

B.Sc. (Hons.)/II-(NS)
CHEMISTRY-Paper-IX
(Physical Chemistry-2)
House Examination-2011
Acharya Narendra Dev College

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:**

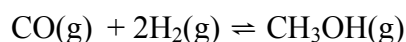
- (i) If the extent of reaction at equilibrium is large, the standard free energy of a reaction has a negative value. Comment.
- (ii) The milk of magnesia which contains $\text{Mg}(\text{OH})_2$ is used to treat acid indigestion. Explain.
- (iii) For a pure substance that can exist in the crystalline forms, α , β , γ and δ , all the four crystalline forms are never found in equilibrium. Comment.
- (iv) The vapour pressure of a system in the metastable region is greater than the stable system at a given temperature. Explain.
- (v) Molecular mass of acetic acid in benzene calculated from osmotic pressure measurement is more than its normal molecular mass. Explain.
- (vi) For spontaneous mixing of gases μ_i must be smaller than μ_i^* . Comment.
- (vii) The chemical potential can be identified with the escaping tendency of a substance. Justify.
- (viii) The synthesis of ammonia is carried out at a low temperature and high pressure. Explain.

(2x4)

2. (i) Calculate the pH of $0.036 \text{ mol dm}^{-3}$ solution of nitrous acid (HNO_2). Given the K_a value of the acid is 4.5×10^{-4} . State the approximations used in the above calculations.
- (ii) The cation and the anion of a salt of weak acid and weak base undergo hydrolysis. Write the chemical equations of various equilibria existing in the aqueous solution of the salt. Derive the expression of pH of the salt solution using appropriate approximations. State the condition under which the solution will be neutral.

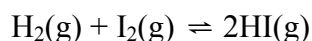
(2,4)

3. (i) Methanol is manufactured industrially by the reaction



The equilibrium constant (K_c) for the reaction is 10.5 at 200°C . Calculate the values of K_p and K_x at this temperature.

- (ii) The equilibrium constant K_p is 54.3 at 430°C for the formation of hydrogen iodide according to the reaction



In a certain experiment, 0.25 mol of H₂, 0.15 mol of I₂ and 2.0 mol of HI are placed in a one litre flask at 430°C. Will there be a net reaction to form HI. Explain.

- (iii) Derive the relation $\frac{d \ln K_c^o}{dT} = \frac{\Delta U^o}{RT^2}$. Show that K_c^o depends on temperature and is independent of pressure.

(2,2,2)

4. (i) 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.
 (ii) Starting from Gibbs-Duhem-Marguelles equation prove that if the solute obeys Henry's law, the solvent will obey Raoult's law.
 (iii) 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.

(2,2,2)

5. (i) Derive the relation between degree of association, α , and van't Hoff factor, i , for an electrolyte that undergoes association in water.
 (ii) The osmotic pressures of solutions of B in solvent A at 298K are given below. The pressures are expressed in terms of the heights of solution (of density $\rho=0.980\text{cm}^{-3}$) in balance with the osmotic pressure. Determine the molar mass of the solute.

C/g dm ⁻³	1.00	2.00	4.00	7.00	9.00
h/cm	0.28	0.71	2.01	5.10	8.00

(2,4)

6. (i) Latent heat of fusion of water is 80cal/g. What will be its melting point at 5atm if density of water and ice are 1.0 and 0.9 g/ml respectively?
 (ii) Derive an expression of phase rule as applicable to reactive system.

(3,3)

7. (i) Explain whether the melting point of a solid substance A will be raised or lowered by pressure, given that solid A does not float on liquid A. Illustrate your answer by suitable equations.
 (ii) Draw a well labelled phase diagram of water. Explain the changes taking place when water below the triple point is compressed at a constant temperature.

(2,4)

8. (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) From the concept of chemical potential derive an expression for the elevation of boiling point of a solvent.

(3,3)