

## 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).

# **USEFUL FORMULARS**

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

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

 $Log K_c = \frac{nE_{cell}^o}{0.0591} \qquad E = E^O - \frac{0.059\nu}{n} \log k \qquad \qquad \mu = \frac{\lambda}{zF}$ 

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

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

#### **SECTION A**

### **QUESTION ONE (30 MARKS)**

a)	State three advantages of potentiometric titration.	(3 marks)	
b)	Differentiate between electrowinning and electrorefining as used in	electrolysis.	
		(2 marks)	
c)	Calculate the reduction potential of $Cu^{2+}/Cu$ electrode at 25°C when [Cu	<sup>2+</sup> ]=0.010M.	
		(3 marks)	
d)	State two differences between electronic conductance and electrolytic	conductance.	
		(4 marks)	
e)	Explain the principle of the hydrogen -oxygen fuel cells and state two adv	vantages over	
	other ordinary cells.	(4 marks)	
f)	Calculate the equilibrium constant of the reaction.	(3 marks)	
	$Cu_{(s)} + 2Ag^+_{(aq)} \to Cu^{2+}_{(aq)} + 2Ag_{(s)}$ $E^0 = 0.4$	$E^{O} = 0.46V$	
g)	State three disadvantages of standard hydrogen electrode (SHE) ov	er the other	
	secondary reference electrodes.	(3 marks)	
h)	The standard electrode potential for a Daniell cell is 1.1V. Calculate the sta	ctrode potential for a Daniell cell is 1.1V. Calculate the standard Gibb's	
	energy for the reaction. $Zn_{(s)} + Cu_{(aq)}^{2+} \rightarrow Zn_{(aq)}^{2+} + Cu_{(s)}$ $E^0 = 1.1V$	(3 marks)	
i)	State three physical limitations of battery performance.	(3 marks)	
j)	Define junction potential as used in electrochemistry.	(2 marks)	

#### **SECTION B**

#### **QUESTION TWO (20 MARKS)**

- a) i) Define the term molar conductivity. (2 marks)
  ii) one half cell in a voltaic cell is constructed from a silver wire dipped in a silver nitrate solution of unknown concentration. Its other half cell consists of zinc
  - electrode dipped in 1 M solution of zinc nitrate. A voltage of 1.48 V is measured for this cell. Use the information below to calculate the concentration of silver nitrate solution used.

$$E_{Zn2+/Zn}^{o} = -0.76 V \text{ and } E_{Ag+/Ag}^{o} = +0.80 V$$
 (8 marks)

b) At  $25^{0}$ C the molar conductivities of Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> are 3.87 mSm<sup>2</sup>mol<sup>-1</sup> and 5.01mSm<sup>2</sup>mol<sup>-1</sup> and 7.35 mSm<sup>2</sup>mol<sup>-1</sup> respectively. Calculate the mobilities of Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>. (4 marks)

- c) Calculate the amount of electric energy available from a dry cell with EMF of 1.5 V which consumes 10g of zinc. (Zn=63.5). (4 marks)
- d) Define a concentration cell.

### **QUESTION THREE (20 MARKS)**

a) Two half-cell reactions of an electrochemical cell are given below

$$\begin{split} MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e &\to Mn^{2+}_{(aq)} + 4H_2O_{(l)} \\ Sn^{2+}_{(aq)} &\to Sn^{4+}_{(aq)} + 2e \\ \end{split} \qquad \qquad \qquad E^o = 0.15V \\ E^o = 0.15V \end{split}$$

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. (5 marks)

b) The following chemical reaction is occurring in an electrochemical cell

$$Mg_{(s)} + 2Ag^{+}(aq)(0.0001M) \longrightarrow Mg^{2+}(aq)(0.1M) + 2Ag_{(s)}$$

The  $E^o$  electrode values for the half cells are given as;

$$Mg^{2+}(aq)/Mg(s) = -2.36 V$$
  
 $Ag^{+}(aq)/Ag(s) = 0.81 V$ 

Using the above information calculate/write;

i.	$E^o$ value for the electrode $2 Ag^+(aq)/2Ag(s)$ .	(1 mark)
ii.	Standard cell potential (E°).	(2 mark)
iii.	Cell potential ( $E_{cell}$ ).	(3 marks)
iv.	Symbolic representation of the above cell.	(1 mark)
v.	Will the cell reaction be spontaneous?	(1 mark)

- c) The electrical resistance of a column of 0.05mol/L NaOH of diameter 1cm and length 50 cm is  $5.55 \times 10^3$  ohm. Calculate:
  - i) resistivity ( $\rho$ ). (3 marks)
  - ii) Conductivity. (2 marks)
  - iii) Molar conductivity. (2 marks)

## **QUESTION FOUR (20 MARKS)**

a) Corrosion is essentially an electrochemical phenomenon. Explain the reactions occurring during corrosion of iron kept in an open atmosphere given that  $E_{1}^{Q} = 0.44W$  and  $E_{2}^{Q} = 1.22W$ 

$$E_{Fe^{2+}/Fe}^{0} = -0.44V \text{ and } E_{H+/O_2/H_2O}^{0} = 1.23V$$
 (5 marks)

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

(2 marks)

- c) A constant current of 30.0A is passed through an aqueous solution of sodium chloride for a time of 1 hour. How many grams of sodium hydroxide and litres of chlorine gas at STP will be produced? (6 marks)
- d) The potential of a hydrogen electrode set up at 25°C in an aqueous solution is -0.295
   V. Calculate the pH of the solution. (4 marks)

## **QUESTION FIVE (20 MARKS)**

a) Use the information given below to calculate the equilibrium constant (K<sub>c</sub>) of the electrochemical reaction;  $Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$ , given that

$$E^{o}_{Cd2+/Cd} = -0.40V$$
 and  $E^{o}_{Fe2+/Fe} = -0.44V$ . (5 marks)

b) Use the information below to answer the questions that follow

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s) \quad E^{0} = +0.34V$$
$$Ag^{+}(aq) + e \rightarrow Ag(s) \quad E^{0} = +0.80V$$

- i) Construct a galvanic cell using the above data. (2 marks)
- ii) For what concentration of  $Ag^+$  ions will the EMF of the cell be zero at 25° C if the concentration of Cu<sup>2+</sup> is 0.01M? (5 marks)
- c) The Specific conductivity of a saturated solution of Al(OH)<sub>3</sub> at 298k is 8.5x10<sup>-7</sup> S cm<sup>-1</sup>
   .If molar conductance at infinite dilution of Al(OH)<sub>3</sub> is 140.05 S cm<sup>2</sup>/moL, calculate the solubility and Ksp of Al(OH)<sub>3</sub>. (5 marks)
- d) State and explain three functions of a salt bridge. (3 marks)