ENGINEERING CHEMISTRY—2009

SEMESTER - 2

Time : 3 Hours Full Marks : 70

Group A
(Multiple Choice Type Questions)

1. Choose the correct alternatives for any ten of the following : 10×1=10

(i) van der Waals type of bond is formed by
(a) sharing of electrons (b) transferring of electrons from one atom to the other (c) sharing of electrons by one atom only (d) weak electrostatic force of attraction among fluctuating dipoles.

(ii) Which of the following defects arises due to misplace of ions in a crystal lattice?
(a) Schottky defect (b) Frenkel defect (c) Metal excess defect (d) Non-stoichiometric defect.

(iii) The coupling between base units of DNA is through
(a) Covalent bonding (b) Electrovalent bonding
(c) van der Waals forces (d) Hydrogen bonding.

(iv) CO_2 is isostructural with
(a) C_2H_2 (b) $HgCl_2$ (c) NO_2 (d) NH_3

(v) ZnO is white when cold and yellow when hot, this is due to
(a) charge transfer (b) d-d transition (c) metal excess defect (d) none of these

(vi) The phenomenon of superconductivity was coined by
(a) Carnot (b) C.V. Raman (c) Einstein (d) Kammerlingh Onnes

(vii) The presence of intermolecular and intramolecular hydrogen bonding is distinguished by
(a) UV-Visible spectroscopy (b) IR-spectroscopy
(c) ^{1}H-NMR spectroscopy (d) Both IR and ^{1}H-NMR spectroscopy.

(viii) Caprolactum is a monomer of
(a) Bakeltte (b) PVC (c) Nylon-66 (d) Teflon

(ix) The ion conductance of an ion depends on its
(a) charge only (b) speed only
(c) charge and speed (d) charge, speed and hydration

(x) Anomalous expansion of water from 0°-4°C occurs due to
(a) van der Waals interaction (b) hydrogen bonding
(c) non-covalent weak interaction (d) dipole-induced dipole interaction

(xi) The hybridization of Xe in XeF_2 is
(a) sp (b) sp^3d^2 (c) sp^3 (d) sp^3d.

(xii) $[Co(NH_3)_5 CN]Cl_2$ and $[Co(NH_3)_5 NC]Cl_2$ are
(a) coordination isomers (b) geometrical isomers
(c) linkage isomers (d) ionization isomers.

Ans. Q.1. (i) d ; (ii) a/d ; (iii) d ; (iv) a ; (v) c ; (vi) d ; (vii) b ; (viii) nylon 6 (All the options are incorrect) ; (ix) d ; (x) b ; (xi) d ; (xii) c.

Group - B
(Short Answer Type Questions)

Answer any *three* of the following. $3 \times 5 = 15$

2. Define ionic mobility. Mention the unit of equivalence conductance and ionic mobility. How does equivalence conductance vary with concentration for both strong and weak electrolytes? 1+1+3

Ans. Ionic mobility : The velocity with which an ion moves under a potential gradient of 1 volt/m. or 1 volt/cm in a solution is called absolute ionic velocity or ionic mobility.

$$\text{Ionic mobility} = \frac{\text{velocity}}{\text{voltage / distance}}$$

Unit of Equivalent conductance : $Ohm^{-1}\ cm^2\ gm\text{-}eq^{-1}$ (C.G.S.)
$Ohm^{-1}\ m^2\ gm\text{-}eq^{-1}$ (S.I.)

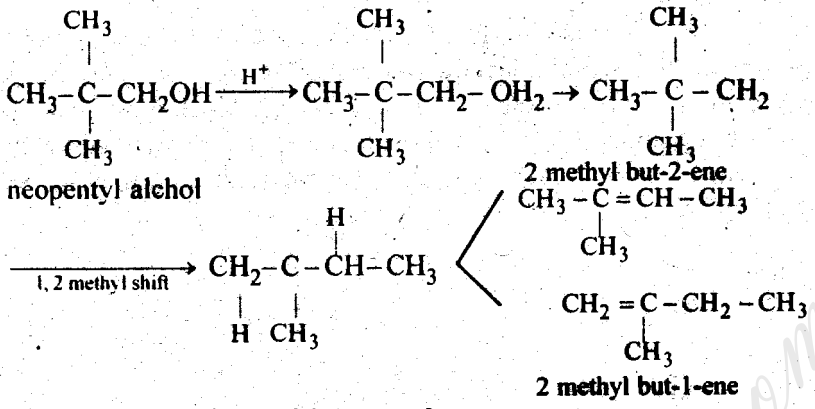
& Ionic mobility : $cm^2\ s^{-1}\ v^{-1}$ (C.G.S.)
$m^2\ s^{-1}\ v^{-1}$

Variation of equivalent conductance with concentration for strong & weak electrolytes : The equivalent conductance or the molar conductance (A_m) of an electrolytes increases with decrease in concentration of electrolyte or with increase in its dilution. Equivalent conductance of strong electrolytes like Hcl, kcl, $CaCl_2$ CH_2 WoN_a, etc with concentration have a comparatively small in crease through they have very high equivalent conductance at or binary temperature ; where as weak electrolyte, like CH_3 COOH show marked increase in equivalent conductance at high dilution.

This is due to the result of an inter ionic attraction between (+)ve and (–) ve ions. The two opposite ions may even give rise to some ion pair of the type (A+B). This type of interionic attraction effectively reduces the speed of the ions and ultimately reduce the equivalent conductance of the electrolytic solution. But when concentration is lowered by increasing the dilution, the ions go far apart, the interionic forces are reduced. Then the ions can move freely. So in that case conductance can be increased with delution.

3. Write down the possible products on the dehydration of neopentryl alcohol. Write down the main features of transition state theory. What is the unit of rate constant of a second order reaction? 2+2+1

Ans. Possible products on the dehy dration of neopentyl alcohol :



Main features of transition sate theory :

(i) The seacting molecular, possesion necessary energy approach to form an activated complex by rearrangement of atoms.

(ii) The energy necessary to approach the seactant molecular to form this transition state or activated complex is the energy of activation.

(iii) For normal or direct reactions, the activated complex formed in assumed to be in equilibrium with reactant.

(iv) The activated complex is not a stable species or a reaction intermediate. It is very short lined.

(v) The potential energy of the activated complex is very high compared to that of the reactant as well as product.

(vi) Transient state does not represent an oberservable, but can be assumed to possess properties such as bond length, molecular weight, enthalpy, etc.

(vii) The activated complex subsequently break up in to products.

The unit of rate constant if a second order reaction is lite $mole^{-1}$ sec^{-1}.

4. (a) What is pseudo-unimolecular reaction ? Give one example.

(b) Explain the physical significance of activation energy. 3+2

Ans. (a) Pseudo-Unimolecular reaction : Those reactions which are bimolecular but are of 1st order are called pseudo unimolecular reaction example : **Hydrolysis of an ester in presence of mineral acid.** Hydrolysis of esters in presence of mineral acids follows first order kineticts. eg. hydrolysis of ethyl acctate in presence of HCl.

$$CH_3\,COO\,C_2H_5 + H_2O \xrightarrow{HCl} CH_3COOH + C_2H_5OH$$

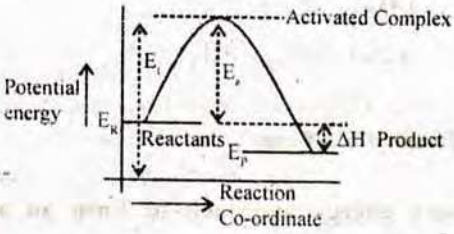
Here HCl act as a catalyet and does not take part in the rate equation. The reaction is bimolecular. However the rate of reaction in given by the rate.

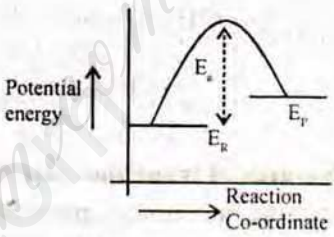
rate = K [ester]

This is because the water is present in large exces and its active mass remain practically constant. Therefore its active mass gets included in ther constant. Since the rate of the reaction

is determined by one concentration term only ie ester, the rection is 1st order. So such reaction is called pseudo-unimolecular reaction.

Ans. (b) A chemical seaction occurs as aresult of collision between reacting molecules possessing sufficient high energy to react. Molecules possessing energy less than threshold energy, simply collide and rebomd without reacting. The extra energy which must be given to molecular to enable them to bring about effective collisions is called activation energy (E_a). Areaction whose activation energy is high will prceed at slowrate and areaction whose E_a value is low will proceed at high rate.





when $\rightarrow E_R > E_P$, the reaction is exothermill

5. **Define lattice energy and hybridization. Arrange the following ionic crystals in order of their increasing lattice energy : LiF, CaF_2 and Mg S.** 3+2

Ans. Lattice Energy : The lattice energy of an ionic compound is defined as the amount of energy released when oppositely charged ions get packed closely to form one mole of crystalline solid. eg.

$Na^+ + Cl^- \rightarrow Nacl + 787$ kJ.

Higher lattice energy means greater stability of ionic compound and greater attarction between the cations and anions.

Hybridization : Hybridization is the concept of intermixing of the orbitals of an atom having nearly the same energy to give exactly equivalent orbitals with same energy, identical shapes and symmetrical orientations in space. eg. Sp hybridization is formed by mixing of S & P orbital of an atom.

The order of the following ionic crystal in order of their in creasing lattice energy is–

$LiF < CaF_2 < MgS$

6. What is LPG ? Why is it used as a domestic fuel ? Define Octance number of a fuel and explain how the Octance number can be improved ? 1+1+3

Ans.: Q.6. Same as Q.6. 2006.

Group - C
(Long Answer Type Questions)

Answer any ***three*** of the following. $3 \times 15 = 45$

7. **(a) Distinguish between SN_1 and SN_2 mechanisms with suitable examples. Discuss the role of solvents in SN_1 reactions.** 4+2

(b) State and explain Hess's law with examples. How does it follow the first law of thermodynamics? 2+2

(c) Using Carnot cycle, prove that the efficiency of a heat engine is always less than one. 6+4+5

Ans. (a) SN^1 follow first order kinetics ie they are unimlecular.

SN^2 follows 2nd order kinetics ie they are bimolecular.

SN^1 onechanism is generally followed by testiary halides. eg. alkaline hydrolyisis of testiary butyl bromide.

$$KOH \rightleftharpoons K^+ + OH^-$$
(aq) (Nu)

$$\text{First step : } CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \underset{\text{r/d step}}{\overset{\text{slow}}{\rightleftharpoons}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\oplus + Pr \xrightarrow{\text{fast}} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

tert. butyl bromide tert. butyl bromide

SN^2 mechanism is generally followed by primary halidex. eg. alkaline hydrolysis of ethyl bromide and is a one step onechanism.

$$OH^{\ominus} \rightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{\overset{H}{|}C}}-Br \xrightarrow{\text{Slow}} \left[HO^{\delta-} \cdots \underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{\overset{H}{|}C}} \cdots Br^{\delta-}\right]^{\neq} \rightarrow HO-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-H + Br^{\ominus}$$

SN^1 mechanism are favoured by weak nucleophiles whereas SN^2 mechanism are favaured by strong mucleophiles in the above example OH^-.

SN^1 mechanism are favoured by polar solvents and SN^2 mechanism are favoured by polar aprolic solvents.

Both, back side and front side attack of nudeophile takes place in SN^1 reaction. In case of optical active substrate, configuration dominates because of back side attack till the formation of canbocation.

The nucleophile ex-clusively attacks from back side of substrate in SN^2 reaction. If the substrate in optically active inversion of config takes place.

The electronic factories influence the reaction rates largely in SN^1 mechanism. For the same halogen, the reactisity sequence is tert. > sec. > primary > CH_3x.

Stenic factors influence the rate if reaction in SN^2 mechanism. The electronic factors do not influence the rate. Thereactivity sequence is CH_3> Primary > Sec.> tert.

Here transition state (T.S.) being more polar man than that of stanting material. This is because, new change is developed and concentrated in the Transition state I (T.S.I) as compared to the stanting material. So in solvents of high polarity, T.S. gets greater stability that of the starting material. As a result, the energy of activation value is decreased and consequently the reaction rate is increased. Moreover, the reaction rate increases with increasing the polarity of solvent, because the stability if carbocation intermediate increases

with increasing the polarity of solvent. Here usually polar profit solvent is used to separate leaving group from carbocation (R^+) is a solvation through inteamolecular H-bonding between X^- and H-atom of the solvent molecule. Some example of polar solvent. H_2O, RoH, R COOH, R CON_2 etc.

Ans. (b) Hess's law : Same as Q. 10(c) 2007.

Hess's law follows 1st law of thermodynamics : From 1st law of thermodynamics we know, $\Delta E = q - w = q - P\Delta V$

ΔE is a state function and its value depend, only on the initial and final states of the system but not on the path of the transformation. However, the values of a and w depend on the path by which the change is carried out.

At constant volume, $\Delta v = 0$, so $w = 0$ $\therefore \Delta E = q$

Since ΔE is a definite quantity, therefore at constant volume, q is also a definite quantity. At constant pressure the work done w becomes a definite quentity. Thus at constant prossure, $q = \Delta E + P\Delta v$. becomes a definite quantity. So at constant volume or pressure, the heat evolved or absorbed in the reaction must therefore, Hen's law is only special case of 1st law of thermodynamics.

Ans. (c) Proof : The efficiency of a heat engine is always less than one using cannot cycle :

When $q = 0$, ie no hert is rejected to the sink.

$W = q - q_1$

$\therefore q - q_1 = q\frac{T - T_1}{T}$ or, $1 - \frac{q_1}{q} = 1 - \frac{T_1}{T}$ or, $\frac{q_1}{q} = \frac{T_1}{T}$ or, $q = q_1\frac{T_1}{T}$

Therefore $W_{max} = q \times \frac{T - T_1}{T} = \frac{q_1}{T_1} \times T \times \frac{T - T_1}{T} = \frac{q_1}{T_1}(T - T_1) = 0$ ie no work can obtained.

Hence to have work, heat must be supplied to the system from the source and more over some heat must be rejected to the sink by the system ie heat flow fromcource to sink. So when system do some work, some amount of heat (q_1) must be rejected to the sink.

$\therefore q - q_1$ must be $< q$

$w < q$ $\therefore \eta$ (efficiency of a heat enjine) < 1

$\frac{q - q_1}{a} < 1$

ie 100% conversion is not feasible. Thus only a fractional quantity of supplied heat can be converted to work and this fraction is, $\frac{T - T_1}{T}$.

8. (a) What is fingerprint region ? Why is methanol a good solvent for UV but not for IR determination ? What solvents are generally used for IR technique ? Which groups are detected if absorption data are 2841(w), 2755(w), 1686(s), 1605, 1460(m) cm^{-1} cm^{-1} ?

(b) What is synthetic metal ? What is electronic polymer ? Write notes on conducting polymers and their importance. 9+6

Ans. (a) Finger print Region : The region 1300 to 625 cm^{-1} known as fringer print region. It is here that the pattern of peaks varies from compound to compound. These are some substancees containing the same functional group show similar absorption above 1500 cm^{-1}. However absorption positions differ in fingerprint region. This region is very useful in identifying an unknown compound by comparing its IR spectrum will a set of standard spectrum recorded under indentical conditions.

UV spectra are recorded by dissolving the compounds in suitable solvents. A good solvent should be transparent over the desired range of coavelengths. Usually solvent, which do not contain conjugated system are most suitable for running the UV spectrum. Methanol is a good solvent for UV because it is obtained as very high grade purity and it is free from UV absorbing substances.

In case if IR spectra, method is not used as solvent because it is not transparent in the IR range and it has strong IR absorption band. It not only dissolve ont the cells made of rock salt but would also give overlapping bands in certain cases.

The most convenient way to obtain IR spectra of solid substance is to use them in solution form. Effective solvent are those which have poor absorption of their own. No one solvent is transparent in the entire region and the solvent has to be selected keeping in view the region where the compound under study is expected to absorb. The most commonly used solvents in IR spectra scopy are CCl_4, $CHCl_3$ and CS_2.

Cm^{-1}	
2841 (W)	Aliphatic C–H, Aldehyde C–H.
2755 (W)	Aldehyde C–H
1686 (S)	Amide, > C = 0
1605	Aromatic
1460 (m)	Ester (aromatic) C = 0, Amine C = N

Ans. (b) Synthetic Metal : Polymer that possess the characteristic properties of metals such as electrical conductivity while retainting the mechanical properties processibility, etc commonly associated with conventional polymers are called intvinsically conducting polymers (ICP) or synthelic metal. Example of syathetic metal is the crystalline poly sulphubmitride polymer $(SN)_n$. It has an appreciable conductivity at room temperature.

Electrinic Polymer : Semiconducting polymers whose conductivity can be increased by several times are generally known as electronic polymers. The conductivity of electronic polymers can be increased by doping.

Conducting polymers and their importance : In general polymers are poor conductors of electricity while metals are good conductors, There are some organic polymers such as poly aniline, poly pyoole, poly this phene, etc. They are good conductors like metals. These polymer compound are wholly composed of elements like carbon, hydrogen and occasiowally nitrogen, oxygen or sulphur. More over they have the mechanical properties of polymers, such as flexibility. Such type of polymers are called conducting by a zieglar-Natta process is a

conductong polymer because the conjugated double bonds in polyacetylene make it possible to conduct electicity down its back bone.

$$HC = CH \xrightarrow[\text{eatalyst}]{\text{Zieglar - Natta}} -CH = CH\,[CH = CH]_n\,CH = CH -$$

Aeetylene Polyacctylene

There are some non conducting polymers can be made conducting by doping will an electron dnar or electron aceptor. Thus non conducting polymers are a physical mixture of non conducting polymers and doping materials. Both n-type and p-type dopants can be used to transform an electronic polymer from an insulator to conductor.

Most of the characteristic shown by inorganic sensiconductors are also shown by semiconducting polymers and the high performance devises such as photovoltic cells, photodetectors, lightemitting diodes, etc made from these polymers have been found to perform to the same levels or even better man the devices made from inorganic semiconductors conducting polymer are such lighter than normal metals and can be used form making light weight batteries. One & their greater flexibility, the electronic devices such as transistors, made from them can be bended like plastics.

9. (a) What are rectifiers? Where are they used?

(b) Why ZnO is white but changes colour on heating ?

(c) What are photovoltaic cells?

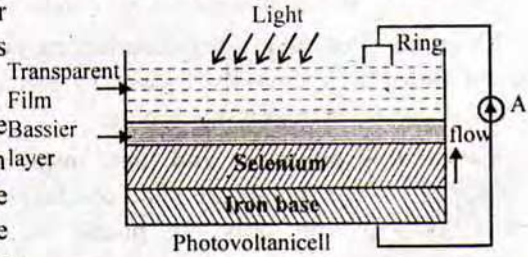
(d) What is the effect of temperature on the conductivity of p-type and n-type semiconductors? 4+3+4+4

Ans. (a) Same as. Q. 8(b) 2002.

Ans. (b) Same as Q. 3(c) 2002.

Ans. (c) Photovoltaic Cells : Photovoltaic Cells in a device that directly converts sunlight to electicity.

The most commonly used photovoltaic cells are of the bassier type like iron–selenium cells or Cu – CuO_2 cells. In the iron selenium cell, a selenium layer is placed on iron disc. Now an extremly thin transparent layer of gold or silver is deposited on the selenium to act as a front electrode. A contact ring on the silver layer acts as one electrode and the iron base as the other.



When light falls on the semiconductor, ie selenium, it ejects electrons which travel from selenium to the front silver electrode through the bassier layer. The flow of electrons in the opposite direction is not permitted by the bassier because it act as a rectifier. The e.m.f generated internally between silver electrode and selenium is directly proportional to the intensity of incident light radiations.

It requires no external battery for its own operations, ie it is self generating.

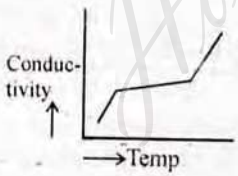
The internal emf and hence current generated by it are large enough to be measured on a pointer galvanometer. Hence, such cells are used in devices like portable expouse meters, direct reading illumination meters and low resistance relays for on/off operations and other monitoring operations in industry.

Ans. (d) Effect of temperature on the Conductivity :

Conductivity of n-type and p-type semiconductors increases with increase in temperature. In case of conductors the free clectorn concentration and hole depends temperature.

n - type Semiconductors : For loop n-type semiconductors close to absolute zero, there are no free carriers in the conduction band, as was in the case of ----- semiconductors. Hence the conductivity is negligible. With increase in temperature, the conductivity increases but after a particular temperature it become constant and then again increases with increase in temperature..

P - type semiconductors : Also for p–type semiconductors, the conductivity increases with increase in temperature, reacting a maximum value and then it becomes constant as in case of n-type semiconductors. However, the increase in conductivity with increase in temperature is mainly due to the increase in number of electrons from the values band of the semiconductors to the acceptor band if the doping agent. When all the acceptor alom get filled up will the electrons from the value band, conductivity becomes constant. Now above this temperature, the rise in conductivity of the semi çonductor is mainly due to the increase in ---- conductivity.



Effect of temp erature on conductivity of type terms conductor.

10. (a) 'Phosphorous forms both PF_3 and PF_5 but nitrogen forms only NF_3. Explain.

(b) Arrange the following in increasing order of bond lengths : O_2, O_2^+, O_2^-.

(c) Using Kohlrausch's law how do we determine the equivalent conductance of acetic acid at infinite dilution?

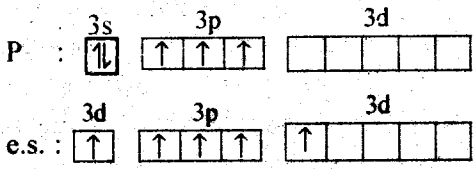
(d) 'Carboxylic acid is stronger acid than phenol.' Explain.

(e) What is calorific value of fuel ? Distinguish between gross and net calorific values.

(f) What are the constituents of coal as determined by proximate analysis?

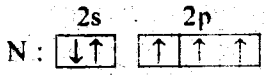
3+2+3+2+3+2

Ans. (a) The ground state electronic configuration of phosphorous is–



Here phosphorous has vacant 3d orbital. In excited state phosphorous may promote an electron from 3s to vacant ed orbital. It PF_5 phosphorous having gained five electrons from fluorine alons and through sp^3d hybridization phosopherous formed PF_5. It can also form PF_3 by Sp^3 d hybridization phosphorous having gained three electrons from ------ atoms in PF_3 molecule.

The ground state electronic of nitrogen is



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Since nitrogen does not have any accant d-orbital, it can only from NF_3 by Sp^3 hybridization.

Ans. (b) $O_2 \Rightarrow$ 16 'e'

$$\sigma_{IS}^2\,\sigma_{IS}^{*2}\,\sigma_{2S}^{7}\,\sigma_{IS}^{*2}\,\sigma_{2Px}^{2}\left\{\begin{matrix}\pi_{2py}^2\\ \pi_{2pz}^2\end{matrix}\right\}\left\{\begin{matrix}\pi_{2py}^{*1}\\ \pi_{2pz}^{*1}\end{matrix}\right\} \quad \text{B.O.} = \frac{10-6}{2} = 2$$

$O_2^+ \Rightarrow$ 15 'e'

$$\sigma_{IS}^2\,\sigma_{IS}^{*2}\,\sigma_{2S}^{2}\,\sigma_{2S}^{*2}\,\sigma_{2Px}^{2}\left\{\begin{matrix}\pi_{2py}^2\\ \pi_{2pz}^2\end{matrix}\right\}\left\{\begin{matrix}\pi_{2py}^{*1}\\ \pi_{2pz}^{*0}\end{matrix}\right\} \quad \text{B.O.} = \frac{10-5}{2} = 2{\cdot}5$$

$O_2^- \Rightarrow$ 17 'e'

$$\sigma_{IS}^2\,\sigma_{IS}^{*2}\,\sigma_{2S}^{2}\,\sigma_{2S}^{*2}\,\sigma_{2Px}^{2}\left\{\begin{matrix}\pi_{2py}^2\\ \pi_{2pz}^2\end{matrix}\right\}\left\{\begin{matrix}\pi_{2py}^{*2}\\ \pi_{2pz}^{*1}\end{matrix}\right\} \quad \text{B.O.} = \frac{10-7}{2} = 1{\cdot}5$$

greater the Bond lower the bond length.

So the in creasing order of bond length is $O_2^+ < O_2 < O_2^-$.

Ans. (c) Equivalent Conductance of acitic acid at infinite dilution using kohlraush's law : Equivalent conductance of eveak electrolytes such as CH_3COOH, can not found out by extra polution of the curve obtained when exponmentally determined values of equivalent conductance of the electrolyte are plotted against $\sqrt{conc}$. However kohlraush's law helps to find out Λ_o for CH_3COOH (weak electrolyte) by knowing Λ_o values for certain strong electrolytes as CH_3COONa, Hel and Nacl.

$\Lambda_o(CH_3COOH) = \lambda^o_{CH_3COO^-} + \lambda^o_{H^+}$

Adding and subtracting limiting ionic conductances of each of Na^+ and cl^- to the R.H.S. we get,

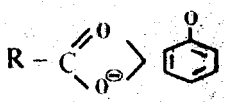
$$\Lambda o\ (CH_3COOH) = \lambda^o_{CH_3COO^-} + \lambda^o_{H^+} + \lambda^o_{Na^+} + \lambda^o_{cl^-} - \lambda^o_{Na^+} - \lambda^o_{cl^-}$$

$$= \left(\lambda^o_{CH_3COO^-} + \lambda^o_{Na^+}\right) + \left(\lambda^o_{H^+} + \lambda^o_{cl^-}\right) - \left(\lambda^o_{Na^+} + \lambda^o_{cl^-}\right)$$

$$\Lambda o\ (CH_3COOH) = \Lambda_o(CH_3COONa) + \Lambda_o(Hcl) - \Lambda_o(Nacl)$$

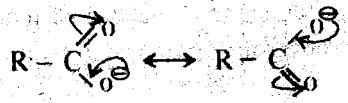
Hence by knowing Λ_o for strong electrolytes ie CH_3COONa, Hcl and Nacl, Λ_o for CH_3COOH can be found out.

Ans. (d) The stability of conjugate bases is in the order

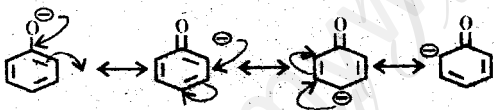


R = alkyl group.

The delocalisation structure of carboxylate anion is as follows :



and the phenside ion is



Phenols are considerably weaker acid than carbonytic acid. This is due to the fact that delocalisation of the (–) ve charge in the carbonylate anion ----- structures of indentical energy content and of the centres of highly electronegative oxygen atom ; where as in the phenoside anion, the structures be higher energy content than the one in which it is on oxygen atom. The relative stabilization of anion w.r. to the undissociated molecule is these likely to be less effective with a ohenol than with a carbolytic acid, leading to the lower relative acidity of the former.

Ans. (e) Carbolitic value of fuel : Calorific value of a fuel may be defined as the amount of heat produced by completely burning of unit man or volume of the fuel. Higher the calorific value better the fuel will be. S.I. unit : J kg^{-1} and C.G.S unit : cal g^{-1}

Distringuish lactocen gross and net calorific value : Same as Q. 9(a) 2003.

Ans. (f) Constitnents of coal as determined by pnzimate analyes. : This analysis provides data for a first general assessment of the quality and type of coal. The properties tested include.

(i) The determination of noister content.

(ii) Volatile Carbonaceons Matter (VCM)

(iii) Ash content

(iv) Fixed carbon

11. Write notes on any three of the following : 3×5

(a) Biodegradable polymers.

(b) Mass spectroscopy and its applications.

(c) Straight run gasoline and jet fuel.

(d) Calomel electrode.

(e) LDPE and HDPE

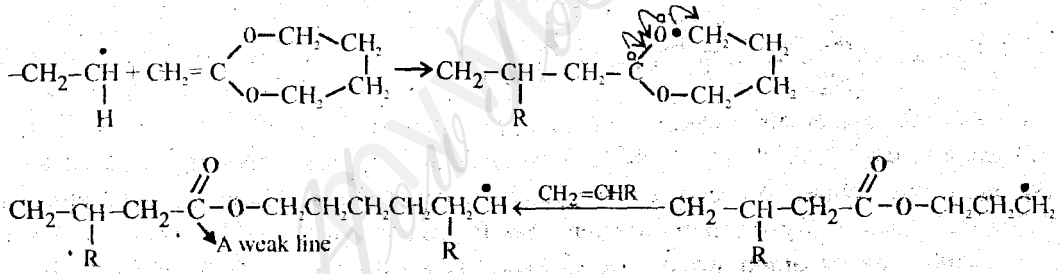
(f) Clausius - Cleyperon equation.

OR

Gibbs - Helmholtz equation.

Ans. (a) Biodegradable Polymers (out of syllabus) : The polymers that can be broken down rapidly by enzymen catalysed seactions are called bio degradable polymers.

The enzymes are produced by micro-organisms. The carbon carbon bonds of chain growth polymers are insert to enzyme satalysed seactions, so they are now biodegradable unless bonds that can be broken by enzymes are inserted into polymer. When the polymer is burried waste, micro-organisms present in the soil can degrade the polymer. One method of making a polymer biodegradable insolves inserting hydrolyzable ester group into the polymer. For example, if the acctal (shown below) is added to an alkene undergoing free radical polymerzation, ester groups will be inserted into the polymer.



The ester link being a weak link is susceptible to enzyme catalysed hydrolysis. Among the most common biodegradable polymers are poly glycolic acid (PGA), poly lactic acid (PLA) and poly hydroxy butyrate (PHB). All are polyester and are therefore suceplible towards enzyme catalysed hydrolysis of there ester link. Co-polymers of PGA and PLA hare found wide variety of uses. For example, a 90/10 co-poly glycolis acid with poly lactic acid used to make absorbable sutures (thread used for goining the edges of wound by stiching). Dextron was the first biodegradable sature. She sutures are entirely degraded and absorbed by the body within 90 days after surgery. Poly hydroxy butyrate which can be used for making films for packaging as well as molded items degrades within fore weaks in land fills. However at present this polymer has limited use due its high cost which is about four times as compared to polypropylene.

Ans. (b) Same as Q.12(c) 2002.

Applications : (i) **Identification of substances :** Man spectrum is highly characteristic of a compound. No two compounds can have exactly similar man spectra.

(ii) Determination of molecular man and formula.

(iii) Determination of molecular structure.

Ans. (c) Same as Q.8(c) 2005.

Ans. (d) Calomel Electrode : Calomel electrodes is an example of secondary reference electrode. A calomel electrode consists of mercury in contact with a paste of spasingle soluble salt of mercurous chloride in mercury and a solution of soluble chloride ions such as Kcl known concentration. It is represented as :

$$Cl\ (aq)/Hg_2Cl_2(\&)/Hg(l)$$

The half cell reaction is

$$Hg_2Cl_2(\&) + 2e \rightleftharpoons 2Hg(l) + 2\ Cl^-\ (aq)$$

Which is the resultant of the following reactions taking place :

$$Hg\ Cl_2(s) \rightleftharpoons Hg_2^{+2}(aq) + 2Cl^-(aq)$$

$$Hg_2^{+2}(aq) + 2e^- \rightleftharpoons 2Hg\ (l)$$

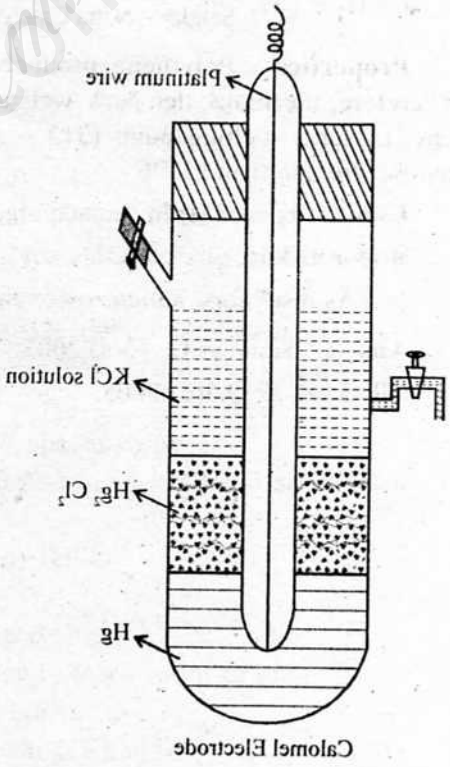
The calomel electrode is, therefore, reversible w.r. to Cl^- ions (anions).

In case a saturated solution of KCl is used, the electrode is called saturated calomel electrode. This electrode is commonly used in laboratory. A dip type saturated calomel electrode is now available for use. The electrode potential of electrode on H-scale, represented as

$KCl(aq)/Hg_2Cl_2(s)/Hg$ depends upon the concentration of KCl solution contained in it and on the temperature.

$$Hg\ Cl_2(S) + 2e \rightleftharpoons 2Hg\ (l) + 2Cl^-(aq)$$

The tenth molar electrode (0.1M KCl) has the lowest temperature Co-efficient and is preferred for accurate work. However, saturated calomel electrode is the most convenient due to the case of replacing the solution and is, thus frequently employed.



Ans. (e) LDPE : It is manufactured by heating ethylene to 350 K to 570 K under a pressure of 1000 – 2000 atm. and in presence of traces of oxygen (0·03 – 0·1y.)

$$n\ CH_2 = CH_2 \xrightarrow[1000-2000\ atm]{350k-570k,O2} (CH_2 - CH_2)_n$$ polyethylene

This polymersiation reaction occurs through a free radical mechanism initiated by oxygen. Poly there produced by this process has a molecular mass around 20,000 and has a branched chain structure. Since branched chain molecule do not pack well, this type of polythene has low density (0·92 gm cm^{-3}) and low melting point (384 K). That is why polythene produced by this method is called low density polythene.

Propertis : It is transparent, has moderate tensile strength and high toughness. It is chens cally insert, slightly flexible and poor conductor of electricity.

Uses : It is used (2) as packing material (in the form of this film, bags, etc. ; (ii) for insulating sires and cables, etc.

HDPE : It is manufactured by heating ethylene at about 333 – 343 K under a pressure 96 – 7 atm. in presence of a catalyst such as trieltyl-aluminium and titeanium tetrachloride (zeiglar–Natta catelyet).

$$n\ CH_2 = CH_2 \xrightarrow[\text{Seigler – Natta Catalyst}]{333-343K,6-7atm} (CH_2 - CH_2)\ \text{Poly ethylene.}$$

Properties : Polythene produced by this process mainly consists of lineear chains. Therefore, the moleculer pack well and hence this type of poly thene has density (0·97 gm cm^{-3}), higher melting point (313 – 423K) and is inert but harder, tongher and has greater tensile strength than LDPE.

Uses : It is used (i) In the manufacture of container (buckets, tubes, etc.)

(ii) for making pipes, bottles, toys, etc.

(iii) As insulators, anticorrosise and packaging material.

Ans. (f) Same as Q. 10(a) 2003.

OR. Same as Q.3(d) 2005.