B.Sc. (Hons.)/II-(NS)
CHEMISTRY-Paper-IX
(Physical Chemistry-2)
House Examination-2010
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) If the standard free energy of a reaction has a small positive value, the extent of reaction at equilibrium is small. Comment.
(ii) The pH=7 is not the correct definition of a neutral solution. Comment.
(iii) Though Li^+ is smaller than K^+, its molar conductance at infinite dilution is less than that of K^+. Explain.
(iv) Transport number of Cl^- in an aqueous solution of HCl is much less than in an aqueous solution of NaCl. Explain.
(v) Walden's rule is not applicable to all the electrolytes. Explain.
(vi) Raoult's law is a special case of Henry's law. Comment.

(2x4)

(2) (i) Show that the molar free energy of mixing for a ternary system of ideal gases is maximum when the gases are present in equimolar amount.
(ii) What is the effect of addition of a non volatile solute on the freezing point and boiling point of a solvent. Explain with the help of a graph of chemical potential versus temperature?
(iii) State the conditions under which the colligative properties can be used to calculate the molar mass of the solute.

(2,3,1)

(3) (i) Starting with Gibbs Duhem equation show that in an ideal binary solution if one component obeys Raoult's law then the second component will obey Henry's law.
(ii) Derive the relation between van't Hoff factor (i) and the degree of dissociation (α) for a weak electrolyte.
(iii) The ideal solution of two volatile liquids A and B is in equilibrium with its vapours under a total pressure of 0.8 atm. The mole fraction of A is 0.5 in the vapour phase and 0.2 in the liquid phase. What are the vapour pressures of pure A and pure B?

(2,2,2)

(4) (i) The blood is isotonic with 0.225M solution of NaCl. Calculate the osmotic pressure of blood at 37ºC.
(ii) The osmotic pressure (π) of a non volatile and inert solute was measured at various concentrations (c) at 27°C in acetone. A plot of π/c versus c yielded a slope of 4.06 J cm^3 g^{-2} and intercept 0.05 J g^{-1}. Calculate the average molar mass of the solute. (R= 8.314 J K^{-1} mol^{-1}.

(3,3)

(5) (i) Give a thermodynamic derivation of the variation of the extent of the reaction at equilibrium with temperature at constant pressure. Using the relation

obtained, discuss the effect of increase in temperature on the extent of reaction at equilibrium.

(ii) Nitrosyl chloride(NOCl) when heated decomposes as: $2NOCl \rightarrow 2NO + Cl_2$. The reaction is endothermic with $\Delta H^o = 77.07$ kJ mol^{-1}. The standard entropies for NOCl, NO and Cl_2 are 261.6, 210.7 and 223.0 J K^{-1} mol^{-1} respectively. Calculate the equilibrium constant for the reaction at 650K. Mention any assumption in the calculation.

(3,3)

(6) (i) Explain briefly Kohlrausch law of independent migration of ions. How can you determine the equivalent conductance at infinite dilution for acetic acid using Kohlrausch law?

(ii) A solution of lithium chloride of concentration 100 mol.m^{-3} and conductivity 1.06 S (mol L^{-1})$^{-1}$ was placed in a moving boundary cell of cross sectional area 1.0×10^{-4} m^2. The solution was electrolyzed for 100 min. With a constant current of 8.0 mA the lithium ion boundary moved a distance of 2.5×10^{-2} m. Calculate the velocity, mobility, transport number and the molar conductivity of Li^+ ion in this solution.

(iii) The conductance of a solution increases if the electric field strength is increased from 25 volts cm^{-1} to 10^5 volts cm^{-1}. Explain.

(2,3,1)

(7) (i) Describe the conductometric titration curve for the titration of acetic acid versus ammonium hydroxide when the base is taken in a burette.

(ii) Calculate the hydrolysis constant and degree of hydrolysis in a 0.1 mol dm^{-3} solution of sodium acetate. What will be the pH of this solution? Given, K_a of acetic acid $=1.8 \times 10^{-5}$.

(3,3)

(8) (i) Describe the sedimentation velocity method to determine the molar mass of a polymer having spherical particles.

(ii) Using the relation $K_w = [H_3O^+][OH^-]$, as also charge balance and material balance equations, derive an exact equation for the ionization constant of a base BOH.

$$K_b = \frac{[OH^-]\{[OH^-] - K_w/[OH^-]\}}{[BOH]_0 - [OH^-] + K_w/[OH^-]}$$

(3,3)

(9) (i) Equal numbers of polymer molecules, having molecular mass 10,000 g mol^{-1} and 1,00,000 g mol^{-1} are mixed to form a sample. Calculate the number average and weight average molecular mass of the sample.

(ii) Why among all the colligative properties, osmometery is considered to be the most applicable for macromolecules?

(iii) What are the concentrations of H_3O^+, HA^-, A^{2-} and H_2A in 0.1 M solution of a diprotic acid H_2A in water? Given: $K_{a1}=1.1 \times 10^{-7}$ $K_{a2}=1.0 \times 10^{-14}$.

(2,2,2)