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Your Roll No. .....

910

B.Sc. (Hons.)/II **C**

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 *six* questions in all. Question No. 1 is compulsory.

Use of scientific calculator is allowed.

$R = 8.314\ JK^{-1}\ mol^{-1}$, $1F = 96500\ C\ mol^{-1}$.

1. Explain, any *four* of the following :

   (*i*) Mixing of ideal gases is purely an entropy effect.

   (*ii*) The transference number of an ion can be positive, negative or zero.

P.T.O.

(*iii*) An aqueous system containing K^+, Na^+ and Cl^- is a three component system whereas K^+, Na^+, Cl^- and Br^- is a four component system.

(*iv*) We observe elevation in boiling point when a non-volatile solute is dissolved in a volatile solvent.

(*v*) Congruent melting point of a two component system is non-variant. 4×2=8

2. (*a*) Define "Chemical Potential".

(*b*) Show that the chemical potential of an ideal gas in a mixture of ideal gases with total pressure 'P' is less than the chemical potential of the pure ideal gas at the same pressure 'P' :

$$\text{i.e. } \mu_i(\text{mix}) < \mu_i(\text{pure}).$$

(*c*) A container is divided into 4 compartments containing 1.0 mol of He, 3.0 mol of Ne, 2.0 mol of Ar and 2.5 mol of Xe at 298 K. The pressure in each compartment is 1 bar. Calculate $\Delta_{mix}G$ and $\Delta_{mix}S$, when the partitions are removed. Assume perfect behaviour. 1,2,3

3. (*a*) Derive the relation :

$$d \ln K°p/dT = \Delta^r H°/RT^2.$$

Also discuss the dependence of Kp° on nature of reaction (endothermic and exothermic reactions).

(*b*) Calculate the hydrolytic constant, degree of hydrolysis and pH of 0.3M NaCN solution.

Given $K_a(HCN) = 4.8 \times 10^{-10}$ M, $Kw = 1.0 \times 10^{-14}$ M^2.

3,3

4. (*a*) Derive Duhem-Margules equation. Using this equation show that if one component of a binary solution behaves ideally, the second component also behaves in the ideal manner.

(*b*) Discuss the principle underlying fractionating column.

(*c*) Two liquids A and B from an ideal solution at temperature T. When the total pressure above the solution is 500 Torr, the amount fraction of A in the vapour phase is 0.4 and in the liquid phase is 0.6. What are the vapour pressure of pure A and pure B at temperature T ? 3,1.5,1.5

5. (*a*) Construct a properly labelled phase diagram for the binary system A + B from the following data :

(*i*) M.Pt. of A = 1060°C

(*ii*) M.Pt. of B = 330°C

(*iii*) A_2B decomposes at 420°C to give a liquid of 45 mol% B.

(*iv*) AB_2 has a peritectic at 255°C and the melt is 71 mol% B.

(*v*) Eutectic is 215°C and 84 mol% of B.

No solid solution formed. Also, describe cooling curve for 10 mol% of B.

(*b*) Describe the sequence of events that take place when the component A (in liquid form) is added to a binary system of two partially miscible liquids B and C. 4.2

6. (*a*) Explain why the variation of equivalent conductance on dilution of strong electrolyte differs from that of a weak electrolyte.

(*b*) In the moving boundary method, a current of 25 mA was passed for 10 min. If the radius of a capillary is 3 mm, calculate the distance moved by H^+ ion in a solution of concentration 50 eq/m^3. 3.3

7. (*a*) Define number average and weight average molecular weight of a polymer.

(*b*) What is gel permeation chromatography ?

(*c*) The relative viscosities of a solution of a sample of polystyrene in toluene were determined with on Ostwald viscometer at 25°C :

$C/10^{-2}$ g cm^{-3}	η/η_0
0.249	1.355
0.499	1.782
0.999	2.879
1.998	6.090

Given $k = 3.7 \times 10^{-2}$ and $a = 0.62$ for this polymer, when the concentrations are expressed in g cm^{-3}. Calculate the molar mass. 2,2,2

8. Write short notes on any *two* of the following :

(*a*) Nernst Distribution Law

(*b*) Phase rule for reactive system

(*c*) Hittorf's method for the determination of transport number. 3,3