follows :

(i) Soda lime glass or soft glass
(ii) Potash glass or hard glass
(iii) Lead glass or flint glass
(iv) Borosilicate glass or pyrex glass or jena glass
(v) Alumino silicate glass
(vi) Optical or crooks glass
(vii) Safety glass or laminated glass
(viii) Tonghened glass
(ix) Wired glass
(x) Glass wool
(xi) Photo chromic glass

Borosilicate glass or pyrex glass or Jena glass : It contains boron trioxide (B_2O_3) and silica with a small amount of alumina and alkali metal oxide.

The percentage composition of different components are as follows :

80.5% silica (SiO_2), 13% B_2O_3, 3% Al_2O_3, 3% K_2O, 0.5% Na_2O.

Al_2O_3 and B_2O_3 gives Al^{+3} and B^{+3} ions for pyrex glass. Al^{+3} may replace Si^{+4} in SiO_4 tetrahedra. Similarly, B^{+3} replaces some Si^{+4} in the tetrahedra skeleton *i.e.*, its thermal coefficient of expansion is very low and chemical resistance is high. Pyrex glasses have very high softening temperature and are shock–proof.

Properties

(i) Low thermal coefficient of expansion
(ii) High chemical resistance
(iii) Excellent shock–resistance
(iv) High softening point

Uses

(i) Superior laboratory apparatus like flasks, beakers etc.
(ii) Television tubes, electrical insulators etc.
(iii) Industry for pipelines for corrosive liquids.

(b) Alumino Silicate Glass : Alumino silicate glass has higher percentage of Al_2O_3 and lower percentage of B_2O_3 with comparison of borosilicate glass. The composition of this type of glass is as follows :

55%, SiO_2, 23% Al_2O_3, 7% B_2O_3, 9% MgO, 5% CaO and 1% ($Na_2O + K_2O$)

Property : It has exceptionally high softening temperatures.

Uses : Alumino silicate glass is used for

1. High pressure mercury discharge tubes
2. Chemical combustion tubes
3. Certain domestic equipments etc.

(c) Optical glass : They contain phosphorous and lead silicate together with a small amount of cerium oxide (CeO_2). Optical glasses are used in optical instruments because they have the following important characteristics :

(i) Low viscosity so that it becomes free from bubbles in molten state.
(ii) It should not be devitrified even upon long annealing.
(iii) The raw material should be free from impurities like (iron) so that glass produced is colorless.
(iv) Its surface should not be spoiled even on long exposure to the atmosphere.

Optical glasses contain cerium oxide which is capable of absorbing the U.V. light (which is injurious to eyes).

Properties : Optical glasses are relatively soft, have low melting point, low durability and low chemical resistance.

Uses : They have high refractive index and used for the manufacturing of lenses.

Prob.4 ***Write short note on Role of Gypsum.*** *[R.T.U. 2014]*

OR

Role of gypsum in cement. *[R.T.U. 2017]*

Sol. Role of Gypsum

When water is mixed with cement, the paste becomes rigid within a short time called flash set or initial setting because of the fast hydration of the basic constituent C_3A.

$$3\ CaO\ Al_2O_3 + 6H_2O \rightarrow 3CaO.\ Al_2O_3.\ 6H_2O\downarrow$$

The formation of hydrated crystal of C_3A prevents further hydration and hydrolysis reactions of remaining constituents (C_3S, C_2S & C_4 4F). In order to make these constituents to react with water, gypsum ($CaSO_4.2H_2O$) is added as retarder to slow down the rate of flash set by forming soluble sulpho aluminate complex.

$$3CaOAl_2O_3 + XH_2O + YCaSO_4.\ 2H_2O \rightarrow 3CaOAl_2O_3\ \underset{(1-3)}{Y}\ CaSO_4 \cdot \underset{(10-33)}{Z}\ H_2O$$

Due to the slow rate of flash set, C_4AF is now in a position to react with water to form the gels and crystals

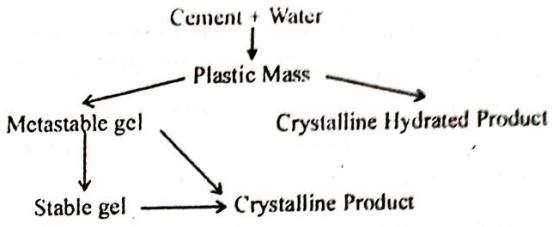
$$4CaO\ Al_2O_3\ Fe_2O_3 + 7H_2O \rightarrow 3CaO\ Al_2O_3\ 6H_2O + CaO\ Fe_2O_3\ H_2O$$

These gels on the passage of time shrinks and leaves capillaries for the water to come out and react with the constituents C_2S and C_3S for their further hydration and hydrolysis reactions which are responsible for the development of ultimate strength in the cement over a period of time.

$$3CaOSiO_2 + X\ H_2O \rightarrow 2CaO\ (X-1).\ H_2O + C(OH)_2$$
$$2CaO\ SiO_2 + X\ H_2O \rightarrow 2CaO\ SiO_2.\ X\ H_2O$$

The formed gels contains free water which is gradually withdrawn by the anhydrous core of cement. Thus, gels begins to harden due to gradual dehydration. This dehydration is followed by crystallization in which 3-dimensional interlocking of reaction product takes place. As degree of crystallization increases hardness and strength of set mass increased. The rate of hardness imported by the basic constituent is in the given order.

$$C_3A > C_3S > C_4AF > C_2S$$



Prob.5 ***What is cement? Explain manufacturing of cement by Rotatory kiln technology with diagram and reactions involved in the process.*** *[R.T.U. 2017]*

Sol. Cement : Cement is a commonly used engineering material, having adhesive and cohesive properties because of which it has been widely used in binding bricks, stones and building blocks. Cement is an anhydrous powder obtained by burning a mixture of various metallic oxides (Ca, Al, Fe & Si etc.) at high temperature of about 1500-1700°C. Cement power on addition of water due to hydrolysis and hydration of its basic constituents. Setting and Hardening of cement takes place and works as binding material.

Rotatory kiln technology : On analysis, the Portland cement is found to contain the lime, silica, alumina, iron oxide, magnesia and other oxides. The percentage composition of the Portland cement is shown as below

Table : Composition

Oxides	Abbreviated form	Percent Limit
Lime (CaO)	C	60-67
Silica $(SiO)_2$	S	17-25
Alumina (Al_2O_3)	A	3-8
Iron Oxide (Fe_2O_3)	F	0.5-6
Magnesia (MgO)	—	0.1-4
Sulphur trioxid (SO_3)	—	1-2
Soda and Potash $(Na_2O + K_2O)$	—	0.5-1.3

As it is clear from the above, lime is the main ingredient forming about two third of the cement. It is very active constituent and its proportion plays an important role on the qualities of cement. A high content of lime generally increases the setting time but gives a high early strength. But too little content of lime reduces the strength of cement.

An excess of lime many make the cement concrete unsound and liable to be disintegrated. Silica and Alumina are also the main and active constituents of cement, having important effects on the properties. A high percentage of silica usually prolongs the setting time but increases the strength. A high percentage of alumina tends to reduce the setting time but to increase the strength.

Iron oxide is not so important constituent, but Portland cement derives its characteristic grey color because of it. It may also combine with lime and silica at a high temperature. The other constituents do not have any effect on the qualities of cement.

(1) Using refractory with high porosity, good thermal conductivity and low coefficient of expansion.

(2) Avoiding sudden temperature changes.

(3) Proper furnace design.

Sol (b) Manufacturing of glass consists of following high level steps :

1. Melting
   (i) Pot furnace
   (ii) Tank furnace
2. Forming and shaping
3. Annealing
4. Finishing

Melting

1. Raw materials in proper proportions (sand, soda ash lime stone) are mixed and finely powdered
2. The homogenous mixture known as Batch is fused with some broken glass, called "Cullet" in any of the two types of furnaces
3. The homogenous mixture is melted either in
   (a) Pot furnace or
   (b) Tank furnace
4. The batch melts and fuses at 1800°C

Forming and Shaping, Annealing and Finishing

1 Molten gas is converted to desired shape by blowing or moulding or pressing between rollers- "Forming and Shaping"

2. Articles are then cooled gradually at room temperature.- "Annealing"
   The longer the annealing period better the quality of glass.
3. After annealing, the articles are subjected to cleaning, polishing, cutting, sand blasting etc.,- "Finishing"

Properties :

1. Incredibly thermally shock resistant (can be taken from red heat and plunged into water without cracking)
2. Low coefficient of thermal expansion
3. Optical transmission properties from ultra violet to infra red
4. Good chemical resistance
5. Excellent electrical insulator

Uses

1. Windows
2. Lenses
3. Mirror substrates
4. Crucibles, trays and boats
5. UV transmitting optics (synthetic fused silica)
6. IR transmitting optics
7. Metrology components

Functions of the Ingredients of Cement

1. Lime is the main constituent of cement. Its proportion must be properly maintained. However, excess of lime reduces the strength of cement, because it makes the cement to expand and disintegrate. On the other hand, presence of lesser amount of lime then required also reduces the strength of cement and makes it quick setting.

2. Silica imparts strength to cement and usually prolongs the setting time.

3. Alumina makes the cement quick–setting. However, excess of Al_2O_3, weakens the cement.

4. $CaSO_4.2H_2O$ (Gypsum) helps to retard the setting action of cement. It actually enhances the initial setting time of cement.

5. Iron oxide provides (a) Color (b) Strength (c) Hardness to the cement.

6. SO_3 (Sulphur trioxide) in small proportion, is desirable when present in small amount, it imparts soundness to cement. However, its excess reduces the soundness of cement.

7. Alkalis : Excess of alkalis causes the cement efflorescent.

Prob.10 *Discuss the use of Seger's cone test and RUL tests for a good refractory.* *[R.T.U. Dec. 2016]*

OR

What are refractories? Discuss the Seger's pyrometric cone test and RUL test. *[R.T.U. Jan. 2016]*

OR

Explain Refractoriness Under Load (RUL) test. *[R.T.U. 2013]*

OR

Write note on Seger cone test and RUL- test. *[R.T.U. 2015]*

OR

How can you measure the refractoriness and refractoriness under load of a refractory material? *[R.T.U. (I Sem.) 2008]*

OR

Explain Segercone test and RUL test of refractory material. *[R.T.U. 2012, 2010, 2009, Raj.Univ.(Back) 2008]*

OR

Pyrometric Cone Equivalent (PCE) test (Seger-cone test) *[R.T.U. 2013]*

OR

Explain Segercone test and RUL test of refractories. *[R.T.U 2007]*

Sol. Refractories : *Refer to Long Answer Prob.3(a)*

Seger's Cone Test : Refractoriness is a measure of fusibility of refractory materials. It represents the softening temperature of refractories. This temperature is observed either with the pyrometers or in terms of Pyrometric Cone Equivalent (PCE) value. In PCE value, refractoriness can be determined on a sample in the form of a cone which is either cut from the material or prepared from the ground sample. The softening of the cone is indicated by the top bending over and the tip touching the plaque on which cone is placed. The PCE is reported in terms of the standard cones and is equivalent to that corresponding in time of softening with test cone. If the test cone softens earlier than one cone and later than other, then the PCE value will be approximately between two cones.

The test refractory in the form of cone generally is 38 mm height and 19 mm base. Size is kept along side the similar sized standard cones and all are heated uniformly at 10° C per minute. Each standard cone is made of a particular refractory material of a definite softening temperature are assigned serial number with increasing softening temperature. When the test cones softens and loses its shape, at the same time one the standard cones whose refractoriness is near to that of the test cone will also soften, the serial number of that standard cone is noted. For example, the silica brick has a PCE of 33 with a softening temperature range 1700 – 1750° C. It indicates that this refractory can be used in furnace with operating temperature.

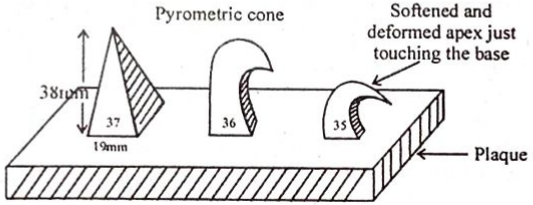


Fig. : Measurement of refractoriness : Seger's cone Test

Refractoriness Under Load (RUL) : This represents the resistance of a refractory material to the combined efforts of heat and load. RUL is the temperature at which the deformation begins and at which at least 10% deformation takes place. It is necessary that refractory material must also possess very high mechanical strength even at operating temperature to bear the maximum possible load without damage.

Strength of Refractory (Refractoriness Under Load) : The high temperature load-bearing characteristics of a refractory material is determined by refractory under load test or R.U.L. test.

In R.U.L. test, the specimen of refractory of size 5cm^2 and height 75cm. under a load of 1.75kg/cm^2 is heated in a carbon resistant furnace. The heating rate is maintained at 10°C/minute.

The temperature at which 10% deformation occurs on test specimen is reported as R.U.L.

The determination of deformation is done by recording the height of the specimen at different temperature

On the basis of R.U.L. test, the refractory material are classified as :

R.U.L.	Refractory material
1350°C	High heat duty brick
1300°C	Intermediate heat duty brick
1100°C	Moderate heat duty brick

Prob.11 *Describe fire clay refractory, its properties and uses.* *[R.T.U. Dec. 2016]*

OR

Write short note on Fire clay refractories. *[R.T.U. Jan. 2016, 2012, 11]*

Sol. Fire Clay Refractories : Fire clays are hydrated aluminium silicates having the general composition, $Al_2O_3.2SiO_2.2H_2O$ with impurities of sand and gravel, alkalies oxide, sulphate and sulphide, silicates and carbonates of Ca and Mg, small quantity of TiO_2. These raw materials are used for making the fire clay refractory.

Preparation : Fire clay refractories are prepared from finely ground raw material, and grog (powdered calcined fire clay). Grog is made by pulverizing rejected crucible, broken sugars. The exact proportions of the constituents depend on the type of bricks to be desired. Spalling character will be lesser when greater is the percentage of grog like, neutral fire clay bricks contain 40% SiO_2 and 55% Al_2O_3, while acidic fire clay bricks 55% SiO_2 and 35% Al_2O_3. Remaining balance consists of K_2O, CaO, FeO, MgO etc.

Manufacturing of Fire Clay :

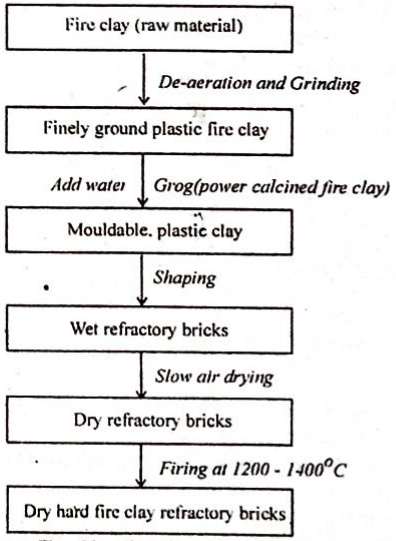


Fig. : Manufacturing of fire clay refractory

The manufactured glass being a bad conductor of heat and if the glass materials are allowed to cool rapidly, the upper layers will cool down first, leaving the inner portions in a state of stress and strain (because the glass is bad conductor of heat). Due to this unequal expansion the glass materials are much likely to crack to pieces. They cannot withstand change of temperature or shock. To avoid such problem, **annealing is needed.**

The manufactured glass material should be kept above critical temperature to reduce internal strain for a sufficiently long time. Then glass must be cooled gradually and slowly at room temperature by passing through different chambers with descending temperature is called **annealing process.**

4. Finishing : After annealing process, all types of annealed glass require finishing. It is carried out by cleaning, washing, grinding, polishing, blasting etc.

Prob.13 ***What is optical fibre? Discuss the structure and working of optical fibres.*** *[R.T.U. Dec. 2016]*

OR

Write short note on Optical Fibre. *[R.T.U. 2012]*

OR

Write short note on total internal reflection in Optical Fibres. *[R.T.U. 2011]*

OR

What is Optical Fibre? Describe the construction, working, advantages and applications of optical fibres. *[R.T.U. 2010, 2009, 2008, Raj. Univ. 2006, 2005]*

Sol. Optical Fibre : A revolutionary new technology based on light wave communication through hair, thin strands of glass called optical fibre, is transforming communication network of the world for communication of voice, video signals and digital data to a distant place. In order to communicate millions of informations at a time, carries waves of extremely high frequencies will be required. It can be achieved, if light rays are used as carrier waves, ordinary method of communication is not suitable for transmitting signals modulated with light rays and atmosphere as medium, is not suitable for transmission of signals due to high attenuations and random fluctuations in the atmosphere. The transmission of informations modulated with carrier light waves through hair thin glass fibre got tremendous impetus.

The study of properties related with propagation of light wave through the fibre is called *fibre optics* and fibre is then called *optical Total Internal Reflection fibre.*

Total internal reflection is a phenomenon that happens when a propagating wave strikes a medium boundary at an angle larger than a particular critical angle with respect to the normal to the surface. If the refrative index is lower on the

other side of the boundary and the incident angle is greater than the crictial angle, the wave can not pass through.

In case of refraction of light, from Snell's law, we have

$$\mu_1 \sin i = \mu_2 \sin r \quad \ldots(1)$$

If light is passing from denser to rarer medium through a plane boundary, then $\mu_1 = \mu_D$ and $\mu_2 = \mu_R$; so with $\left(\mu = \frac{\mu_D}{\mu_R}\right)$ equation (1) reduces to

$$\sin i = \frac{\mu_R}{\mu_D} \sin r \text{ i.e., } \sin i = \frac{\sin r}{\mu} \quad \ldots(2)$$

i.e. $\sin i \propto \sin r$ with $(\angle i) < (\angle r)$ as $[\mu > 1]$

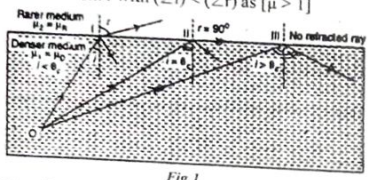


Fig. 1

Case I : As angle of incidence i increases, angle of refraction r will also increase and for certain value of i(< 90°) r will become 90°. The value of angle of incidence for which r = 90° is called **critical angle** and if denoted by θ_c.

$$\sin \theta_c = \frac{\sin 90}{\mu} \text{ i.e., } \sin \theta_c = \frac{1}{\mu} \quad \ldots(3)$$

Equation (2) in terms of critical angle can be written as

$$\sin i = \sin r \times \sin \theta_c \text{ i.e. } \sin r = \frac{\sin i}{\sin \theta_c} \quad \ldots(4)$$

Case II : If $i > \theta_c$, $\sin r > 1$. This means that r is imaginary. Physically, this situation implies that refracted ray does not exist so that total light incident on the boundary will be reflected back into the same medium from the boundary. This phenomenon is called total internal reflection.

Working Principle : The principle of optical fibres is based on light transmission in **total internal reflection.** Optical fibres are extremely thin glass fibres drawn out of ultra high purity, and low dispersion glass. The fibres are coated with a layer of lower refractive index.

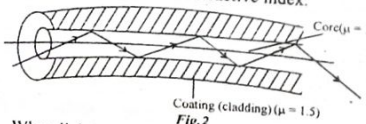


Fig.2

When light enters at one end of the fibre, it undergoes successive total internal reflection from side walls and travel down the length of the fibre along a zig zag path. In fact

total internal reflection takes place at the interface between the high refractive index core, [usually made of vitreous silica doped with germania (Ge_2O)] and the lower refractive index sheath or cladding of pure glass. Light can be transmitted over many kilometers without decrease in its intensity due to total internal reflection by optical fibres.

In this way, ray undergoes repeated total internal reflection until it emerges out of the other end of fibre, even if the fibre is bent. Thus, the light ray is guided through the fibre from one end to other end without any energy being lost due to refraction.

Fibre Construction : An optical fibre is a hair thin fibre made of glass quartz or transparent polymer having radius of 10^{-6} m.

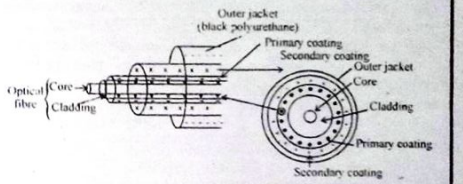


Fig. 3 : Structure of an Optical Fibre

An optical fibre consists of

(i) core
(ii) cladding
(iii) coating

(i) **Core :** It is an innermost cylindrical part which is made up of ultra pure glass having high refractive index ($\mu_1 = 1.7$). The core carries light signals. The core diameter can vary from about 5mm to about 100mm.

(ii) **Cladding :** The core is surrounded by another cylindrical shell of lower refractive index ($\mu_2 = 1.5$) called cladding. The cladding helps to keep the light within the core through the phenomenon of total internal reflection. The cladding diameter is usually 125 mm.

(iii) **Coating :** It is a safeguard for core and cladding against ecological effects. A soft plastic coating (primary coating) is done whose diameter is about 250mm for greater strength and protection of the fibre. This is followed by another layer of coating known as secondary coating.

Applications of Optical Fibre

(1) In Communication : Fibre optics essentially deals with the communications involving voice signals, video signal or digital data by transmission of light through optical fibre.

(2) Transmission of Image : Images can be sent from one place to another place through the optical fibre as optical fibres can be bent in any shape and no obstruction is found in the propagation of light through the fibre. The technology o fibre optics is intimately linked with its applications in medicin and industry.

(i) In Medicine : The instrument based on optica fibre used for searching an ulcer in the stomach of patient i called *fibroscope* in endoscopy. Two thin bundles of optica fibres are inserted down the patients throat. Light introduce at outer end of one bundle, undergoes multiple reflections ... end up illuminating the interior of the stomach. Some of th light reflected from the interior then comes back through th second bundle of the fibres. It is detected and converted int images on TV screen for physician to view.

(ii) In Industry : The fibroscope is also useful i industry. It could be used to examine welds, nozzles an combustion chambers, any defects inside jet aircraft engine which would be inaccessible for observation otherwise.

Advantages of Optical Fibres

1. Have low signal attenuation.
2. Have very large information transmission capacity
3. Have small size, lighter in weight and low cos transmission.
4. Fibre is much more reliable and ease of maintenance
5. Communication is more confidential and private an no cross-talk in optical fibres.
6. Have very wide bandwidth.
7. Have heat and corrosion resistance.
8. Have greater repeater spacing.
9. Optical fibres are immune to electromagneti interface and do not pick up line currents.
10. Fibres are excellent dielectrics, isolation coating i not required.
11. Safer than metal wires and have very long life spa as compared to metal.

Prob.14 ***Write a note on aluminosilicate glasses and it uses.*** *[R.T.U. Dec. 2016]*

Sol. Alumino Silicate Glass : *Refer Q.3(b) (Long Answe Type Questions).*

Prob.15 ***Explain the Steam Emulsification Number .*** *[R.T.U. Dec. 2016]*

OR

Write short note on the Steam Emulsification Numbe (SEN). *[R.T.U. Jan. 2016, 2011]*

Sol. Steam Emulsification Number (SEN) : This is one o the properties of oil that comes into play when and where oi is to be mixed up with water. This property is tested an represented in a manner that time taken by an emulsion t form separate layers of water and oil. By ASTM tests it i carried out as follows :

is fitted with an agate jet that can be kept closed or open by a valve rod fitted with a ball made of brass. The lid of the cup is fitted with a thermometer, which indicates the oil temperature.

(b) **Heating bath :** Oil cup is surrounded by a cylindrical copper bath containing copper with containing water having an outlet for taking out water, a stirrer with four blades and a thermometer.

(c) **Kohlrausch flask :** It is a special type of receiver for receiving the oil. Its capacity is 50 ml to the mark in its neck.

Working : Water is filled in the bath and the brass ball is kept in position to seal the orifice. Test oil is filled in the oil cup upto the tip of the indicator. An empty Kohlrausch flask is kept just below the jet. The desired temperature at which the viscosity is to be measured, maintained by stirring the water and oil in the heating bath and the oil cup respectively. The ball value is lifted and the time is noted for 50 ml of the oil to collect in the flask and the value is immediately closed to stop the overflow of the oil.

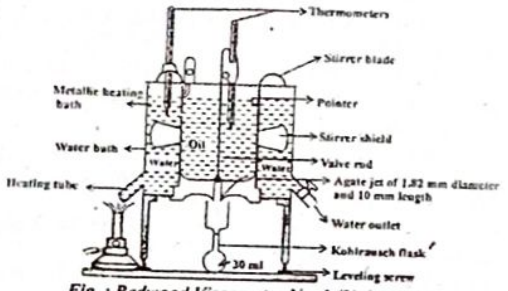


Fig. : Redwood Viscometer No. 1 (Universal)

Prob.21 ***Write short note on Silica Refractories.***

[R.T.U. Jan. 2016]

OR

Explain Silica Refractory. *[R.T.U. 2014, 12, 11]*

Sol. Silica Refractories : It contains 90 to 95% silica and about 2% lime is added during grinding to furnish the **bond preparation**. The raw material used for the manufacturing of silica bricks are quartz, quartzite, ganister, sand, sandstone etc. The silicious rock is first crushed and grounded with 2% lime and water and results the thick paste.

It is converted into bricks either by hand moulding or by machine pressing. The bricks are dried in air and heated. After drying, bricks are burnt in kilns. In about 24 hours, the temperature is slowly raised to about 1500°C. This high temperature is maintained for about 12 hours. This step is very important. Since it allows quartzite to be converted into cristobalite (allotropic transformation). Then, cooling is done carefully and it takes about 7 days to 14 days.

Crystobalite is slowly changed into tridymite during cooling. So that a mixture of tridymite and cristobalite results in the final bricks. In final silica bricks mixture of tridymite and crystobalite is present.

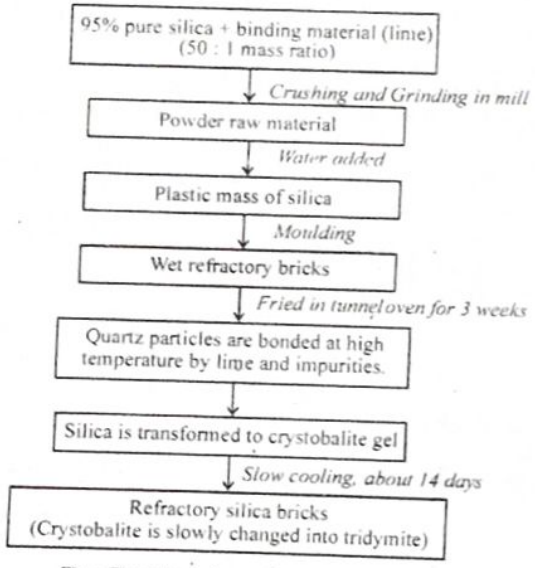


Fig. : Flow chart of manufacturing of Silica Bricks

Properties

1. **Silica Bricks** are yellowish in colour with brown specks (buff coloured). It depends upon the raw materials used for making them.
2. **Composition :** SiO_2 = 95%, Al_2O_3 = 0.75%, Fe_2O_3 = 0.5% CaO = 2%, and MgO = 0.05%
3. **Hardness :** Silica bricks are quite hard and abrasion resistant.
4. **Texture :** Silica bricks have homogenous texture free from air-voids and other moulding defects.
5. **Thermal Conductivity :** It is greater than that of fire clay bricks and is 0.0013 gm cal. per second at 200°C.
6. **Porosity :** 20-30% porosity which imparts low spalling and good thermal characteristics to silica bricks.
7. **Refractoriness :** The fusion temperature of silica refractory is about 1700° C, thus, the refractoriness is high, therefore, it can be used at an operating temperature of 1690°C.

8. **Refractoriness Under Load (RUL) or Load Bearing Strength :** It is 5 kg/cm² at 1700° C.
9. **Chemical Nature :** These are acidic in character. They are not affected by acidic furnace charges, slags etc. except HF. Silica refractories are attacked by alkalies and basic slag specially at higher temperature.
10. **Spalling Resistance :** On heating silica undergoes following allotropic changes

$$\text{Quartzite} \underset{}{\overset{870°C}{\rightleftharpoons}} \text{Tridymite} \overset{1470°C}{\rightleftharpoons} \text{Crystobalite}$$

(Sp.gr.=2.65) (Crystalline) — Sp. gr = 2.26 (α-Form of silica) — Sp. gr. = 2.32 (β-Form of silica)

Silica bricks do not contract in use, but they have a permanent expansion of about 15%, when heated again. This effect is reversible and the brick returns to its original size when cooled. This expansion is caused by reversible allotropic transformation.

Sudden changes in temperature and pressure would not convert quartzite into tridymite and crystobalite and this would cause the bricks to expand to the extent of about 17% during use in the furnace and the structure of refractory will fall, therefore, these bricks are heated and cooled very slowly.

Heating at 1500°C for about one complete day is necessary during the manufacture of silica bricks, otherwise spalling will take place.

The most important characteristics of a silica refractory are:

(i) High crushing strength
(ii) High tensile strength in hot condition
(iii) Refractoriness as high as 1690° C
(iv) High percentage of silica, but low concentration of other oxides
(v) No volume change as far as possible when used
(vi) Little or no spalling when subjected to sudden fluctuation in temperature

Uses :

Silica bricks can be used where-

(i) No shrinkage in refractory is required and
(ii) High resistance to heat is required

Silica bricks are used in lining roof arches of open hearth furnaces and reverberatory furnaces, gas retort and walls of coke ovens copper stove domes, glass furnaces etc. due to their high thermal conductivity.

Prob.22 ***What is the importance of annealing in glass making process?*** *[R.T.U. Jan. 2016]*

OR

Write short notes on annealing in glass manufacturing. *[R.T.U. 2014]*

Sol. Annealing : *Refer to Long Answer Prob.12.*

Importance of Annealing : *Refer to Short Answer Prob.3.*

Prob.23 ***Write effect of different constituents in glass. Describe the manufacturing process of glass with chemical reaction.*** *[R.T.U. Jan. 2016]*

every 1° C rise a flame is introduced for a moment with the hel of shutter. Flash point is recorded at the temperature when flash appears in the form of weaker sound and light. The procedu is continued as before until the oil vapor catches fire, which stay upto a minimum for five seconds. This is fire point of an oil.

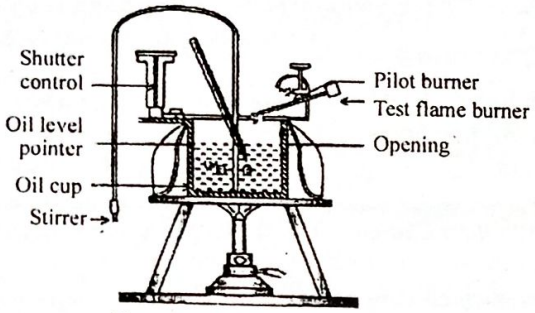


Fig. : Pensky-Marten's Apparatus

Prob.31 ***Explain Classification of lubricants.*** *[R.T.U. 201*

OR

Write note on Classification of lubricants. *[R.T.U. 201*

Sol. Classification of Lubricants

Lubricants are classified on the basis of consisten as:

1. Liquid lubricants or Lubricating oils
2. Semisolid lubricants or Greases
3. Solid lubricants

Their use in machinery depends on the workir conditions of the machinery.

1. Liquid Lubricants

Liquid lubricants are also known as lubricating o Lubricating oils reduce friction and wear between two movi metallic bodies by providing a continuous fluid film in betwe them.

A good liquid lubricant must possess:

(i) Low vapour pressure or high boiling point
(ii) Adequate viscosity for particular service conditions
(iii) Low freezing point
(iv) High oxidation resistance and heat stability
(v) Non corrosive properties
(vi) Resistance to decomposition at higher and elevat temperatures.

Liquid lubricants also act as:

(i) Cooling medium
(ii) Sealihg agent
(iii) Corrosion preventors

They are further classified as-

(A) Animal and Vegetable oils
(B) Mineral oils or Petroleum oils
(C) Blended oils
(D) Synthetic oils

2. Semi–solid Lubricant or Greases

Lubricating grease is a semi–solid lubricant obtained by combining lubricating oil with a thickening (gelling) agent (soap). Lubricating oil is the principal component and it can either petroleum oil or a synthetic hydrocarbon of low to high viscosity. The thickeners consist primarily of special soaps of **lithium, sodium, calcium, barium, aluminium** etc. Non soap thickeners include carbon black silica gel, poly urea, other synthetic polymers and bentonite clay etc. They improve heat resistance. The fibrous structure of the thickeners traps the oil and enables lubricant to cling to moving parts.

Applications

Greases have the following uses:

1. Where lubricating oil cannot remain in place due to high load, low speed, intermittent operation, sudden jerks etc. e.g. rail axle boxes.
2. Grease works at high temperatures in bearings and gears.
3. In machines used for textile, edible materials, paper etc. where dripping of oil is undesirable.
4. Greases are also used in the situations where bearing needs to be sealed against entry of dust, dirt, grit or moisture etc.

3. Solid Lubricant

Where oils and greases are either undesirable or inadequate. Then, solid lubricants are used in dry power form or mixed with water/oil, solid lubricants are preferred over oils and greases due to following reasons:

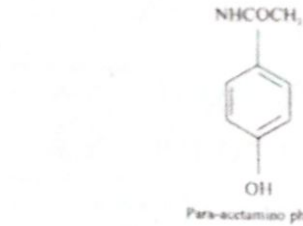
1. Where operating conditions are such that a lubricating film cannot be secured by use of oils or grease.
2. Where operating temperature or load is extremely high, such that oil or grease does not stay at desired place.
3. Where a lubricating film cannot be maintained due to their contamination by dust or grit particles, e.g. in commutator bushes of electric generators and motors.
4. Where combustible lubricants cannot be used.

An ideal solid–film lubricant should have the following characteristics:

(i) Good thermal conductivity
(ii) Low shear strength (frictional resistance)
(iii) Chemical inertness
(iv) Strong adhesion to the applied surface and
(v) Stability at operating temperatures.

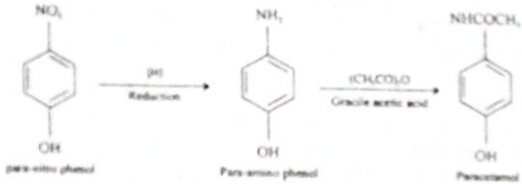
Prob.32 ***Define lubrication. Explain extreme pressure lubrication with suitable example.*** *[R.T.U. 2013, 12]*

Sol.



Para-acetamino phenol

Synthesis



Properties and uses : Paracetamols exist as white crystalline powder, sparingly soluble in water, soluble in alcohol, and very slightly soluble in methylene chloride. Paracetamols produce antipyresis by acting on the death have been observed following over dosage; hepatic damage is likely in an adult who takes more than 10g in a single dose or if a 2-year old child takes more than 3g.

II. Long Answer Type Questions

Prob.1 ***Explain substitution reaction with the help of example.***

Sol. Substitution Reactions : These reactions involve the displacement of an atom or a group by another atom or group.

$$RCH_2CH_2X + Y^- \xrightarrow{\text{Substitution Reaction}} RCH_2CH_2Y + X^-$$

Substrate — Attacking Reagent — Product — Leaving Group

It takes place at

1. sp^3 hybridised carbon (alkane, haloalkane, alcohol)
2. sp^3 hybridised carbon (benzene)

A substitution reaction can be uncleophilic, electrophilic or free radical substitution reaciton.

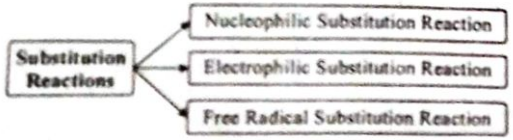


Fig. 1 : Types of Substitution Reaction

1. Nucleophilic Substitution (SN) Reactions

These reactions involves the attack of a nucleophile and are more common in aliphatic compounds. For example, hydrolysis of alkyl halides by aqueous KOH.

$$R - X + K - OH \rightarrow R - OH + KX$$

In general it may be represented as :

$$Nu: + R - X \longrightarrow R - Nu + X:^{\ominus}$$

These reactions may follow two mechanism :

(i) Unimolecular Mechanism (S_N 1)

The rate or such reactions depends only on the concentration of alkyl halide (susbstrate) and is independent of nucleophile.

$$\text{Rate} \propto [RX] \quad \ldots (1)$$

Such reactions are belived to be completed in two steps. The first step is the rate determining step (slow) in which they alkyl halide ionizeds to give carbonium ion. In the second step, the carbonium ion combines with the nucleophile to give the substituted product. This can be explained by the hydrolysis of ter-butyl bromide.

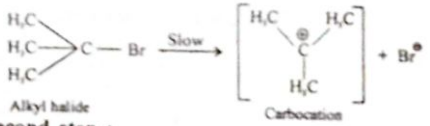
$$HO^{\ominus} + (CH_3)_3CBr \longrightarrow (CH_3)_3COH + Br^{\ominus}$$

The rate of above reaction depends only on the concentration of t-butyl bromide

$$\text{Rate} = k[(CH_3)_3C - Br] \quad \ldots(2)$$

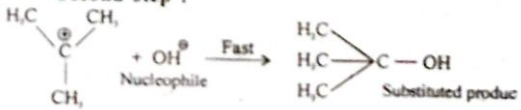
Based on the kinetics, the reaction takes place in following two steps:

First Step



Alkyl halide — Carbocation

Second step :



Nucleophile — Substituted produc

The energy profile diagram of a two step S_N1 reactior is shown in fig. (2)

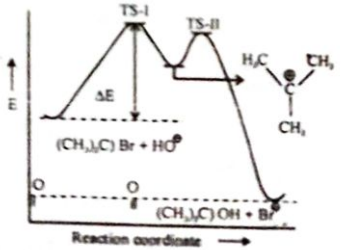


Fig. 2 : Energy Profile for an S_N1 Reaction

Solvents play very important role in S_N1 reactions as the ionization is facilitated by solvation of carbocation.

(ii) Bimolecular (S_N 2) Mechanism

The rate of such reactions depends on the concentration of alkyl halide (substrate) as well as the base (nucleophile).

$$\text{Rate} \propto [RX]\,[OH^-] \quad \ldots(3)$$

Such reactions are completed in one step. Consider the hydrolysis of methyl bromide by aqueous NaOH.

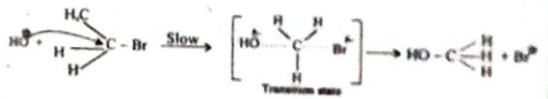
$$HO^{\ominus} + CH_3 - Br \rightarrow HO - CH_3 Br^{\ominus}$$

Kinetic studies of this reaction reveals that the rate of such a reaction depends upon the concentration of alkyl halide as well as the hydroxide ion.

$$\text{Rate} \propto [CH_3Br]\,[OH^-] \quad \ldots(4)$$

If the concentration of any of them is doubled then the rate of reaction is also doubled and when the rate or reaction of any one of them is halved, the rate of reaction is also halved.

In such a process the hydroxide ion (nucleophile) attacks the carbon atom from the side opposite to that of the bromine (leaving group). This is because of the fact that both hydroxide ion and the bromine are electron rich. So, the bond breaking and bond making are simultaneous processes and such a reaction, therefore, involve a transition state in which the carbon atom appears to be pentavalent. In transition state, carbon atom is joined to three substituents by full covalent bonds and to the nucleophile and leaving group by partial bonds. The three substituents acquire a coplanar geometry.



Transition state

The energy profile of such a reaction is shown in Fig. (3).

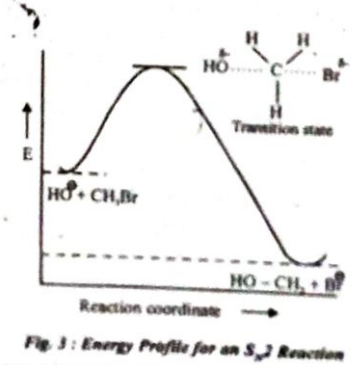
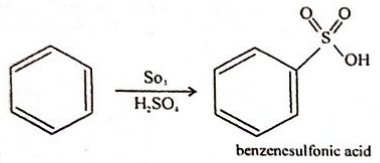


Fig. 3 : Energy Profile for an S_N2 Reaction

Prob.2 ***Give the difference between S_N1 and S_N2 reaction.***

(b) Sulphonation : In this reaction sulphur trioxide (SO_3) acts as an electrophile.



benzenesulfonic acid

(ii) Free Radical Substitution Reactions

Such reactions begin with the formation of a free radical which substitutes a group or atom present in the reactant molecule. The reaction of methane with chlorine in the presence of light is a free redical substitutiion reaction.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

The first step is initiation i.e free radical formation by homolytic cleavage of bonds. Second step is chain propagation and finally chain termination step

Initiation

Initiation step may happen spontaneously or may be induced by heat or light depending on the type of bond.

$$Cl_2 \rightarrow 2Cl\bullet$$

Chain Propagation

In this step, a molecule reacts with a free radical to generate a new radical.

$$CH_4 + Cl\bullet \rightarrow CH_3\bullet + HCl$$
$$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$$

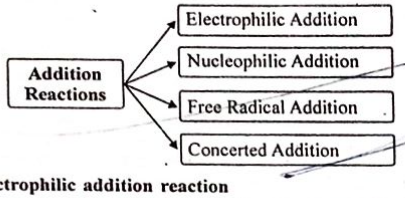
Chain Termination

This step is also known as destruction of free radicals. This step involves a combination of two like or unlike radicals to form a new bond.

$$2Cl\bullet \rightarrow Cl_2$$
$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$$
$$CH_3\bullet + CH_3\bullet \rightarrow CH_3CH_3$$

Problem *Explain addition reaction with the help of example.*

Sol. These reactions are characteristic of compounds containing multiple bonds. The alkene (=), alkynes (≡), C = O, C ≡ N react by addition to multiple bond. Thus in addition reaction there is increase in the number of groups attached to the substrate and decrease in its unsaturation. Addition reactions are of four type namely electrophilic, nucleophilic, free radical and concerted. The first three are the two-step processes, with initial attack by electrophile, nucleophile or a free radical. The second step consists of a combination of the resulting intermediate with a negative species, a positive species or a neutral entity. In addition, attack at the two carbon atoms of the double or triple bond is simultaneous.



1. Electrophilic addition reaction

These reactions are brought about by the attack of electrophiles and are generally given by compounds containing carbon-carbon double and triple bonds. For example addition of HBr to propene. This reaction takes place in following steps :

Step 1 : H^+ from HBr is added to propene to form a π-complex, which then forms isopropyl carbocation (2°-carbocation, which is more stable than 1°-carbocation).

$$\underset{\text{Propene}}{CH_3-CH=CH_2} \rightarrow CH_3-CH=CH_2 \rightarrow CH_3-\overset{\oplus}{C}H-CH_2 + Br^{\ominus}$$

$\overset{\delta+}{H}-\overset{\delta-}{Br}$ (π-Complex); $\overset{\oplus}{C}H-CH_2-H$ (Isopropyl carbocation)

Step 2 : The bromide ion (nucleophile) combines with the carbocation to give isopropyl bromide.

$$\underset{\text{Propene}}{CH_3-\overset{\oplus}{C}H-CH_3} + Br^{\ominus} \rightarrow \underset{\text{Isopropyl bromide}}{CH_3-\underset{Br}{CH}-CH_3}$$

The product formed in above reaction follows Marknownikoff's Rule, according to which the negative part of the addendum is added to that doubly bonded carbon atom which bears the minimum number of hydrogens.

In the above case during first step : two carbocations may be formed giving two different products in following manner.

$$CH_3-CH=CH_2 + H^{\oplus} \longrightarrow \underset{\text{2°-Carbocation}}{CH_3-\overset{\oplus}{C}H-CH_3} \xrightarrow{Br^{\ominus}} \underset{\text{2-Bromopropane}}{CH_3-\underset{Br}{CH}-CH_3}$$

$$CH_3-CH_2-\overset{\oplus}{C}H_2 \xrightarrow{Br^{\ominus}} \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2Br}$$

(1° Carbocation)

The major product of the reaction is 2-bromopropane as the secondary carbocation formed is more stable than primary carbocation forming 1-bromopropane. Thus, Markownikoff's rule is obeyed.

Anti-Markownikoff's Addition or Peroxide Effect : According to this effect, the addition of HBr to propene in presence of peroxides gives 1-bromopropane as major product rather than 2-bromopropane.

$$\underset{\text{(Not formed)}}{CH_3-\underset{Br}{CH}-CH_3} \xleftarrow[\text{Peroxide}]{HBr} \underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\text{Peroxide}]{HBr} \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br}$$

This is because in the presence of peroxides the addition involves free radical mechanism. This effect was put forth by Kharasch and Mayo, so it is also called Kharasch effect.

2. Radical Addition Reactions

The addition reactions of alkenes catalyzed by small amount of peroxides or irradiated by ultraviolet light are nearly always free radical chain reactions and often lead to the formation of polymetric products. These reactions are illustrated by some examples.

Addition of HBr to Olefins : This is most famous 'abnormal' addition to alkenes and the entire mechanism consists of chain initiation, propagation and finally termination.

Chain Initiation : It starts with light or by thermal decomposition of initiators such as peroxides. The peroxides present in most olefin samples due to autoxidation, are sufficient to initiate the chain. In fact, olefins must be carefully purified to suppress the radical processes.

$$\underset{\text{Dibenzoyl peroxide}}{C_6H_5-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5} \xrightarrow{\Delta,\ 60-80°C} \underset{\text{Dibenzoyl oxy radical}}{2C_6H_5CO_2}$$

$$C_6H_5CO_2 + HBr \longrightarrow C_6H_5COOH + Br^{\bullet}$$

Chain Propagation : With propylene the chain propagating steps are as follows :

$$Br^{\bullet} + CH_2=CH-CH_3 \longrightarrow Br-CH_2-\dot{C}H-CH_3 + \underset{\text{exothermic}}{9\ kcal/mol}$$

$$Br-CH_2-\dot{C}H-CH_3 + HBr \longrightarrow BrCH_2-CH_2-CH_3 + Br^{\bullet} + \underset{\text{exothermic}}{7\ kcal/mol}$$

Thus, the overall result is 'anti-Markownikoff, addition, i.e. reverse of the normal addition to the olefin. The bromine adds to the less hindered end of the bond and forms a more stable radical. Therefore, we find that with the decomposition of a single initiator molecule, a large number of molecules of the product are formed.

This abnormal addition of bromine is a good method of preparing primary bromides from terminal olefins.

Chain Termination : Chain termination occurs by combination with bromine atoms, or with alkyl radicals or by coupling or disproportionation of alkyl radicals.

$$2Br^{\bullet} \longrightarrow Br_2$$

$$Br-CH_2-\dot{C}H-CH_3 + Br^{\bullet} \longrightarrow Br-CH_2-\underset{Br}{CH}-CH_3$$

$$2Br-CH_2-\dot{C}H-CH_3 \longrightarrow Br-CH_2-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2-Br$$

It is interesting to note that in presence of polar solvents or in presence of inhibitors like thiophenol or hydroquinone. the above addition becomes a heterolytic process. It is homolytic in conditions in which it is described. So we can say that homolytic addition is the result of peroxide effect and distinguishes it from ionic reactions.

We can explain the anology in orientation in the same manner as we explain orientation in heterolytic addition. In heterolytic addition, just as the secondary carbocation $CH_3-\overset{\oplus}{C}HR$ is more stable than primary $\overset{\oplus}{C}H_2-CH_2R$, so is the secondary radical CH_2Br-CR is assumed to be more stable than the primary radical $\bullet CH_2-CHR-Br$. Therefore, the basic difference is not that in one, the process is heterolytic and in the other it is homolytic, but in one case the addition begins with the formation of a new C–H bond whereas in the other it is the C–Br bond, which is formed first. However, if somehow the reaction conditions could be so altered that the initial attack at the double bond were by a H radical, than Markownikoff's type of addition would be expected.

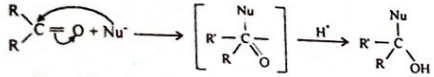
Having read the mechanism of addition of HBr to olefins in presence of peroxides, it is pertinent to ask if HCl of HI also combine by radical addition? In this connection it has to be noted that HCl or HI do not undergo abnormal addition to olefins under normal conditions. The reasons for failure are different for the two compounds. The H-Cl bond is too strong to be broken readily in the atom abstraction reaction. The hydrogen iodide bond breaks up easily to give atoms but these do not add rapidly to double bonds.

$$R^{\bullet} + HI \xrightarrow{Fast} RH + I^{\bullet}$$

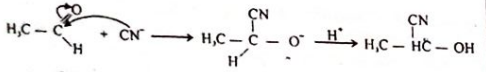
$$I^{\bullet} + >C=C< \xrightarrow{Slow} I-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}^{\bullet}$$

3. Nucleophilic Additions

The carbonyl group of aldehydes and ketones facilitates addition reactions by both nucleophilic as well as electrophilic pathways. The electron deficient carbonyl carbon atom can react with nucleophiles while the electron rich carbonyl oxygen can react with electrophiles. The typical reaction of aldehydes and ketones is nucleophilic addition involving a base can be represented in general as



One of the simplest addition reactions to the carbonyl group is the cyanohydrin reaction. Cyanide ion adds to the carbonyl carbon atom to give an unstable intermediate oxyanion (alkoxide). The alkoxide being a strong base then abstracts a proton from the solvent or another molecule of the weak acid HCN to form the cyanohydrin.



Other examples of nucleophilic additions include the addition of acids (HCl), alcohols to hemiacetals or hemiketals, addition of Grignard reagents, addition of organozinc compounds (Reformatsky reaction), etc. An interesting example is the aldol condensation.

Prob.5 ***What is Elimination Reaction? Explain its reaction mechanism with an example.***

Sol. These reactions are reverse of addition reaction and involve the loss of atoms or groups from the same molecule to form multiple linkage. On the basis of mechanism, elimination reactions may be of two types.

1. α-Elimination : This type of elimination is very rare and involves elimination of two groups or atoms from the same carbon atom. For example,

$$\underset{\text{Chloroform}}{CHCl_3} \longrightarrow \underset{\text{Dichlorocarbene}}{:CCl_2} + HCl$$

2. β-Elimination : It involves the removal of two groups or atoms from the two adjacent (α and β) carbon atoms of the molecule. For example,

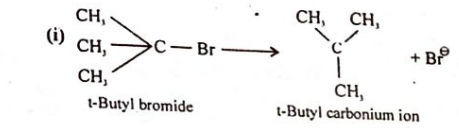
$$>\overset{\beta}{C}-\overset{\alpha}{C}< \longrightarrow >C=C< + HX$$

$$CH_3-CHBr-CH_3 \xrightarrow{\text{alc. KOH}} CH_3-CH=CH_2 + HBr$$

These reactions proceed via unimolecular (E_1) or bimolecular (E_2) mechanism.

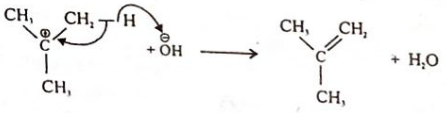
1. Unimolecular (E_1) mechanism

When the rate of an elimination reaction depends only on the concentration of the substrate. Like S_N1 reactions these also occur in two steps. For example, dehydrohalogenation of T-alkyl halides. The first step involves the ionisation of alkyl halide to give carbonium ion (slow) and the second step involves that fast abstraction of a proton by the base adjacent to β-carbon leading to the formation of alkene.



t-Butyl bromide — t-Butyl carbonium ion

(ii)



2-Methyl propene

When there is a possibility of formation of two types of alkenes, then the main product is most highly substituted alkene as per Saytzeff rule. For example

$$\underset{\text{Br}}{CH_3-CH_2-CH-CH_3} \xrightarrow[\text{KOH}]{\text{Alc}} \underset{\text{2-Butene (80\%)}}{CH_3CH=CHCH_3} + \underset{\text{1-Butene (20\%)}}{CH_3CH_2CH=CH_2}$$

The other common example of E_1 reaction is dehydration of alcohols, Which occurs as :

(i) $CH_3-CH_2-OH \xrightarrow{H^+} CH_3-\overset{\oplus}{C}H_2-H_2O$

(ii) $CH_3-\overset{\oplus}{C}H_2 \longrightarrow CH_2=CH_2 + H^{\oplus}$

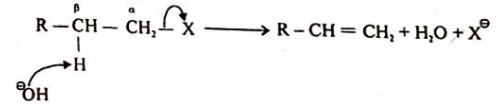
2. Bimolecular (E_2) Mechanism

When the rate of an elimination reaction is dependent both upon the concentration of substrate as well as the attacking reagent, the reaction is of second order and is represented by E_2. For example, reaction of alkyl halide with alc. KOH.

$$CH_3-CH_2-Br + KOH \xrightarrow[\text{(alc)}]{} CH_2=CH_2 + H_2O + KBr$$

Rate = k [CH_3CH_2Br] [KOH] ...(1)

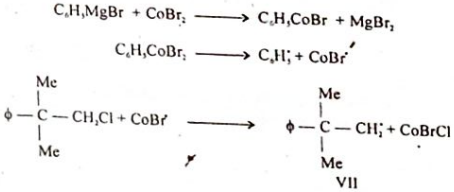
The mechanism is a one step process in which the abstraction of the proton from the β-carbon and the expulsion of the leaving group, i.e., halide ion from the α-carbon atom occur simultaneously.



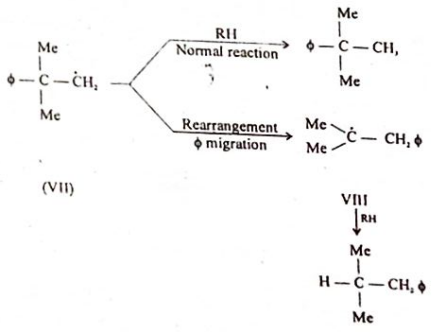
This is also known as dehydro halogenation reaction.

Prob.6 ***What is free radicals? How they are formed.***

Sol. Free radicals, compared to many other electron deficient species, show less tendency to undergo rearrangements. The largest number of radical rearrangements known are those in which an aryl group migrates to an adjacent position. However, no example of a hydrogen or alkyl shift in a monoradical has been reported. The first case of a phenyl migration scheme was observed in 1944 by Urry and Kharasch. Treatment of 1-chloro-2-methyl-2-phenylpropane with phenylmagnesium bromide, in the presence of cabaltous bromide, afforded a mixture of products. The following radical mechanism was proposed to rationalize the products. The neopentyl radical (VII) may abstract a hydrogen atom to give the normal product:

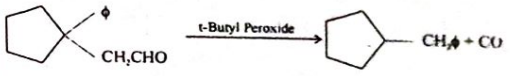


VII



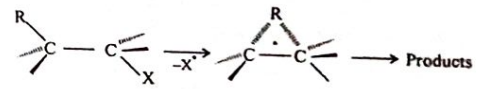
(VII) VIII

t-butylbenzene, or it may also rearrange to a more stable tertiary radical (VIII) which then forms isobutylbenzene. Both the radicals, (VII) and (VIII), dimerize and are disproportionate in their yields. This sequence of steps was confirmed by sub sequent workers who generated the radicals by different methods and observed exclusive migration of the phenyl group. In cycle compounds, equation (1)

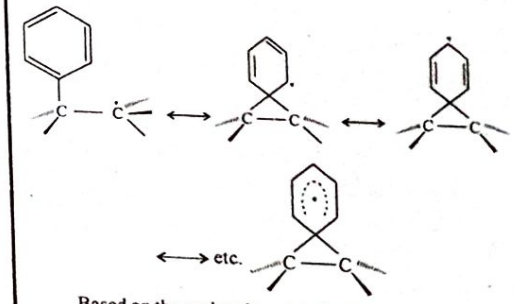


...(1)

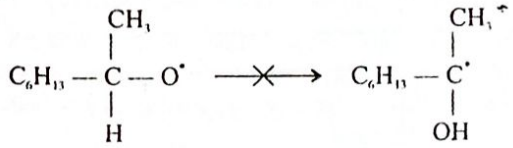
of the migration of a phenyl group was reported by Wild and Philip. The mechanism of radical rearrangements has not been investigated in detail but the intramolecular 1, 2-shift, in general, may be described. This assumes the formation of a triangular non-classical radical (IX) which presumably provides a path of lower activation energy compared to the dissociation and coupling processes. Moreover, for aryl migration additional resonance structures are available for the delocalization of the odd electron, as shown, and thus stabilization is possible an in (X).



(IX)



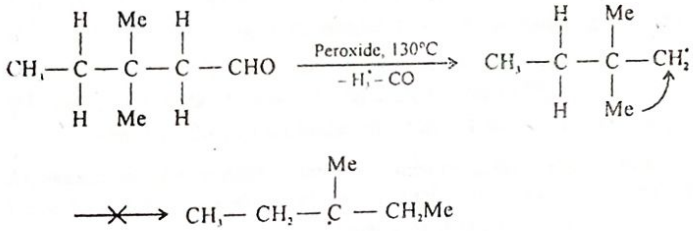
Based on the molecular orbital treatment of Huckelx, it has been argued that the transition state (IX) is less stable than either the initial or the rearranged product when R is hydrogen or an alkyl group. This implies that there is no reason to expect 1,2-alkyl or hydrogen shifts in radical reactions though they are well known in the corresponding carbocations. No unambiguous case of an alkyl or hydrogen migration is yet known in simple radicals. Kornblum and coworkers pyrolyzed optically active 2-octyl nitrite and obtained an optically active octanol. They concluded that the radical (XI) does not undergo a 1, 2 hydrogen shift to carbon to give XI (a) but, rather, abstracts a hydrogen atom from the solvent to yield actanol. Brown and Russel found similar negative



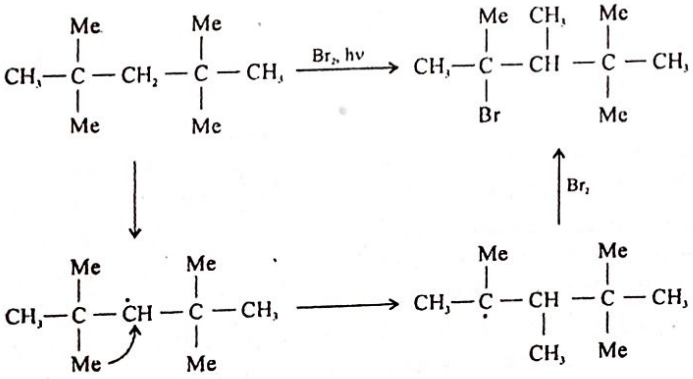
(XI)

evidence of hydrogen migration in the photochlorination of isobutane because the isobutyl radical did not rearrange to the t-butyl radical. Similar results by other workers have demonstrated that such rearrangements are unlikely. Considerations of orbital symmetry do not apply to reactions proceeding through bridged intermediates. Thus intermediates of the above type are possible.

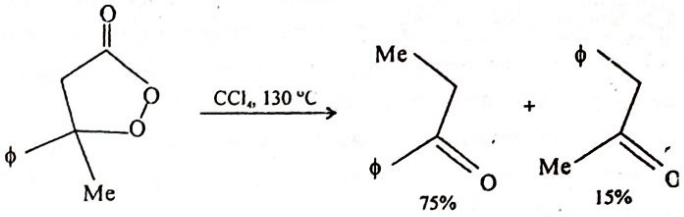
The migration of an alkyl group in carbocations is frequencly observed, but the free radicals show no tendency to rearrange. Seubald observed no rearrangement of 2,2-dimethylpentanal to t-amyl radical on decarbonylation in the liquid phase.



Kharasch and cowrkers brominated 2,2,4,4-tetramethylpentane under u.v. light in the gaseous phase and obtained a rearranged product, 2-bromo 2,3,4,4-tetramethylpentane. The bromo derivative was identified by treatment with silver nitrate which yielded 2,3,4,4-tetramethylpentane.



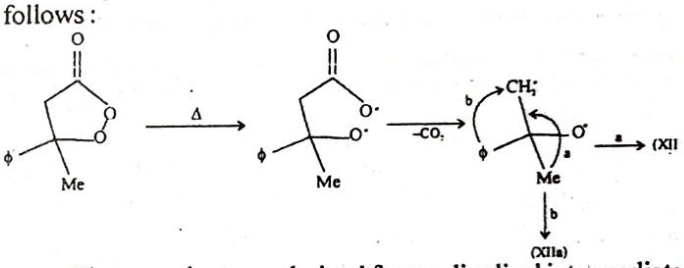
These authors postulated the formation of the original product as the result of the initially formed secondary to the rearranged tertiary radical by a 1, 2-shift. The validity of this interpretation was questioned later and it was suggested that the rearrangement actually took place on reaction of the rearranged bromide with silver nitrate. Nevertheless, recently, several reactions have been reported in which the alkyl group



(XII) (XIIa)

migration has been observed to be even faster than that of the phenyl group. Green and coworkers, for instance, among others, isolated two major products (XII) and XIIa) in the decarbonylation of β-methyl-β-phenyl-β-peroxypropiolactone.

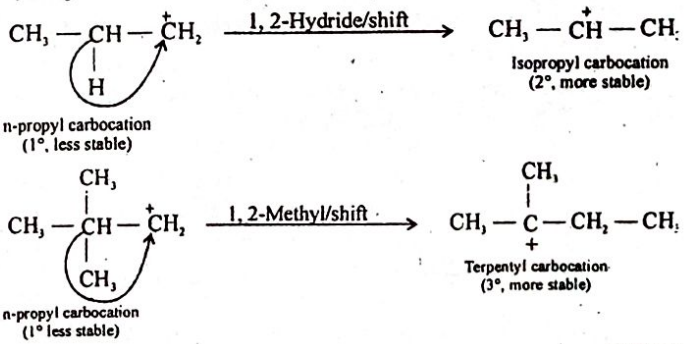
A possible mechanism for this may be postulated as follows :



These products are derived from a diradical intermediate and the yield of (XII) via methyl migration (path a) is almost five times more than that obtained from phenyl migration (path b). The formation of these products can, however, be explained alternatively by a two-step rather than an intramolecular rearrangement. According to the latter pathway, the migrating group may fragment and then recombine in the cage to form the product. Though alkyl migrations have been suggested to take place at high temperatures, the complexity and low yields of the products obtained in such cases a re still ambiguous.

Prob.7 *Write short note on Rearrangement of Carbocations.*

Sol. Carbocations are prone to rearrangements. During these rearrangements, less stable (1° or 2°) carbocations are converted into more stable (2° or 3°) carbocations either by 1, 2-hydride shift or by 1, 2-methyl shift. For example :



□□□