



MACHAKOS UNIVERSITY

University Examinations 2019/2020 Academic year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

FOURTH YEAR FIRST SEMESTER EXAMINATION FOR

BACHELOR OF EDUCATION (SCIENCE)

SCH 401: ELECTROCHEMISTRY

DATE: 29/11/2019

TIME: 8.30-10.30 AM

INSTRUCTIONS TO CANDIDATES

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 20 marks).

Required data

- $F = 96500 \text{ C}$
- Atomic mass of Cu = 64, Ag = 107, N = 14, O = 16

SECTION A - COMPULSORY.

QUESTION ONE (30 MARKS)

- a) Explain the following terms as used in electrochemistry:
- Mobility of an ion (1 mark)
 - Transference number (1 mark)
 - Molar conductivity (1 mark)
 - Standard electrode potential (1 mark)
 - Faradaic current (1 mark)
- b) Given the metals zinc and copper and solutions of $\text{Zn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ at 25 °C;
 $(\text{Zn}^{2+}(0.01 \text{ M})/\text{Zn}, E^\theta = -0.762 \text{ V}$ and $\text{Cu}^{2+}(0.01 \text{ M})/\text{Cu}, E^\theta = +0.337 \text{ V})$,
- Construct a cell which will operate spontaneously (give your answer in short-hand notation) (1 mark)
 - Write the equations at the anode, cathode and the overall reaction (3 marks)
 - Calculate the E^θ cell (2 marks)
 - Calculate the ΔG^θ of the reaction (2 marks)
 - Given that the concentration of $\text{Zn}(\text{NO}_3)_2$ is 0.01 M and $\text{Cu}(\text{NO}_3)_2$ is 0.05 M, calculate the EMF of the cell (3 marks)
 - Calculate the equilibrium constant (K_{eq}) for the reaction (2 marks)
- c) In a Hittorf cell experiment, a solution of silver nitrate was electrolysed between silver electrodes. The amount of silver nitrate in the anode compartment was 0.227 g before electrolysis and 0.2819 g after electrolysis. During electrolysis, 0.0194 g of copper was deposited on the cathode of copper coulometer in series with the Hittorf cell.
- Calculate the transport number of Ag^+ and NO_3^- ions . (3 marks)
 - Which of the ions (between Ag^+ and NO_3^-) carry majority of the current? (1 mark)
- d) The ability of electrolytic solution to conduct an electric current is the evidence that different electrolytes have different abilities to conduct electric current. Explain four factors that affect the electrical conductance of an electrolyte (8 marks)

SECTION B: ANSWER ANY TWO QUESTIONS

QUESTION TWO (20 MARKS)

- a) Explain how a fourth-year chemistry student would be able to determine the transport number of H^+ ions in an aqueous solution of HCl using moving boundary method. Include diagrams and equations where necessary (7 marks)
- b) In a moving boundary experiment a current of 1.6 mA was applied to 0.02 M NaCl solution at 25 °C using $\text{CdCl}_{2(\text{aq})}$ as the indicator solution. It was found out that the boundary had moved 10 cm in 3453 seconds in a tube of cross-sectional area 0.1115 cm^2 . The conductivity of the sodium chloride at 25 °C was $2.313 \times 10^{-3} \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Calculate:
- The transport number of Na^+ ions (4 marks)
 - The mobility of Na^+ ions (3 marks)
- c) Using relevant examples, explain the following types of electrodes used in electrochemical analysis;
- Electrodes of the first kind (2 marks)
 - Electrodes of the second kind (2 marks)
 - Redox electrodes (2 marks)

QUESTION THREE (20 MARKS)

- a) i) Using examples, distinguish between chemical cells with transference and chemical cells without transference (4 marks)
- ii) Given the following cell;
- $$\text{Ag} / \text{AgCl} / \text{HCl} (a_1) / \text{HCl} (a_2) / \text{AgCl} / \text{Ag}$$
- If the EMF of the cell with transference at 298 K is 0.02802 V and the EMF of the corresponding cell without transference is 0.01696 V. Calculate the transport number of;
- The hydrogen ions (4 marks)
 - The chloride ions (1 mark)
- b) The variation of molar conductivities with concentrations of an aqueous solution of a given salt is as shown in the table below;

Concentration (mol dm^{-3})	0.0005	0.001	0.005	0.01	0.02	0.05	0.1
Molar conductivity ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	131.4	130.5	127.2	124.8	121.4	115.2	109.1

- i) By plotting a graph, determine the molar conductance at infinite dilution of the solution (7 marks)
- ii) Calculate the apparent degree of ionization (α) for the solution at concentration of $0.015 \text{ mol dm}^{-3}$ (2 marks)
- iii) Based on information in Q 2c ii) classify the above solution. Justify your answer (2 marks)

QUESTION FOUR (20 MARKS)

- a) State the Kohlrausch law of independent migration of ions (2 marks)
- b) The table below shows the conductance data at infinite dilution at 25°C .

Electrolyte	$\lambda \text{ (}\Omega^{-1}\text{cm}^2\text{mol}^{-1}\text{)}$
Sodium butyrate (NaBu)	82.6
Hydrochloric acid (HCl)	426.2
Sodium Chloride (NaCl)	126.5

- Calculate the molar conductance of Butyric acid (HBu) at infinite dilution. (3 marks)
- c) Electrical biosensors have been the subject of basic and applied research for over fifty years. State and explain three types of electrochemical biosensors outlining their working principles (9 marks)
- d) Discuss quantitatively the way in which conductivity and molar conductivity changes with increase in dilution for strong, intermediate and weak electrolytes (6 marks)

QUESTION FIVE (20 MARKS)

- a) Explain the working and the electrochemistry principles of;
 - i. Alkaline fuel cells (5 marks)
 - ii. Phosphoric acid fuel cells (5 marks)
- b) Explain the basic working principles of the following electroanalytical techniques:
 - i) Anodic stripping voltammetry (5 marks)
 - ii) Polarography (5 marks)