

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

**EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF
SCIENCE AND BACHELOR OF EDUCATION (SCIENCE)**

CHEM 325: ELECTROCHEMISTRY**STREAMS: BSc, B.ED (SCI)****TIME: 2 HOURS****DAY/DATE: WEDNESDAY 20/12/2023****11.30 A.M. – 1.30 P.M.****INSTRUCTIONS**

- Answer question *one* and any other *two* questions

[*Constants: $F = 96500 \text{ C mol}^{-1}$ $2.0303RT/F = 0.0592\text{V}$]*

QUESTION ONE [30 marks]

- a) (i). On what basis are electrical materials classified? **[2 marks]**
- (ii) Explain why the resistance of a metallic conductor increases on raising the temperature while that of electrolytic conductor decreases on raising the temperature. **[2.5marks]**
- b) (i). Enumerate the major differences between metallic and electrolytic conductors. **[5marks]**
- (ii) Illustrating with a diagram, account for the differences in conduction process of a metallic conductor, semiconductor and an insulator **[3 marks]**
- c). Distinguish between the following pairs. Show how they are related and

give their units of measurement [4.5 marks]

(i). Resistivity and Cell Constant

(ii) Conductance and Conductivity

(iii) Molar conductance and Specific Conductance

d). Calculate the ionic strength and the mean activity of the following electrolytes [5 marks]

(i) 0.5M BaCl₂ (mean activity coefficient (γ_{\pm}) of BaCl₂ = 0.034)

(ii) 0.5M LaCl₃ (mean activity coefficient (γ_{\pm}) of LaCl₃ = 0.056)

e). A conductivity cell was calibrated by filling it with 0.02M solution of KCl whose conductivity is 0.0278Ω⁻¹ cm⁻¹. The resistance was found to be 457.3Ω. The cell was filled with CaCl₂ solution containing 0.555g of CaCl₂ per litre. The measured resistance was 1050 Ω. Calculate

(i). The cell constant for the cell [2 marks]

(ii). The conductivity of CaCl₂ solution [3 marks]

(iii). The molar conductance of CaCl₂ at this concentration [3 marks]

[Atomic mass: Ca = 40.08 Cl = 35,45]

QUESTION TWO [20marks]

a) Outline the experimental procedure for the determination of conductance of an electrolytic solution. Why is an AC rather than a DC current employed in this experiment? [4 marks]

b)(i).State Kohlrausch's law of independent ion migration [2 marks]

(ii). Mention and briefly explain applications of Kohlrausch's law of independent migration of ion migration [4 marks]

(iii).The molar conductance of a weak electrolyte at infinite dilution (Λ^0_m)

cannot be determined by extrapolation of the plot of (Λ_m) against concentration. However, that of a strong electrolyte can. Explain with the help of a diagram . **[3 marks]**

c). At 25°C a solution of KCl having a conductivity of $0.014088 \Omega^{-1} \text{cm}^{-1}$ exhibits a resistance of 654Ω in a given conductivity cell. In this same cell, a 0.10 M solution of NH_4OH has a resistance of **2554 Ω** . Given that the limiting molar ionic conductivities are: $\lambda^\circ \text{NH}_4^+ = 73.52 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ and $\lambda^\circ \text{OH}^- = 198.3 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Calculate

(i) The cell constant **[2 marks]**

(ii) The molar conductance of 0.10 M NH_4OH **[3 marks]**

(iii) The degree of dissociation of 0.10M NH_4OH **[2 marks]**

d). At 18 °C the specific conductance of a saturated solution of AgCl in water was $2.40 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. Given that the molar conductance at infinite dilution of $\text{AgNO}_3 = 116.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ of $\text{NaCl} = 110.3 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ and $\text{NaNO}_3 = 105 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ and on assumption that AgCl is completely dissociated in solution, calculate

(i). The solubility of AgCl **[3 marks]**

(ii) The solubility product of AgCl **[2 marks]**

QUESTION THREE [20marks]

a) (i). State the main postulates on which Debye – Huckel theory of interionic attraction for strong electrolytes is based. **[2.5 marks]**

(I). Briefly discuss the relaxation (asymmetric effect) **[3 marks]**

(II). Electrophoretic effect **[2 marks]**

b). Conductometric measurements are used to determine the end points of acid base titrations. Sketch and discuss the conductometric titrations curves of the following acid–base reactions : (i) HCl and NaOH (ii) CH₃COOH and NaOH

[3 marks]

b).(i) What do you understand by the term transport number of an ion.

[2 marks]

(ii) In a moving boundary experiment to determine transport number of K⁺ and Cl⁻, 0.2M KCl was floated in 0.65M LiCl indicator solution in a tube of diameter 4.15mm. A steady current of 1.82mA was passed and the formed boundary was observed to have moved a distance of 6.4mm in 20 minutes.

Calculate the transport number of K⁺ and Cl⁻

[4 marks]

c). Given the following standard half reactions and their standard reduction potentials

Half cell reaction	E⁰(V)
(i). Br ₂ (l) + 2e \longrightarrow 2Br ⁻	1.09
(ii) Fe ³⁺ _(aq) + e \longrightarrow Fe ²⁺ _(aq)	0.77
(iii) MnO ₄ ⁻ _(aq) + 8H ⁺ + 5e \longrightarrow Mn ²⁺ _(aq) + H ₂ O	1.51
(iv). Cu ²⁺ _(aq) + 2e \longrightarrow Cu(s)	0.34
(v). O ₂ (g) + H ⁺ _(aq) + 4e \longrightarrow 2H ₂ O	1.23

i) Identify the strongest and the weakest oxidizing agent. Give reasons for your answer

[2 marks]

(ii) Arrange the above substances in order of the increasing strength of oxidizing agent.

[1.5marks]

QUESTION FOUR [20marks]

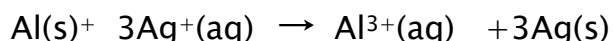
a) (i). Distinguish between a galvanic (voltaic) cell and electrolytic cell

[1.5marks]

(ii) Explain why is it necessary to use a salt bridge or a porous disc in a galvanic cell?. Give suitable electrolytes that are used as salt bridge and their characteristics

[1.5marks]

b).A galvanic cell utilizes the following reaction



What is effect on the cell emf of each of the following changes

(i). Water is added to the anode compartment diluting the solution [1.5marks]

(ii)The size of the aluminum electrode is increased [1.5marks]

(iii) A solution of AgNO₃ is added to the cathode compartment increasing quantity of Ag⁺ but not changing its concentration [1.5marks]

(iv). HCl is added to the AgNO₃ solution, precipitating some of the Ag⁺ as AgCl [1.5marks]

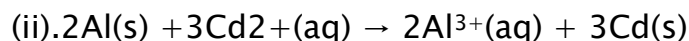
c) (i). How are the Gibb's free energy change and cell electromotive force related? [1 mark]

(ii). Explain what happens to E_{cell} when a battery is charged and as it discharges in relation to changes in Gibb's free energy [1 marks]

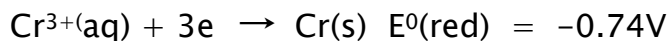
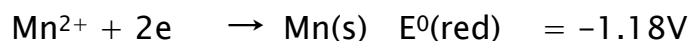
d) Write the anode and cathode half reactions and the respective standard shorthand notation for the galvanic cells that use the following reactions

[2.5marks]

(i). $\text{Cd(s)} + \text{Sn}^{2+}(\text{aq}) \rightarrow \text{Cd}^{2+}(\text{aq}) + \text{Sn(s)}$



(d) A galvanic cell is to be designed at standard –state conditions using the following two half reactions



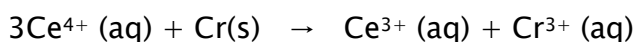
(i). write a balanced chemical equation describing the spontaneous cell reaction
[2 marks]

(ii). calculate the E°_{cell} and ΔG° of the above cell (2.5marks)

(iii) Sketch a diagram showing the above galvanic cell based on the overall cell reaction Label all the components and indicate the direction of the electron flow and the direction of ion migration. Identify the cathode and the anode [2 marks]

QUESTION FIVE [20marks]

(a) A galvanic cell utilizes the following reaction and operates at 298K



(i). Write the two half–cell reactions [2 marks]

(ii). Write the overall cell reaction [2 marks]

(iii) Calculate E°_{cell} of the cell [2 marks]

(iv) What is the emf of the cell when $[\text{Ce}^{4+}] = 2.0\text{M}$ $[\text{Ce}^{3+}] = 0.01\text{M}$ and
 $[\text{Cr}^{3+}] = 0.01\text{M}$ [3 marks]

(v) What is the emf of the cell when $[\text{Ce}^{4+}] = 0.35\text{M}$ $[\text{Ce}^{3+}] = 0.85\text{M}$ and
 $[\text{Cr}^{3+}] = 1.2\text{M}$? [3 marks]

(vi.) What is the equilibrium constant for the cell reaction at 298K [2 marks]

(vii). If the temperature coefficient of the cell is $1.86 \times 10^{-4}\text{V}/\text{degree}$ calculate

ΔG , ΔH and ΔS for the reaction

[6 marks]

