B.Tech.

SECOND SEMESTER EXAMINATION, 2009-10

ENGINEERING CHEMISTRY

(EAS-202/102)

Time : *3 Hours]* *[Total Marks : 100*

Note : *(1) Attempt **all** questions.*

Section A

Q. 1. Choose / Fill correct answers :

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

Ans. (a) Di ie moment

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

Ans. Scum or precipitate

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

(i) Ionic **(ii) vander Walls**

(iii) Hydrogen **(iv) Covalent**

Ans. Hydrogen bond

(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. 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. $SiCl_4$

(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. Teflon

(h) Bakelite is a :

(i) Natural polymer **(ii) Additional polymer**

(iii) Condensation polymer **(iv) Homopolymer**

Ans. Condensation polymer

(i) The relationship between absorbance and transmittance is, A= ________.

Ans. $A = -\log T$

or

$$A = \log \frac{1}{T}$$

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

Ans. Lower wave number

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

Ans. H atom, C-atom

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

Ans. Hydrogen bond

(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. 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. K = mol $litre^{-1}$ $time^{-1}$

(p) The _______ cells convert the energy from the combustion ______ of into the electrical energy.

Ans. fuel, H_2/fuel

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

Ans. oxidation Fe_3O_4

(r) The following reaction is known as :

Ketoxime $\xrightarrow{H_2SO_4}$ N-substituted amide

(i) Aldol condensation **(ii) Beckmann rearrangement**

(iii) Diels-Alder Reaction **(iv) Hoffmann rearrangement**

Ans. Beckmann rearrangement

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

Ans. Zigler 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)

Section B

Q. 2. Attempt any three parts of tbe following.: –

Q. 2. (a) (i) Explain tbe bonding and antibonding molecular orbitels and fferentiate between them.

Ans. Bonding molecular orbital: Molecular orbital formed by the addition of two omic orbital wave functions is known as bonding molecular orbital i.e. $\psi = \psi_A + \psi_B$

Antibondlng molecular orbltal : Molecular orbital formed by substraction of two omic orbital wave functions is known as antibonding molecular orbital.

$\psi_O = \psi_A - \psi_B$

Difference between bonding and antibonding molecular orbital

Bc ling M.O.	Antibonding M.O.
.) Formed by additıon of two atomic orbital wave functions.	(1) Formed by substraction of two atomic orbital wave function.
!) The electron density in BMO is greater than that in individual atomic orbitals. $\psi_b^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B > \psi_A^2 + \psi_B^2$	(2) The electron density in ABMO in is less than that in individual atomic orbitals. $\psi_a^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B < \psi_A^2 + \psi_B^2$
.) Bonding M.O. are represented as σ, π etc.	(3) ABMO represented by σ^*, π^* etc.
.) The energy level of BMO is less as compared to that of individual atomic orbitals.	(4) The energy level of ABMO is more as compared to that of individual atomic orbitals.
;) Electrons present in bonding MO helps in the formation of bonds.	(5) Electrons present in ABMO decrease the tendency to form bonds.

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

Ans. $N_2 = KK\,\sigma(2s^2)\,\sigma*(2s^2)\,\pi(2px^2) = \pi(2py^2)\,\sigma(2pz^2)$

Bond order $= \frac{10-4}{2} = 3.0$ Magnetic property = Diamagnetic

$N_2^+ = KK\,\sigma(2s^2)\,\sigma*(2s^2)\,\pi(2px^2) = \pi(2py^2)\,\sigma(2pz^1)$

Bond order $= \frac{9-4}{2} = 2.5$ = Paramagnatic

$N_2^- = KK\,\sigma(2s^2)\,\sigma*(2s^2)\,\pi(2px^2) = \pi(2py^2)\,\sigma(2pz^2)\,\pi*(2px^1)$

$$\text{Bond order} = \frac{10-5}{2} = 2.5 = \text{Peramagnetic}$$

$N_2^{=} = KK\,\sigma(2s^2)\,\sigma^*(2s^2)\,\pi(2px^2)\,2\pi(2py^2)\,\sigma(2p_z^2)\,\pi^*(2p^2x)$

$$\text{Bond order} = \frac{10-6}{2} = 2 = \text{Diamagnetic}$$

order of stability $= N_2 > N_2^+ \approx N_2^- > N_2^{=}$

Q. 2. (b) (i) Derive the equation for half life of a first order reaction.

Ans. Half life for First order reaction :

For First order Reaction :

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

when $t.\ t_{\frac{1}{2}}\ x = a/2$

$$K_1 = \frac{2.303}{t_{\frac{1}{2}}}\log\frac{a}{a-\frac{a}{2}} = \frac{2.303}{t_{\frac{1}{2}}}\log_2$$

$$t_{\frac{1}{2}} = \frac{2.303 \times 0.3010}{K_1} \qquad \boxed{t_{\frac{1}{2}} = \frac{0.693}{K}}$$

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

Ans. EMF of a Cell : 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 electromotive force (emf) of the cell. It is expressed in volt and measured by voltmeter.

$E_{cell} = E_{Right} - E_{Left}$

E_{right} = Reduction potential of right hand electrode

E_{Left} = Reduction potential of left hand electrode

Electrochemical Cell : An electrochemical cell is a device for the conversion of electricsl energy into chemical energy or vice-versa. It is divided into two classes.

(i) Galvanic Cell : Converts Chemical energy into electric energy. ex-Dry cell or Lead storage battery.

(ii) Electrolytic Cell : The electrical energy from an external source is used to bring about a chemical change.

Example : Charging of lead storage battery, Electrolytic purification of metals.

EMF of an Electrochemical Cell :

$E_{cell} = E_{cathode} - E_{anode}$

$E_{cell} = E_{right} - E_{left}$

The cell reaction is feasible only when E_{cell} has positive value.

Q. 2. (c) (i) Describe preparation, properties and applications of :

(A) Buna-N

(B) Nylon -6, 6

Ans. Buna N- Preparation : It is prepared by the copolymerisation of butadiene and acrylonitrile in emulsion system.

$$CH_2 = CH - CH = CH_2 + nCH_2 = \underset{\displaystyle CN}{\underset{|}{CH}} \xrightarrow[\text{- zation}]{\text{copolymeri}} \left[CH_2 - CH = CH - CH_2 - \underset{\displaystyle CN}{\underset{|}{CH}} - CH_2 \right]$$

Propertiea :

(1) Excellent resistant to oils, chemicals, aging (sunlight)

(2) Nitrite rubber has more heat resistance aod it may be exposed to high temperatures.

(3) It has good abrasion resistance, even after immersion in gasoline or oils.

Applicationa : (1) Convey or belts (2) Hoses (3) Adhesives (4) Gaakets

(5) Lining of tanks (6) Printing rollers (7) oil-resistance foams (8) Automobile parts and high attitude aircraft componenta.

Nylon - 6, 6 : Preparation : It is made by the condensation polymerisation of hexamethylene diamine and Adipic acid in 1 : 1 molar ratio.

$$\underset{\text{Hexamethyene Diamine}}{H_2N - (CH_2)_6 - NH_2} + nHOOC - (CH_2)_4 - COOH \xrightarrow[\text{- zation}]{\text{Polymeri}}$$

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

Polyhexa methylene adipamide

Propertiea :

(1) High strength, high melting point, elasticity, toughness, abrasion resistance.

(2) Retention of good mechanical properties upto 125°*C*.

(3) They are also sterilisable.

(4) Good hydrocarbon resistance.

Applicatlons :

(1) Used for fibers

(2) In mechanical engineering like Gears, Bearings, Bushes, Cams etc.

(3) In medicine and pharmacy because of sterilisability.

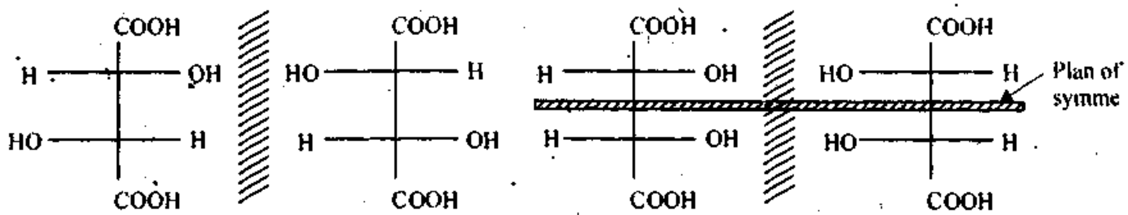
(4) Used for jacketing electrical ware to provide a tough, abrasion resistant outer cover to protect the primary electrical insulation.

(5) for making tyre cords.

(il) Discuas in brief the diastereomers and meso compounds with auitable examples.

Ans. (ii) Deastereomers : Stereoisomers that are not mirror images of each other are known as diastereomers. They have different physical and chemical properties even towards achirsl reagenta, solvents and catalysts. This is due to the fact that they have different amounta of free energy.

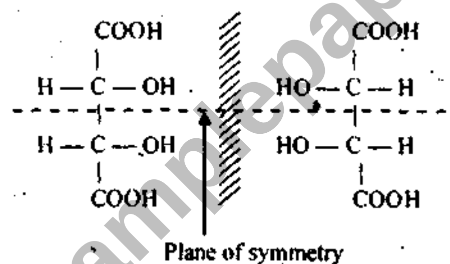
ex. (+) tartaric acid is diastereomeric with meso tartaric acid.



(a) (+) tartaric acid | (b) (–) tartaric acid | (c) | (d)

(a) and (c) or (c) and (d) are not mirror images of each other so they are diasteroisomers.

Meso compounds : The compounds which have optical rotation zero are call meso-compound. This is due to plane of symmetry in the molecule. The plane of symmetry divi into two equal halves in any plane and thus the atoms or groups on one side of the plane fro mirror image of those on the other side of Mesotartaric acid.



Q. 2 (d) (i) Distinguish between thermosetting and thermoplastic resins. Classi the following as thermosetting and thermoplastic :

Polystyrene, polyethylene, urea-formaldehyde, bakelite, teflon and nylon.

Ans.

Thermosetting	Thermoplastics
1. These once hardened can't be softened	1. These polymers are softened on heating an hardened on cooling.
2. These can't be remoulded.	2. Can be moulded again and again
3. Formed by condensation polymerisation	3. Formed by addition polymerisation
4. Have cross linked three dimensional network type structure.	4. have linear structure. The different chains ar held together by weak Vander waal's forces.
5 hard strong and more brittle	5. Soft, weak and less brittle.
6 Insoluble in organic solvents	6. Soluble in organic solvents.

Polystyrene – Thermoplastics
Polyethylene – Thermoplastics
Urea-Formaldehyde – Thermosetting
Bakelite – Thermosetting
Teflon – Thermoplastics
Nylon – Thermoplastics

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

Ans. Zeolite Process for removing hardness of water : (Permutit process) :

Zeolite is hydrated sodium aluminium silicates

$Na_2O . Al_2O_3 . 2SiO_2 . 6H_2O$

Zeolites are insoluble and they exchange Na^+ for Ca^{++} and Mg^{++}.

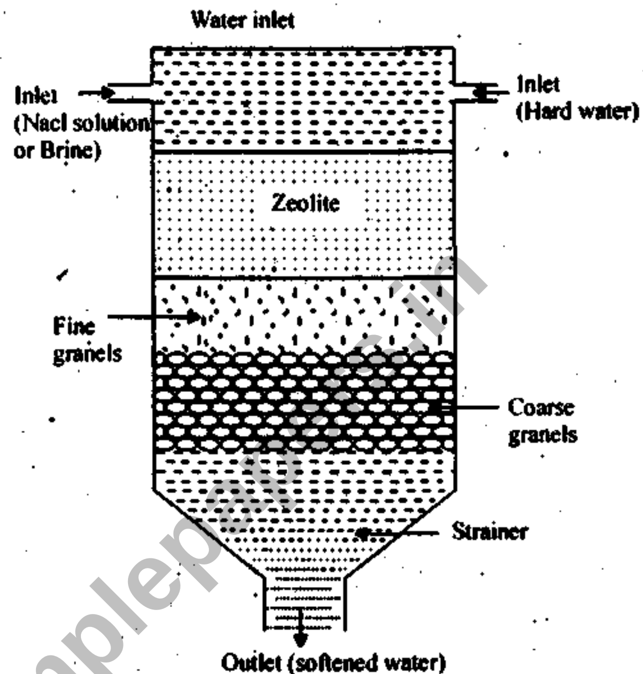
$Ca(HCO_3)_2 + Na_2Ze \longrightarrow 2NaHCO_3 + CaZe$

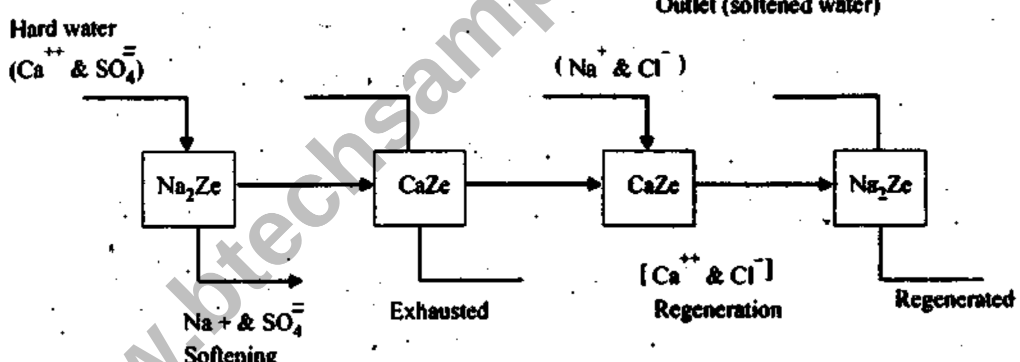
$MgSO_4 + Na_2Ze \longrightarrow Na_2SO_4 + MgZe.$

$CaZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2$

$MgZe + 2NaCl \longrightarrow Na_2Ze + MgCl_2$

The overall softening process by zeolite is given as :





The reactions involved in zeolite process are :

$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2NaHCO_3$

$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2NaHCO_3$

$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2Nacl$

$Na_2Ze + CaSO_4 \longrightarrow CaZe + Na_2SO_4$

$Na_2Ze + MgCl_2 \longrightarrow MgZe + 2Nacl$

$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$

$Na_2Ze + Fe(HCO_3)_2 \longrightarrow FeZe + 2NaHCO_3$

$Na_2Ze + Mn(HCO_3)_2 \longrightarrow MnZe + 2NaHCO_3$

Q. 2. (e) (i) Two organic compounds have same molecular formula C_2H_6O. In NMR spectra one shows only one signal while the other has three signals. Identify them with proper explanation.

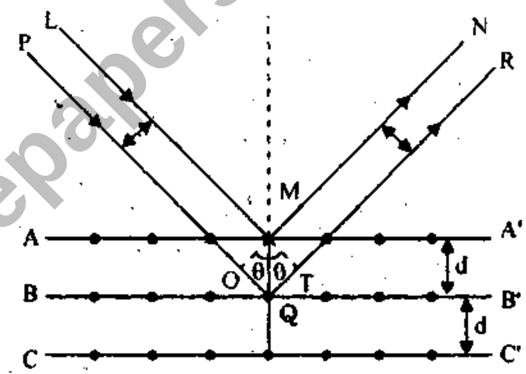
Ans. Molecular formula = C_2H_6O

Isomers possible = two

One signal = two identical groups. that can be $-CH_3$ group because due to 6H only one signal can be observed in NMR. So it may be CH_3OCH_3 (Dimethylene)

Three signal = three different hydrogen that can be CH_3, CH_2 and OH. So it may be CH_3CH_2OH (Ethanol)

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



Ans. Bragg's Law : A simple equation was developed by H. Bragg for the study of internal structure of crystals. Bragg is pointad out that the scattering of x-raya by crystals could ba considered as "reflections" from auccessiva planes of the atoms in the crystal.

In Δ QMT

$\angle OMQ = \angle QMT = \theta$

$$\sin\theta = \frac{QT}{MQ} = \frac{QT}{d}$$

$QT = d \sin\theta$

$OQ = d \sin\theta$

Path difference between PQR and LMN

$= OQ + QT$

$= d \sin\theta + d \sin\theta$

$= 2d \sin\theta$

For the waves raflected from first layer and second layer to be in the same phase this path difference must be integral multiple of wavelength i.e. $n\lambda$

where n = Integer = 1, 2, 3, ...

So $n\lambda = 2d \sin\theta$ This ia known aa Bragg's equation.

Section C

Q. 3. Attempt any one of the following :

Q. 3. (a) Explain Beer Lambert Law. Discuss Electronic transitions. Calculate absorhance if %T=80.

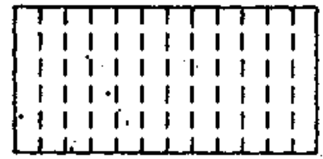
Ans. Bear Lambert Law : Lambert is law states that, whan a monochromatic light is passed through a solution. The decrease in the intensity of light with tha thickness of the solution is directly proportional to the intensity of incidant light

$I_t = I_0 e^{-kx}$ I_t = Intensity of the transmitted light

I_0 = intensity of tha incident light

x = thickness of tha medium

(iii) Cholesteric Liquid crystal : Cholesteric liquid crystals have properties of both nematic and smectic liquid crystals to some extent. It is callled cholesteryl because it is obtained in cholesteryl derivatives.



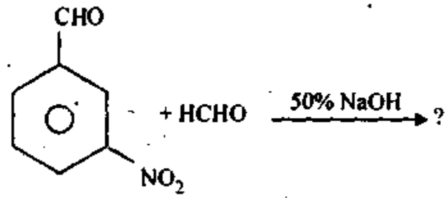
Difference between Nematic and Smectic liquid crystals :

(1) Nematic has thread like structure while smectic has soap like layer arrangement.

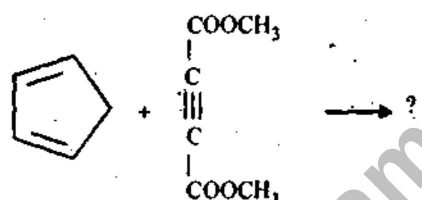
(2) Smectic liquid crystal is formed at lower temp than nematic liquid crystals.

Q. 4. (b) Complete the following reactions and write their mechanism

(i)

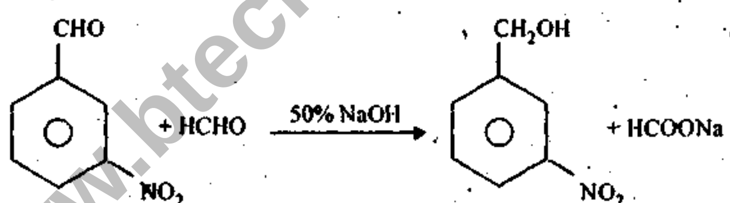


(ii)



Write one application of the above named reactions.

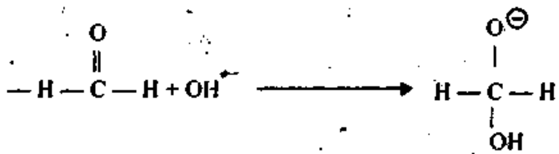
Ans. (i)



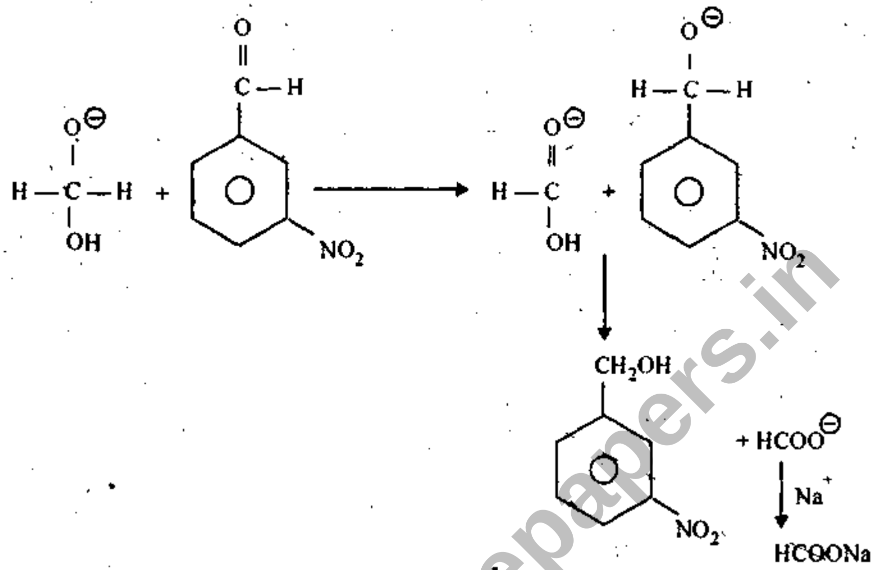
This is crossed Cannizarro Reaction.

Mechanism : Step I : $NaOH \rightarrow Na^+ + OH^-$

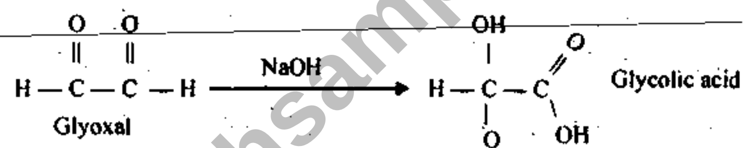
Step II :

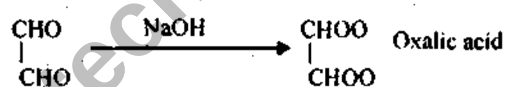


Step III :

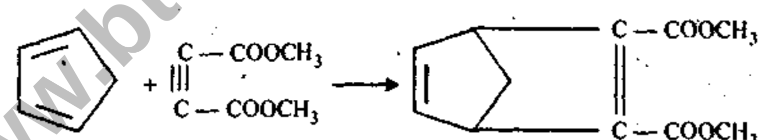


Application : It is used to prepare glycolic acid and oxalic acid

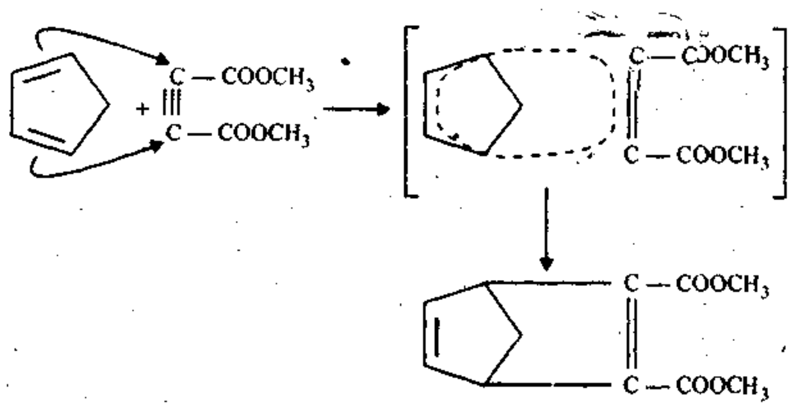




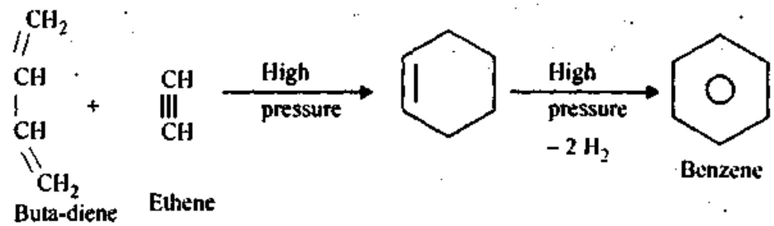
(II)



Mechanism :



Applications : It is used to prepare benzene from butadiene and ethene.



Q. 5. Attempt any four parts of the following :

Q. 5. (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. Component : The least number of independent chemical constituents in term of which the composition of every phase can be expressed by means of a chemical equation is called conponent

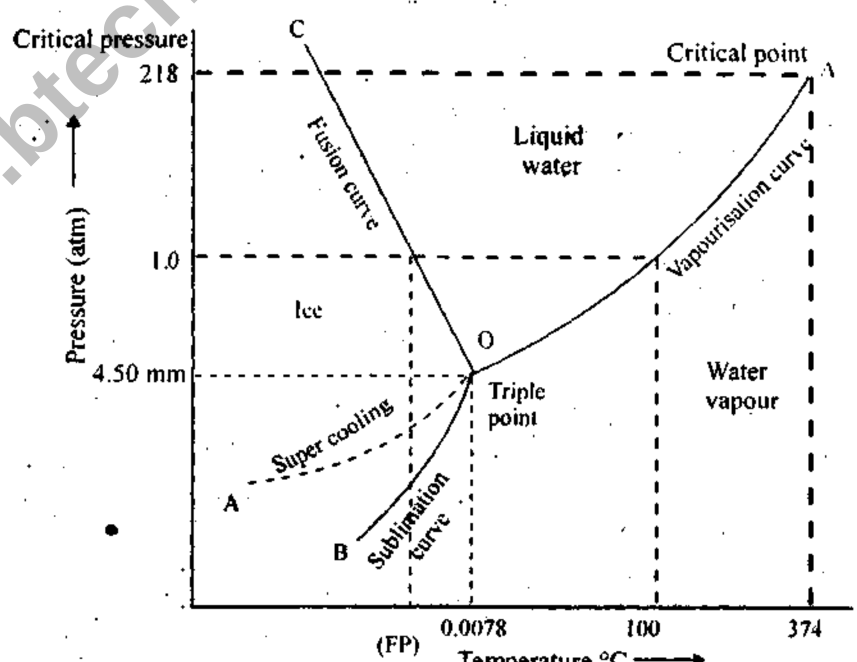
eg. water system has three phases : ice, water and water vapour. The composition of all the three phases is expressed in terms of one chemical individual H_2O. Thus water system has one component only.

Phase : Any homogeneous part of a system having all physical and chemical properties the same throughout is called a phase.

ex. If a system containing only liquid water is one phase or 1– phase system (P = 1)

(2) A system containing liquid water and water vapour /gas is a two phase or 2-phase system (P = 2)

(3) A system containing liquid water, water vapour, and solid ice is three phase or 3-phase system.



Degree of Freedom : The least number of variable factors (concentration, pressure and temperature) which must be specified so that the remaining variables are fixed automatically and the system is completely defined is called Degree of freedom".

eg. For water system – F = 0 because ice – water-vapour system

In this system the three phases coexists at the freezing point of water. Since the freezing temperature of water has fixed value the vapour pressure of water has also a definite value. The system has two variables (temperature and pressure) and both these are already fixed. Thus the system is completely defined automatically, these being no need to specify only variable. Hence it has no **Degree** of freedom ($F = 0$)

For a one-component system

$F = C - P + 2$

$1 - P + 2 = (3 - P)$

Case -1 : Only one phase is present

$F = 3 - 1 = 2$

System = bivariant= two variables (temp. & pressure)

Case -2 : two phases are in equilibrium

$F = 3 - 2 = 1$

System = univariant (monovariant)

= one variable *i.e.* (pressura)

Case - 3 : three phases are in equilibrium

$F = 3 - P = 3 - 3 = 0F = 0$ (nonvariant or invariant).

At Tripie point 'O' : The vapour pressure curve (OA), the sublimation curve (OB) and the fusion curve (OC) meet at the triple point 'O' where all the three phases liquid water / ice/ vapour are in equilibrium. This occurs at 0.0076°C and vapour pressure 4.58 mm fig. Since there are three phases and one component.

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

i.e. the system at the triple point is invariant or nonvariant. Thus if pressure or temperature is changed, the three phases would not exist and one of the phase would disappear.

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

Ans.

Addition	Condensation
1 It requires the presence of double bond in the monomer.	1. It requires two reactive functional groups to be present at both ends of the monomer .There should be at least two different bi-or poly functional monomers having functional groups with affinity for each othe
2 No by product is formed	2. Generally a by-product is formed
3 Homo-chain Polymar, generally a thermoplastic is obtained.	3. Hetero-chain polymer either thermoplastic or thermoset can be obtained.
4 The growth of chain is at one active centre.	4. The growth of chain occurs at minimum of two active centres.
eg. Polymerization of ethylena → polyethylene Vinyl chloride → polyvinylchlorida styrene → polystyrena	**eg** hexamethylenedrame + Adipic acid → nylon 6, 6 (polyamide) Caprolactum → nylon 6

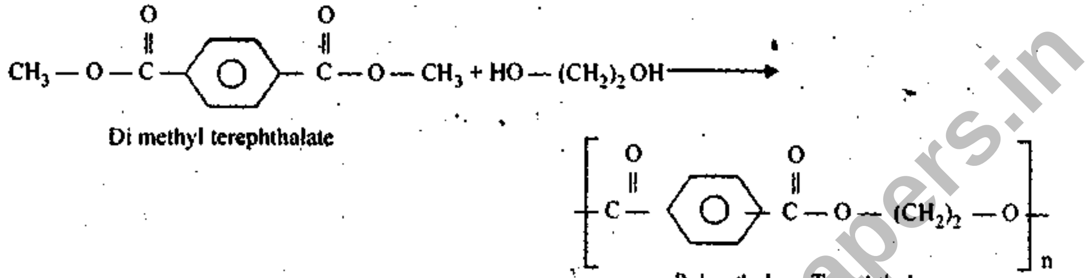
Monomers of Neoprene :

$$CH_2 = CH - \underset{\substack{|\\Cl}}{C} = CH_2 \longrightarrow -\!\!\left[CH - CH = \underset{\substack{|\\Cl}}{C} - CH_2\right]_n$$

2, chloro -1, 3-butadiene   Neoprene

Chloroprene

Monomer of Decron :



Poly ethylene Terephthalate
(Dacron) (Terylene) (PET)

Monomer of Nylon 6, 6 :

$$H_2N - (CH_2)_6 - NH_2 + HOOC - (CH_2)_4 - COOH \longrightarrow \left[HN - (CH_2)_6 - \underset{|}{\overset{}{N}}(H) - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}}\right]_n$$

Hexamethylene   Adipic acid

(Nylon 6-6)

Monomer of PTFE (Teflon) :

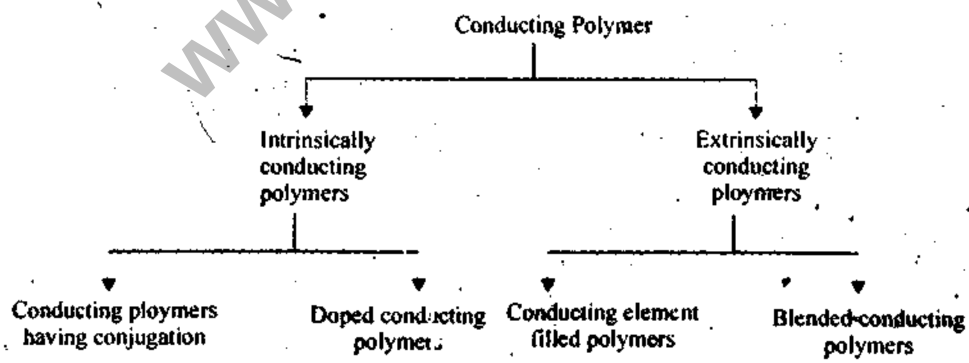
$$nF_2C = CF_2 \longrightarrow -\!\!\left[CF_2 - CF_2\right]_n$$

Tetrafluroethylene   Teflon

Conducting Polymers : A polymer which can conduct electricity is termed as conducting polymers.

eg. Polyaniline (2) Polypyrrole (3) Polyacetylene (4) polythiophene

Classification of Conducting Polymers :



Application of Condncting Polymers :

(1) In rechargeable batteries

(2) In analytical sensors

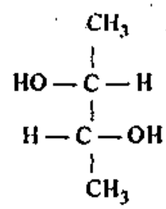
(3) For making ion- exchangers

(4) In electrochromic displays and optical fibres.

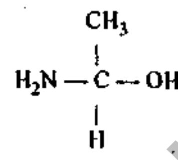
(5) In electronics

(6) In photovoltaic devices.

Q. 6. (a) Assign (R) or (5) configuration to the following compounds :

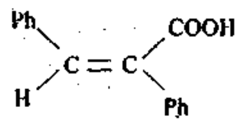


(A)

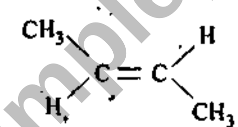


(B)

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



(A)



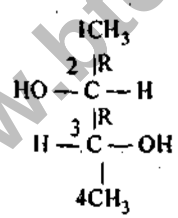
(B)

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

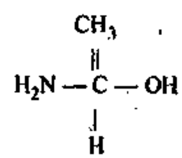
(iv) The following compounds are optically active or not ? Explain.

(A) 1, 3-Diphenyl propadiene . (B) 1, 7-Dicarboxylspirocycleheptane.

Ans. (i)

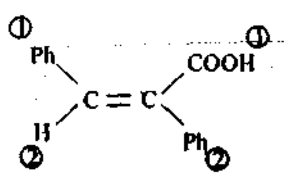


$C_2 = R$
$C_3 = R$

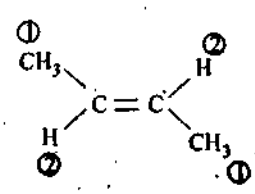


It has R-configuration It has R-configuration

(ii)



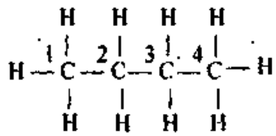
Z-isomer



E-isomer

(iii) Conformational isomer of *n*-Butane :

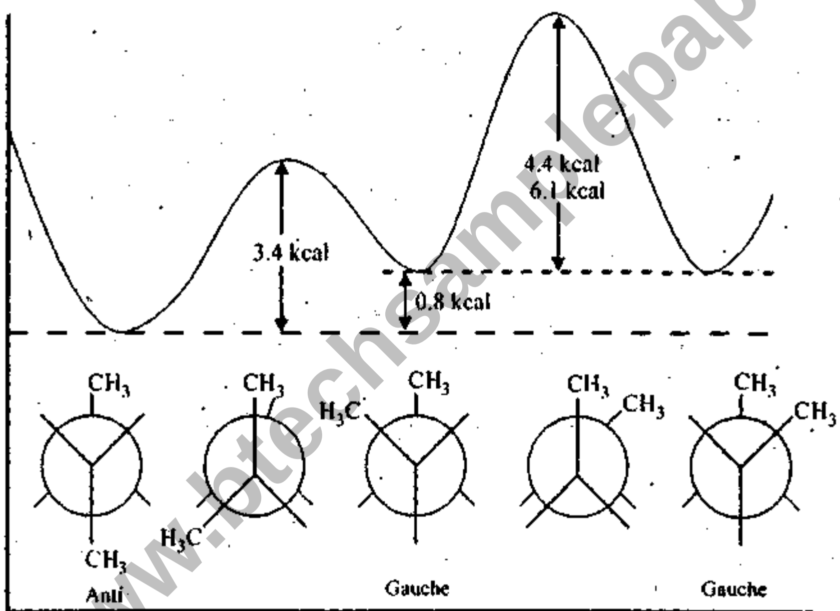
n-butane has the structure



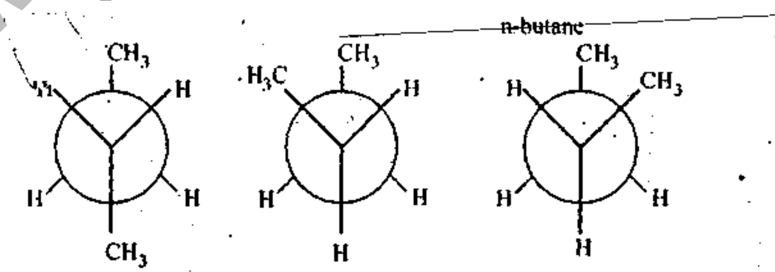
Due to presence of the methyl groups, there are several different staggered conformations.

There is the anti conformation A_1 in which the methyl groups are as far apart as they can be (*B*) and (*C*) are the two Gauche conformations in which the methyl groups are only 60° apart.

The conformation (*A*) is 0.8 K Cal/mol more stable than (*B*) or (*C*). Both anti and Gauche conformations are free of torsional strain. But in Gauche conformations, there is Vander waals repulsion (steric repulsion) between the methyl groups, and the molecule is less stable because of Vander waals strain (or steric strain).



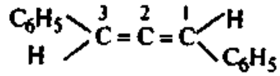
Potential energy changes during rotation about the C (2) – C(3) bonding



(A) (B) (C)

Anti conformation

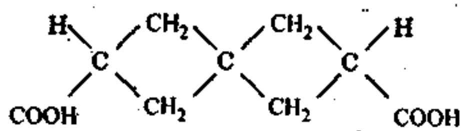
Gauche conforamation of n-Butane

(iv) 1, 3-Diphenyl propadiene = 

It is an allene and allenes are optically active. It is optically active compound withou chiral center.

Central C-atom has *sp* and 1,3 carbon has sp^2 hybridisatio

1,7-Dicarboxylspirocycloheptane.



It is an spirane derivative which is also optically active due to restricted rotation. So it i also optically active.

Q. 6. (b) Deduce the kinetic equation for the reaction of the first order. A firs order reaction is 25% completed in 30 min. Calculate (i) rate constant (ii) half life tim and (iii) time required for 75% of the reaction to be completed.

Ans. In first order reaction

$$A \xrightarrow{k} \text{Product}$$

At starting	a	0
At equilibrium at t (sec)	$(a-x)$	x

rate of reaction $\frac{dx}{dt} = k(a-x)$

or $\int \frac{dx}{(a-x)} = k\int dt$

$-ln\,(a-x) = kt + c$

when $t = 0$ $x = 0$

$-lx\,a = c$

$-ln\,(a-x) = kt - ln\,a$

$ln\,a - ln\,(a-x) = kt$

$kt = \frac{ln\,a}{ln\,(a-x)} = ln\,\frac{a}{(a-x)}$

$k = \frac{1}{t}\,ln\,\frac{a}{(a-x)}$

$$\boxed{k = \frac{2.303}{t}\log\frac{a}{(a-x)}}$$

Solution : 25% completed $t = 30$ min

(i) **Rate constant** $k = \frac{2.303}{30}\log\frac{100}{100-25}$

$$= \frac{2.303}{30} \log \frac{100}{75}$$

$$= \frac{2.303}{30} [\log 100 - \log 75]$$

$$= \frac{2.303}{30} [2 - \log 75] = \frac{2.303}{30} [2 - 1.8751] = 0.0096 \text{ min}^{-1}$$

(ii) Half life time $= t_{1/2} = \frac{0.693}{k} = \frac{0.6930}{0.0096} = \frac{6930}{96} \approx 72$ min

(iii) When 75% reaction complete

$$t_{75\%} = \frac{2.303}{k} \log \frac{100}{100 - 75}$$

$$= \frac{2.303}{0.0096} \log \frac{100}{25}, \frac{2.303}{0.0096} \times 2 \times .3010 \approx 144 \text{ min}$$

Q. 7. Attempt any one of the following :

(a) (i) Write the relationship between high and low calorific values. If HCV of a coal sample its 7500 cal/g and % H=5. Calculate is LCV. Given; latent heat of condensation of steam= 580 cal/g.

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

Ans. The relationship between high and low calorific value is

Net calorific value (LCV) = Gross calorific value (HCV) $- 0.09 \times H \times L$

where H = % of hydrogen in the fuel

l = latent heat of steam

Solution: HCV = 7500 Cal/gm % $H = 5$ $l = 580$ Cal/g

$$\text{LCV} = \text{HCV} - 0.09 \times \text{H} \times \text{L}$$

$$= 7500 - 0.09 \times 5 \times 580$$

$$= 7500 - 261 = 7239 \text{ cal}$$

(ii) Prohlems created hy Hard water in boiler :

(1) Sludge and scale formation: The increase in the concentration of dissolved salts due to boiling, lead to th... n out as precipitates.

If the ppt formed are soft loose and slimy, these are known as sludges, while if the precipitate is hard and adhering on the inner wall, it is called scale.

(2) Priming and foaming : Priming refers to the propulsion of water into steam drum by extremely rapid, almost explosive boiling of water at the heating surface.

Foaming is the formation of small but presistent foam or bubbles the water surface in boilers, which do not break easily.

(3) Boiler corrosion : Boiler corrosion is 'decay' or 'disintegration' of boiler body material either due to chemical or electrochemical reaction with its environment having O_2 and CO_2 and minerals acids.

(4) Caustic Embrittlement : It is a phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

Hardness of hard water in sample = 500 ppm

In **French** (°Fr)

1°Fr = 1 part of $CaCO_3$ equivalent hardness per 10^5 parts of water.

Hence 1 ppm = 0.1° Fr

= 500 × 0.1 = 50° Fr

In Clarke (°Cl)

1°Cl = 1 part of $CaCO_3$ per 70, 000 parts of water.

Hence 1 ppm = 0.07° Cl = 500 × 0.07 = 35° Cl

Q. 7. (b) What are fullerenes ? Discuss their applications.

Ans. Fullerenes : It is an allotrope of carbon. Its molecular formula C_{60}. It was discovered by H.W. Kroto and R.Smatley at Rice university USA in 1985. It is popularly known as Buck minister fullerence in honour of american architect Buck minister fuller, who designed geodesic dome structure based on hexagons and pentagons.

Preparation : These are prepared by vapouring a graphite rod in 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 of Fullerene :

Structure : 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 (– 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 a double bond. C_{60} is also known as bucky ball as it is or spherical cluster of carbon atom arranged in series of 5 and 6-membered rings to form a soccer ball shape.

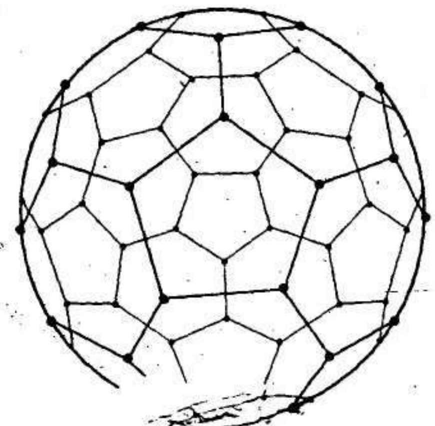


Fig. Structure of a buckyball.

Applications : (1) Used as lubricant

(2) Used as superconductor when mixed with alkali metals ($C_{60}k_x$)

(3) Used as soft ferromagnet (eg. TDAE C_{60})

(4) In electronic and Microelectronic devices

(5) In Non-linear optical devices.