B.TECH.

[EAS-202]

SECOND SEMESTER THEORY EXAMINATION 2010-11

ENGINEERING CHEMISTRY

Time: 3 Hours *Total Marks: 100*

Note: Attempt all questions.

SECTION—A

1. Choose/Fill correct answer: (20×1=20)

(*i*) Which of the following molecule possesses the smallest bond length?

(*a*) F_2 (*b*) Cl_2

(*c*) Br_2 (*d*) I_2

Ans. (*a*) F_2

(*ii*) Which one is not the allotropy of carbon?

(*a*) Graphite (*b*) Fullerene

(*c*) Diamond (*d*) Bakelite

Ans. (*d*) Bakelite

(*iii*) The rate of a reaction does not depend upon:

(*a*) Temperature

(*b*) Pressure

(*c*) Concentration

(*d*) Catalyst

Ans. (*b*) Pressure

(*iv*) For a system Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Vapur, degree of freedom, is .....

Ans. Zero

(*v*) S_N^2 reaction is accompanied by ..... of configuration.

Ans. Inversion

(*vi*) Optical isomerism in compounds due to restricted rotation around a single bond is called .....

Ans. Biphenyl comounds

(*vii*) The number of conformation of ethane is:

(*a*) 3 (*b*) 5

(*c*) 7 (*d*) None

Ans. (*d*) None

(*viii*) Polypyrrol is .....polymer.

Ans. Conducting

(*ix*) $F_2C = CF_2$ is a monomer of:

(*a*) Teflon (*b*) Glyptal

(*c*) Nylon-6 (*d*) Bunna-S

Ans. (*a*) Teflon

(*x*) The electrode potential of SHE (Standard Hydrogen Electrode) is:

(*a*) 1 (*b*) 2

(*c*) 1.018 (*d*) Zero

Ans. (*d*) Zero

(*xi*) The chemical formula of Zeolite is:

(*a*) $FeSO_4 \cdot 7H_2O$

(*b*) $Al_2(SO_4)_3 \cdot 18H_2O$

(*c*) $Na_2Al_2O_4$

(*d*) $Na_2O \cdot Al_2O_3 \cdot x\ SiO_2\ _yH_2O$

Ans. (*d*) $Na_2O \cdot Al_2O_3 \cdot x\ SiO_2\ _yH_2O$

(*xii*) Corrosion is a process of:

(*a*) Oxidatiion

(*b*) Reduction

(*c*) Electrolysis

(*d*) Erosion

Ans. (*c*) Electrolysis

(*xiii*) Finger Print region of 1R spectroscopy is .....

Ans. In range of 1300-900 cm^{-1}

(xiv) A good fuel should possesses:

(a) High calorific value

(b) Low ignition temperature

(c) High moisture content

(d) Both (a) and (b)

Ans. (a) High calorific value

(xv) The oxidation number of Fe in $K_4[Fe(C_N)_6]$ is:

(a) +2 (b) +3

(c) +1 (d) +4

Ans. (a) +2

(xvi) The relation between HCV and LCV is:

(a) LCV = HCV – 0.09HL

(b) LCV = HCV + 0.09HL

(c) HCV = LCV – 0.09HL

(d) HCV = LCV + 0.09HL

Ans. (a) LCV = HCV – 0.09HL

(xvii) For preparation of N/20 $K_2Cr_2O_7$ solution, the amount of $K_2Cr_2O_7$ required to dissolve in 250 ml water is:

(a) 0.6125 g (b) 6.125 g

(c) 61.25 g (d) 612.5 g

Ans. (a) 0.6125 g

(xviii) The total number of NMR signals in 2-bromopropane is:

(a) 3 (b) 2

(c) 4 (d) 1

Ans. (c) 4

(xix) The reaction $N_2O_5(g) \rightarrow N_2O_4(g) + 1/2O_2(g)$ is:

(a) Zero order

(b) First order

(c) Second order

(d) Fractional order

Ans. (b) First order

(xx) Carbon having four different groups attached to it is called ..... carbon.

Ans. chiral

SECTION — B

Q.2. Attempt any three of the following: **(10×3=30)**

(a) (i) Explain metallic bond on the basis of molecular orbital theory.

(ii) Calculate the bond order of O_2, O^{+2}, O^{-2}, and O_2^{-2} and arrange them in increasing order of their stability.

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

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

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

Explanations of metallic bond on the basis of molecular orbital theory: This is the quantam mechanical treatment of the metallic crystal and is similar to molecular orbital theory of covalent molecules.

Molecular orbital theory: According to this theory electorns in the metal are considered to cover the whole crystal lattice and are not localised between any two atoms. Therefore metallic bonding is formed by the delocalisation of all orbitals containing free electrons.

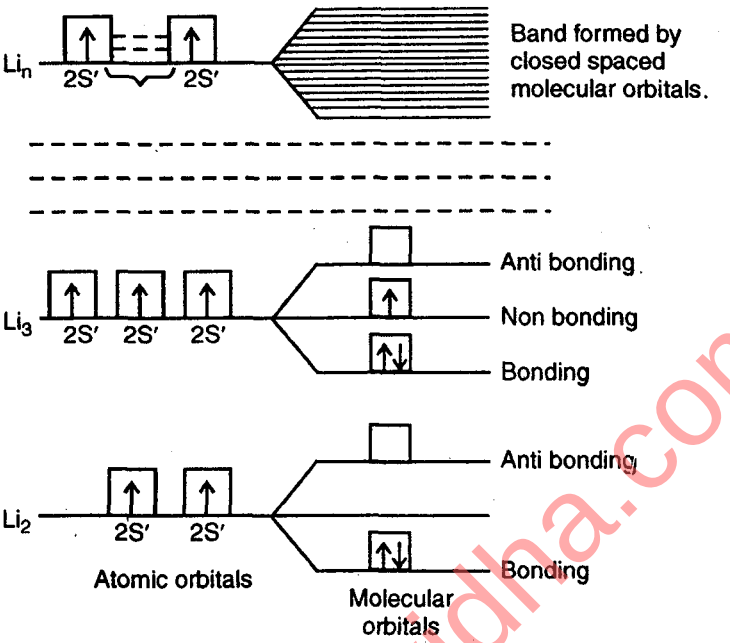
According to molecular orbital theory when two atomic orbitals combine, two molecular orbitals are found one of which is bonding molecular orbital and the other is antibonding molecular orbital. When three atomic orbitals combine three molecular orbitals e.g. bonding, antibonding and nonbonding are formed. Similarly when n-atomic orbitals combine n-molecular orbitals are formed. In case of metallic crystals n is of the order of 10^{23}.

e.g. $Li(3): 1S^2 2S^1$

$$\underset{\text{Atom I}}{Li} + \underset{\text{Atom II}}{Li} \rightarrow Li_2$$

$$\underset{\text{Atom I}}{Li} + \underset{\text{Atom II}}{Li} + \underset{\text{Atom III}}{Li} \rightarrow Li_3$$

$$Li + Li + Li + \text{----------} \rightarrow Li_n$$

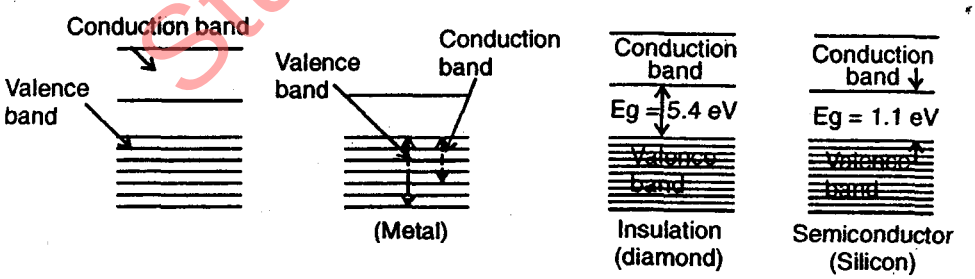


Formation of Bands

Therefore 10^{23} molecular orbitals are formed and these are so closely spaced that they form a continuum known as quasi-continuous energy band. That is why the theory is known as Band theory.

The outermost energy band that is completely filled or partially filled is known as valence band while the band that is above the valence band is empty at OK is known as conduction band. The gap between valence band and conduction band is known as energy gap or band gap. Depending upon the band gap materials are clasified as:

1. **Metals:** Band gap is zero that is valence band overlaps with the conduction band.
2. **Semi conductors:** Band gap is of the order of 1 eV.
3. **Insulators:** Band gap is large i.e. in case of diamond it is 5.4 eV.



(*ii*) Molecule/ion	M.O Configuration	B.O
O_2	$\sigma 1S^2 \overset{*}{\sigma} 1S^2\ \sigma\ 2S^2 \overset{*}{\sigma}\ 2S^2 \sigma 2P_z^2 \pi 2P_x^2 = \pi 2y^2, \overset{*}{\pi}\ 2P_x' = \overset{*}{\pi}\ 2P_y'$	$\frac{1}{2}(10-6) = 2$

O_2^{+2} $\quad \sigma 1S^2 \overset{*}{\sigma} 1S^2 \sigma 2S^2 \overset{*}{\sigma} 2S^2 \sigma 2P_3^2 \pi 2P_x^2 = \pi(2P_y') \overset{*}{\pi} 2P_x'$ 2.5

O_2^{-} $\quad \sigma 1S^2 \overset{*}{\sigma} 1S^2 \sigma 2S^2 \overset{*}{\sigma} 2S^2 \sigma 2P_z^2 \pi 2P_x^2 = \pi(2P_y^2) \overset{*}{\pi} 2P_2^2 = \overset{*}{\pi} 2P_2^1$ 1.5

O_2^{-2} $\quad \sigma 1S^2 \overset{*}{\sigma} 1S^2, \sigma 2S^2 \overset{*}{\sigma} 2S^2 \sigma 2P_z^2 \pi 2P_x^2 = \pi 2P_y^2 \overset{*}{\pi} 2P_x^2 = \overset{*}{\pi} 2P_y^2$ 1.0

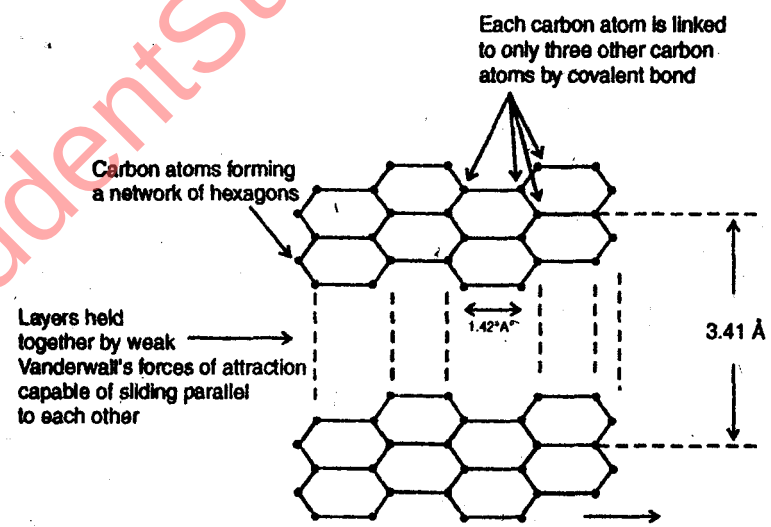
∵ Band order ∝ Stability

$$O_2^{+} > O_2 > O_2^{-} > O_2^{2-}$$
Order of Stability

(b) (i) Explain the structure of graphite. Also explain the reasons for its electrical and lubricating properties.

(ii) A body centered cubic element of density 10.3 g cm^{-3} has a cell edge of 314 pm. Calculate the atomic mass of the element. (Avogadro's constant = 6.023×10^{23} mol^{-1}).

Ans. (i) Structure of Graphite: In graphite each carbon atom Sp^2-hybridised and is linked to three other carbon atoms in the same plane. In this way hexagons of six carbon atoms are formed in one layer which may be regarded as benzene rings fused together. The bonding between atoms within a layer is strong covalent. Several such layers are held together by weak vanderwaals forces. Therefore, grpahite is composed of flat two dimensional layers.



Graphite has thus a two dimensional structure. The distance between the atoms is 0.142 nm. The distance between the adjacent layers is 0.335 nm. Weak binding between the layers results in the graphitte crystals being slipping and it is due to this fact that graphite is very good lubricant and has condensation properties. The energy required to separate network solids into constituent atoms is usually large. Thus graphite has a very high melting point.

Ans. (*ii*) Given

Density $\rho = 10.3$ gm/cm^3

Cell edge length $a = 314$ Pm $= 3.14 \times 10^{-8}$ m

In B.C.C. structure, no of effective atoms $N_e = 2$

We know that $$\rho = \frac{A_w \times N_e}{N_a \times a^3}$$

where A_w = Atomic weight

N_A = Avagadro's number

or $$A_w = \frac{10.3 \times 6.023 \times 10^{23} \times (3.14 \times 10^{-8})^3}{2}$$

or $$A_w = 960.3 \times 10^{23} \times 10^{-24}$$

or $$A_w = 96.03$$

or $$A_w = 96 \text{ Ans.}$$

(c) (i) Give the mechanism of following reactions:

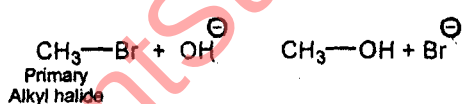
Beckmann rearrangement

Diels-Alder reaction.

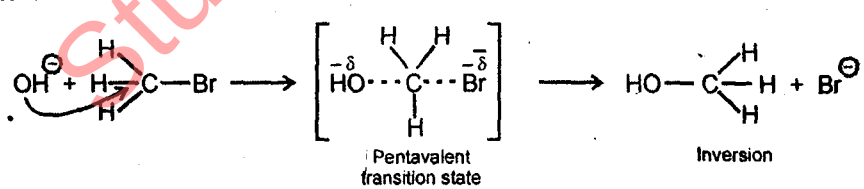
(ii)Show, how does S_N^2 reaction give rise to inverted product.

Ans. (i) Please See Q.No. 2(iv) of Ist Sem. 2008-09.

Ans. (*ii*) SN^2 reaction: SN^2 reaction proceeds in a single step.



Mechanism: In SN^2 reaction breaking of bond and formation of bond takes place simultaneously. Such reactions proceed via transition state in which carbon atom appears to be pentavalent. As the reagent attacks from the rear side (backside), S_N^2 reaction is often accompanied by inversion of configuration.



(d) A sample of coal was analysed as follows: Exactly 1.51 gm of coal was weighed into a silica crucible. After heating for 1 hr at 110°C, the residue weighed 1.415 gm. The crucible was then strongly heated for exactly 7 min at 950°C. The residue weighed 0.528 gm. The crucible was then heated until a constt weight of residue was obtained. The lost residue was found to be 0.254 gm. Calculate the percentage results of above analysis.

Ans. Weight of moisture in coal = 1.51 – 1.415 = 0.095 gm

Weight of volatile matter = 1.415 – 0.528 = 0.887 gm

Weight of ash $= 0.254$ gm

$$\% \text{ of moisture} = \frac{0.095}{1.4} \times 100 = 6.8\%$$

$$\% \text{ of volatile matter} = \frac{0.887}{1.4} \times 100 = 63.4\%$$

$$\% \text{ Ash} = \frac{0.254}{1.4} \times 100 = 18.2\%$$

$$\% \text{ of fixed carbon} = 100 - (6.8 + 63.4 + 18.2) = 11.6\% \quad \textbf{Ans.}$$

(e) (i) What is optical activity? Give the stereoisomers of Tartaric acid.

(ii) Distinguish between hydrogen evolution and oxygen absorption theory of corrosion.

Ans. (i) Please See Q.No. 3(c) of Second Sem. of 2006-07.

(ii) Oxygen Absorptiion Mechanism or Rusting of Iron in alkaline/neutral medium: Usually the surface of metal is covered with a thin layer of oxide. When this oxide layer is broken, bare surface is exposed to environment and this area acts as an anode while the remaining area acts as cathode.

Since the medim is exposed to the atmosphere, it contains dissolved oxygen. Thus at cathode oxygen reduction takes place while at anode iron corrodes.

$Fe \longrightarrow Fe^{+2} + 2e$ Oxidation At anode

$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$ Reduction At cathode

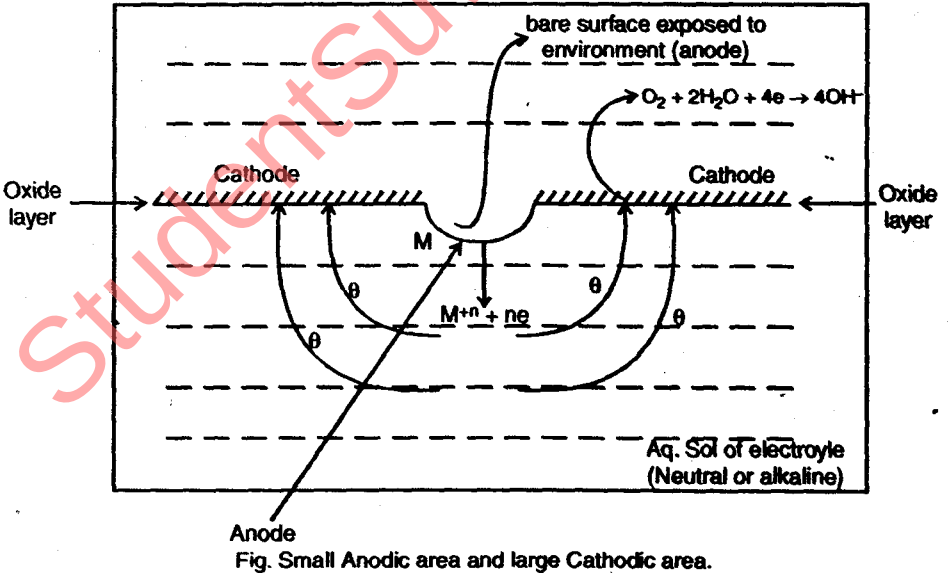


Fig. Small Anodic area and large Cathodic area.

The electrons liberated at anode flow towards cathode where they are consumed in reduction reaction. The Fe^{+2} and OH^- thus formed react to form ferrous hydroxide. Since during corrosion there in no net accomulation of charge hence the overall reaction is

$$[Fe \longrightarrow Fe^{+2} + 2e] \times 2$$
$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$$
$$2Fe + O_2 + 2H_2O \longrightarrow \underbrace{2Fe^{+2} + 4OH^-}$$
$$\downarrow$$
$$2Fe(OH)_2\downarrow$$
Ferrous hydroxide

Depending upon the availability of oxygen two types of corrosion products are formed.

(*i*) In excess supply of oxygen: In excess supply of oxygen ferrous hydroxide is easily oxidised into ferric hydroxide.

$$\underset{\text{Ferrous hydroxide}}{4\,Fe(OH)_2} + 2H_2O + O_2 \longrightarrow \underset{\text{Ferric hydroxide}}{4Fe(OH)_3\downarrow}$$
$$\downarrow$$
$$4\,Fe_2O_3 \cdot xH_2O$$
Yellow rust

(*ii*) In limited supply of oxygen: In limited supply of oxygen black magnetite Fe_3O_4 or ferrosoferric oxide is formed

$$6Fe(OH)_2 \longrightarrow \underset{\text{Black}}{Fe_2O_3 \cdot FeO \cdot 6H_2O}$$

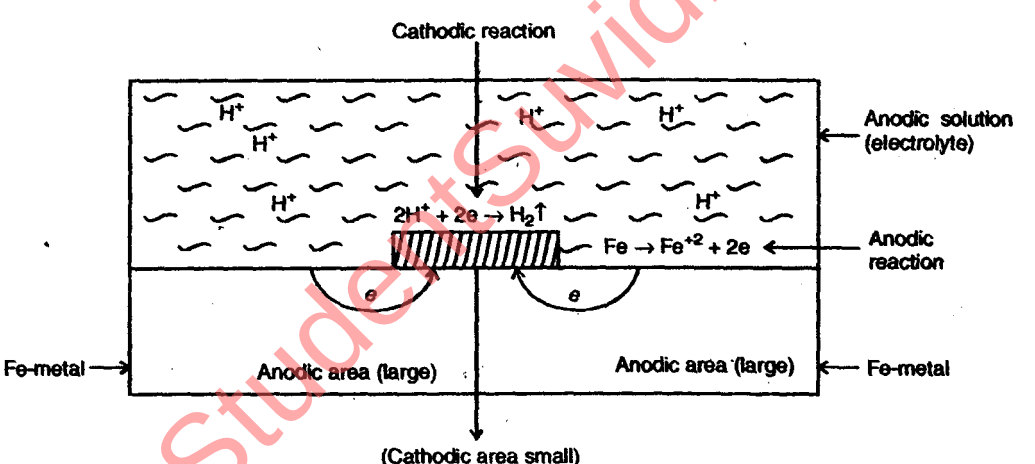


Fig. *Mechanism of wet corrosion by hydrogen evolution mechanism.*

(b) Hydrogen evolution mechanism: In acidic solution corrosion of iron metal takes place by hydrogen evolution mechanism. Iron undergoes oxidation at anode to form Fe^{+2}.

The electrons liberated at anode are consumed at cathode by H^+ liberating hydrogen gas.

$Fe \longrightarrow Fe^{+2} + 2e$	Oxidation	At anode
$2H^+ + 2e \longrightarrow H_2$	Reduction	At cathode

The overal reaction is $Fe + 2H^+ \longrightarrow Fe^{+2} + H_2\uparrow$

All the metals which are palced above hydrogen in electrochemical series, corrodes in acidic solution by hydrogen evolution mechanism.

SECTION — C

Note: Attempt all five questions: **(10×5=50)**

Q.3. Attempt any one of the following:

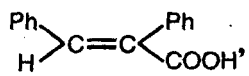
(a) (i) Distinguish between thermoplastic and thermosetting polymers.

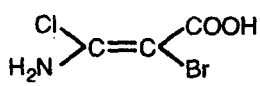
(ii) How will you prepare Bakelite and Presplex polymers?

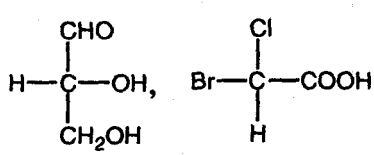
Ans. (i) Please See Q.No. 2(c) of Ist Sem. 2007-08.

(ii) Please See Q.No. 2(e) of Ist Sem. 2007-08.

(b) (i) Assign E, Z and R, S configuration of the following:

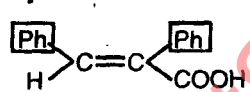






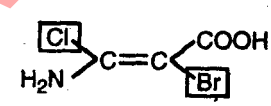
(ii) Explain the term chirality. What is the condition essential for optical activity?

Ans. (i)



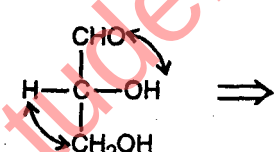
(Z)

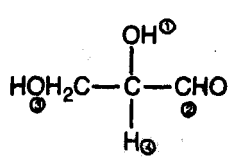
Higher Priority groups are on the same side of carbon.



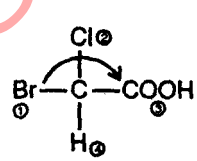
(E)

Higher Priority groups are on the opposite side.





R Configuration



R Configuration

(ii) Chirality: "A carbon atom which is bonded to four different atoms or groups is known as chiral or asymmetric carbon, and this is known as the condition of chirality."

Essential Condition for Optical Activity: The necesary and sufficient condition for a compound to exhibit optical isomerism is that it should be disymmetric i.e. the gemetrical structure of the molecule should not superimpose on its mirror. A compound is dissymmetric in nature if it is devoid of the followign elements of symmetry:

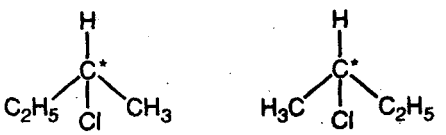
(*i*) Plane of symmetry

(*ii*) Centre of Symmetry

(*iii*) Alternating axis of symmetry

(*i*) Molecules containing only one asymmetric carbon atom are disymmetric in nature and hence exhibit optical activity. These chiral molecules are non superimposable on their mirror image.

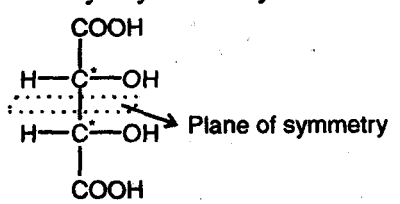
2 — Chlorobutane



Optically active compound (non-superimposable mirror image)

(*ii*) However molecules containing two or more asymmetric carbon atoms may not necessarily be optically active as they may not be disymmetric because of the presence of any element of symmetry.

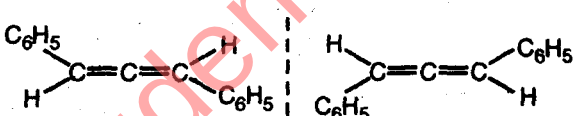
e.g.



(Optically inactive although it contains two asymmetric carbon atoms)

(*iii*) Although large number of compounds are optically active because of the presence of asymmetric carbon atom. But there are some compounds which donot passess any asymmetric carbon atom but are optically active because the molecule as a whole is disymmetric.

e.g. (a) Allenes



Non-Superimposable mirror image 1, 3 Diphenyl propadiene

"Hence disymmetry is the only condition for optical activity."

(c) The following data is obtained in a bomb calorimeter experiments:

Weight of crucible	=	**3.649 g**
Weight of fuel	=	**1.029 g**
Mass of water in calorimeter	=	**2200 g**
Water equivalent of calorimeter	=	**570 g**
Observed rise in temeprature	=	**2.3°C**
Cooling correction	=	**0.047°C**
Acid correction	=	**62.6 calories**
Fuse wire correction	=	**3.8 calories**
Cotton thread correction	=	**1.6 calories**

Calculate GCV of fuel sample. If the fuel contains 6.0% H, determine the NCV.

Ans.
$$HCV = \frac{(w+w)(t_2 - t_1 + C_c) - C_A + C_F + C_{C_T}}{m}$$
$$= \frac{(2200+570)(2.3+0.047) - (62.6+3.8+1.6)}{(4.687-3.649)}$$
$$= \frac{(2770 \times 2.347) - 68}{1.038}$$
$$\therefore \quad HCV = 6197.67 \text{ Cal/gm}$$

Since the fuel containing 6.0% hydrogen

$$\therefore \quad LCV = (HCV - 0.09 \times H \times 587) \text{ Cal/gm}$$
$$LCV = 6261 - 0.09 \times 6 \times 587$$
$$LCV = 6261 - 316.98$$
$$\therefore \quad LCV = 5944.02 \text{ Cal/gm.}$$

Q.4. Attempt any one of the following:

(a) Calculate the temporary, permanent and total hardness of a sample of water that is analysed as: $Mg(HCL_3)_2 = 7.3$ mg/L, $Ca(HCO_3)_2 = 16.2$ mg/L $MgCl_2 = 9.5$ mg/L and $CaSO_4 = 13.6$ mg/L.

Ans. Sample of water analysed as—

$Mg(HCO_3)_2 = 7.3$ mg/l $\quad Ca(HCO_3)_2 = 16.2$ mg/l

$MgCl_2 = 9.5$ mg/l and $CaSO_4 = 13.6$/l

$$\text{Temporary Hardness} = \left[\frac{16.2 \times 100}{162} + \frac{73 \times 100}{1460}\right] = 15 \text{ mg/l}$$

$$\text{Permanent Hardness} = \left[\frac{52 \times 100}{95} + \frac{13.6 \times 100}{136}\right] = 65 \text{ mg/l}$$

Total hardness $= (15+65) = 80$ mg/l **Ans.**

(b) (i) Explain the term chemical shift.

(ii) Indicate the number and splitting of signals in the NMR spectra of the anhydrous ethanol.

Ans. (i) Chemical Shift: The magnetic field at which a free or bare nucleus resonates is quite different from the field at which the same nucleus in a molecule resonates. It is thus clear that the electorns in a molecule affect the NMR frequency of a given nucleus in the molecule. The electrons are said to shield or dishield a nucleus from the applied magnetic field depending upon whether the magnetic field generated by their motion opposes or reinforces the field. The applied external magnetic field affects the motion of the electrons surrounding the nuclei thereby inducing local magnetic field. The magnitude of the local magnetic field is determined by the electron distribution around a nucleus.

"The difference between the magnitude of the magnetic fields at which 'free' nuclei and molecular nuclei resonates is called **chemical shift.**"

We defined chemical shift of a sample as

$$\delta = \frac{\beta_{sample} - \beta_{ref}}{\beta_o} \times 10^6 \text{ ppm}$$

where β_{sample} = Magnetic field of sample

β_{ref} = Magnetic field of reference

(ii) Ethanol contains three types of proton marked a, b, c. Hence it will show-three signals in NMR spectrum.

Splitting of Signals:

S.No.	Proton type	Number of neighbouring Proton (n)	Multiplicity (n + 1)
1.	a (1 H)	0	1
2	b (2H)	3 (of CH_3)	4
3	c (3H)	2 (of CH_2)	3

(c) (i) Explain S_N1 reaction with an example.

(ii) Complete and name the following reactions:

$2CH_3CHO \xrightarrow{NaOH} ?$

$2HCHO \xrightarrow{NaOH} ?$

$(CH_3)_2C(=O)-N-OH \xrightarrow{H^{\oplus}} ?$

$CH_3-C(=O)-NH_2 \xrightarrow{NaOH+Br_2} ?$

Ans. *(i)* Please See Q.No. 3(b) of IInd Sem. 2007-08.

(ii) $2CH_3CHO \xrightarrow{NaOH} CH_3-CH(OH)-CH_2-CHO$ (β-hydroxyal dehyde)

Above reaction is **Aldol condensation.**

$2HCHO \xrightarrow{NaOH} CH_3OH + NCOONa$

Above reaction is Cannizaro's Reaction

$(CH_3)_2C(=O)-N-OH \xrightarrow{H^{\oplus}} CH_3-C(=O)-NH-CH_3$

Above reaction is Beckmann's rearrangement.

$CH_3-C(=O)-NH_2 \xrightarrow{NaOH+Br_2} CH_3NH_2 + eve$

Above reaction is Hoffmann rearrangement.

Q.5. Attempt any one of the following:

(a) (i) Distinguish between order and Molecularity of a reaction.

(ii) Calculate the order and molecularity of the following reactions:

$N_2O_5(g) \rightarrow N_2O_4(g) + \frac{1}{2}O_2(g)$

$H_2(g) + I_2(g) \rightarrow 2HI(g)$

$CH_3CHO \xrightarrow{\Delta} CH_4 + CO_2$

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^{\oplus}} CH_3COOH + C_2H_5OH$$

Ans. (*ii*) Please See Q.No. 6(2i) of IInd Sem. 2008-09.

(*ii*) $N_2O_5(g) \longrightarrow N_2O_4(g) + \frac{1}{2}O_2(g)$

→ Above reaction is unimolecular and having order = 1

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

→ Bimolecular but the order of the above reaction is zero.

$$CH_3CHO \xrightarrow{\Delta} CH_4 + CO_2$$

→ Unimolecular but the order of the reactions 3/2.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^{\oplus}} CH3COOH + C_2H_5OH$$

→ Bimolecular and its order is one.

(b) What is phase rule? Draw and explain phase diagram of water.

Ans. Please See Q.No. 4(a) of Ist Sem. 2006-07.

(c) Discuss the titrimetric analysis of Acid-base and Redox titration.

Ans. Acid-Base Titration: This titration involves titration of base with standard and or titration of an acid with a standard base.

The neutralisation titration essentially involves the combinatiion of hydroxyl ions with the hydrogen ions to form water.

$$H^+ + OH^- \longrightarrow H_2O$$

e.g. Titration of sodium hydroxide with hydrochloric acid

$$NaOH + HCl \longrightarrow NaCL + H_2O$$

i.e. $OH^- + H^+ \longrightarrow H_2O$

Redox Titration: This titration involves the change in oxidation numbers or transfer of electrons among the reacting substances. The standard solutions ae either of the two (i.e. oxidising agent or reducing agent.). This is also known as "Redox titration". The important oxidising and reducing agents generally used in redox titration are

Oxidising agent	Reducing agent
Potassium dichromate	Ferrous compounds
Potassium permagnate	Stannous copounds
Iodine potassium iodate etc.	Oxalic acid sodium thiosulphate

Q.6. Attempt any one of the following:

(a) (i) For a first order reaction, the rate constant is found to be 7×10^{-7} at 7°C and 9×10^{-4} at 57°C. Calculate the energy of activation of the reaction.

($\log_{10}7 = 0.8451$, $\log_{10}9 = 0.9542$)

(ii) What are biopolymers? Give their uses.

Ans. $k_1 = 7 \times 10^{-7}$, $T_1 = 273 + 7 = 280°K$

$k_2 = 9 \times 10^{-4}$, $T_2 = 273 + 57 = 330°K$

$E_a = ?$

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

$$\log \frac{9\times10^{-4}}{7\times10^{-7}} = \frac{E_a}{2.303\times8.314}\left[\frac{330-280}{330\times280}\right]$$

$$\log \frac{9}{7} + \log 10^3 = \frac{E_a}{2.303\times8.314}\left[\frac{50}{330\times280}\right]$$

$$3 + (0.9542 - 0.8451) = \frac{E_a}{2.303\times8.314\times66\times28}$$

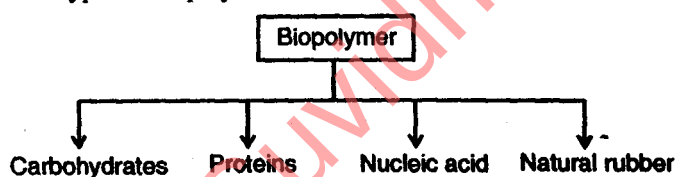
$$E_a = 3.1\times2.303\times8.314\times66\times28$$

$$E_a = 109.69 \text{ kJ/Mol.}$$

(*ii*) Biopolymer's: Biopolymers are the polymers which are present in living matter, animals or plants.

In general bipolymers are the complex lifeless organic substances which build up living organism and are required for their growth and maintenance. They form the basis of life.

Mainly there are four types of biopolymer.



Uses:

(*i*) As a principal food storage polysaccharide in plants and animals. It is encountered daily in the form of rice, bread, potatoes, cakes etc.

(*ii*) Used as an indicator in iodometric titration.

(*iii*) Used in the manufacture of ethyl alcohol, glucose dextrin etc.

(*iv*) Starch nitrate is used as an explosive.

(*v*) It finds used in textiles, paper and plastic industries.

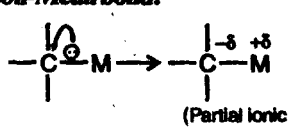
(b) What are organometallic compounds? Give the classification and preparation of organometallics.

Ans. Organometallics:

Definition: "Compounds which contain direct Carbon–Metal bond are known as organometallic compounds".

Since metals are less electronegative than carbon hence the difference in electronegativity makes such compounds polar in nature. Carbon centre acquires partial negative charge ($-\delta$) whereas metal acquires partial positive charge ($+\delta$) as shown below. The extent of polarity depends upon the difference in electronegativity of carbon and metal.

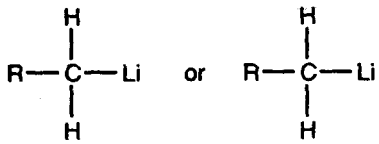
Carbon-Metal bond:

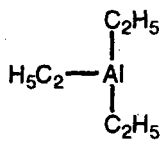


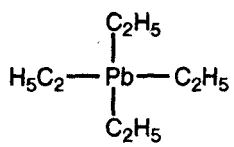
where, M may be Mg, Ca, Na, Li, Al, Sn, Pb etc.

They are named after the name of the metal attached to the carbon centre as alkyl or aryl derivatives.

Example:

Alkyl lithium  Methyl Lithium

Triethyl aluminium 

Tetraethyl lead 

The reactivity of organometallic compound depends upon the percentage ionic character (i.e., the electropositivity of the metal) of the carbon-metal bond. The greater the percentage ionic character of crabon-metal bond the higher is the reactivity of the compound.

Compound	% Ionic character	Reactivity
C-Pb	12%	↓ increases
C-Al	22%	
C-Mg	35%	
C-K	51%	

One of the most versatile reagents in organic chemistry is RMgX (Alkyl magnesium halide), popularly known as 'Grignard Reagent' after the name of its discoverer Victor Grignard, is also an organometallic compound. The versatility of this class of compound is evident from the fact that almost all classes of organic compounds can be prepared from them.

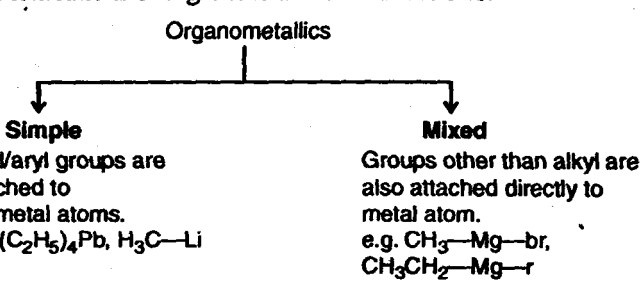
RMgX may be represented as

$$R^{-\delta} - Mg^{+\delta} - X$$

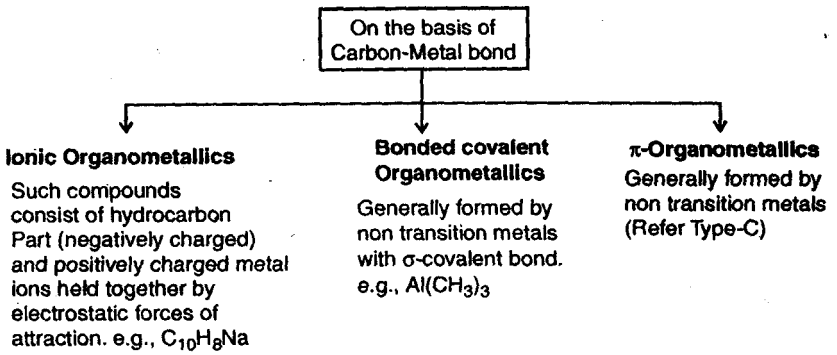
R-may be alkyl or aryl group.

The various classifications of organometallics are as follows:

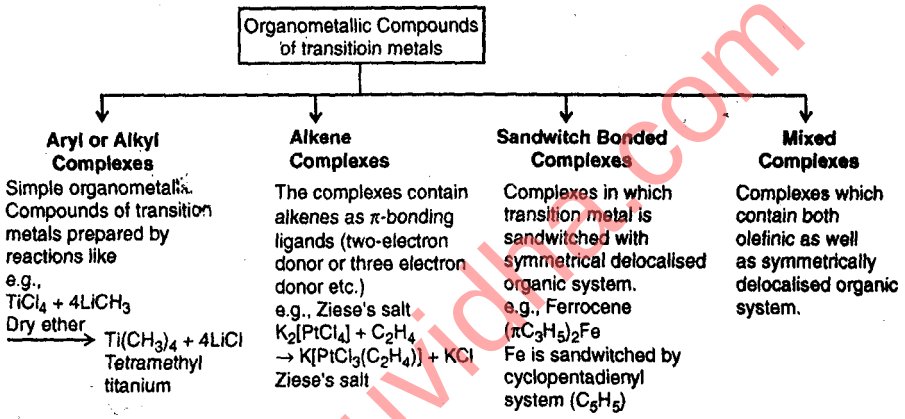
[A]



[B]



[C]



Ferrocene $[\pi\text{–}(C_5H_5)_2Fe]$ Di-π-cyclo pentadienyl iron

Preparation

(a) In laboratory ferrocene is prepared by the action of grignard reagent with metal halides.

$$FeCl_2 + 2C_5H_5MgBr \longrightarrow \underset{\text{Ferrocene}}{Fe(C_5H_5)_2} + 2MgBrCl$$

(b) Commercially it is prepared by the action of cyclopentadene with finally divided iron at 300°C.

$$Fe + 2C_5H_6 \xrightarrow{300^\circ C} \underset{\text{Ferrocene}}{Fe(C_5H_5)_2}$$

(c) Define the term liquid crystals. Describe the classification and applications of liquid crystals.

Ans. Please See Q.No. 3(a) of Ist Sem. 2008-09.

Q.7. Attempt any one of the following:

(a) (i) Differentiate between an electro-chemical cell and an electrolytic cell.

(ii) Calculate the electrode poential of the copper wire dipped in 0.1 M $CuSO_4$ solution at 25°C. The standard electrode potential of copper is 0.34 V.

Ans. (*i*) Electrochemical Cell: In these cells, two like electrodes at different concentrations are dipping in the same solution. The hydrogen electrodes at unequal gas pressures immersed in the same solution of hydrogen ions constitute an electrode - concentration cell. This may be represented as follows:

Pt; $H_2(p_1)$ | solution of H^+ ions, say, HCl | $H_2(p_2)$; Pt

The reactions occuring are

R.H.E	$2H^+ + 2e^- \longrightarrow H_2(p_2)$	(Reduction)
L.H.E.	$H_2(p_1) \longrightarrow 2H^+ + (2e^-)$	(Oxidation)

Overall reaction; $H_2(p_1) \longrightarrow H_2(p_2)$

This reaction is evidently independent of the concentration of the electrolyte.

Electrolyte Concentration Cells: In these cells, the two electrodes of the same metal are dipping in solutions of metal ions of different concentration. One such cell is represented below:

$$Zn, Zn^{2+}(a_+)_1 \| Zn^{2+}(a_+)_1, Zn$$

In this case, both the electrodes are of the same metal (Zn) and these are in contact with solution of the same ions (Zn^{+2}). The concentration and hence activities of the ions, are however, different. Let $(a_+)_1$ and $(a_+)_2$ be the activities of zinc ions in the two electrolytes surrounding the electrodes. The two electrolytes, which are generally $ZnSO_4$ solution, are separated from each other by a salt bridge. This is represented by the double line put in between the two half cells. The reactions occurring are:

R.H.E.	$Zn^{2+}(a_+)_2 + 2e^- \longrightarrow Z_n(S)$	(Reduction)
L.H.E.	$Zn(S) \longrightarrow Z_n(a_+)_1 + 2e^-$	(Oxidation)
Overall reaction	$Zn^+(a_+)_2 \longrightarrow Zn^{+2}(a_+)_1$	

The net process thus involves the transfer of 1 mole of Zn^{2+} ions from the solution in which the activity is $(a_+)_2$ to the solution in which the activity is $(a_+)_1$.

(ii) $\underset{(0.1M)}{Cu^{2+}(aq)} + 2e^- \longrightarrow Cu(S), \quad E^o = 0.34\ V$

$$E = E^o - \frac{0.0591}{2} \log \frac{[Cu]}{[Cu^{2+}]}$$

$$E = 0.34 - \frac{0.0591}{2} \log \frac{10}{0.1}$$

$$E = 0.34 - \frac{0.0591}{2} \times 1$$

$E = 0.369$ Volt **Ans.**

(b) What is meant by corrosion inhibitors? How is corrosion prevented by cathodic protection?

Ans. Corrosion inhibitors: "Substances which are added from outside to reduce the rate of corrosion are known as inhibitors."

Inhibitors reduce the rate of corrosioin either:

(*i*) By forming a layer in between which acts as a barrier between the material and environment.

(*ii*) Or by retarding the anodic or cathodic or both processes.

Cathodic inhibitors: They retard the rate of cathodic reaction and hence the overall rate of corrosion. In acidic medium the cathodic reaction taking place is

$2H^+(aq) + 2e \longrightarrow H_2(g)$ Reduction, at cathode

organic inhibitors like amines, mercaptans, substituted areas having lone pair of electrons reduce the rate of cathodic reaction, considerably by reacting with H^+.

Anodic inhibitors: Inhibitors which retard the rate of anodic reaction by polarising it are known as anoidic inhibitors. These inhibitors generally form a layer in between material and environment.

e.g. — Chromates, phosphates, tungstates are generally used as anodic inhibitors.

Prevention by cathodic protectioin: Please See Q.No. 5(i) of IInd Sem. 2007-08.

(c) (i) Write a short note on biogas.

(ii) Write a short note on softening of water by Zeolites.

Ans. (i) Please See Q.No. 5(c) of IInd Sem. 2006-07.

(ii) Please See Q.No. 2(c)(ii) of IInd Sem. 2009-10.