

**LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034**

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FOURTH SEMESTER – APRIL 2010

**CH 4808 - ELECTROCHEMISTRY**

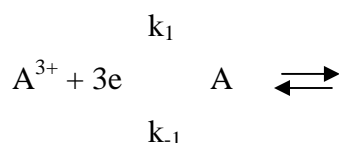
Date & Time: 15/04/2010 / 9:00 - 12:00 Dept. No.

Max. : 100 Marks

**PART – A**

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

1. Account for the abnormal ionic mobilities of  $H^+$  (aq) and  $OH^-$  (aq)
2. Compare the thickness of the ionic atmosphere of 0.01 m electrolytic solutions of  $PQ$  and  $P_2 Q_3$ .
3. The thermodynamic dissociation constant of a weak acid (HA) at  $25^\circ C$  is  $2 \times 10^{-5}$ . Calculate its degree of dissociation in 0.01 M solution of the acid in the presence of 0.01 M  $KNO_3(aq)$ .
4. What is zeta potential?
5. What is Walden's rule?
6. Explain the applicability of Nernst & Butler-Volmer equations.
7. Write the expression for the cathodic current density of the following reaction in terms of its free energy of activation.



8. The reaction resistance of an electrode at 298 K was found to 1265 ohm. What will be its exchange current density?
9. Define stoichiometric number. How is it related to transfer coefficients?
10. What is phase over potential? Give an example.

**PART – B**

Answer **ANY EIGHT** questions (8 x 5 = 40)

11. Calculate the stability constant of  $[ZnX_4]^{2-}$  is the EMF of the cell  
 $Zn | [ZnX_4]^{2-} 0.06M, X^- (0.15M) || SHE$  is 1.07 V at  $25^\circ C$ .  $E^\circ$  red. of  $Zn^{2+}|Zn$  is  $-0.76V$ .
12. Mention the postulates of Debye – Huckel theory. How is Debye – Huckel limiting law equation verified?
13. Explain the evidences for the existence of ionic atmosphere around an ion.
14. Derive the linearised Poisson – Boltzmann equation.
15. Calculate the free energy of ion – solvent interactions for  $K^+$  (aq). The radius of the ion is 133 pm and dielectric constant of water is 78.3 at 298K.
16. Explain electrokinetic phenomena and mention their significance.
17. Discuss the behavior of an electrode having cathodic symmetry factor 0.75.
18. The Tafel cathodic slope of the plot of  $\Delta\phi$  vs  $\log i$  for a two electron electrode process was found to be 0.12. Determine the transfer coefficient for the reduction process.
19. Explain the condition under which an electrode (i) will obey anodic Tafel equation (ii) will be non-polarisable
20. Compare the current vs over potential diagram for an electrode under the following conditions: (a)  $\beta = 0.25$  & High field (b)  $\beta = 0.75$  & Very Low field

21. What is Pourbaix diagram? Mention its characteristics.

22.  $Zn^{2+}$  has the diffusion co-efficient of  $6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . The values of  $m$  and  $t$  are  $13 \text{ mg s}^{-1}$  and  $14 \text{ s}$  respectively. Calculate the diffusion current of  $2.6 \times 10^{-4} \text{ M}$  solution of  $Zn^{2+}$ .

**PART – C**

Answer **ANY FOUR** questions

(4 x 10 = 40)

23. a) Derive Lippmann equation and explain. (5)

b) Explain electro capillarity curves. (5)

24. Explain any two of the following

a) Bjerrum's theory

b) Evaluation of thermodynamic quantities from EMF.

c) Helmholtz – Perrin model & its defects

d) Verification of Debye – Huckel – Onsager equation. (5+5)

25. a) Calculate the mean activity of  $10^{-4} \text{ M KCl (aq)}$ . What is the activity change of KCl if  $0.01 \text{ m}$

$ZnCl_2$  is added to 1 lit of the above solution? What will happen to Debye – Huckel reciprocal length after adding  $ZnCl_2$ ? (6)

b) Calculate the radius of the moving (NaI) entity in acetone given  $\wedge\eta = 5.7 \times 10^{-8} \text{ C}^2 \text{ cm}^{-1} \text{ eq}^{-1}$  and  $\epsilon = 20.7$  at  $25^\circ\text{C}$  (4)

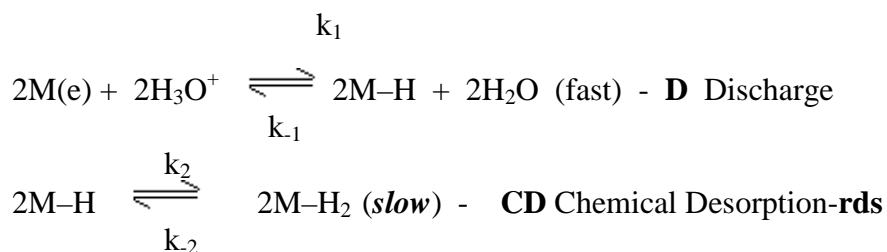
26. (a) Derive the equation relating current and over potential for a one electron electrode system.

(b) Explain the condition under which the Butler-Volmer relation get reduced to Tafel equation?

27. (a) Explain the factors contributing to concentration over potential.

(b) Obtain an expression for the limiting current on the basis of concentration polarization.

28. The discharge of hydrogen ion in acidic medium follows the following mechanism :



Determine the anodic transfer coefficient of the reaction.

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