Time: 3 Hours   *Maximum Marks* :38

Attempt *Six* questions in all. Question No. 1 is compulsory. Use of calculator is allowed.

1. Answer any four of the following:

    (i)   Give the number of components in the following system and justify.

    (a) $NH_4Cl(s)$ in a closed container containing $NH_3(g)$.

    (b) KCl, NaCl, H_2O

    (ii)   A given solid has a definite composition and sharp melting point. How can you prove that it is not a compound.

    (iii) An aqueous solution of sodium carbonate is alkaline, ferric chloride is acidic and potassium chloride is neutral. Explain.

    (iv)   Molecular weight of KBr in water from osmotic pressure measurement is half its normal molecular weight. Explain.

    (v)   Which of the following are the expressions for chemical potential?

    (a) $(\partial A/\partial n_i)_{T,P,nj}$ (b) $(\partial A/\partial n_i)_{T,V,nj}$ (c) $(\partial U/\partial n_i)_{T,P,nj}$ (d) $(\partial H/\partial n_i)_{S,P,nj}$

    (vi)   For the following exothermic reaction state the conditions of temperature and pressure that will increase the extent of the reaction at equilibrium.

    (vii) A pure compound X can exist in vapour, liquid and two crystalline forms, namely, α and β. Give the number of two phase and four phase equilibria that can exist in this system.

    (2 x 4)

2. (i) Show that the molar entropy of mixing in a binary ideal mixture of gases is maximum when the mole fraction of one component of the gas is 0.5.

    (ii) Derive an expression of phase rule as applicable to a non-reactive system in which one component is missing in one phase.

   (iii) What is electroneutrality principle?

    (2,3,1)

3. (i) A substance X exists in two solid modifications α and β as well as liquid and vapour phase. α is more stable than β at lower temperatures. β melts at a still higher temperature to form the liquid. α is denser than the liquid but β is less dense than the liquid. No meta stable state is observed. Draw a well labelled phase diagram and describe each point, line and region.

   (ii) How many components are present if a solution contains the following: Na^+, Cl^-, Ag^+, H^+, OH^-, NO_3^-, $AgCl(s)$, H_2O ?

   (4,2)

4. (i) Derive a relationship between K_p and K_x. Show their dependence on pressure.

   (ii) At 300 K the vapour pressures of pure toluene and benzene are 37 torr and 118 torr respectively. They form ideal solutions. Determine the composition of the solution that boils at 300 K and a pressure of 50 torr.

   (4,2)

5. (i) Derive the expression for pH of an aqueous solution of a salt of weak acid and weak base. Show the condition under which the aqueous solution of the salt is acidic.

   (ii) Derive the following relation:
   $(\partial \ln K_c / \partial T)_P = \Delta U^\circ / RT^2$

   (4,2)

6. (i) From the concept of chemical potential derive an expression for the depression in freezing point of a solvent.

   (ii) A solution containing 0.54 g of naphthalene (molar mass 128 g mol^{-1}) in 50.0 g of CC_4 boils at a temperature that is higher than the boiling point of pure CCl_4 by 0.42°C. If a solution of 0.63 g of another non-volatile Y solute in the same quantity of CCl_4 yields a boiling point elevation of 0.64°C, calculate the molar mass of Y.

   (3,3)

7. (i) The pH of 0.1 mol dm^{-3} solutions of three sodium salts NaX, NaY and NaZ are respectively 7.0, 9.0 and 11.0. Arrange the acids HX,

HY and HZ in the order of their increasing strength. Calculate the Ka of these acids wherever possible.

(ii) What are the concentrations of H^+, HSO_4^-, SO_4^{2-} and H_2SO_4 in a 0.2 mol dm^{-3} solution of sulphuric acid? Given, first step dissociation of sulphuric acid is strong and $K_2 = 1.3 \times 10^{-2}$.

(iii) Derive the relation between degree of dissociation, α, and van't Hoff factor, i, for an electrolyte that undergoes dissociation in water.

(2,2,2)

8. (i) Phosphorous pentachloride dissociates according to the equation

   PCl_5 (g) $\rightarrow PCl_3$ (g) $+ Cl_2$ (g)
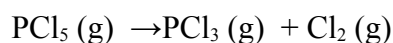
   Show that $K_P = \alpha^2 (P/p^\circ)/(1- \alpha^2)$ where P is the total pressure and α is the degree of dissociation.

   (ii) Explain why in a phase diagram of a one component system, the solid-vapour and liquid-vapour lines always have a positive slope, while the solid-liquid line may have a negative or a positive slope.

   (3,3)

9. Write short notes on any two of the following:

   (i) Conductometric titration of weak acid and strong base.

   (ii) Van't Hoff factor and its significance

   (iii) Phase diagram of a system forming incongruently melting compound.

   (iv) Raoult's law

   (3,3)