LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

FOURTH SEMESTER – **APRIL 2025**

PCH 4502 – ELECTROCHEMISTRY

Date: 25-04-2025 Dept. No. Max. : 100 Marks

Time: 01:00 PM - 04:00 PM

SECTION A

Answer ANY FOUR of the following. **(4 x 10 = 40)**

1. Discuss the role of the Debye-Falkenhaegen and Wien effects in providing evidence for the existence of ionic atmosphere.
2. (a) Distinguish between chemical and electrochemical potentials.
   (b) Determine the freezing point of 0.6 molal aqueous solution of a weak base, HB, if it is 15% ionized. (K_f of water is 1.86 °C/molal) (5+5)
3. Distinguish the following:
   (a) Outer and Inner Helmholtz planes (b) Electrophoresis and Electroosmosis (5+5)
4. Outline the principle of polarography and explain Ilkovic equation.
5. (a) Explain the conditions for polarizable and non-polarisable electrodes.
   (b) What is symmetry factor? How is it related to electron transfer coefficient in an oxidation reaction? (5+5)
6. Derive the Butler-Volmer equation for an elementary electron transfer reaction and explain the condition to resemble Ohm's law equation.
7. In the light of Pourbaix diagram and polarization curves, illustrate the fact that metallic iron is stable at negative potentials and ferric ions are stable at highly positive potentials.
8. (a) Define phase and activation over potentials.
   (b) For the electrode process, $Fe_3O_4 + 8H^+ + 2e \rightleftharpoons 3Fe^{2+} + 4H_2O$, that occurs on iron electrode in an aqueous solution, calculate the cell potential at pH = 3.5. (Given: S.R.P for the system = 0.98 V) (5+5)

SECTION B

Answer ANY THREE of the following. **(3 x 20 = 60)**

9. (a) Derive Debye-Huckel limiting law and explain any one application of it.
   (b) Prove that ion-solvent interaction is always spontaneous. (10+10)
10. (a) Describe viscous, electrophoretic and asymmetry effects in explaining Debye-Huckel-Onsager equation.
    (b) For the cell reaction, $Zn + 2AgCl_{(s)} \rightarrow 2Ag + Zn^{2+} + 2Cl^-$, E^o cell at 298 K is 1.4 V. Evaluate ΔG^o, ΔH^o, and ΔS^o for the cell reaction if the temperature coefficient of cell EMF is equal to -2.54×10^{-4} VK^{-1}. (1 Faraday = 96500 C)
    (c) Explain the different modes of mass transport in voltammetry. (10+5+5)
11. (a) Describe Helmholtz-Perrin model of electrical double layer. Mention its limitations.
    (b) Derive Lippmann equation relating interfacial tension and applied potential and mention the significance of electrocapillary curves. (10+10)
12. (a) Obtain an expression for the anodic current density of a multistep electron transfer reaction and mention the significance of anodic transfer coefficient.
    (b) Mention the significance of stoichiometric number and propose a possible mechanism for an electrochemical reaction with the following parameters. $\overleftarrow{\gamma} = 2$; $\overrightarrow{\gamma} = 2$; r = 0; $\gamma = 2$; and n = 4. (12+8)

13. (a) Determine the transfer coefficients and prove that the second step in the mechanism of the reduction of Fe^{2+} is the rate limiting step.

$$Fe^{2+} + H_2O \leftrightharpoons FeOH^+ + H^+$$
$$FeOH^+ + e \leftrightharpoons FeOH$$
$$FeOH + H^+ + e \leftrightharpoons Fe + H_2O$$

(b) The Tafel anodic and cathodic slopes ($\partial\Delta\emptyset/\partial \log i$) are 0.023 and 0.021 respectively. Obtain the essential parameters and predict the mechanism of the electrochemical reaction.

(12+8)

14. (a) Explain the advantage of the plot of ln i *vs* $\Delta\varphi$ over ln i *vs* η and mention the significance of the intercept.

(b) What are batteries? Distinguish between primary and secondary batteries with suitable examples.

(10+10)
