MUMBAI UNIVERSITY PAPER SOLUTION

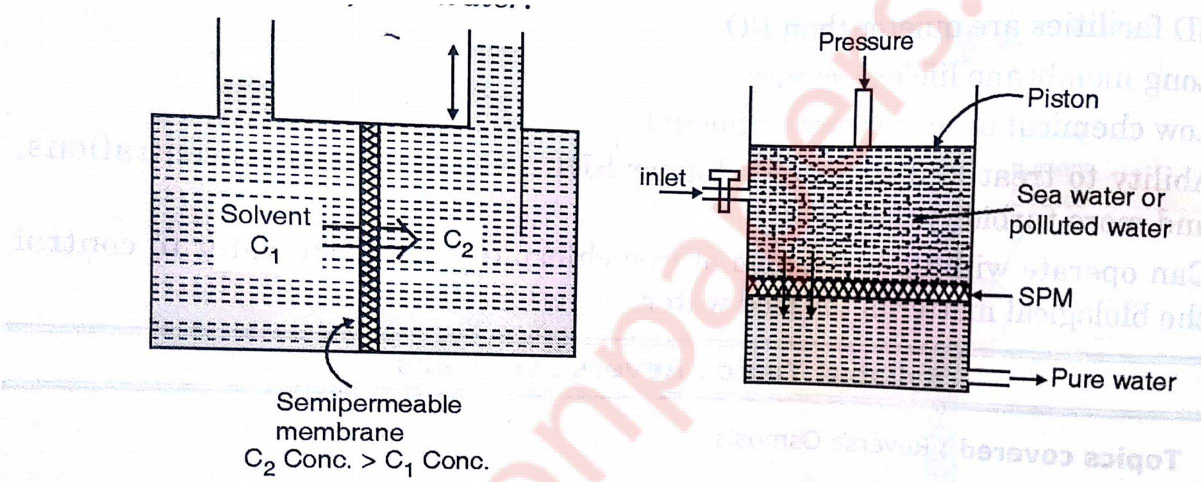
APPLIED CHEMISTRY I MAY 2019

Q1)(a) Write a brief note on Reverse Osmosis . **(3M)**

Ans : 1. When two solution of unequal concentration are separated by semipermeable membrane, flow of solvent takes place from dilute to concentrated section due to osmosis.

2. If hydrostatic pressure, which is slightly higher than the osmotic pressure is applied on the concentrated section of solution, the flow of solvent reverses, i.e. solvent moves from high concentration to low concentration across the membrane. This is known as Reverse Osmosis (RO).

3. In RO, pure solvent (water) is separated from its contaminants.



4. In one section, pressure of 15-40 kg is applied to seawater/impure water so that pure water is forced through semi permeable membrane, leaving behind dissolved solids.

5. This process is used for getting water for high pressure boilers.

6. The advantage of reverse osmosis process is that it removes ionic, non-ionic, colloidal, high molecular weight organic matter. It also removes colloidal silica which is not removed by filtration.

Q1)(b) Write methods of preparation, properties and uses of polyurethane rubber . **(3M)**

Ans: Preparation:

Properties :

1. Polyurethane rubber has high resistance to oxidation because of saturated character.

2. Good resistance to many organic solvents.

3. It gets attacked by acids and alkalies (hot and concentrated).

4. Polyurethane is light, tough, resistant to heat, abrasion chemicals, weather, etc.

Uses :

1. For manufacture of foams, spandex fibres.

2. For surface coatings.

3. For shoe soles.

Q1)(c) Define and discuss giving significance of the following (3M)

(i) Viscosity (ii) Cloud Point

Ans : i) Viscosity

Viscosity is defined as the property by virtue of which a liquid or fluid (oil) offers resistance to its own flow.

Significance of Viscosity :

1. A lubricating oil selected for a job should have viscosity as high as possible.

2. It helps in achieving desired results to control wear and tear of machine parts.

3. It also helps to decide about the addition of blending agents to improve the property of lubricating oil.

ii) Cloud Point :

Cloud point is defined as the temperature at which the oil becomes cloudy or hazy in appearance.

Significance of cloud point :

1. It helps us to know the lowest temperature upto which the oil can be suitable as a liquid lubricant.

2. The lubricating oils used in machines working at low temperatures should have lower cloud point than the working temperature.

3. Knowledge of this can help the machines to be prevented from getting jammed in places from cold region or during winter season in some areas in India.

Q1)(d) Write advantages and drawbacks of Phase Rule . (3M)

Ans : Advantages of phase rule :

1. It applies to physical as well as chemical phase reaction.

2. It provides a convenient basis for classification of equilibrium states of systems with the help of phases, components and degree of freedom.

3. It applies to microscopic systems.

4. It indicates that different systems having the same degrees of freedom behave in a similar fashion.

5. It helps in predicting the behaviour of a system under different conditions of the governing variables.

6. It helps in deciding whether the given number of substances together would exist in equilibrium under a given set of conditions or whether some of them will have to be inter converted or eliminated.

7. Phase rule does not take any cognizance of the nature of the amounts of substances present in the system.

Disadvantages of phase rule :

1. Phase rule can be applied for systems in equilibrium only.

2. It is not of much help in case of systems which attain the equilibrium state very slowly.

3. It applies to a single equilibrium state. It does not indicate the other possible equilibria in the system.

4. Phase rule considers only the number of phases but not their quantities.

5. All the phases of the system must be present under the same conditions of temperature, pressure and gravitational forces.

6. The solid, liquid phases should not be so finely sub-divided as to bring about deviation from their normal values of vapour pressure.

Q1)(e) A hard water sample contains following impurities (in mg/L) **(3M)**

$Mg(HCO_3)_2$ = 150 ; NaCl = 77 ; $CaCl_2$ = 150 ; $MgSO_4$ = 85 .

Calculate temporary, permanent and total hardness of the given sample of water.

Ans :

Salt	Concentration	Multiplication Factor	$CaCO_3$ Equivalents	Hardness
$Mg(HCO_3)_2$	150	$150 \text{ X } \frac{100}{146} =$ 102.73	102.73	Temporary
NaCl	77	-	-	Doesn't impart hardness
$CaCl_2$	150	-	-	Doesn't impart hardness
$MgSO_4$	85	$85 \text{ X } \frac{100}{120} =$ 70.83	70.83	Permanent

Temporary Hardness = 102.73 ppm.

Permanent Hardness = 70.83 ppm.

Total Hardness = 173.56 ppm.

Q1)(f) Discuss the effect of temperature on polymers . **(3M)**

Ans :

1. The hard and brittle state is the glassy state and soft-flexible state is the viscoelastic state. If the viscoelastic state of polymer is heated further, the polymer becomes a viscous liquid and can flow. This state is known as viscofluid state.
2. Below T_g the molecules in polymer do not move apart and do not have movements within the molecular chains. Therefore stress transfer property is lost and polymer below T_g is brittle.
3. Above the T_g , the chain segments within the long molecules move locally like a person moving his hands, legs, leaning forward-backward but standing at one place, during exercise. Thus the polymers in the viscoelastic state have flexibility or stress transfer property.
4. Above the temperature T_m ; the kinetic energy of the polymer molecules is high enough to cause movement within the chain segments as well to move from one position to another. Therefore this state has flow character like liquids .
5. Some polymers have thermal degradation at and above T_m .

Polymer	T_g °C	T_M °C
Polyethylene	-125	115
Polypropylene	-18	175
Polystyrene	100	240
Polyvinyl chloride	80	212
Polyacrylonitrile	97	241

Q1)(g) Why gypsum is added during manufacturing of the cement? **(3M)**

Ans : 1) When water is added to cement, tricalcium aluminate (C_3A) starts setting first.

2) C_3A combines with water very rapidly with evolution of large amount of heat.

$$C_3A + 6H_2O \rightarrow C_3A.\ 6H_2O + \Delta\ .$$

3) If gypsum is added to cement, it doesn't set very quickly by forming insoluble tricalcium sulphoaluminate ($3CaO.Al_2O_3.xCaSO_4.7H_2O$).

4) Thus it acts as retarding agent for early setting of cement.

$$3CaO.Al_2O_3 + xCaSO_4.7H_2O \rightarrow 3CaO.Al_2O_3.xCaSO_4.7H_2O$$

C_3A Gypsum Tricalcium Sulphoaluminate (Insoluble)

This reaction prevents high concentration of alumina and is retarding initial set of cement.

Q2)(a) A hard water sample has following composition **(6M)**

CaSO4 = 170 mg/L ; Ca(HCO3)2 = 130 mg/L ; Mg(HCO3)2 = 95 mg/L ; HCl = 58 mg/L ; KNO3 =75 mg/ L

Calculate lime (90% pure) and soda (95% pure) required for complete softening of one million litres of above hard water sample .

Ans :

Salt / Impurity	Quantity	Multiplication Factor	$CaCO_3$ Equivalents	Requirement of Lime or Soda
$CaSO_4$	170	$\frac{100}{136}$	125	S (Permanent)
$Ca(HCO_3)_2$	130	$\frac{100}{162}$	80.24	L (Temporary)
$Mg(HCO_3)_2$	95	$\frac{100}{146}$	65.07	2L (Temporary)
HCl	58	$\frac{100}{136}$	42.64	L+S
KNO_3	-	-	-	-

Lime Requirement = $\frac{74}{100}$ [Temporary Ca^{2+} + 2 X Temporary Mg^{2+} + H^+] X $\frac{Volume\ of\ water}{1000000}$ X 100/%purity

$$= \frac{74}{100}[80.24+2X65.07+42.64] \text{ X } \frac{1000000}{1000000} \text{ X } \frac{100}{90}$$

= 208.04 kg .

Soda Requirement = $\frac{106}{100}$ [Permanent Ca^{2+}+H^+] X $\frac{Volume\ of\ water}{1000000}$ X $\frac{100}{\%\ of\ purity}$ kg

Soda Requirement = $\frac{106}{100}$ [125+42.64] x $\frac{1000000}{1000000}$ x $\frac{100}{95}$ kg .

Soda Requirement = 187.05 kg .

Ans : Soda requirement of the water sample is 208.04 kg and lime requirement is 187.05 kg.

Q2)(b)(i) What is glass transition temperature ? **(3M)**

Ans:

1)There is a temperature boundary for almost all amorphous polymers and many crystalline polymers, only above which the substance remains soft, flexible, rubbery and below which it becomes hard, brittle and glassy.

Eg. An ordinary rubber ball if cooled below -70°C becomes so hard and brittle that it will break into pieces like a glass ball falling on a hard surface.

2)The temperature below which a polymer is hard, brittle and glassy and above which it is soft and flexible is called as 'Glass Transition Temperature'(Tg).

3)A polymer is not preferred to be used at temperatures below its glass transition temperature since it becomes hard, stiff and brittle.

4)A polymer material should have much lower Tg than the operating temperature.

Eg. polymers to be used for refrigerators, air conditioners or used in cold countries should have lower Tg, so that they do not break during use.

5)At glass transition temperature, the internal energy of the polymer increases to that extent where chain segments of a polymer molecule just start leaving their lattice sites.

(ii) What are semi solid lubricants? Under which conditions they are used? (2M)

Ans :

1) Semisolid lubricant consists of an emulsion of soap with mineral/vegetable oil , with or without addition .It consists of soap dispersed throughout liquid lubricating oil .
2) The semisolid lubricants are used under working conditions such as ,
   i) Low speed and high pressure, and high temperature (upto 80 ℃) .
   ii) Machineries used in textile mills, paper and food product manufacturing, etc. where spilling and spurting of lubricant is harmful to the product .
   iii) Machines where liquid lubricant cannot be maintained in position due to intermittent operations of machine parts such as shaft , etc .
   iv) In places where the bearing has to be sealed against entry of dirt, water , dust and grit .

Q2)(c)Explain briefly Carbon nanotubes by CVD method . (4M)

Ans :

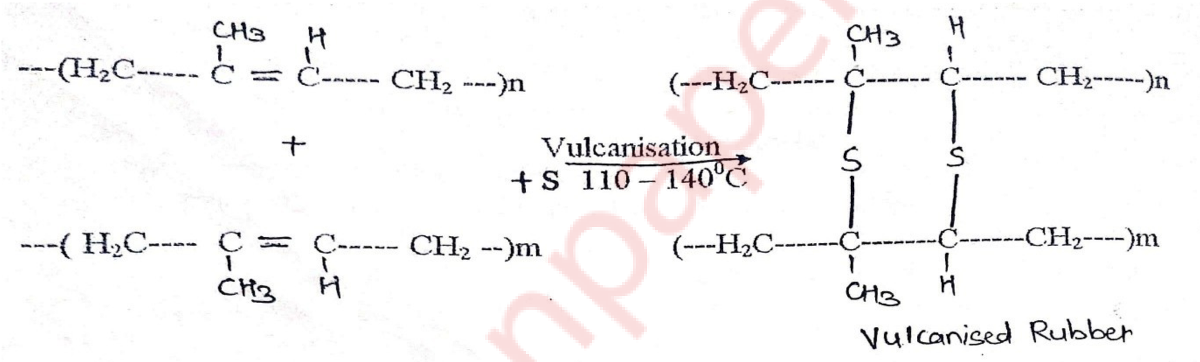
1. It is a method of preparation of mostly single walled nanotube .
2. It is obtained by chemical vapour of hydrocarbon over metal catalyst (such as Co, Fe) supported on silica or zeolite.
3. The carbon deposition activity depends upon
   i) Co content of the catalyst
   ii) pH in catalyst preparation
4. Ethylene/methane is used in reaction with temperature of 545 ˚C .For nickel-catalysed CVD and 900 ℃ for an uncatalyzed process to give single walled nanotube. Resultant carbon tubes have open ends. It is used to obtain nanotube chips containing isolated single walled nanotubes at controlled locations .
5. High yields of single walled nano tubes have been obtained by catalytic decomposition of H_2/ CH_4 mixture over well dispersed metal particles such as Co, Ni or Fe on MgO at 1000 ℃ .
6. Fullerenes and bundles of single walled nanotubes are obtained on carbonyl zeolite catalysts.

7. Method is established for last 20 years and has been in use for producing various carbon materials such as carbon fibres, filaments, etc .

Q3)(a) What is natural rubber? What is vulcanization of rubber? Compare the properties of vulcanized rubber over natural rubber . (6M)

Ans :

1) Natural rubber is a high polymer which has elastic properties and can be stretched to 4-10 times of its original length and as soon as stretching force is removed, it returns to its original length.
2) Natural rubber is obtained from soaps of range of rubber plants like Havea Brasillians. The rubber latex is obtained by making in cis ions in the bark of rubber trees and allowing the soaps to flow into small vessels. Tapping is done at intervals of 6 months.
3) Latex is diluted to contain between 15-20% of rubber and filtered to remove any dirt present in it.Then it is treated with acetic/formic acid where rubber is coagulated .



Vulcanization of rubber :To improve properties of rubber, it is compounded with substances like sulphur,H_2S, benzoyl chloride, etc .Generally, vulcanization is done by heating low rubber with sulphur to 110-140 ℃ .The added sulphur combines chemically at double bonds forming cross-linked structure which gives stiffness to rubber molecule .

Properties of vulcanized rubber over natural rubber :

1) It has good tensile strength and extensibility when tensile force is applied.
2) It possesses low water absorption tendency .
3) It has higher resistance to oxidation and to abrasion.
4) It has much higher resistance to wear and tear.
5) It is a better electrical insulator.
6) It is resistant to organic solvent, fats and oils.
7) It is easy to manipulate the vulcanized rubber to produce the desired shapes.
8) It's useful temperature range is 40-150 ℃.
9) It's tackiness is only slight.

Q3)(b)(i) What is 'Triple Point'? Write the condition for which triple point exists for water system. (3M)

Ans:

1) The point where all the three curves ,i.e. Vapour Pressure Curve, Sublimation Curve and Fusion Curve meet is called as the 'Triple Point' .At triple point 'O' , all the three phases solid, liquid and vapour are simultaneously in equilibrium .
2) This triple point occurs at 0.0075 ˚C and 4.58 mm Hg pressure. Since there are three phases and one component, therefore
   F = C - P + 2
   F = 1 - 3 + 2
   F = 0 .
3) The system at triple point is zero variant or nonvariant. Thus, neither pressure nor temperature can be altered .

(ii) What are Fullerenes? Write important properties and uses of Fullerene. (2M)

Ans :

1. Fullerenes are hollow, pure carbon molecules in which carbon atoms lie at the vertices of a polyhedron with 12 pentagonal faces and any number of hexagonal faces .
2. Each carbon is bound to other three carbons in a pseudo-spherical arrangement consisting of alternating pentagonal and hexagonal rings, in the manner of a soccer ball .

Properties of Fullerenes :

i) All atoms lie on surface of sphere symmetrically as seen in truncated icosahedrons .
ii) With changes in temperature, fullerene shows variation in behaviour and structure .
iii) Fullerene 60 resembles to an electrophile in chemical reactions.
iv) Fullerene exhibits ferromagnetism and can be methylated, hydrogenated, ammoniated and fluorinated .

Uses of Fullerenes :

a) Fullerenes are used in synthetic, pharmaceuticals and industrial applications, as inhibitor of HIV protease .
b) They can be useful in light emitting diodes (LED), molecular electronics and computing, as lubricants, rocket fuel, etc .

Q3)(c) In the process of determination of hardness, a standard hard water sample was prepared by dissolving 2.5g $CaCO_3$ and making solution upto one litre.

50 ml of above hard water required 45 ml of EDTA. 50 ml of unknown hard water sample was titrated it required 30 ml of same EDTA. The unknown hard water sample was boiled and filtered. 50 ml of this boiled sample required 20 ml of EDTA. Calculate hardness of all types of unknown hard water sample. (4M)

Solution:

Given data: Concentration of SHW = 1g/lit

Quantity of SHW (1 g/lit) = 50 ml

Quantity of EDTA consumed by 50 ml SHW = 45 ml

Quantity of hard water sample = 50 ml

Quantity of EDTA consumed = 30 ml

Quantity of EDTA consumed after boiling = 20 ml

Hardness = ?

Standardization of EDTA:

Standard hardwater has 1g I.e. 1 X 1000 = 1000 mg of $CaCO_3$ equivalent hardness per litre

= 1000 mg/lit

= 1000/1000 = 1 mg/ml $CaCO_3$ equivalent hardness

50 ml SHW = 50 X 1 mg $CaCO_3$ = 50 mg $CaCO_3$

45 ∴ ml SHW = 50 ml SHW = 50 mg $CaCO_3$

1 ml EDTA = 50/45 = 1.11 mg of $CaCO_3$ equivalent hardness

Calculation of total hardness:

50 ml Hard water sample = 30 ml EDTA = 30 X 1.11 mgs of $CaCO_3$ per 50 ml

= 33.3 mgs of $CaCO_3$

∴Total Hardness per litre = 666 mgs of $CaCO_3$

Calculation of permanent hardness:

50 ml boiled water = 20 ml of EDTA = 20 X 1.11 mgs of $CaCO_3$ in 100 ml

= 22.2 mgs of $CaCO_3$

∴ per litre = 444 mgs of $CaCO_3$

$H_{Temporary} = H_{Total} – H_{permanant}$ =666 – 444 = 222 mgs of $CaCO_3$

Total Hardness = 666 ppm

Permanent Hardness = 222 ppm

Temporary Hardness = 444 ppm

Q4)(a) Draw a neat labelled diagram and explain zeolite process of softening of hard water. Discuss its merits and demerits. **(6M)**

Ans :

1) The zeolite, i.e. the boiling stone, is a group of naturally occurring minerals which release their water of hydration in the form of steam. Eg Na-zeolite $Na_2O.Al_2O_3.xSiO_2.yH_2O$
X = 2-10 , Y = 2-6
2) Thus zeolite is hydrated sodium aluminosilicate, capable of exchanging their sodium ions for the hardness producing ions in water.
3) Zeolites are of two types :
   i) Natural Zeolites : These are non-porous. These are derived from green sands by washing, heating and treating with caustic soda. Eg Natrolite .
   ii) Synthetic Zeolites : These are porous and gel structures .It is prepared by heating together china clay ,feldspar and soda ash, following by cooling and granulating the resultant mass or prepared by heating solutions of Na-silicate, $Al_2(SO_4)_3$ and $NaAlO_2$.These have higher exchange capacity but less durable.
4) If water containing Ca^{2+}, Mg^{2+} ions are passed over zeolite bed, Ca^{2+}, Mg^{2+} are exchanged for sodium as
   a) $CaCl_2 + Na_2Ze \rightarrow CaZe + 2NaCl$
   b) $MgSO_4 + Na_2Ze \rightarrow MgZe + Na_2SO_4$

   Here Na – Zeolite is converted into Ca^{2+} and Mg^{2+} Zeolites whereas water becomes free from $Ca^{2+}$and Mg^{2+} but richer in sodium salts.

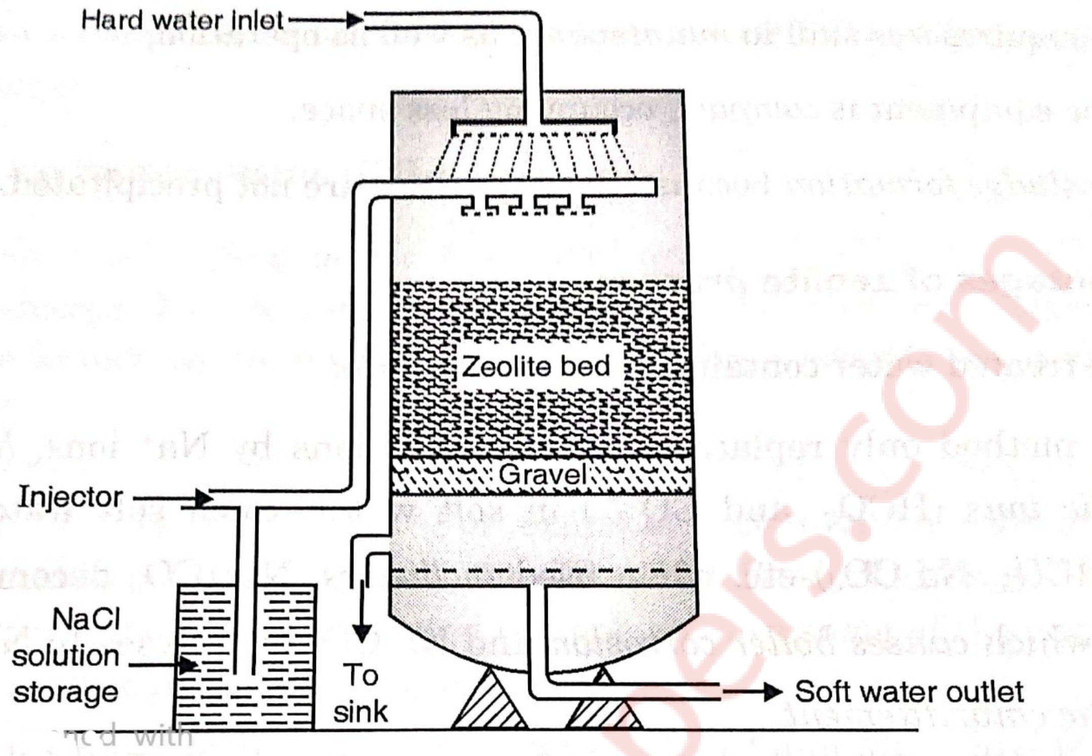


Fig. 1.11.3 : Zeolite Softner

5) Regeneration: When zeolite is exhausted, it is regenerated by washing bed with concentrated brine solution (NaCl) .

   $CaZe/MgZe + 2NaCl \rightarrow Na_2Ze + CaCl_2/MgCl_2$

6) Process: For softening of water, hard water is percolated at a specific rate through zeolite bed kept in a cylinder. The calcium and zeolite ions are retained by zeolite bed and water becomes rich in sodium salts.
   $Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2NaHCO_3$
   $Na_2Ze + MgCl_2 \rightarrow MgZe + 2NaCl$

Merits of using zeolite:

1) It removes hardness almost upto 10 ppm.

2) The equipment is compact.

3)No sludge formation takes place. Hence it is clean operation.

4)It requires less time for softening.

5)It removes Fe and Mg from water.

Demerits of using zeolite :

1) The treated water contains more sodium salts.

2) The method only replaces calcium and magnesium ions by sodium ions, but leaves all acidic ions in soft water.

3) Such soft water containing carbonates and bicarbonates is used in boilers, sodium bicarbonate decomposes to give carbon dioxide which causes boiler corrosion and sodium carbonate hydrolyses to sodium hydroxide, causing caustic embrittlement.

Q4)(b)(i) 10g of lubricating oil was heated with 25 ml of 50% alcohol, the resultant mixture required 25 ml of N/10 KOH. The blank reading was obtained to be 8 ml of same KOH. Calculate acid value of the lubricating oil . (3M)

Solution:

Given : Weight of oil = 10 g , Normality of KOH = 1/10=0.1 N , Volume of KOH = 25 ml

To Find : Acid Value

Acid Value = $\frac{Volume\ of\ KOH\ X\ Normality\ of\ KOH\ X\ 56}{Weight\ of\ oil \in grams}$.

Acid Value = $\frac{25\ X\ 0.1\ X\ 56}{10}$.

Acid Value = 14 mgs of KOH .

Ans : The Acid Value of the oil is 14 mgs of KOH .

Q4)(b)(ii) Explain the terms : (a) Concrete (b) RCC (2M)

Ans : Concrete

1) Concrete is a building and structural material obtained by mixing a binding material (cement/lime), inert mineral aggregates (such as sand, crushed stone, gravel, bricks) and water in suitable proportion and which can be readily worked or moulded into almost any desired shape which is compact, rigid, strong and durable .
2) Concrete is of two types , lime concrete and cement concrete .
3) More amount of cement in concrete gives water proofness to concrete. Next to steel, it is important in construction works .

RCC

1) RCC (Reinforced Concrete Construction) is the combination of steel and concrete structure which has high load-bearing capacity .
2) Plain concrete has a great compressive strength but little ability to withstand tension. Hence when steel and concrete are together used, embedded steel takes up tension and strength is given by concrete .
3) RCC is easy to make and cast into desired shape which can bear any type of load .

Q4)(c) Explain the importance of polymers in the field of surgery and medicine . (4M)

Ans :

1) Biomaterials are materials that can be implanted in the body to provide special prosthetic functions or used in diagnostic, surgical, therapeutic applications, without causing adverse effect on blood and other tissues.
2) These materials are versatile and can be modified to suit specific body functions.
3) Biomaterials should possess following characteristics:
   i) Purity and reproducibility
   ii) Easy sterilization and should not be toxic or allergic.
   iii) Optimum physical and chemical properties.
   iv) Should be fabricated into desired shape or form.
   v) Should be chemically inert and not affect body fluids.
   vi) Should be flexible.
4) Applications of polymeric biomaterials:
   i) To construct artificial replacement for human organs:
      Some man made polymers are used for complete replacement of organs like artificial heart, heart lung machines, artificial kidneys, legs, artificial faces, in plastic surgery, etc.
   ii) To repair, sustain and augment function of organs:
      Polymers find application in clothing, glasses for sight, dentures, vascular prostheses, heart valves, pace makers, meshes and forms for reconstructive surgery, cannulae for haemodialysis, etc.
   iii) To provide biochemical function:
      Some polymers have specific and definite chemical interaction with the biochemistry of body.
      Eg. Synthetic ion exchange resins for absorbing metaboiles from blood, synthetic polyelectrolytes capable of absorbing specific viruses, polymers for production of interferon (antiviral agent), synthetic polypeptides, enzymes having higher biological activity.
      Silicone Rubber is used in heart valves, plastic surgery.
      Polyurethane rubber: artificial rubber, reconstructive surgery.
      PMMA: contact lenses, dental restoratives.
      PVC: disposable syringes.
      Polylactic acid: dialysis media, drug delivery, plastic surgery.

Q5)(a) What is compounding of plastic? Explain the role played by various constituents used during manufacturing of plastic . (6M)

Ans :

1) Compounding of plastic consists of preparing plastic formulations by mixing or blending polymers and additives in a molten state, these blends are automatically dosed with fixed setpoints usually through feeders/hoppers.
2) The moulding constituents of plastic are :
   i) Binders e.g. resins
      Binders hold other constituents together during manufacture and influence the properties of plastic. Usually natural or synthetic resins or cellulosic derivatives are used as binders. Resins can be either thermoplastic or thermosetting.
   ii) Fillers or extenders

Fillers are those substances which reduce the cost per kg of polymers and introduce some specific property in resin like better tensile strength, hardness, finish, workability, opacity etc to the plastic material.
Eg quartz, mica improve hardness.
Ba salts, when introduced, make the sheet impervious to X-rays.

iii) Pigments or dyes or colouring agents
These impart desired colour to plastic. Organic dyestuffs and inorganic pigments are used for this in small proportion.

iv) Catalysts or accelerators
These are added only to thermosetting resins. These substances accelerate the process of cross linking of polymer to form infusible cross linked form during moulding operations.
Eg. hydrogen peroxide, benzoyl peroxide, metallic oxides.

v) Plasticizers
These are substances that are added to resins to increase plasticity and flexibility. These substances reduce intermolecular force of attraction between macromolecules of resin.
Eg. oils (non-drying type), camphor, esters of stearic/phthalic acid .

vi) Lubricants
These when added make moulding of plastic easier and impart glossy, flawless finish to the products. Even it presents plastic material from sticking to moulding equipment .

vii) Stabilizers
It is to improve thermal stability during processing. These are required especially in the processing stage for plastics, which have tendency to decompose or change their colours at moulding temperatures.
Opaque moulding compound- Salts of lead- Red lead, White lead.
Transparent moulding compound- Stearates of lead, Cadmium, Barium .

Q5)(b)(i) Define and briefly explain **(3M)**

Biological Oxygen Demand (BOD)

Chemical Oxygen Demand (COD)

Ans : BOD

1. The Biochemical Oxygen Demand (BOD) of water is a measure of amount of oxygen required for the biological oxidation of organic matter under aerobic conditions, at 20 and for a period of five days.

2. BOD is directly related to the extent of pollution in waste water and industrial effluent.

3. The higher the BOD of a sample, higher will be the pollution caused by it. Drinking water should have BOD preferably less than 1 ppm.

4. BOD = $[(DO)_1-(DO)_2]/x$ ppm where $(DO)_1$=DO in blank titration, $(DO)_2$=DO of the sample water

x = Volume of sample/Total Volume to which it was diluted.

COD

1.The amount of oxygen required by organic matter in a sample water for its oxidation by strong oxidizing agent is known as Chemical Oxygen Demand or COD of the sample.

2. It helps in designing the water treatment plant and deciding the disposal of domestic effluents in various types of water streams.

3.COD = (V_2-V_1)X NX 8X 1000/V where V_1 = Volume of FAS for sample titration,

V_2=Volume of FAS for blank titration, V= Volume of sample taken for the test, N=Normality of FAS

Q5)(b)(ii) Write important functions of lubricant. (2M)

Ans : The functions of lubricants are :

1) Lubricants act as coolants, thereby avoiding loss of energy. They reduce the frictional heat, thereby controlling expansion of metals. It helps to maintain shape, size and dimensions of metal parts of machines.
2) Lubricants reduce the wastage of power, eg in internal combustible engines, the lubricant applied between the piston and the cylinder acts as a coolant.
3) Lubricant acts as a sealant, as it does not allow the escape of gases from engine under high pressure.
4) Lubricant prevents the attack of moisture on machine surface. This helps to control corrosion of the metal parts.
5) Lubricant act as cleansing agents, because they have the tendency to wash off solid particles produced due to combustion or wear.
6) Lubricants help to reduce maintenance cost of machines, because a thin film of a lubricant reduces friction and thus controls wear.

Q5)(c) Draw and explain phase diagram of Pb-Ag system . (4M)

Ans : Lead Silver system has two components and four phases. The phases are:

1) Solid Silver
2) Solid Lead
3) Solution of molten silver and lead
4) Vapour

Since pressure has nearly no effect on equilibrium, so gaseous phase is practically absent, the condensed phase rule F = C-P+1 will be applicable.

In the phase diagram of Pb-Ag System, following salient features are observed.

1) Curve AO (Freezing curve of Ag)
2) Curve BO (Freezing curve of Pb)
3) Eutectic Point ‘O’
4) Area AOB

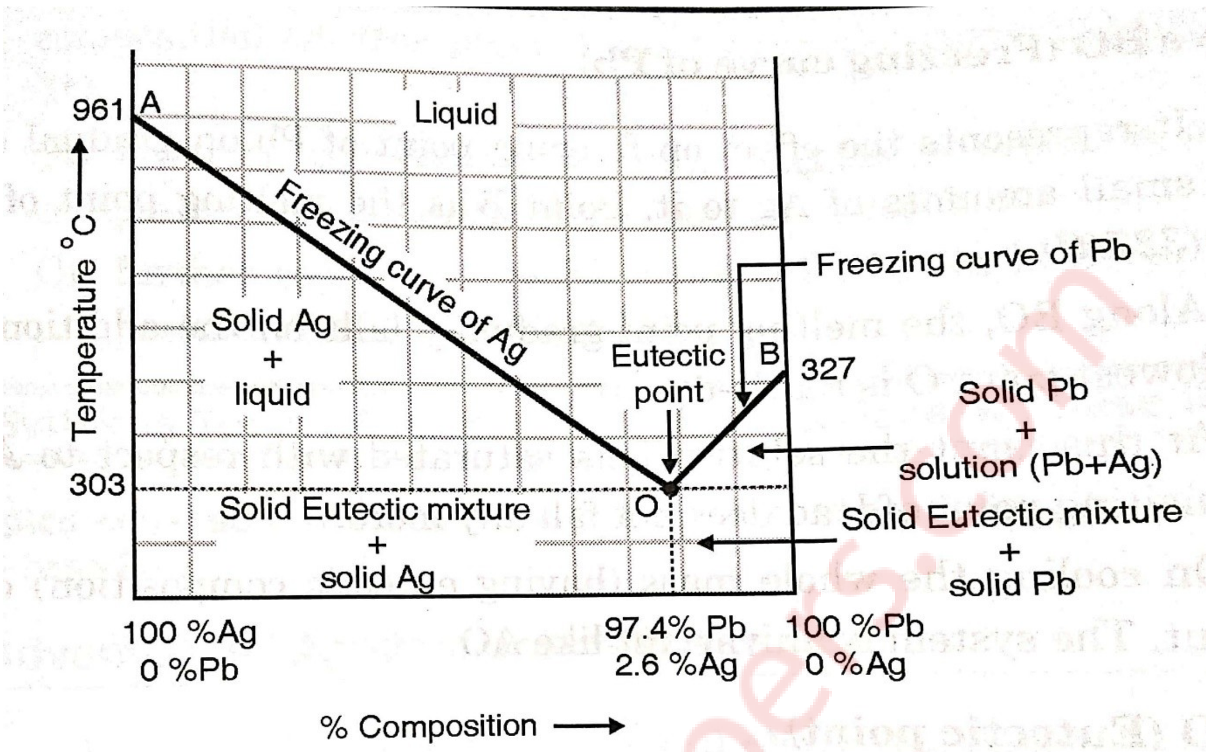


Fig. 4.6.1 : The phase diagram of Pb- Ag system

Curve AO :

i) When Pb is added to Ag, freezing point of Ag decreases till the lowest point (303 ℃) is reached, where solution gets saturated with Pb.

ii) At point O, no more lead can go in solution and on further addition of Pb, it separates as the solid phase.

iii) Along the curve OA, solid Ag and solution co-exist. Hence F=C-P+1=2-2+1=1 i.e. System is Univariant .

Curve BO :

i) When Ag is added to Pb, freezing point of Pb (327 ℃) decreases till the lowest point (303 ℃) is reached , where solution gets saturated with Ag.

ii) On cooling further, the whole mass (eutectic composition) crystallizes out .

iii) Number of phases = 2 (solid Pb + solution) .
F = C - P + 1 = 1 .

Point O :

i) The curve AO and BO meet at point O (303 ℃) where all three phases (that is solid Pb, solid Ag and then solution) coexist.

ii) Therefore F=0, this represents zero variant system at point O because it is fixed composition (Ag=2.6% and Pb=97.4%).

iii) No mixture of lead and silver has melting point lower than eutectic temperature.

iv) Below this temperature, we have two regions :
1) eutectic + solid Ag in which crystalline silver and solid eutectic are stable.
2) eutectic + solid Pb in which crystalline lead and solid eutectic are stable.

Area AOB :

i) It represents solution of Ag and Pb .

ii) If a sample of lead containing less than 2.6% Ag is taken, at an arbitrary point on the curve. On allowing the mass to cool, the temperature gradually falls without any change in composition till this point is reached on the curve BO .

iii) Since Number of Phases (P) = 1, F = 2-1+1 = 2 .
Therefore, the system is bivariant.

Q6)(a) Draw a neat diagram and explain the mechanism of thick film lubrication . (6M)

Ans :

1) In this type of mechanisms, a liquid lubricant with high viscosity is applied in the form of thick film between two moving surfaces. The film is at least 1000 ˚A thick .
2) Such film helps to avoid surface to surface contact of moving surfaces. The hydrodynamic lubrication helps to reduce the coefficient of friction μ to about 0.001 to 0.003, which is much lower as compared to that of unlubricated surfaces .
3) The mechanism of hydrodynamic lubrication can be better understood by considering the operation of a journal bearing.
4) The bearing consists of a shaft rotating at a fair speed, with moderate load. The lubricant is applied in annular space.
5) When journal bearing is stationary, the two surfaces remain in contact, but as the shaft (journal) begins to rotate, the film of lubricant also rotates between the two metallic surfaces.
6) Due to the presence of thick oily layer, all the asperities of the metal surfaces are filled up and a pressure is developed which practically keeps the two surfaces away from each other, thereby reducing wear.
7) The motion is smooth as the resistance to the motion is restricted amongst the particles of lubricant. Essential characteristics of lubricants required are :
   i) Adequate viscosity, oiliness and higher viscosity index .
   ii) Lubricant should be resistant to seasonal impact.
8) The blending oils used in hydrodynamic or thick film lubrication are vegetable oils or mineral oils blended with antioxidants or organometallic compounds .The machines in which this mechanism is used are sewing machines, clocks, watches, scientific instruments .

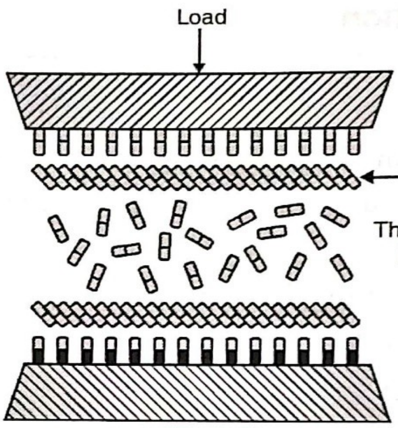


Fig. 3.3.1(a) : Hydrodynamic lubrication or fluid film lubrication

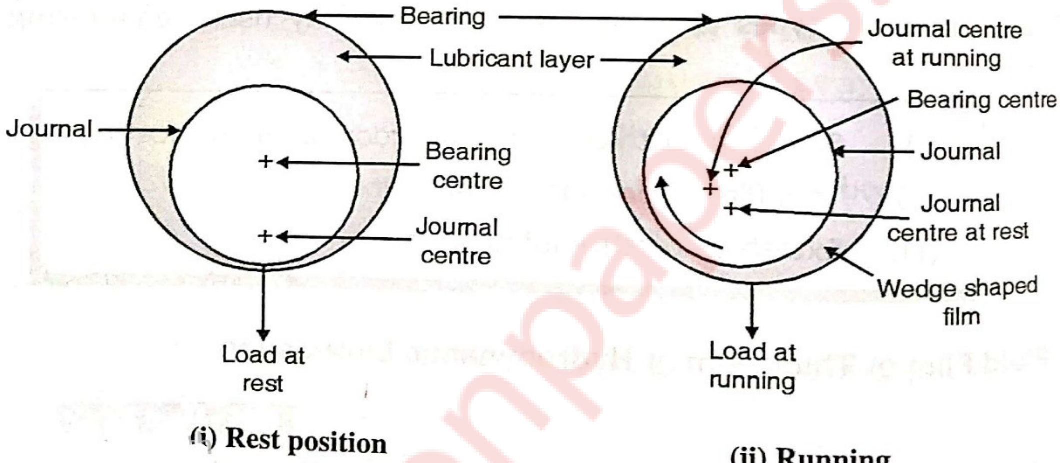


Fig. 3.3.1(b) : Fluid film lubrication

Q6)(b)(i) Write Gibb's mathematical equation of phase rule and define the terms involved in it.

(3M)

Ans : 1) Gibb's mathematical equation for phase rule may be stated as, The number of degrees of freedom (F) of the system is related to the number of components (C) and phases (P) by the phase rule equation provided equilibrium between any number of phases is not influenced by gravitational, electric or magnetic forces or by surface action, but only by temperature, pressure and concentration for any system at equilibrium at definite temperature and pressure.

F = C - P + 2

2) A Phase is defined as any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts of the system by definite boundary surfaces.

3) Component is defined as the smallest number of independently variable constituents taking part in the state of equilibrium by means of which the composition of each phase can be expressed directly or in the form of chemical equation.

4) Degree of freedom is defined as the minimum number of independently variable factors such as temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system.

Q6)(b)(ii) With chemical equation, explain role played by bleaching powder in water treatment.

(2M)

Ans: 1) Bleaching powder reacts with water as

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

$Cl_2 + H_2O \rightarrow HCl + HOCl$

Hypochlorous Acid

$HOCl \rightarrow HCl + [O]$

Nascent Oxygen

2)In these reactions above, the HOCl deactivates the enzymes present in the cells of micro-organism.

3)Thus the metabolic activity of micro-organism gets affected, thereby making the micro organism inactive and finally the organism dies.

Q6)(c) Explain manufacturing of the cement by wet process materials . (4M)

Ans : Wet process manufacturing of cement involves the following operations:

1) Mixing of Raw Material:
   i) The calcareous raw materials are crushed, powdered and stored in big silos. The argillaceous materials are thoroughly mixed with water and then both are passed to 'Grinding Mills' to get fine paste of slurry of raw materials. The slurry contains about 38-40% of water. It is stored in storage tanks and kept ready for feeding to a rotary kiln.
2) Burning of Raw Material:
   i) The collected slurry is injected into rotary kiln at its upper end. Due to slope and slow rotation of kiln, the materials move towards higher and higher temperature sections of kiln, to get clinkers of cement.

Rotary Kiln:

1) A rotary kiln is a steel tube about 2.5-3 m in diameter and 90-120 m in length, lined inside with refractory bricks. It rests on roller bearings, which are supported on concrete structure. It is inclined around 4-5 ˚ and rotating at 1 rpm. Burning fuel and air are injected at lower end, which heats interior of kiln upto 1750 ℃ .
   a) Drying Zone: It is upper part of kiln, where water is completely removed from slurry.
   b) Calcining Zone (upto 1000 ℃) :

i) In this zone, lime stone of slurry undergo decomposition to form quick lime and carbon dioxide, which is latter space out.

ii) The material forms small lumps. The following reaction takes place in this zone

$CaCO_3 \leftrightarrow CaO + CO_2$

c) Clinkering Zone (upto 1700 ℃):

i) Here lime and clay undergo chemical reactions to give clinkers of cement:

$2CaO + SiO_2 \rightarrow Ca_2SiO_4(C_2S)$

Dicalcium silicate

$3CaO + SiO_2 \rightarrow Ca_3SiO_5(C_3S)$

Tricalcium silicate

$3CaO + Al_2O_3 \rightarrow Ca_2Al_2O_6(C_3A)$

Tricalcium Aluminate

$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow Ca4Al2Fe_2O_{10}(C_3A)$

Tetracalcium Alumino Ferrite

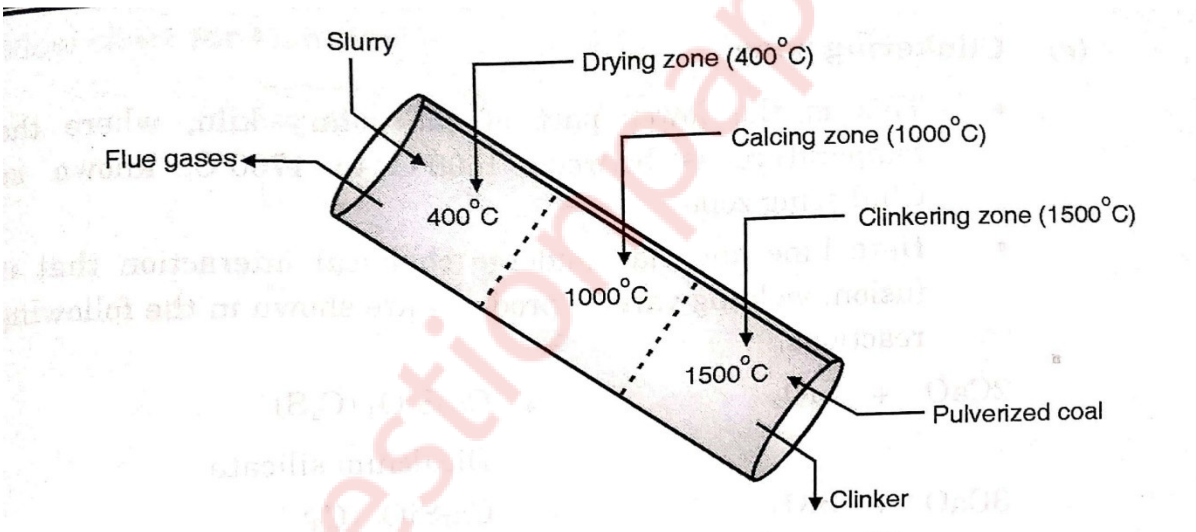


Fig. 5.2.1 : Schematic diagram of rotary kiln

ii) The aluminates and silicates of calcium then fuse together to form small, hard greyish stones called clinkers. These clinkers are very hot and hence they are cooled with air-counter-blast. This hot air so produced is used for burning powdered coal/oil. The cooked clinkers are collected in trolleys.

3) Grinding and Packaging:

i) The cooled clinkers are ground to a fine, powder in ball mills/ tube mills.

ii) During final grinding 2-3% gypsum is added, to enhance setting time of cement.

iii) This ground cement is stored in silos through automatic machines.