CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE

CHEM 325: ELECTROCHEMISTRY

STREAMS: BSC **TIME: 2 HOURS**

DAY/DATE: MONDAY 12/07/2021 **2.30 P.M. – 4.30 P.M.**

INSTRUCTIONS:

- **Answer question ONE and any other TWO questions.**

QUESTION ONE (30 MARKS)

1. (a) (i) Explain the following:

(I) During measurement of conductive a.c is used. (4 marks)

(II) The electrodes used in conductance measurements are platinized. (3 marks)

(III) Why the changes in equivalent conductance of KCI and HOAC with concentration are widely different. (5 marks)

(ii) Account for the abnormal high value of the mobilities of $H^{+¿¿}$ and $OH^{-¿¿}$ ions in water. (5 marks)

(iii) Compare between electrolytic and metallic conduction. (4 marks)

(b) (i) A conductance cell on being filled with a 0.02 molar solution of KCI at $25^0\,C$ showed a resistance of 165 ohms. The specific conductance of the KCI solution used is $2.77\times10^{-3}\,mho\,cm^{-1}$. The same cell containing 0.01 molar $NaCI$ solution gave an electrical resistance of 3840 hms. Calculate the specific and equivalent conductance of the $NaCI$ solution. (3 marks)

(ii) (I) State Kohlrausch law of independent migration of ions. ($\frac{1}{2}$ mark)

(II) The equivalent conductance at infinite dilution of $HCI, NaCI \wedge NaOAC$ are 426.2 $0 h m^{-1} cm^2$ 126.5 $oh m^{-1} cm^2$ and 91.0 $oh m^{-1} cm^2$ respectively at $25^0 C$. Calculate equivalent conductance at infinite dilution for CH_3COOH. A conductance cell filled with 0.01 M KCI has a resistance of 257.3 ohms at $25^0 C$. The same cell filled with $0.2 N CH_3COOH$ has a resistance of 508.6 $ohms$. Calculate the dissociation constant of $HOAC$.
$[K of\ 0.01\ MKCI = 1.41 \times 10^{-3} Ohm^{-1} CM^{-1}]$

(4 $\frac{1}{2}$ marks)

QUESTION TWO (20 MARKS)

2. (a) (i) At $25^0 C$ the specific conductance of a saturated solution of $S_r S 0_4$ and that of water used are $1.482 \times 10^{-4} oh m^{-1} cm^{-1} \wedge 1.5 \times 10^{-6} ohm^{-1} cm^{-1}$ respectively. Given the ion conductance of $S_r^{2+¿¿}$ and $SO_4^{2-¿¿}$ to be 59.46 $oh m^{-1} cm^2 gm-eq^{-1}$ and 79.8 $ohm^{-1} cm^2 gm-eq^{-1}$ respectively at this temperature. Calculate the solubility of the salt in $gm\, lit^{-1} (m\, wt\, of\, Sr\, SO_4 = 182)$ (2 marks)

(ii) In an electrolysis of copper suphate between copper electrodes the total mass of copper deposited at the cathode was 0.153 g and the masses of copper per unit volume of the anode liquid before and after electrolysis were 0.79 and 0.91 g respectively. Calculate the transport number of the $Cu^{2+¿¿}$ and $SO_4^{2-¿¿}$ ions.
(2 marks)

(b) (i) Describe the moving boundary method employed in determining the transport number of an ion. (4 marks)

(ii) Calculate the transport number of $H^{+¿¿}$ ion from the following obtained by moving boundary method. Concentration of HCI solution = 0.10 N weight of silver deposited in the coulometer = 0.12g. Distance moved by the boundary = 7.5 cm cross-section of the tube = 1.2559 cm equivalent weight of silver = 108 {F=96500C}.
(2 marks)

(c) A conductivity cell of constant $1 cm^{-1}$ shows a resistance of 6667 ohms when filled with 0.001 M KCI Solution at $25^0 C$ the same cell records a resistance of 2353 ohms when filled with 0.001 MHCI solutions at $25^0 C$.

(i) Calculate equivalent conductance values for KCI and HCI solutions.

($2\frac{1}{2}$ marks)

(ii) Calculate ion conduction of $H^{+¿¿}$ assuming that $K^{+¿¿}$ and $CI^{-¿¿}$ have the same mobility. Consider the solutions to be infinitely dilute. (2 marks)

(iii) How far will $H^{+¿¿}$ move in 10 seconds when a potential difference of 2 volts is applied between two electrodes placed 2 cm apart. ($2\frac{1}{2}$ marks)

(d) Discuss the principles underlying the conductometric titrations. (3 marks)

QUESTION THREE (20 MARKS)

3. (a) (i) Write a note on concentration cells. (3 marks)

(ii) For the electrode concentration cell

$Zn(X_1)-Hg/Zn\,SO_4/Zn(x_2)-Hg$
$E\,at\,298\,K\,is\,0.0594\,V.$
X_1 and X_2 the mole fractions of zin in Hg, are respectively
$3\times10^{-2}\wedge3\times10^{-4}$. Calculate the ratio of the activity coefficient of Zn (on mole fraction basis) in the two amalgams. (2 marks)

(iii) Discuss electrolyte concentration cells without transference and electrolyte concentration cells with transference using suitable examples. ($4\frac{1}{2}$ marks)

(iv) The emf of the concentration cell

$Pb/PbSO_4/CuSO_4(a_{\pm}=0.022)/¿CuSO_4¿$ ($1\frac{1}{2}marks¿$

Calculate the EMF of the cell.

(b) (i) The cell without liquid junction describe below has a potential of 0.520523V

$Pt, H_2(1.0\,atm)/HCI(3.215\times10^{-5}M), AgCI(sat'd)/Ag$. Calculate the standard electrode potential for the half reaction $AgCl(s)+e^{-¿\rightleftarrows Ag(s)+CI^{-¿¿}¿}$
{The effective diameter of the hydrated ion in nanometers for $H^{+¿,CI^{-¿¿}¿}$ are 0.9, 0.3 respectively} (5 marks)

(ii) One beaker contains a solution of $0.02\,m\,kmno_4, 0.005\,m\,mnso_4 \wedge 0.5\,m\,H_2SO_4$ and a second beaker contains 0.15 $MFeSO_4$ and 0.0015 $M\,Fe_2$¿ The two beakers are connected by a salt bridge and platinum electrodes are placed in each. The electrodes are connected via a wire with a voltmeter in between. Calculate the potential of each half cell.

(I) Before reaction ($1\frac{1}{2}$ marks)

(II) After reaction (2 marks)

(III) Calculate the measured cell voltage at the start of the reaction and after the reaction reaches equilibrium. Assume $H_2SO_4$to be completely ionized and in equal volumes in each beaker.

MnO_4^-¿$+8\,H^+$¿$+5e^-$¿$\rightleftharpoons Mn^{2+}$¿$+4H_2O$¿$E^0=1.51V$¿¿¿

Fe^{3+}¿$+e^-$¿$\rightleftharpoons Fe^{2+}$¿$E^0=0.771V$¿¿¿ ($1\frac{1}{2}$ marks)

QUESTION FOUR (20 MARS)

4. (a) (i) A chemist wanted to measure the concentration of Cu^{2+}¿¿ in a large number of samples of water in which the copper ion concentration was expected to be quite small. The apparatus that was used consisted of a silver electrode, dipping into a 1.00 M solution of $AgNO_3$ connected by a salt bridge to a second half cell containing a copper electrode that was able to be dipped into each water sample, one after another in the analysis of one of the samples, the cell potential was measured to be 0.62V. Calculate the concentration of copper ion in this particular sample of water.

Ag^+¿$aq+e^-$¿$\rightleftharpoons Ag|s|E^0=+0.80\,V$¿¿

Cu^{2+}¿ $aq+2e^-$¿$\rightleftharpoons Cu|s|E^0=+0.34\,V$¿¿ ($4\frac{1}{2}$ marks)

(ii) The EMF of the cell $cd/cdcl_2.2\frac{1}{2}H_20/satd.soln/AgCl/Ag$ is found to be 0.6753 volt at 25^0C. Temperature coefficient of EMF in this case is $6.5\times10^{-4}\,volt\,deg^{-1}$. Calculate $\Delta G, \Delta H, \Delta S$ and thermodynamic equilibrium constant of the cell reaction (assume E^0_{cell}=0.6225) F=96500 C .

($5\frac{1}{2}$ marks)

(b) (i) Calculate the potential when 0.1A of electricity is drawn from the galvanic cell

$cd/cd^{2+}(0.01\ M)//Cu^{2+}(0.01\ M/Cu$

Assume a cell resistance of $4.0\ \Omega$

$Cu^{2+}+2e^{-} \rightleftharpoons Cu(s)\ E^{0}\ at\ 25^{0}C = +0.337$

$Cu^{2+}+2e^{-} \rightleftharpoons cd(s)\ E^{0}\ at\ 25^{0} = -0.403$ (4 marks)

(ii) Calculate the potential required to generate a current of 0.1A in the reverse direction in the foregoing cell $\{F = 96491\ C\}$ (1 mark)

(c) (i) Write short notes on characteristics of overvoltage caused by charge transfer polarization. (3 marks)

(ii) Differentiate between decomposition potential and discharge potential. (2 marks)
