

# ENGINEERING CHEMISTRY—2007

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) The change in internal energy of a system depends on  
(a) Initial and final states of the system (b) The reversible path  
(c) The irreversibility in the process (d) The initial state of the system only
- (ii) The Joule-Thomson expansion is  
(a) Isobasic (b) Isentropic (c) Isothermal (d) Isenthalpic
- (iii) In normal hydrogen electrode, the activity of H<sup>+</sup> ion is  
(a) 0.1 (b) 0.2 (c) 2 (d) 1
- (iv) Which of the following has the least bond angle?  
(a) NH<sub>3</sub> (b) H<sub>2</sub>O (c) CH<sub>4</sub> (d) BeF<sub>2</sub>
- (v) The half-life period of a reaction is found to be directly proportional to the initial concentration. The order of the reaction is  
(a) Zero (b) One (c) Two (d) Three
- (vi) A conducting polymer is  
(a) Polyethylene (b) Polypropylene (c) Polyaniline (d) Bakelite
- (vii) The highest ranking coal is  
(a) Anthracite (b) Bituminous (c) Lignite (d) Peat
- (viii) Which of the following is true always for a spontaneous change at all temperatures?  
(a)  $\Delta H > 0$  and  $\Delta S < 0$  (b)  $\Delta H < 0$  and  $\Delta S < 0$   
(c)  $\Delta H < 0$  and  $\Delta S > 0$  (d)  $\Delta H > 0$  and  $\Delta S > 0$
- (ix) If the rate of a reaction becomes twice for every 10<sup>0</sup> rise in temperature by what factor the rate of the reaction increases when temperature is raised from 30°C to 80°C?  
(a) 16 (b) 32 (c) 64 (d) 128
- (x) NMR spectra are normally carried out on  
(a) Liquids or solutions (b) Gases  
(c) Solids (d) Suspensions
- (xi) The calorific value should be the highest for  
(a) Water gas (b) LPG (c) Producer gas (d) Carburetted water gas
- (xii) Most commonly used vulcanising agent is  
(a) Graphite (b) Sulphur (c) Lampblack (d) Softsoap

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

## Group-B

## [ Short Answer Type Questions ]

Answer any three questions.

3 × 5 = 15

2. State and explain the first law of thermodynamics. Deduce the expression for the maximum work done when an ideal gas expands isothermally and reversibly. 1 + 2 + 2

Ans. Same as Question No. 3.(a) & (b), of 2005.

3. Explain the principle of Ultra-violet spectroscopy in determining the constitution of an organic compound. Write down the mathematical form of Lambert-Beer's law and explain each term.

Ans. Ultra-violet Spectroscopy : Same as Q. 5.(a)(ii), of 2003.

Mathematical form of Lambert law :

$$\frac{I}{I_0} = e^{-kl}$$

where  $k$  = Absorption co-efficient

$I_0$  = Intensity of the incident light

$I$  = Intensity of transmitted light

$l$  = thickness of the medium

Lambert-Beer's Law :

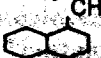
$$\frac{I}{I_0} = e^{-\epsilon c l} \quad \epsilon = \text{molar absorption co-efficient}$$

$\log_{10} (I_0/I) = \epsilon l c$ .  $C$  = Concentration of the absorbing solution

Octane Number : Same as Q. 6.(b) of 2004.

Cetane Number : It is a measure of the ease with which a fuel will ignite under compression.

Cetane ( $C_{16}H_{34}$ ) has very short ignition lag and its number is taken as 100 and that  $\alpha$ -methyl

naphthalene ( $C_{11}H_{10}$ , ) which has very long lag and its number taken as zero. The cetane

number is defined as the percentage by volume of cetane in a mixture of cetane and  $\alpha$ -methyl naphthalene which is equivalent in ignition quality to the fuel under test. Oils for high speed, medium speed and low speed diesel engines should have cetane number not less than 45, 35 and 25 respectively. Cetane number depends on the nature and composition of its hydrocarbon.

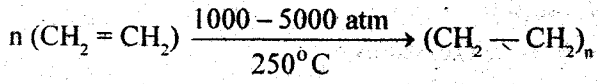
n-alkane > naphthalene (i.e. cycloalkane) > alkenes > branched alkenes > aromatics.

Biofuel : Fuel obtained from any biomass (wood, sewage, cattle dung, agricultural wastes or crop residue, etc.) is known as biofuel. Gobar gas is an example of biofuel.

4. What do you understand by polymerisation? What is the degree of polymerisation? Write down the structure and use of Nylon-66 and PVC.

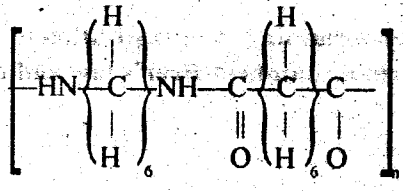
Ans. Polymerisation : The chemical process leading to the formation of polymer molecule by linking of the simple monomer molecule is known as polymerisation.

Number of monomer unit joining together to form polymer is called the degree of polymerisation. For example poly ethylene. In polyethylene 'n' numbers of ethylene monomers joined under certain condition to form polyethylene (PE) polymer. Here 'n' is the degree of polymerisation.

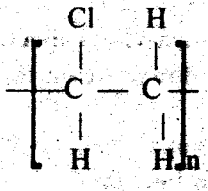


ethylene in presence of free radical initiator (O<sub>2</sub>) Polyethylene (PE)

Structure of Nylon - 66 and PVC :



Nylon 66



PVC

Use of Nylon 66 : (i) It is used as a plastic and also as a synthetic fibre.

(ii) It is primarily used for fibres which find use in making socks, hoses, under garments, etc.

(iii) It is also used for making filaments to ropes, bristles for tooth brush and films etc.

Use of PVC : (i) It is used for making rain coat, table, PVC cloth, etc.

(ii) It is also used for making helmets, tires, motor cycles, mud guard, etc.

5. Deduce the expression for the rate constant of a second order reaction where the initial concentrations of the two reactants are same.

Ans. Same as Q. 4.(b) of 2004.

6. Discuss about SN<sup>1</sup> and SN<sup>2</sup> reactions with examples.

Ans. Same as Q. 6.(d) of 2005.

Group-C

[ Long Answer Type Questions ]

Answer any three questions.

3 × 15 = 15

7. Tabulate the products available from the distillation of crude petroleum against the range of temperature. Define octane and cetane numbers. What is biofuel? 7 + 6 + 2

Ans. Distillation of crude petroleum against the range of temperature :

Same as Q. 10.(a) of 2006.

8. State and explain the basic features of High and Low temperature carbonisations of coal. Write the usefulness of both the processes. Define gross and net calorific values of a fuel. What are proximate and ultimate analysis of coal? 7 + 2 + 2 + 4

Ans. Low temperature carbonisation : In this process, the heating of coal is carried out 500 - 700°C. The yield of coke is about 75-80% and it contains about 5-15% volatile matter. It is not mechanically strong, so it can not be used as a metallurgical coke. However it burns easily giving practically a smokeless, hot and radiant fire. Hence it is suitable for domestic purpose. The by product gas produced (about 130-120 m<sup>3</sup>/tonne) by this process is richer in heating value (about 6,000 - 9,500 k cal/m<sup>3</sup>) and is therefore, a more valuable gaseous fuel. So for production of coke for domestic purpose LTC is done. LTC gives coal gas of higher calorific value but the amount of coal gas obtained by this process is much lower than that of HTC. Amount of coal tar obtained by LTC is higher than that of HTC.

**High temperature carbonisation :** It is carried out at 900 - 1200°C with object of producing coke of the right porosity, hardness, purity, strength etc, so that it can be used in metallurgy. Nearly all the volatile matter of coal is driven off and the yield of coke is about 65-75% containing 1-3% volatile matter. The by product gas produced is high in volume (about 300 - 390 m<sup>3</sup>/tonne), but its calorific value is low (about 5000 - 6000 k cal/m<sup>3</sup>). The major products of HTC are coal gas, coke, coal tar and ammoniacal liquor.

**Gross and Net Calorific value :** Same as Q. 9,(a) of 2003.

**Proximate analysis :** Proximate analysis is so called because the data collected vary with the procedure adopted. It gives the valuable information about the practical utility of coal. We can assess the quality of coal by proximate analysis. It includes the determination of moisture, volatile matter, ash and fixed carbon.

$$(i) \% \text{ moisture content} = \frac{\text{Loss in weight}}{\text{Weight of coal taken}} \times 100$$

(ii) % volatile matter

$$= \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal sample taken}} \times 100$$

$$(iii) \% \text{ Ash} = \frac{\text{Weight of Ash}}{\text{Weight of dry coal}} \times 100$$

(iv) % fixed carbon = 100 - % of (moisture + volatile matter + ash)

**Ultimate Analysis of Coal :** In order to ascertain the quality of coal, it is subjected two types of analysis, one is ultimate analysis. The ultimate analysis is useful for combustion calculations. It include the determination of constituents present in dry coal like carbon, hydrogen, Nitrogen, sulphur, Ash and oxygen.

Ultimate analysis involves in the following determination :

- (i) Carbon & hydrogen content
- (ii) Nitrogen content
- (iii) Sulphur content
- (iv) Ash content
- (v) Oxygen content

9. (a) Explain addition and condensation polymerisation with example. 4
- (b) Distinguish between thermoplastic and thermosetting resins citing examples. 4
- (c) Deduce Gibbs-Helmholtz equation in any of its standard forms. 3
- (d) What is the difference between p-type semiconductor and n-type semiconductor? 2
- (e) What is the 'Finger Print Region' in IR-spectroscopy? 2

Ans. (a). Same as Q. 7.(a) of 2005.

Ans. (b) Same as Q. 8.(a) of 2003.

Ans. (c) Same as Q. 3.(d) of 2005.

Ans. (d) Same as Q. 7.(a) of 2004.

**Ans. (e) Finger Print Region in IR Spectroscopy :** The region  $1400-650 \text{ cm}^{-1}$  of any IR spectrum is known as **Finger Print Region** ; this is the region usually checked for identification, since it is the region associated with vibrational and rotational energy changes of the molecular skeleton and so is characteristic of the compound.

**10. (a) Draw the conductometric titration curve for the titration of HCL vs NaOH and explain the salient features in the curve.** 5

**(b) Define specific conductance and equivalent conductance. Show how they are related.** 6

**(c) State and explain Hess' law with examples.** 4

**Ans. (a).** Same as Q. 9.(b) of 2004.

**Ans. (b). Specific Conductance :** The reciprocal of specific resistance is known as **Specific**

**conductance.** It is represented by  $K$  (kappa). Thus  $K = \frac{1}{\rho} = \frac{l}{A \times R} = \frac{l \times C}{A}$ , where  $R$  (resistance) is the reciprocal of electrical conductance ( $C$ ) and  $l/A = \text{cell constant}$ . Unit of  $C$  is  $\text{ohm}^{-1} = \text{mho}$ . Unit of specific conductance is  $\text{ohm}^{-1} \text{ cm}^{-1}$ .

The specific conductance increases with (i) ionic concentration & (ii) speed of the ions concerned.

**Equivalent conductance ( $\wedge$ ) :** Equivalent conductance ( $\wedge$ ) of a solution at a dilution  $V$  may be defined as the conductance of all ions produced from 1 gm equivalent of electrolyte dissolved in  $V$  c.c. of the solution when the distance between the two electrode is 1 cm and the area of the electrode is so large that whole solution is contained between them.

$\wedge = K \times V$ , where  $K = \text{specific conductance}$  and  $V = \text{volume of solution in c.c. containing 1 gm equivalent of electrolyte}$ . Unit of equivalent conductance is  $\text{ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}$ .

**Relation :** Equivalent conductance is the product of the specific conductance ( $K$ ) and the volume  $V$  in c.c. containing one gm equivalent of the electrolyte at the dilution  $V$ . Thus  $\wedge = K \times V$ .

In general, if an electrolyte solution contains  $N$  gram-equivalents in 1000 c.c. of the solution, the volume of the solution containing 1 gram equivalent will be  $1000/N$ . Thus

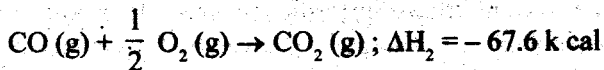
$$\wedge = \frac{K \times 1000}{N}$$

**Ans. (c). Hess's Law :** This law states that the total heat change ( $\Delta H$ ) i.e. heat evolved or absorbed accompanying a chemical reaction is same whether the reaction takes place in one step or more steps.

It means that the heat of a reaction depend only on the initial reactants and final products and not on the intermediate products that may formed. e.g., carbon can be converted into carbon dioxide either directly or via the formation of carbon monoxide. The heat change ( $\Delta H$ ) in both process and found to be same.

e.g., formation of  $\text{CO}_2$  directly.  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) ; \Delta H = -94 \text{ k cal}$ .

**Formation of  $\text{CO}_2$  via  $\text{CO}$  :**  $\text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO(g)} ; \Delta H_1 = -26.4 \text{ k cal}$



$$\Delta H = \Delta H_1 + \Delta H_2 = -(26.4 + 67.6) = -94 \text{ k cal}$$

11. Write explanatory notes on *any three* of the following :

3 × 5

- Schottky and Frenkel defects
- Order and molecularity of a reaction
- Gibbs-Duhem equation for a two component system
- Nernst's electrode potential
- Arrhenius equation
- Ligand.

Ans. (a). Same as Q. 3.(a) of 2002.

Ans. (b). Same as Q. 4(a) of 2003.

Ans. (c). **Gibb's – Duhem equation for a two component system :**

Let us consider a solution composed of two components and  $n_1$  &  $n_2$  be the number of moles of two components present. Let  $G$  be any extensive property of the system. Then  $G$  must be function of  $P$ ,  $T$  and  $n_1$  &  $n_2$ .

$$G = f(P, T, n_1, n_2) \dots\dots\dots (i)$$

Partial differentiation of equation (i) yields for  $dG$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2} dx_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1} dx_2 \dots\dots (ii)$$

at constant  $P$  and  $T$ , the equation (ii) be comes

$$dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 \dots\dots\dots (iii)$$

By use of Enber's theorem of homogeneous function equation (iii) can be integrated to yield

$$G = \bar{G}_1 n_1 + \bar{G}_2 n_2 \dots\dots\dots (iv)$$

Equation (iv) on complete differentiated, we obtain

$$\begin{aligned} dG &= \bar{G}_1 dn_1 + n_1 d\bar{G}_1 + \bar{G}_2 dn_2 + n_2 d\bar{G}_2 \\ &= (\bar{G}_1 dn_1 + \bar{G}_2 dn_2) + n_1 d\bar{G}_1 + n_2 d\bar{G}_2 \end{aligned}$$

Since  $dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2$

$$\therefore n_1 d\bar{G}_1 + n_2 d\bar{G}_2 = 0 \dots\dots\dots (v)$$

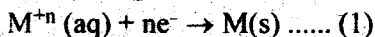
$$d\bar{G}_1 = -\frac{n_2}{n_1} d\bar{G}_2 \dots\dots\dots (vi)$$

These are two forms of Gibbs – Duhem equation.

Ans. (d). **Nernst's Electrode Potential :**

The electrode potential depends on the concentration of metallic ions in solution and variation of electrode potential with concentration of metallic ion solution is given by Nernst equation.

Consider a general electrode reaction :



$$\therefore \Delta G = \Delta G^{\circ} + RT \ln \frac{a_{\text{product}}}{a_{\text{reactant}}} \dots\dots (2)$$

Since  $\Delta G = -nFE$  and  $\Delta G^{\circ} = -nFE^{\circ}$

$$\text{Hence, } E = E^{\circ} - \frac{2 \cdot 303 RT}{nF} \log \left( \frac{a_{\text{product}}}{a_{\text{reactant}}} \right) \dots\dots (3)$$

This **Nernst equation** where  $E$  is electrode potential,  $E^{\circ}$  standard electrode potential,  $F$  is Faraday of electricity ;  $T$  is temperature,  $R$  is gas constant and  $a$  is activity. At  $25^{\circ}\text{C}$  i.e.  $T = (273 + 25) \text{ K} = 298\text{K}$ , putting the value of  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $F = 96500\text{C}$ .

$$\text{We get, } E = E^{\circ} - \frac{0.0591}{n} \log \frac{a_{\text{Product}}}{a_{\text{reactant}}}$$

In dilute solution, activities may be replaced by molar concentration terms,

$$\therefore E = E^{\circ} - \frac{0.0591}{n} \log \frac{[M(\text{s})]}{[M^{+n}(\text{aq})]}$$

For pure solid  $[M(\text{s})] = 1$

$$\therefore E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{+n}(\text{aq})]} \dots\dots (4)$$

The above equation is **Nernst Equation** for the electrode at  $25^{\circ}\text{C}$  and the electrode potential is called **Nernst electrode potential**.

At any temperature ( $T$ ) the above equation can be written as

$$E = E^{\circ} - \frac{2 \cdot 303 RT}{nF} \log \frac{1}{[M^{+n}(\text{aq})]} \dots\dots (5)$$

From the above equations, it can be concluded that

- (i) Electrode potential ( $E$ ) increases as  $[M^{+n}]$  is increased
- (ii) The electrode potential ( $E$ ) decreases as temperature is increased.

**Ans. (e). Arrhenius Equation :**

Arrhenius first pointed out that the variation of the rate constant with temperature. He suggested a simple relationship between the rate constant,  $k$  for a reaction and the temperature of the system.

$$k = Ae^{-E_a/RT} \dots\dots (1)$$

Where  $k$  = rate constant

$T$  = Temperature

A = Arrhenius constant

g = gas constant

$E_a$  = Activation energy of the reaction

In equation (1),  $e^{-E_a/RT}$  represents the fraction of mole units having energies equal to greater than the energy of activation.

Taking logarithm of equation (1),

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

$$\text{or, } \ln k = \ln A - \frac{E_a}{RT} \dots\dots(2)$$

$$\text{or, } \log k = \log A - \frac{E_a}{2.303 RT}$$

Thus a plot of  $\log k$  versus  $\frac{1}{T}$  should be a straight line (Fig.) with slope equal to  $-\frac{E_a}{2.303 R}$  and intercept equal to  $\log A$  so from the slope of this plot the activation energy can be evaluated.

Let  $k_1$  = rate constant of a reaction at temperature  $T_1$  and

$k_2$  = rate constant of same reaction at temperature  $T_2$ .

So from equation (2), we get

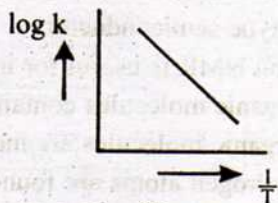
$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \dots\dots(3)$$

$$\text{and } \ln k_2 = \ln A - \frac{E_a}{RT_2} \dots\dots(4)$$

from equations (3) & (4),

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

$$\text{or, } \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \dots\dots(5)$$



Figure

Thus if we know rate constants at two different temperatures, we can calculate activation energy from equation (5).

**Ans. (f).** Same as Q.7.(b) of 2003.