LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

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

FOURTH SEMESTER – **APRIL 2025**

PCH4MC02 – ELECTROCHEMISTRY

Date: 28-04-2025 Dept. No. Max. : 100 Marks

Time: 01:00 PM - 04:00 PM

	SECTION A – K1 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
1	**Fill in the blanks**	
a)	According to Walden's rule, at a given temperature, the product of equivalent conductance at infinite dilution of an electrolyte and _____ of the solvent is a constant.	
b)	The model that describes the behaviour of metal electrodes in an electrochemical system is _____.	
c)	Ohmic behavior of an electrode refers to the linear dependence of over potential with _____.	
d)	The equation that establishes the relation between electron transfer coefficient and symmetry factor in a multi electron oxidation process is _____.	
e)	In voltammetry, the desired electrochemical reaction occurs at _____ electrode.	
	SECTION A – K2 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
2	**True or False**	
a)	The thickness of ionic atmosphere around an ion in an electrolyte is measured as Debye-Huckel reciprocal length.	
b)	If mercury is used as an electrode, generally hard bases adsorb very strongly on the electrode.	
c)	The net current density is found to be dependent on symmetry factor when $\eta < 0.01$.	
d)	Evans diagram is a plot of potential vs pH.	
e)	Nafion can be used as an electrolyte in proton exchange membrane fuel cells.	
	SECTION B – K3 (CO2)	
	Answer any THREE of the following	**(3 x 10 = 30)**
3	(a) Apply Born model to find out the thermodynamic parameters for ion-solvent interactions. (b) For KCl, the lattice energy and the heat of solution are found to be -702.5 and +17.5 kJ mol^{-1} respectively. Calculate the enthalpy of salt-solvent interaction.	(7+3)
4	Derive Lippmann equation and explain the electrocapillary curves of various electrolytes.	
5	(a) Explain the various modes of transport of analyte in voltammetry. (b) Calculate the equilibrium constant for the reaction, $Fe + CuSO_4 \rightleftharpoons FeSO_4 + Cu$, at 25°C. (Standard oxidation potentials of Fe and Cu are +0.5V and -0.4V respectively.)	(6+4)
6	(a) What is electrode rectification? Explain the conditions for anodic and cathodic electrode rectifications. (b) Distinguish between polarizable and non-polarizable electrodes.	(6+4)
7	(a) Obtain the total number of steps involved in an electrochemical reaction which contains the following parameters: $\vec{\gamma} = 1$: $\overleftarrow{\gamma} = 1$; $\upsilon = 2$; $r = 1$. (b) How will you theoretically predict that the first step in the given mechanism could be the rate limiting step? $A + e \leftrightarrows B$ $B + e \leftrightarrows C$.	(5+5)

	SECTION C – K4 (CO3)	
	Answer any TWO of the following	**(2 x 12.5 = 25)**
8	(a) Obtain the solution for linearized Poisson-Boltzmann equation to find the electrostatic potential of an ion. (b) 3.45 g of a solute with a van't Hoff factor of 4, is dissolved in 22.0 g of water. The solution boils at 101.2^0C. Calculate the molecular weight of solute. (K_b of water is 0.51^0C/molal)	(8+4.5)
9	(a) What is membrane potential? How is it measured? (b) Explain the construction, working and advantages of solid oxide fuel cells.	(5+7.5)
10	(a) Discuss the modifications of Butler-Volmer equation when (i) $\eta = 0$ and (ii) $\eta < 0.01$V. (b) Compare the kinetics of the reaction $Cd^{2+} + 2e \rightarrow Cd$ carried out at an over potential of i) + 2mV ii) – 2mV.	(8+4.5)
11	(a) Obtain an expression for the reverse current density of a multistep electron transfer reaction and explain the terms involved in the anodic transfer coefficient. (b) Find the number of electrons that participate in the rate determining step of a reaction with the following parameters: $\vec{\alpha} = 1$, $\vec{\gamma} = 1$ and $\upsilon = 2$.	(8+4.5)
	SECTION D – K5 (CO4)	
	Answer any ONE of the following	**(1 x 15 = 15)**
12	(a) Show that Wien's effect is an evidence for the existence of ionic atmosphere. (b) Differentiate electroosmosis from electrophoresis. (c) Sketch and explain a polarogram.	(6+4+5)
13	(a) Discuss the importance of Pourbaix diagram to understand the thermodynamic stability of iron at different pH. (b) The Tafel anodic and cathodic slopes ($\partial\Delta\emptyset/\partial \log i$) are 0.023 and 0.021 respectively. Calculate the transfer coefficients and obtain the essential parameters to interpret the mechanism of the electrochemical reaction.	(8+7)
	SECTION E – K6 (CO5)	
	Answer any ONE of the following	**(1 x 20 = 20)**
14	(a) Explain the viscous and relaxation effects which lower the conductance of strong electrolytes. (b) Discuss Helmholtz – Perrin model of electrified interface. What are its limitations? (c) Consider the following cell, $Ag_{(s)}$, Ag^+ (a = 0.001 m) // Ag^+ (c = 0.01 m), $Ag_{(s)}$. Emf of the cell is +0.11 V at 25^0C. Write the cell reaction and calculate the activity coefficient of Ag^+ in 0.1 m solution.	(7+8+5)
15	(a) Explain the high field approximation of Butler-Volmer equation. Mention its experimental significance. (b) Predict the anodic and cathodic orders and transfer coefficients for the reduction of Fe^{2+} that follows the given mechanism when the second step is the rate limiting step. $Fe^{2+} + H_2O \leftrightarrows FeOH^+ + H^+$ $FeOH^+ + e \leftrightarrows FeOH$ $FeOH + H^+ + e \leftrightarrows Fe + H_2O$ (c) How do Lead-acid batteries act as both Voltaic cell and Electrolytic cell? Explain.	(6+8+6)
