# LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FOURTH SEMESTER – **NOVEMBER 2016**

**CH 4814/CH 4808 – ELECTROCHEMISTRY**

Date: 10-11-2016 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

## Part-A

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

1. Calculate the thickness of ionic atmosphere in 0.01 M KCl at 25□C in ethanol as solvent (dielectric constant is 24.3).
2. Tetraisoamyl ammonium nitrate is an intermediate electrolyte. Account for this.
3. Calculate the equilibrium constant at 25 °C for the cell reaction,
   $2Ag^{+} + Zn \rightleftharpoons Zn^{2+} + 2Ag$ ($E^{\circ}_{cell}$ = 1.56 V)
4. State Walden's rule.
5. What is zeta potential? Mention its significance.
6. State the condition for an electrode to act as cathodic rectifier.
7. How will you account for the role of platinum in reference electrodes?
8. Mention the importance of anodic and cathodic transfer coefficients.
9. The discharge of $H^{+}$ ions on mercury surface is difficult – Justify.
10. Define stoichiometric number.

## Part-B

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

11. Explain the theoretical basis for Debye-Huckel-Onsager equation.
12. Distinguish between electrophoresis and electro osmosis.
13. Account for the abnormal conductance of $H_3O^{+}$ and $OH^{-}$ ions in protic solvents.
14. Calculate the freezing point of 0.01 m aqueous solution of potassiumhexacyano-ferrate(III), if it is 60% dissociated. $K_f$ for water is 1.86 K kg $mol^{-1}$.
15. Derive Lippmann equation and explain the significance of electrocapillary curves.
16. Explain how convection and migration modes of mass transfer can be minimized in an electrochemical cell.
17. Explain symmetry factor and exchange current density.
18. What are reaction over potential and concentration over potential?
19. The exchange current density of an electrode was found to be 0.60 mA $cm^{-2}$ at 25ºC. Calculate the current density across it when the over potential is 200 mV given that the anodic transfer coefficient is 0.5. The electrode involves three electron processes with rate determining step occurring twice per overall reaction.
20. Discuss Butler-Volmer equation for different symmetry factors, β (<0.05 & >0.05).
21. What is a polarizable electrode? How is it related to exchange current density?
22. Calculate the minimum potential required for the discharge of $Cu^{2+}$ from its $5\times10^{-3}$ M solution at 298K. (SRP: $Cu^{2+}$/ Cu = 0.34V).

## Part-C

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

23. Give an account of 'Parallel Plate Condenser Model' to describe the double layer structure. What are its limitations? How are they overcome in Stern's model?
24. Derive Debye Huckel limiting law. How is it verified? Mention its applications.
25 a. Derive an expression to calculate the work done in transferring an ion from vacuum to solvent.
   b. The thermodynamic solubility product of $BaSO_4$ is $10^{-10}$ $mol^2/lit^2$ at 25□C. What is the solubility of salt in water at the same temperature in the presence of $10^{-3}$ M sodium chloride solution? (5+5)

26a. Compare the following High field approximation plots i) i vs +ve η ii) log i vs –ve η.

b. The Tafel slope of the plot of ln i vs η for positive over potential was found to be 58.42. Determine the corresponding transfer coefficient. (6+4)

27a. Explain the modification of Butler-Volmer equation for potential as a function of concentration.

b. How will you differentiate experimentally a simple electrode reaction from a multistep reaction? (6+4)

28. The deposition of iron follows the mechanism given below;

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

$FeOH^+ + e \rightleftharpoons FeOH$ (2) $K_2$

$FeOH + H^+ + e \rightleftharpoons Fe + H_2O$ (3) $K_3$

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

**********