

FIRST SEMESTER EXAMINATION, 2010-11

ENGINEERING CHEMISTRY

Time : 3 Hours

Total Marks : 100

SECTION – A

1. Choose/Fill correct answer:

(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. (iii) Intermolecular hydrogen bonding in o-nitrophenol

(b) which of the following possess lowest energy?

- (i) NO (iii) N₂
(ii) O₂ (iv) CO

Ans. (iv) CO

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

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

Ans. (iii) 1, 2, 4

(d) An electrophilic reagent is:

- (i) Carbanion (iii) Alcohol
(ii) Chloride ion (iv) FeCl₃

Ans. (iv) FeCl₃

(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. (iii) nucleophilic substitution

(f) SN1 reaction is facilitated by:

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

Ans. (i) Bulky groups

(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

(h) Glyptal is a polymer of:

- (i) Alkanal and HCHO
(ii) Glycol and Phthalic acid
(iii) Glycerol and Phthalic acid
(iv) CH₃COOH and Phthalic acid

Ans. (ii) Glycol and Phthalic acid

(i) Wacker process uses the catalyst:

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

Ans. (iii) Zeise's salt

(j) Inflexion point is when:

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

Ans. (iii) pH changes abruptly

(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-ray studies of crystals

Ans. (iii) X-ray studies of crystals

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

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

Ans. (iii) 2

(m) Optical isomerism is shown by:

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

Ans. (ii) Butanol-2

(n) The angle between two covalent bonds is minimum in:

- (i) BeF_2 (iii) H_2O
- (ii) CH_4 (iv) NH_3

Ans. (iii) H_2O

(o) On increasing the temperature, the vapour pressure of liquid:

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

Ans. (ii) increases

(p) The crystalline compound A_xB_y is characterized by a body-centred cell. The compound has the formula:

- (i) AB (iii) A_2B
- (ii) A_4B (iv) AB_4

Ans. (i) AB

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

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

Ans. (iv) both zero variant

(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

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

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

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

(t) $E_{\text{cell}} + E_{\text{anode}} \rightarrow ?$

Ans. E_{cathode}

SECTION - B

2. Attempt any three of the following:

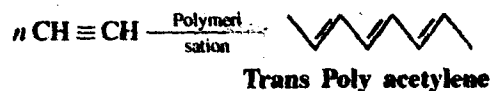
(10 × 3 = 30)

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

Ans. Conducting Polymers: A polymer which can conduct electricity is known as conducting polymer.

- Polymers having extensive conjugation of p bonds in the polymeric back bone or ring structure increase their conductivities to a large extent

e.g. Trans - Poly acetylene



The conductivities of polymers, with extensive double in conjugation, can be increased by doping then with suitable impurities.

Application: Some of the potential applications of conducting polymers area as follows

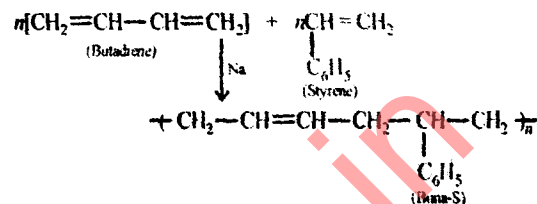
- In rechargeable batteries.
- In smart (variable transmission) windows.
- Making conducting series.
- Non linear optical materials
- Electromechanical actuators
- Sensors for pH, glucose and various gases like H_2O_2 , SO_2 etc.

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

Ans. Elastomers: The group of polymers exhibiting high degree of elasticity, stretching at least twice of their original length under the action of tensile force and recover their dimensions after the removal of the applied force,

just like rubber are known as elastomers.

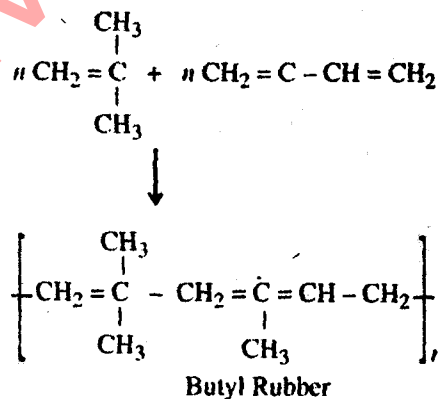
Preparation, structure and uses of Buna-S: It is obtained by the polymerisation of butadiene and styrene in presence of sodium metal.



Buna-S are extremely resistant towards wear and tear and used for manufacture of tyres, rubber tubes.

Butyl Rubber: Butyl Rubber is a copolymer

Preparation: Butyl rubber is obtained by the copolymerisation of isobutene with small amount of isoprene.



Uses:

- It is used for making cycle and automobile tyre.
- In the insulation of high voltage wires and cables.
- For tank linings.
- In making conveyor belts

- (a) With the help of molecular orbital diagram, calculate the bond order of O_2^- , O_2^{2-} , He_2^+ , N_2^- . Also write their magnetic character.

Ans.

$$O_2^- (17) = \sigma(15^2) \uparrow \downarrow (15^2) \sigma(25^2) \uparrow \downarrow (25^2) \sigma(P_z^2)$$

$$\pi(2P_x^2) = \pi(2P_y^2) \uparrow \downarrow (2P_x^2) = \uparrow \downarrow (2P_x^2) = \uparrow \downarrow (2P_y^2)$$

$$B.O = \frac{1}{2}(10 - 7) = 1.5$$

One electron is unpaired so it is paramagnetic in nature.

$$O_2^{2-} (z=18) = \sigma 15^2, \uparrow \downarrow (15^2), \sigma(25^2) \uparrow \downarrow (25^2) \sigma(2P_z^2)$$

$$\pi(2P_x^2) = \pi(2P_y^2) \uparrow \downarrow (2P_x^2) = \uparrow \downarrow (2P_x^2) = \uparrow \downarrow (2P_y^2)$$

$$B.O = \frac{1}{2}(10 - 8) = 1.0$$

All the electrons are paired so it is diamagnetic in nature.

$$He_2^+ (z=3) = \sigma 15^2, \uparrow 15^1$$

$$B.O = \frac{1}{2}(2 - 1) = 0.5$$

It has one unpaired electron. So it is paramagnetic.

$$N_2^- (z=16) = \sigma(15^2) \uparrow \downarrow (15^2), \uparrow \downarrow (25^2) \sigma(2P_z^2)$$

$$\pi(2P_x^2) \pi(2P_y^2) = \pi(2P_x^2) \uparrow \downarrow (2P_x^2)$$

$$B.O = \frac{1}{2}(10 - 6) = 2$$

It has no unpaired e^- so it is diamagnetic.

- (b) Derive an expression for the density (e) of a cubic crystal.

Ans. Density of a cubic crystal: Let the edge length of the cube = a cm

$$\therefore \text{Volume of unit cell } a^3 \text{ cm}^3$$

$$\therefore \text{Density of unit cell}$$

$$= \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\therefore \text{Mass of unit cell} = \text{Number of atoms per unit cell} \times \text{Mass of each atom}$$

$$= z \times m \quad \dots(1)$$

$$z = \text{no. of atoms per unit cell}$$

$$m = \text{Mass of each atom}$$

$$\text{But } m = \frac{\text{Atomic mass}}{\text{Avogadro's No.}} = \frac{M}{N_0} \quad \dots(2)$$

$$\text{from eqn (1) and Mass of unit cell} = z \times \frac{M}{N_0}$$

$$\therefore \text{Density of unit cell} = \frac{z \times M}{a^3 \times N_0} \text{ gm/cm}^3$$

If edge length is expressed in picometer then
edge length = $a \times 10^{-12}$ m = $a \times 10^{-10}$ cm

$$\text{Volume of unit cell} = a^3 \times 10^{-30} \text{ cm}^3$$

Therefore, eqn (4) becomes

$$\text{Density of unit cell} = \frac{z \times M}{a^3 \times 10^{-30} \times N_0} \text{ gm/cm}^3$$

- (iii) (a) Classify fuel cells. Give some examples with their electrode reactions.

Ans. Fuel Cell: An electrochemical conversion device which converts chemical energy of the fuel directly into electrical energy is known as fuel cell.

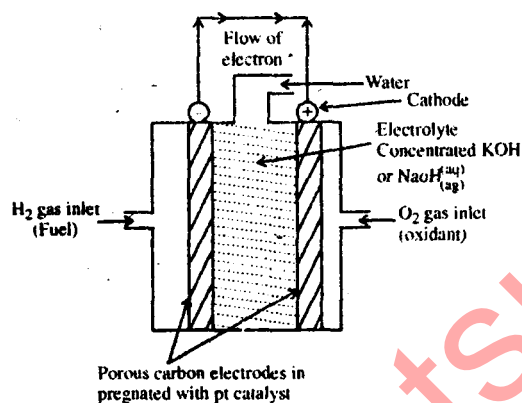
Examples: (i) H_2/O_2 fuel cell (ii) Propane/Oxygen fuel cell.

Classification fuel Cell: Depending upon the type of electrolyte used in the cell it may be classified as:

- (i) Alkaline fuel cells.
- (ii) Molter carbonate fuel cells.
- (iii) Proton exchange membrane fuel cell etc.

The schematic diagram of H_2/O_2 fuel cell is shown ahead.

When hydrogen and oxygen are bubbled through anode and cathode respectively in the electrolyte the following reaction take up place.



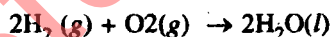
Reduction Half cell



Oxidation half cell



Overall cell reaction



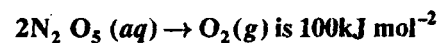
$$\therefore E_{\text{cell}} = E_R^\circ - E_L^\circ = -0.40 - (-0.83)$$

$$E_{\text{cell}}^\circ = 1.23 \text{ V}$$

However, the actual emf of the cell lies in between 0.8 to 1.0V. Therefore, is a fuel cell following reaction takes place.



(b) 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. From Arrhenius equation,

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$K_1 = 2.35 \times 10^{-4} \text{ s}^{-1}, K_2 = ?, T_1 = 293 \text{ K},$$

$$T_2 = 303 \text{ K}$$

$$\log \frac{K_2}{2.35 \times 10^{-4}} = \frac{100}{2.303 \times 8.314} \times \left[\frac{303 - 293}{303 \times 293} \right]$$

$$\log \left(\frac{K_2}{2.35 \times 10^{-4}} \right) = \frac{100}{2.303 \times 8.314} \times \frac{10}{303 \times 293}$$

$$\log \left(\frac{K_2}{2.35 \times 10^{-4}} \right) = \frac{100}{2.303 \times 8.314} \times \frac{10}{303 \times 293}$$

$$\log \left(\frac{K_2}{2.35 \times 10^{-4}} \right) = 5.883 \times 10^{-4}$$

Taking antilog we get

$$\text{or } \left(\frac{K_2}{2.35 \times 10^{-4}} \right) = 1.00056$$

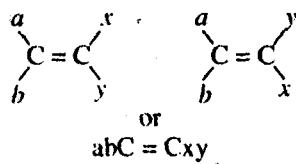
$$\text{or } K_2 = 2.35 \times 10^{-4} \text{ s}^{-1}$$

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

Ans. E-Z Nomenclature: The configuration of geometrical isomers can be designated as cis or trans. The different possible geometrical isomers may be classified as:

S.N.	Type	Cis	Trans
I.	$abC = Cab$		
II.	$abC = Cax$		

The cis and trans-system of assigning configuration of geometrical isomers fails when all the four groups attached to the two carbon atoms (doubly bonded carbons) are different.



In order to specify the configuration of this type of geometrical isomers a new system known as E-Z system was introduced and is based on the priorities of groups in the Cahn, Ingold and Prelog system. Further E and Z system of nomenclature can be applied in all cases.

E and Z nomenclature is assigned according to the following rules:

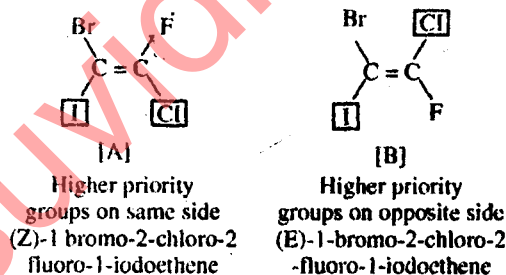
- Group of highest priority is determined on each doubly bonded carbon atom in accordance with the sequence rule.
- If the two groups of higher priority on each carbon are on the same side of the double bond. The alkene is designated as Z isomer [Z (German word) Zusammen-together].
- If the two groups or atoms of higher priority on each carbon are on opposite sides of the double bond, the alkene is designated as E isomer [E (German word) Entgegen-opposite].

Sequence rule

- Atoms of higher atomic number get higher priority. In case of isotopes, atom with higher mass number will have a higher priority.
- If the atomic number of atoms attached to the doubly bonded carbon atom is same, the priority is determined by comparing the atomic number of second atom.

-I and -Cl are on the same side of the double bond in structure [A] and hence it is assigned as configuration 'Z'.

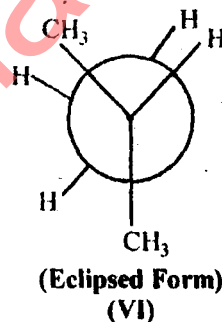
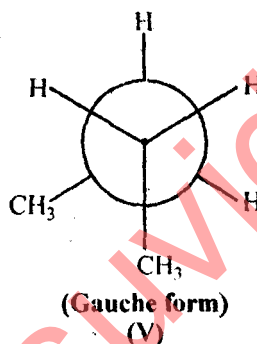
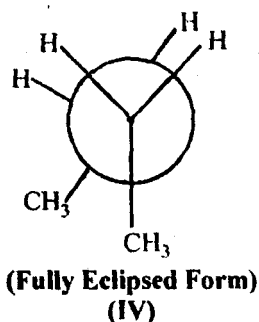
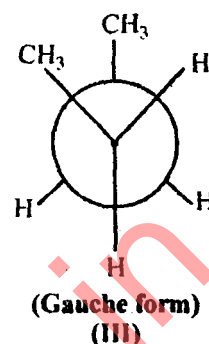
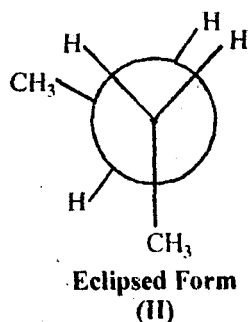
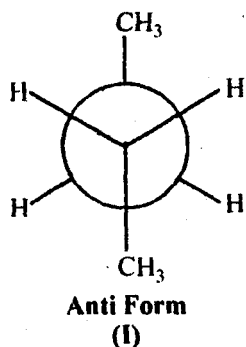
In compound [B] -I and -Cl are on the opposite side of the double bond and hence it is assigned the configuration 'E'.



Conformation of n-butane: n-butane is derived from ethane of four carbon in which one hydrogen is substituted by methyl.

In the completely staggered conformation (I), known as antiform, the methyl group lie as far apart as possible. If we assume that the angle of rotation about the central C_2-C_3 bond is zero for (I), then on rotating one of the C_2 or C_3 carbon atom through the angle of 60° , the eclipsed form (II) appears. In its back, hydrogen, rather than the methyl group is attached to the other carbon. If we rotate it by another 60° , we get staggered conformation (III), also known as gauche form, in which the two methyl groups are only at 60° gives rise to eclipsed form (V), in which the two methyl groups are again at 60° apart. Further rotation by 60° gives rise to eclipsed form (VI).

which if rotated by another 60° will give the anti form (I).



(v) Show how does S_N2 reaction give rise to inverted product.

Ans. Please see Q. 3(b) of IInd Sem 2007-08.

SECTION-C

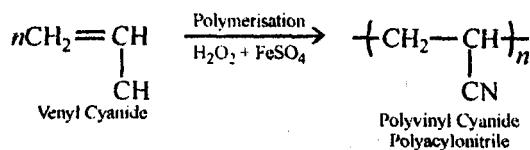
3. Attempt any one of the following:

(10 × 5 = 50)

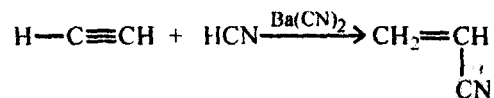
(a) Write the method of preparation for the following compounds:

(i) Polyacrylonitrile

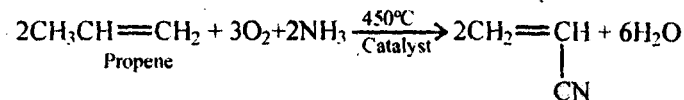
Ans. **Polyacrylonitrile:** Polyacrylonitrile is prepared by the polymerisation of acrylonitrile in presence of FeSO_4 and H_2O_2 as a catalyst.



This is also known as orlon or Acrilan. The monomer vinyl cyanide was initially obtained by the action of HCN on acetylene in presence of $\text{Ba}(\text{CN})_2$.

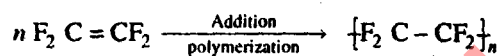


But now a days it is prepared by the following method:

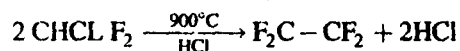


(ii) Polytetrafluoroethylene (PTFE)

Ans. Polytetrafluoroethylene (PTFE): PTFE is prepared by the polymerization of aqueous suspension of tetrafluoro ethylene under presence of benzyl peroxide.



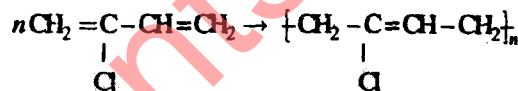
The monomer tetrafluoro ethylene is obtained by heating chlorodifluoro methane at 900°C in presence of HCL.



Tetrafluoro ethylene

(iii) Neoprene

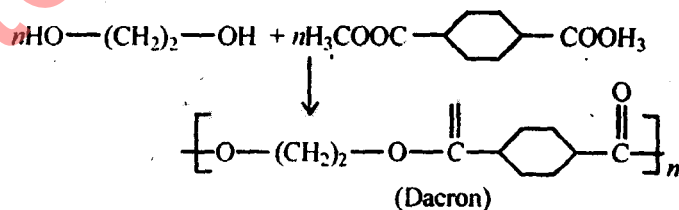
Ans. Neoprene: (Preparation) Neoprene is prepared by the polymerisation of chloroprene which is 2-chloro 1-3 butadiene



Neoprene

(iv) Dacron

Ans. Dacron: Dacron is prepared by heating excess of ethylene glycol with dimethyl terephthalate in presence of basic catalys at 200°C

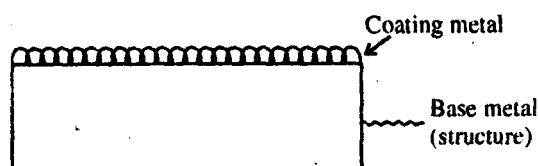


- (b) (i) Explain the term cathodic protection. Indicate how metal coatings can effectively prevent corrosion.

Ans. Cathode Protection: The basic principle involved is to force the metal / structure to be protected to behave as or function as cathode.

If electron enters through the external circuit to the structure then it is protected or if current enters to the structure from electrolyte then the structure is protected.

Metal Coating: Metal is coated on base structure



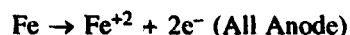
Metallic coating is done by electrolysis or electro deposition. In this process of electrolysis, the electrolytic solution of metal on whose coating is to be provided is electrolysed and the metal which is to be coated is made up the cathode, by using direct current.

On electrolysis the cathode will be coated up. Anode is either made up of coating metal itself or an inert material of good electrical conductivity like graphite while the base metal to be plated of is made the cathode.

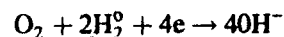
- (ii) Explain why a pure metal rod half immersed vertically in water starts corroding the bottom.

Ans. A pure metal rod half immersed vertically in water starts corroding at the bottom because part of the rod which is above the water level is more oxygenated and acts as cathode while the part just below the water line is poorly oxygenated acts as anode and suffers corrosion.

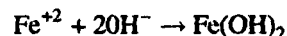
Less oxygenated part



More oxygenated part



Overall reaction



Ferrous hydroxide

4. Attempt any one of the following:

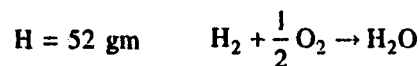
- (a) A sample of coal was found to have the following percentage composition: C = 75%, H = 5.2%, N = 3.2% and ash = 4.5%. Calculate the minimum air required for complete combustion of 1 kg of coal.

Ans. Given that weight of coal = 1 kg

wt of O₂ required % of component combustion reaction



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



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

Total weight of oxygen required = 2416 gm

Oxygen present in the fuel = 121 gm

∴ Net oxygen required for combustion

$$= 2416 - 121$$

$$= 2295 \text{ gm}$$

$$= 2.295 \text{ kg}$$

∴ Minimum weight of air required for combustion

$$= 2.295 \times \frac{100}{23} = 9978 \text{ kg} \quad \text{Ans.}$$

(b) Give the mechanism of 1 kg of coal.

(i) Hoffmann re-arrangement

(ii) Aldol Condensation

(iii) **Canizzaro reaction.**

Ans. Please see Q. 3(a) of IInd Sem. 2006-07.

5. Attempt any one of the following:

- (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. Please See Q. 4(c) of IInd Sem. 2006-07.

- (ii) What are the advantages and disadvantages of gaseous fuels?

Ans. Advantages:

1. They are very fast combustion fuel.
2. They do not produce ash and smoke
3. They have highest calorific value.
4. They have highest thermal efficiency

Disadvantages:

1. They are costly except natural gas.
 2. Transportation and storage is not easy. Chance of spontaneous explosion is possible.
 3. Fire hazards are possible
- (b) Describe the various types of liquid crystals. Distinguish between nematic and smectic liquid crystals.

Ans. Please See Q. 4(a) of IInd Sem. 2009-10.

6. Attempt any one of the following:

- (a) What is the potential of a half-cell consisting of zinc electrode in 0.01 M ZnSO_4 solution at 25°C ? $E^\circ = 0.763\text{V}$.

Ans. $E = E^\circ - \frac{0.0591}{n} \log C$

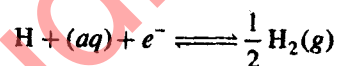
$$E_{\text{cell}} = 0.763 - \frac{0.0591}{2} \log 0.01$$
$$E_{\text{cell}} = 0.763 - \frac{0.591}{2} \times (-2)$$
$$E_{\text{cell}} = 0.763 + 0.591$$

$$E_{\text{cell}} = 1.354 \text{ volt}$$

- (b) (i) What is a reference electrode? Describe the construction of normal hydrogen electrode.

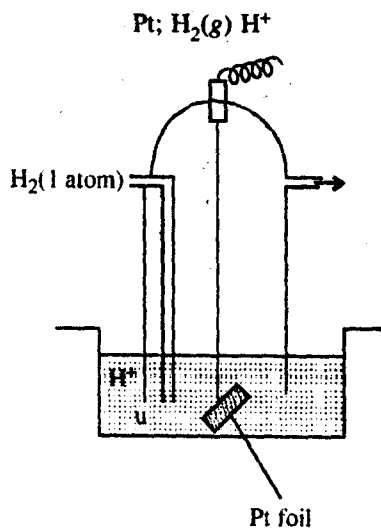
Ans. **Reference Electrode:** Reference electrode consists of two reversible electrode, one of which acts as the cathode and the other as the anode. Each electrode along with the electrolytic reagent associated with it is called the half cell and the reaction that occurs in the half cell is called the half cell reaction.

Hydrogen electrode: Hydrogen gas bubbling in a solution of an acid forms an electrode of this type. The equilibrium in this case is represented as



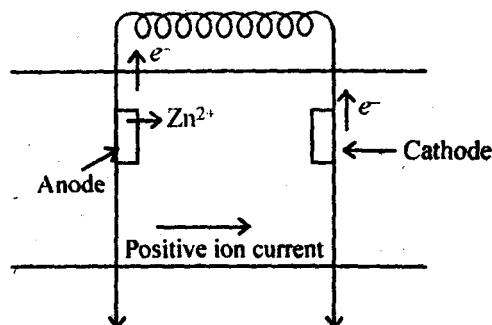
The electrode is reversible with respect to hydrogen ion.

Since hydrogen gas is non conducting, platinum or some other metal which is not attacked by the acid and easily comes into equilibrium with hydrogen, is used for making electrical contact in the circuit the electrode is represented as



(ii) Write short note on Galvanic cell.

Ans.

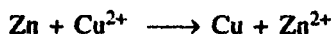


On Galvanic cell the metal which is higher up in electrochemical series, with more negative electrode potential will act as anode. In the Zn-Cu galvanic cell Zn acts as anode where oxidation occurs and Cu acts as cathode where reduction occurs.

In anode



In Cathode $\text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu}$



$$E = E_o - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

7. Attempt any one of the following:

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

Ans. Properties of good fuel:

- High calorific value:** A good fuel have high calorific values. Since the amount of heat librated and thus temperature obtained depends upon this factor.
- Moderate ignition temperature:** The minimum temperature at which a fuel catches foil is known as ignition temperature. If the ignition temperature is high the kindling of fuel becomes difficult. A good fuel must have moderate ignition temperature.
- Moderate rate of combustion:** If the rate of combustion is high it becomes difficult to control and if the rate of combustion is low, the required high temperature may not be attained.
- Low moisture content:** Moisture reduces the calorific value of the fuel. A considerable amount of heat is wasted is the evaporation of moisture present in the fuel during combustion.
- Low ash content:** Ash reduces the calorific values of the fuel.
- Price and availability:** A good fuel should be cheap and readily available is bulk.
- Harmful products:** The products of combustion should be free from objectionable gases like H_2S , CO, CO_2 etc.

8. **Storage and transportation:** A good full should have low storage cast easily transportable from one place to another.

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

Ans. Please See Q. 3(e) of Ist Sem. 2007-08.

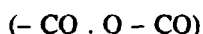
(b) (i) What is 'SHIELDING' and 'DESHIELDING'?

Ans. Please See Q. 2(b) of Ist Sem. 2008.

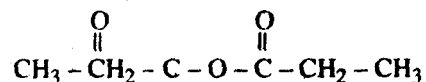
(ii) An organic compound with molecular weight 130 shows the following band in the infrared spectrum: (i) 3082-2860 (m), (ii) 1825 (s), (iii) 1755 (m) and 1455 cm^{-1} (m).

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

Ans. The infrared spectrum, we see two bonds at 1825 cm^{-1} (s) and 1755 cm^{-1} (m). out of these one is strong and the other is less intense. These two bands are characteristic of acyclic anhydride i.e.



The band at 3081 - 2860 cm^{-1} (m) indicates C-H stretching the NMR spectrum, a triplet and a quartet are in the ratio 7.3 : 4.9 i.e., 1.5 : 1 or 3 : 2 the three triplet at 8.75 and a tune proton quartet at 7.8 τ indicates $\text{CH}_3 - \text{CH}_2 -$ as a part of the structure clearly, a structure of the compound can be written as



This structure is in accordance with the give data and its molecular weight is 130.