



Date: 17-06-2022

Dept. No.

Max. : 100 Marks

Time: 01:00 PM - 04:00 PM

PART A**Answer ALL questions.****10 x 2 = 20 marks**

- Calculate the thickness of the ionic atmosphere for 0.1 M BaCl₂ solution in water at 298 K (The dielectric constant of water is 78.5).
- Define the term solvation number.
- What is a non-polarizable interface? Give an example.
- What is sedimentation potential?
- Prove that electrochemical reactions follow zero order kinetics.
- Mention the condition for an electrode to show rectification behavior.
- Write the Nernst equation as a function of pH for the following redox equilibrium

$$4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}.$$
- What is breakdown potential? Mention its significance?
- How is the EMF of a battery influenced by the redox equilibrium?
- How is the migration current eliminated in polarography?

PART B**Answer ANY EIGHT questions.****8 x 5 = 40 marks**

- How are ion-ion interactions correlated with activity co-efficient of a species? Mention the limitations of Debye-Hückel limiting law.
- Write the expression to calculate hydration number of water using mobility method. For an electrical field of 0.05 Vm⁻¹ in an electrolytic solution, a drift velocity of 2 x 10⁹ ms⁻¹ is observed for an ion. Calculate the absolute velocity.
- Calculate the ΔG° and equilibrium constant for the cell at 298 K:
 Pt | I₂, I₂ || Fe²⁺, Fe³⁺ | Pt. $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.769 \text{ V}$, $E_{\text{I}_2/\text{I}^-}^0 = 0.534 \text{ V}$
- Discuss the merits and demerits of a parallel-plate condenser model of a double layer.
- Draw the Lippmann capillary electrometer and electrocapillary curve for q_m vs V . Mention their significances.
- Discuss the modification of the Butler-Volmer equation at zero over potential.
- The exchange current density of a certain electrode and its anodic symmetry factor are 0.80 mA cm⁻² and 0.504, respectively. Calculate the net current density at an over potential of -200mV.
- Derive an expression for the anodic current density in a multistep electrochemical reaction.
- Predict the values of anodic and cathodic transfer coefficients for the evolution of hydrogen in acidic solution having the following mechanism.

$$2\text{M} + 2\text{e}^- + 2\text{H}_3\text{O}^+ \rightleftharpoons 2\text{MH} + 2\text{H}_2\text{O} \text{ (slow)}$$

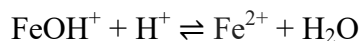
$$2\text{MH} \rightleftharpoons 2\text{M} + \text{H}_2 \text{ (fast)}$$
- The Tafel equation for the evolution of oxygen in acidic medium was found to be
 $i = i_0 e^{\frac{2(1-\beta)\eta F}{RT}}$. Calculate the value of the slope for the plot of η vs log i (Given: β = 1/4).
- What is over voltage? Explain phase and concentration over voltage.
- How is polarography helpful in determining the stability of a complex.

PART C

Answer ANY FOUR questions.

4 x 10 = 40 marks

23. Derive the Debye-Hückel-Onsager equation for an uni-univalent electrolyte. Mention the limitations of this equation.
24. (a) Derive an expression for an electro-osmotic mobility.
(b) Explain the salient features of the Stern model of electrified interface.
25. (a) 2 molal NaCl solution in water has elevation in boiling point of 1.88 K. If K_b for water is 0.52 K kg/mol, calculate the van't Hoff factor and degree of dissociation for NaCl.
(b) How will you discuss the kinetics of corrosion in different regions of the Pourbaix diagram of a metal?
26. (a) Explain the conditions for an electrochemical system to register equal and unequal currents anodically and cathodically. **(6)**
(b) The equilibrium constant for the reaction $X + ne^- \rightleftharpoons Y$ is 5.8×10^{20} at 298 K. The equilibrium concentrations of X and Y are 0.4 and 0.6 M respectively. Calculate the number of electrons involved in the reaction (Given applied potential = 0.608 V). **(4)**
27. Dissolution of iron is found to have the following mechanism. Prove that the second step is the rate limiting step.



28. (a) Explain the major differences between pulse and AC voltammetric techniques.
(b) What are Fuel cells? Discuss briefly the thermodynamics of Fuel cells. **(5+5)**
