 LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FOURTH SEMESTER – APRIL 2012

# CH 4808 - ELECTROCHEMISTRY

 Date : 16-04-2012 Dept. No. Max. : 100 Marks

 Time : 1:00 - 4:00

***PART – A***

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

1. Mention the factors that favour ion association in an electrolytic solution.
2. Determine the mean activity coefficient of 10-3 m La(NO3)3 in water using

Debye – Huckellimitting law at 25oC.

1. Calculate the work of charging Li+ in vacuum. The radius of Li+ is 59 pm

(∈0 = 1.112 x 10-10 C2 J-1 m-1).

1. Mention the evidences for the existence of ionic atmosphere around an ion of an electrolyte.
2. What is zeta potential?
3. What is voltametry? How does it differ from potentiometry?
4. The Butler-Volmer equation under certain condition(s) can be expressed in the form: i = A Sinh(kη). Express the values of A and k in terms of the corresponding physical constants?
5. Explain the condition under which an electrode will (i) show ohmic behavior (ii) act as a rectifier.
6. Define stoichiometric number. How can it be determined experimentally?
7. Explain concentration polarization**.** What are the factors contributing to it?

***PART – B***

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

1. For the cell, Zn + 2 AgCl(s)→ 2 Ag + Zn2+ + 2Cl-.Eo cell at 298 K is 1.034 V. Evaluate ΔGo, ΔHo and ΔSo for the cell if the temperature coefficient of EMF is −2.54 x 10-4 V/K.
2. Calculate the thickness of the ionic atmosphere in 0.1 M KCl at 298 K in

nitro benzene (∈ = 34.8). (∈o = 8.85 x 10-12 C2J-1 m-1).

1. Differentiate chemical potential and electrochemical potential and deduce the relevant equations.
2. Discuss the salient features of Helmholtz – Perrin model of electrical double layer.
3. How is Debye- Huckel – Onsagar equation verified experimentally?
4. Calculate the molar conductivity of NaI in acetone. The viscosity of acetone is 3.16 milli poise. The radii of Na+and I- ions are 260 and 300 pm respectively. (1 poise = 10-7 ohm C2 om-3).
5. The cathodic symmetry factor, β of an electrode is less than 0.5. Draw the following curves in a plot of current density vs applied potential:

 (i) Anodic current density, ia (ii) Cathodic current density, ic

(iii) Net current density, i

1. The current density of an electrode for an over potential 10 mV was found to be 0.62mAcm-2. What will be the current density when the over potential applied is 100 mV, if its cathodic symmetry factor is 0.56.
2. Calculate the minimum potential required for the discharge of Cu2+ from its 5x10-3M solution at 298K (SRP of Cu2+/ Cu = 0.34V).
3. The reduction of Fe2+ to Fe follows the following mechanism:

Fe2+ + H2O FeOH+ + H+ eqconts K1…….(1) Fast

FeOH++ e FeOH eq conts K2……. (2) Fast

FeOH + H+ + e Fe +H2O eq conts K3…….(3) Slow

Write the expression for the current density of the rate determining step and step-2.

1. Derive the relation between applied potential and current density for a cathodic reaction on a mercury surface.
2. Define residual, diffusion and limiting currents. How do they arise and how are they related to each other?

***PART – C***

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

1. a) Mention the assumptions of Debye – Huckel theory of activity coefficients.

 b) Derive linearised Poisson – Boltzmann equation and mention its

 significance.

1. Explain any two of the following

 a) Electrocapillarity b) Grotthus type conduction

 c) Electrokinetic phenomena d) Diverse ion effect.

1. a) Discuss the theoretical basis for Debye – Huckel – Onsager equation.

 b) How is solvation number determined?

1. (a) Derive the relation between current and over potential for a simple

 one electron electrode system.

 (b) Deduce Nernst equation from the above relation.

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

(b) Discuss Butler-Volmer equation for different symmetry factors,

β (<0.5 , 0 &>0.5)

1. The evolution of hydrogen on a metal surface follows a two-step mechanism, viz., a fast equilibrium discharge of H3O+ followed by the slow chemical desorption of the adsorbed H atoms. Write the mechanism of the reaction and hence determine the order and the transfer coefficient for the discharge process.

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