

B.TECH.

EAS-202/102

SECOND SEMESTER THEORY EXAMINATION, 2009-10

ENGINEERING CHEMISTRY

Time : 2 Hours

Total Marks : 100

Attempt All questions.

SECTION-A

1. Choose/Fill correct answers :

(a) IR active compounds are those compounds which undergo a net change in

Ans. Rotational and vibrational levels

(b) Hard water does not give lather with soap because it forms,

Ans. Insoluble white scum which do not possess any cleaning action.

(c) Which of the intermolecular bonds are caused by induced dipoles?

- (i) Ionic (ii) Vander Walls
(iii) Hydrogen (iv) Covalent

Ans. (iv) Covalent

(d) Which of the following statements about graphite is not correct?

- (i) The coordination of carbon atom is 4.
(ii) The carbon atoms are arranged layers
(iii) The layers in graphite are attractive to each other by weak forces.
(iv) The carbon atoms use only three of their four outer electrons for covalent bonding.

Ans. (i) The coordination of carbon atom is 4.

(e) Which of the following has the greatest covalent character?

- (i) NaCl (ii) $MgCl_2$

(iii) $AlCl_3$

(iv) $SiCl_4$

Ans. (iv) $SiCl_4$

(f) Example of geometrical isomerism is :

- (i) 2-Butanol (ii) 2-Butene
(iii) 2-Butanal (iv) 2-Butyne

Ans. 2-Butene

(g) The polymer which is used in non sticky kitchen is :

- (i) PVC (ii) Teflon
(iii) Rayon (iv) Isoprene

Ans. (ii) Teflon

(h) Bakelite is a :

- (i) Natural polymer
(ii) Additional polymer
(iii) Condensation polymer
(iv) Homopolymer

Ans. (iii) Condensation polymer

(i) The relationship between absorbance and transmittance is, $A = \dots\dots\dots$

Ans. $\log\left(\frac{I}{T}\right)$

(j) Hydrogen bonding in IR spectroscopy results the shifting of absorption band towards wave number.

Ans. Functional group region

- (k) In NMR spectroscopy the number of splitted peaks = $n + 1$, where n is the number of atoms on the neighbouring atoms.

Ans. Hydrogen, Carbon

- (l) The abnormal boiling point of H_2O is due to

Ans. Hydrogen bonding

- (m) Which of the following is diamagnetic in nature?

- (i) H_2^+ (ii) H_2
(iii) H_2^- (iv) None of these

Ans. H_2

- (n) Which of the following is an example of cubic structure?

- (i) NaCl (ii) SnO_2
(iii) ZnO (iv) $NaNO_3$

Ans. (i) NaCl

- (o) The unit of k of zero order reaction is :

- (i) $time^{-1}$
(ii) $mol\ litre^{-1}\ time^{-1}$
(iii) $litre\ mol^{-1}\ time^{-1}$
(iv) $litre^{-1}\ time^{-1}$

Ans. (ii) $mol\ litre^{-1}\ time^{-1}$

- (p) The cells convert the energy from the combustion of in to the electrical energy.

Ans. Fuel, Hydrogen

- (q) Corrosion involves the of iron and the formula of rust is

Ans. Rusting, $Fe_2O_3 \cdot xH_2O$

- (r) The following reaction is known as :

Ketoxime H_2SO_4 N-substituted amide.

- (i) Aldol condensation
(ii) Beckmann rearrangement
(iii) Diels-Alder Reaction
(iv) Hoffmann rearrangement

Ans. (ii) Beckmann rearrangement

- (s) $Et_3Al.TiCl_3$ is known as

Ans. Ziegler Natta Catalyst

- (t) The titration of ferrous ammonium sulphate versus potassium dichromate is known as titration.

Ans. Redox

- (u) The major component of bio-gas is

Ans. Methane (CH_4) Le 50-60

SECTION-B

2. Attempt any three of the following :

- (a) (i) Explain the bonding and antibonding molecular orbitals and differentiate between them.

Ans. Bonding and Antibonding Molecular orbits : Molecular orbital formed by the addition of two atomic orbital wave function is known as bonding molecular orbital.

Molecular orbitals which do not take part in bonding are known as Non-bonding molecular orbitals.

Difference between bonding and antibonding molecular orbitals :

Bonding molecular orbital

1. BMO is obtained by addition of two atomic orbital wave function.
2. The electron density in BMO is greater than that in individual atomic orbitals

$$\psi_b^2 = \psi_A^2 + \psi_B^2 + 2\psi_A \psi_B > \psi_A^2 + \psi_B^2$$

3. The energy level of BMO is less as compared to that of individual atomic orbitals.
4. Electrons present in bonding MO helps in the formation of bond.
5. Bonding molecular orbitals are represented as σ , π etc.

Antibonding molecular orbital

1. ABMO is obtained by subtraction of two atomic orbital wave function.
2. The electron density in ABMO is less than that in individual atomic orbitals.

$$\psi_a^2 = \psi_A^2 + \psi_B^2 - 2\psi_A \psi_B < \psi_A^2 + \psi_B^2$$

3. The energy level of ABMO is more as compared to that of individual atomic orbitals.

4. Electrons present in ABMO decrease the tendency to form bond.

5. They are represented as σ^* , π^* etc.

(ii) Write the electronic configurations of N_2 , N_2^+ , N_2^- and N_2^{2-} . Establish their stability order based on calculation of bond order. Also write their magnetic character.

$$\text{Ans. } N_2(14) \rightarrow kk\sigma(2s^2)\dot{\sigma}(2s^2)\pi(2p_x^2)$$

$$= \pi(2p_y^2)\sigma 2p_z^2$$

$$B.O = \frac{1}{2}(8-2) = 3 \quad (\text{Diamagnetic})$$

$$N_2^+ B = kk\sigma(2s^2)\dot{\sigma}(2s^2)\pi(2p_x^2) = \pi(2p_y^2)\sigma p_z$$

$$B.O = \frac{1}{2}(7-2) = \frac{5}{2} = 2.5 \quad (\text{Paramagnetic})$$

$$N_2^-(1s) = kk\sigma(2s^2)\dot{\sigma}(2s^2)\pi(2p_x^2)$$

$$= \pi(2p_y^2)(\sigma 2p_z^2)\dot{\pi}(2p_x^1)$$

$$B.O = \frac{1}{2}(8-3) = 2.5 \quad (\text{Paramagnetic})$$

$$N_2^{2-}(16) = kk\sigma(2s^2)\dot{\sigma}(2s^2)\sigma(2p_z^2), \pi(2p_x^2)$$

$$= \pi(2p_y^2)\dot{\pi}(2p_x^1) = \dot{\pi}(2p_y^1)$$

$$B.O = \frac{1}{2}(8-4) = 2 \quad (\text{Paramagnetic})$$

$$N_2 > N_2^+ > N_2^- = N_2^{2-}$$

order of stability

(b) (i) Derive the equation for half life of a first order reaction.

Ans. Please see Q. No 4(b), Ind I sem exam of 2006-07

(ii) Define EMF of a cell and write a short note on electrochemical cell.

Ans. Electromotive Force (E.M.F) : The difference in potential which causes the flow of current from the electrode having higher potential to the electrode having lower potential is known as E.M.F. of the cell. It is expressed in volt.

Electro-chemical Cell : "An electrochemical cell is a device which converts chemical energy into electrical energy and vice-versa". This conversion is due to redox reaction occurring in the cell.

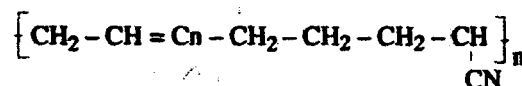
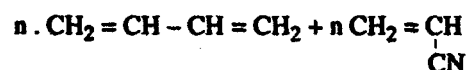
(c) (i) Describe preparation, properties and applications of:

(A) Buna-N

(B) Nylon-6, 6

Ans. (A) Buna - N or GR-A or Nitrile Butadiene Rubber

Properties



Proportion

(i) Buna - N is resistant to heat, sunlight, oil and acid

(ii) Nitrile Rubber is less resistant than natural rubber

(iii) It has good abrasion resistance

(iv) In vulcanised form nitrile rubber has high temperature resistance.

Application : It is used for making to following

1. Automobile parts
2. Oil Resistant foams because of its excellent resistance to oils.
3. Conveyer belt
4. High altitude air crafts components
5. Printing Rollers
6. Adhesive

Ans. Nylon 6,6

(a) (i) Condensation polymer,

(ii) Copolymer,

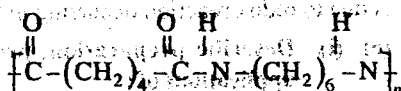
(iii) Thermoplastic

(b) Monomers

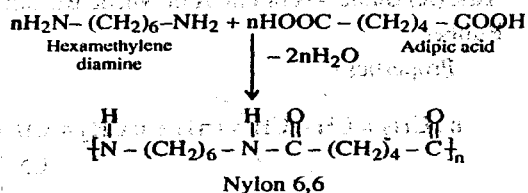
(i) $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$ — Hexamethylene diamine

(ii) $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ — Adipic acid

(c) Structure

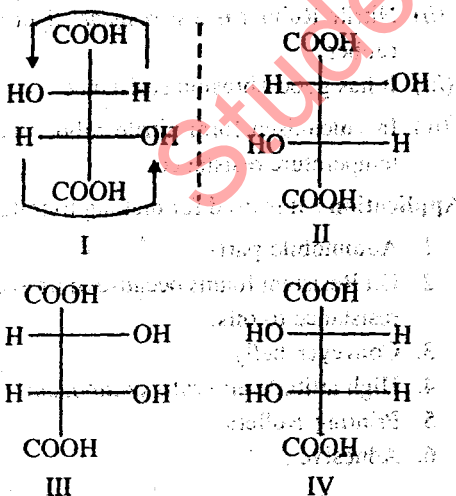


Preparation : Nylon 6,6 is obtained by the poly condensation of hexamethylene diamine and adipic acid in the ratio of 1:1.



(ii) Discuss in brief the diastereomers and meso compounds with suitable examples.

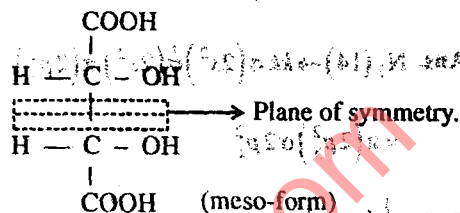
Ans. Dia-Stereomers : Optical isomers that are not mirror images of each other are known as diastereomers. They have different physical properties like M.P, B.P, density, refractive index.



I and III, II and IV — Diastereomers

I and IV, II and III — Diastereomers.

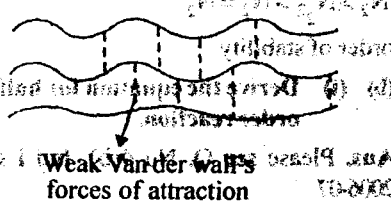
Meso Compound : A compound having two or more asymmetric carbon atoms, which superimposes on its mirror image and hence is optically inactive is known as meso compound. For example, Tartaric Acid.



(d) (i) Distinguish between thermosetting and thermoplastic resins. Classify the following as thermosetting and thermoplastic: Polystyrene, polyethylene, urea-formaldehyde, bakelite, teflon and nylon.

Ans. Difference between Thermoplastic and Thermosettings :

1. Polymers which are softened on heating and hardened on cooling are known as thermoplastics.
2. They can be moulded again and again.
3. They are generally formed by addition polymerisation.
4. They have linear structure and the different chains are held together by weak Van der waal's force of attraction.
5. On heating secondary bonds break (Vanderwaal's forces of attraction) hence they get softened.
6. They are usually soft, weak and less brittle.
7. They are generally soluble in some organic solvents.
8. Structure



9. **Example :** PE, PVC, PMMA, Nylons, Polystyrene.

Thermosetting

1. Polymers which once hardened can't be softened again are known as thermosets.
2. They can't be removed.
3. They are generally formed by condensation polymerisation.
4. They have cross linked three dimensional network type of structure.
5. On heating thermosets undergo hardening rather than softening because of taking place of any left over polymerisation. One prolonged heating they undergo degradation and the process is known as charring.
6. They are usually hard, strong and more brittle.
7. They are generally insoluble in organic solvents.
8. Structure



Three dimensional network type of structure

9. **Example :** Phenolic resin, Epoxy resin, Bakelite.

Polystyrene — Thermoplastic

Polyethylene — Thermoplastic

Bakelite — Thermosetting

Teflon — Thermoplastic

Nylon — Thermoplastic

- (ii) **Discuss** the zeolite process for removing the hardness of water.

Ans. Zeolite Process : Zeolites are hydrated sodium alumina silicates capable of exchanging its sodium ions reversibly with the hardness producing cation in water.

The formula of sodium zeolite is $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x = 2$ to 10 and $y = 2$ to 6 . They are also known as permutit.

1. Natural zeolites

2. Synthetic zeolites

Zeolite are of two types :

1. **Natural zeolites :** are amorphous and non-porous in nature. They are derived from green sands by washing, heating and treating with NaOH.

2. **Synthetic zeolites :** are porous and gel structured synthetic zeolites are prepared by heating together solutions of

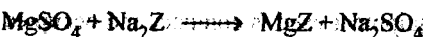
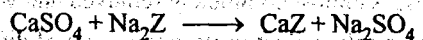
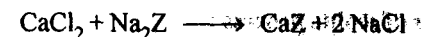
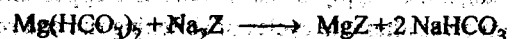
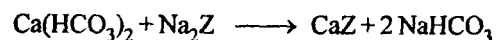
(a) Sodium silicate, aluminium sulphate and sodium aluminate.

(b) China clay, feldspar and soda ash.

They possess higher exchange capacity per unit weight and are less durable than natural zeolites.

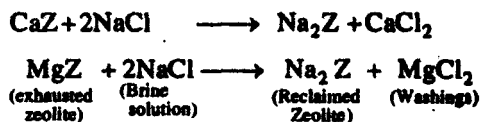
Principle :

A. Zeolites can be simply represented as Na_2Z where Z represents insoluble radical frame work. They hold sodium ion loosely. When hard water is passed through a bed of zeolite, the hardness causing ions are retained by zeolite as CaZ and MgZ . Therefore water becomes free from the main hardness producing cation but gets more concentrated with respect to sodium salts and eventually zeolite gets exhausted.



B. **Regeneration:** During softening, zeolites exchange its sodium ions with magnesium and calcium ions and after some time they are completely converted into calcium and

magnesium zeolites and the zeolite bed ceases to soften water, i.e., gets exhausted. "The process by which the exhausted zeolite is reclaimed by treating it with 10% brine solution is known as regeneration."



The regenerated zeolite is again used for softening.

Process : Hard water is percolated at a definite rate through the bed of zeolite housed in a cylindrical unit. The hardness causing Ca^{+2} and Mg^{+2} ions are retained by zeolite as CaZ and MgZ respectively. The outgoing water contains sodium salts. After sometime the bed gets exhausted.

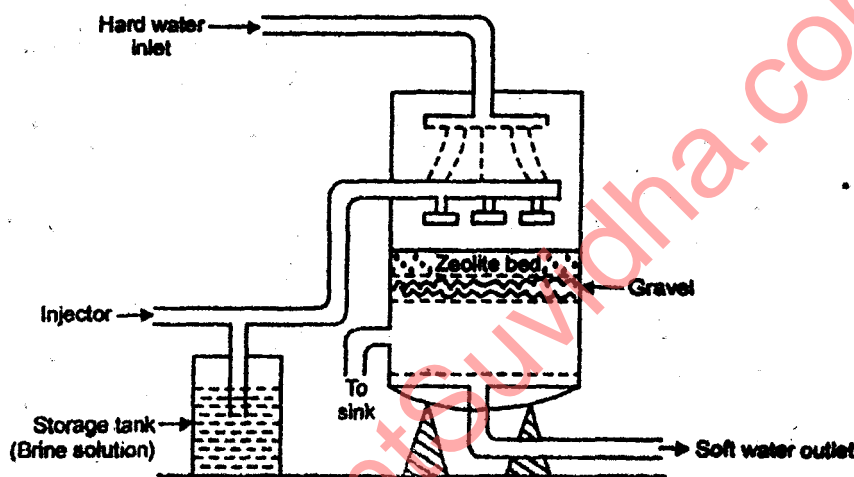


Fig. Zeolite softner

At this stage, the supply of hard water is stopped and regeneration is carried out. Thus softening by zeolite involves alternate cycles of softening run and regeneration.

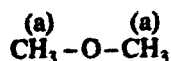
The regeneration step comprises of (1) backwashing (2) brining (3) rinsing before reuse. The soft water thus obtained has hardness less than 30 ppm.

Advantages of zeolite process :

- 1. Hardness is almost completely removed and water of about 15 ppm hardness is produced.
- 2. It automatically adjust itself to the water of different hardness.
- 3. The equipment used is compact and occupies less space.
- 4. It requires less time for softening.
- 5. Less skill is required for maintenance as well as operation.
- 6. There is no danger of sludge formation because impurities are not precipitated.

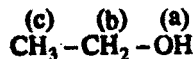
- (e) (i) Two organic compounds have same molecular formula C_2H_6O (Ethyl alcohol). In NMR spectra one shows only one signal while the other has three signals. Identify them with proper explanation.

Ans. C_2H_6O shows only one signal so there will be only one type of proton present. Hence the formula will be



Number of N.M.R. signal = 1

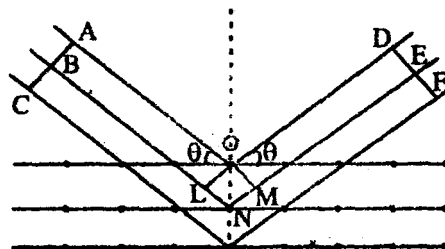
⇒ Other shows three N.M.R signals so there will be three types of proton in the formula. Hence the formula will be



- (ii) Write a short note on Bragg's law.

Ans. **Bragg's equation.** Bragg pointed out that scattering of X-rays by crystal could be considered as reflection from successive planes of atoms in the crystal. However, unlike reflection of ordinary light, the reflection of X-rays can take place. Only at certain angles which are determined by the wavelength of the X-rays and the distance between the planes in the crystal. The fundamental equation which gives a simple relation between the wave length of the X-rays, the interplaner distance in the crystal and the angle of reflection, is known as Bragg's equation.

Derivation: Let the planes ABC and DEF be drawn perpendicular to the incident and reflected beams, respectively. The waves reflected by different layer planes will be in phase with one another (i.e will coincide with the another in planes DEF) only "when the difference in the path lengths of the waves reflects from successive planes is equal to an integral number of wavelength.



Let δ be the difference in the paths lengths of the waves reflected from the first two planes. The value of δ can be obtained by drawing perpendiculars OL and OM on the incident and reflected beam. Then,

$$\delta = LN + NM \quad \dots (i)$$

But δ should be equal to an integer of wavelength (λ) i.e.,

$$n\lambda = LN + NM \quad \dots (ii)$$

When n is an integer known as the order of reflection.

Since triangles OLN and OMN are congruent. Thus,

$$LN = NM$$

$$\therefore n\lambda = 2LN \quad \dots (iii)$$

$$\text{But, } LN = d \sin \theta$$

$$\therefore n\lambda = 2d \sin \theta \quad \dots (iv)$$

This is known as Bragg's equation. If value of θ , n & λ are known, we can drive the value of d by this equation.

The integer n has the successive values of 1, 2, 3, etc. as θ increases. The maximum diffraction changes with n and known as first, second, etc. order when $n = 1, 2, \dots$ etc. respectively.

SECTION-C

3. Attempt any one of the following :

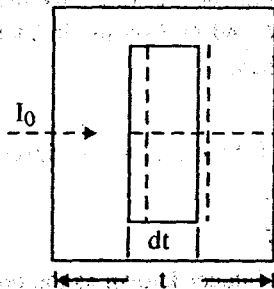
- (a) Explain Beer Lambert Law. Discuss Electronic transitions. Calculate absorbance if %T = 80.

Ans. Absorption of light by the molecule is governed by two laws :

(i) Lambert's Law

(ii) Beer's Law.

Lambert's Law : This law states that "when a beam of monochromatic light is passed through an absorbing medium, the rate of decrease of intensity of light radiation with the thickness of the absorbing medium is directly proportional to the intensity of the light". Let I be the intensity of light radiation passing through a medium having thickness ' t '.



dl = Infinitesimal decrease in the intensity of light radiation after passing through thickness ' dt '.

$-\frac{dl}{dt}$ = Rate of decrease of Intensity of radiation with the thickness.

$$-\frac{dl}{dt} \propto I \quad \dots(1)$$

or $\frac{dl}{dt} = -KI$

Where I = proportionality constant

or $\int_{I_0}^I \frac{dl}{I} = -K \int_{t=0}^t dt$

or $\ln \frac{I}{I_0} = -Kt$

or $I = I_0 e^{-Kt} \quad \dots(2)$

K depends upon

(i) Wavelength of light used.

(ii) Absorbing medium used.

Equation (2) may also be written as

$$I = I_0 10^{-at} \quad \dots(3)$$

where $a = \frac{K}{2.303}$ = Extinction coefficient of the absorbing medium.

I_{abs} be the intensity of radiation absorbed, then

$$I_{abs} = I_0 - I = I_0 - I_0 e^{-Kt}$$

$$I_{abs} = I_0 (1 - e^{-Kt})$$

Beer's Law : This law states that "when a beam of monochromatic radiation is passed through a solution of an absorbing medium, the rate of decrease of intensity of radiation with thickness of the absorbing medium is directly proportional to the intensity of incident radiation as well as the concentration of the solution."

Mathematically,

$$-\frac{dl}{dt} \propto IC \quad \dots(1)$$

or $-\frac{dl}{dt} = K'IC$

where,

K' = Molar absorption coefficient which depends upon the nature of absorbing medium

C = Concentration of solution in mol/L.

Let,

I_0 = Intensity of light radiation before entering the absorbing medium.

I = Intensity of radiation after passing through a thickness ' t ' of the medium.

$$\therefore \int_{I_0}^I \frac{dl}{I} = - \int_{x=0}^x K' C dt$$

$$\text{or } I = I_0 e^{-K'c} \quad \dots(2)$$

This equation may also be written as

$$I = I_0 10^{a'cl} \quad \dots(3)$$

$$\text{or } \boxed{\log \frac{I_0}{I} = a'cl} \quad \dots(4)$$

where,

$$a' = \frac{K'}{2.303} = \text{Molar extinction coefficient of the absorbing medium.}$$

Types of Electronic Transition : The various types of electronic transition, which are possible in organic molecule by absorption of UV-visible light are as follows:

1. **$\sigma - \sigma^*$ transition :** This type of transition is possible in saturated hydrocarbons (alkane) where only σ bands are formed and no atom has non-bonding (n) electrons. Such transitions require energy in the range of 150 nm which is not available in ultraviolet region. e.g., CH_4 .

$$\lambda_{\text{max}} \approx 121.9 \text{ nm}$$

2. **$n - \sigma^*$ transition :** Compounds which contain non-bonding electron exhibit this type of transition. Organic compounds containing nitrogen, oxygen, sulphur or chlorine etc. as an element have non bonding electrons.

e.g., Saturated halide, CH_3Cl

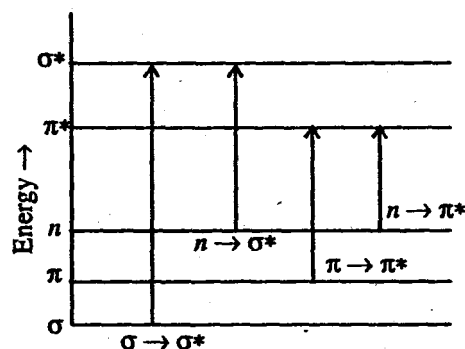
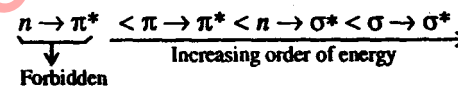
Alcohols, ether, aldehyde, ketone, amine

3. **$\pi - \pi^*$ transition :** This type of transition takes place in saturated compounds containing double or triple bond. Aromatic compounds also exhibit this type of transition. $\pi - \pi^*$ transition requires less energy. Simple chromophores having multiple bonded units like $> \text{C} = \text{C} <$, $\text{C} \equiv \text{C} - \text{C} \equiv \text{C} -$, $-\text{C} \equiv \text{N}$, $-\text{N} = \text{N} <$, $> \text{C} = \text{O}$ undergo $\pi - \pi^*$ transition, e.g., ethylene ($\text{H}_2\text{C} = \text{CH}_2$) shows an intense band at 174 nm and weak band at 200 nm due to $\pi - \pi^*$ transition.

4. **$n \rightarrow \pi^*$ transition :** This type of transition occurs in compounds containing non-bonding electrons on hetero atom. The electron gets excited to π^* antibonding orbital. This type of transition requires least energy and hence occurs at longer wavelength. e.g., aldehyde and ketone exhibit this type of transition.

$\begin{matrix} \text{R} \\ \diagup \\ \text{C} = \text{O} \\ \diagdown \\ \text{R} \end{matrix}$ this saturated aldehyde show both types of transition, i.e., $n - \pi^*$ (λ_{max} 290 nm) and $\pi - \pi^*$ (λ_{max} 180 nm)

Out of these transition $n - \pi^*$ transition is forbidden according to selection rule and the increasing order of energy of various transitions are given below (Fig.)



- (b) Write the various regions in IR spectrum. Discuss the fingerprint region. Determine the structure of the compound, $\text{C}_3\text{H}_6\text{O}$ showing the following absorption bands in IR spectrum; (i) 2950 cm^{-1} and (ii) 1720 cm^{-1} . The compound gives negative test with Tollen's reagent.

Ans. The entire IR-region is divided into two broad regions :

- (i) Functional group region
- (ii) Finger Print region.

Finger Print region : The region below 1500 cm^{-1} is very useful for establishing the identity of a compound. Two identical compounds under similar conditions and their same medium, differ in their IR spectra in the region below 1500 cm^{-1} and hence can be identified easily. The region below 1500 cm^{-1} is

- (a) Rich in many absorptions caused by bending vibration. Rich in many absorptions resulting from the stretching vibrations of C – C, C – O and C – N bonds.
- (c) Rich in absorption bands and shoulder's because the number of bending vibration is usually more than the number of stretching vibrations. Therefore it is called finger print region.

(i) At 2950 cm^{-1} , C–H stretching

(ii) At 1720 cm^{-1} , $\text{C}=\text{O}$ stretching vibration of saturated ketones.

So the structure will $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$ (Acetone)

It also shows –ve tollens reagent test.

4. Attempt any one of the following :

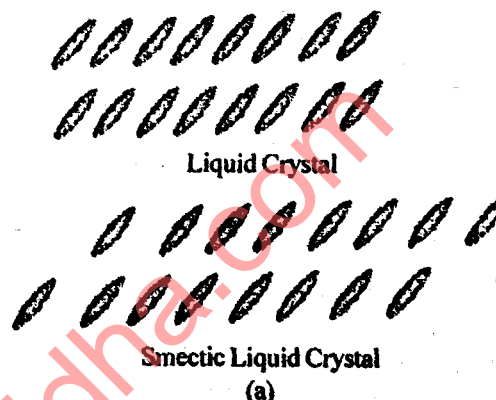
- (a) Describe the various types of liquid crystals. Distinguish between nematic and smectic liquid crystals.

Ans. Types of Liquid Crystals : The various types of liquid crystals are :

- (i) **Smectic (Soap like) liquid crystals :** It is the type of liquid crystal in which the molecules maintain the general orientational order (tendency of molecules to align along the director on long-range basis) as well as they tend to align themselves in layers or planes, i.e., positional order.

Therefore smectic liquid crystals flow in layers. The layers are held together by weak inter layer forces and hence they flow past each other. In deformed state also they still contain the lattice. X-ray diffraction of such crystals confirms the existence of layers (Fig.)

Example : Cholesteryl mylistate have more than one smectic phase.



- (ii) **Nematic (thread like) liquid crystal :** Nematic liquid crystals contain thread like textures. With no positional order (translational symmetry) but tend to point along the direction i.e., parallel to the director.



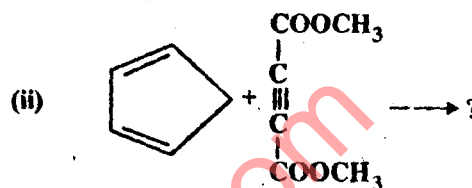
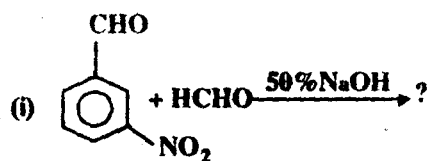
When an external electric or magnetic field is applied, the molecules orient themselves in one direction and it becomes clear (Fig. b)

Nematic phase is less ordered than the smectic phase.

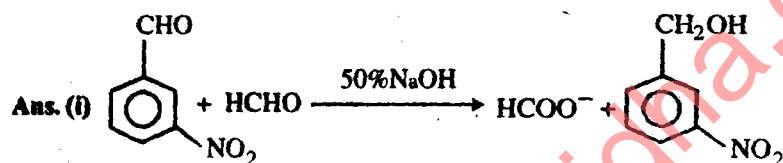
Example : p-methoxy cinamic acid.

Applications of Liquids Crystals :

- (i) In LCD (Liquid crystal display) devices (LCD projector, LCD TV. etc.)
- (ii) As lubricant.
- (iii) In thermography for detecting tumors.
- (iv) In liquid crystal thermometers for measuring skin temperature.
- (b) Complete the following reactions and write their mechanism.

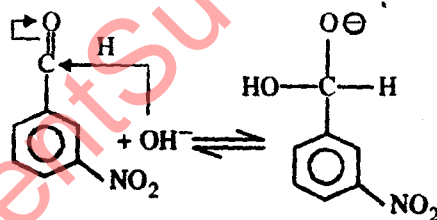


Write one application of the above named reactions.

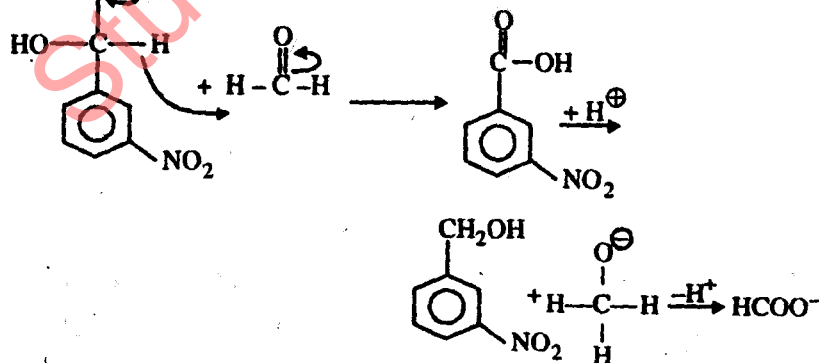


Mechanism :

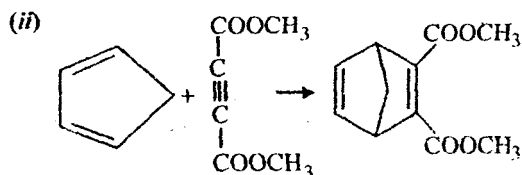
Step (I)



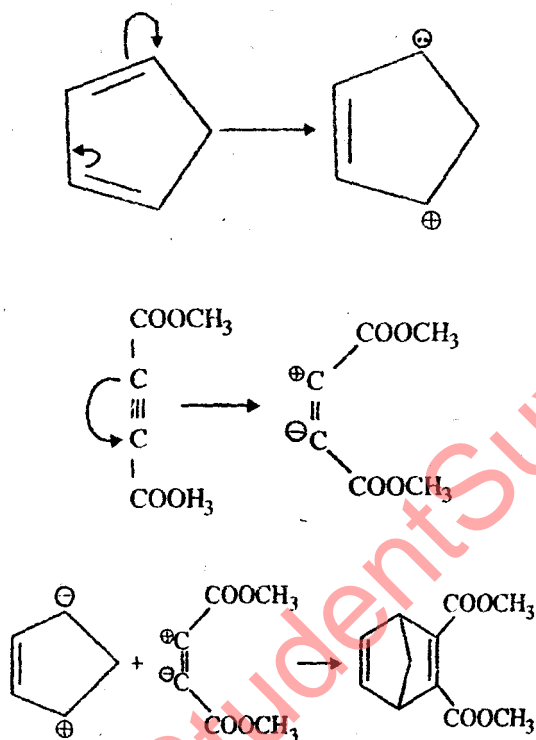
Step (II)



Application : Product of cannizzaran reaction (tetranitrate) is used as vasodilator and an explosive.



Mechanism:



5. Attempt any one of the following :

- (a) Explain the terms: component, phase and degree of freedom with the help of phase diagram of water. Calculate the degree of freedom at triple point.

Ans. Phase: A phase is chemically homogeneous, physically distinct and mathematically separable part of a system. It is denoted by 'P'.

Component : The minimum number of chemical constituents taking part in equilibrium by means of which composition of each phase can be expressed either directly or by means of a chemical equation is known as component. It is denoted by 'C'

e.g., $\text{Ice}(s) \rightleftharpoons \text{water}(L) \rightleftharpoons \text{vapour}(g)$

Water is one component system because the composition of each phase namely Ice, water and vapour can be expressed in terms of only one constituent H_2O . Hence water system is a three phase and one component system.

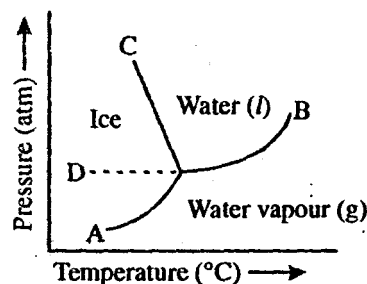
Degree of Freedom : Degree of freedom of a system at equilibrium is the minimum number of variables such as pressure, temperature & concentration on which must be specified in order to define the system completely denoted by (F).

Phase Rule: Phase rule may be stated as: when the equilibrium between any number of phase is influenced only by temperature, pressure and concentration but not influenced by gravity, or electrical or magnetic forces or by surface action then the number of degrees of freedom (F) of system is related to the number of components (C) and of phases (P) by the phase rule equation

$$F = C - P + 2$$

Water system (Phase Diagram)

The Water System: In this case water is the only chemical compound involved hence, $C = 1$; water can exist in three phase viz. solid, liquid and vapour. The phase which are in equilibria can be one, two, three.



In *One-phase equilibria*, only one phase exists solid (Area on the left of the curve *AOC*), liquid (Area between *OC* and *OB*) and vapour (Area below the curve *AOB*).

Here $P = 1$

$$\therefore F = C - P + 2$$

$$\Rightarrow = 1 - 1 + 2 = 2$$

System is bivariant and both T and P must be specified to define the state of the system.

In *two phase equilibria*, two phases are in equilibrium and they can be

Solid \rightleftharpoons Liquid (along *OC*)

Solid \rightleftharpoons Vapour (along *AO*)

Liquid \rightleftharpoons Vapour (along *OB*)

Here $p = 2$

$$\therefore F = C - P + 2 = 1 - 2 + 2 = 1$$

Then, system is univariant only one variable is sufficient to completely describe the state of the system.

In *three-phase equilibria*, three phases are in equilibrium

Solid \rightleftharpoons Liquid \rightleftharpoons Vapour

Here $P = 3$

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

Then, system is therefore invariant at the triple point O (0.0098°C and 4.58 mm Hg).

It is clear that for water system, the maximum value of F is two. Therefore, such a system can be represented completely by a pressure-temperature diagram, as shown in figure.

Curve OA: Along *OA*, Ice \rightleftharpoons Water vapour.

This curve is known as sublimation curve of ice. This curve *OA* starts from point O and should extend up to the absolute zero of temperature.

Curve OB: Along the curve *OB*, Water (l) \rightleftharpoons Water vapour (g)

This curve is known as vapour pressure curve of water. With rise of temperature, the vapour pressure increase. For any given vapour pressure on the vice versa. Above the curve *OB*, liquid is stable phase while below it vapour is the stable phase. The curve *OB* extends up to the critical point of water and below liquid phases are no longer distinguishable from each other.

Curve OC: Along the curve *OC*, Ice \rightleftharpoons Water (l).

This curve is known as freezing point curve of ice and indicates the influence of pressure on the melting point of ice. The slope of the curve *OC* is negative which implies that ice melts with a decrease in volume.

Metastable curve OD: The Curve *OD* is a continuation of curve *BO*. The curve *OD* represents water (l) and water (Vapour) phase in *metastable equilibrium*. It is sometimes Possible to cool liquid water below the point O without solidification as is shown by the dotted curve *OD*. The liquid below the freezing point is in the super cooled state which is not quite stable and is known as *metastable state*. The metastable state is spontaneously converted into stable state by the addition of a small amount of stable phase.

The point O: The point O is called the triple point because at this point all the, three phase, ice, water (l) and water (v) coexist in equilibrium. System is invariant at triple point (since $F = 0$). If either the temperature or the pressure or both are changed, the three phases would not longer coexist and at least one of them would disappear.

(b) Differentiate between addition and condensation polymers. Identify the monomers in the compounds: Neoprene; Dacron; Nylon 6, 6; Polytetrafluoroethylene (PTFE). And also explain conducting polymers with their applications.

Ans. Difference between Addition and Condensation polymerisation.

Addition polymerisation

1. The process of polymerisation in which monomers undergo polymerisation to form polymer without elimination of any atom or group is known as addition polymerisation.
2. Only one type of monomers are generally involved.
3. The molecular formula of repeating unit is exactly same as that of the starting monomer.
4. Molecular weight of the polymeric disperse rises at once.
5. Alkenes and their derivatives are generally used as monomers.
6. This is also known as chain reaction polymerisation.
7. Initiator is needed.
8. Addition polymerisation gives rise to homopolymers.
9. Example: PE, PVC, PMMA etc.

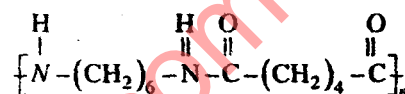
Condensation Polymerisation

1. The process of polymerisation in which monomers undergo polymerisation to form polymer with elimination of small molecules like NH_3 , H_2O , CH_3OH etc. is known as condensation polymerisation.
2. More than one type of monomers are generally involved.
3. The molecular formula of repeating unit is different from that of starting monomer.
4. Molecular weight of the polymeric disperse rises steadily throughout the process of polymerisation.
5. Bifunctional monomers are generally used as monomers e.g., adipic acid, hexamethylene diamine.
6. This is also known as step growth polymerisation.

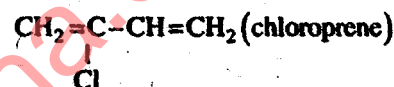
7. No initiator required.
8. Generally copolymers are formed.
9. Example: Nylon 6,6; Bakelite etc.

Polytetrafluoroethylene (PTFE) : It is addition polymer whose monomer is $(\text{CF}_2 = \text{CF}_2)$ and structure is $\{\text{CF}_2 - \text{CF}_2\}_n$

Nylon 6,6 : It is condensation polymer with monomer $\text{H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2$ and its structure is



Neoprene : It is homopolymer. Its monomer is



and its structure is $\left[\text{CH}_2 - \underset{\text{Cl}}{\underset{|}{\text{C}}} = \text{CH} - \text{CH}_2 \right]_n$

Conducting Polymers : Polymers, in general, are bad conductor of electricity and hence some of them find applications in electrical insulations. The poor conductivity of polymers may be attributed to the non-availability of large number of free electrons required for conduction. The electrical conductivity of some polymers/metals is summarised in the table.

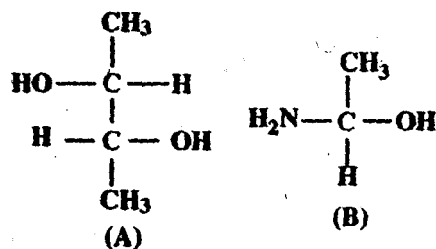
Table

Polymers	Conductivity (Seimen cm^{-1}) (S cm^{-1})
Teflon (excellent insulator)	10^{-18}
Polyethylene	10^{-22}
Polyacetylene (doped)	1.5×10^5
Polythiophene (doped)	10^4
Polypyrrole (doped)	$5 \times 10^2 - 7.5 \times 10^3$
Copper	6×10^5
Silver	10^6

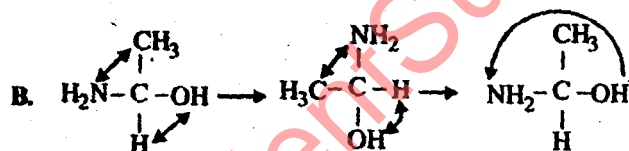
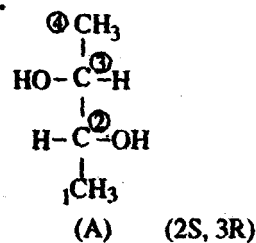
In recent years, polymers with electrical conductivities comparable with metals has been synthesised "A polymer which can conduct electricity is known as conducting polymer."

6. Attempt any one of the following :

(a) (i) Assign (R) or (S) configuration to the following compounds:

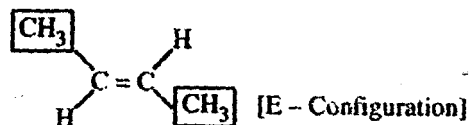
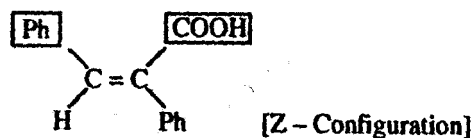


Ans. A.

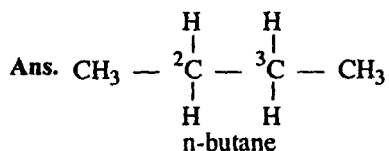


(ii) Assign E or Z configuration to the following compounds :

Ans. Assign in E or Z configuration



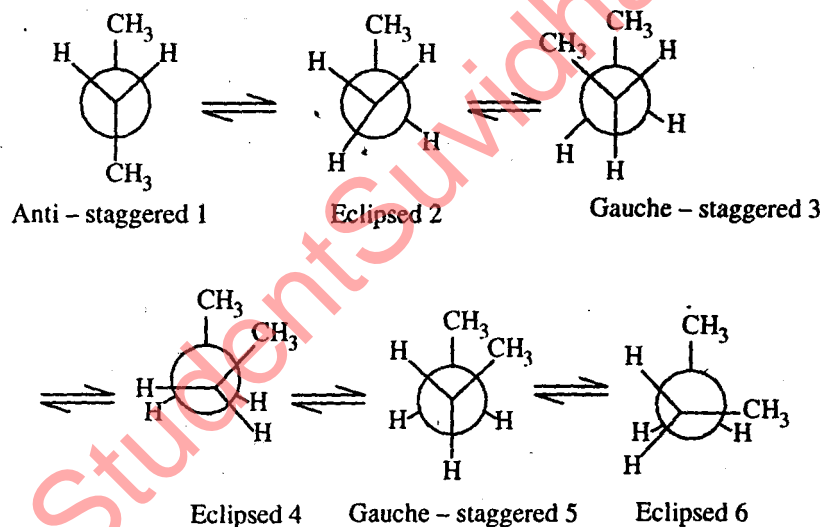
(iii) Describe the conformational isomers of n-Butane.



The middle C–C single bond in n-butane is similar to ethane but one hydrogen atom at each carbon atom is replaced by $-\text{CH}_3$. The rotation about C–2 and C–3 single bonds gives many conformations of normal butane.

1. The staggered conformation in which the $-\text{CH}_3$ groups are as far apart as possible is known as anti or trans conformation. It is the most stable conformation.
2. The staggered in which two methyl groups only 60° apart is known as Gauche conformation.
3. The other possible conformation is the eclipsed conformation, in which eclipsing occurs between hydrogen atoms and methyl group.

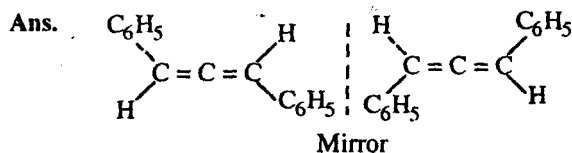
The various conformations of n-butane is shown in the following figure.



(iv) The following compounds are optically active or not? Explain.

(A) 1,3-Diphenyl propadiene

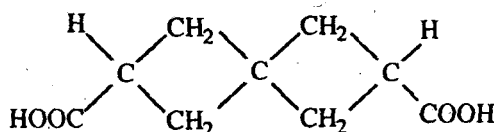
(B) 1,7-Dicarboxylspirocycloheptane



Non-Superimposable mirror image 1,3 diphenyl propadiene

Two p-orbitals of central carbon atom form π bonds with the p-orbitals of the terminal carbon atoms. These π -bonds are perpendicular to each other. The substituent at one end of the molecule are in a plane which is perpendicular to that of the substituent at the other end so that the compound exists in two forms which are non-superimposable mirror images and are optically active.

(B) 1,7-Dicarboxylspirocycloheptane :



The condition for chirality in spirans are quite analogous to those in allenes since here the two rings are perpendicular to each other, and hence suitable substitution of either of the system or within the ring will make the molecule dissymmetric and optically active.

(b) Deduce the kinetic equation for the reaction of the first order. A first order reaction is 25% completed in 30 min. Calculate (i) rate constant (ii) half life time and (iii) time required for 75% of the reaction to be completed.

Ans. Let us consider a general first order reaction A \rightarrow Product

Initially $t=0$, a 0

At time t. a-x x

$$\therefore \frac{dx}{dt} K_1 (a-x)$$

$$\text{or } \frac{dx}{dt} k_1 (a-x) \quad [K_1 = \text{rate constant}]$$

$$\text{or } \int \frac{dx}{a-x} = \int K_1 dt$$

$$-\log (a-x) = K_1 t + c \quad \dots(1)$$

$$\text{at } t=0, x=0$$

$$-\log a = C$$

Putting the value of C in eqn (1)

$$-\log (a-x) = K_1 t - \log a$$

$$K_1 = \frac{1}{t} \log \left(\frac{a}{a-x} \right)$$

or

$$K_1 = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

Above in the expression for the first order rate constant.

Give $t = 30$ min, reaction 25% complete, so initial concentration = a,

$$(a-x) = (a - 0.25a) = 0.75a$$

$$K_1 = \frac{2.303}{30} \log \frac{a \times 10}{75a}$$

$$K_1 = \frac{2.303}{30} \log \frac{4}{3}$$

$$K_1 = \frac{2.303}{30} (\log 4 - \log 3)$$

$$(ii) t_{1/2} = \frac{0.693}{K_1}$$

$$(iii) t = \frac{2.303}{K_1} \log \frac{a}{a-x}$$

Initial concentration = a

$$a-x = a - 0.75a = 0.25a$$

$$t = \frac{2.303}{K_1} \log \frac{a}{0.25a}$$

7. Attempt any one of the following :

(a) (i) Write the relationship between high and low calorific values. If HCV of a coal sample is 7500 cal/g and % H = 5.

Calculate is LCV. Given; latent heat of condensation of steam = 580 cal/g.

Ans. Relationship between LCV & HCV : Lower calorific value (LCV) = HCV – Latent heat of water vapour formed

$$\text{Also, } LCV = HCV - \frac{H}{100} \times 9 \times 587$$

$$\text{or } LCV = HCV - 0.09 \times H \times 587 \text{ Cal/gm or } \frac{\text{Kcal}}{\text{Kg}}$$

where,

H = percentage of hydrogen present in the fuel.

587 = Latent heat of condensation of steam.

Numerical Part :

Given HCV = 7500 Cal/gm

% H = 5

Latent Heat of condensation = 580 Cal/gm

$$\therefore LCV = (7500 - 0.09 \times 5 \times 580) \text{ Cal/gm}$$

$$\text{or } LCV = 7239 \text{ Cal/gm}$$

(ii) Discuss the problems created by hard water in boiler. A sample of hard water has a hardness 500 ppm. Express the hardness in °French and °Clark.

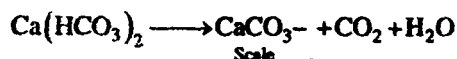
Ans. Problems created by Hard water in boiler : If hard water is fed directly into the boilers, it may lead to the following problem.

1. Scale and sludge formation.
 2. Caustic embrittlement.
 3. Boiler corrosion.
 4. Priming and foaming
1. **Scale & Sludge :** If precipitate formed is soft, loose and floats in boiler water, it is called sludge.
- Scale :** "Scales are the hard deposits firmly sticking on the inner wall of the boiler and can't be removed easily by scrapping." They may be formed in boilers due to following reasons :

(i) Hydrolysis of magnesium salts :



(ii) Decomposition of calcium bicarbonate



(iii) On continuous heating CaSO_4 present in hard water gets precipitated as hard scale.

(iv) If silica is present in small amount in water it may form calcium silicate (CaSiO_3) and magnesium silicate (MgSiO_3) scales which adhere very firmly to the inner walls of the boiler. Scales are generally removed by chemical reactions.

Disadvantages of sludge formation

- (i) Sludges are bad conductor of heat and hence a portion of heat generated is wasted which decreases the efficiency of boiler.
- (ii) Excessive sludge may cause choking of pipe in the region where there is less water circulation.

Prevention of sludge formation : Formation of sludges can be prevented by frequent blow down operation (which consist of removal of a portion of concentrated water from boiler and replacing it with fresh water.)

Disadvantages of scale formation

- (i) **Wastages of fuel :** Scales are bad conductor of heat which considerably reduces the heat transfer from boiler to inside water. Therefore water has to be heated at higher temperature continuously, which increases the fuel consumption.
- (ii) **Decrease in efficiency :** Sometime scales are deposited in the valves and condensers of the boiler choking them partially. It reduces the water circulation thereby impairing the efficiency of boiler.

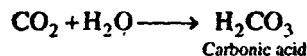
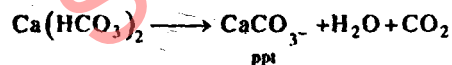
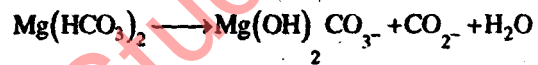
(iii) **Lowering of boiler safety:** Scale being bad conductor of heat prevents efficient heat transfer from boiler to inside water. Hence boiler has to be overheated in order to maintain a constant supply of steam. The overheating makes the boiler material softer and weaker and boiler becomes unsafe to bear the pressure of steam particularly at high pressure.

(iv) **Danger of explosion :** On overheating thick scales crack due to uneven expansion. Water comes suddenly in contact with overheated metal and large quantity of steam is formed instantaneously. This leads to development of very high pressure which may cause explosion of boiler.

2. **Boiler Corrosion :** "Loss of boiler body material or its, useful properties by chemical or electrochemical interaction with its environment is known as boiler corrosion."

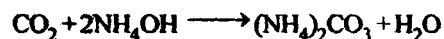
Corrosion in boiler may be due to the following reasons :

(i) **Dissolved carbon dioxide :** CO_2 gas dissolved in water forms carbonic acid which has a corrosive effect on boiler material like any other acid. CO_2 is also produced in water by the decomposition of bicarbonates.



Removal: Carbon dioxide can be removed,

(a) By addition of calculated amount of ammonium hydroxide (NH_4OH)



(b) By mechanical deaeration along with oxygen.

3. **Caustic Embrittlement :** "Caustic embrittlement is a type of boiler corrosion due to which boiler material becomes brittle in presence of high concentration of caustic and static tensile stress (thermal stress). It is characterised by the formation of intergranular cracks on the boiler metal particularly at places of high stress like bends, joints, riveted seams etc.

4. **Priming and Foaming:** As steam rises from the surface of boiling water in boiler, it may be associated with small droplets of water. Steam containing liquid water is called wet steam. "The process of wet steam formation is known as priming". Priming is mainly attributed to the presence of

1. Suspended impurities and to some extent to dissolve some impurities in water.

2. Sudden boiling

3. High steam velocity

4. Faulty boiler design

Priming can be minimised by:

1. Proper designing

2. Maintaining low water levels

3. Controlled rate of steam velocity

4. Efficient softening.

"The formation of persistent bubbles in boiler which do not break easily is known as foaming."

Foaming is generally caused by the presence of oils and alkalis in water.

Clay or organic matter in raw water, oil and grease in condensed make up water and finely divided particles of sludge may also cause foaming.

Foaming can be minimised by :

1. Removal of foaming agent like oil, grease from boiler water.

2. Addition of castor oil and antifoaming chemical.

Numerical part :-

Hardness of sample = 500 ppm

We know that

1 ppm = 0.1 French = 0.07° Clark

$\therefore 500 \text{ ppm} = 500 \times 0.1^{\circ} \text{ French}$
 $= 50^{\circ} \text{ French}$

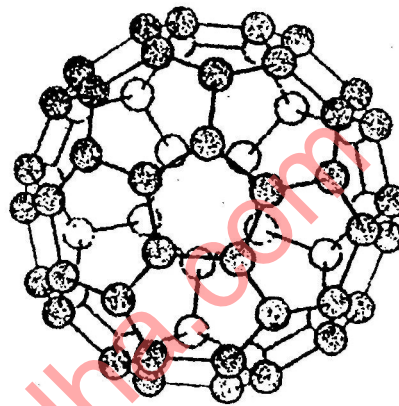
Also $500 \text{ ppm} = 500 \times 0.07^{\circ} \text{ Clark}$
 $= 35^{\circ} \text{ Clark}$

(b) What are fullerenes? Discuss their applications.

Ans. Fullerenes : "The phenomenon of existence of an element in two or more solid modifications is known as allotropy and the solid modifications are known as allotropes." Diamond and graphites are two important allotropes of carbon.

In 1985, a new allotropic form of carbon (C_{60}) was discovered by Engineer and Architect Richard Buckminster Fuller. C_{60} exists as discrete molecule consisting of clusters of carbon atoms. Apart from C_{60} , some other discrete molecules with clusters of carbon atoms like C_{32} , C_{50} , C_{70} have also been isolated. These allotropes are collectively known as "fullerenes" C_{60} is also known as "Buckminster fullerene."

Unlike carbon and graphite, fullerenes have definite molecular formula. C_{60} has the most symmetrical 'Soccer ball' shaped structure (a bucky ball) as shown in the Fig. It contains 20 six-membered rings and 12 five membered rings.



C_{60} buckminster fullerene

Applications : Applications of fullerenes are

1. Making super conductors
2. Making soft ferromagnets
3. Making Electronic devices and optical (non-linear) devices.