

B.Tech.

**FIRST SEMESTER EXAMINATION, 2010-11**

**ENGINEERING CHEMISTRY**

(EAS-102)

[Total Marks : 100]

Time : 3 Hours]

Note : (1) Attempt All questions.

**SECTION-A**

Q. 1. Choose/Fill correct answer :

20 × 1 = 20

(a) o-nitrophenol is more volatile than p-nitrophenol due to :

- (i) Inductive effect
- (ii) Electromeric effect
- (iii) Intermolecular hydrogen bonding in o-nitrophenol
- (iv) Intramolecular hydrogen bonding in o-nitrophenol.

Ans. (iv) Intramolecular hydrogen bonding in o-nitrophenol.

Q. 1. (b) Which of the following possesses lowest energy ?

- (i) NO
- (ii) O<sub>2</sub>
- (iii) N<sub>2</sub>
- (iv) CO

Ans. (ii) N<sub>2</sub>

Q. 1. (c) The number of atoms per unit cell in a simple cubic, fcc and bcc arrangement are, respectively :

- (i) 8, 14, 9
- (ii) 1, 4, 2
- (iii) 1, 2, 4
- (iv) 4, 1, 2

Ans. (ii) 1, 4, 2

Q. 1. (d) An electrophilic reagent is:

- (i) Carbanion
- (ii) Chloride ion
- (iii) Alcohol
- (iv) FeCl<sub>3</sub>

Ans. (iv) FeCl<sub>3</sub>

Q. 1. (e) The formation of cyanohydrin from a ketone is an example of:

- (i) electrophilic addition
- (ii) nucleophilic addition
- (iii) nucleophilic substitution
- (iv) electrophilic substitution

Ans. (ii) Nucleophilic addition

Q. 1. (f) S<sub>N</sub>1 reaction is facilitated by :

- (i) Bulky groups
- (ii) Simple non-bulky groups
- (iii) Both (i) and (ii)
- (iv) None of these

Ans. (i) Bulky groups

**Q. 1. (g) Which of the following compounds, will have zero dipole moment ?**

- (i) 1, 1-Dichloroethene (ii) cis-1, 2-Dichloroethene  
(iii) trans-1, 2-Dichloroethene (iv) None of the compounds

**Ans. (iii) Trans-1, 2-Dichloroethene**

**Q. 1. (h) Glyptal is a polymer of**

- (i) Alkanal and HCHO (ii) Glycol and Phthalic acid  
(iii) Glycerol and Phthalic acid (iv)  $\text{CH}_3\text{COOH}$  and Phthalic acid

**Ans. (ii) Glycol + phthalic acid**

**Q. 1. (i) Waker process uses the catalyst:**

- (i) Wilkinson catalyst (ii) Zeigler Natta catalyst  
(iii) Zelse's salt (iv) Nickel

**Ans. (iii) Zeise's salt**

**Q. 1. (j) Inflexion point is when**

- (i) pH remains constant (ii) pH changes abruptly  
(iii) pH changes slowly (iv) None of these

**Ans. (iii) pH changes abruptly**

**Q. 1. (k) Bragg's equation is based on:**

- (i) IR studies of crystals (ii) UV studies of crystals  
(iii) X-ray studies of crystals (iv) Y-rays studies of crystals

**Ans. (iii) X-ray studies of crystals**

**Q. 1. (l) Number of signals obtained in the  $^1\text{H NMR}$  of  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$  shall be :**

- (i) 10 (ii) 2  
(iii) 1 (iv) 4

**Ans. (ii) 2**

**Q. 1. (m) Optical isomerism is shown by:**

- (i) Butanol-1 (ii) 3-Pentanol  
(iii) Butanol-2 (iv) 4-Hexanol

**Ans. (ii) Butanol-2**

**Q. 1. (n) The angle between two covalent bonds is minimum in :**

- (i)  $\text{BeF}_2$  (ii)  $\text{H}_2\text{O}$   
(iii)  $\text{CH}_4$  (iv)  $\text{NH}_3$

**Ans. (iii)  $\text{H}_2\text{O}$**

**Q. 1. (o) On increasing the temperature, the vapour pressure of liquid:**

- (i) decreases (ii) increases  
(iii) remain constant (iv) first increases then decreases

**Ans. (ii) Increase**

**Q. 1. (p) The crystalline compound  $\text{A}_x\text{B}_y$  is characterized by a body-centred cell.**

**The compound has the formula :**

- (i) AB (iii)  $\text{A}_8\text{B}$   
(ii)  $\text{A}_4\text{B}$  (iv)  $\text{AB}_4$

Ans. (i) AB

Q. 1. (q) Eutectic point of a system and triple point are :

- (i) identical (ii) always same  
(iii) different (iv) both zero variant.

Ans. (ii) different

Q. 1. (r) The role of salt bridge is :

- (i) To keep e.m.f. of the cell positive  
(ii) To keep e.m.f. of the cell negative  
(iii) To maintain electrical neutrality of the solution in two half cells  
(iv) None of the above

Ans. (iii) To maintain electrical neutrality of the solution in two half cells.

Q. 1. (s) With increased polarity of solvent the absorption band shifts to shorter wavelength for :

- (i)  $\pi \rightarrow \pi^*$  (ii)  $n \rightarrow \pi^*$   
(iii)  $n \rightarrow \delta^*$  (iv)  $\delta \rightarrow \delta^*$

Ans. (ii)  $n \rightarrow \pi^*$

Q. 1. (t)  $E_{\text{cell}} + E_{\text{anode}} \longrightarrow ?$

Ans.  $E_{\text{cathode}}$

## SECTION-B

Q. 2. Attempt any three of the following :

(10 × 3 = 30)

Q. 2. (i) (a) Describe in brief about conducting polymers with their applications.

Ans. **Conducting polymers** : A polymer which can conduct electricity intermed as conducting polymer. e.g. polyaniline, polypyrrole, conducting, polymer, may be used in place of metals because of their lighter weight and they do not corrode.

**Synthesis** : 0.1M oAniline Hydrochloride + 1.0M aqueous HCl

Exothermic  
3-4°C

↓

0.1M ammonium persulphate  $(\text{NH}_4)_2 \text{S}_2\text{O}_8$   
(cassoln) slowly added with stirring.

During polymerisation reaction vessel is placed in an ice path for one to two hours and colour changes.

Light blue → Blue green → Copper tint → Green

↓  
get precipitated in green form filter washed

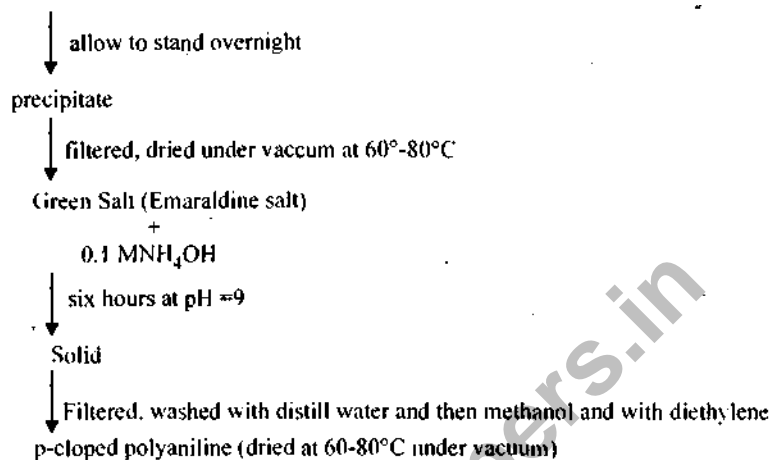
Polyaniline

↓  
washed with methyl alcohol or acetone

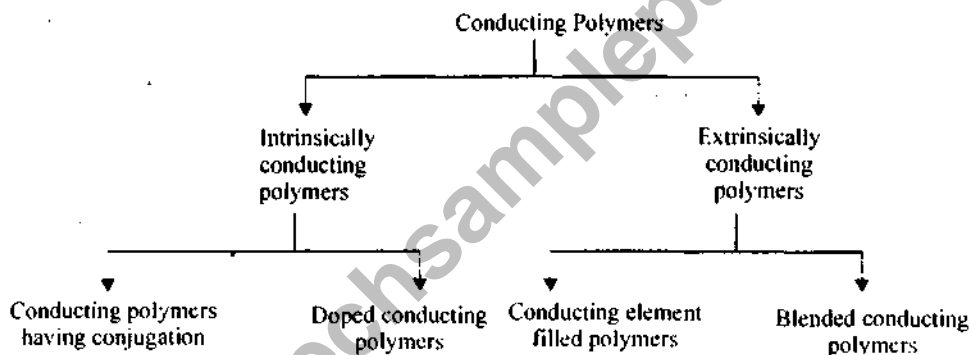
Polyaniline

↓  
washed with methyl alcohol or acetone

Residue + 1.0 M ag. HCl



### Classification of Conducting Polymers



**Applications: 1. In Rechargeable Batteries :** These rechargeable batteries are small in size, longer lasting, do not involve heavy metals.

**2. In Analytical sensors :** Also used for making sensors for pH, O<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub> and glucose.

**3. For making Ion Exchangers :** Membrane made up of conducting polymers can show boundary layer effects with selective permeability for ions, gases etc. Hence they are useful for ion-exchangers and controlled release of drugs.

**4. In Electrochromic displays and optical fibres :** ICP's can absorb visible light to give coloured products so can be useful for electrochromic displays and optical filters. Thus conducting polymers can be used as electrochromic materials.

**5. In Electronics:** Photostructural lacquers based on ICP's are useful for electron beam lithography LED's and Data Storage.

**6. In photovoltaic devices :** Al | conducting polymer | Au photovoltaic.

**Q. 2. (ii) (b) What are elastomers ? Give the preparation, structure and uses of Buna-S and Butyl rubber.**

**Ans. Elastomers :** When a polymer is vulcanized into rubbery products exhibiting good strength and elongation, it is called on elastomers.

The elastomers possesses the tendency to recover their original shape after they have been greatly deformed.

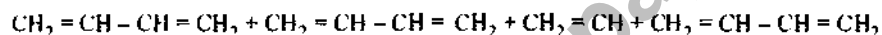
The elastomeric molecules are long and thin and flexible which become lined up when the material is stretched. But as soon as the stretching force is removed, the molecules return to their original random conformation.

Molecules in Elastomers have weak intermolecular forces.

**Essential requirements of an Elastomers :** (1) Long flexible chains

(2) Weak intermolecular forces

(3) occasional cross-linking

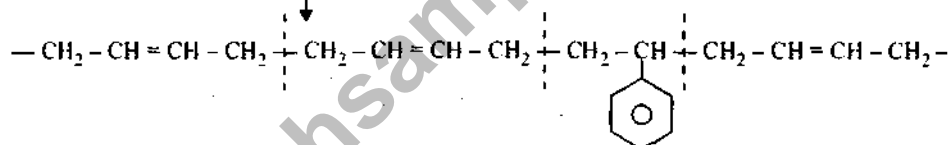


Butadiene

Copolymerization



Styrene



(Styrene Butadiene Rubber having repeating units of mainly 1, 4 - addition product)

**Buna-S : Preparation and Structure :** It is prepared by the copolymerisation of butadiene (75%) and styrene (25%).

**Uses :** (1) used in motor tyres (2) used in shoe soles (3) Foot wear components

(4) Insulation of wire and cables

(5) Carpet backing (6) Gaskets

(7) Adhesives

(8) Tank-lining etc.

**Butyl Rubber :** It is prepared by copolymerisation of Isobutylene (98%) and Isoprene (2%).

**Preparation and Structure :**



Butyl rubber

**Uses :** (1) In making cycle and automobile tyre.

- (2) In the insulation of high voltage wires and cables.  
 (3) In tank linings  
 (4) In making conveyer belts.

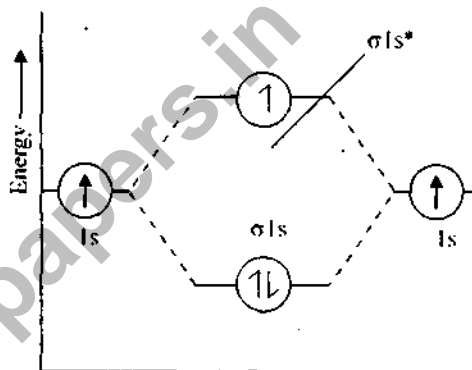
**Q. 2. (ii) (a) With the help of molecular orbital diagram, calculate the bond order of  $O_2^-$ ,  $O_2^{2-}$ ,  $H_2^+$ ,  $NO^-$ . Also write their magnetic character.**

**Ans. Molecular orbital Theory :** It states that

(i) The valence electrons are considered to be associated with all the nuclei in the molecule. Thus the atomic orbital from different atoms must be combined to product molecular orbitals.

(ii) Electrons may be considered either as particles or waves. An electron in an atom may therefore be described as occupying an atomic orbital  $1^B$  by a wave function  $\psi$  (which is a solution to the schrodinger wave equation). Electrons in a molecule are said to occupy molecular orbitals.

(iii) The wave function describing a molecular orbital may be obtained by linear combination of atomic orbitals.



**Bond Order of  $H_2^+$  :** Molecular orbital Electronic configuration of  $H_2^+$  molecule

$$= \sigma 1s^2, \sigma^* 1s^1$$

$$\text{Bond order} = \frac{1}{2}$$

magnetic behaviour = Paramagnetic

**Bond Order of  $NO^-$  :** The electronic configuration, bond order and magnetic character of  $NO^-$  is as

$$NO^- - 16 - KK \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2px)^2 \pi(2py)^2 \pi(2pz)^2 \pi^*(2py)^1 \pi^*(2pz)^1$$

$$\text{Bond Order} = \frac{8 - 4}{2} = 2$$

Magnetic Character = Paramagnetic

**Bond order of  $O_2^-$  (Superoxide ion) :** The ion is formed when the  $O_2$  molecule gains one electron.

The electronic configuration is:

$$O_2^- = KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2px)^2 (\pi 2py)^2 (\pi 2px)^2 (\pi^* 2py)^2 (\pi^* 2pz)^1$$

$$\text{Bond Order} = \frac{1}{2} [N_b - N_a] = \frac{1}{2} [8 - 5] = 1 \frac{1}{2}$$

Magnetic character = paramagnetic

**Bond Order of  $O_2^{2-}$  :**

$$\text{Electronic Configuration} = 14 = KK \sigma(2s)^2 \sigma^*(2s)^2, \sigma(2px)^2 \pi(2py)^2 \pi(pz)^2 \pi^*(2py)^2 \pi^*(2pz)^2$$

$$\text{Bond Order} = \frac{8-6}{2} = 1,$$

Magnetic character = Diamagnetic

**Q. 2. (ii) (h) Derive an expression for the density ( $\rho$ ) of a cubic crystal.**

**Ans. Density for Cubic crystal :**

Let  $V$  = Volume of cube

$m$  = atomic mass

$N$  = Avogadro's number

“ $n$ ” = Effective number of particle in unit cell (cube)

Mass of  $N$  atoms =  $m$  gm

mass of one atom =  $\frac{m}{N}$  gm

if unit cell has in effective no of particles, mass of cubic cell =  $n \left( \frac{m}{N} \right)$  gm

$$\text{density} = \frac{\text{Mass}}{\text{Volume}} = \left( \frac{n m}{N \times V} \right)$$

$$\text{hence } \rho = \left( \frac{n m}{N V} \right) \text{ gm/cm}^3$$

**Q. 2. (iii) (a) Classify fuel cells. Give some examples with their electrode reactions.**

**Ans. Fuel Cells :** A Fuel cell is a device that generates electricity by a chemical reaction. Every fuel cell has two electrodes, one positive and one negative, called cathode and anode respectively. The reactions that produce electricity takes place at the electrodes. Every fuel cell has an Electrolyte, which carries electrically charged particles from one electrodes to the other, and a catalyst, which speeds the reactions at the electrodes.

Therefore, it may be defined as “A fuel cell converts the chemical energy of the fuels directly to electricity.”

**Working of fuel Cells :** The purpose of a fuel cell is to produce an electric current than can be directed outside the cell to do work, such as powering an electric motor or illuminating a light bulb, because of the way electricity behaves. This current returns to the fuel cell completing an electrical circuit.

In general terms, hydrogen atoms enter a fuel cell at the anode where a chemical reaction strips them of their electrons. The hydrogen atoms are then ionized and carry a positive electrical charge. The negatively charged electrons provide the current through wires to do work. If AC is needed, the DC output of the fuel cell must be routed through a conversion device called an inverter.

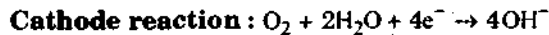
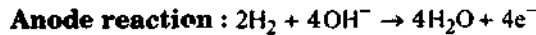
**Types of Fuel Cells :**

The fuel cells may be classified into following categories :

- (i) Alkaline fuel cells (AFC)
- (ii) Phosphoric Acid fuel cells (PAFC)

- (iii) Molten Carbonate fuel Cells (MCFC)
- (iv) Polymer Electrolyte Membrane Fuel Cells (PEMFC)
- (v) Solid oxide fuel cells (SOFC)
- (vi) Direct Methanol fuel cells (DMFC)
- (vii) Regenerative fuel cells (RFC)

**Alkaline Fuel Cells :** The chemical reactions, occurred at the anode and cathode in an AFC are as under :



**Phosphoric Acid Fuel Cells (PAFCs) :** Phosphoric acid fuel cells were the first fuel cells to cross the commercial threshold in the electric power industry. More than 265 of these, "first generation", power units were placed in operation in stationary power applications in the united states and overseas : out of which over 200 units currently in use.

PAGCs operate at around 150 – 200°C, above the boiling point of water. The overall efficiencies of PAC can approach up to 80% and the electricity generating efficiency is 37-42%.

**Molten Carbonate Fuel Cells (MCFCS) :** Molten carbonate fuel cells are currently-being developed for natural gas and coal based power plants for electrical utility, industrial and military application. It is a high temperature fuel cells that use an electrolyte compased of a molten carbonate salt mixture (carbonated of sodium or magnesium) suspended in a porous, chemically inert ceramic lithium aluminium. oxide ( $\text{LiAlO}_2$ ) Matrix. MCFCS are operated at 650°C, therefore, non-precious metals can be used as catalysts at the anode and cathode to reduce cost.

**Polymer Electrolyte Membrane Fuel Cells (PEMFCs)**

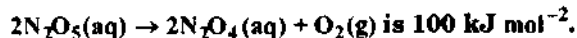
**Solid Oxide Fuel Cells (SOFCs) :** Solid oxide fuel cells use a hard ceramic compound of metal oxides, e.g., calcium or zirconium oxides, as electrolyte. Since the electrolyte is a solid, the cells do not have to be constructed in the plate like configuration.

**Direct Method Fuel Cells (DMFCs) :** The above mentioned as well as other fuel cells are powered by hydrogen, which can be fed the cell system directly or can be generated with in the fuel cell system by reforming hydrogen rich fuels, e.g., methanol, ethanol and hydrocarbon fuels, Here in this case, DMFCs, however are powered by pure methanol which is mixed with steam and fed directly to the fuel cell anode, like other fuel cells, DMFCs do not have the fuel storage problems, as the methanol has a higher energy density than hydrogen-through less than gasoline or diesel fuel, Methanol is also easier to transport and supply to the public as it is liquid like gasoline.

**Regenerative Fuel Cells (RFCs) :** Regenerative fuel cells produce electricity from hydrogen and oxygen and generate heat and water as by products just like other fuel cells. However, regenerative fuel cell systems can also use electricity from solar power or some other source to divided the excess water into oxygen and hydrogen fuel. Process is called as electrolysis. This is a comparatively young fuel cell technology being developed by NASA, USA and others.



**Q. 2. (iii) (h) The activation energy for the reaction:**



The rate constant of the reaction is  $2.35 \times 10^{-4} \text{ s}^{-1}$  at 293 K. What is the rate constant of the reaction at 303 K ?

Ans.  $K, Ae^{-E_a/RT}$

Given  $k_1 = 2.35 \times 10^{-4} \text{ T}_1 = 293^\circ \text{K}$   $E_a = 100 \text{ kJ/mol}^2$

$k_2 = ? \text{ T}_2 = 303^\circ \text{K}$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{k_2}{2.35 \times 10^{-4}} = \frac{100}{2.303 \times 8.3} \left[ \frac{10}{293 \times 303} \right]$$

$$\log \frac{k_2}{2.35 \times 10^{-4}} = 0.5881$$

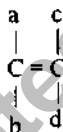
$$\frac{k_2}{2.35 \times 10^{-4}} = \text{Antilog}(0.5881) = 3.874$$

or

$$k_2 = 9.11 \times 10^{-4} \text{ sec}^{-1}$$

**Q. 2. (iv) Write short notes on : E, Z Nomenclature, Conformation of n-butane.**

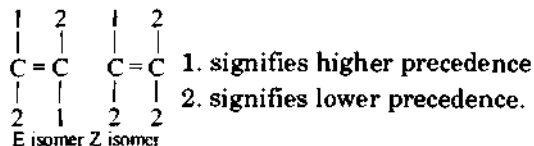
**Ans. E and Z System of Nomenclature :** If four different atoms or groups are attached to the carbon atoms of a double bond, then cis and trans designations cannot be employed.



In such cases, Cahn, Ingold and Prelog developed **E** and **Z** system of nomenclature, which is based on a priority system. In this system, the two atoms/groups attached to each carbon atom of the doubly bond carbons are put in order of precedence based on sequence rules;

(i) The symbol '**E**' (from German word *Entgegen* = across or opposite) is assigned to the isomers in which atoms/groups of higher precedence are on the opposite side.

(ii) The symbol '**Z**' (from German word *Zusammen* = together) is assigned to the isomer in which the atoms/groups of higher precedence are on the same side. Thus :



**Note :** In large number of cases, **E** isomer is trans while **Z** isomer is cis. However, there are many exceptions also.

**Sequence rules : 1.** Higher the atomic number, higher is the priority assigned to the atom. For example:

Precedence order : I > Br > Cl > H

At. No. 53 35 17 1

(ii) In case of groups, the precedence is decided on the basis of atomic number of first atom of the group. For example :

Precedence order  $-Cl > -SO_3H > -OH > -NHCH_3 > -COOH$

$\uparrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow$

At. No. of first atom 17 16 8 7 6

(iii) If the precedence order of groups cannot be settled on the basis of atomic number of first atom, then second atom or the subsequent groups are considered. For example :

Precedence order  $-COOH > -CH_2-CH_3 > -CH_3$

$\uparrow \quad \uparrow \quad \uparrow$

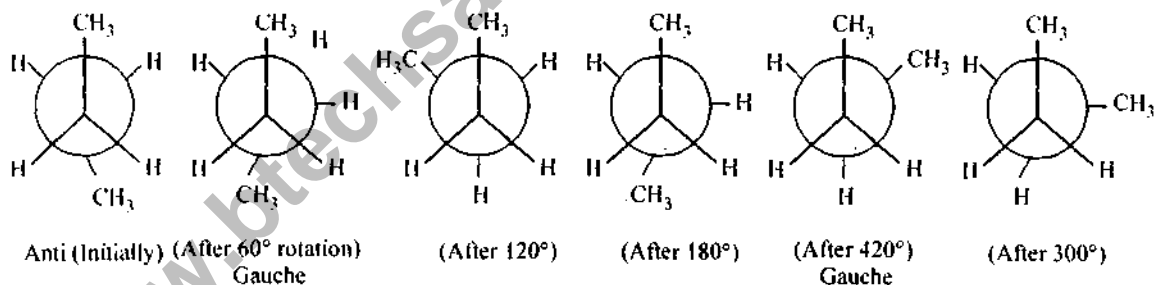
At. No. of second atom 6 6 1

**Conformation of n-butane :**

$CH_3 - CH_2 - CH_2 - CH_3$  n-Butane

1 2 3 4

n-Butane has free rotation about  $C_2 - C_3$   $\sigma$  bond. Different conformers of n-butane are as follows :



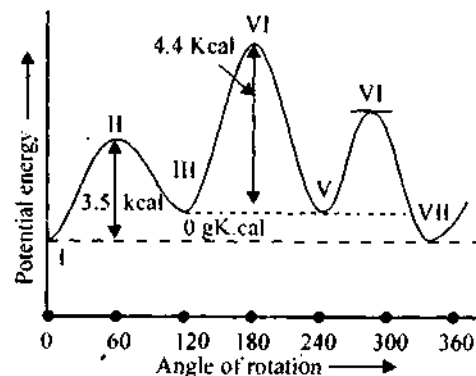
I is called as Anti form, III and V are called as Gauche form IV is completely eclipsed form, II and VI are Partially eclipsed form.

**Energy order is :** I < II = VI < III = V < IV

I is have minimum energy because both  $CH_3$  groups are anti to each other.

III and V are identical in energy, both the gauche forms are free from torsional strain, so they are more stable than partially eclipsed II and VI forms.

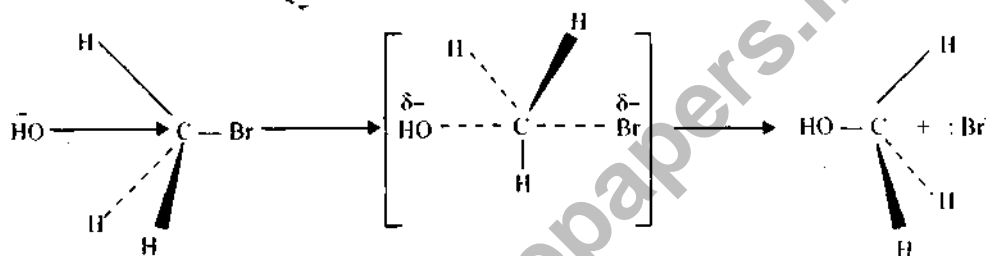
**Q. 2. (v) Show how does  $S_N2$  reaction give rise to inverted product.**



**Ans.  $S_N2$  Mechanism (Bimolecular Nucleophile Substitution Reactions) :** When the rate of a nucleophile substitution reaction depends on the concentration of both the substrate and the nucleophile the reaction is of second order and known as  $S_N2$ .

Rate  $\propto$  [Substrate] [Nucleophile]

Evidently, the rate-determining step involves the participation of both the substrate and the nucleophile. A typical example of  $S_N2$  reactions is the hydrolysis of methyl bromide by aqueous NaOH.



The hydroxide ion attacks the substrate carbon from the side opposite the bromine atom (leaving group). It is because both the hydroxide ion and bromine atom are electron rich species. It is natural that they stay as far apart as possible (same charges repel). The transition state can be pictured as a structure in which both —OH and —Br are partially bonded to carbon atom of substrate. The C — Br bond is not completely broken and C — OH bond is not completely formed in the transition state; The —OH ion has a diminished negative charge because it has begun to share its electron with the substrate carbon, while the —Br atom has also developed a small negative charge as it has partially removed the shared pair of electrons from the substrate carbon. The three C—H bonds lie in one plane and the C—OH and C—Br bonds are perpendicular to the plane of C—H bonds in transition state. The energy required for the breaking of C—Br bond is partially provided by the energy liberated by the formation of C—OH bond.

In final product, the configuration of the carbon is inverted, rather like as umbrella blown inside out (in strong wind). This change in configuration is called Walden Inversion.

### SECTION—C

(10 × 5 = 50)

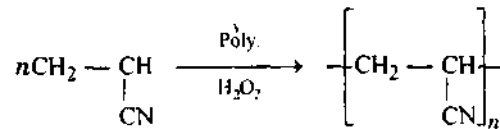
**Q. 3. Attempt any one of the following**

(a) Write the method of preparation for the following compounds:

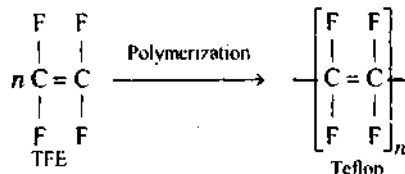
- (i) Polyacrylonitrile
- (ii) Polytetrafluoroethylene (PTFE)
- (iii) Neoprene
- (iv) Dacron.

**Ans. Preparation :**

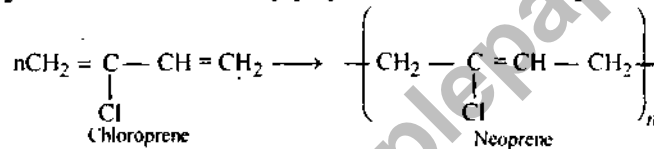
(i) **Polyacrylonitrile** : It is also known as acrilan formed by the polymerization of acrylonitrile.



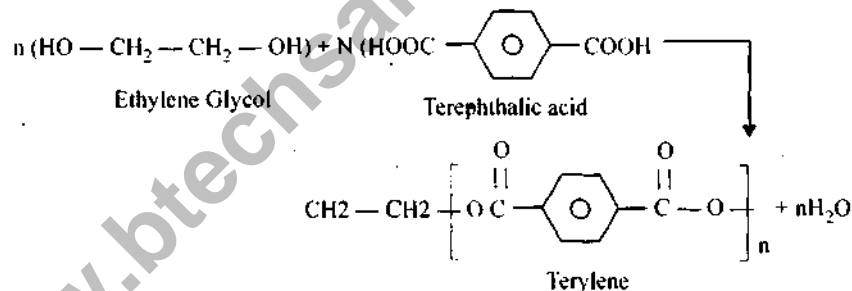
(ii) **Poly tetrafluoroethylene (PTFE)** : It is also known as teflon and is obtained by polymerization of tetrafluoro ethylene (TFE) under pressure in the presence of benzoyl peroxide as catalyst.



(iii) **Neoprene**: It is obtained by polymerization of chloroprene



(iv) **Decron**: It is also known as Terylene and obtained by the polymerization of terephthalic acid with ethylene glycol.



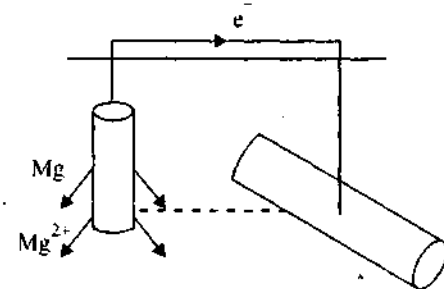
**Q. 3. (h) (i) Explain the term cathodic protection. Indicate how metal coatings can effectively prevent corrosion.**

**Ans. Corrosion Control (Protection Against Corrosion)**

Some of the corrosion control methods are described as follows:

**1. Cathodic protection** : The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur. There are two types of cathodic protection :

(i) **Sacrificial anodic protection method** : In this protection method, the metallic structure (to be protected) is connected by a wire to a more anodic



**Fig.** In cathodic protection, an anode a more strongly reducing metal is sacrificed to maintain the integrity of the protected object (e.g. a pipeline)

metal, so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly; while the parent structure (cathodic) is protected. The more active metal so employed is called "sacrificial anode". The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are **magnesium, zinc, aluminium and their alloys**. Important applications of sacrificial anodic method include protection of buried pipelines, underground cables, marine structures, ship-hulls, water-tanks, piers, etc. (See Fig.)

**(ii) Impressed current cathodic protection :**

In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. Usually, the impressed current is derived from a direct current source (like battery or rectifier on A.C. line) with an insoluble anode (like graphite, high silica iron, scrap iron, stainless steel or platinum). Usually, a sufficient D.C. current is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium), and connected to the metallic structure to be protected (see fig). The anode is usually, in a **backfill** (composed of coke breeze or gypsum) so as to increase the electrical contact with the surrounding soil. This type of cathodic protection has been applied to open water-box coolers, water-tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid-up ships, etc. **This kind of protection technique is particularly, useful for large structures for long-term operation.**

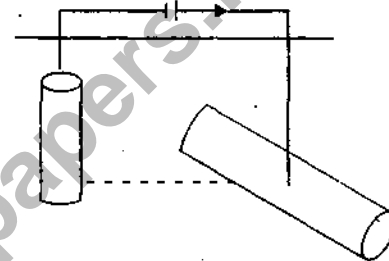


Fig. In impressed-current cathodic protection, electrons are supplied from an external cell so that the object itself becomes cathodic and is not oxidized.

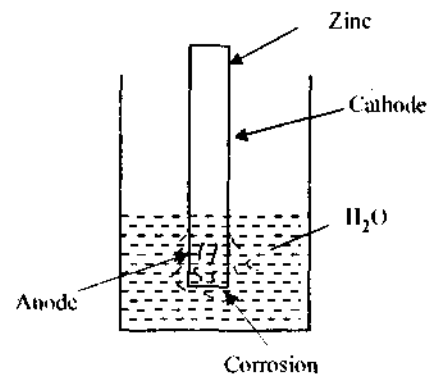
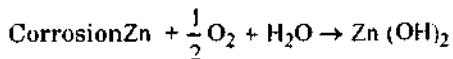
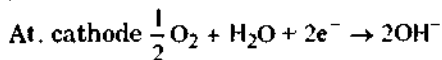
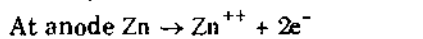
usually, in a **backfill** (composed of coke breeze or gypsum) so as to increase the electrical contact with the surrounding soil. This type of cathodic protection has been applied to open water-box coolers, water-tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid-up ships, etc. **This kind of protection technique is particularly, useful for large structures for long-term operation.**

**Q. 3. (b) (ii) Explain why a pure metal rod half immersed vertically in water starts corroding at the bottom.**

**Ans.** When a metal is half dipped under water, there will be formation of differential aeration corrosion. The position of metal above, water will be acting as cathode and inside acts as anode. It is anode where corrosion will take place

ex. Zinc.

Reaction



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

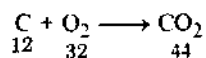
**Q. 4. (a) A sample of coal was found to have the following percentage composition : C = 75%, H = 5.2%, N = 3.2% and ash = 4.5%. Calculate the minimum air required for complete combustion of 1 kg of coal.**

**Ans.** C = 75%, H = 5.2%, N = 3.2% Ash = 4.5%

Rest is oxygen % =  $100 - (75 + 5.2 + 3.2 + 4.5) = 12.1\%$

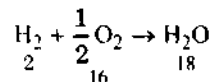
In one 1 kg coal C = 750 gm H = 52 gm N = 32 gm Ash = 45 gm

Oxygen = 121 gm



oxygen required by carbon

$$= 750 \times \frac{32}{12} = 2000 \text{ gm}$$



oxygen required by Hydrogen

$$= 52 \times \frac{16}{2} = 416 \text{ gm}$$

Total oxygen required = 2416 gm

Required oxygen from Air =  $2416 - 121 = 2295 \text{ gm}$

Air has 23% Oxygen, Hence Air required for combustion =  $2295 \times \frac{100}{23}$   
= 9978 gm or 9.978 kg.

**Q. 4. (b) Give the mechanism of following reactions:**

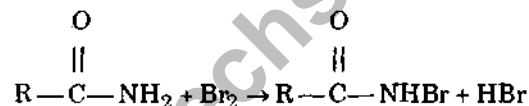
(i) Hoffmann re-arrangement

(ii) Aldol Condensation

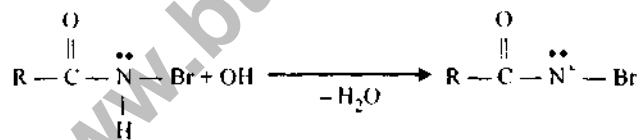
(iii) Canizzaro reaction.

**Ans. (i) Hoffmann re-arrangement**

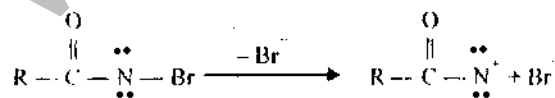
Step 1 : Hoffmann of an amide



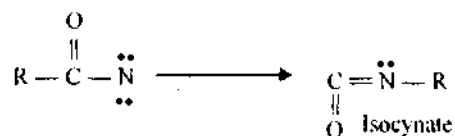
Step II : Removal of proton by hydromide ion



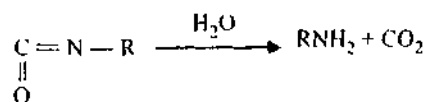
Step III : Separation of halide ion



Step IV : Migration of alkyl/aryl group from carbonyl carbon to  $e^-$  deficient

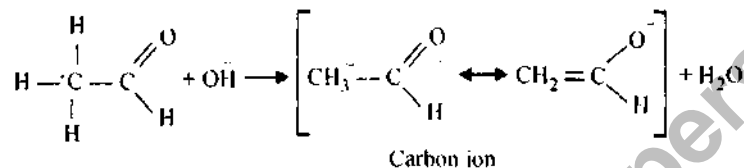


**Step V : Hydrolysis of an isocyanate to form a 1 amine .**

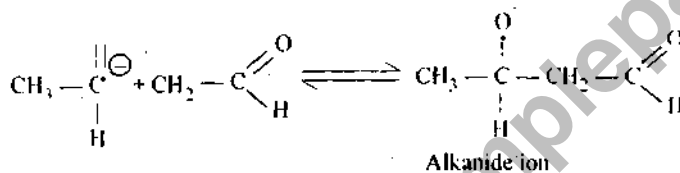


**(ii) Aldol Condensation**

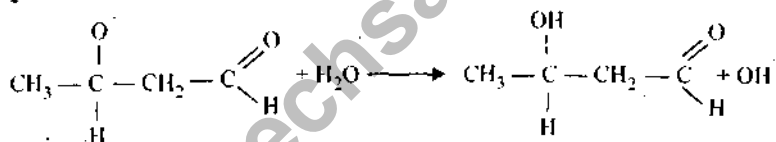
**Step I :**



**Step II :**

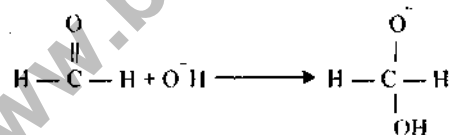


**Step III :**

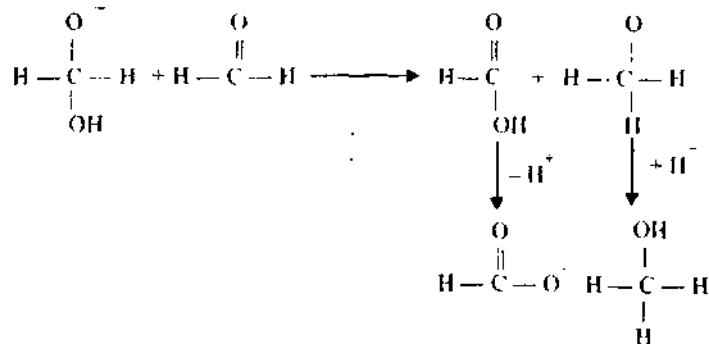


**(iii) Cannizzaro reaction**

**Step I :**



**Step II : Hydride Transfer**



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

**Q. 5. (a) (i) Outline the salient features of the phase diagram of water system highlighting the name of system (areas, curves and point), phases in equilibrium and degree of freedom in each case.**

**Ans. Phase rule :** This rule was put forward for heterogeneous systems and stated by American physicist willard Gibbs in 1874.

This rule may be stated as

$$F = C - P + 2$$

where  $F$  = number of degree of freedom.

$C$  = number of component

$P$ , phase of the system.

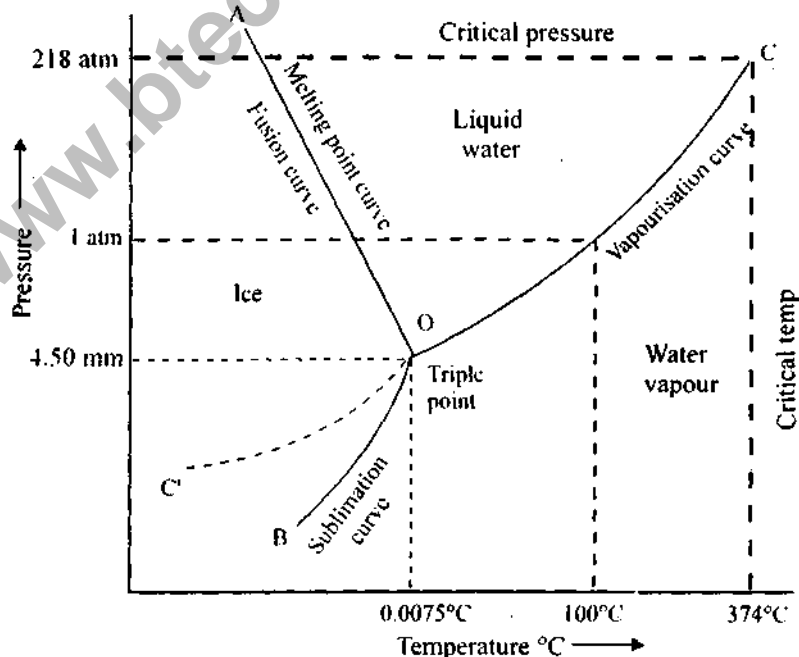
**Phases :** The homogeneous parts of a heterogeneous in equilibrium, which are physically distinct and mechanically separable and termed as phases.

**eg.** In the water system there are three phases —  
ice (solid) water (liquid) vapour (gas) in equilibrium.

**Component :** The number of components of a system are the smallest number of independently variable constituents taking part in equilibrium by means of which the composition of each phase can be expressed either directly or in terms of chemical equations :

**eg.** (i)  $\text{Ice (s)} \rightleftharpoons \text{water} \rightleftharpoons \text{vapour (g)}$

This is one component system because the composition of each phase namely ice, water and vapour can be expressed in term of only one constituent  $\text{H}_2\text{O}$ . Therefore water system is a three phase and one component system.





**Degree freedom of Variance :** The degree of freedom of a system at equilibrium is the minimum number of variables such as pressure, temperature and concentration which must be specified in order to define the system completely. It is also known as 'Variance of the system' and is denoted by 'F'.

**Water system :**

Water system is an important example of one component system consisting of three phases namely Ice (solid) water (liquid), vapour (gaseous)

The salient features of water system are as follows : —

S.N.	Area/curve/point	Phase/equilibrium	$F = C - P + 2$	Remark
1.	Area OAB	Ice $P = 1$	$F = 2$	Bivariant P and T can be varied
2.	Area OAC	Water $P = 1$	$F = 2$	Bivariant P and T can be varied
3.	Area OBC	Vapour $P = 1$	$F = 2$	Bivariant P and T can be varied
4.	Curve OA	Ice $\rightleftharpoons$ water $P = 2$	$F = 1$	Fusion curve, univariant P or T can be varied
5.	Curve OB	Ice $\rightleftharpoons$ vapour $P = 2$	$F = 1$	Sublimation curve univariant, P or T can be varied
6.	Curve OC	Water $\rightleftharpoons$ vapour $P = 2$	$F = 1$	Vapourisation curve, univariant, P or T can be varied
7.	Curve OC'	Water $\rightleftharpoons$ vapour $P = 1$ at metastable equilibrium	$F = 1$	Metastable curve
8.	Point O	Ice $\rightleftharpoons$ water $\rightleftharpoons$ vapour	$F = 0$	Triple point, invariant $P = 3$

Triple point 'O': At point 'O' all the three phases are in equilibrium.



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

Therefore triple point is invariant, i.e. all the three phases co-exist only at a particular temperature and particular pressure.

Temperature at triple point = 0.0075°C

Pressure at triple point = 4.58 mm of Hg

Metastable curve : OA' is metastable curve along which super cooled liquid is in equilibrium with vapour without separation of ice. As soon as the system is disturbed (by addition of ice, mechanical disturbance etc) entire supercooled liquid solidifies.

**Q. 5. (a) (ii) What are the advantages and disadvantages of gaseous fuels ?**

**Ans. Gaseous Fuel-Advantages :**

(1) Can be manufactured at a central location and distributed over a wide area through pipelines.

- (2) These are very clean to operate and are ashless and smokeless.
- (3) They can be used in internal combustion engines.
- (4) Their calorific value is very high.
- (5) Their burning can easily be controlled
- (6) They can be ignited spontaneously and air needed is must less.

**Disadvantages :** (1) Large storage tanks are required for storage.

- (2) They are highly inflammable, hence risk of hazards are quite high.
- (3) Their cost of production is quite high.

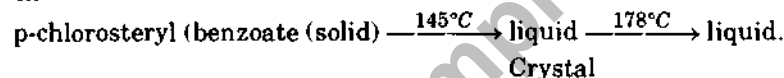
**Q. 5. (b) Describe the various types of liquid crystals. Distinguish between nematic and smectic liquid crystals.**

**Ans. Liquid Crystalline State :** Solid substance on heating undergo two sharp transformations.



The turbid liquid shows on isotropy. This turbid liquid is called liquid crystal. It does not have property of crystalline solid state. The liquid crystals are more like liquid having mobility, Surface tension and viscosity etc. They are is mesomorphic states.

ex.

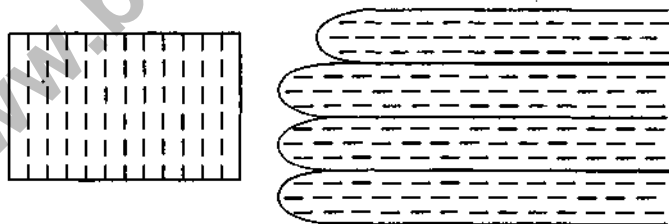


**Classification of liquid crystals :** They are three types of liquid crystals.

(1) **Smectic liquid crystal :** The meaning of smectic is soap like. These liquid crystals do not flow like normal liquid. They have limited mobility. They flow smectic liquid crystals blow in layers one over another. They form a series of strata.

Smectic liquid crystal also give x-ray diffraction patterns like solid crystals but it is in one direction only. They are always uniaxial and are not affected by a magnetic field.

ex : Ethyl-p-azoxy benzoate, Ethyl-p-azoxy cinnamate n-octyl-p-azoxy cinnamate etc.

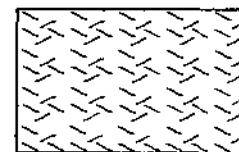


(2) **Nematic Liquid crystal :** In this type of crystals the molecules are lined up in such a way that their long axis are parallel to each other but the molecules are not arranged in layers. This type of liquid crystals show near normal flow of liquids. Nematic phases are turbid and anisotropic.

ex : p-azoxy anisole, p-azoxy phenetole, p-methoxy cinnamic acid etc

(3) **Cholestric liquid crystal :** This type of liquid crystals have properties of both nematic and smectic liquid crystals to some extent.

ex. cholesterol Benzoate.



- Applications :** (1) In flate television screen  
 (2) In wrist watches  
 (3) In laptop screen  
 (4) In digital thermometer  
 (5) In digital clock  
 (6) In switchable windows  
 (7) In detection of jot points in microcircuits  
 (8) In finding fractures and tumors in human.

**Q. 6. Attempt any one of the following :**

**Q. 6. (a) What is the potential of a half-cell consisting of zinc electrode in 0.01 M ZnSO<sub>4</sub> solution at 25°C ? E° = 0.763 V.**

**Ans.**

$$E = E^\circ - \frac{RT}{nF} \log(\text{ion})$$

$$= 0.763 - \frac{0.591}{n} \log 0.01$$

for Zn,  $n = 2$  and  $0.01 = 10^{-2}$

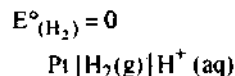
$$E = 0.763 - \frac{0.591}{2} \log 10^{-2}$$

$$= 0.763 + \frac{0.0591}{2} \times 2 = 0.763 + 0.0591 = 0.822 \text{ V}$$

**Q. 6. (b) (i) What is reference electrode ? Describe the construction of normal hydrogen electrode.**

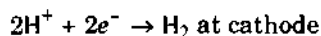
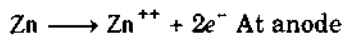
**Ans. Reference Electrode:** Electrode with the half of which, we measure the electrode potential of a single electrode is called Reference electrode. It has its E° value zero. It can act as anode as well cathode.

**Normal Hydrogen electrode:** It is made of glass cylindrical vessel having Pt wire inside fitted with a platinum plate at the bottom H<sub>2</sub> gas is bubbled at 1 Atm. pressure in 1 N HCl.

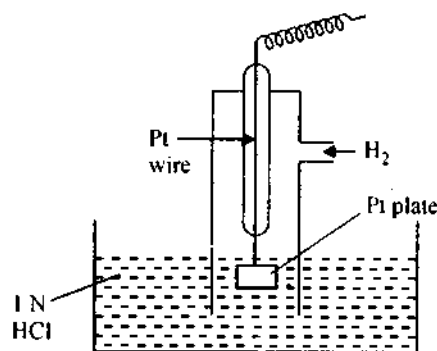


Let us take example of determination of electrode potential of Zn.

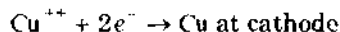
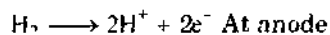
NHE acts as cathode with Zn and reaction will be as



$$E^\circ_{\text{Zn}^{++}/\text{Zn}} = -0.76 \text{ V}$$



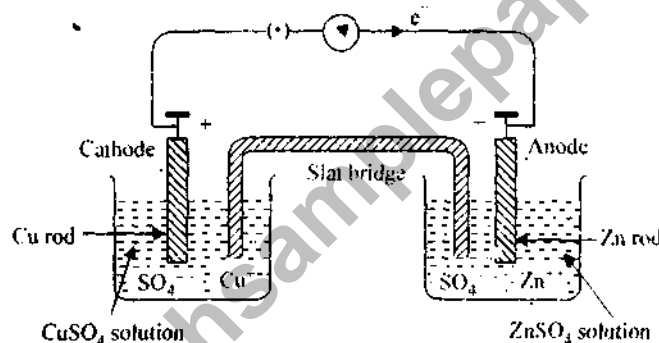
It can act as anode when  $E^{\circ} \text{Cu}^{++} / \text{Cu}$  is measured.



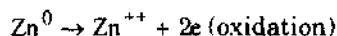
**Q. 6. (b) (ii) Write short note on Galvanic cell.**

**Ans. Galvanic or electric cells :** The cells used for electrolysis are called electrolytic cells while those used for generation of electrical energy from chemical reactions are called galvanic or voltaic cells. A galvanic or electric cell (chemical battery) can be obtained by combining any two half cells having different electrode potentials. Thus, if a standard zinc-half cell is coupled with a standard copper half cell by wire and a salt bridge as shown in Fig., the resulting cell will have a voltage of

$$E_{\text{Cu}}^{\circ} - E_{\text{Zn}}^{\circ} = 0.345 - (-0.762) = 1.107 \text{ volts}$$



In the Daniell cell so formed, the electrons flow from the zinc electrode to the copper electrode through the connecting metal wire, while the  $\text{Cu}^{++}$  ions in the solution move to the copper cathode where they reduce their electron "pressure" and get deposited. The electron "pressure" is maintained by the generation of the corresponding stream of zinc ions from the dissolution (or "corrosion") of the zinc anode :



For concentrations other than 1 gm ion per litre, the e.m.f. of the cell may be calculated from the Nernst equation :

$$\begin{aligned} E_C &= \frac{0.059}{n} \log \frac{C}{K} \\ &= \frac{0.059}{n} \log \frac{1}{K} + \frac{0.059}{n} \log C \\ &= E_0 + \frac{0.059}{n} \log C \end{aligned}$$

For example, if the concentration of  $\text{Cu}^{++}$  and  $\text{Zn}^{++}$  are 0.01M and 0.1 M respectively, then the voltage of the resultant Daniell cell would be

$$\begin{aligned}
 E_{\text{Cu}} - E_{\text{Zn}} &= \left\{ E_{\text{Cu}}^0 + \frac{0.059}{2} \log [\text{Cu}^{++}] \right\} - \left\{ E_{\text{Zn}}^0 + \frac{0.059}{2} \log [\text{Zn}^{++}] \right\} \\
 &= \{0.345 + 0.0295 \log 10^{-2}\} - \{0.762 + 0.0295 \log 10^{-1}\} \\
 &= 0.345 - 0.059 + 0.762 - 0.0295 = 1.0775 \text{ volts.}
 \end{aligned}$$

**Q. 7. Attempt any one of the following :**

**Q. 7. (a) (i) What are the properties of a good fuel ? Define, High and Low calorific values.**

**Ans. Properties of a good fuel :** (a) A good fuel should possess high calorific value, since the amount of heat liberated and temperature attained there by depends upon this property of fuel.

(b) A good fuel must have moderate ignition temperature because low ignition temperature can causes fire hazards during storage and transport of fuel. The fuel with high ignition temperature show difficulty during ignition of fuel.

(c) A fuel must have low moisture content because the moisture is paid at the same rate as the fuel containing moisture reduces its heating value.

(d) A fuel should have low content of non-combustible matter because non-combustible matter remains in the form of ash or clinker after combustion. It also reduce the heating value.

(e) A fuel must burn with a moderate rate of combustion because if the rate of combustion is low, than a part of the heat liberated may get radiated, instead of raising the temperature hence the required high temperature may not be attained. Also too high combustion rates are also not required because then it gets out of control.

(f) A good fuel should not pollute the atmosphere by emitting Co,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  and other poisonous gas.

(g) A good fuel must has low cost.

(h) A good fuel must be easy to transport.

(i) A good fuel must have low storage cost.

(j) It must have controllable combustion so that combustion can be started or stopped when required.

(k) In case of solid fuel, the size should be uniform so that combustion is regular

(l) A fuel should burn in air with efficiency without. much smoke

**High Calorific Value : or Gross Calorific value :** The total amount of heat liberated, when unit mass or unit volume of the fuel has been burnt completely and the products of combustion are cooled to room temperature.

$$\text{HCV of Fuel (L)} = \frac{(W + w)(T_2 - T_1)}{x} \text{ cal/gm or } \frac{\text{Kcal}}{\text{kg}}$$

**Lower or Net Calorific Value :** The net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion produced are allowed to escape.

$$\text{LCV} = (\text{HCV} - 0.09 \text{ H} \times 587) \text{ cal/gm}$$

where x = mass of fuel sample in gm taken in crucible

$W$  = mass of water in calorimeter (in gms)

$w$  = water equivalent in gms of calorimeter, stirrer thermometer, bomb etc.

$T_1$  &  $T_2$  = initial and final temperature of water in calorimeter respectively.

$L$  = Higher or gross calorific value of fuel in  $\frac{\text{Cal}}{\text{gm}}$

**Q. 7. (a) (ii) What is 'Optical activity' ? How do you specify a particular configuration as R and S ?**

**Ans. Ans. Optical activity :** "When plane polarised light is passed through the solutions of certain organic compounds they rotate the plane polarised light either to the left or to the right. Substances which rotate the plane of polarised light are known as optically active compounds and the phenomenon is known as optical activity."

Depending upon the rotation of plane polarised light, optically active compounds are of two types :

(a) **Laevo rotatory :** "Compounds which rotate the plane of polarised light towards the left is known as laevo rotatory compounds." Such compounds are designated as  $l$  or by the sign (-).

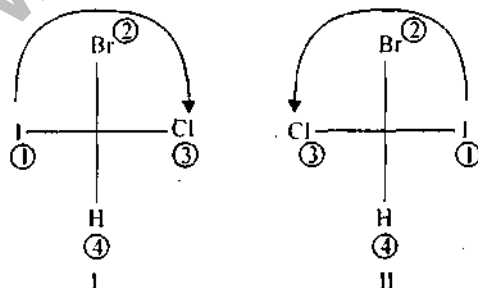
(b) **Dextra Rotatory :** "Compounds which rotates the plane of polarised light towards the right (clockwise) are known as dextro-rotatory compounds." They are designated as 'd' or by the sign (+).

**R and S Nomenclature :** This system specifies the absolute configuration of asymmetric molecules. This system of configuration was given by Cahn, Ingold and Prelog. The symbol R and S stand for the Latin words Rectus and Sinister respectively. The important features of R and S systems are as follows :

- (1) The four groups attached to the asymmetric carbon atom/atoms are assigned priority in accordance with the sequence rule.
- (2) After Assigning the priority of atoms or groups the molecule is rotated in such a way that atom or group of lowest priority is directed away from the viewer.
- (3) The arrangement of remaining three atoms or groups are viewed from the group of highest priority to the second priority and then to third. In looking so, if eye moves in anticlockwise direction it is specified as 's' and if eye moves in clockwise direction it is specified as R.

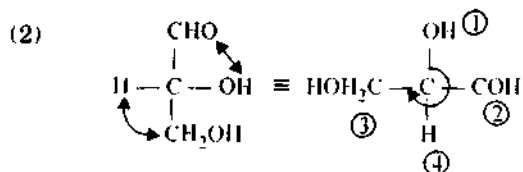
**R-S Nomenclature of some important organic Compounds :**

(1)

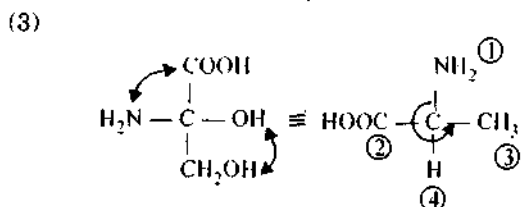


Priority order  $I > Br > Cl > H$

R configuration in (I) and S-configuration (II)



Priority order  $\text{OH} > \text{CHO} > \text{CH}_2\text{OH} > \text{H}$   
R configuration



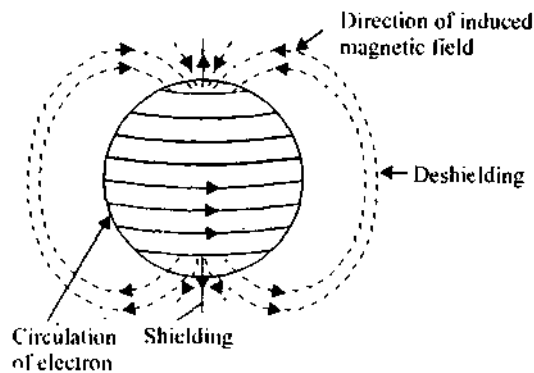
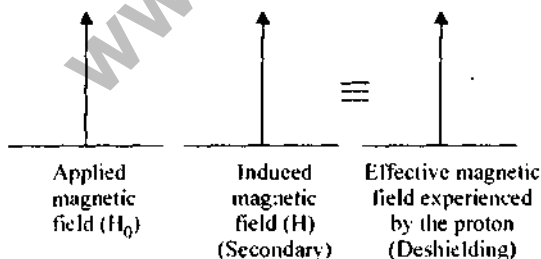
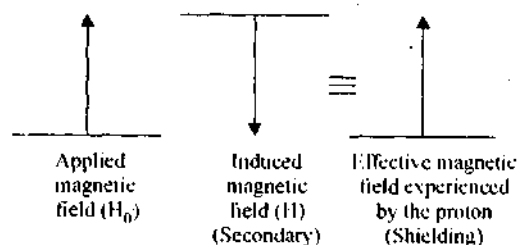
Priority order  $\text{NH}_2 > \text{COOH} > \text{CH}_3 > \text{H}$   
S-Configuration

Q. 7. (b) (i) What is 'SHIELDING' and 'DESHIELDING' ?

**Ans. Shielding and Deshielding :** When a molecule is placed in an external magnetic field ( $H_0$ ) its electrons are caused to circulate in a manner producing secondary magnetic fields or induced magnetic field. This may lead to following situations :

(a) **Shielding of protons :** If the secondary magnetic field produced by the circulation of electrons opposes the applied magnetic field at a proton, the effective field experienced by it is less than the applied field and the proton is said to be shielded. Shielding shifts the absorption up field.

(b) **Deshielding of Protons :** If the secondary magnetic field produced by the circulation of electrons reinforces the applied magnetic field at a proton, the effective field experienced by it



Shielding and Deshielding of proton

is more than the applied field and the proton is said to be deshielded. Deshielding shifts the absorption down field.

**Q. 7. (b) (ii) An organic compound with molecular weight 130 shows the following band in the infra-red spectrum :**

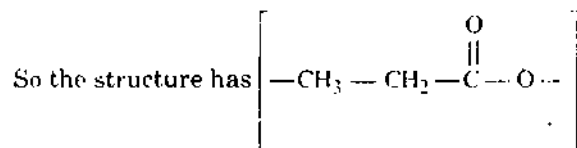
(i) 3082-2860 (m), (ii) 1825 (s), (iii) 1755 (m) and 1455  $\text{cm}^{-1}$  (m)

**In its NMR spectrum, two signal result (i) Triplet 8.7  $\tau$  (7.3 squares,  $J = 7.1$  cps), (ii) quartet 7.8  $\tau$  (4.9 squares,  $J = 7.1$  cps). Determine the structure of the compound.**

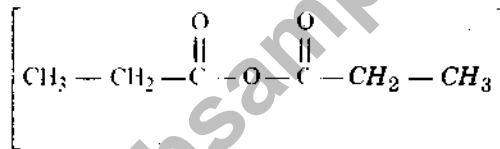
**Ans.** Molecular wt = 130

NMR = 2 signal splitting into triplet and quartet means  $-\text{CH}_2 - \text{CH}_3$  groups are attached.

IR Bands are in favour of C—H bonds, C = O and C—O



As molecule wt is 130, it is formed only when the organic compound is —



Acetic anhydrate