ENGINEERING CHEMISTRY—2008

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 x 1 = 10**

i) A living system is thermodynamically an example of
   a) an Isolated system b) a closed system
   c) an adiabatically closed system d) an open system.

ii) For an ideal gas undergoing free expansion
   a) $\Delta T = 0$ and $\Delta S > 0$ b) $\Delta T = 0$ and $\Delta S = 0$
   c) $\Delta T < 0$ and $\Delta S > 0$ d) $\Delta T < 0$ and $\Delta S = 0$.

iii) Structure of SF_6 is
   a) planar b) octahedral c) trigonal bipyramidal d) square pyramidal.

iv) Two elements, whose electronegativities are 1.2 and 3.0, form
   a) ionic bond b) covalentbond c) co-ordinate bond d) metallic bond.

v) Germanium is an example of
   a) intrinsic semiconductor b) n-type semiconductor
   c) p-type semiconductor d) insulator.

vi) Proton NMR is useful for investigating structure of organic molecules because
   a) organic molecules contain carbon atoms
   b) organic molecules are mostly covalent
   c) hydrogen atoms are found in most of the organic molecules
   d) organic compounds are low boiling.

vii) The half-life of a first order reaction is 20 minutes. The time required for 75% completion of the reaction is
   a) 30 minutes c) 40 minutes b) 50 minutes d) 60 minutes.

viii) The half-life of a first order reaction is 20 minutes. The time required for 75% completion of the reaction is
   a) H_2O b) H_2S c) PH_3 d) NH_3

viii) Which one has the largest bond angle ?
   a) H_2O b) H S c) PH d) NH

ix) Which of the octahedral complexes (M = metal atom, A and B are ligands) exhibits geometrical isomerism ?
   a) $[MA_6]$ b) $[MA_5B]$ c) $[MA_4B_2]$ d) $[MA_3B_3]$

x) The most stable carbonium ion is
a) $(CH_3)_2CH^+$ b) $Ph\ C^+$ c) $CH_3CH_2^+$ c) $CH_2=CH-CH_2^+$.

xi) An example of thermosetting plastic is
a) PVC b) nylon c) polythene d) bakelite

xii) The calorific value is highest for
a) water gas b) LPG c) producer gas d) carburetted water gas.

Ans.: Q.1. (i)(d) ; (ii)(a) ; (iii)(b) ; (iv)(a) ; (v)(a) ; (b)(c) ; (vi)(c) ; (vii)(b) ; (viii)(d) ; (ix)(c)(d) ; (x)(b) ; (xi)(d) ; (xii)(b).

GROUP - B

(Short Answer Type Questions)

Answer any three of the following **3 x 5 = 15**

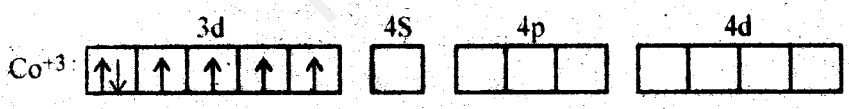
2. Show that for an ideal gas undergoing reversible adiabatic expansion or compression PV^γ = constant. A diatomic ideal gas ($\gamma = 1.4$), initially at 600 K and 10 atm undergoes reversible adiabatic expansion till the final pressure becomes 2 atm. Find out its final volume.

Ans. Proof PV^γ = Constant : Same as Q.2 (b) '2005

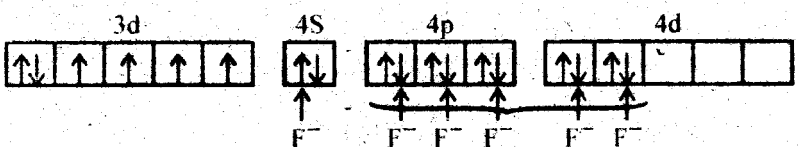
Numerical Problem : Number of moles, the final temperature and the initial volume are not given here. Hence the problem cannot be solved on the basis of pure assumption.

3. Explain why the anion $[CoF_6]^{3-}$ is paramagnetic while the anion $[Co(CN)_6]^{3-}$ is diamagnetic.

Ans. $[c_0b_6]^{-3}$:



$[CoF_6]^{-3}$:



$Sp3d^2$ Hybridisation

(Six electron pairs from six F^- ligand)

The complex anion $[Co(CN)_6]^{-3}$ has octahedral geometry and due to presence of paired electrons and also involvement of inner d-orbital ie low spin complex, it is diamagnetive.

Q.4. Write down the Arrhenius equation for the temperature dependence of specific rate and explain the terms used. What is the unit of the frequency factor for a first order reaction ? Plot logk vs $\frac{1}{T}$ and explain the significance of the slope of the plot.

Ans. : Arrhenius equation for the temperature dependence of specific rate :

$k = Ae^{-Ea/RT}$

where k = Rate constant

A = Arrhenius constant as frequency factor ie frequency of collision of the reacting molecules.

R = Universal gas constant

Ea = Activation energy

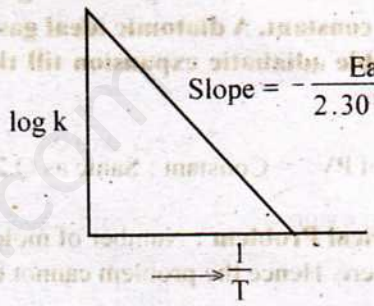
Unit of frequency factor (A) for 1st order reaction :

Collision per second / litre

Explanation of Plot log k VS $\frac{1}{T}$

$\ln k = \ln (Ae^{-Ea/RT})$

$\therefore \log k = \log A - \frac{Ea}{2.303RT}$



So if we plot log k against $\frac{1}{T}$ a straight line having a slope equal to — Ea / 2.303R and an intercept log A can be obtained. From the slope we can calculate the activation energy.

Q. 5. Predict the shape of the following molecules using VSEPR theory :

BF_3, CO_2, PCl_5, SF_6, XeF_4.

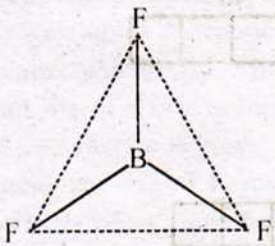
Ans. BF_3 : Central atom B $\Rightarrow 3 + 3 = 6 \Rightarrow$ ep = 3 $\Rightarrow$ plane traingle

bp = 3

lp = ep – bp

= 3 – 3

= 0



$\therefore F - \hat{B} - F = 120^o$

CO_2 : Central atom C $\Rightarrow 4 + 0 = 4 \Rightarrow$ ep = 2 $\Rightarrow$ linear

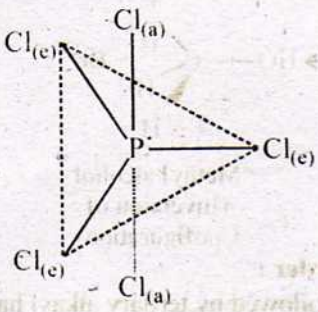
bp = 2

lp = 0

$0 = C = 0$ $\quad 0 - \hat{C} - 0 = 180^o$

PCl_5 : Central atom P $\Rightarrow 5 + 5 = 10 \Rightarrow$ ep = 2 $\Rightarrow$ linear
bp = 2
lp = 0

a = axial
e = equiatorial

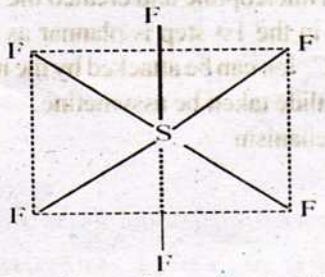


$Cl_{(e)} - \hat{P} - Cl_{(e)} = 120^o$

$Cl_{(e)} - \hat{P} - Cl_{(a)} = 90^o$

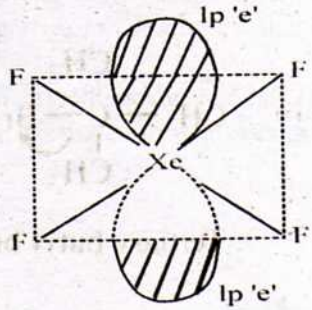
$Cl_{(a)} - \hat{P} - Cl_{(a)} = 180^o$

SF_6 : Central atom S $\Rightarrow 6 + 6 = 12 \Rightarrow$ ep = 6 $\Rightarrow$ Octahedral (Oh)
bp = 6
lp = 0



$F - \hat{S} - F = 90^o$

XeF_4 : Central atom Xe $\Rightarrow 8 + 4 = 12 \Rightarrow$ ep = 6 $\Rightarrow$ Square plannar
bp = 4
lp = 2



$F - \hat{S} - F = 90^O$

Q.6. Account for the following :

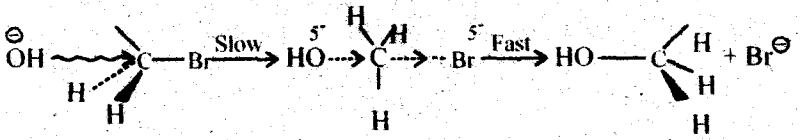
i) SN^2 reaction occurs with inversion of configuration and SN^1 reaction occurs with retention of configuration.

ii) Formic acid is more acidic than acetic acid and acetic acid is more acidic than phenol.

Ans. SN^2 : Substitution Nucleophilie bimolecular and 2nd order :

This SN^2 mechanism is generally followed by primary alkyl halides (e.g. Methyl bromide). It is a single step reaction. The breaking and making of bond occurs simaltaneously. The nucleophile (e.g. OH^-) approaches the carbon atom attached to the halogen (here bromine in example) from the side opposite to that carrying the halogen. This occurs due to the fact that the attack from the side halogen (Br) is hindered, as both nucleophile and halogen (Br) atom are electron rich and cause repulsion. So the product formed has opposite configuration to that of the methyl bromide (like an inverted umbrella). The change in configuration is called the walden Inversion. Then we can say the SN^2 reaction

proceed with the inversion of configuration.



Methyl bromide

Methyl alcohol (Inversion of Configuration)

SN 1 : Substitution Nucleophilic Unimolecular and 1st order :

This SN1 reaction is a two step process and it is generally followed by tertiary alkayl halide (e.g. Tatiary butyl bromide). In the 1st step a carbocation is generated by breaking of carbon-halogen (bromine) bonds. And in the 2nd step that carbonium ion is attakced by a nucleophile and created the substituted product (Tertiary butyl alcohol). The carbonium ion formed in the 1st step is plannar as the central positively charged carbon atom is sp^2 hybridised. The plannar C^+ ion can be attacked by the nucleophile (OH) on either side to give two isomers (d & l), if the alkyl halide taken be assymetine.

Alkaline hydrolysis of tertiary butyl bromide Via SN 1 mechanism

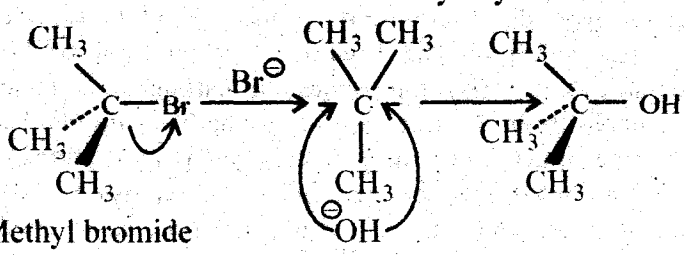
$$KOH\ (or) \rightleftharpoons K^+ OH^-$$

(i) $CH_3-C(CH_3)_2-Br \overset{Slow}{\rightleftharpoons} CH_3-C^{\oplus}(CH_3)_2 + Br^{\ominus}$

Tertiary butyl bromide Tertiary butyl $C^{\oplus}$ ion

(ii) $CH_3-C^{\oplus}(CH_3)_2 + OH \xrightarrow{fast} CH_3-C(CH_3)_2-OH$

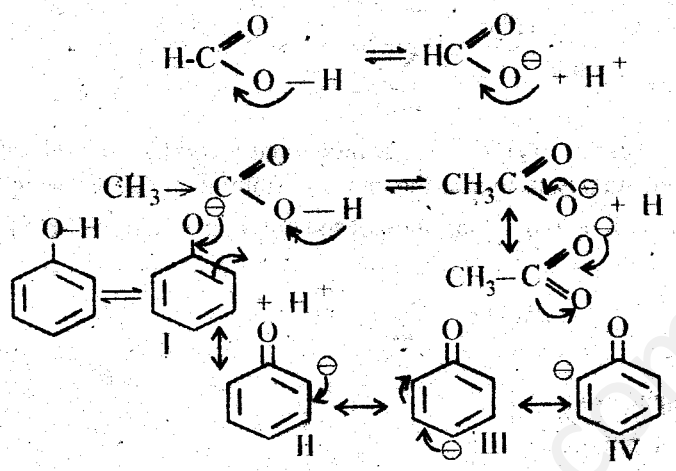
Tertiarybutyl alcohol



Methyl bromide

(Retention of Configuration)

Q.6. Ans.



(ii) Formic acid is more acidic than acetic acid because in formic acid no + I effect and no + R effect, conjugate base is most stable where as in acetic acid has + I effect (CH_3 gr) and no + R effect, conjugate base is less stable.

Acetic acid is more acidic than phenol (no + I effect and + R effect) Phenoxide ion has four resonating structures but are non equivalent whereas acetate ion although has two equivalent resonating structures and hence more stable than phenoxide ion.

GROUP - C
(Long Answer Type Questions)

Answer any three of the following **3 x 15 = 45**

7. a) What are raw rubber and vulcanized rubber ? **3**

Ans. Same as Q.10(a) '2002

b) Give the outlines of preparation, structure and uses of SBR and NBR. **6**

Ans. Same as Q.10(b) '2002

c) Explain number average and weight average molar mass of a polymer. **4**

Ans. Number Average Molecular Weight : Number average molecular weight is determined by colligative property measurement and it is defined as the total weight of all the molecules present in the polymer sample divided by the total number of molecules present.

Thus if a polymer sample contains $n_1, n_2 \ldots\ldots\ldots n_i$ number of molecular species having mas M_1, M_2, M_3 respectively, then the numeber average molecular weight $\overline{M_n}$ is given as :

$$\overline{M_n} = \frac{\text{Total mass of the polymer sample}}{\text{Number of molecular species present in the sample}}$$

$$= \frac{n_1M_1 + n_2M_2 + \ldots\ldots\ldots\ldots + n_iMi}{n_1 + n_2 + \ldots\ldots\ldots\ldots + n_i} = \frac{\sum_i n_iMi}{\sum_i n_i}$$

Weight Average Molecular Weight : Weight average molecular weight is generally determined by light scattering measurement and it is defined as the total contribution of various weight fractions of polymeric species towards the total molecular mass of the polymeric sample. So $\overline{M_w}$ is given as

$$\overline{M_w} = w_1M_1 + W_2M_2 + \ldots\ldots\ldots + W_iM_i = \sum_i W_iM_i$$

where $W_i = \frac{\text{Mass of species i}}{\text{Total Mass of polymer}}$

$$= \frac{n_iM_i}{n_1M_1 + n_2M_2 + \ldots\ldots\ldots\ldots n_iM_i} = \frac{n_iM_i}{\sum_i n_iM_i}$$

$$\therefore \overline{M_w} = M_1 \frac{1}{\sum_i n_iM_i} + M_2 \frac{n_2M_2}{\sum_i n_iM_i} + \ldots\ldots\ldots\ldots + M_i \frac{n_iM_i}{\sum_i n_iM_i}$$

$$= \frac{1}{\sum_i n_iM_i} \left(n_1M_1^2 + n_2M_2^2 + \ldots\ldots\ldots\ldots + n_iM_i^2 \right)$$

$$= \frac{\sum_i n_iM_i^2}{\sum_i n_iM_i} = \frac{\sum_i n_iM_i^2}{W}$$

W_i = fractional weight of corresponding polymer unit (i)
W = Total weight of the Polymer Sample
M_i = Molecular mass of the Polymeric Unit i

The weight average molecular mass is always greater than the number average molecular mass. Moreover since $\overline{M_w} = \overline{M_n}$ in case of monodisperse system.

d) Define intrinsic and extrinsic semiconductors. 2

Ans. : Same as Q.3(b) '2002

8. a) What is meant by transport number of an ion ? How is it related with ionic conductance ? The ionic radius of Li^+ is less than that of K^+. However, in aqueous solution Li

$^{+}$ ions are less mobile than K^{+} ions. How can you explain this observation ? **1 + 1 + 1**

Ans. : Transport number of an ion : The fraction of total current carried by a particular type of ion is known as the transference number or transport nuber of that ion.

If λ_{+}^{o}, λ_{-}^{o} are ionic conductance and u_{+}, u_{-} are mobility's of cation and anion respectively then the transport number of cation & anion can be written as,

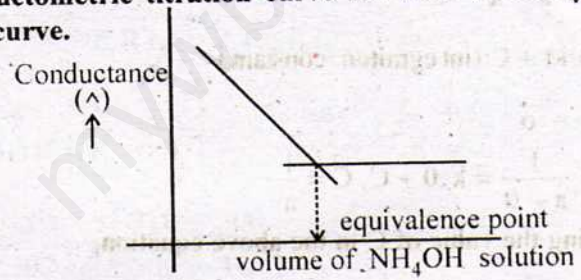
$$t_{+} = \frac{\lambda_{+}^{o}}{\lambda_{+}^{o} + \lambda_{-}^{o}} = \frac{Fu_{+}}{F(u_{+} + u_{-})} = \frac{u_{+}}{u_{+} + u_{-}}$$

$$t_{-} = \frac{\lambda_{-}^{o}}{\lambda_{+}^{o} + \lambda_{-}^{o}} = \frac{Fu_{-}}{F(u_{+} + u_{-})} = \frac{u_{-}}{u_{+} + u_{-}}$$

The ionic conductance of Li^{+} ion is less than of K^{+} ion in aqueous solution or in other words Li^{+} ion less mobile in aqueous solution than K^{+} ion, The probable cause in the hydration of ions. The Li^{+} ion being smaller compaired to K^{+} ion, the electric field in Li^{+} is much stronger than K^{+} ion and hence it can capable of associating or attracting large number of water molecules than the K^{+} ion, The net result is the higher hydration contributing the larger dimensions, lowering the speed and hence lowering the ionic conductance. The hydration number of Li^{+} is "6" and K^{+} is '2'

b) Draw the conductometric titration curve for HC1 vs NH_4OH and explain the features of the curve. **4**

Ans. :



During titration of strong acid (HCl) by a weak base (NH_4OH), the following reaction taken place :

$$H^{+} + Cl^{-} + NH_4OH \rightarrow NH_4^{+} + Cl^{-} + H_2O$$

Here neutralisation reactions means, the replacement of highly conducting H^{+} ion by low conducting NH_4^{+} ion. So the overall conductance of the solution decreases progressively with the addition of NH_4OH and reaches the lower limit at the equivalence point. after the equivalence point, the conductance of the solution reamain almost constant, as NH_4OH, the unused base used further, is a weak base and has a very low ionic conductance.

c) What do you mean by half-decomposition period of a reaction? Consider a second order reaction A + B → products. Assuming the initial concentrations of both the reactants to be same, show that the half-decomposition period of the reaction is

inversely proportional to the Initial concentration. 1+3

Ans. : Half decomposition period of a reaction : For a chemical reaction, the time for half decomposition is called half decomposition period of that chemical reaction. It is denoted by $t_{\frac{1}{2}}$

Let us consider a second order reaction and the initial concentration of both reaction are same. Say a mole / lit and at time 't' x mole / lit of each is decomposed to form products.

$$\underset{\text{at } t = 0}{A\ (a)} + \underset{B\ (a)}{} \rightarrow \underset{0}{\text{Products}} \quad \text{(2nd order reaction)}$$

$$\text{at } t = t \quad (a - x) \quad (a - x)$$

a = initial concentration at $t = 0$

under such conditions, the rate of the above reaction

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

$$\text{or, } \frac{dx}{dt} = k\,(a - x)^2 \qquad \text{or, } \frac{dx}{(a - x)^2} = kdt$$

Now integrating, $\int \frac{dx}{a - x} = k \int dt$

$$\frac{1}{a - x} = kt + C \text{ (integraiton constant)}$$

when $t = 0,\ x = o$

$$\text{Hence, } \frac{1}{a - 0} = k.0 + C,\ C = \frac{1}{a}$$

∴ Now substituting the value of C in the above equation,

$$\frac{1}{a - x} = kt + \frac{1}{a} \qquad \text{or, } kt = \frac{x}{a(a - x)}$$

$$\text{or, } \frac{1}{a - x} - \frac{1}{a} = kt \quad \therefore k = \frac{x}{t\,a(a - x)}$$

so the rate constant of the above reaction is $k = \frac{x}{t\,a(a - x)}$

Now at $t = t_{\frac{1}{2}}$, so $x = \frac{a}{2}$

$$\therefore t_{\frac{1}{2}} = \frac{\frac{a}{2}}{ka\,(a - \frac{a}{2})} = \frac{\frac{a}{2}}{k.a.\frac{a}{2}} = \frac{1}{ka} \qquad \therefore t_{\frac{1}{2}} \propto \frac{1}{a}$$

So we can say the half life period ($t_{\frac{1}{2}}$) of a second order reaction, having the reactant same initial concentration is inversely proportional to the initial concentration of any reactant.

d) Rate constants of a reaction at 300 K and 310 K are $4.5 \times 10^{-5}s^{-1}$ and $9 \times 10^{-5}s^{-1}$ respectively. Evaluate the activation energy and the pre-exponential factor (frequency factor) of the reaction. What is the order of the reaction ? 4

Ans. We know, $k = A.e^{-Ea/RT}$

whose k = rate constant

A = Arrhenius constant as frequency factor

R = Universal gas constant

Ea = Activation Energy

taking log on both side

$$\log k_1 = \log A - \frac{Ea}{2.303RT_1}, \quad k_1 = 4.5 \times 10^{-5} \text{ sec}^{-1} \text{ at } T_1 = 300K$$

$$\log k_2 = \log A - , \frac{Ea}{2.303RT_2}, \quad k_2 = 9 \times 10^{-5} \text{ sec}^{-1} \text{ at } T_2 = 310K$$

$$\text{Now, } \log k_1 - \log k_2 = -\frac{Ea}{2.303RT_1} + \frac{Ea}{2.303RT_2}$$

$$\text{Now, } \log \frac{k_1}{k_2} = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = -\frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\text{or, } \log \frac{k_1}{k_2} = -\frac{Ea}{2.303 \times 2}\left[\frac{310 - 300}{300 \times 310}\right]$$

$$\log \frac{45 \times 10^{-5}}{9 \times 10^{-5}} = -\frac{Ea}{2.303 \times 2}\left[\frac{10}{300 \times 310}\right]$$

$$\text{or, } Ea = -\log(0.5) \times 2.303 \times 2 \times \frac{300 \times 310}{10} \text{ cal} = 1.2895 \text{ K.Cal}$$

$$\therefore Ea = 53.604 \text{ kJ}$$

$$\log A = \log 4.5 - \log 5 + \frac{12895}{2.303 \times 2 \times 300}$$

$$\therefore A = 9.6659 \times 10^4$$

9. a) Explain optical isomerism in case of co-ordination compounds with suitable examples. 4

Ans. : Same as Q.7.(c) 2002

b) Write down the order of the bond energy of the following bonds and give reason for your answer : C = 0, C = N, C – I, C – F.

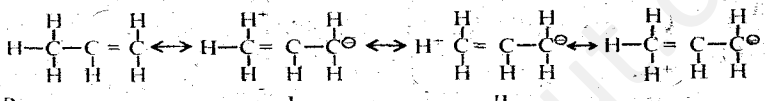
Ans. : In case of Co the bond order is 3 and for CN the bond order is 2.5. In C–I and C–F, the bond present is single bond. We know that the higher the bond order higher will be bond energy. So the bond energy of C ≡ 0 is greater than C ≡ N.

Now the bond length of C–I is 0.214 nm and C – F is 0.132 nm. We know that lower the bond length greater will be bond energy. So bond energy C – F is greather than C – I.

So the bond energy order C ≡ O > C ≡ N > C – F > C – I.

c) Explain the term 'hyperconjugation', citing examples. 4

Ans. : Hyper conjugation or (Baker Nathan) effect involves the delocalization of sigma (σ) electrons through the overlapping of p-orbital of double bond with σ- orbital of the adjacent single bond. As for example propene :



Propene I II

on other hand we can say that : (i) hyper conjugation is also called no bond resonance, since no bond exist between free H^+ and C–atom, (ii) the H^+ions are not free to move, since they still bound quite firmly to the π could, (iii) the hyper conjugation occurs through H-atom present on α-hydrogen atom is on the C-atom adjacent of double bond, (iv) the higher the number of α-hydrogen atoms, the higher is the hyper conjugative effect. Consequently, the order of hyper conjugative effect is :

CH_3–> CH_3CH_2–> $(CH_3)_2CH$–> $(CH_3)_3C$–

d) Distinguish between coking coal and caking coal. 3

Ans. : Coals that soften on heating in the absence of air, producing a 'Pasty' or 'Plastic' mass which fuse together to large Coherent masses impervious to air are called caking Coals. Coals from which very little of such plastic material is formed are either non coking or weakly caking coal.

On the other hand coals on heating produce residue, which is hard, porous strong and usable for metallurgical purpose are called Coking Coal. All coking coals are Caking coals but all caking coals are not coking coals.

The moisture content of coking coals is about 2% but that of weakly caking and non-caking coals is 3 to 12%

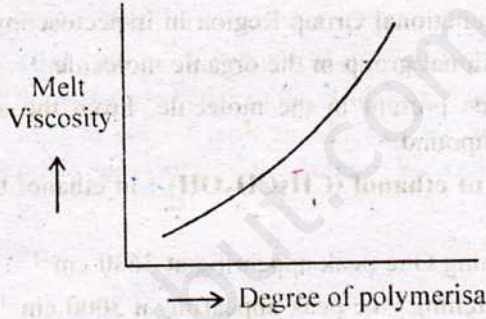
10.a) How do the properties such as (i) tensile strength (ii) physical state of the polymer (iii) impact strength (iv) melt viscosity of a polymer vary with degree of polymerization ? 4

Ans. : Tensile Strength : Tensile strength of a polymer depends on degree of polymerisation of the polymer. It increases with increase of degree of polymerisation and after a certain tensile strength it stabilises.

Physical state of Polymer : Physical strength of a polymer increases with increase of degree of polymerisation.

Impact strength of Polymer : Impact strength of a polymer increases with increase of degree of polymerisation.

Melt viscosity of polymer : Melt viscosity of a polymer follow the relation with degree of polymerisation, shown by the graph below :

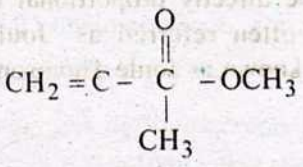


b) Discuss the difference among isotactic, syndiotactic and atactic polymers. 3

Ans. : Same as Q.8.(d) '2003

c) Degree of polymerization of a sample of poly methylmethacrylate (PMMA) is found to be 1000. What is the number average and the weight average molar masses of PMMA ? 4

Ans. : PMMA is polymethyl methacrylate. It is a polymer of Methylmethacrylate.



Molecular weight of methylmethacrylate (M_o) is 100. Degree of poly merisation = 1000

Number Average molecular weight $\overline{M_n} = \frac{M_o}{1 - p_n} = \frac{100}{1 - \frac{999}{1001}} = 50050$ (Ans.)

where $p_n = \frac{n-1}{n+1} = \frac{1000-1}{1000+1} = \frac{999}{1001} = 0.998$

Weight average molecular weight $\overline{Mw} = Mo \frac{1 + p_n}{1 - p_n}$

$$= 100 \times \frac{1 + 0.998}{1 - 0.998}$$

$$= \frac{100 \times 1.998}{.002} = \frac{199.8}{.002} = 99900 \text{ (Ans.)}$$

d) What is the importance of 'functional group region' in IR spectroscopy ? What are the different absorption peaks possible for methanol and ethanol ? 1+3

Ans.Importance of "Functional Group Region In Irspectoscopy".

(a) To detect the functional group in the organic molecule.

(b) to detect the bonds present in the molecule. From the above we can determine the structure of a organic compound.

IR absorption peaks of ethanol (CH_3CH_2OH) : In ethanol three characteristic peaks are obtained.

(i) Due to O–H stretching One peak appearing at 3630 cm^{-1}

(ii) Due to C–H stretching One peak appearing at 3000 cm^{-1}

(iii)Due to C–C Stretching one peak appearing at ≤ 1000 cm^{-1}

IR absorption peaks of methanol (CH_3OH) :

11. a) Write notes on the following :

Joule-Thomson expansion and inversion temperature.

Ans : (a) Joule Thomson Expansion : When a gas is allowed to expand from one higher pressure to lower through the porous plug, which acts us a throttle in thermaly insulated apparatus so that the process is adiabatic. A lower temperature can be observed at lower pressure region and this cooling observed is found to be directly proportional to pressure difference. The above adibatic expansion of the gas often referred as 'Joule-thomson expansion' and the temperature change upon expansion is known as Joule Thomson effect.

In case of Joule - Thomson expansion, dH = 0

We know, $\left(\frac{\partial H}{\partial T}\right)p = Cp$ (Specifcn heat at constant pressure) dh = 0

$$\mu = \frac{1}{c_p}\left(\frac{\partial H}{\partial p}\right)$$

μ = Joule Thomson coefficient

when $\mu = 0$, $\frac{2a}{RT_i} - b = 0$, Or $T_i = \frac{2a}{Rb}$ T_i = Inversion temp.

μ and b are Vander Waal's constant

For every gas there is a temperature when these is neither cooling nor heating observed and it is known as Inversion temperature T_1

Thus inversion temperature of a gas, $T_i = \frac{2a}{Rb}$

The co-efficient of J-T expension is important in the liquification of gases because it predicts whether a gas cools or heats or expand. The co-efficient is a decreasing function of temperature and it passes through & so at inversion temperature T_i. In order to liquify a gas by J-T expansion, the gas must be cooled below the J-T inversion temperature.

Ans : (b) Chemical Potential (μ) : The chemical potential of a given substance is the change in free energy (G) of the system when 1 mole of that particular substance, at constant temperture and pressure is added to such a large quantity of the system so that there is no appreciable change in the overall composition of the system. We know

$G = f(P, T, n_1, n_2, n_3 \ldots\ldots n_j)$

We can write,

$$\therefore \left(\frac{\partial G}{\partial n_j}\right)_{T,p,n_j} = \mu_i \quad \ldots\ldots\ldots\ldots (i) \qquad [\mu_i = \text{Chemical potential of i th component}]$$

The eq^n (i) may written as :

$$\therefore dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_j} dT + \left(\frac{\partial G}{\partial t}\right)_{T,n_j} dp + \mu_1 dn_1 + \mu_2 dn_2 + \ldots\ldots\ldots + \mu_i dn_j \quad \ldots\ldots (ii)$$

where $\mu_1, \mu_2 \ldots\ldots\ldots\ldots \mu_j$ are the respective chemical potential of the components 1, 2, ...j

If T and P remain constant, then

$$(\partial G)_{T,P} = \mu_i dn_1 + \mu_2 dn_2 + \ldots\ldots\ldots + \mu_j dn_j \qquad \text{(iii)}$$

If a system has definite composition having n_1, n_2 ....., n_j moles of the constituents 1, 2, ...j respectively, then integration of (iii) gives ;

$$(G)_{T,p,nj} = n\mu_1 + n_2\mu_2 + \ldots\ldots\ldots + n_j\mu_j \ldots\ldots\ldots\ldots (iii)$$

So we can also say chemical potential may also be defined as the contribution per mole of each particular constituent of the mixture to the total free energy of the system under condition of constant temperature, pressure and definite composition.

Significance of chemical potential in explaining equilibrium of reacting system.

Chemical potential is an intensive property and it may be regarded as the force which

drives the chemical system to equilibrium. At equilibrium the chemical potential of the substance in the reacting system must have the same value through the system.

In other words, the matter flows spontaneously from a region of high chemical potential to low chemical potential. Chemical potential may also be regarded as the escaping tendency of that system. Greater the Chemical potential of a system greater will be its escaping tendency.

Condition for the equilibrium is : $\sum \mu_i . dn_i = 0$

Ans. (c) Hydrogen bond : Same as Q.5 '2004

Effects of Hydrogen bond on properties of Compound :

(i) Boiling points of liquid compound in creases because of bydrogen bonding leads to increase in intermolecular attractions which leads to increase in heat of vapourization. eg. Boiling pt H_2O (373K) > CH_3OH (336K) > CH_3OCH_3 (268 K)

(ii) Solubility of organic compounds in water is attributed to hydrogen bond formation eg. CH_3OCH_3 is completely miscible with water whereas CH_3SCH_3 is partially miscible.

(iii) Viscosity of liquid compound increases due to intermolecular hydrogen bonding.

(iv) Unique properties of water due to hydrogen bonding.

(d)Non-stoichiometric defects.

Ans. (d) Same as Q. 7. (a) '2003

Ans. (e) **Carburetted wate gas :** We know cracking of crude oil generates some hydrocarbons and if these gaseous hydrocarbons are mixed with water gas [CO(g) + H_2(g)], calorific value of water gas increases. Hence Carburetted wate gas is a mixture of water gas and some gaseous hydrocorbons. This carburelted water gas contains about 35% H_2, 25% CO, 25% N_2 + CO_2, Its Calorific vlaue is about 45000 k Cal / m^3 and it is used for heating and illuminating purposes.

Semi water Gas : Same as Q. 11. '2006

Q. 11. F. Perfect and Inperfect Complex

Ans. : Question is Out of Syllabus.