LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FOURTH SEMESTER – **APRIL 2016**

CH 4814 / CH 4808 - ELECTROCHEMISTRY

Date: 18-04-2016 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

Part-A

Answer ALL questions. **(10 x 2= 20)**

1. What are the factors that favour the association of ions in an electrolytic solution?
2. Calculate the mean activity coefficient of 0.01 M aqueous solution of KCl at 25 ºC (value of constant, A= 0.51).
3. How many grams of silver would be deposited by passing 0.2 F of electricity through an electrolyte containing Ag^+ ions? (Equivalent weight of Ag = 108)
4. What is an inner Helmholtz plane in the electrical double layer model?
5. Mention the role of a supporting electrolyte used in polarography technique.
6. Calculate the applied potential for the reduction of aqueous 1.0 M Na^+. Given: E_{eq} = -2.71V.
7. How are transfer coefficients related to symmetry factor in a complex multistep reaction?
8. What is phase over potential?
9. Why is it that Hg electrode does not allow charge to flow through itself?
10. Mention the significance of stoichiometric number.

Part-B

Answer any EIGHT questions. **(8 x 5= 40)**

11. Explain how electrophoretic and relaxation effects affect the mobility of an ion in solution.
12. Show that the conductance of electrolytic solutions at high potential gradient is an evidence for the existence of ionic atmosphere.
13. Calculate ΔG^o and equilibrium constant for the reaction in cell, $Cr_{(s)} / Cr^{3+}_{(aq)} // Cd^{2+}_{(aq)} / Cd_{(s)}$ (E^o_{cell} = 0.34 V).
14. Derive Lippmann equation and explain the significance of electrocapillary curves.

15a. Calculate Debye-Huckel reciprocal length for 0.001 M $CaCl_2$ in ethanol at 300 K. (Dielectric constant of ethanol is 24.3)

b. The molar conductances at infinite dilution for Al^{3+} and SO_4^{2-} ions are 189 and 160 Ω^{-1} cm^2 mol^{-1} respectively. Calculate the molar conductance at infinite dilution for $Al_2(SO_4)_3$. (3+2)

16. Distinguish between streaming and sedimentation potentials.
17. Calculate the effective resistance across 1 cm^2 of the electrode Pt, H_2, H^+ when $\eta < 0.01$V. Given i_0 = 0.79 mA/ cm^2 and β = 0.5.
18. How will you obtain the slope and intercept when anodic current density dominates?
19. How is the electro catalytic activity of metals determined for hydrogen evolution reaction?
20. How does symmetry factor influence the efficiency of the rectification of an electrode?
21. The exchange current density and the anodic symmetry factor of an electrode are 1.75×10^{-4} Acm^{-2} and 0.45 respectively. Determine the net current density of the electrode at 298 K under the over potentials a) 0.05 V b) -0.25 V.
22. Predict the conditions for an electrode to show i) no anodic tendency ii) no cathodic tendency.

Part-C

Answer any FOUR questions. **(4 x 10= 40)**

23a. Derive Debye-Huckel limiting law. How is it verified?

b. The solubility product of silver chloride is 1.77×10^{-10} mol^2dm^{-6} at 25 ºC. What is the solubility of salt in water at the same temperature in the presence of 10^{-4} M potassium chloride solution assuming Debye- Huckel limiting law to apply? **(6+4)**

24a. Derive linearized Poisson-Boltzmann equation for interionic interactions.

b. Calculate the weight of sodium chloride needed to decrease the freezing point of 500 ml of water to -8 ºC. (K_f of water = 1.86 ºC/molal; Molecular weight of NaCl = 58.5 g/mol) **(6+4)**

25a. Discuss the salient features of Gouy-Chapman model of electrical double layer.

b. With a neat sketch explain the important features of a polarogram. **(6+4)**

26. Derive the Butler-Volmer equation for a one electron electrode reaction and explain the low and high field approximations.

27a. How will you determine the anodic and cathodic orders for the mechanism of reduction of I_3^-?

b. The Tafel slope of the plot of ln i vs η for positive over potential was found to be 48.53. Calculate the corresponding transfer coefficient. **(6+4)**

28a. How will you modify the Butler-Volmer equation into an equation for potential as a function of concentrations?

b. Compare the kinetics of the reduction of H^+ over the surfaces of Hg and Pt. **(6+4)**

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