LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FOURTH SEMESTER – **APRIL 2024**

PCH 4502 – ELECTROCHEMISTRY

Date: 03-04-2024 Dept. No. Max. : 100 Marks

Time: 09:00 AM - 12:00 NOON

Part-A

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

1. State Bjerrum hypothesis for ion pair formation.
2. Find the osmotic pressure of 0.1 M aqueous solution of sodium chloride at 25°C. ($R = 0.0821$ atm L mol^{-1} K^{-1})
3. Diagrammatically represent the outer and inner Helmholtz planes.
4. Write the factors affecting zeta potential.
5. Mention the disadvantages of dropping mercury electrode used in polarography.
6. Prove that Faraday's law is a kinetic expression.
7. What is the condition for an electrode to behave as an anodic rectifier?
8. Define stoichiometric number.
9. How are the symmetric factor and transfer coefficient related in a multistep anodic oxidation process?
10. Mention the significance of pitting potential.

Part-B

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

11. Apply Born model to find the change in free energy of ion solvent interaction.
12. (a) Obtain the solution for the linearised Poisson-Boltzmann equation for interionic interactions.
    (b) For the cell reaction, $Zn + 2AgCl_{(s)} \rightarrow 2Ag + Zn^{2+} + 2Cl^-$, E^o cell at 298 K is 1.4 V. Evaluate ΔG^o, ΔH^o, and ΔS^o for the cell reaction if the temperature coefficient of cell EMF is equal to -2.54×10^{-4} VK^{-1}. (1 Faraday = 96500 C) (6+4)
13. Distinguish the following electrokinetic phenomena.
    (i) Electro osmosis and Electrophoresis
    (ii) Streaming and Sedimentation potentials (5+5)
14. (a) Explain the construction and working principle of solid oxide fuel cell.
    (b) Mention the various types of amperometric titration curves. (6+4)
15. (a) Discuss the Ohmic and non-Ohmic behavior of electrodes.
    (b) Compare the kinetics of the reaction $M^{n+} + ne^- \rightarrow M$ at the over potentials
    (i) – 0.2 V (ii) + 0.2 V (6+4)
16. Obtain the Butler-Volmer equation for an elementary electron transfer reaction and explain the modification of the equation when the over potential is zero.
17. (a) Discuss the low field and high field approximations of Butler-Volmer equation.
    (b) The exchange current density and the anodic symmetric factor of an electron transfer reaction are 1.26×10^{-5} Acm^{-2} and 0.53 respectively. Calculate the net current density at an over potential of -200 mV. (6+4)
18. Explain the following.
    (i) polarizable and non-polarisable electrodes.
    (ii) phase and activation over potentials. (5+5)

Part-C

Answer any TWO questions. **(2 × 20= 40)**

19. (a) Derive Debye-Huckel limiting law. Explain any one application of the law.
(b) Explain the theoretical background of Debye-Huckel-Onsager equation.
(c) Calculate the mean activity coefficient of 0.0015 M aqueous solution of calcium chloride at 298 K. (10+6+4)

20. (a) Discuss in detail Gouy-Chapman diffuse charge model of electrified interface. What are its limitations?
(b) Explain Wiens and Debye-Falkenhagen effects which are the evidences for the theory of electrolytic conductance.
(c) Find the thickness of ionic atmosphere for 0.01 M aqueous solution of KNO_3 at 25 ºC. (Dielectric constant of water is 78.6) (10+6+4)

21. (a) For a multistep electron transfer reaction,
(i) derive an expression for its cathodic current density
(ii) write the expression for its net current density and mention the terms involved.
(b) Calculate the potential at which $Cr_2O_7^{2-}$ is reduced to Cr^{3+} in a solution of pH = 5. Given: SRP of $Cr_2O_7^{2-}/ Cr^{3+}$ = + 1.33 V. (13+7)

22. (a) The reduction of triiodide to iodide takes place through the following mechanism.

$$I_3^- \leftrightharpoons I_2 + I^-$$
$$I_2 \leftrightharpoons 2I$$
$$2(I + e \leftrightharpoons I^-)$$

Evaluate the transfer coefficients and prove that the third step is the rate determining step.
(b) Explain the formation of various regions in a Pourbaix diagram with an example and mention its importance. (12+8)
