LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FOURTH SEMESTER – **APRIL 2014**

CH 4814 - ELECTROCHEMISTRY

Date : 07/04/2014 Dept. No. Max. : 100 Marks

Time : 01:00-04:00

Part-A

Answer *all* the questions. Each carries *two* marks.

1. State Bronsted-Bjerrum hypothesis for ion pair formation.
2. Calculate the osmotic pressure of 0.24 M aqueous solution at 28 □ (the value of R is 0.0821 L atmmol^{-1}K^{-1}).
3. Account for the abnormal mobility of OH^- ions in aqueous solution.
4. Calculate zeta potential of a particle in aqueous solution if the electrophoretic mobility is 3.5×10^{-8} $m^2s^{-1}V^{-1}$ ($\eta = 8.94 \times 10^{-4}$ $Kgm^{-1}s^{-1}$; $\varepsilon = 78.5$).
5. Walden's rule holds good only for large ions in solution. Why?
6. Mention the condition under which Butler-Volmer equation resembles Ohm's law.
7. Predict the conditions for the dominance of forward and reverse current densities.
8. Bring out the difference between symmetry factor and transfer coefficient.
9. How will you obtain the number of electrons involved in a concerted redox reaction?
10. How are resistance and exchange current density related?

Part-B

Answer any *eight* questions. Each carries *five* marks.

11. For the cell, $Zn + 2\ AgCl_{(s)} \rightarrow 2Ag + Zn^{2+} + 2Cl^-$, E^o cell at 298 K is 1.034 V. Evaluate ΔG^o, ΔH^o, and ΔS^o for the cell if the temperature coefficient of cell EMF is -2.54×10^{-4} VK^{-1}.
12. Apply Born's model to find out the expression for energy of ion solvent interaction.
13. The thermodynamic solubility product of $BaSO_4$ is 10^{-10} at 25 □. What is the solubility of salt in water at the same temperature in the presence of 10^{-4} M potassium nitrate solution?
14. What are electrocapillary curves? Mention their importance.
15. Calculate the thickness of the ionic atmosphere in 0.1 M sodium chloride in ethylenedichloride (ε = 10.4) and ethyl alcohol (ε = 24.3) at 25 □.
16. Write a note on Wien's effect.
17. Define symmetry factor and mention its significances when its value is 0.5.
18. What are polarisable and nonpolarisable electrodes? Give examples.
19. Discuss the modification of Butler-Volmer equation at equilibrium condition.
20. The exchange current density of Pt/H_2, H^+ is 0.79 $mAcm^{-2}$ at 25□. Calculate the current density across the electrode when the over potential are:i)10mV ii)-200mV.
21. How will you obtain the slope and intercept when the reverse current density dominates?
22. Obtain the transfer coefficients for the dissolution of iron when the second step determines the rate.

Part-C

Answer any *four* questions. Each carries *ten* marks.

23. Derive Debye Huckel limiting law. How is it verified? Mention its applications.
24. Discuss in detail Gouy-Chapman diffuse charge model of electrified interface. How the limitations of this model are overcome in Stern's theory?

25a. Explain the theoretical basis of Debye-Huckel-Onsager equation. (6)

b. Evaluate Onsager constants A and B for methyl alcohol. ε and η of methyl alcohol are 31.5 and 0.00545 poise, respectively. (4)

26a. Explain any three types of over voltages. (6)

b. What is cathodic rectifier? When does an electrode show such a tendency? (4)

27a. Obtain the anodic and cathodic orders for the reduction of I_3^- ion. (6)

b. Arrive at the mechanism of a reaction containing four steps over all. There is one step prior to and one step after the slowest step. The transfer coefficients are found to be one each. (4)

28a. Obtain the order and the transfer coefficient for the evolution of hydrogen when the second step determines the rate. (6)

b. Calculate the effective resistance across 1 cm^2 of the electrode $Hg/H_{2(g)}/H^+$. Given the exchange current density = 0.79×10^{-12} A cm^{-2}. (4)

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