

THE CATHOLIC UNIVERSITY OF EASTERN AFRICA

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MAIN EXAMINATION

SEPTEMBER –DECEMBER 2021

FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

REGULAR PROGRAMME

CHEM 309: ELECTROCHEMISTRY

Date: DECEMBER 2021

Duration: 2 Hours

INSTRUCTIONS: Answer Question ONE and any TWO Questions

Useful Information

$$F = 96490 \text{ C mol}^{-1}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$0^\circ \text{ C} = 273 \text{ K}$$

$$\ln x = 2.303 \log x$$

$$\text{At } 25^\circ \text{C} \quad \frac{2.303RT}{nF} = \frac{0.0591}{n}$$

- Q1. a) (i) Using the Debye-Huckel limiting equation, calculate the mean activity coefficient of 0.004M Zinc Sulphate. **(6 marks)**

$$\left(A = 0.51 \text{ mol}^{1/2} \text{ dm}^{3/2} \right) \text{ at } 25^\circ \text{C for aqueous solutions}$$

- (ii) Calculate the activity of 0.004M zinc sulphate. **(3 marks)**

- b) The conductivity of $1.25 \times 10^{-1} \text{ mol dm}^{-3}$ solution of a monobasic acid is $2.39 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$. Its molar conductivity of infinite dilution is

$400\Omega^{-1}cm^2mol^{-1}$. Calculate the degree of dissociation of the acid and its dissociation constant. **(6 marks)**

c) Briefly explain how the conductance of electrolytes can be measured. **(5 marks)**

d) Given

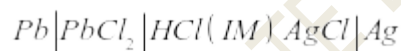
$$E^0(Co^{2+}|Co) = -0.2770V$$

$$E^0(Cc^{4+}|Cc^{3+}) = 1.610V$$

- (i) Represent the above information by a cell diagram. **(1 mark)**
- (ii) Determine E^0 for the cell **(2 marks)**
- (iii) Write the overall cell reaction and the Nernst expression for the cell. **(3 marks)**

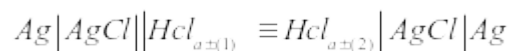
e) Discuss the principle involved in conductimetric titrations.

Q2. a) Given the following electrochemical cell **(4 marks)**



The emf at 298K is 0.490V. If the rate of change of emf with temperature is $1.8 \times 10^{-4}V/deg$. calculate;

- (i) ΔG of the cell **(2 marks)**
 - (ii) ΔH of the cell **(2 marks)**
 - (iii) ΔS of the cell **(2 marks)**
- b) A hydrogen electrode and normal calomel (reference electrode) electrode, gives an emf of 0.435V when placed in a certain solution of 25°C.
- (i) what is the pH of the solution? **(2 marks)**
 - (ii) what is the value of a_{H^+} ? **(2 marks)**
- c) For the following cell with transference



given emf the emf with transference at 298K is 0.0289V and that of corresponding cell without transference is 0.0169V. Calculate;

- (i) The transference number of H^+ and Cl^- ions **(6 marks)**
- (ii) The liquid junction potential **(2 marks)**
- (iii) By considering individual electrode reaction, write the overall cell reaction. **(2 marks)**

- Q3. a) The specific conductivity of a saturated sparingly soluble salt MSO_4 at $25^\circ C$ was found to be $4.63 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. That of pure water was $1.11 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$, calculate
- (i) The solubility of MSO_4 **(2 marks)**
 - (ii) The solubility product of MSO_4 **(2 marks)**

$$\Lambda^0_{MSO_4} = 287 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

- b) Briefly describe how the emf of an electrochemical cell can be determined. **(5 marks)**
- c) Calculate the equilibrium constant of the cell $Zn | Zn^{2+} || Fe^{3+}, Fe^{2+} | Pt$ at 298K given $Zn | Zn = -0.762V, Fe^{3+}, Fe^{2+} | Pt = 0.771V$ **(3 marks)**
- d) Briefly discuss the factors that affect the rate of which ions of an electrolyte carry charge. **(8 marks)**

- Q4. a) The resistance R, of an electrical conductor is proportional to its length and inversely proportional to its cross-sectional area (A). Derive a relationship between the conductivity (K) with current density (j) and electric field intensity (E). **(6 marks)**
- b) (i) State Kohlrausch law of independent ionic migration **(1 mark)**
 (ii) Discuss briefly the Arrhenius theory of ionization. Considering acetic acid show that the molar conductivity and the limiting molar conductivity at infinite dilution are related in the Ostwald's dilution relationship. **(6 marks)**
 - c) Explain how a hydrogen electrode is used to measure pH. **(7 marks)**

- Q5. a) (i) Briefly explain how the Hirtoff method is used to determine the transport numbers of ions in an electrolyte. **(6 marks)**
- (ii) Perform the analysis of the anode and cathode compartments when IF of electricity is passed through a solution of copper (II) chloride using platinum electrodes. **(6 marks)**
- b) A one liter solution of sea water was analysed and found to have the following ionic components.
- 29.31g of NaCl, 1.83g of MgSO₄, 3.99g of MgCl₂, 1.34g of CaSO₄ and 0.85g of K₂SO₄.
- Calculate the ionic strength of this solution.
- Na=23, Mg = 24, Ca=40, K=39, Cl=35.5, S=32 and O=16. **(6 marks)**
- c) Define Over-potential. **(2 marks)**

END

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