MACHAKOS UNIVERSITY

University Examinations 2023/2024 Academic Year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

FOURTH /THIRD YEAR FIRST SEMESTER EXAMINATION FOR

BACHELOR OF EDUCATION SCIENCE (SPECIAL NEEDS)

BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY.

BACHELOR OF EDUCATION (SCIENCE)

SCH 401/310: 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).

USEFUL FORMULARS

$R = \rho(\frac{l}{A}), \pi = 3.142$ $\kappa = \frac{1}{R} \times Cell\ constant$

$\Lambda_m = \frac{\kappa \times 1000}{C}$ $\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty}$ $\mathrm{K} = \frac{C\alpha^2}{1-\alpha}$

$Log\ K_c = \frac{nE^o_{cell}}{0.0591}$ $E = E^O - \frac{0.059v}{n}\log k$ $\mu = \frac{\lambda}{zF}$

$1C\Omega = 1As\Omega = 1Vs$

$\Delta G^o = -nFE^O_{cell}$ where F=96500c/mol

SECTION A

QUESTION ONE (30 MARKS)

a) State two differences between electronic conductance and electrolytic conductance. (4 marks)

b) Calculate the equilibrium constant for the following reaction at 25°C. (4 marks)
$Sn_{(s)} + 2Cu^{2+}(aq) \rightleftarrows Sn^{2+}(aq) + 2Cu^{+}(aq)$.

c) Describe the working principle of the hydrogen -oxygen fuel cells. (3 marks)

d) A galvanic cell consist of $Mg/Mg^{2+}(aq, 1.0\ M)$ and $Ag/Ag^{+}(aq, 1.0\ M)$. Calculate the standard EMF of this electrochemical cell at 25°C. (3 marks)

e) Using suitable equations describe how lead-acid battery discharges. (3 marks)

f) Predict using balanced equations what will happen when molecular bromine is added to solution containing sodium iodide solution at 25°C. (3 marks)

g) Calculate the reduction potential of Ag^{+} /Ag electrode at 25°C when [Ag]=0.010M. (3 marks)

h) Differentiate between electro-winning and electro-refining as used in electrolysis. (2 marks)

i) Define junction potential as used in electrochemistry. (2 marks)

j) State three disadvantages of standard hydrogen electrode (SHE) over the other secondary reference electrodes. (3 marks)

SECTION B

QUESTION TWO (20 MARKS)

a) A voltaic cell is made of Zn/Zn^{2+} and $Pt/H_2/H^{+}$. In a certain experiment the EMF of the cell is found to be 0.54 V at 25°C. Given that $[Zn^{2+}] = 1.0\ M$ and $\left[P_{H_2}\right] = 1.0\ M$. Calculate the concentration of H^{+}. (7 marks)

b) Describe three modes by which analyte move from bulk solution to electrode surface and state how the undesirable effects of the modes are minimized. (6 marks)

c) Define a sensor and describe its three major components. (7 marks)

QUESTION THREE (20 MARKS)

a) Write a balanced ionic equation to represent the oxidation of iodide ion by permanganate ion in basic solution to yield molecular iodine and manganese (IV) oxide

$MnO_4^- + I^- \rightarrow MnO_2 + I_2$. (8 marks)

b) Aqueous solution of a platinum salt is electrolysed by passing a current of 2.5 A for two hours. As a result 9.09 grams of metallic platinum is deposited at the cathode. Calculate the charge on the platinum ion in this solution (RFM of platinum salt is 195.1g). (6 marks)

c) Two half cells reactions of an electrochemical cell are given below

$$MnO_{4(aq)}^- + 8H_{(aq)}^+ + 5e \rightarrow Mn_{(aq)}^{2+} + 4H_2O_{(l)}$$

$$Sn_{(aq)}^{2+} \rightarrow Sn_{(aq)}^{4+} + 2e$$

Construct a redox equation from the above half-cell reactions and predict if this reaction favours formation of reactants or products shown in the equations.

(6 marks)

QUESTION FOUR (20 MARKS)

a) Predict whether the following reaction will proceed spontaneously in the given direction at 298 K.

$Co_{(s)} + Fe_{(aq)}^{2+} \rightarrow Co_{(aq)}^{2+} + Fe_{(s)}$.

Given that $[Co^{2+}] = 0.15M \quad [Fe^{2+}] = 0.68M$ (7 marks)

b) Corrosion is essentially an electrochemical phenomenon. Explain the reactions occurring during corrosion of iron kept in an open atmosphere given that $E^O_{Fe^{2+}/Fe} = -0.44V \ and \ E^O_{H+/O_2/H_2O} = 1.23V$ (8 marks)

c) The conductivity of 0.001M acetic acid is $4.0 \times 10^{-5}\ S\ cm^{-1}$. Calculate the dissociation constant (k_a) if Λ_m^o for acetic acid is $390.5\ S\ cm^2 mol^{-1}$. (5 marks)

QUESTION FIVE (20 MARKS)

a) A current of 0.452 A is passed through an electrolytic cell containing molten calcium chloride for 1.5 hours. Write the electrode reactions and calculate the quantity of products (in grams) formed at the electrodes (RFM Ca=40, Cl=35.5). (7 marks)

b) Calculate the standard free energy change for the following reaction at 25°C and state whether the reaction is spontaneous under the given condition.

$2Au_{(s)} + 3Ca^{2+}(aq, 1\ M) \rightarrow 2Au^{3+}(aq, 1\ M) + 3Ca(s)$. (6 marks)

c) A voltaic cell is made of Cu/Cu^{2+} and Ag/Ag^{+}.

i) Write the cell diagram for the above cell. (2 marks)

ii) Determine the concentration of Ag^{+} ions will the EMF of the cell be zero at 25° C if the concentration of Cu^{2+} is 0.01M? (5 marks)

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

*For all half-reactions the concentration is 1 *M* for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.