

This question paper contains 7 printed pages]

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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

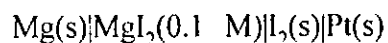
(a) Usually a saturated solution of KCl or  $\text{NH}_4\text{NO}_3$  is used in the salt bridge.

Explain.

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

P.T.O.

- (c) Given the  $E^\circ$  values for the electrodes  $\text{Fe}^{2+}(\text{aq.})|\text{Fe}(\text{s})$  and  $\text{Pt}(\text{s})|\text{Fe}^{3+}(\text{aq.})$ ,  $\text{Fe}^{2+}(\text{aq.})$  as  $-0.44$  V and  $+0.77$  V respectively, calculate the  $E^\circ$  value for the electrode  $\text{Fe}^{3+}(\text{aq.})|\text{Fe}(\text{s})$ .
- (d) The amide ion in liquid ammonia has abnormally high transference number. Explain.
- (e) Why does conductivity of an electrolyte solution decrease 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  $25^\circ\text{C}$



Given that :

$$E^\circ_{\text{I}_2|\text{I}^-} = 0.535 \text{ V} \text{ and } E^\circ_{\text{Mg}^{2+}|\text{Mg}} = -2.363 \text{ V}$$

- (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  $5.5 \times 10^{-6} \text{ S m}^{-1}$  at  $25^\circ\text{C}$ . Given  $\lambda(\text{H}^+) = 0.0350 \text{ S m}^2 \text{ mol}^{-1}$ ;  $\lambda(\text{OH}^-) = 0.0199 \text{ S m}^2 \text{ mol}^{-1}$ . determine  $K_w$  at  $25^\circ\text{C}$ .
- (c) It is found that at  $25^\circ\text{C}$ , 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  $126.8 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$  at  $25^\circ\text{C}$ . whereas that for KCl is known to be  $138.3 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ . 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  $0.01 \text{ mol dm}^{-3}$  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  $\text{Ag}^+$  ion.

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

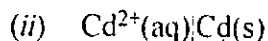
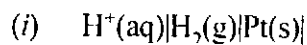
4. Write short notes on any *three* of the following : 5.5.5

- (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.

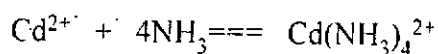
### Section B

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

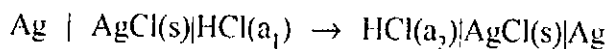


(c) Determine the equilibrium constant for the reaction at 298 K :

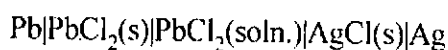


$$E^\circ_{\text{Cd}^{2+}|\text{Cd}} = -0.40 \text{ V} \text{ and } E^\circ_{\text{Cd}(\text{NH}_3)_4^{2+}|\text{Cd}} = -0.61 \text{ V.} \quad 5.5.5$$

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



(b) For the following cell



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  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the reaction at 45°C.

- (c) For the cell  $\text{Pt}|\text{H}_2(\text{g}, 1 \text{ bar})|\text{HCl} (m = 0.1 \text{ mol kg}^{-1})|\text{AgCl}(\text{s})|\text{Ag}(\text{s})$ , the EMF is 0.3524 V at 25°C. Calculate the mean ionic activity coefficient  $\gamma_{\pm}$  of 0.1 mol  $\text{kg}^{-1}$  HCl at 25°C if the standard electrode potential,  $E^{\circ}$ , of  $\text{AgCl}(\text{s})|\text{Ag}(\text{s})|\text{Cl}^{-}$  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.