LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FOURTH SEMESTER – **JULY 2024**

PCH4MC02 – ELECTROCHEMISTRY

Date: 13-06-2024 Dept. No. Max. : 100 Marks

Time: 10:00 AM - 01:00 PM

	SECTION A – K1 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
1	**Fill in the blanks**	
a)	According to Bjerrum hypothesis, the ion pairs are formed when the Bjerrum critical distance is ____ the sum of the radii of ions.	
b)	When the coefficient of viscosity of ionic solution increases, Zeta potential _____.	
c)	_____ shows the relation between symmetry factor and transfer coefficient in a complex multistep reduction process.	
d)	In Pourbaix diagram the redox equilibria involving H^+ and OH^- ions are represented by_____.	
e)	In the cyclic voltammogram of one electron transfer redox reactions, the value of ΔE_P is equal to ___.	
	SECTION A – K2 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
2	**True or False**	
a)	Arrhenius theory of electrolytic dissociation is applicable only to concentrated solution of strong electrolytes.	
b)	The adsorption of biomolecules onto metals from solution can be studied by atomic force microscopy.	
c)	The resistance of a totally non-polarizable electrode should be zero.	
d)	Evans diagram refers to the plot of E vs pH.	
e)	Nafion is a perfluorosulfonic acid polymer used in solid polymer electrolyte fuel cell.	
	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) Account for the abnormal conductance of H_3O^+ ion in protic solvents.	(7+3)
4	(a) Explain the mechanism of electrochemical enzyme catalyzed oxidation of styrene. (b) Diagrammatically represent the outer and inner Helmholtz planes near the electrode surface.	(8+2)
5	Explain the conditions to obtain (i) low field (ii) high field approximations of Butler-Volmer equation and mention the parameter obtained from the slope of the plot of ln i vs η in each case.	
6	The Tafel anodic and cathodic slopes $(\partial \Delta \emptyset / \partial \log i)$ for a two-step process were found to be 0.04 and 0.12 respectively. Determine the transfer coefficients, stoichiometric number and predict the mechanism of the reaction.	
7	(a) Define Debye-Huckel reciprocal length and obtain an expression to measure the same. (b) Discuss the principle of sodium ion battery with a suitable example.	(5+5)

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) An aluminium-air battery has E^0_{cell} of 2.73 V and it involves 12 electrons process. Calculate the free energy change of battery.	(10+2.5)
9	(a) Discuss Helmholtz – Perrin model of electrified interface. What are its limitations? (b) Mention the various modes of transfer of electroactive materials to an electrode surface. How are they minimised?	(8.5+4)
10	(a) Define symmetry factor. How does it determine the tendencies of electrodes to show rectification behaviour anodically and cathodically? (b) For the following oxygen evolution reaction in acidic medium $2H_2O \leftrightharpoons O_2 + 4H^+ 4e^-$ the current at high anodic overpotential is given as $i_a = 4Fke^{[(1-\beta)\eta F/RT]}$. Prove that the slope $(\partial\eta/\partial \ln i)$ is 0.05.	(8.5+4)
11	(a) Discuss with an example the importance of the construction of polarization curve for the determination of corrosion current and corrosion potential. (b) How will you express Nernst equation as a function of pH for the formation of Fe from its oxide, Fe_3O_4 in an aqueous solution?	(8.5+4)

SECTION D – K5 (CO4)

	Answer any ONE of the following	**(1 x 15 = 15)**
12	(a) Explain any one application of Debye-Huckel limiting law. (b) Deduce Lippmann equation and arrive at the expression for determining the capacitance of an electrified interface. (c) Mention the significance of diffusion current and half-wave potential measured by a polarogram.	(5+7+3)
13	(a) Compare the kinetics of the reaction $Ag^+ + e^- \rightarrow Ag$ carried out at an over potential of (i) + 0.2 V (ii) – 0.2 V? (b) Obtain an expression for the cathodic current density of a multistep electron transfer reaction. (c) What are primary and secondary batteries? Give suitable examples.	(4+7+4)

SECTION E – K6 (CO5)

	Answer any ONE of the following	**(1 x 20 = 20)**
14	(a) 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) (b) Distinguish between streaming and sedimentation potentials. (c) Explain the construction, working and disadvantages of phosphoric acid fuel cell.	(5+7+8)
15	(a) Obtain the cathodic Tafel equation and discuss the experimental determination of symmetry factor, exchange current density and equilibrium potential. (b) Dissolution of iron takes place in terms of the mechanism mentioned below with second step as the rate limiting step. $Fe + H_2O \leftrightharpoons FeOH + H^+ + e^-$ $FeOH \leftrightharpoons FeOH^+ + e^-$ $FeOH^+ + H^+ \leftrightharpoons Fe^{2+} + H_2O$ Derive an expression for the net current density to evaluate the transfer coefficients and stoichiometric number.	(10+10)
