

**B.Sc. (Hons.)/II-(NS)**  
**CHEMISTRY-Paper-IX**  
**(Physical Chemistry-2)**  
**House Examination-2008**  
**Acharya Narendra Dev College**

*Time: 3Hours*

*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) The phase diagram of water system is useful to explain survival of aquatic life in sub zero conditions. Comment.
  - (ii) Molality of a solution does not depend on temperature. Comment.
  - (iii) If partial molar volume of one of the components in a mixture increases, that of the other decreases. Explain.
  - (iv) If the standard free energy of a reaction is zero, the extent of reaction at equilibrium is small. Comment.
  - (v) Explain why the aqueous solution of sodium acetate is alkaline while that of  $\text{CuSO}_4$  is acidic in nature.
  - (vi) The pH of pure water at  $40^\circ\text{C}$  is 6.75 still it is not acidic. Explain.
  - (vii) Molecular mass of acetic acid in water calculated from osmotic pressure measurement is less than its normal molecular mass.
- (2x4)
2. (i) The pH of  $0.1\text{ mol dm}^{-3}$  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  $K_a$  of these acids wherever possible.
- (ii) What are the concentrations of  $\text{H}^+$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{SO}_4$  in a  $0.2\text{ mol dm}^{-3}$  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 for pH of a solution of a salt whose cation and anion both undergo hydrolysis.
- (2,2,2)

3. (i) Derive the relation between degree of dissociation,  $\alpha$ , and van't Hoff factor,  $i$ , for an electrolyte that undergoes dissociation in water.
- (ii) A solution containing 0.64g of naphthalene (molar mass  $128 \text{ g mol}^{-1}$ ) in 50.0g of  $\text{CCl}_4$  boils at a temperature higher than that of pure  $\text{CCl}_4$  by  $0.45^\circ\text{C}$ . If a solution of 0.722g of another no-volatile solute in the same quantity of  $\text{CCl}_4$  yields a boiling point elevation of  $0.65^\circ\text{C}$ , calculate the molar mass of the solute.
- (iii) What is molal depression in freezing point constant of a solvent? What are the assumptions made while deriving its expression?  
( $2\frac{1}{2}, 2, 1\frac{1}{2}$ )
4. (i) A substance X exists in two crystalline forms  $\alpha$  and  $\beta$ .  $\alpha$  exists at lower temperature and  $\beta$  exists at higher temperature. The density of liquid X is less than that of solid X. No metastable state exists. Draw a well labeled phase diagram. From the graph identify the minimum and maximum temperature at which X can exist in liquid state.
- (ii) Give the number of components in the following systems. Justify your answer.
- (a)  $\text{KBr-NaBr-H}_2\text{O}$ .
- (b) Thermal decomposition of ammonia in a closed vessel  
(3,3)
5. (i) Explain why the tie line within the binodal curve of a three component system are parallel neither to the sides of the triangle nor to each other.
- (ii) Derive a relation between degree of freedom, number of components and number of phases for a C component non reacting system in which two components are missing in one phase.
- (iii) A one component system exhibits vapour phase, liquid phase and three solid modifications. Can the five phase equilibria be present in the system?  
(2,3,1)

6. (i) Derive the expressions for free energy and entropy of mixing for an ideal gas mixture at constant temperature and pressure. What will be the volume of mixing when equal moles of two ideal gases are mixed?
- (ii) The partial molar volumes of acetone and chloroform in a solution containing equal moles of the two liquids are  $74.0\text{cm}^3\text{mol}^{-1}$  and  $80.0\text{cm}^3\text{mol}^{-1}$  respectively at constant temperature and pressure. Calculate the volume of 1kg of this solution.
- (3,3)
7. (i) Give a thermodynamic derivation of the variation of the extent of reaction at equilibrium with temperature at constant pressure.
- (ii) For a chemical reaction the equilibrium constant at 300K and 400K are 100 and 400 respectively. Calculate the standard enthalpy of reaction and mention any approximation made.
- (3,3)
8. (i) Using the Duhem-Margules equation show that if the solvent obeys Raoult's law then the solute will obey Henry's law for the same composition range.
- (ii) Show that the saturated vapour in equilibrium with its binary solution is richer in that component whose addition to the solution increases the total vapour pressure at constant temperature.
- (iii) It has been found that CST for phenol-water system is increased by the addition of small amount of potassium chloride and decreased by the addition of small amount of succinic acid. Explain why.
- (2,2,2)
9. Write short notes on any three of the following:
- (i) Azeotropic mixture
  - (ii) Steam distillation
  - (iii) Raoult's law
  - (iv) Konowaloff's rule
  - (v) Solid solution
- (2x3)