LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FOURTH SEMESTER – **APRIL 2015**

CH 4814 - ELECTROCHEMISTRY

Date : 17/04/2015 Dept. No. Max. : 100 Marks

Time : 09:00-12:00

Part-A

Answer all questions. Each question carries two marks. ***(10x2=20)***

1. What are intermediate electrolytes? Cite an example.
2. The lattice energy and heat of solution of KCl are -702.49 and +17.15 KJ/mol respectively. Calculate the enthalpy of salt-solvent interaction.
3. Why the mobility of H^+ is the highest among cations in aqueous solution?
4. Differentiate streaming potential from sedimentation potential.
5. Find the charge in coulombs on one mole of N_3^- ion.
6. Why is it that the discharge of H^+ is difficult on Hg surface?
7. Distinguish between symmetry factor and transfer coefficient.
8. Mention the condition to modify Butler-Volmer equation to Nernst equation and Tafel equation.
9. What is the effect of symmetry factor on current density?
10. Predict the anodic orders in the reduction of I_3^-.

Part-B

Answer any eight questions. Each question carries five marks. ***(8x5=40)***

11. The standard potential, E^0 of $Pt/H_{2(g)}$ / $HBr_{(aq)}$ // $AgBr_{(aq)}$ / $Ag_{(s)}$at 298 Kis +0.07131 V. Evaluate ΔG^o, ΔH^o, and ΔS^o for the cell if the temperature coefficient of cell EMF is -4.99×10^{-4} VK^{-1}.
12. Derive an expression for the thickness of ionic atmosphere using ion-cloud theory.
13. Write a note on Wien's effect.
14. Derive Lippmann equation and mention its importance.
15. Explain how convection and migration of mass transport can be avoided in an electrochemical cell?
16. A solution containing 8 g HF in 500 g of water freezes at -1.76 ℃. Find the degree of ionization of HF, (Molecular weight of HF is 20 and K_f of water is 1.86 ℃/molal)
17. Compare the plots: a) i vs η at negative HFA and b) log i vs η at positive HFA.
18. Calculate the minimum potential at which Zn can be deposited from 0.01 M aq. solution. Given: SRP Zn^{2+}/Zn = +0.76 V.
19. Explain i) Phase over potential ii) Reaction over potential.
20. How is the electrocatalytic activity of metals determined for hydrogen evolution reaction?
21. Deduce Nernst equation from Butler-Volmer equation.
22. The exchange current density and the symmetry factor of an electrode are 1.65 $mAcm^{-2}$ and 0.35, respectively. Determine the net current density of the electrode at 298 K under the over potentials i) -0.005 V ii) 0.05 V

Part-C

Answer any four questions. Each question carries ten marks. ***(4x10=40)***

23a. Explain the theoretical basis of Debye-Huckel-Onsager equation. **(7)**

b. State Walden's rule and mention its significance. **(3)**

24a. Derive Debye-Huckel limiting law. How is it verified? **(6)**

b. Calculate the mean activity coefficient of 0.1 M potassium ferrocyanidesolution at 25 ^{0}C using Debye-Huckel limiting law. (Value of A is 0.51) **(4)**

25. Explain parallel plate condenser model of electrified interface. What are its limitations? How are they overcome in Stern's model?

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

27a. Explain i) electrode as anodic rectifier ii) three electrode system **(6)**

b. The Tafel slope of the plot of ln i vs η for positive over potential is 55.89. Determine the corresponding transfer coefficient. **(4)**

28. Consider the following mechanism for the deposition of iron.

$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+$ (1) k_1

$FeOH^+ + e \rightleftharpoons FeOH$ (2) k_2

$FeOH + H^+ + e \rightleftharpoons Fe + H_2O$ (3) k_3

How will you prove that step-2 is the rate determining step?

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