LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FOURTHSEMESTER – APRIL 2018

16PCH4MC02/CH4814/CH4808- ELECTROCHEMISTRY

Date: 20-04-2018 Dept. No. Max. : 100 Marks
Time: 01:00-04:00

Part-A

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

1. How does the added inert electrolyte affect the solubility of a sparingly soluble salt?
2. Write the effect of ion-pair and triple ion formation on molar conductivity of $LiBF_4$ in dimethoxy ethane solution at 25 ºC.
3. How is zeta potential determined from the streaming potential?
4. Calculate Helmholtz capacitance per unit area in $\mu F/cm^2$ when a double layer is separated by a distance of 4Å in aqueous electrolyte solution. The permittivity of vacuum is 8.854×10^{-12} F/m and the permittivity of water is 78.
5. How are the symmetric factor and transfer coefficient related in a multistep reduction reaction?
6. Obtain the number of electrons that participate in the rate determining step of a reaction with the parameters: $\vec{\alpha} = 1$: $\vec{\gamma} = 1$ and $\gamma = 2$.
7. Mention the significance of polarization curve.
8. Define the term concentration over potential.
9. Write the equation which relates the diffusion current with the analyte concentration.
10. Distinguish between primary and secondary batteries.

Part-B

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

11. Determine the relationship between the mean ionic concentration $C_{\pm}$ and the ordinary molar concentration, C for binary electrolytes of the type 1:3 and 2:3.
12. Derive the Bronsted-Bjerrum equation for the effect of added salt on rate constants in ionic reactions.
13. Calculate the energy per unit area of an electric double layer for a surface potential of 40 mV in an aqueous solution containing 0.01 monovalent ions (Debye length is 30.4 nm).
14. Discuss the sedimentation potential of the moving particle in a medium.
15. Obtain the Tafel equation for the cathodic process of a multi step reaction.
16. Modify Butler-Volmer equation into an equation for potential as a function of concentration.
17. How are symmetric factor and equilibrium potential determined experimentally?

18. The exchange current density of $Pt/Cu^{2+}, Cu^{+}$ is 4.8 $mAcm^{-2}$. Calculate the net current density across the electrode at 25 ºC with a applied voltage of 2 V when $[Cu^{+}]$ = 0.1 M and $[Cu^{+}]$ = 0.2 M. (SRP = 0.15 V and β = 0.54)

19. Predict the conditions for i) an electrode to act as an anodic rectifier ii) the net current density to be independent of symmetric factor.

20. Discuss the influence of pH and polarization of the electrode surface on the rate of corrosion.

21. Explain with examples any two types of titration curves obtained in amperometry.

22. How will you compare the kinetics of the reaction $M \rightarrow M^{n+} + ne$ carried out at two over potentials + 0.3 V and - 0.3 V?

Part-C

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

23. Derive an expression for Debye-Huckel length and electrostatic potential, $\varphi_j(r)$.

24 a. Derive the Debye-Huckel-Onsager equation for strong electrolytes. (8+2)

b. At 25ºC the molar ionic conductivity of Na^{+} is 5.01 mSm^2mol^{-1}. Calculate its mobility.

25a. How is the differential capacitance of the electric double layer determined using the Gouy-Chapman diffuse-charge model? (6+4)

b. Calculate Stokes frictional force of the spherical object with 1 m radius, moving in a 1 Pa.s viscous fluid. The flow velocity relative to the object is 1 m/s.

26. The reduction of Fe^{2+} to Fe follows 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

How will you prove that the second step is the rate determining step?

27. a. Describe the construction and working of a solid oxide fuel cell. (6)

b. How will you express Nernst equation as a pH dependent equation for the redox system MnO_4^{-} / Mn^{2+} ? (4)

28 a. Discuss the steps involved in an anodic stripping voltammetry technique.

b. Predict the cathodic orders involved in the reduction process of I_3^{-}.

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