

B.Tech.

FIRST ODD SEMESTER EXAMINATION, 2009-10

ENGINEERING CHEMISTRY -I

Time : 3 Hours

(EAS-102)

[Total Marks : 100

SECTION-A

Q. 1. Choose/Fill Correct Answer.

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

2 × 1 = 20

(a) CO (b) NO (c) He²⁺ (d) O₂⁻

Ans. No

(ii) Hydrogen bonding is maximum in

(a) Ethyl chloride

(b) Ethanol

(c) Diethyl ether

(d) Triethyl amine

Ans. 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. in which rate is independent of reactants concentration.

(iv) Rusting of iron is

(a) Enhanced by dry air.

(b) Prevented by cleaning

(c) Retarded in the presence of dissolved salts.

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

Ans. prevented if the article is connected with a piece of Mg.

(v) The most stable carbanion is

(a) methyl carbanion (b) primary carbanion

(c) secondary carbanion (d) tertiary carbanion.

Ans. 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. not super impossible on their mirror image.

(vii) Bakelite is

(a) gel (h) solid (c) liquid (d) gas

Ans. solid

(viii) The vulcanized rubber contains

(a) sulphur (h) Iron (c) herrylium (d) zinc

Ans. sulphur

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

(a) Chromatography (h) Mass spectroscopy
(c) IR spectroscopy (d) X-rays diffraction.

Ans. IR spectroscopy

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

(a) Phenolphthalein (h) methyl red
(c) methyl orange (d) none of these

Ans. Phenolphthalein

(xi) Fill in the blanks :

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

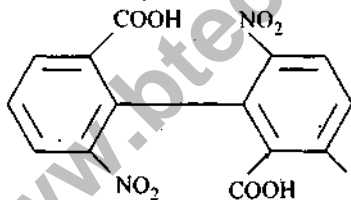
(ii) Graphite is an _____ of carbon.

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

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

(v) _____ is electrochemical disintegration of a metal.

(vi) _____ will show _____ isomerism



(vii) In cannizzaro reaction aldehyde must consist of

(viii) The monomer of natural rubber is

(ix) The main component of biogas is

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

Ans. (i) Weaker (ii) Allotrop (iii) Y8 (iv) Zero (v) Corrosion

(vi) Optical (vii) No α -H-atom

(viii) Isoprene or C_5H_8 or $CH_2 = \underset{\begin{array}{c} | \\ CH_3 \end{array}}{CH} - CH = CH_2$

(ix) Methane

(x) $CaCO_3$

SECTION-B

Q. 2. Attempt any three of the following :

10 × 3 = 30

Q. 2. (i) (a) What is metallic bond ? Explain it on the basis of bond theory.

Ans. Metals are neither held by ionic nor by covalent bonds. The properties of metals are explained by a special type of bond called metallic bond. It may be defined as :

- (a) The force that bonds a metal ion to a number of electrons with in its sphere of influence.
- (b) A bond which is formed between electropositive elements.
- (c) The attractive force which holds the atoms of two or more metals together in a metal crystal or in an alloy.

There are three major theories applied for bonding in metals. They are

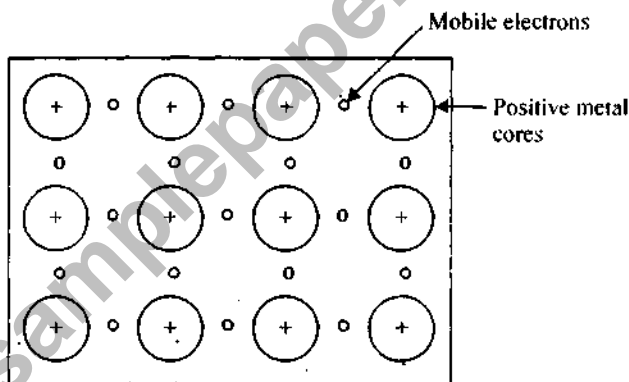
- (i) Free Electron theory or Electron sea theory
- (ii) Valence Bond theory or

Resonance theory

(iii) Molecular Orbital theory

(i) **Free Electron Theory :**

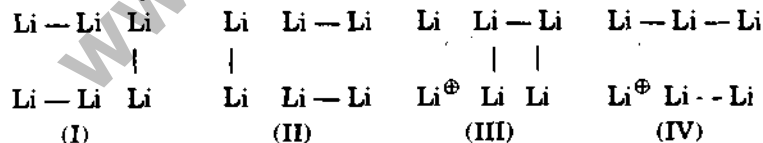
According to this theory, each atom in a metal crystal loses all its valency electrons due to low ionization energy of metal atoms. These electrons form an electron pool or gas. Now a metal is regarded as a group of the metal ions are believed to be held together in a regular geometric pattern by this electron pool or gas. The force that binds a metal ion to the mobile, electrons with in its sphere of influence is known as metallic bond.



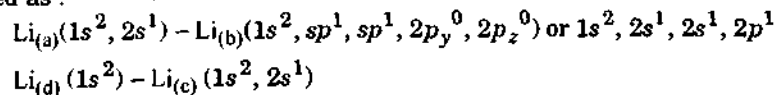
Structure of a metallic crystal : electron Sea model

(ii) **Valence Bond Theory :** According to this theory, the metallic bonding is essentially covalent in origin and the metallic structure involves resonance of electron pair bonds (ordinary covalent bond) between each atom and its nearest neighbours, so there is a resonance of large number of canonical forms.

Consider the metallic crystal of lithium (${}_{3}\text{Li} - 1s^2, 2s^1$) metal in which each atom has eight nearest neighbours as shown :



Here, only the four atoms are shown but actual bonding includes all the atoms of the crystal and is three dimensional, the contributing structures III, IV contains lithium atoms with a negative charge bonded to other two lithium atoms by covalent bonds. Covalent bonds are formed as :

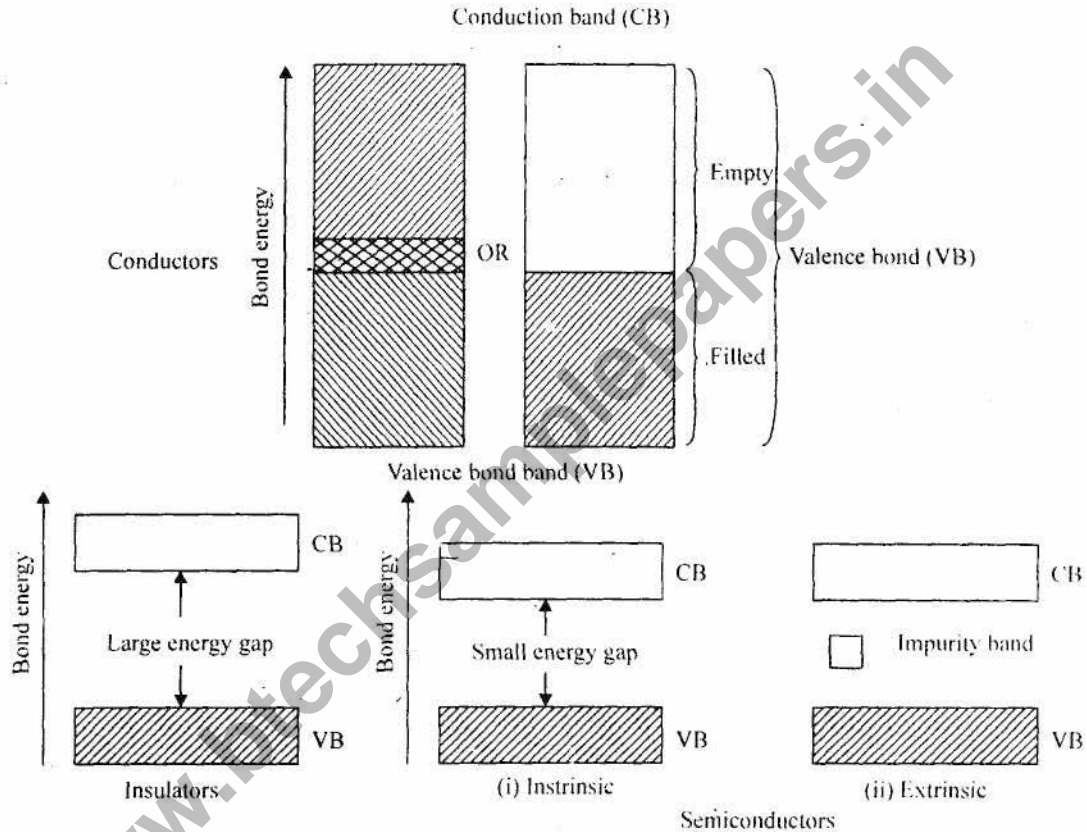


(iii) **Molecular Orbital Theory or Band Theory** : According to this theory, Metallic bond results from the delocalization of the free electrons orbitals over all the atoms of a metal structure.

With the help of Molecular orbital theory of metals, materials can be classified into following three categories, depending on the energy gap between the valence and conduction bands :

(a) Conductors (b) Insulators (c) Semiconductors

The above three energy bands are diagrammatically represented as



Q. 2. (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 ?

$$\text{Ans. } \rho = \frac{nM}{NV}$$

$$= \frac{4 \times 58.5}{6 \times 10^{23} \times (0.564)^3}$$

$$= 2.166 \text{ g/c.c}$$

for NaCl $n = 4$ (Facecentered cubic crystal)

$$N = 6.023 \times 10^{23}$$

$$M = 58.5 = (\text{Na} = 23, \text{Cl} = 35.5)$$

Q. 2. (ii) State and Explain phase rule. Discuss the salient features of phase diagram of water system.

Ans. Phase rule states, "the number of degree of freedom (F) of the system is related to the number of components (C) and of phases (P) present at equilibrium by the equation

$$F = C - P + 2$$

The water system : In water system there can be three forms of equilibria :

(1) Liquid \rightleftharpoons Vapour

(2) Solid \rightleftharpoons Vapour

(3) Solid \rightleftharpoons Liquid

Each equilibrium involves two phases.

Curve OA : Vapour

pressure curve of water.

Ice \rightleftharpoons water vapour

Degree of freedom-one

System -Univariant

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

Curve OB : Vapour

pressure curve of ice or

sublimation curve of

ice water (l) \rightleftharpoons

water vapour

Degree of freedom =

one

System - univariant

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

Curve OC : Fusion

curve of ice

Ice \rightleftharpoons Water (l)

Degree of freedom

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

$$= 1 - 2 + 2 = 1$$

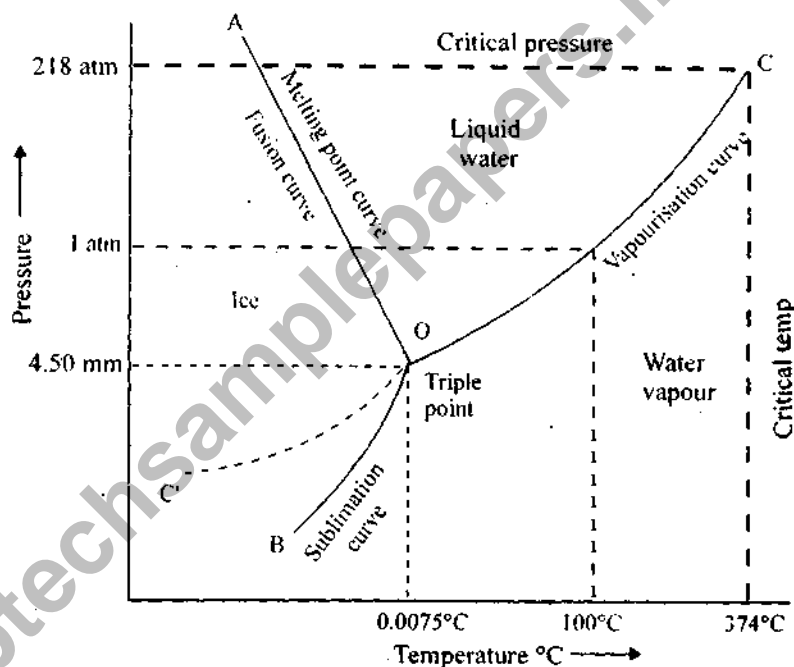
System is univariant

At Triple Point 'O' : The three curves OA, OB, OC meet, at the point O where the three phases, ice, water and vapour coexist in equilibrium. The system represented by this point is non-variant.

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

Q. 2. (iii) (a) Describe the conformational isomers of n-butane.

Ans. In butane, two hydrogens of ethane are replaced by methyl groups. The internal rotation of a substituted ethane is not usually symmetrical and therefore it may have maxima



and minima of different heights. In n-butane, we have to consider several types of conformations obtained by rotating butane molecules six times, each time by 60° .

(i) **Anti-staggered (I)** : It is most stable form in which the two methyl groups are as far apart as possible. It is a fully staggered conformation of lowest energy.

(ii) **Partially Eclipsed (II)** : In this form two methyl groups are nearer an overlap the hydrogen atoms. It is less stable than anti-form and the energy difference is 3.4 Kcal/mole energy.

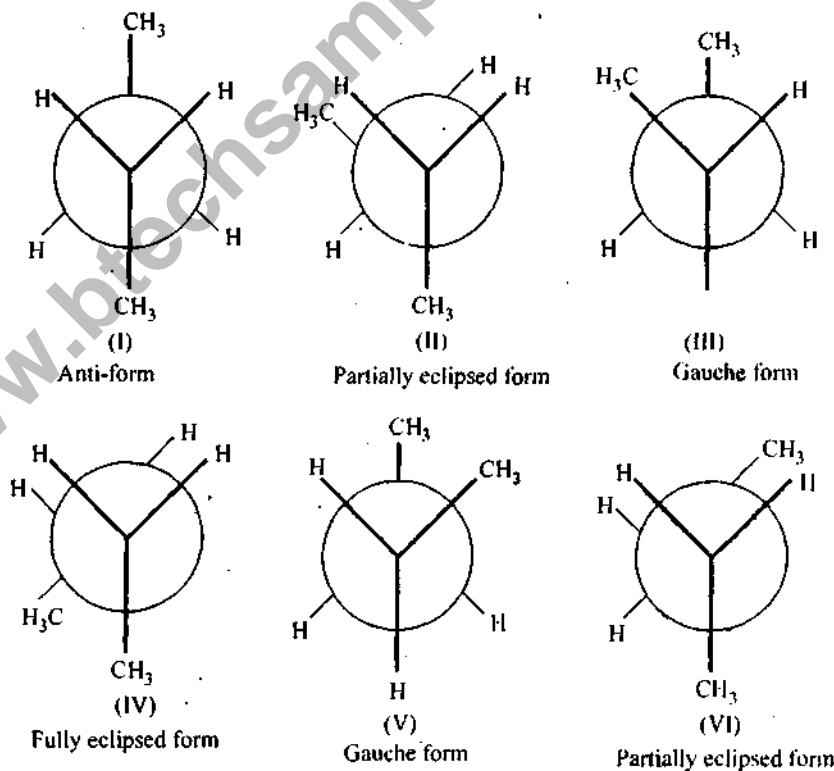
(iii) **Gauche Staggered (III)** : In this form two methyl groups are nearer to each other but do not overlap. It is less stable than I but more stable than II. The energy difference with II is 0.8 K cal/mole energy.

(iv) **Fully Eclipsed (IV)** : In this form, the two methyl groups are eclipsed. It requires about 4.4 K cal/mole of energy.

(v) **Gauche staggered (V)** : Here, two methyl groups are closer, to each other. It requires 0.8 Kcal/mole energy.

(vi) **Partially Eclipsed (VI)** : In this form the methyl groups overlap the hydrogens. It requires 3.4 Kcal/mole energy.

Thus, the anti-form (I) is the most stable and the fully eclipsed form (IV) is the least stable conformation of n-butane. These can be represented by Newmann projection formula as :

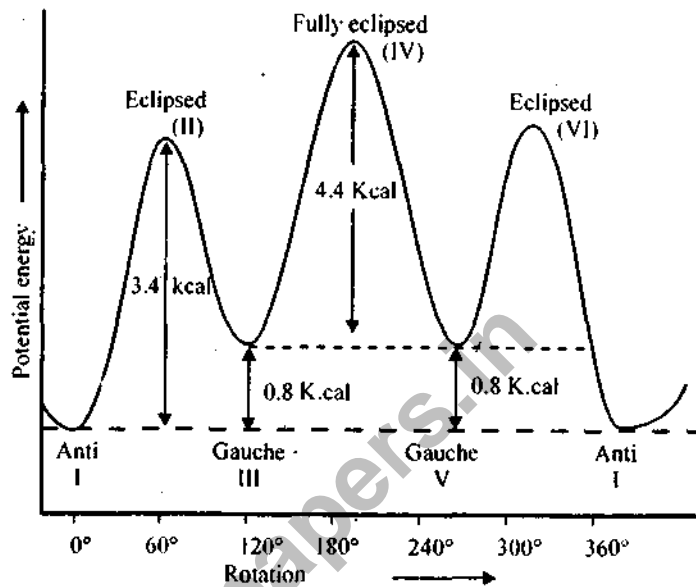


Potential energy changes during rotation around the C-C bond in n-butane

Energy Consideration :

Consider the energy profile diagram of n-butane conformation. Gauche or skew (III and V) are of somewhat higher energy than the anti form (I) and this energy difference is computed at about 0.8 kcal/mole and is commonly known as n-butane skew interaction. In rotating the n-butane molecule, we come across two different eclipsed forms (IV and II or VI). The corresponding energy barriers are 4.4 Kcal/mole and 3.4 Kcal/mole, respectively.

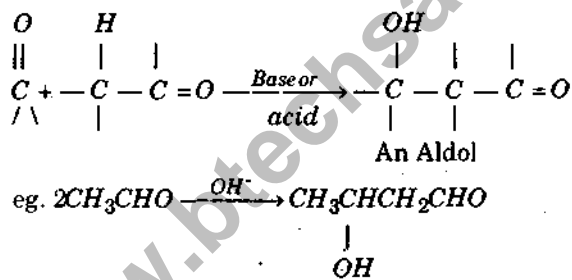
Thus, at ordinary temperatures and in most reactions the molecule is expected to exist predominantly in anti form (I). Here also the conformers have never been isolated since the energy barriers to small.



Q. 2. (ii) (b) Write the mechanism of the following reactions :

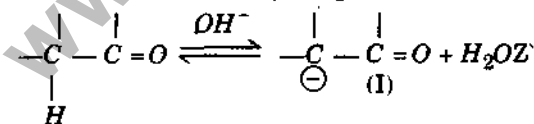
(i) Aldol condensation (ii) Beckman rearrangement

Ans. (i) Aldol condensation : Two molecules of an aldehyde or a ketone may combine (under the influence of dilute acid or dilute base) to form a β -hydroxy aldehyde or β -hydroxy ketone. This reaction is called the Aldol condensation.

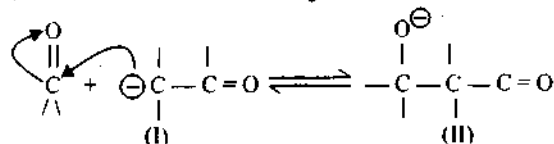


Mechanism

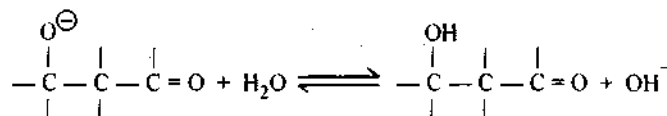
(1) Abstraction of hydrogen ion



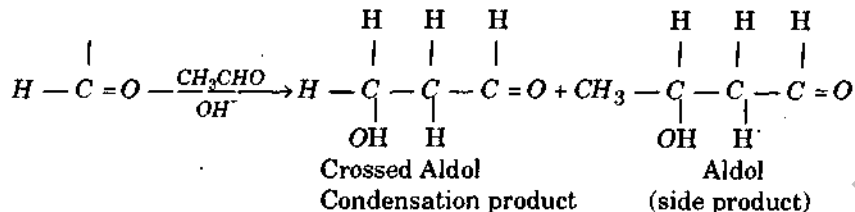
(2) Attack on the carbonyl carbon



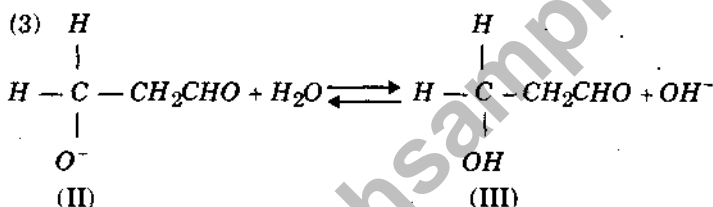
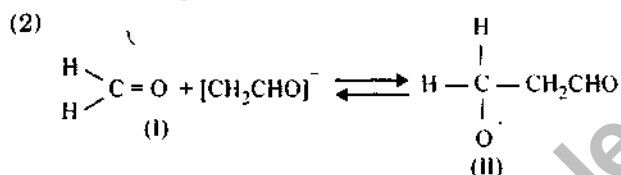
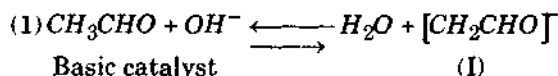
(3) Formation of Aldol



Cross Aldol condensation

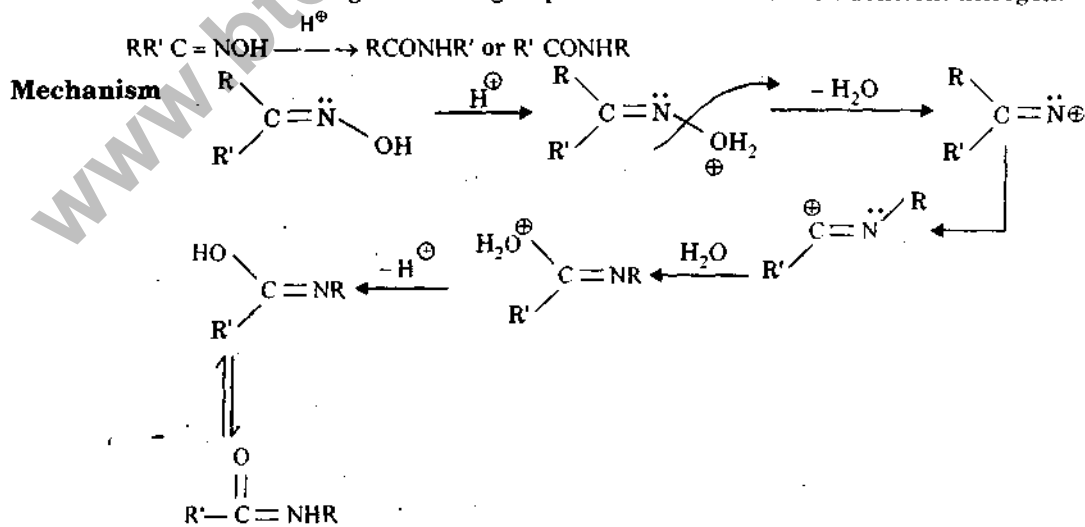


Mechanism

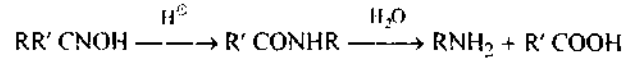


(ii) **Beckman rearrangement** : The acid catalysed conversion of ketoximes to N-substituted amide is known as Beckmann rearrangement.

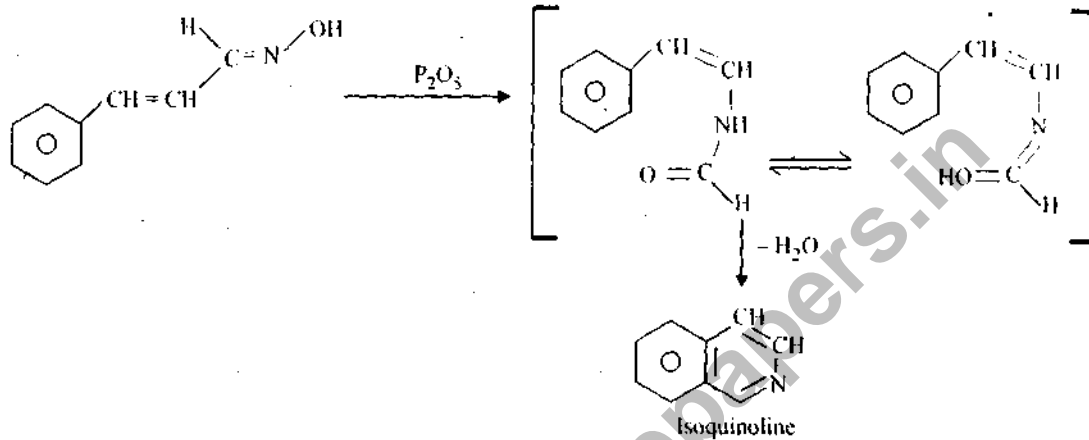
The reaction involves the migration of a group from carbon to electron deficient nitrogen.



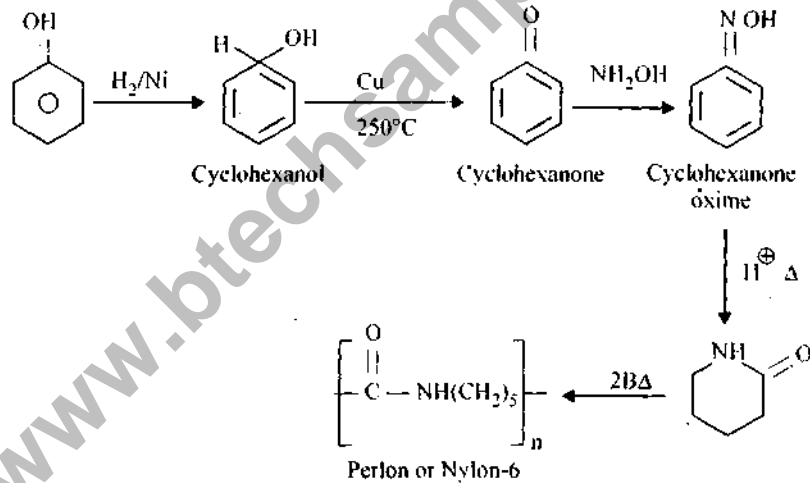
Applications : (1) Configuration of ketoximes can be assigned.



(2) **Synthesis of isoquinoline**



(3) **Synthesis of Lactams :**

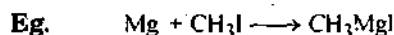


Q. 2. (iv) (a) Describe preparation, properties and application of

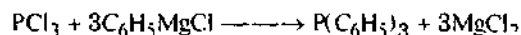
(i) **Buna-S**

(ii) **Nylon 6, 6**

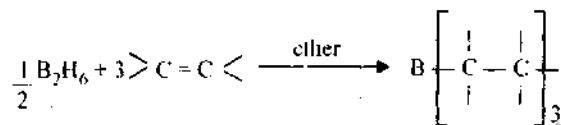
Ans. (i) Buna-S : Preparation : Copolymerisation of Butadiene (75%) and styrene (25%).



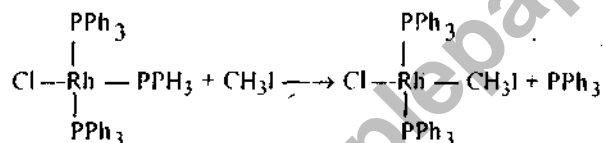
(2) **Use of alkylating agents** : The alkylation is generally done either in ether or hydrocarbon solvents. Alkylating agents can be Grignard and lithium reagents, aluminium and mercury alkyls etc.



(3) **Interaction of metal or non-metal hydrides with alkenes or alkynes** : It can also be regarded as insertion of alkene in M — H bond.

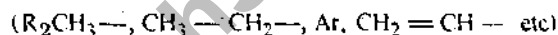


(4) **Oxidative addition reaction or oxid or reactions** : In this metal-carbon bonds are made by the addition of alkyl or aryl halides to coordinatively unsaturated transition metal compounds.

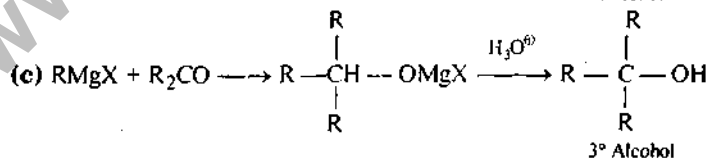
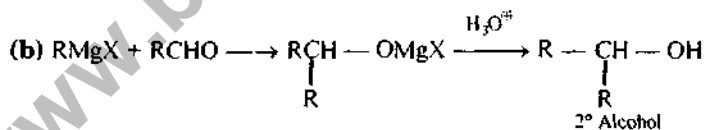
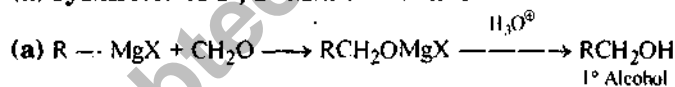


Application of organometallic Compound of Mg : Organomagnesium halide (R — Mg — X) is used in the synthesis of many compounds.

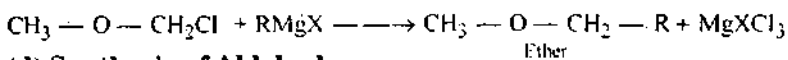
(a) **Synthesis of hydrocarbons** :



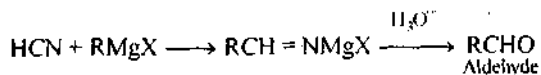
(b) **synthesis of 1°, 2° and 3° alcohols** :

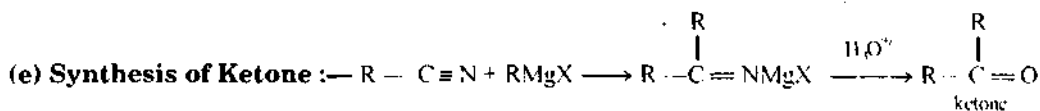


(C) **Synthesis of Ethers** :

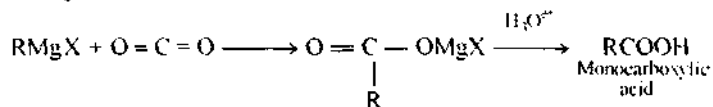


(d) **Synthesis of Aldehydes** :





(f) **Synthesis of acid** :



Q. 2. (v) (a) What is importance of IR spectroscopy in finger print region ?

Ans. An IR spectrum can be divided into two areas :

(1) **Functional group region** : absorption Band observed in (4000 – 1400 cm^{-1}).

(2) **Finger print region** : The region 1400 cm^{-1} to 650 cm^{-1} is referred to as the finger print region. The absorption pattern in this region is complex. This portion is extremely valuable when examined with reference to other regions, for ex. if alcoholic or phenolic (O-H) stretching frequency appears in the high frequency region and absorption also occurs at 1260 cm^{-1} to 1000 cm^{-1} (finger print region). The latter is used to confirm the assignment of the former i.e. alcoholic or phenolic nature with highly specific structures. This is the region usually checked for identification, since it is associated with vibrational (and rotational) energy changes of the molecular skeleton, and so is characteristic of the compound.

Functional Group	Found in	Range (cm^{-1})	No of bands
C = O	Acyclic ketones cyclohexanones	1725–1705	
$\begin{array}{c} C = O \\ \\ H \end{array}$	Aldehydes	1740–1720	
C = O	Cyclopentanones	1750–1720	
C = O	Cyclobutanones	~1775	
C = C – C = O	$\alpha\beta$ -unsaturated ketones	1685–1665	
Ar C = O	Aromatic aldehydes & Ketones	1700 – 1680	
$\begin{array}{c} C = O \\ \\ OH \end{array}$	Carboxylic acids	1710 – 1700	
$\begin{array}{c} C = O \\ \\ OR \end{array}$	Esters & δ -lactones γ -lactones	1750–1735 1780–1760	
$\begin{array}{c} C = C - C = O \\ \\ OR \end{array}$	Aromatic and conjugated Esters	1725–1710	

$\begin{array}{c} \text{C}=\text{O} \\ \\ \text{NH}_2 \end{array}$	Primary amide	1700 - 1650	
$\begin{array}{c} \text{O} \\ \\ \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{O} \\ \\ \text{O} \end{array}$	Anhydrides	1850-1800 1790-1740	Two bands
$\text{C} \equiv \text{N}$	Nitriles	2280-2200	
$\text{C} \equiv \text{C}$	Alkynes	2300-2100	
OH	Alcohols (free)	3650-3560	
OH	Alcohols (H-bonded)	3400-3200	
OH	Carboxylic acid (H-bonded)	2700-2500	Several bands
NH	Secondary amines	3500-3300	one bands
NO_2	Nitro compounds	1570-1550	Two bands
	Caromatic	1370-1300	
NO_2	Nitrocompound (alepactic)	1570-1550 1380-1370	Two bands

Q. 2 (v) (b) 0.72 gm 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 the fuel. Give answer in KJ/Kg.

$$\begin{aligned} \text{Ans. HCV} &= \frac{(w + W)(t_2 - t_1)}{m} \\ &= \frac{(250 + 150)(29.1 - 27.3)}{0.72} = \frac{400 \times 1.8}{0.72} \text{ Cal/gm} = 1000 \text{ cal/gm} \quad 1 \text{ cal} = 4.2 \text{ J} \\ &= 4200 \text{ KJ/Kg} = \frac{400 \times 1.8 \times 4.2}{0.72} = \frac{4001.8}{0.72} \times 4.2 \text{ KJ/Kg} = 4200 \text{ KJ/Kg} \end{aligned}$$

SECTION-C

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

10 × 5 = 50

Q. 3. (a) Discuss the classification of Liquid crystals and write down its applications.

Ans. Liquid crystals was discovered by Frederich Reinitze in 1988. It was observed that solid substances on heating undergo two sharp transformations. Firstly, it gives turbid liquid just after melting and on further heating it changes to a clear liquid.



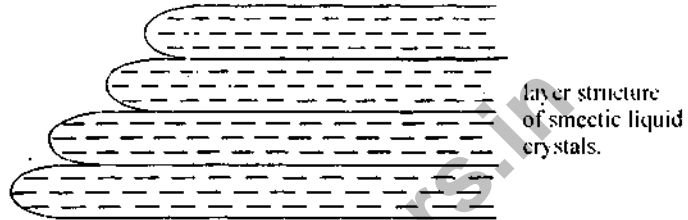
eg. p-chloro steryl benzoate (solid) $\xrightarrow{145^{\circ}\text{C}}$ Liquid crystal $\xrightarrow{178^{\circ}\text{C}}$ Liquid

Thus, these are four states of matter -solid, liquid, Gas and Liquid crystal (Mesomorphic state)

Classifications : Liquid crystals are mainly of three types :

(1) Smectic Liquid Crystal :

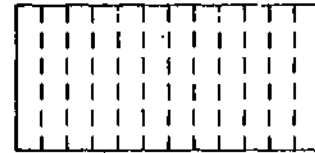
Smectic = Soap like. These liquid crystals do not flow like normal liquid. They have limited mobility. They flow smectic liquid crystals flow in layers one over another. They edge of different layers show finer lines in ordinary as well as polarized light.



The molecules are arranged in nearly parallel layers at regular spacing from each other. Molecules in every layer are not equally spaced. It, therefore, results in anisotropic property i.e. double refraction.

(2) Nematic Liquid Crystals : Nematic = Thread like. In flow behaviour nematic liquid crystals are similar to liquids. Being turbid, nematic liquid crystals are very close to liquid in most of the properties. In polarized light, these liquid crystals appear like thread. They are affected by strong magnetic field.

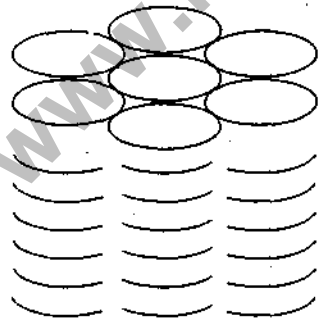
In nematic liquid crystals, molecules are parallel but not in layers. The molecules have more face as there is no regular arrangement.



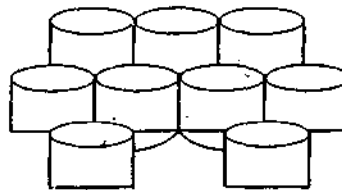
(3) Cholesteric liquid Crystal : Cholesteric liquid crystals have properties of both nematic and smectic liquid crystals to some extent.

(4) Disc-Shaped Liquid Crystals : Molecular arrangement of this type of liquid crystals have two phases

(a) columnar phase (b) Nematic phase.



(a) Columnar phase



(b) Nematic phase

Applications of Liquid crystals :

(1) In laptop screen. (2) In Writs watches.

- (3) In flat television screen
 (4) In switchable windows
 (5) In finding fractures and tumors in humans.
 (6) In digital thermometer.
 (7) In detection of hot points in microcircuits.
 (8) In digital clock.

Q. 3. (b) Describe the preparation, structure and applications of fullerene.

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 also known as Buckminster fullerene. 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. C_{60} is also known as buckyball as it is a spherical cluster of carbon atoms arranged in series of 5 and membered rings, to form soccer ball shaped.

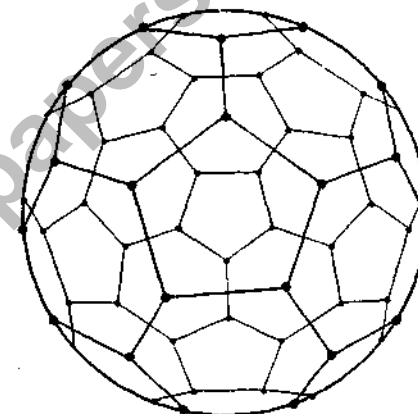


Fig. Structure of C_{60} fullerene molecule

Properties : 1. It is a black powdery material.

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

3. It is very tough and thermally stable.

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

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

Applications : (1) Metal fullerenes are used as super conductors.

(2) Fullerenes are used as charge carriers in batteries.

(3) They are used in non-linear optical devices.

(4) Fullerenes are used in several electronics and microelectronic devices.

(5) Very useful soft ferro-magnets are made by fullerenes.

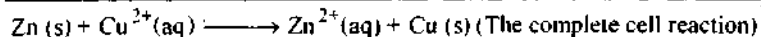
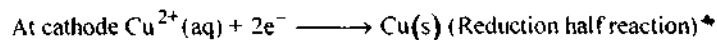
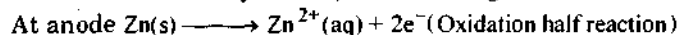
Q. 4. Attempt any one part of the following :

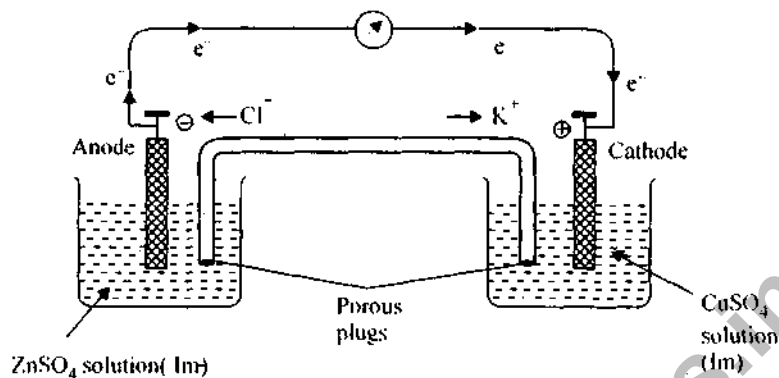
Q. 4. (a) Describe the construction of galvanic cell. Write down the electrode reactions and formula of its e.m.f.

Ans. Galvanic Cell : It converts chemical energy into electric energy. Eg. Dry cell or lead storage battery.

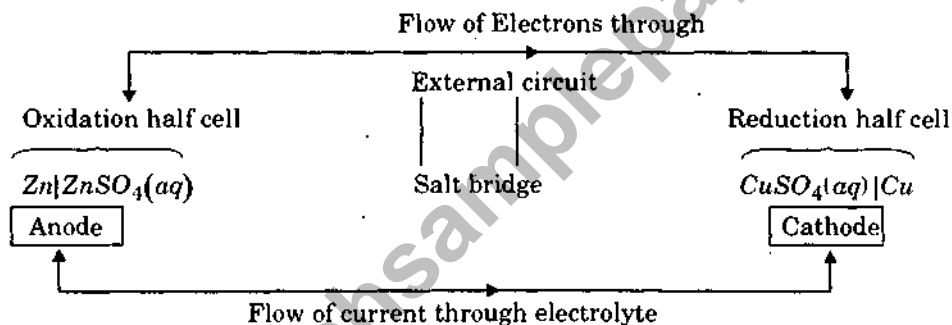
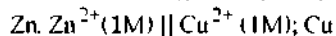
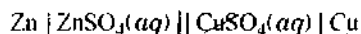
The practical application of galvanic cell is Daniel cell. It consists of Zinc electrode, dipping in $ZnSO_4$ solution (say 1 M) and a copper electrode, dipping in $CuSO_4$ solution (say 1M) taken in two different beakers.

The two solutions are connected by means of a salt bridge. The moment when the two electrodes are connected by a wire, the following reactions occur at different electrodes :





Representation of Galvanic cell :



Left



The potential of the electrode is given by

$$E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Reduced State}]}{[\text{Oxidised State}]}$$

Right

Q. 4. (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 $5.2 \times 10^{-3} \text{ mol}^{-1} \text{ L minute}^{-1}$. What is the initial concentration of the reactant.

Ans. For a second order reaction when conc. of both reactants are same –

$$t_{y_2} = \frac{1}{k} \times \frac{1}{a}$$

t_{y_2} = half life k = rate constant

a = initial conc.

given $t_{y_2} = 60 \text{ min}$

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

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

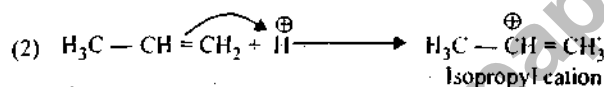
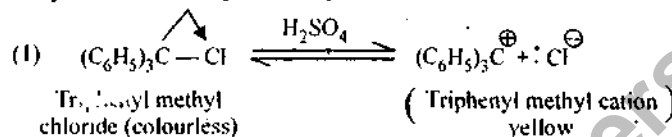
$$a = \frac{1}{5.2 \times 60} \times 10^3 = \frac{1000}{6 \times 52} = \frac{1000}{312} = 3.2 \text{ mol/lit}$$

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

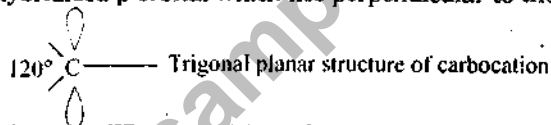
Q. 5. (a) What are Carbocations ? Show hybridization in Carbocations and discuss stability of primary, secondary, and tertiary carbocations.

Ans. A species in which the carbon bears a positive charge is called carbocation. The formation of carbocation can be detected by NMR spectroscopy. It acts as an electrophile and also a Lewis acid.

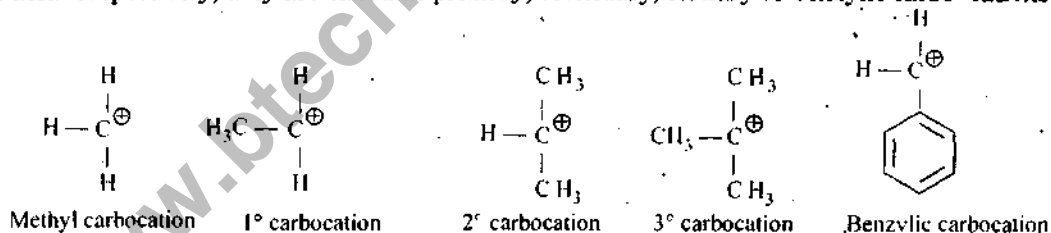
Formation : They are formed by heterolysis of covalent bond.



Structure : In the carbocations, the central carbon bearing positive charge is bonded to three other atoms or molecules and is in sp^2 hybridized state. The structure is thus planar with bond angles of 120° . There is a vacant unhybridized p-orbital which lies perpendicular to the plane of σ bonds.



Types of Carbocations : When positive charge is present on 1° , 2° , 3° or benzylic carbon-atom respectively, they are called as primary, secondary, tertiary or benzylic carbocations.



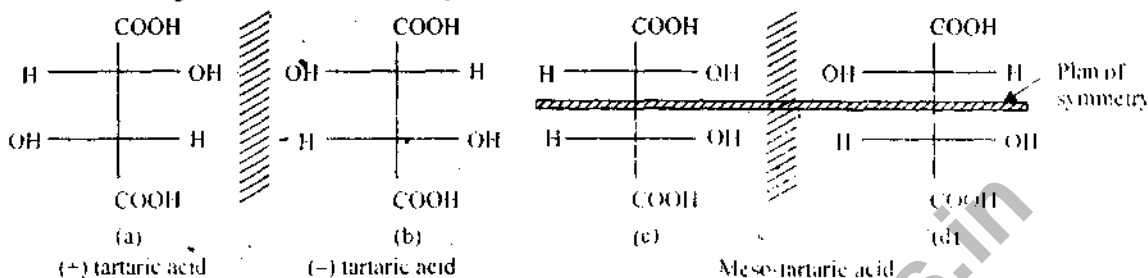
Stability : Carbocations are stabilized by the dispersal of charge. Positive charge of carbocations can be dispersed either by (+ I) effect of the alkyl group or by resonance in alkyl or benzylic carbocations, or by hyper conjugation in 1° , 2° , 3° carbocations.

Stability of carbocations: $\text{Benzyl} > 3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

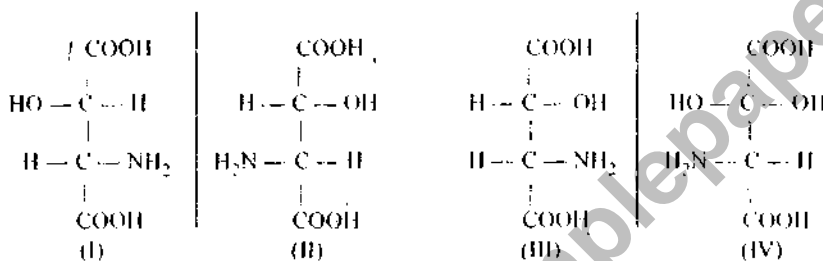
Q. 5. (b) Discuss Stereochemistry of tartaric acid. What will happen if one of the OH groups of tartaric acid is replaced by NH_2 group.

Ans. Tartaric acid is an example diastereomer. Diastereomers have different physical and chemical properties even towards achiral reagents. Solvents and Catalysts. This due to the fact that they have different amounts of free energy. (+) - Tartaric acid is diastereomeric with meso-tartaric acid.

(a) and (b) being mirror images of each other, are enantiomers. (a) and (c) or (c) and (d) are not mirror images of each other so they are diastereomers.



In case of replacement of one OH group by NH_2 group.



In the case two pairs of enantiomers exist (I, II) and (III, IV).

Also there are 4 pairs of diastereomers

(I, III), (I, IV), (II, III) and (II, IV)

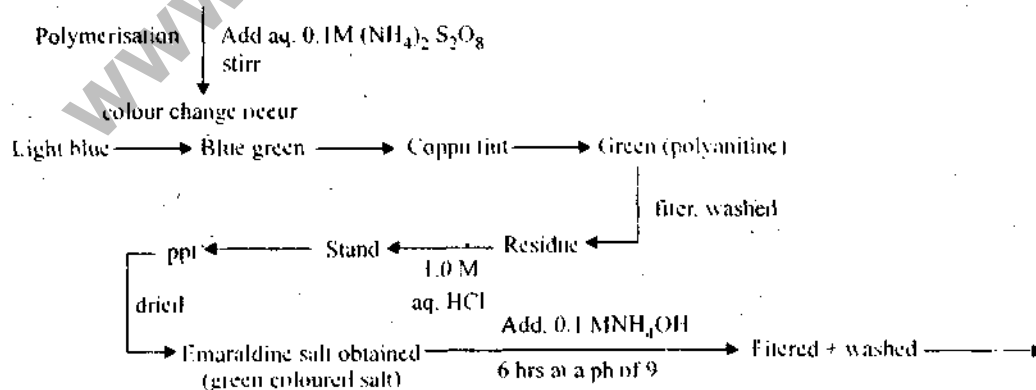
Enantiomers have equal angle of rotation of plane of polarized light with opposite direction. But diastereomers have different magnitude of angle of rotation.

Q. 6. (a) Write a short note on conducting polymers.

Ans. A polymers which can conduct electricity is termed as conducting polymer.

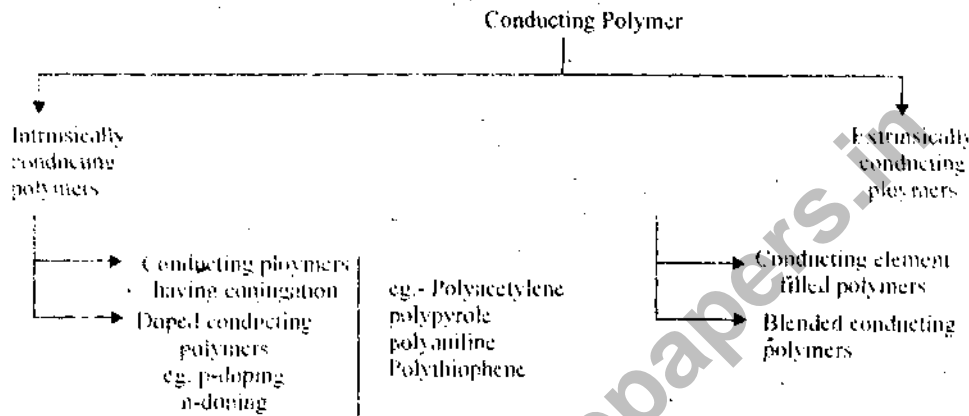
Ex. Polyaniline & polypyrrole.

Synthesis :



0.1 M aniline hydrochloride solution + 1.0 M aq. HCl
 Resulting solid (p-doped polyaniline) conducting polymer.

Classification



- Application :** (1) In Rechargeable batteries.
 (2) In Analytical sensors
 (3) For Making Ion Exchangers.
 (4) In Electrochromic displays and optical fibres.
 (5) In electronics.
 (6) In photovoltaic devices.

Q. 6. (b) What are the differences between

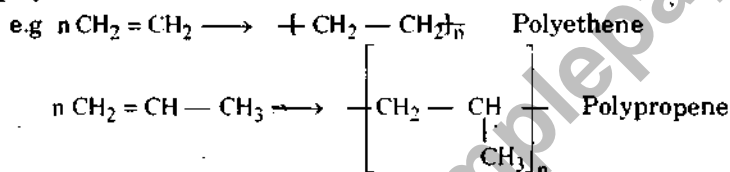
- (a) **Thermosetting and thermoplastics polymers.**
 (b) **Homopolymers and copolymers.**

Ans.

Thermoplastics	Thermosets
(a) They are formed either by addition or by condensation polymerisation reactions.	(a) They are formed by condensation polymerisation reactions.
(b) They have either linear or branched structures.	(b) They have three dimensional, cross linked network structure.
(c) Adjacent polymer chains are held together by either vander walls forces, or by dipole-dipole forces or by H-bonds.	(c) Adjacent polymers chains are held together by strong covalent bonds called cross-links.
(d) They softens on heating and stiffen on cooling.	(d) They do not soften on heating.

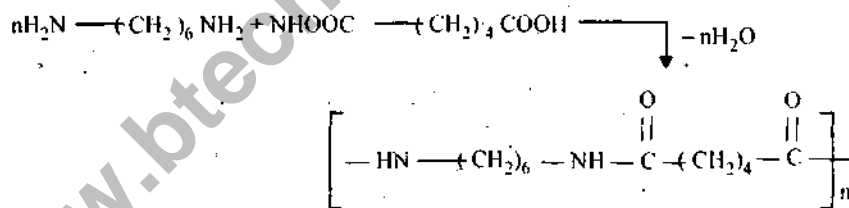
- | | |
|--|---|
| (e) Low molecular weight thermoplastics, are soluble in their suitable solvents. | (e) They are generally insoluble in any solvent. |
| (f) They can be remoulded, reshaped and reused. | (f) They cannot be re-moulded and hence cannot be re-used. |
| (g) They can be reclaimed from waste i.e., they can be recycled. | (g) They cannot be reclaimed from waste. They cannot be recycled. |
| (h) During moulding of thermoplastics, there is no change in their chemical composition. | (h) They undergo chemical changes such as further polymerisation and cross-linking during moulding process. |
| (i) They are tough materials. | (i) They are brittle materials. |

(II) Homopolymers : When a polymer is formed by identical monomers is called homopolymers.



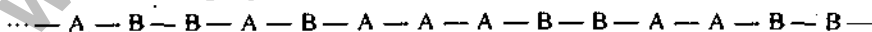
It is formed by addition polymerisation.

Copolymers : When a polymer is formed by two types of monomer units, it is called copolymer. This polymer is formed by condensation polymerisation. ex. **Nylon 66.**

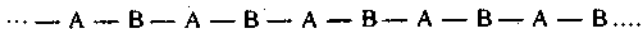


Copolymers are of different types :

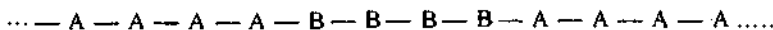
(a) **Random Copolymer :** Monomer units are randomly distributed.



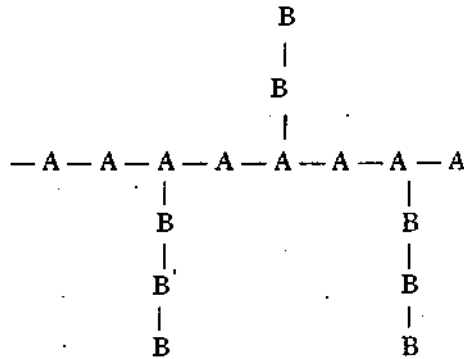
(b) **Alternate copolymer :** monomer units are arranged in regular manner of polyesters, polyamide, styrene-acrylonitrile etc.



(c) **Block copolymers :** a block of monomer unit is followed by another kind of monomer unit.



(d) **Graft Polymer :** a monomer unit attached in side chain and form a Backbone of the polymer.



Q. 7. (a) Describe proximate and ultimate analysis of fuels.

Ans. Coal is mainly composed of C, H, N and O, besides non-combustible inorganic matter. The assessment of quantity of Coal is carried out by the following two types of analysis :

- (a) Proximate analysis
- (b) Ultimate analysis.

(a) Proximate analysis : This involves the following determinations.

(1) Moisture :

One gram finely powdered coal $\xrightarrow[\text{heat one hour } 105^{\circ}\text{C}-110^{\circ}\text{C}]{\text{insilica crucible}}$ Crucible cooled
in dessicator & weighed

The amount of weight loss is reported as moisture

$$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{wt. of coal taken}} \times 100$$

(2) Volatile Matter : The dried sample of coal left in the crucible from (1) is then covered with a lid and kept in a muffle furnace at $925 \pm 25^{\circ}\text{C}$ for 7 minutes.

After 7 minutes the crucible is taken out and cooled first in air and then inside the dessicator and weighed again. Loss of weight is volatile matter.

$$\text{percentage of volatile matter} = \frac{\text{Loss in wt. due to removal of volatile matter}}{\text{wt of coal sample taken}} \times 100$$

(3) Ash : The residual coal in the crucible obtained from (2) is heated without lid in a muffle furnace at a temperature of nearly 800°C for nearly 30 minutes. The crucible is taken out cooled first in air then in a dessicator and weighed. Heating cooling and weighing are repeated till a constant weight is obtained.

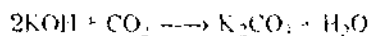
$$\text{Percentage of ash} = \frac{\text{wt. of ash left}}{\text{wt of coal sample taken}} \times 100$$

(4) Fixed Carbon : The percentage of fixed carbon is reported as under :

$$100 - \% \text{ of (Moisture + Volatile matter + Ash)}$$

(b) Ultimate Analysis : It involves the following determinations.

(1) **Carbon and Hydrogen**: At least two gram of coal sample is burnt in a combustion apparatus to convert carbon and hydrogen into CO_2 and H_2O respectively. These are absorbed respectively in KOH and CaCl_2 absorption tubes of known weight. The percentage of carbon and hydrogen are calculated from the increase in weight of the respective absorption tubes.



$$\% \text{ of C} = \frac{\text{Increase in wt of KOH absorption tube}}{\text{wt. of the sample taken}} \times \frac{12}{44} \times 100$$

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

(2) **Nitrogen** : It is determined by taking 1 gm of Coal sample in Kjeldahl flask with conc. H_2SO_4 , K_2SO_4 and HgSO_4 , So that the nitrogen present in the sample is converted into ammonium salt. The sample solution is then made alkaline with NaOH and liberated ammonia is distilled over into a measured amount of standard acid solution, where it is absorbed. The unused acid is then determined by back titration with standard NaOH solution. From the volume of the acid used by liberated ammonia, the percentage of nitrogen in coal is calculated as under :

$$\text{Percentage of nitrogen} = \frac{\text{Volume of acid used} \times \text{Normally} \times 1.4}{\text{Weight of Coal taken}}$$

(3) **Sulphur** : It is determined from the washings obtained from the known mass of coal used in a bomb calorimeter for the determination of calorific value. During this process, sulphur is converted into sulphate. The washings are heated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$\% \text{ of Sulphur} = \frac{\text{wt. of BaSO}_4 \text{ obtained}}{\text{wt. of Coal sample taken in bomb}} \times \frac{32}{233} \times 100$$

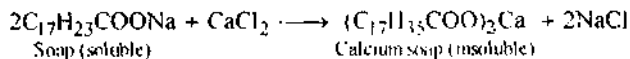
(4) Ash determination is carried out as in proximate analysis.

(5) The % of oxygen is found by difference.

$$\% \text{ of O} = 100 - \text{Percentage of (C + H + S + N + ash)}$$

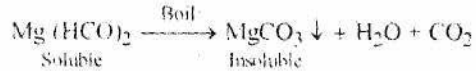
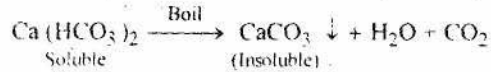
Q. 7. (b) What is hardness of water ? Describe Zeolite process for making soft water from hard water.

Ans. Hardness of water : Soap consuming capacity of water is called Hardness. It is mainly due to the presence of calcium and magnesium ions. These ions react with the sodium salt of long-chain fatty acids present in the soap to form insoluble soaps of calcium and magnesium which do not possess any detergent value.



Hardness is of two types :

(1) **Temporary hardness** : This is due to the presence of soluble salts of bicarbonates of calcium and magnesium and removed by boiling

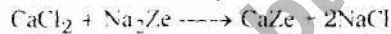
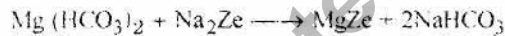


The insoluble calcium and magnesium carbonates can easily be removed by filtration.

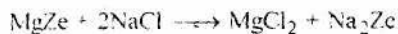
(2) **Permanent hardness** : This is due to the sulphides, chlorides and nitrates of calcium, magnesium and other metals. It cannot be removed by boiling.

Zeolite Process of softening of water : In this process, the Zeolite or permutit is used for water softening. The permutit is Sodium aluminium orthosilicate, $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$ or Na_2Ze where $\text{Ze} = \text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$. The Zeolite may be natural or synthetic. The Zeolite have the property of exchanging their sodium ions easily with calcium or magnesium ions when they come in contact with hard water.

When water enters at the top and passes through the bed of zeolite, the chemical reactions occur are as :

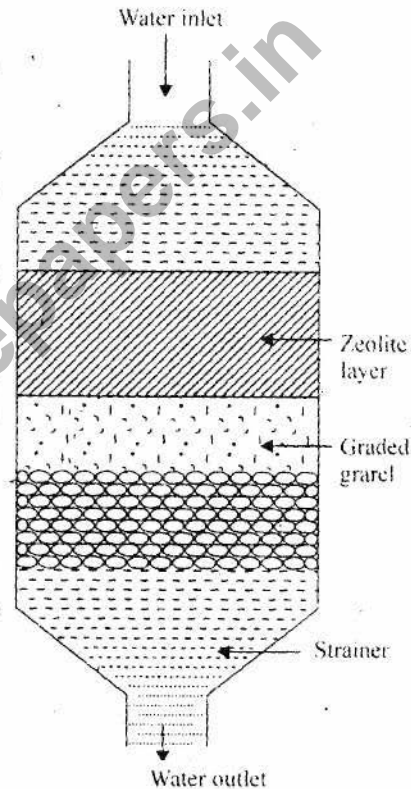


The process removes both temporary as well as permanent hardness. When the permutit is completely converted into calcium or magnesium zeolites then it gets exhausted and it ceases to soften water. The permutit can be made active by passing 10% solution of NaCl.



The soluble salt of Ca and Mg can thus easily be removed.

Limitations : (1) The water must be free from suspended matter, otherwise the permutit gets clogged.



(2) If water contains some acids, it must be neutralised with base, because the mineral acid destroys the zeolite.

(3) Coloured in should be removed by pre-treatment because the calcium and magnesium zeolite cannot be easily converted into zeolite.

(4) Lead cannot be removed by this because it cannot be converted into lead zeolite.

Advantages : (1) The method can produce zero hardness.

(2) The equipment occupies a small space and it easy to operate.

(3) No sludge formation occur during the process.

(4) This process can automatically adjust itself for different types of hardness of water.

(5) This method is very cheap because the regenerated permutit can again be used.

Disadvantages : (1) After treatment water contains more sodium salt.

(2) The method leaves all the acidic ions such as HCO_3^- and CO_3^{2-} in the softened water.

(3) High turbidity in water cannot easily be heated by this method.

(4) When such water is boiled in boiler, the CO_2 is liberated free CO_2 is weakly acidic in nature and highly corrosive to boiler material.