

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 325: ELECTROCHEMISTRY

STREAMS: BSC CHEM

TIME: 2 HOURS

DAY/DATE: WEDNESDAY 08/04/2020

8.30 A.M. – 10.30 A.M.

INSTRUCTIONS:

Answer question ONE and any other TWO questions.

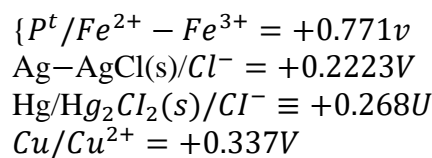
USEFUL DATA

IF = G6500 C

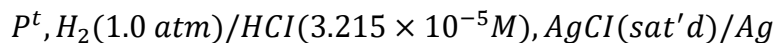
IR = 8.316 J mol⁻¹ K⁻¹

1. (a) Briefly explain the following terms
 - (i) Electrochemical cell ($\frac{1}{2}$ mark)
 - (ii) Electrode potential ($\frac{1}{2}$ mark)
 - (iii) Electromotive Force (EMF) ($\frac{1}{2}$ mark)
 - (iv) Standard reduction potential ($\frac{1}{2}$ mark)
- (b)
 - (i) Explain how you can increase the value of reduction potential. (1 mark)
 - (ii) Why do electrochemical cells stop working after some time? (1 mark)
 - (iii) Why is hydrogen electrode not generally used in pH measurement? ($1\frac{1}{2}$ mark)
 - (iv) The e.m.f. of the cell $Tl|TlCl(s)|KCl(0.1M)|Hg_2Cl_2(s)|Hg$ is 0.73 volts and $dE/dT = 7.5 \times 10^{-4}$

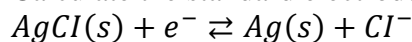
- (I) Write the individual electrode reaction and the overall cell reaction. (1½ marks)
- (II) Calculate enthalpy change (ΔH), change in Gibbs free energy (ΔG) and entropy change (ΔS) $\{F = 96500C\}$ (3½ marks)
- (c) Give the cell reactions of the following cells and calculate their standard e.m.f. at 25° C



- (i) $Hg/Hg_2Cl_2(s)/Cl^- || Cu^{2+}/Cu$ (1½ marks)
- (ii) $Pt/Fe^{2+}, Fe^{3+} // Cl^- / AgCl(s) / Ag$ (2 marks)
- (iii) The cell without liquid junction given below has a potential of 0.52053V



Calculate the standard electrode potential for the half-reaction



{The effective diameter of the hydrated ion in nanometers for H^+ , Cl^- are 0.9, 0.3 respectively} (8 marks)

- (d) (i) Describe the construction and working of the calomel electrode. (8 marks)

QUESTION TWO (20 MARKS)

2. (a) (i) Briefly discuss the factors that influence transport numbers. (6½ marks)
- (ii) In a moving boundary experiment 0.002 M HCl solution was floated on a lithium chloride solution. The tube used had a diameter of 2 cm. When a current of 8 milliamperes was passed for 40 minutes the H^+ ions $-Li^+$ ions boundary moved through 26.8 cm. Calculate the transport number of H^+ and Cl^- ions in the HCl solution used. (2½ marks)
- (iii) A solution of $AgNO_3$ was electrolyzed with silver electrodes. Before electrolysis 25 g of the solution contained 26.50 mg of silver while after electrolysis 25 g of anode solution contained 42.94 mg of silver. During the time of electrolysis 32.10 mg. of silver was deposited in a silver voltameter. Calculate the transport number. (4½ marks)

- (b) (i) Give a brief outline of the main ideas of Debye-Huckel theory. ($2\frac{1}{2}$ marks)
- (ii) The specific conductance of a saturated aqueous solution of barium sulphate at 298 k is $1.84 \times 10^{-3} \text{ sm}^{-1}$ and that of water is $1.60 \times 10^{-4} \text{ sm}^{-1}$. The ionic conductivities at infinite dilution of Ba^{2+} and SO_4^{2-} ions at 298k are $63.6 \times 10^{-4} \text{ sm}^2 \text{ mol}^{-1}$ and $79.8 \times 10^{-4} \text{ sm}^2 \text{ mol}^{-1}$ respectively. Calculate the solubility and solubility product of barium sulphate at 298k. (2 marks)
- (iii) Explain the principle behind conductometric titrations. (1 mark)
- (iv) Why does the conductivity of the solution rise quickly after the equivalence point. (1 mark)

QUESTION THREE (20 MARKS)

3. (a) (i) Explain what you understand by temperature compensation (reference temperature conversion) or a test solution in conductivity measurement. (3 marks)
- (ii) Discuss the effect of dilution on the equivalent and molar conductance. ($6\frac{1}{2}$ marks)
- (iii) State Kohlrausch law of independent migration of ions. ($\frac{1}{2}$ mark)
- (b) Conductivity cell of cell constant 1 cm^{-1} shows a resistance of 6667 ohms when filled with 0.001M KCl solution at 25°C . The same cell records a resistance of 2353 ohms when filled with 0.001 m HCl solution at 25°C .
- (i) Calculate equivalent conductance values for KCl and HCl solutions. (3 marks)
- (ii) Calculate ion concentration of H^+ assuming that K^+ and Cl^- have the same mobility considering the solutions to be infinitely dilute. ($1\frac{1}{2}$ marks)
- (iii) How far will H^+ move in 10 seconds when a potential difference of 2 volts is applied between two electrodes placed 2 cm part. ($2\frac{1}{2}$ marks)
- (c) Using appropriate values from table 1 below
- (i) Calculate the equivalent conductance at infinite dilution of NH_4OH , CH_3COOH and H_2O at 25°C . ($1\frac{1}{2}$ marks)
- (ii) Λ_0 values of HCl, NaCl, CH_3COONa be respectively 426.1, 126.4 and 91.0. Calculate equivalent conductance at infinite dilution (Λ_0) ($\frac{1}{2}$ mark)

- (iii) Equivalent conductance of benzoic acid in a 0.10 M solution is $8.8 \text{ s-cm}^2\text{-equiv}^{-1}$ at 25°C . The equivalent ionic conductance of benzoate ion at infinite dilution at 25°C is $32.3 \text{ s cm}^2 - \text{equiv}^{-1}$. Calculate the degree of dissociation of benzoic acid in 0.10M solutions at 25°C . (1 mark)

Table (1)

Equivalent ionic conductances at infinite dilution at 25°C

Cations	λ_+^0	Anions	λ_-^0
H^+	349.8	OH^-	197.6
K^+	73.52	CH_3COO^-	40.9
Na^+	50.11	HCO_3^-	44.5
NH_4^+	73.4	Cl^-	76.3

QUESTION FOUR (20 MARKS)

4. (a) Briefly explain a reason for the following statements:
- Very dilute solutions can be titrated by amperometric method. ($\frac{1}{2}$ mark)
 - A rotating platinum electrode has largely confined its employment to anodic reactions. (1 mark)
 - Amperometric titration is capable of greater accuracy than non-titrative polarographic method. ($\frac{1}{2}$ mark)
 - The use of rotating platinum electrode in place of the DME (Dropping Mercury Electrode) in titration increases sensitivity. ($\frac{1}{2}$ mark)
 - The number of titrations to which the amperometric method can be applied is much greater than that for potentiometric titration. ($1\frac{1}{2}$ mark)
- (b) (i) To determine the purity of a sample of $Na_2S_2O_3$, a sample is titrated coulometrically using I^- as a mediator and I_3^- as the titrant. A sample weighing 0.1342 g is transferred to a 100 ml volumetric flask and diluted to volume with distilled water. A 10.00 ml portion is transferred to an electrochemical cell along with 25 ml of 1 M KI, 75 ml of a pH 7.0 phosphate buffer and several drops of a starch indicator solution. Electrolysis at a constant current of 36.45 mA requires 221.8 s to reach the starch indicator end point. Determine the sample's purity.
{ $F = 96487 \text{C mol}^{-1}$ } ($3\frac{1}{2}$ marks)
- (ii) Write short notes on chronopotentiometry. (4 marks)

- (c) Cyclic voltammetry of ferrocene carboxylic acid was performed and the results obtained are shown in the figure below.

- (i) Suggest some possible sources of errors which contributed to DEP not being approximately 59 mV as expected. (1½ marks)
- (ii) What happens to the peak current (i_p) as the potential scan rate (v) changes? Explain why this occurs? (1½ marks)
- (iii) Why do current signals decay after the peak currents (i_p) are reached, even though Oxidizing or reducing potentials are still being applied to the working electrode? Why is this more pronounced at faster scan rates? (1 mark)

- (iv) What do you predict will occur if a working electrodes with a smaller surface area is used to perform cyclic voltammetry? What would be the advantages and disadvantages of using the smaller electrodes? (2 marks)
- (d) (i) Outline the features of the polarogram. (2 marks)
- (ii) State basic problems with the DC polarogram. ($\frac{1}{2}$ mark)
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