B.TECH.　EAS-102

ENGINEERING CHEMISTRY - I

Time : 3 Hours　　　　　　　　　　　*Total Marks : 100*

SECTION – A

Q.1. Choose/Fill Correct answer (20×1=20)

(*i*) Which of the following has a bond order of 2.5?

(a) CO　　　　(b) NO

(c) He^{2+}　　　(d) O_2^-

Ans. (b) NO

(*ii*) Hydrogen bonding is maximum in

(a) Ethyl chloride　(b) Ethanol

(c) Diethyl ether　(d) Triethyl amine

Ans. (b) Ethanol

(*iii*) A zero order reaction is one

(a) in which rate is independent of reactants concentration

(b) in which one of the reactants is in large excess

(c) whose rate is not affected by time

(d) whose rate increases with time.

Ans. (a) in which rate is independent of reactants concentration

(*iv*) Rusting of iron is

(a) Enhanced by dry air

(b) Prevented by cleaning

(c) Retarted in the presence of dissolved salts.

(d) Prevented if the article is connected with a piece of Mg.

Ans. (a) Enhanced by dry air

(*v*) The most stable carbanion is

(a) methyl carbanion

(b) primary carbanion

(c) secondary carbanion

(d) tertiary carbanion

Ans. (a) methyl carbanion

(*vi*) Chiral molecules are those which are

(a) not superimposable on their mirror image

(b) are superimposable on their mirror image

(c) show geometrical isomerism

(d) unstable molecules.

Ans. (a) not superimposable on their mirror image

(*vii*) Bakelite is

(a) gel　　　　(b) solid

(c) liquid　　　(d) gas

Ans. (b) solid

(*viii*) The vulcanized rubber contains

(a) sulphur　　(b) iron

(c) beryllium　(d) zinc

Ans. (a) sulphur

(*ix*) Presence of fuctional group in a compound can be established by using

(a) Chromatography

(b) Mass spectroscopy

(c) IR.spectroscopy

(d) X-rays diffraction

Ans. (a) Chromatography

(x) Which indicator have pH range of 8.3-10

    (a) Phenolphthalein   (b) methyl red

    (c) methyl orange   (d) none of these

Ans. (a) Phenolphthalein

(xi) Fill in the blanks:

    (i) Hydrogen bond is a _____ than a covalent bond.

Ans. weaker

    (ii) Graphite is an _____ of carbon.

Ans. allotrope

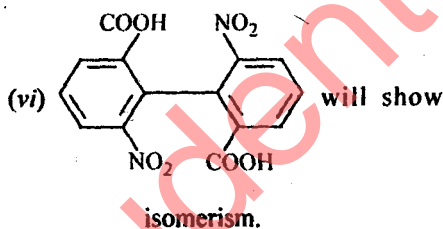   (iii) An atom at the corner of a cubic unit cell makes _____ contribution to particular unit cell.

Ans. 1/8

    (iv) The degree of freedom of a triple point is _____.

Ans. zero

    (v) _____ is electrochemical disintegration of a metal.

Ans. corrosion

    (vi) will show _____ isomerism.

Ans. geometric

    (vii) In cannizzaro reaction aldehyde must consist of _____.

Ans. no. of α-hydrogen

    (viii) The monomer of natural rubber is _____.

Ans. isoprene $\left(H_2C = C - HC = CH_2 \atop \qquad | \atop \qquad CH_3 \right)$

    (ix) The main component of biogas is _____.

Ans. CH_4

(x) Hardness of water is expressed in terms of equivalent of _____.

Ans. $CaCO_3$

SECTION—B

Q.2. Attempt any three of the following:

$$(10 \times 3 = 30)$$

(i)   **(a)** What is metallic bond? Explain it on the basis of bond theory.

Ans. Metallic Bond: "Metals are the elements having strong tendency to loose the electron and hence to form cations."

$$\underset{(metal)}{M} \longrightarrow M^{+n} + ne$$

"The force of attraction that binds a metal ion to a number of electrons within its sphere of influence is known as metallic bond."

Molecular orbital theory of metallic bond: Please see Q.No. 1(b) of Ist Semester 2001-02.

(i)   **(b)** A unit cell of sodium chloride has four formula units. The edge length of unit cell is 0.564. What is the density of sodium chloride?

Ans. NaCl has F.C.C. crystal structure. It has four formula units, it means there are 4 sodium ions and 4 chloride ions.

No. of effective atoms per unit cell in FCC structure,

$$N_e = \left(\frac{8}{8} + \frac{6}{2} \right) = 4$$

Molecular weight of NaCl = At weight of Na + At. weight of Cl

    $Aw = 23 + 35.5 = 58.5$ grams

Edge length of unit cell, $a = 0.564$

Note: Here unit of edge is not given. From

    $a = 5.63$ Å

On standard books, it is

    $a = 0.563$ Å

or $\quad a = 5.63 \times 10^{-10}$ m

Volume $V = a^3$

$$\text{Density } \rho = \left(\frac{\text{Mass of unit cell (M)}}{\text{Volume of unit cell}} \right)$$

where $\qquad M = m \cdot Ne \qquad\qquad$ {where m = Mass of one atom}

and $\qquad m = \left(\dfrac{\text{Atomic weight}}{\text{Avogadro's number}} \right) = \dfrac{Aw}{NA}$

$\therefore \qquad \rho = \left(\dfrac{Aw \times Ne}{N_A \cdot a^3} \right) = \dfrac{58.5 \times 4}{6.023 \times 10^{23} \times (5.63 \times 10^{-10})^3}$

$$\rho = \frac{0.218 \times 1}{10^{23} \times 10^{-30}} \, g/m^3 = \frac{0.218 \times 10^7 \, g}{m^3}$$

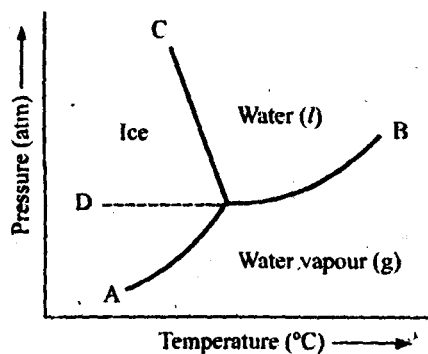or $\qquad \rho = 0.2180 \times 10^4$ kg/m^3

$\Rightarrow \qquad\quad = 2180$ kg/m^3

(ii) **State and explain phase rule. Discuss the salient features of phase diagram of water system.**

Ans. Phase Rule: Phase rule may be state as: When the equilibrium between any number of phases is influenced only by tempere. 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 componants (C) and of phases (P) by the phase rule equation

$$F = C - P + 2$$

Water System (Phase Diagram)

The Phase diagram for water system

The Water System: In this case water is the only chemical compound involved whence, $C = 1$, Water can exist in three phase viz. solid, liquid and vapour. The phases which are in equilibria can be one, two and 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 $\rightleftharpoons$ Vapor (along OB)

Here $P = 2$

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

Then, system is univariant and 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 increases. For any given vapour pressure on the curve there is only one value of the temperature and 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 the 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) phases 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 phases, 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

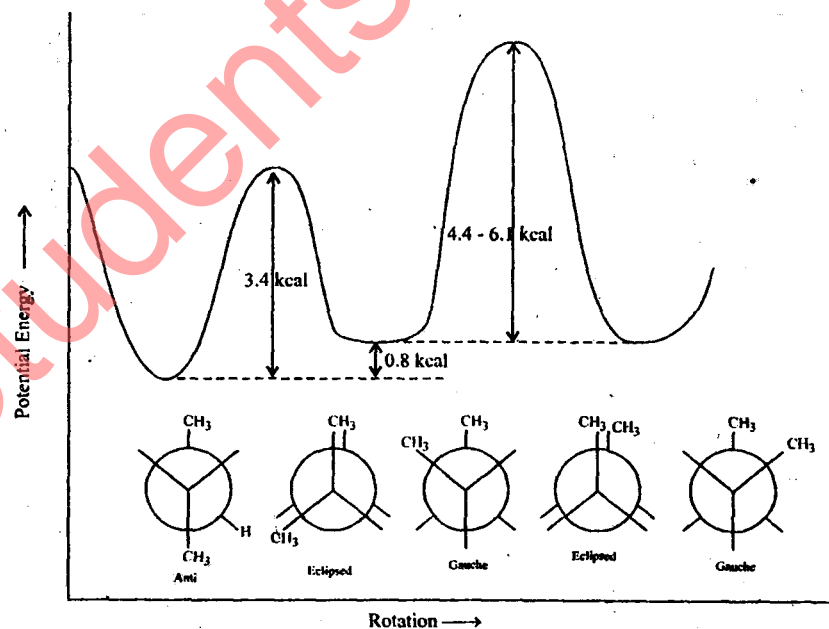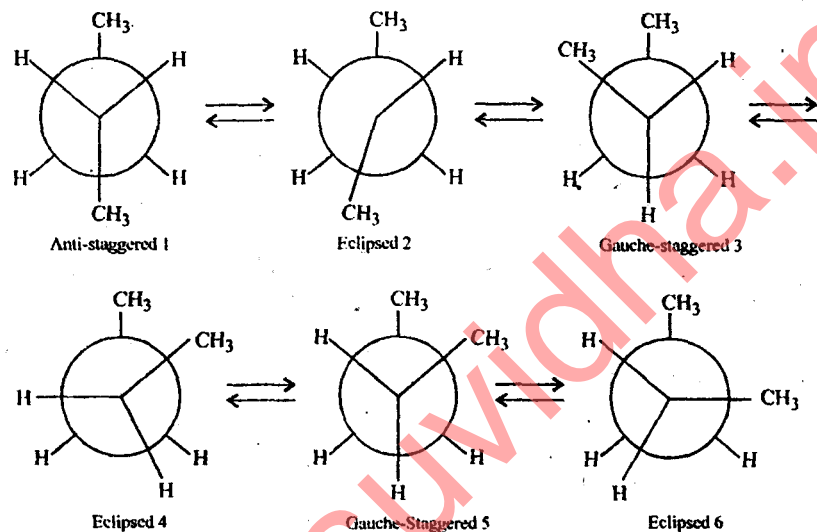longer coexist and at least one of them would disappear.

(iii) **(a)** **Describe the conformational isomers of n-butane.**

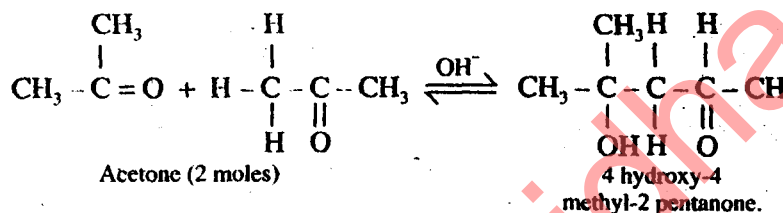**(b)** **Write the mechanism of the following reactions:**

(i) Aldol condenstion

(ii) Beckmann rearrangement

Ans. (a) Conformation of *n*-butane:

Anti-staggered 1   Eclipsed 2   Gauche-staggered 3

Eclipsed 4   Gauche-Staggered 5   Eclipsed 6

Potential Energy →

3.4 kcal

4.4 - 6.1 kcal

0.8 kcal

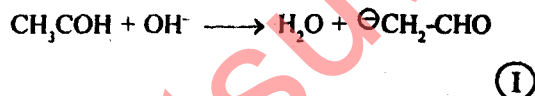Anti   Eclipsed   Gauche   Eclipsed   Gauche

Rotation →

(b) (i) Aldol condenstion: Aldol condensation : Condensation between two molecules of an aldehyde or a ketone to form β-hydroxy aldehyde or a β-hydroxy ketone.
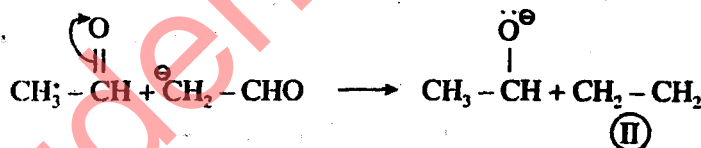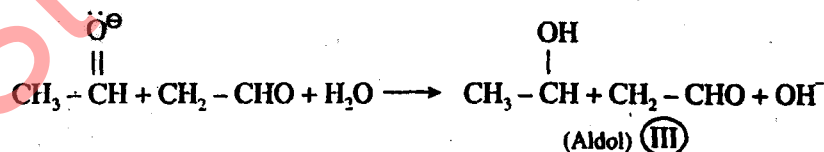
$$\underset{\text{Acetaldehyde (2 moles)}}{\overset{\overset{H}{|}}{CH_3 - C = O} + \overset{H\quad H}{\underset{\overset{|}{H}}{H - \overset{|}{C} - \overset{|}{C} = O}}} \quad \overset{OH^-}{\rightleftharpoons} \quad \underset{\substack{\text{(Aldol)}\\(\beta\text{-hydroxy butyraldehyde})}}{\overset{H\quad H\quad H}{CH_3 - \underset{\underset{OH}{|}}{\overset{|}{C}} - \underset{\underset{H}{|}}{\overset{|}{C}} - \overset{|}{C} = O}}$$

$$\underset{\text{Acetone (2 moles)}}{\overset{\overset{CH_3}{|}}{CH_3 - C = O} + \overset{H}{\underset{\overset{||}{O}}{H - \underset{\overset{|}{H}}{\overset{|}{C}} - C - CH_3}}} \quad \overset{OH^-}{\rightleftharpoons} \quad \underset{\substack{\text{4 hydroxy-4}\\\text{methyl-2 pentanone.}}}{\overset{CH_3 H\quad H}{CH_3 - \underset{\underset{OH}{|}}{\overset{|}{C}} - \underset{\underset{H}{|}}{\overset{|}{C}} - \underset{\overset{||}{O}}{C} - CH}}$$

Mechanism. It takes three steps.

1st step. First step of the reaction is the formation of resonance stabilised carbanions.

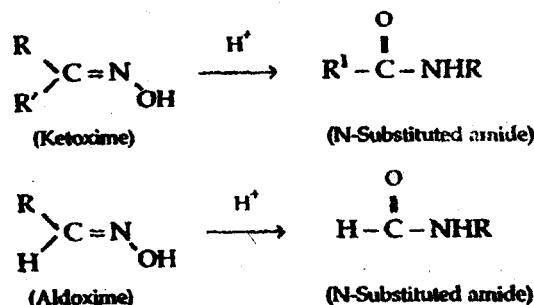$$CH_3COH + OH^- \longrightarrow H_2O + {}^{\ominus}CH_2\text{-}CHO \qquad \text{①}$$

II step. Carbanions attack on the carbonyl group of second aldehyde molecule to form an addition product an alkoxide.

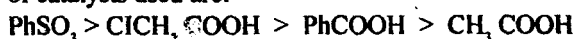$$\overset{\curvearrowright O}{CH_3 - \overset{||}{CH}} + {}^{\ominus}CH_2 - CHO \longrightarrow CH_3 - \overset{\overset{..}{O}{}^{\ominus}}{\underset{|}{CH}} + CH_2 - CH_2 \qquad \text{②}$$

III step. Alkoxide II, abstract a hydrogen ion form water to form β-hydroxy aldehyde (aldol) III

$$CH_3 - \overset{\overset{..}{O}{}^{\ominus}}{\overset{||}{CH}} + CH_2 - CHO + H_2O \longrightarrow CH_3 - \overset{OH}{\underset{|}{CH}} + CH_2 - CHO + OH^- \\ \underset{\text{(Aldol) ③}}{}$$
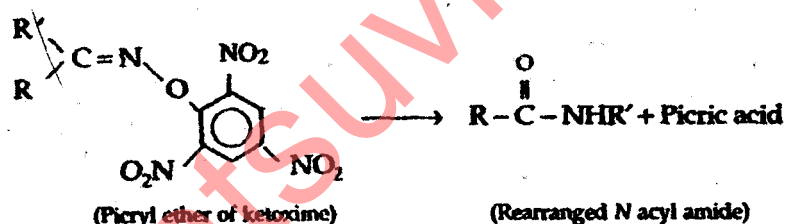
(ii) Beckmann rearrangement: Beckmann rearrangement is the acid-catalysed conversion of ketorimes to *N*-substituted acid amides. Few aldoximes can also undergo rearrangement under these conditions.
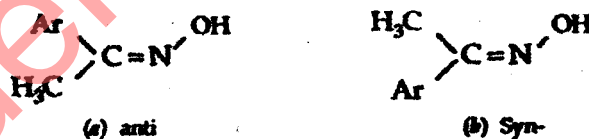
$$\underset{R'}{\overset{R}{\diagdown}} C = N \overset{}{\diagdown} OH \xrightarrow{H^+} \overset{\overset{O}{\|}}{R^1 - C - NHR}$$

(Ketoxime)   (N-Substituted amide)

$$\underset{H}{\overset{R}{\diagdown}} C = N \overset{}{\diagdown} OH \xrightarrow{H^+} \overset{\overset{O}{\|}}{H - C - NHR}$$

(Aldoxime)   (N-Substituted amide)

The rearrangement is catalysed by many acidic reagents such as sulfuric acid (H_2SO_4), thionyl chloride ($SOCl_2$), phosphorus pentachloride (PCl_5), phosphorus pentaoxides (P_2O_5) etc. The role of catalyst is to convert the – OH of the oxime (which by itself is a very poor leaving group) into a better leaving group. Thus, if a stronger acid is used as a catalyst, rearrangement is faster. The reactivity order of catalysts used are:

$PhSO_3 > ClCH_2COOH > PhCOOH > CH_3COOH$

Some of the esters and ethers of oximes also undergo Beckmann rearrangement example, the picryl ether of oxime undergo Beckmann rearrangement to form N-acyl amide. Since picrate is a very good leaving group, catalyst is not required.

(Picryl ether of ketoxime)   (Rearranged N acyl amide)

Oximes exhibit geometrical isomerism, since there is no free rotation about the C = N bond.

(a) anti   (b) Syn-

In the form :

(a) CH_3 and OH are on the opposite side of the double bond, that is they are *anti* to each other. But in the form

(b)   these two groups are *syn* (or *cis*) to each other.

The Beckmann rearrangement is stereo specific as the migration of group from carbon to nitrogen is 'anti'

While

(a)   is subject to Beckmann rearrangement, the prod-uct is $\overset{\overset{O}{\|}}{Ar - C - NHCH_3}$.

(b) would give $\overset{\overset{O}{\|}}{CH_3 - C - NH\,Ar}$.
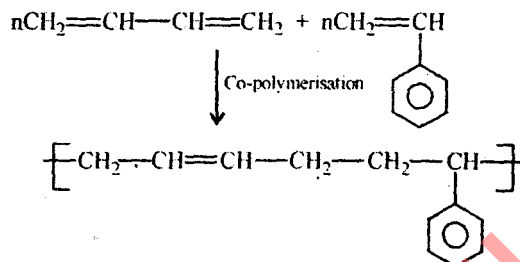
(iv) *(a)* **Describe preparation, properties and application of**

     (i) Buna-S

     (ii) Nylon 6, 6.

Ans. Buna-S: It is produced by copolymerisation.

Preparation: Preparation of 1, 3 butadiene and styrene in the ratio of 3 : 1 in presence of cummene hydroperoxide as catalyst.

$$nCH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}CH$$

Co-polymerisation

$$-[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH]-$$
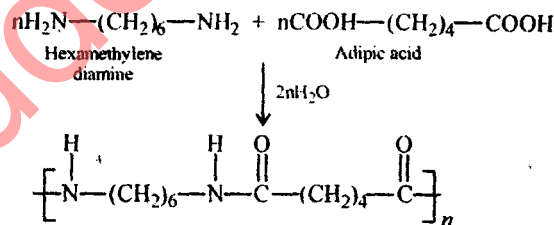
Properties: SBR has the following properties:

(i) High load bearing capacity.

(ii) High abrasion resistance.

(iii) Low oxygen and ozone resistance.

(iv) Swell in oils and solvents.

Application: SBR in used for making:

(i) Shoe soles and foot wear components.

(ii) Floor title

(iii) Wire and cable insulations

Nylon 6'6:

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

$$nH_2N{-}(CH_2)_6{-}NH_2 + nCOOH{-}(CH_2)_4{-}COOH$$

Hexamethylene diamine   Adipic acid

$$2nH_2O$$

$$-\left[\underset{H}{N}{-}(CH_2)_6{-}\underset{H}{N}{-}\underset{O}{C}{-}(CH_2)_4{-}\underset{O}{C}\right]_n$$

Properties: (i) Nylons hae high m.p and posses high temperature stability.

(ii) They have good resistance.

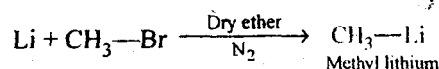(iii) They are resistant to chemicals.

Application: (i) Nylon 6,6 is primarily used for fibres which in-turn is used for making socks, dresses, carpets etc.

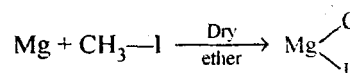(ii) In making filaments for ropes, bristles for brushes tyre cords etc.

    (b) **Discuss general methods for the preparation of organometallic compounds. What are applications of organometallic compound of Mg.**

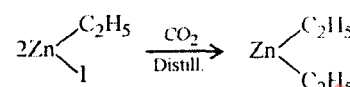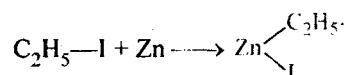**Ans. Methods of Preparation of Organometallic Compound:**

(i) Organolithium compound is prepared by the reaction of alkyl halide with metallic lithium in either. N_2 or He is used to maintain inert atmosphere during the reaction.

$$Li + CH_3—Br \xrightarrow[N_2]{Dry\ ether} \underset{\text{Methyl lithium}}{CH_3—Li}$$

(ii) Grignard reagent (alkyl magniumhalide) is prepared by the action of alkyl halide on Mg-rubbon in presence of dry ether.

$$Mg + CH_3—I \xrightarrow[ether]{Dry} Mg\Big\langle{CH_3 \atop I}$$

(iii) Organozinic compounds are prepared by heating alkyl halide with zinc in the atmosphere of carbon dioxide.

$$C_2H_5—I + Zn \longrightarrow Zn\Big\langle{C_2H_5 \atop I}$$

$$2Zn\Big\langle{C_2H_5 \atop I} \xrightarrow[Distill.]{CO_2} Zn\Big\langle{C_2H_5 \atop C_2H_5} + ZnI_2$$

Application of organometallic compounds:

(i) Synthesis of different class of organic compound.

(ii) In catalysis

(iii) **In Polymerisation:** Zegler Natta catalyst consist of organometallic compound and is widely used as a co-ordination catalyst in the synthesis of a number of polymers.

(v) **(a) What is importance of IR spectroscopy in finger print region?**

Ans. Importance : With the help of finger print region it is possible to distinguish between two chantiomers. It is possible to distinguish the infra red spectra of straight chain alkanes containing 30 carbon atoms or more.

Finger print region can be divided into three regions as follows:

(i) 1500 – 1350 cm^{-1}

(ii) 1350 – 1000 cm^{-1}

(iii) Below 1000 cm^{-1}

(i) **Region: 1500 – 1350 cm^{-1}:** The appearance of doublet near 1380 cm^{-1} (m) and 1365 cm^{-1} shows the presence of certaining butyle group in the compound.

(ii) **Region: 1350 – 1000 cm^{-1}:** All classes of compound viz. alcohols, esters, lactones, acid anhydrides shows characteristic absorptions in this region due to C O steching.

(iii) **Region: Below 1000 cm^{-1}:** At 970 – 960 cm^{-1} (s) distinguish between cis and trans alkenes are possible.

(b) 0.72 g of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3°C to 29.1°C. If the calorimeter contains 250 grams of water and its water equivalent is 150 gram, calculate the HCV of fuel. Give answer in kJ/kg.

Ans. Data Given

Mass of fuel burnt (m) = 0.85 g

Final temperature of calorimeter t_2 = 29.1°C

Initial temperature of calorimeter t_1 = 27.3°C

Mass of water in calorimeter W = 250 g.

Water equivalent of calorimeter ω = 150 g

We know that higher calorific value (HCV) is given by

$$HCV = \frac{(W + \omega)(t_2 - t_1)}{m}\ (\text{cal/g})$$

$$= \frac{(250 + 150)(29.1 - 27.3)}{0.85}$$

$$= \frac{400 \times 1.8}{0.85} = 847.06\ \text{cal/g}$$

$$= 847.06 \times 4.18\ \text{J/g}$$

$$= 847.06 \times 4.18 \times \frac{10^3}{10^3}\ \text{J/g}$$

$$= 3540.7\ \text{kJ/kg}$$

SECTION—C

10×5=50

Q.3. Attempt any ONE part of the following:

(a) Discuss the classification of liquid crystals and write down its applications.

Ans. Classification of liquid crystal: Liquid crystals are classified in two types:

(i) Smectic liquid crystals: It is the type of liquid crystal in which the molecules maitain the general orientational order as well as they lend 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 interlayer forces and hence they flow past each other.

Example: Cholestryl mylistate have more than one smectic phase.

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

Example: p-methoxy cinamic acid.

Application of liquid crystals:

(i) In LCD (liquid crystal displays) devices (LCD projector, LCD TV etc.)
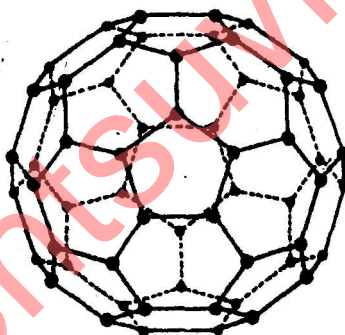
(ii) As lubricant

(*iii*) In thermography for detecting tumours.

(*b*) Describe the preparation, structure and applications of fullerenes.

Ans. Fullerene is an allotrope of carbon. It is a molecule of formula C_{60}. It was discovered by H.W.Kroto and R.Smalley at Rice University, USA in 1985. It is popularly known as Buckminster fullerene in honour of the american architect Buckminster Fuller, who designed geodesic dome structures based on hexagons & pentagons. The shape of C_{60} resembles that of such domes designed by Fuller.

Preparation. Fullerenes are prepared by vaporizing a graphite rod in a helium atmosphere. Mixture of fullerenes like C_{60}, C_{70} etc., are formed which are separated by solvent extraction. Pure C_{60} is isolated from this mixture by column chromatography.

Structure. The C_{60} molecule has a truncated icosahedron structure. An icosahedron is a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. A carbon atom is present at each vertex of this structure. The molecule is aromatic and has several resonance structures. The valencies of each carbon atom are satisfied by two single and one double bond. C_{60} is also known as *buckyball* as it is a spherical cluster of carbon atoms arranged in series of 5-and 6-membered rings to form a soccer ball shape.

Fig. *Structure of a buckyball.*

In the solid state, C_{60} form a normal face-centred cubic lattice just as is observed for cubic-close packing of spheres.

The solid state NMR spectrum of C_{60} gives a sharp single line at 143 ppm without any magic angle spinning (instead of a broad line, expected for a normal solid). This means the solid is acting like a liquid, and the molecules must be tumbling on their lattice sites. X-ray diffraction shows this to be true. As with a normal face-centred cubic lattice, the C_{60} array generates tetrahedral and octahedral holes which can accept intercalated species. As the two holes have significant size differences so fullenes show selectivity for intercalated ions. For example, cesium fits comfortably into the octahedral holes but it is too large to be accommodated in the tetrahe-dral holes.

Properties of Fullerenes :

1. Fullerene is a black powdery material.

2. It forms deep magenta solution, when dissolved in benzene.

3. It is very tough and thermally stable (it can be sublimed at 600°C under vacuum).

4. It exists as a discrete molecule, unlike the other two allotropes of carbon viz. diamond and graphite).

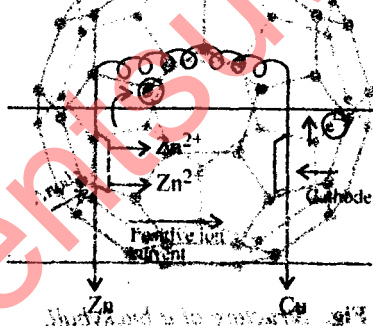5. It can be compressed to lose 30% of its volume without destroying its carbon cage structure.

Potential applications of fullerenes:

1. It is suitable for use as a lubricant due to its spherical structure. The bucky balls would act as molecular ball bearings.

2. It can be used as a superconductor when mixed with alkali metals. (e.g., $C_{60}K_x$)

3. It can also be used as soft ferromagnet (e.g., TDAE C_{60})'

4. Other possible areas of uses are; (i) Electronic and Microelectronic devices, (ii) Non-linear optical devices.

Q.4. Attempt any ONE part of the following:

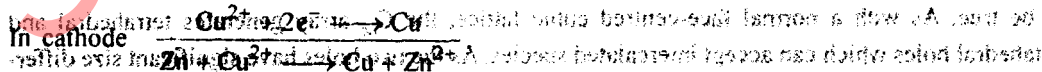(a) Describe the construction of galvanic cell. Write down the electrode reactions and formula of its emf.

Ans. Galvanic Cell: In galvanic cell the metal which is higher up in electrochemical series, with more negative electrode potential will act as anode. In the Zn-Cu galvanic cell, in acts as anode where oxidation occurs and Cu acts as cathode where reduction occurs.
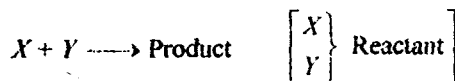

In anode

$$Zn \rightarrow Zn^{2+} + 2e^-$$

and

$$E = E_0 - \frac{0.059}{n} l \frac{[Zn^{+}]}{[Cu^{2+}]}$$

In cathode

$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$$

(b) In a second order reaction, where the initial concentration of the reactants is the same, half of the reactants are consumed in 60 minutes. If the specific reaction rate is 5.2×10^{-3} mol^{-1} L min^{-1}. What is the initial concentration of the reactant.

Ans. The rate constant for a second order reaction for which the concentration of both the reactants is given by

$$K_2 = \frac{1}{at}\left(\frac{X}{a-X}\right)$$

$$X + Y \longrightarrow \text{Product} \qquad \begin{bmatrix} X \\ Y \end{bmatrix} \text{Reactant}$$

$$\begin{array}{cccc} a & a & & 0 \\ a/2 & a/2 & & a/2 \end{array}$$

$$k_2 = 5.2 \times 10^{-3} \text{ mol}^{-1} \text{ L/min}$$

$$5.2 \times 10^{-3} = \frac{1}{a \times 60}\left[\frac{a/2}{a - a/2}\right]$$

$$5.2 \times 10^{-3} = \frac{1}{60a}$$
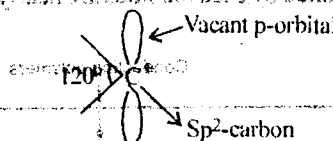
$$a = \frac{1}{60 \times 5.2 \times 10^{-3}}$$

$$a = 3.205 \text{ mol/L}$$

Q.5. Attempt any ONE part of the following:

(a) What are carbocations? Show hybridization in carbocations and discuss stability of primary, secondary and tertiary carbocations.

Ans. Carbocation: "A carbocation is our organic species which has only six paired electrons and a positive change at its carbon centre. They are generally represented by R⁺."

Hybridisation: In carbocation ion carbon is sp^2-hybridised and is planar with a vacant p-orbital perpendicular to the plane of three covalent bonds to carbon."
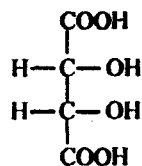

Stability: Stability of a charged system is increased by dispersal of the charge. Thus any factor which tends to disperse the positive charge of the electron deficient carbon will enhance the stability of carbocation. Therefore the electron releasing groups exhibiting +I effect will enhance the stability of carbocation.

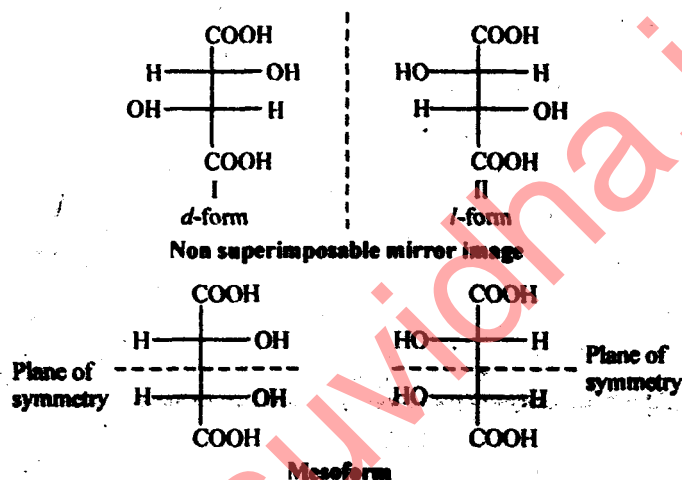The relative stability of carbocation has the following order:

$$(CH_3)C^+ > (CH_3)_2{}^+CH > CH_3{}^+CH_2 > {}^+CH_3$$

(b) Discuss stereochemistry of tartaric acid. What will happen if one of the OH groups of tartaric adic is replaced by NH_2 group?

Ans. Tartaric acid

$$
\begin{array}{c}
COOH \\
| \\
H\!-\!C\!-\!OH \\
| \\
H\!-\!C\!-\!OH \\
| \\
COOH
\end{array}
$$

Theoretically four isomeric forms $2^2 = 4$ are possible.

I
d-form

II
l-form

Non superimposable mirror image

Plane of symmetry

Plane of symmetry

Mesoform
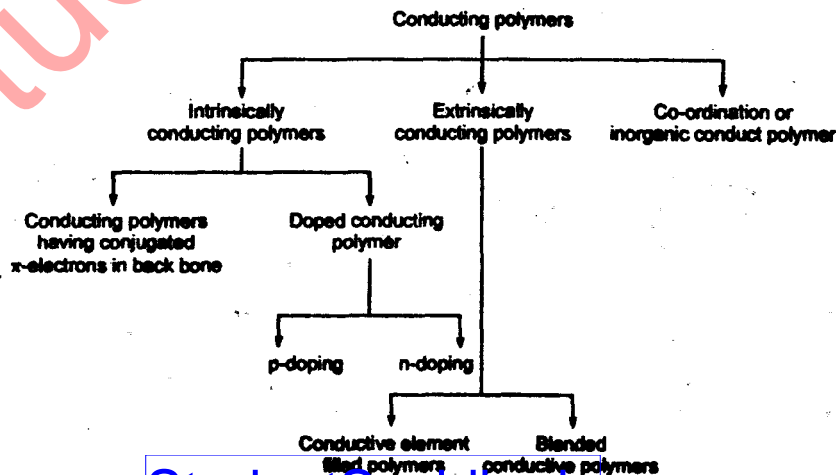
Hence tartaric acid exists in three rather than four isomeric form.

If one of the OH group of tartaric acid is replaced by NH_2, then tartaric acid will exist in four isomeric form.

Q.6. Attempt any ONE part of the following:

(a) Write short note on conducting polymers.

Ans. Conducting Polymers : Polymers which can conduct electricity are called conducting polymers. Ordinary polymers obtained by used methods are nearly insulators. However, some specific polymers may act as conductors.

Conducting polymers

Intrinsically conducting polymers — Extrinsically conducting polymers — Co-ordination or inorganic conduct polymer

Conducting polymers having conjugated π-electrons in back bone — Doped conducting polymer

p-doping — n-doping

Conductive element filled polymers — Blended conductive polymers

Applications of Conducting Polymers :

1.　In rechargeable batteries.
2.　In making analytical sensors for pH, O_2, SO_2, NH_3 etc.
3.　In preparation of ion exchangers.
4.　In controlled release of drugs.
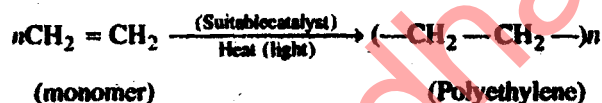5.　In photovoltaic devices.

(*b*) What are differences between:
(*i*) Thermosetting and thermoplastic polymers
(*ii*) Homopolymers and copolymers.

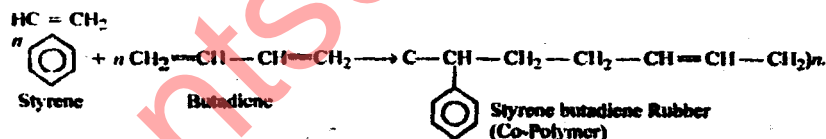Ans. (*i*) Please see Q.No. 2(*a*)(*v*) of Ist Semester 2008-09.

(*ii*) **Homopolymer & Copoly-mer:** Monomers containing a double bond combine without loss to give a product which is an exact multiplication of the starting monomeric material e.g. polymerisation of ethylene.

$$nCH_2 = CH_2 \xrightarrow[\text{Heat (light)}]{\text{(Suitable catalyst)}} (-CH_2 - CH_2 -)n$$

(monomer)　　　　　　　　　　　　　　(Polyethylene)

This process is known as addition polymerisation and the resulting product is called a 'homopolymer'.

Simultaneous addition polymerisation of two different monomers gives rise to co-polymers which have properties intermediate between the homopolymers formed from individual monomers but different from the properties of their mechanical mixture.

Example:

Styrene　　　Butadiene　　　　　　Styrene butadiene Rubber
　　　　　　　　　　　　　　　　　　(Co-Polymer)

Q.7. Attempt any ONE part of the following:

(*a*) Describe proximate and ultimate analysis of fuels.

Ans. A *fuel cell* is an electrochemical cell which converts chemical energy contained in a easily available fuel oxidant system into electrical energy.

The basic principles of a fuel cell are identical to those of the well known electrochemical cell, the only difference is that in fuel cell, the chemical energy is provided by a fuel and an oxidant stored outside the cell. However, the fuel and the oxidizing agent are cont-inuously and separately supplied to the electrodes of the cell, at which they undergo reactions. Fuel cells are also primary cells and they are capable of supplying current as long as the reactants are supplied.

Important characteristics of fuel cells

(*i*)　They have high efficiency,
(*ii*)　Their emission levels are far below the permis-sible limits,
(*iii*)　They are modular and hence can be built in a wide range of power requirements,
(*iv*)　Their noise levels are also low,
(*v*)　They are free from vibration, heat transfer and thermal pollution.

(*b*) What is hardness of water? Describe zeolite process for making soft water from hard water.

Ans. **Hardness of Water:** "Hardnes is the property of water which prevent the lather formation with soap." Hardness in water is done to the presence of bicarbonates, chlorides and sulphates of Ca, Mg and other heavy metals.

Zeolite process:

Inorganic cation exchangers. These are complex inorganic salts like hydrated sodium-aluminium silicate, $Na_2Al_2Si_2O_8.xH_2O$ which have interesting property of exchanging cations such as calcium and magnesium ions in hard water with sodium ions. These complex salts are known as zeolites. These can be either naturally occurring or artificially synthesised substances. Their technical name is permutit. For artificial synthesis of permutit, a mixture of soda ash (Na_2CO_3), sand (SiO_2) and alumina (Al_2O_3) is fused. The product is washed with water to remove soluble impurities leaving behind a porous mass of permutit.

The permutit is loosely packed in a big tank over a layer of coarse sand. Hard water is introduced into the tank from the top. Water reaches the bottom of the tank

Fig. Zeolite method for softening of hard water.

and then slowly rises through the permutit layer in the tank. The cations present in hard water are exchanged for sodium ions.

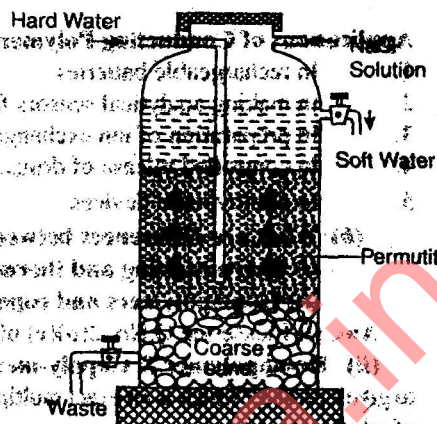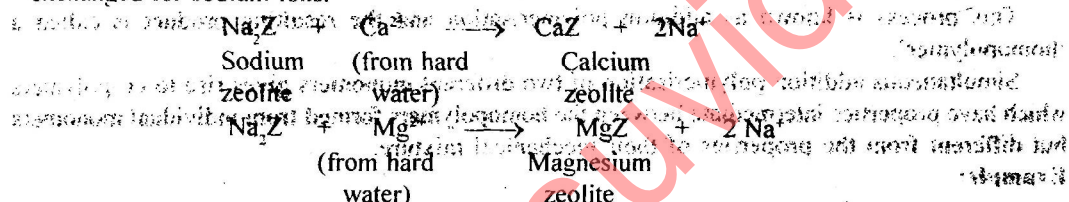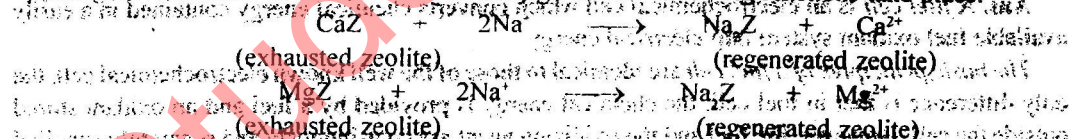$$Na_2Z + Ca^{2+} \longrightarrow CaZ + 2Na^+$$

Sodium zeolite   (from hard water)   Calcium zeolite

$$Na_2Z + Mg^{2+} \longrightarrow MgZ + 2Na^+$$

(from hard water)   Magnesium zeolite

where $Z = Al_2Si_2O_8.xH_2O$

The calcium and magnesium ions remain attached to the zeolite and the water becomes soft. The soft water contains sodium salts (which are soluble in water). These sodium salts do not precipitate the soap and do not interfere with lather formation.

Regeneration of Permutit. As the process continues, the zeolite gets exhausted because the whole of sodium zeolite gets converted to calcium or magnesium zeolite. It may be regenerated by passing 10% solution of sodium chloride through it. The following reactions take place:

$$CaZ + 2Na^+ \longrightarrow Na_2Z + Ca^{2+}$$
(exhausted zeolite)   (regenerated zeolite)

$$MgZ + 2Na^+ \longrightarrow Na_2Z + Mg^{2+}$$
(exhausted zeolite)   (regenerated zeolite)

The regenerated sodium zeolite can be used again for the softening of water.

Merits over soda-lime process:
(i) Equipment is portable and covers less space.
(ii) Can be operated easily.
(iii) Total (100%) Hardness can be remove.
(iv) Slug formation is removed.
(v) Water of any Hardness can be entertained.
(vi) Cheaper than soda-lime process.