

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 KCl 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 KCl at  $25^{\circ}C$  showed a resistance of 165 ohms. The specific conductance of the KCl used is  $2.77 \times 10^{-3} \text{ mho cm}^{-1}$ . The same cell containing 0.01 molar solution gave an electrical resistance of 3840 hms. Calculate the specific equivalent conductance of the NaCl solution. (3 marks)

- (ii) (I) State Kohlrausch law of independent migration of ions.  $\left(\frac{1}{2}\right)$  mark
- (II) The equivalent conductance at infinite dilution of  $HCl, NaCl \wedge NaOAc$  are  $426.2 \text{ ohm}^{-1} \text{ cm}^2$ ,  $126.5 \text{ ohm}^{-1} \text{ cm}^2$  and  $91.0 \text{ ohm}^{-1} \text{ cm}^2$  respectively at  $25^\circ C$ . Calculate equivalent conductance at infinite dilution for  $CH_3COOH$ . A conductance cell filled with  $0.01 \text{ M KCl}$  has a resistance of  $257.3 \text{ ohms}$  at  $25^\circ C$ . The same cell filled with  $0.2 \text{ N } CH_3COOH$  has a resistance of  $508.6 \text{ ohms}$ . Calculate the dissociation constant of  $HOAc$ .  
 $[K \text{ of } 0.01 \text{ M KCl} = 1.41 \times 10^{-3} \text{ Ohm}^{-1} \text{ CM}^{-1}]$
- $\left(4 \frac{1}{2}\right)$  marks

**QUESTION TWO (20 MARKS)**

2. (a) (i) At  $25^\circ C$  the specific conductance of a saturated solution of  $SrSO_4$  and that of water used are  $1.482 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$  and  $1.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  respectively. Given the ion conductance of  $Sr^{2+}$  and  $SO_4^{2-}$  to be  $59.46 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm}^{-1} \text{ eq}^{-1}$  and  $79.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm}^{-1} \text{ eq}^{-1}$  respectively at this temperature. Calculate the solubility of the salt in  $\text{gm lit}^{-1}$  ( $m \text{ wt of } SrSO_4 = 182$ ) (2 marks)
- (ii) In an electrolysis of copper sulphate between copper electrodes the total mass of copper deposited at the cathode was  $0.153 \text{ g}$  and the copper per unit volume of the anode liquid before and after were  $0.79$  and  $0.91 \text{ g}$  respectively. Calculate the transport number of  $Cu^{2+}$  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  $HCl$  solution =  $0.10 \text{ N}$  of silver deposited in the coulometer =  $0.12 \text{ g}$ . Distance moved by the boundary =  $7.5 \text{ cm}$  cross-section of the tube =  $1.2559 \text{ cm}$  weight of silver =  $108$  { $F=96500C$ }. (2 marks)
- (c) A conductivity cell of constant  $1 \text{ cm}^{-1}$  shows a resistance of  $6667 \text{ ohms}$  when filled with  $0.001 \text{ M KCl}$  Solution at  $25^\circ C$  the same cell records a resistance of  $2353 \text{ ohms}$  when filled with  $0.001 \text{ M HCl}$  solutions at  $25^\circ C$ .
- (i) Calculate equivalent conductance values for  $KCl$  and  $HCl$  solutions.

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

- same marks)
- (ii) Calculate ion conduction of  $H^{+}$  assuming that  $K^{+}$  and  $Cl^{-}$  have the 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



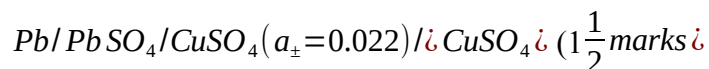
$E$  at 298 K is 0.0594 V.

$X_1$  and  $X_2$  the mole fractions of Zn in Hg, are respectively

$3 \times 10^{-2}$  and  $3 \times 10^{-4}$ . 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



Calculate the EMF of the cell.

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

$Pt, H_2(1.0 \text{ atm}) / HCl(3.215 \times 10^{-5} M), AgCl(sat'd) / Ag$ . Calculate the standard electrode potential for the half reaction  $AgCl(s) + e^{-} \rightleftharpoons Ag(s) + Cl^{-}$

{The effective diameter of the hydrated ion in nanometers for  $H^{+}$  and  $Cl^{-}$  are 0.9, respectively}

(5 marks)

0.3

(ii) One beaker contains a solution of  $0.02\text{ M KMnO}_4$ ,  $0.005\text{ M MnSO}_4$  and  $0.5\text{ M H}_2\text{SO}_4$  and a second beaker contains  $0.15\text{ M FeSO}_4$  and  $0.0015\text{ M Fe}_2\text{SO}_4$ . 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)

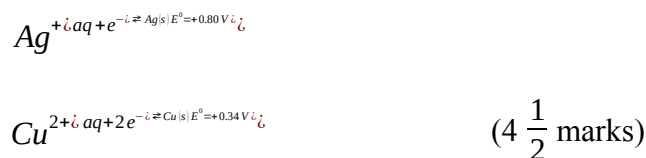
(II) After reaction (2 marks)

(III) Calculate the measured cell voltage at the start of the reaction and after the reaction reaches equilibrium. Assume  $\text{H}_2\text{SO}_4$  to be completely ionized and in equal volumes in each beaker.



#### QUESTION FOUR (20 MARKS)

4. (a) (i) A chemist wanted to measure the concentration of  $\text{Cu}^{2+}$  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  $1.00\text{ M}$  solution of  $\text{AgNO}_3$  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 samples, the cell potential was measured to be  $0.62\text{V}$ . Calculate the concentration of copper ion in this particular sample of water.

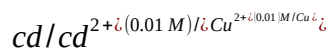


(ii) The EMF of the cell  $\text{Cd} / \text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O} / \text{satd. soln} / \text{AgCl} / \text{Ag}$  is found to be  $0.6753\text{ volt}$  at  $25^\circ\text{C}$ . Temperature coefficient of EMF in this case is

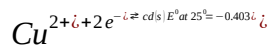
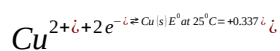
$6.5 \times 10^{-4}\text{ volt deg}^{-1}$ . Calculate  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  and thermodynamic equilibrium constant of the cell reaction (assume  $E_{\text{cell}}^0 = 0.6225\text{V}$  at  $25^\circ\text{C}$ ).

F=96500  
( $5\frac{1}{2}$  marks)

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



Assume a cell resistance of  $4.0 \Omega$



(4 marks)

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