LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

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

FOURTH SEMESTER – **NOVEMBER 2024**

PCH4MC02 – ELECTROCHEMISTRY

Date: 09-11-2024 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	**Answer the following**	
a)	Define electrochemical potential.	
b)	Diagrammatically represent the inner Helmholtz plane.	
c)	How is transfer coefficient related to symmetry factor in a reduction process?	
d)	Mention the significance of breakdown potential.	
e)	Write one disadvantage of using dropping mercury electrode in polarography.	
	SECTION A – K2 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
2	**Fill in the blanks**	
a)	If the dielectric constant of the medium increases then the thickness of ionic atmosphere ____.	
b)	According to Stern model of electrified interface, at higher concentration of electrolytes, the double layer obeys _____ model.	
c)	For an electrode to act as a cathodic rectifier, its symmetry factor should be _____.	
d)	The sum of the transfer coefficients is _____ for a multistep electrochemical reaction.	
e)	An electrochemical cell that converts chemical energy directly into electricity is called _____.	
	SECTION B – K3 (CO2)	
	Answer any THREE of the following	**(3 x 10 = 30)**
3	(a) Prove that ion-solvent interaction is always spontaneous. (b) Calculate emf of the cell, Zn/Zn^{2+} (0.001 m) // Ag^{+} (0.1 m) / Ag and comment on the spontaneity of the reaction. ($E^{0}_{Ag+¿_{Ag}}$ = 0.8 V; $E_{Zn/¿^{0}_{Zn2+¿}¿¿}$ = - 0.76 V)	(7+3)
4	Discuss Helmholtz–Perrin model of electrified interface. What are its limitations?	
5	Define over potential and discuss the modifications of Butler-Volmer equation when the over potential is (i) zero volt (ii) 100 mV.	
6	Predict the anodic and cathodic orders in the mechanism of the reduction of I_3^-.	
7	(a) Explain Debye-Falkenhagen effect, which is an evidence for the existence of ionic atmosphere. (b) Bring out the differences between primary and secondary batteries with suitable examples.	(6+4)
	SECTION C – K4 (CO3)	
	Answer any TWO of the following	**(2 x 12.5 = 25)**
8	(a) Explain the various factors to be considered in deriving Debye-Huckel-Onsager equation. (b) Evaluate Onsager constants A and B for methyl alcohol at 298 K. (Dielectric constant (ε) and Coefficient of viscosity (η) of methyl alcohol respectively are 31.5 and 0.00545 poise)	(8.5+4)
9	(a) Distinguish between electrophoresis and electroosmosis.	

	(b) Explain the cyclic voltammogram of ferri-ferro cyanide system.	(8+4.5)
10	(a) Obtain the cathodic Tafel equation. How is it modified for the experimental determination of symmetry factor and exchange current density? (b) Predict the current that is registered anodically and cathodically in an electrochemical system for a symmetry factor of 0.5 when the over potential is + 1.0 V.	(8+4.5)
11	(a) How will you express Nernst equation as a function of pH? Give an example. (b) Calculate the potential at which $Cr_2O_7^{2-}$ is reduced to Cr^{3+} in a solution of pH = 4. Given: SRP of $Cr_2O_7^{2-}/Cr^{3+}$ = +1.33V.	(8+4.5)
	SECTION D – K5 (CO4)	
	Answer any ONE of the following	**(1 x 15 = 15)**
12	(a) Derive Debye-Huckel limiting law. How is it verified? (b) Deduce Lippmann equation connecting interfacial tension and applied potential. (c) Mention the factors affecting diffusion current.	(7+5+3)
13	(a) Obtain an expression for the cathodic current density of a multistep electron transfer reaction and predict the cathodic transfer coefficient. (b) Discuss with an example the application of electrochemical polarization curves and Pourbaix diagram to understand the kinetics of corrosion.	(8+7)
	SECTION E – K6 (CO5)	
	Answer any ONE of the following	**(1 x 20 = 20)**
14	(a) Define Debye-Huckel reciprocal length and obtain an expression to measure the same. (b) What is meant by membrane potential? Explain the mechanism of electrochemical enzyme catalyzed oxidation of styrene.	(10+10)
15	(a) Compare the kinetics of the reaction $Zn \rightarrow Zn^{2+} + 2e$ carried out at over potential (i) + 200 mV and (ii) – 200 mV (b) Evaluate the transfer coefficients and prove that the reduction of iron follows the given mechanism if the slowest step is the second step. $Fe^{2+} + H_2O \leftrightharpoons FeOH^+ + H^+$ (1) $FeOH^+ + e^- \leftrightharpoons FeOH$ (2) $FeOH + H^+ + e^- \leftrightharpoons Fe + H_2O$ (3) (c) Explain the construction, working principle and disadvantages of solid oxide fuel cells.	(5+8+7)
