This question paper contains 7 printed pages]

Roll No. | | | | | | | | | | | |

S. No. of Question Paper : **2380**

Unique Paper Code : **2171403** **F-4**

Name of the Paper : **Physical Chemistry Electrochemistry (Paper No. 11)**

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

Semester : **IV**

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

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

Attempt *five* questions in all, selecting any *two* questions

from each Section. Question No. **1** is compulsory.

Use of scientific calculator is allowed.

1. Answer any *five* of the following : 5×3=15

(*a*) Usually a saturated solution of KCl or NH_4NO_3 is used in the salt bridge. Explain.

(*b*) Metallic conductance decreases while electrolytic conductance increases with temperature. Comment.

P.T.O.

(*c*) Given the E° values for the electrodes Fe^{2+}(aq.)|Fe(s) and Pt(s)|Fe^{3+}(aq.), Fe^{2+} (aq.) as –0.44 V and +0.77 V respectively, calculate the E° value for the electrode Fe^{3+}(aq.)|Fe(s).

(*d*) The amide ion in liquid ammonia has abnormally high transference number. Explain.

(*e*) Why does conductivity of an electrolyte solution decease with dilution while the molar conductivity increases ?

(*f*) How does ionic velocity differ from ionic mobility ?

(*g*) Determine the cell reaction and EMF for the cell at 25°C

$$Mg(s)|MgI_2(0.1\ M)|I_2(s)|Pt(s)$$

Given that :

$$E^\circ_{I^-|I_2} = 0.535\ V \text{ and } E^\circ_{Mg^{2+}|Mg} = -2.363\ V$$

(*h*) Explain why the use of quinhydrone electrode is restricted to acidic solutions only ?

Section A

2. (*a*) State and explain Kohlrausch's law of independent migration of ions. How does it help in determining the molar conductivity at infinite dilution of a weak electrolyte ?

(*b*) The conductivity of water was found to be 5.5×10^{-6} S m^{-1} at 25°C. Given $\lambda(H^+) = 0.0350$ S m^2 mol^{-1}; $\lambda(OH^-) = 0.0199$ S m^2 mol^{-1}, determine K_w at 25°C.

(*c*) It is found that at 25°C, the resistance of a certain conductivity cell is 2.20.000 ohms when it is filled with water. 100 ohms when filled with 0.02 M KCl, and 1.02,000 ohms when filled with water saturated with AgCl. The equivalent conductivity of AgCl is calculated to be 126.8×10^{-4} S m^2 mol^{-1} at 25°C. whereas that for KCl is known to be 138.3×10^{-4} S m^2 mol^{-1}. Assuming that the solutions are prepared with water of the same resistance as given above

and neglecting the variation of the equivalent conductivity with concentration, calculate :

(*i*) The cell constant

(*ii*) The specific conductivity of the saturated solution of AgCl

(*iii*) The solubility and solubility product of AgCl at 25°C. 5.5.5

3. (*a*) Show that though cations and anions move with different speeds the ions are discharged in equivalent amounts at the two electrodes.

(*b*) A solution of 0.01 mol dm^{-3} in silver nitrate is used with silver electrodes in a Hittorf's device. 32.10 mg of silver is deposited in a silver coulometer in series with Hittorf's cell. At the end of the run, 20.09 g of the solution in the anodic compartment was found to contain 39.66 mg of silver. 27.12 g of solution in the cathodic compartment contained 11.14 mg of Ag. Calculate transference number of Ag^+ ion.

(*c*) The molar conductivity of an aqueous solution of 0.0008 M aniline hydrochloride is 120×10^{-4} S m^2 mol^{-1}. When few drops of aniline were added to the solution, its molar conductivity is reduced to 105×10^{-4} S m^2 mol^{-1}. Calculate the degree of hydrolysis and hydrolysis constant of the salt. Given Λ_m(HCl) = 415×10^{-4} S m^2 mol^{-1}. 5.5.5

4. Write short notes on any *three* of the following : 5.5.5

(*a*) Debye-Huckel–Onsagar theory of ionic atmosphere

(*b*) Various applications of conductance measurements

(*c*) Effect of pressure, viscosity and dielectric constant of the solvent on the conductivity measurements

(*d*) Moving boundary method.

Section B

5. (*a*) Describe an accurate method for determining the EMF of an electrochemical cell.

(*b*) Derive an expression for the electrode potential in terms of chemical potential for the half cells

(*i*) $H^+(aq)|H_2(g)|Pt(s)|$

(*ii*) $Cd^{2+}(aq)|Cd(s)$

(*c*) Determine the equilibrium constant for the reaction at 298 K :

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

$E°_{Cd^{2+}|Cd} = -0.40$ V and $E°_{Cd(NH_3)_4^{2+}|Cd} = -0.61$ V. 5.5.5

6. (*a*) Derive an expression to calculate the liquid junction potential for the following cell

$$Ag \mid AgCl(s)|HCl(a_1) \rightarrow HCl(a_2)|AgCl(s)|Ag$$

(*b*) For the following cell

$$Pb|PbCl_2(s)|PbCl_2(soln.)|AgCl(s)|Ag$$

The potential at 25°C is 0.490 V and the variation of EMF with temperature is given by

$$E = 0.490 - (1.86 \times 10^{-4} \text{ V deg}^{-1})(t - 25)$$

where t is the temperature in degree Celsius, calculate ΔG, ΔH and ΔS for the reaction at 45°C.

(*c*) For the cell $Pt|H_2(g.\ 1\ bar)|HCl\ (m = 0.1\ mol\ kg^{-1})|AgCl(s)|Ag(s)$. the EMF is 0.3524 V at 25°C. Calculate the mean ionic activity coefficient $\gamma_{\pm}$ of 0.1 mol kg^{-1} HCl at 25°C if the standard electrode potential. E°. of $AgCl(s)|Ag(s)|Cl^-$ is 0.2224 V. 5.5.5

7. Write short notes on any *three* of the following : 5.5.5

(*a*) Concentration cells without transference

(*b*) Determination of pH of a solution

(*c*) Applications of potentiometric measurements

(*d*) Primary and secondary cells.