CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

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

CHEM 325: ELECTROCHEMISTRY

STREAMS: **TIME: 2 HOURS**

DAY/DATE: MONDAY 23/12/2024 **11.30 A.M – 1.30 P.M**

INSTRUCTIONS: ANSWER QUESTION ***ONE*** AND ANY OTHER **T*WO*** QUESTIONS

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

QUESTION ONE [30 Marks]

(a)(i). Define an electrical current and show what constitutes the flow of current in a given conductor? **[3marks]**

(ii). Discuss the main differences between metallic and electrolytic conductors**.** **[5marks]**

(b) (i) Illustrating with a sketch, account for the differences in conduction process of a metallic conductor, semiconductor and an insulator and elaborate why copper is a metallic conductor while silicon is a semiconductor **[3marks]**

c). Distinguish between the following pairs, show how they are related and give their units. [**4marks]**

(i). Resistivity and Cell Constant

(ii) Conductance and Conductivity

(iii) Molar conductance and conductivity

d) Give explanations to **ANY TWO** of the following observations. **[4marks].**

(i) The resistance of a metallic conductor increases on raising the temperature while that of electrolytic conductor decreases on raising the temperature.

(ii) Experimental determination of conductance of an electrolyte employs use of an AC current rather than a DC current.

(iii) When the concentration of an electrolyte is increased its conductivity increases but it its molar conductance decreases.

(iv). The limiting molar conductances of hydrogen and hydroxyl ions are much greater than those of other ionic species. **[2marks]**

(e). Discuss briefly the Arrhenius theory of electrolytic dissociation and rationalize its weakness. **[4marks]**

(f). Calculate the ionic strength and the mean activity of 0.05M Na_3PO_4 (mean activity coefficient ($Y_{\pm}$) of Na_3PO_4 =0.066) **[5marks]**

QUESTION TWO. [20marks]

a) Outline the experimental procedure for the determination of conductivity of an electrolytic solution and show how it is related to the molar conductance. Why is an AC rather than a DC current employed in this experiment? **[4marks]**

(b). A conductivity cell was calibrated by filling it with 0.02M solution of KCl whose conductivity is $0.0278\Omega^{-1}$ cm^{-1}. The resistance was found to be 457.3Ω. The cell was filled with $CaCl_2$ solution containing 0.555g of $CaCl_2$ per litre. The measured resistance was 1050 Ω. Calculate

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

(ii). The conductivity of $CaCl_2$ solution. **[3marks]**

(iii). The molar conductance of $CaCl_2$ at this concentration. **[3marks]**

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

(c). At $25^{O}C$, a solution of KCl having a conductivity of 0.014088 Ω^{-1} cm^{-1} exhibits a resistance of 654 Ω in a given conductivity cell. In this same cell a

0.10M solution of NH_4OH has a resistance of 2554 Ω. Given that the limiting molar ionic conductivities are: λ^o_{NH4+} = 73.52 Ω^{-1} cm^2mol^{-1} and λ^o_{OH-} = 198.3 Ω^{-1} cm^2mol^{-1}calculate

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

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

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

(d). At 18^0C, the conductivity of a saturated solution of silver chloride in water was $2.40x10^{-6}$ $\Omega^{-1}cm^{-1}$ and that of water used to prepare it is$1.6 x10^{-6}$ $\Omega^{-1}cm^{-1}$. Given that the molar conductance at infinite dilution of $AgNO_3$ = 116.5 $\Omega^{-1}cm^2mol^{-1}$, of NaCl = 110.3 $\Omega^{-1}cm^2mol^{-1}$ and of $NaNO_3$ = 105 $\Omega^{-1}cm^2mol^{-1}$ and assuming that AgCl is completely dissociated in solution, calculate

(i) Solubility of AgCl **[4marks]**

(ii) Solubility product of AgCl **[2marks]**

d) Sketch and discuss the conductmetric titrations curves of the following acid-base pairs:
[4marks]

(i) HCl and NaOH (ii) CH_3COOH and NaOH

QUESTION THREE [20marks]

a) (i). State Kohlrausch's law of independent ion migration and briefly explain

its applications. **[3marks]**

(ii). The values of molar conductance at infinite dilution (Λ^0_m) for HCl, NaCl NaAc (Sodium acetate) are 420, 126 and 91 $\Omega^{-1}cm^2mol^{-1}$respectively. A conductivity cell filled with 0.1M acetic acid gave resistance of 510 Ω and drops to 120 Ω when enough solid NaCl is added to make the solution 0.1M.

Determine

(i). Cell constant of the conductivity cell **[1.5marks]**

(ii) Molar conductance at infinite dilution of acetic acid. **[2marks]**

(iii). The degree of dissociation of acetic acid [**1.5marks]**

b) (i)Enumerate the main postulates that governs Debye –Huckel –Onsager theory of interionic attraction for strong electrolytes. **[2marks]**

(ii) Write Debye-Huckel- Onsager equation and explain the terms in the

Equation.
[1.5marks]

c). Briefly discuss the following

(i). Relaxation or asymmetric effect **[2.5marks*]***

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

d)(i) Explain the meaning of the term transport number of an ion. **[1.5marks]**

(ii) The boundary formed between aqueous solution of 0.001M HCl and NaCl contained in a vertically mounted tube of internal diameter 5mm moved a distance of 7.2mm in 5 minutes with a constant current flow of 5.5mA. Calculate the transport number of hydrogen and chloride ion**.** **[3marks]**

QUESTION FOUR (20 MARKS)

(a) Use the reaction given below to answer questions that follow

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Distinguish between the following pairs

(i) Oxidation and reduction. On which side of an oxidation half reaction and reduction half reactions do the electrons appear? **[2 marks]**

(ii) Oxidizing and reducing age**n**ts [**2 marks]**

(iii) Show by an arrow which substance is oxidized and which substance is reduced. Give reasons for your answer **[2 marks**].

(iv) Which substance acts as oxidizing agent and which substance acts as a reducing agent? Give reasons for your answer. **[2 marks]**

(b) Balance ***ANY ONE*** of the following oxidation-reduction reactions that occur in acidic solution using the half-reaction method **[3 marks]**.

(i) Cu(s) + $HNO_3(aq) \longrightarrow Cu^{2+}(aq) + NO(g)$

(ii) $Cr_2O_7^{2-}(aq) + Cl^-(aq) \longrightarrow Cr^3 + (aq) + Cl_2(g)$

(c) Specify which of the following are oxidation-reduction reactions and identify the oxidizing agent, the reducing agent, the substance being oxidized and the substance being reduced. **[5 marks]**

(i) Zn (s) + 2HCl$(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

(ii) $Cr_2O_7^{2-}(aq) + 2OH\text{-}(aq) \rightarrow 2CrO_4^{2-}(aq) + H_2O(I)$

(iii) $O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$

(iv) $2H_2O_2(I) \rightarrow 2H_2O(I) + O_2(g)$

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

Half cell reaction	E^0(V)
(i). $Br_2(l) + 2e \longrightarrow 2Br^-$	1.09
(ii) $Fe^{3+}_{(aq)} + e \longrightarrow Fe^{2+}(aq)$	0.77
(iii) $MnO^-_{4(aq)} + 8H^+ + 5e \longrightarrow Mn^{2+}(aq) + H_2O$	1.51
(iv). $Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$	0.34
(v). $O_2(g) + H^+(aq) + 4e \longrightarrow 2H_2O$	1.23

i) Identify the strongest and the weakest oxidizing agent. Give reasons for your answer.
[2.5marks]

(ii)Arrange the above substances in order of the increasing strength of oxidizing agent. **[1.5marks]**

QUESTION FIVE (20 MARKS)

(a) Distinguish between a galvanic cell and an electrolytic cell **[2 marks]**

(b) A galvanic cell operates using the following reaction

$Al(s) + Cd^{2+}(aq) \longrightarrow Al^{3+}(aq) + Cd(s)$

(i) Write the individual cell reactions **[1 mark]**

(ii) Write the overall cell reaction **[1 mark]**

(iii) Calculate E^{o}_{cell} of the cell **[1 mark]**

(iv) What is the emf of the cell when: $\left[Cd^{2+}\right] = 3.00M$ and $\left[Al^{3+}\right] = 0.100$ **[2 marks]**

Given: $Al^{3+}(aq) + 3e \rightarrow Al(s)$ E⁰= -1.66V

$Cd^{2+}(aq) + 2e \rightarrow Cd(s)$ E⁰= -0.403V]

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

$3Ce^{4+}(aq) + Cr(s) \rightarrow Ce^{3+}(aq) + Cr^{3+}(aq)$

(i) Write the two half-cell reactions **[1 mark]**

(ii) Write the overall cell reaction **[1 mark]**

(iii) Calculate E^{o}_{cell} of the cell **[1 mark]**

(iv) What is the emf of the cell when $\left[Ce^{4+}\right] = 2.0M$ $\left[Ce^{3+}\right] = 0.01M$ and $\left[Cr^{3+}\right] = 0.01M$ **[2 marks]**

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

(vi) If the temperature coefficient of the cell is $1.86x10^{-4}V$/degree calculate ΔG, ΔH and ΔS for the reaction. **[6 marks]**

Given: $Ce^{4+}(aq) + e \rightarrow Ce^{3+}(aq)$ E⁰= -1.61V

$Cr^{3+}(aq) + 3e \rightarrow Cr(s)$ E⁰= -1.41V
