MACHAKOS UNIVERSITY

University Examinations for 2021/2022 Academic Year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR SECOND SEMESTER EXAMINATION FOR

BACHELOR OF SCIENCE (ANALYTICAL CHEMISTRY)

SAN 310: ELECTROCHEMISTRY

DATE: **TIME:**

INSTRUCTIONS:

- 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 C
- Atomic mass of Cu = 64, Ag = 107, N = 14, O = 16

SECTION A – COMPULSORY

QUESTION ONE (30 MARKS)

a) Define the following terms as used in electrochemistry:

i) Transport number (1 mark)

ii) Molar conductivity (1 mark)

iii) Mobility of an ion (1 mark)

iv) Degree of ionization (1 mark)

v) Electrolysis (1 mark)

b) i) Distinguish between faradaic and non-faradaic currents (2 marks)

ii) 5 g of copper were deposited when a current of 0.120 A was passed through a solution of copper (II) sulphate using copper electrodes (Cu = 64). Determine the time taken to deposit the 5 g of copper. (3 marks)

iii) In a moving boundary experiment a current of 1.6 mA was applied to 0.02 M NaCl solution at 25 ºC using $CdCl_2$ 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 ºC was 2.313 x 10^{-3} $\Omega^{-1}cm^2mol^{-1}$. Calculate:

i) The transport number of Na^+ ions (3 marks)

ii) The mobility of Na^+ ions (2 marks)

iv) 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.

i) Calculate the transport number of Ag^+ and NO_3^- ions (4 marks)

ii) Which of the ions (between Ag+ and NO_3^-) carry majority of the current? (1 mark)

v) Given the metals silver and copper and solutions of $AgNO_3$ and $Cu(NO_3)_2$ at 25 ºC;

(Cu^{2+}/Cu, E^{θ} = +0.337 V and Ag+/Ag, E^{θ} = +0.7991 V),

i) Construct a cell which will operate spontaneously (give your answer in short-hand notation) (1 mark)

ii) Write the equations at the anode, cathode and the overall reaction (3 marks)

iii) Given that the concentration of $Cu(NO_3)_2$ is 0.01 M and $AgNO_3$ is 0.05 M, calculate the EMF of the cell (3 marks)

iv) Calculate the equilibrium constant (K_{eq}) for the reaction (2 marks)

v) Calculate the ΔG^o of the cell reaction (1 mark)

SECTION B: ANSWER ANY TWO QUESTIONS

QUESTION TWO (20 MARKS)

a) The principles of conductance and resistance are key in the analysis of electrolytes. Explain five (5) factors that determine the conductance of an electrolyte (10 marks)

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 ($\Omega^{-1}cm^2mol^{-1}$)	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 (6 marks)

ii) Calculate the apparent degree of ionization (α) for the solution at concentration of 0.015 mol dm^{-3} (2 marks)

iii) Based on information from Q 2b ii) classify the above solution. Justify your answer (2 marks)

QUESTION THREE (20 MARKS)

a) An electrolyte is one of the key components of an electrochemical cell;

i) Distinguish between a strong electrolyte and a weak electrolyte. (2 marks)

ii) Briefly describe any **two** roles of a supporting electrolyte in an electrochemical cell. (2 marks)

iii) Describe **three** modes of mass transfer in an electrochemical cell. (6 marks)

b) A third year student pursuing a course in Analytical Chemistry was interested in determining the transference number of Na^+ ions in an aqueous solution of NaCl using moving boundary method. Using appropriate diagrams and equations where necessary, explain how the third year student would achieve the transference number. (6 marks)

c) Given the following cell with transference;

$Ag/AgCl/HCl\ (a_1)/HCl\ (a_2)/AgCl/Ag$

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 and chloride ions (4 marks)

QUESTION FOUR (20 MARKS)

Explain the basic working principles of the following electroanalytical techniques:

i) Anodic stripping voltammetry (4 marks)

ii) Polarography (4 marks)

iii) Cyclic voltammetry (4 marks)

iv) Chronoamperommetry (4 marks)

v) Chronocoulommetry (4 marks)

QUESTION FIVE (20 MARKS)

a) Fuel cells are electrochemical cells that convert the chemical energy of a fuel into electricity;

i) Describe two (2) advantages of fuel cells over conventional energy sources (4 marks)

ii) Explain the working and the electrochemistry principles of;

I) Alkaline fuel cells (5 marks)

II) Phosphoric acid fuel cells (5 marks)

b) State and explain **three** types of electrochemical biosensors (6 marks)