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Your Roll No. .....

1254

B.Sc. (Hons.) / II A

CHEMISTRY – Paper IX

(Physical Chemistry - II)

Time : 3 Hours **Maximum Marks : 38**

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt any **six** questions. Graph paper will be provided. Use of scientific calculator is allowed.

1. (a) Derive thermodynamically an expression for the entropy of mixing (Δ_{mix} S) of ideal gases.

   (b) Two dm^3 of a gas A under 400 KPa and 298 K and four dm^3 of a gas B under 200 KPa and 298 K are forced into a three dm^3 evacuated reaction vessel, the temperature being maintained at 298 K. Calculate the change in entropy of gases assuming they are ideal. **3, 3**

2. (a) What is the effect of temperature change on the equilibrium constant ? Derive a relation between K_p^o and T starting from the Gibbs-Helmholtz equation.

(b) In an experiment, for the reaction :

$$2SO_2(g) + O_2(g) = 2SO_3(g)$$

0.1 mole each of SO_2 and SO_3 were mixed in a 3 dm^3 flask at 300 K. The pressure at equilibrium was 207.75 KPa. Calculate (a) the mole fraction of O_2 at equilibrium and (b) K_p^o and K_c^o. **3, 3**

3. (a) Construct a phase diagram for the Zn and Mg system given the following data :
Melting point of Magnesium = 655 °C
Melting point of Zinc = 500 °C
One eutectic point at 350 °C with 20 mol % of Zn and another at 430 °C with 92 mol % of Zn. A solid compound of Mg Zn_2 is formed which melts at 540 °C. The maximum is not very sharp. Comment on the stability of the compound.

(b) A mixture of 40. mol % Zn and 60 mol % Mg is cooled from 650 °C to 200 °C. Describe the cooling curve. **4, 2**

4. (a) Derive an expression relating depression in freezing point with molality of a dilute solution of a non-volatile solute starting from the concept of chemical potential.

(b) A solution of sodium chloride of molality m has an osmotic pressure of 2.0 atm. at 25 °C. Calculate ΔG at 25 °C for the process :

H_2O (Solution, 25 °C) $\rightarrow H_2O$ (Pure. 25 °C)

Give the answer in S.I. units. **4, 3**

5. (a) Derive the relation between the number of phases (p), components (c) and degrees of freedom (F) for a non-reactive system in which one component is present in all but one phase and another one is present in only two phases. Rest of the components are present in all the phases.

(b) An equimolar mixture of two polymers has a number average molar mass of 1.00 kg mol^{-1}, as determined by osmotic pressure measurements, and a mass average molar mass of 1.2 kg mol^{-1}, as determined by ultra centrifugation method. Determine the molar masses of the two polymers. **3, 3**

6. (a) Show that an exact equation to calculate $[H_3O^+]$ in an aqueous solution containing a salt formed from a strong acid and a weak base is given by :

$$\frac{K_w}{K_b} = \frac{([H_3O^+] - (K_w/[H_3O^+]))\,[H_3O^+]}{C + (K_w/[H_3O^+]) - [H_3O^+]}$$

where K_w, K_b and c have their usual meanings.

(b) Calculate the concentrations of H_3O^+, CN^-, HCN and OH^- in a 0.01 M solution of HCN in water, given K_a(HCN) as 6.8×10^{-10} and K_w as 1.0×10^{-14} at 25 °C. Solve by writing the mass balances, charge balance and the proton condition. Indicate and justify the approximations you make in the calculations. **3, 4**

7. (a) Derive an expression for the transport number of an ion in terms of ionic mobilities at ∞ dilution for a dilute solution of a single electrolyte.

(b) A solution of HCl was electrolysed in a transport cell using Pt electrodes. Analysis of the cathode solution gave the following results – mass of Cl^- before electrolysis is 0.160 g per 20.0 g of water, mass of Cl^- after electrolysis is 0.146 g per 20.0 g of water. A silver coulometer connected in series showed a deposit of 0.28 g Ag. Calculate the transport number of Cl^- ions. Molar mass of Cl is 35.5 g mol^{-1} and that of Ag is 107.8 g mol^{-1}. **3, 3**

8. (a) Starting from Gibbs-Duhem equation, derive the Duhem-Margules equation as applicable to a binary liquid system, and show that if one component shows positive deviation, so also must the other.

(b) When a mixture of H_2O and chlorobenzene (mutually immiscible) is distilled at an external pressure of 740.2 mm Hg, the mixture boiled at 90.3 °C, at which temperature the vapor pressure of pure water is 530.1 mm Hg. Calculate the mass % of chlorobenzene in the distillate, molar mass 112 g mol^{-1}. **3, 3**
