CHEMISTRY PAPER–XI

## (Physical Chemistry-A)

Time Allowed : 3 Hours   Max. Marks : 22

Note : (i) Attempt five questions in all, selecting at least one question from each Section. Sections-A to D carry equal marks. Section–E is compulsory. (ii) Use of log tables and simple calculator is allowed.

SECTION–A

1. (a) What are liquid crystals ? Why are they so called ? Describe different types of liquid crystals. How is thermography used in detecting cancer ?

    (b) Apply Le-Chatelier's principle to predict suitable conditions for getting maximum yield of the products in each of the following cases :

    (i) Manufacture of nitric acid by Birkland-Eyde process :

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO$$
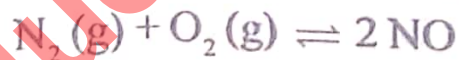
$$\Delta H = +\,ve$$

(ii) Manufacture of sulphuric acid by contact process (key step) :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
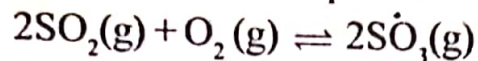
$$\Delta H = - \text{ve}$$

2. (a) What are 'London Dispersion Forces' ? How do they originate ? What are the factors on which their magnitude depends ?

(b) Taking suitable examples explain the difference between crystalline solids, liquid crystals and liquids.

(c) With the help of Le-Chatelier's principle explain :

(i) Effect of temperature and pressure on the solubility of gases in liquids.

(ii) Effect of temperature on the solubility of sugar in water.

SECTION-B

3. (a) Derive Van't Hoff equation in terms of K_p as well as K_c.

(b) Calculate the vapour pressure of water at 80° C. Given that latent heat of vaporisation of water is 540 Cal/gm and R is 1.987 Cals k^{-1} mol^{-1}.

4. (a) Derive the equation :

$$\Delta G = - RT\, ln\, K_p + RT\, ln\, Q_p$$

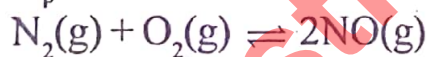(b) Write expressions for equilibrium constant in terms of :

(i) Concentrations (K_c)

(ii) Pressure (K_p)

(iii) Mole fraction (K_x)

Relate K_x with K_c as well as K_p.

(c) K_p value for the reaction :

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

at 298 K is 0.14. Calculate K_c (R = 0.082 lit atm K^{-1} mol^{-1}).

SECTION-C

5. (a) On the basis of reversible Carnot's cycle, how the concept of entropy was developed ? Define entropy and state its units. Is it a state function ?

(b) Derive an expression for the entropy change of an ideal gas, when the temperature changes from T_1 to T_2 and pressure changes from P_1 to P_2.

6. (a) State and explain Carnot's theorem and explain how thermodynamic scale of temperature was developed.

(b) How do you explain that entropy change of the system plus that of the surroundings ($\Delta S_{system} + \Delta S_{surroundings}$) increases in an irreversible process, whereas it remains constant in a reversible process.

(c) A heated copper block at 150° C loses 500 J of heat to the surroundings which are at room temperature i.e. 35°C. Calculate :

    (i)   Entropy change of the copper block

    (ii) Entropy change of the surroundings

    (iii) ΔS_{total}

assuming the temperature of the block and of the surroundings to be constant.

SECTION–D

7. (a) Derive Gibb's Helmholtz equation in the form :

$$\frac{\partial}{\partial T}(\Delta G/T)_p = -\frac{\Delta H}{T^2}.$$

   (b) The Volume occupied by 2.0 mole of an ideal gas increases from 2.0 dm³ to 20.0 dm³ during isothermal reversible expansion of an idal gas. Calculate the change in entropy and change in free energy of the gas at 350 K.

8. (a) Derive an expression for the change in free energy, when a system undergoes a change in temperature as well as a change in pressure in a reversible manner.

   (b) State third law of thermodynamics. How does the law help in the determination of absolute entropies of chemical compounds at any desired temperature ?

   (c) What do you understand by criterion of spontaneity ? Explain it in terms of ΔG.

SECTION–E

9. Attempt any six :

   (a) What type of liquid crystals are used in electronic industry ?

   (b) Relate K_p with K_c of a reversible reaction.

   (c) Which of the properties of a system remain constant at thermodynamic equilibrium ?

   (d) Under what conditions $\Delta G°$ obtained from K_p and K_c has same value ?

   (e) Which will have a greater entropy, a normal protein or a denatured protein ?

   (f) What is the effect of temperature on ΔS_{mixing} of ideal gases ?

   (g) Relate entropy of fusion of a solid with its freezing point.

   (h) What do you understand by temperature coefficient of emf of an electrochemical cell ?

   (i) What is the difference between Gibb's free energy and Helmholtz free energy of a system ?

$6\times1=6$