[This question paper contains 6 printed pages.]

Sr. No. of Question Paper : 2045 **GC-3** **Your Roll No.....**

Unique Paper Code : 32171303

Name of the Paper : C–7 Physical Chemistry–III : Phase Equilibria and Electrochemical Cells

Name of the Course : **B.Sc. (H) Chemistry – CBCS**

Semester : III

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on the receipt of this question paper.
2. Question number **1** is compulsory.
3. Attempt **six** questions in all, selecting at least two questions from each section.

Use of Scientific calculator is permitted.

Graph papers may be provided.

Values of constants : R = 8.314 J K^{-1} mol^{-1}; F = 96500 C mol^{-1};

(2.303RT/F) at 298 K = 0.0591.

1. Attempt any **five** questions from the following :

   (a) Is it possible to cut through a slab of ice with a knife without separating the slab into two ? Explain using the phase diagram of water system.

   (b) How will you distinguish between a compound and its eutectic mixture both of which have sharp melting points ?

   (c) What is the effect of adding naphthalene on the CST of phenol-water system at constant pressure ? Explain with reasons.

(d) Name the most commonly used electrolyte in constructing a salt bridge. Why is it chosen over other electrolytes ?

(e) What is a standard hydrogen electrode ?

(f) Can we use quinhydrone electrode to measure pH of solution from 0-14 ? Justify your answer.

(g) What is an azeotrope ? Can the components of azeotrope be separated by simple boiling ? Give reasons for your answer.

(h) Most adsorption processes are exothermic in nature. Explain.

(i) Adsorption of gases on solid suface is not monolayer at high temperature and low pressure. Give reason. (3×5)

Section A

2. (a) Using Duhem-Margules equation and Raoult's law, show that in a binary solution if one component shows positive deviation, then the other component also does so. (3)

(b) The vapour pressures of pure ethylene bromide and propylene bromide are 22.93 kPa and 16.93 kPa at 300 K. These two compounds form a nearly ideal solution. When 3 moles of ethylene bromide and 2 moles of propylene bromide are mixed and allowed to attain equilibrium at 300K, the total pressure is 20.4 kPa. Calculate the mole fractions of the two components in the liquid phase. (4)

(c) Draw and discuss the phase diagram of sulphur which exhibits the phenomenon of enantiotropy. (5)

3. (a) Deduce Gibbs phase rule for a non - reactive system at equilibrium, in which one component is absent in one phase, while the other components are present in all phases. (3)

(b) Describe the method of cooling curves for construction of phase diagram. Draw and explain the cooling curves for a system A-B exhibiting a simple eutectic phase diagram when the composition is (i) 100% A (ii) a eutectic mixture of composition 50% (iii) a mixture of A and B of composition 25% (other than eutectic mixture). (4)

(c) Construct a well labelled phase diagram for the two component system consisting of X and Y using the following data. Also comment on the nature of the compound formed.

Melting point of X = 700°C; Melting point of Y = 480°C

One eutectic point is at 330 °C and 20 mol% of X

Another eutectic point is at 410°C with 80 mole percent of X.

A solid compound XY_2 is formed which melts at 590°C. (5)

4. (a) Phenol and water are partially miscible in each other. What will be your observation on

(i) No. of phases and Degrees of freedom

(ii) Composition of each phase

(iii) Quantities of layers if there is a phase separation,

as phenol is added progressively to a definite quantity, say 10 mL of water at constant temperature below its CST. (3)

(b) What is steam distillation ? Write the expression for determining the molar mass of a liquid using steam distillation ? (4)

(c) Draw a well labelled triangular phase diagram of chloroform – acetic acid – water system and explain the various regions in it. (5)

5. (a) State and explain the Nernst distribution law and its limitations. (3)

(b) Calculate the number of components in a solution containing H^+, OH^-, Na^+, Cl^-, Ag^+, NO_3^-, AgCl(s) and $H_2O(l)$. (4)

P.T.O.

(c) An aqueous solution contains 10 g of solute per litre of solution. When 1 litre of solution is treated with 100 mL of ether, 6 g of the solute are extracted. Calculate the distribution coefficient, K_D, for the distribution of solute between ether and water. How much more of solute would be extracted from the aqueous phase by a further 100 mL of ether. Assume that the molecular state of the solute is the same in ether and water. (5)

Section B

6. (a) Using Freundlich isotherm expressed in terms of mass of solute adsorbed per kg of adsorbent (x) and concentration C in g/dm^3 i.e.,

$$x = kC^{1/n}$$

calculate the mass of acetic acid in grams that 900 g of charcoal would absorb from 0.817 mol/dm^3 vinegar solution. The value of the constants k and n are 0.16 and 2 respectively. (3)

(b) What is e.m.f (potential) of a cell ? Describe the method of measuring the e.m.f of an electrochemical cell using a potentiometer. (4)

(c) The following table gives the potential of Harned cell at 25°C at various molalities of HCl : Pt(s) | H_2(g,1bar) | HCl(m) | AgCl(s) | Ag(s)

$m/10^{-3}$	3.215	5.619	9.138
E_{cell}/V	0.52	0.49	0.47

Determine the standard electrode potential of silver-silver chloride electrode graphically. (5)

7. (a) Explain, with example, the difference between a reversible and an irreversible cell. State the condition for a thermodynamically reversible cell. (3)

(b) Construct the galvanic cell for the following reactions and write the expression for cell potential :

(i) $2Cr(s) + 3Hg_2Cl_2(s) \rightleftharpoons 2Cr^{3+}(aq) + 6Cl^-(aq) + 6Hg(l)$

(ii) $Fe(s) + Cl_2(g) \rightleftharpoons FeCl_2(aq)$ (4)

(c) Derive the following expression for liquid junction potential of the following concentration cell with transference involving 1:1 electrolyte, HCl and in which the electrodes are reversible with respect to cation.

H_2 (1 bar)|HCl(a_1)|HCl (a_2)|H_2 (g, 1 bar)

$$E_{lj} = (1-2t_-)\frac{RT}{F}\ln\frac{(a_\pm)_{1,HCl}}{(a_\pm)_{2,HCl}}$$

where t_- is the transference number of the anion, Cl^-. (5)

8. (a) Given the E° values for the electrodes $Cu^{2+}(aq)|Cu(s)$ and $Cu^+(aq)|Cu(s)$ as +0.340 V and + 0.522 V respectively, calculate the E° value for the electrode $Cu^{2+}(aq)|Cu^+(aq)$. (3)

(b) Write the cell with which the equilibrium constant of the following reaction can be determined.

$$Cd^{2+} + 4NH_3 \rightleftharpoons Cd(NH_3)_4^{2+}$$

Also, determine the standard equilibrium constant for the reaction at 298 K, given that

$$E^0_{Cd^{2+}/Cd} = -0.4V \quad \text{and} \quad E^0_{Cd(NH_3)_4^{2+}/Cd} = -0.6V$$ (4)

(c) Starting from Gibbs Helmholtz equation and the relation $\Delta G = -nFE$, derive the relations for ΔH and ΔS in terms of temperature coefficient of cell potential. What are the units of ΔH and ΔS if F is expressed in coulomb $mole^{-1}$ and E in volt. (5)

9. (a) A concentration cell formed from a metal and its nitrate is given below :

$$M(s) \mid M(NO_3)_x (0.01M) \parallel M(NO_3)_x (0.1M) \mid M(s)$$

The potential of the cell was found to be 0.0295 V at 298 K. Determine the molecular formula of the metal nitrate. (3)

(b) What is the principle underlying potentiometric titrations ? What are the advantages of potentiometric titrations over the conventional volumetric titrations ? (4)

(c) What are the assumptions of Langmuir adsorption theory ? On the basis of Langmuir theory of adsorption, show that

$$\theta = \frac{Kp}{1+Kp} \qquad (5)$$