LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - **CHEMISTRY**

FOURTH SEMESTER – **APRIL 2013**

CH 4808 - ELECTROCHEMISTRY

Date : 25/04/2013 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

PART – A

Answer any ALL questions: 10 x 2 = 20

1. Calculate the mean ionic activity coefficient of 10^{-3} M $BaCl_{2(aq)}$ using Debye-Huckel limiting law equation at 25°C.

2. E° red Fe^{3+} | Fe^{2+} is 0.771V and for Fe^{2+}|Fe is -0.44V calculate E° red for Fe^{3+}|Fe (all at 25°C)

3. Mention the factors that promote ion association in an electrolytic solution.

4. What is electrochemical potential?

5. Define streaming potential.

6. Derive the relation between rate and current density of an electrochemical reaction.

7. Define exchange current density. What are the factors determining its magnitude?

8. Explain the condition under which an electrode shows ohmic behavior.

9. Define stoichiometric number.

10. Defineconcentration over potential**.** What are the factors contributing to it?

PART – B

Answer any EIGHT questions 8 x 5 = 40

11. Explain Walden rule and mention its significance.

12. Calculate the thickness of the ionic atmosphere in 0.01M KCl in the following solvents at 25°C: nitrobenzene (D=34.8) and ethanol (D=24.3).

13. Deduce the values of Debye-Huckel-Onsager constants for CH_3OH at 25°C if the dielectric constant is 31.5 and the coefficient of viscosity is$5.45x10^{-4}$ $kgm^{-1}s^{-1}$.

14. Explain any one method of determining solvation number.

15. Outline the evidences for the existence of electrical double layer and explain.

16. E_{cell} for Ag|AgBr|Br^- (0.1M)||KCl (satd) | Hg_2Cl_2|Hg is 0.11V at 298K. E_{red} of saturated calomel electrode and $E°_{red}$for Ag^+|Ag are 0.2412V and 0.7994V respectively. Calculate K_{sp} of AgCl.

17. What do you mean by polarisable electrode? How is it related to exchange current density?

18. The exchange current density of an electrode and its symmetry factor are 1.35 $mAcm^{-2}$ and 0.45, respectively.Calculate its anodic current density at an over potential of 200mV.

19. Explain oxygen and hydrogen evolution in (i) acidic (ii) neutral media.

20. Calculate the minimum potential required for the discharge of Cu^{2+} from its $5x10^{-3}$M solution at 298K (SRP: Cu^{2+}/ Cu = 0.34V)

21. The reduction of M^{2+} to M follows the following mechanism

$M^{2+} + 2H_2O \rightarrow MOH^+ + H_3O^+$

$MOH^+ + e \rightarrow MOH$

$MOH + H^+ + e \rightarrow M + H_2O$

Determine the cathodictransfer coefficient if step-3 is RDS.

22. Discuss any five types of over-potential for an electrode system

PART – C

Answer any FOUR questions: **4 x 10 = 40**

23. Explain any two of the following. (5+5)

a) Applications of Debye – Huckellimiting law equation

b) Significance of electrocapillaritycurves

c) Electrokinetic phenomena

d) Zetapotential and its significance.

24. a) Mention the assumptions of Debye-Huckel theory and derive the linearised Poisson-Boltzmann equation. (2+5)

b) Calculate the potentials at distances $3\kappa^{-1}$due to the cation in 0.001NKCl$_{(aq)}$ at 298K (3)

$\kappa^{-1} = 9.607 \times 10^{-9}$ m

$4\pi\varepsilon_o = 1.112x\ 10^{-10}\ C^2J^{-1}m^{-1}$ and the dielectric constant of water is 80.

25. a) Discuss the salient features of Gouy-Chapmann model of electrical double layer (7)

b) How is Debye-Huckel-Onsager equation verified? (3)

26. (a) Derive the relationship between current density and over potential for an electrode system involving one electron.

(b) Deduce Nernst equation from the above relation.

27. (a) What do you mean by electrode rectification?

(b) Discuss Butler-Volmer equation for different symmetry factors,β (<0.5 , 0 &>0.5)

28. The deposition of iron follows the following mechanisum:

$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+$ Eqcont K_1…….(1)

$FeOH^+ + e \rightleftharpoons FeOH$ Eq cont K_2……. (2)

$FeOH + H^+ + e \rightleftharpoons Fe + H_2O$ Eq cont K_3…….(3)

Determine the reaction order with respect Fe^{2+} and the transfer coefficients in both directions if step-2 is RDS.