

4th Semester Examination, 2022*Time : 3 hours**Full Marks : 60***Answer from all the Parts as per direction***The figures in the right-hand margin indicate marks**Candidates are required to answer in their own words
as far as practicable***(PHYSICAL CHEMISTRY-IV)****PART – I****1. Answer all the questions :****1 × 8**

(a) If Λ_{eqv} is equivalent conductivity and Λ_{m} is molar conductivity, then

$$\Lambda_{\text{eqv}} \text{Al}_2(\text{SO}_4)_3 = \text{————} \Lambda_{\text{m}} \text{Al}_2(\text{SO}_4)_3$$

(Turn Over)

- (b) Dispersion of conductance at high frequencies is _____ effect.
- (c) The velocity with which anion moves under a potential gradient of 1 volt per cm in a solution is called _____.
- (d) If K_a is dissociation constant of weak acid and its concentration is 'C' moles dm^{-3} , then $[K_a / C]^{\frac{1}{2}}$ is _____.
- (e) If Q is quantity of charge in coulombs and F is Faraday, then the number of moles of electrons is given by the formula _____.
- (f) In electroplating, the article to be electroplated is _____ electrode.
- (g) The titrations in which the e.m.f. of a cell is measured with addition of a titrant are called _____ titrations.
- (h) The C.G.S and S.I. units of dipole moment are respectively Debye(D) and Coulomb-metre. Hence $1\text{D} =$ _____ Coulomb-metre.

PART – II

2. Answer any *eight* of the following questions : $1\frac{1}{2} \times 8$

(a) Define electrolytic conductivity (k) and mention its unit in C.G.S. system.

(b) Deduce the relation between equivalent conductivity (\wedge_m), electrolytic conductivity (k) and concentration "C" (in moles per C.C.).

(c) The equivalent conductivities of a given sample of CH_3COOH at 0.05N and at infinite dilution are $0.39 \text{ S cm}^2 \text{ eqv}^{-1}$ and $0390 \text{ S cm}^2 \text{ eqv}^{-1}$ respectively. Calculate its degree of dissociation.

(d) What is wien effect. What happens to this effect if the concentration of electrolyte is increased ?

(e) Define transport number of cation and anion. Find the relation between them.

(f) What are conductometric titrations ?

(4)

- (g) State Faraday's first law and second law of electrolysis.
- (h) Name the factors on which the electrode potential depend ?
- (i) What are the advantages of potentiometric titrations ?
- (j) What is induced polarisation ? Name two types of induced polarisation.

PART – III

3. Answer any *eight* of the following : 2 × 8

- (a) Explain why equivalent conductance increases with dilution but the electrolytic conductivity decreases.
- (b) Give reasons why there is no limiting value of electrolytic conductivity ?
- (c) Define equivalent and molar conductances. Mention their units in C.G.S. system.

- (d) What is Walden's rule ? In which cases it is not applicable ?
- (e) Explain conductometric titration of a strong acid with a strong base.
- (f) How are transport numbers of cations and anions are related to their ionic mobilities ?
- (g) What is the mass of copper deposited (in gram) by 0.68 moles of electrons during electrolysis of molten CuCl_2 ?
- (h) Calculate standard emf of the cell
 $\text{Zn (s)} | \text{ZnSO}_4 \text{ (aq)} || \text{CuSO}_4 \text{ (aq)} | \text{Cu (s)}$
if $E^{\circ}_{\text{zn}/\text{zn}^{+2}} = + 0.76$ volt and
 $E^{\circ}_{\text{cu}/\text{cu}^{+2}} = - 0.35$ volt.
- (i) Write Clausius-Mosotti equation for polar molecules and indicate the meaning notations used.

- (j) Write the most general form of Lorentz-Lorenz equation for determination of molar refractivity. Mention the meaning of notations used.

PART – IV

Answer all questions as directed : 6×4

4. (a) Derive Debye-Huckel-Onsager conductance equation for a solution of uni-uni valent strong electrolyte.

Or

- (b) State and explain Kohlrausch's law of independent migration of ions.

If Λ_0 values of NaCl, HCl and CH_3COONa are $126.45 \text{ scm}^2 \text{ eqv}^{-1}$, $426.16 \text{ scm}^2 \text{ eqv}^{-1}$ and $91.2 \text{ scm}^2 \text{ eqv}^{-1}$ respectively, then calculate Λ_0 value of CH_3COOH .

1 + 2 + 3

5. (a) Describe Hittorf's method of determining the transport number of ions when

(i) electrodes are not attacked by ions

(ii) electrodes are attacked by ions. 3 + 3

Or

(b) Explain conductance measurement method of determining solubility and solubility product of a sparingly soluble salt. 6

6. (a) What is Nernst equation for electrode potential for a metal-metal ion electrode ?

Calculate the potential of a half-cell consisting of Zn electrode in 0.01 M ZnSO_4 solution at 25°C (Given $E^0_{\text{oxdn}} = 0.76$ volt).

3 + 3

Or

(b) Explain how ΔG , ΔH and ΔS of a cell reaction can be determined by emf measurement. 6

7. (a) What are concentration cells ? Derive the emf of a concentration cell with transference.

1+5

Or

- (b) Write notes on :

3+3

(i) Liquid junction potential

(ii) Salt bridge.