46 — 15|12|18 (M)

Roll No. ☐☐☐☐☐☐☐☐☐☐☐

S. No. of Question Paper : **43**

Unique Paper Code : **32171303**   **I**

Name of the Paper : **Physical Chemistry-III : Phase**

Equlibria, Electrochemical Cell

Name of the Course : **B.Sc. (Hons.) Chemistry**

Semester : **III**

Duration : **3 Hours**   Maximum Marks : **75**

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

Question No. 1 is compulsory.

Attempt *six* questions in all,

selecting at least *two* questions from each Section.

Use of scientific calculator is permitted.

Graph paper may be provided.

Values of constant : R = 8.314 JK^{-1} Mol^{-1}; F = 96500 C Mol^{-1}.

I. Attempt any *five* questions from the following :   5×3

  (a) Why a saturated solution of KCl or NH_4NO_3 should be used in the salt bridge ?

  (b) Polarities of cathode and anode in a galvanic cell are opposite to those in an electrolytic cell.

  (c) Langmuir equation is more suitable for chemisorption than physisorption.

  (d) Adsorption is an exothermic process.

  (e) For a one component system, the maximum number of phases that can exist in equilibrium is three.

  (f) Find out the number of components present in the solution containing Na^+, Cl^-, Ag^+, NO_3^-, $AgCl(s)$ and H_2O.

Section-A

2.   (a) The EMF of the following cell :

$$Cd/CdCl_2(satd.)//AgCl(s)/Ag$$
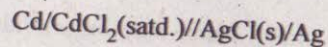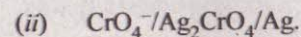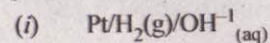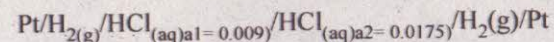
is 0.6753 V at 25°C and 0.6915 V at 0°C.

Calculate ΔG, ΔH and ΔS for the cell reaction at 25°C.

  (b) Derive an expression for the electrode potential for the following half cells :

    (i) $Pt/H_2(g)/OH^{-1}_{(aq)}$

    (ii) $CrO_4^-/Ag_2CrO_4/Ag$.

  (c) Explain with examples, the difference between reversible cell and irreversible cells.   6,3,3

3.   (a) Given the cell,

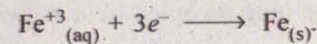$$Pt/H_{2(g)}/HCl_{(aq)a1=0.009}/HCl_{(aq)a2=0.0175}/H_2(g)/Pt$$

E_{cell} = 0.028 V at 25°C

    (i) Derive an expression for EMF of cell with transference.

    (ii) Calculate the liquid junction potential associated with this cell. The transference no. of H^+ ions is 0.83.

  (b) You are given the following reduction reactions and E^0 values :

$$Fe^{+3}_{(aq)} + e^- \longrightarrow Fe^{+2}_{(aq)}; \quad E^0 = 0.771 \text{ V}$$

$$Fe^{+2}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}; \quad E^0 = -0.447 \text{ V}.$$
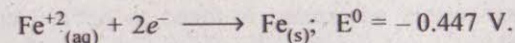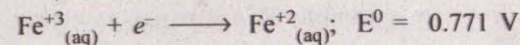
Calculate E^0 for half cell reaction :

$$Fe^{+3}_{(aq)} + 3e^- \longrightarrow Fe_{(s)}. \qquad 8,4$$
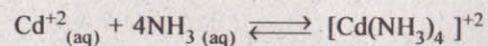
4.   (a)   Construct the appropriate cell and to determine the equilibrium constant for the reaction at 298 K :

$$Cd^{+2}_{(aq)} + 4NH_{3\,(aq)} \rightleftharpoons [Cd(NH_3)_4]^{+2}$$

$E^0_{Cd^{+2}/Cd} = -0.40$ V and $E^0_{[Cd(NH_3)_4]^{+2}/Cd} = -0.61$ V.

   (b)   Explain, how the pH of a solution is determined by using the quinhydron electrode.

   (c)   What other electrodes can also be used to determine the pH of the solution ?   6,3,3

5.   (a)   Give the postulates on which Langmuir's adsorption isotherm is based and develop an expression for the same. What form does the equation take under conditions of low pressure and high pressure ?

   (b)   At 0°C and 1 atm pressure, volume of N_2 gas required to cover a sample of silica gel assuming Langmuir monolayer adsorption is found to be 130 cm³ g⁻¹ of the gel. Calculate the surface area per gram of silica gel. Given that the area occupied by a N_2 molecule is 0.162 nm².   6,6

Section-B

6.   (a)   Using Clausius-Clapeyron equation, draw the labelled phase diagram for water.

   (b)   A mixture of an organic liquid A and water is distilled under 1 atm pressure at 372.2 K. What mass of steam would be condensed to obtain 1 g of liquid A in the distillate ? The vapour pressure of H_2O at 372.2 K is 739 torr and molar mass of A = 123 g mol⁻.

   (c)   What are the azeotrops ? Can they be purified by fractional distillation ? Justify your answer.   4,4,4

7.   (a)   Construct a well labelled phase diagram for zinc and magnesium system using the following data :

     (i)   Melting point of magnesium, 655°C

     (ii)   Melting point of zinc, 500°C

     (iii)   One eutectic point at 350°C with 20 mole per cent of zinc and another at 430°C with 92 mole per cent of zinc.

(ii) A solid compound of $MgZn_2$ is formed which melts

congruently at 540°C.

Draw the cooling curves at 20% mole and 40% mole

of Zinc.

(b) A solute distributes itself between two immiscible

solvents α and β. If the solute was found to be associated

in phase β while it remained unaffected in the other, find

out the distribution coefficient of the solute between

phase α and β.

(c) Starting from Duhem-Margules equation, show that if one

component behaves ideally, the second component also

behave in the ideal manner.   6,3,3

8. (a) Derive an expression of phase rule for the reactive and

non-reactive system.

(b) When a liquid, which is immisible with water, was steam

distilled at 95.2°C at a total pressure of 747.3 torr, the

distillate contained 1.27 g of the liquid per gram of water.

Calculate the molar mass of the liquid. The vapour pressure

of water is 638.6 torr at 95.2°C.

(c) What is the effect of different types of impurities on

CST ? Explain with examples.   4,4,4

9. Write short notes on any *three* :

(a) Calomel electrode

(b) Physical adsorption and Chemical adsorption

(c) BET equation

(d) Fractional distillation of ideal and non-ideal

solutions.   4,4,4