CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR BACHELOR OF SCIENCE (CHEMISTRY)

CHEM 325: ELECTROCHEMISRTY

STREAMS: BSc **TIME: 2 HOURS**

DAY/DATE: THURSDAY 01/04/2021 **8.30 A.M. – 10.30 A.M.**

INSTRUCTIONS

- ***Answer question one and any two questions***
- ***Do not write on the question paper***

1. a) (i) Explain why the LI+ ion moves slower than K+ ion in water. (3 marks)

   ii) Explain why the equivalent conductance of an electrolyte at finite concentration is less than at infinite dilution. (3 marks)

   (iii) Explain why the changes in equivalent conductance of KCl and CH3COOH with concentration are widely different. (4 marks)

   (iv) Account for the abnormal high value of the mobilities of H+ and OH^- ions in water. (4 marks)

   (v) Criticize the statement given below.

   "Conductance of H+ ion increase as temperature increases" (2 marks)

   b) (i) The resistance of a electrolyte solution A is 450hms in a given cell and that of electrolyte solution B is 100 Ohns in the same cell. Equal volumes of solutions of both A and B are mixed. Calculate the resistance of this mixture when the same cell is used. (3 marks)

(ii) The equivalent conductance at infinite dilution of HCl, NaCl and CH3COONa are 426.2 $Ohm^{-1}cm^2$, 126.50hm^{-1} cm^2 and 91.0 Ohm^{-1} cm^2 respectively at 25^0C.

I. Calculate molar conductance at infinite dilution for CH3COOH. (2½ marks)

II. Calculate the dissociation constant of CH3OOH given that, a conductance cell filled with 0.01M KCl has a resistance of 257.3Ohms at 25^0C and the same cell filled with 0.2 N CH3COOH has a resistance of 508.6 Ohms. {conductivity of 0.01MKCl = 1.41 x 10^{-3} $Ohm^{-1}cm^{-1}$} (2½ marks)

C) At 25^0C in a saturated solution of $BaSO_4$, Ba^{2+} and $SO_4 2^-$ ions take 151 sec and 121 sec respectively to cover a distance of 1cm across which a potential difference of 10volts is applied. The solubility product of $BaSO_4$ at 25^0C is 10^{-10} (considered in gm-eq lit^{-1} unit). The conductance of the solution is 2.2 x 10^{-6} Ohm^{-1} in a cell of which the conductance of water is 0.8 x 10^{-6} Ohm^{-1} at 25^0C. If in the same cell conductance of 0.01NKCl be 1.40 x 10^{-3} Ohm^{-1} at 25^0C calculate its specific conductance at the same temperature. (F = 96484). (6 marks)

QUESTION TWO (20 MARKS)

2. a) (i) A current of 10mA was passed through a $AgNO_3$ solution in a Hittorf cell with Ag-electrodes for 80 minutes. After electrolysis, the cathode solution weighed 40.28gm and was titrated with 86cm^3 of 0.0200 molar KSCN. The anode solution weighed 40.40gm and required 112cm^3 of 0.0200 molar KSCN. Calculate the transport number of Ag^+ {F=96484C, RMM of $AgNo_3$ = 169.8} (6 marks)

(ii) In a moving boundary experiment with 0.01 mole LiCl, the boundary in a tube having across sectional area of 0.125cm^2 moves through 7.3cm in 1490 sec when a current of 1.80 x 10^{-3} ampere is used. Calculate t_+ (t = the transport number)

b (i) Explain why the decomposition potential of most acid solutions is 1.7 volts. (2 marks)

(ii) Distinguish between single electrode potential and standard electrode potential (1 mark)

C) Construct cell where the following reactions take place.

(i) $2KMnO_4 + 3H_2SO_4 + 5H_2O_4 \rightarrow 2MnSO_4 + 8H_2O + 5O_2$ (2 marks)

(ii) $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$ (½ marks)

d) (i) show $\frac{d(\frac{E^0}{T})}{d(\frac{1}{T})} = \frac{DH^0}{nF}$ (2½ marks)

(ii) For the electrochemical cell

$Pt/H_2(g,P=1atm)/HClaqa=1)/AgCl(s)$

The EMF at temperature near 298k obeys the following equation

$E^0/V = -0.00558 + 2.6967 \times 10^{-3}T +$

$8.2299 \times 10^{-6} T^2 + 5.869 \times 10^{-9}T^3$

Where T is the absolute temperature measured at K. Calculate $\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$ for the reaction at 298K $\Delta G^\ominus$ =change in standard

G1bb's Free energy, $\Delta S\Theta$ = entropy change of standard F=96485.3 $CMol^{-1}$ (5 marks)

QUESTION THREE (20 MARKS)

3. a) (i) Derive cell that can be used to

I. Obtain the solubility product (KsP) of Cu(OH)2 (2½ marks)

II. Obtain the equilibrium constant (Kc) for the reaction

$Zn(s) + 4H^{+}_{aq} + PbO_2\ (s) \leftrightharpoons Pb^{2+}_{aq} + Zn^{2+}_{aq} + 2H_2O\ (l)$ (2½ marks)

(ii) For the reduction of ClO_4^- to ClO_3^- the standard electrode potential under alkaline conditions is +0.37V, while under acidic conditions it is +1.20v. Write a balanced half-cell reaction for each reduction and deduce the value for the ionic product of water, KW (R=8.314) (2½ marks)

(iii) The overall cell reaction occurring in a direct methanol fuel cell is

$$\frac{1}{6}\ CH_3OH + \frac{1}{4}O_2 \rightarrow \frac{1}{3}H_2O + \frac{1}{6}CO_2$$

$\Delta G^{\Theta} = -177 KJ\ Mol^{-1}$

$\Delta H^{\Theta} = -121\ KJ\ Mol^{-1}$

I. Write an equation describing how the cell potential varies with temperature, and also calculate the cell potential for this reaction at 100^0C. (2½ marks)

II. What drawbacks arise from operating a fuel at low temperature? (2 marks)

b) (i) Calculate the standard electrode potential for the aqueous couple

$[Fe\ (OX)_3]^{3-}_{aq}/\ [Fe(OX)_3]^{4-}_{aq}$

From the following data (298K), where OX^{2-} refers to the Oxalate anion, $C_2O_4^{2-}$

$Fe^{3+}aq + e^- \leftrightharpoons Fe^{2+}aq$ $E^{\Theta} = 0.0770V$

$Fe^{2+}aq + 3OX^{2-} \leftrightharpoons [Fe\ (OX)_3]^{4-}aq$ $K=1.7X10^5$

$Fe^{2+}aq + 3OX^{2-} \leftrightharpoons [Fe\ (OX)_3]^{3-}aq$ $K=2.0\ X10^{20}$ (3 marks)

(ii) (I) The calomel and silver/silver Chloride electrodes are commonly used in aqueous solution voltammetry. Identify the potential determining equilibria and the associated Nernst equation for each electrode comment on any implications of the latter. (2 marks)

(II) Suggest a reference electrode suitable for voltammetry in non-aqueous solutions. Can the calomel and Ag/AgCl redox couple be used in these media? (2 marks)

QUESTION FOUR (20 MARKS)

4. (i) Derive an equation that describes how the current varies as a function of time in a chronoamperometric experiment with a surface bound redox species. Hence suggest a suitable plot to assess the magnitude of the electron transfer rate associated with the process. (4 marks)

   (ii) Explain what you understand by the term chronopotentiometry and how you can distinguish it from constant current coulometric analysis, coulometric titrimetry and galvanostatics. (2½ marks)

   b) During a chronoamperometric experiment with 100ml of 0.01m solution of an oxidant, the measured current was 55 milliamp, 10^{-2} seconds after the experiment commenced.

   (i) What will be the value of the current after 100 seconds and also after 10,000 seconds? (1 mark)
   (ii) What fraction of the original oxidant will be reduced after 100 seconds if a two electron electrode reaction is involved? (4 marks)
   (iii) Why do the currents become so small even though most of the oxidant has not been reduced? (1 mark)

C) A chronocoulometric experiment was conducted with a 1mM solution of a reactant molecule which absorbs on the electrode surface to produce a layer in which each adsorbed molecule occupies $100A^2 = 10\text{-}14\ cm^2$.

(i) If the reactant undergoes a two-electron reduction at the electrode, calculate the electrical charge that will be consumed by the reduction of the adsorbed molecules in microcoulombs cm^{-2} (1 mark)

(ii) If the reactant has a diffusion coefficient of $2 \times 10^{-5} cm^2 sec^{-1}$. Calculate the additional electrical charge that will be consumed by molecules that diffuse to the electrode within 10^{-2}, 10^{-1} and 1 sec. (2½ marks)

(iii) How would the accuracy of measurements of the quantity of adsorbed reactants by chronocoulometry depend on the duration of the chronocoulometric experiment.

(1 mark)

d) For the determination of cyanide ion, baker and Morrison {Anal. Chem, 27, 1306 (1955) employed a silver and platinum electrode pair, connected together through a microniam meter, solution to which the cyanide sample is added.

(i) Draw the cell representing the reaction (½ marks)

(ii) The electrode reaction involved (1 mark)

(iii) Why does a reaction, nevertheless proceed spontaneously. (½ marks)

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