CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

FOURTH YEAR EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF EDUCATION (SCIENCE), BACHELOR OF SCIENCE

CHEM 425: ELECTROCHEMISTRY

STREAMS: BED (SCI), BSC **TIME: 2 HOURS**

DAY/DATE: TUESDAY 05/12/2017 **8.30 A.M. – 10.30 A.M.**

INSTRUCTIONS: ANSWER QUESTION ONE AND ANY OTHER TWO QUESTIONS

QUESTION ONE (30 MARKS)

(a) Differentiate between decomposition potential and discharge potential. [4 marks]

(b) (i) Calculate the equilibrium constants for the following reaction at 25˚C

$Pb + Sn^{2+} \rightleftharpoons Pb^{2+} + Sn$

Given:

$Sn^{2+} + 2e^{-} \rightleftharpoons Sn\ E^{o}(volts) = -0.136\ V$

$Pb^{2+} + 2e^{-} \rightleftharpoons Sn\ E^{o}(volts) = -0.126\ V$

F = charge on one mole of electrons = 96, 500 coulombs

R = 8.314 J mol^{-1} K^{-1} [4 marks]

(ii) The EMF of the cell cd/$cdcl_2$. 2½ H_2O/ satd sol/AgCl/Ag is found to be 0.6753 volts at 25˚C.Temperature coefficient of EMF in this case is $-6.5x10^{-4}$ volt – $degre^{-1}$. CalculateΔG, ΔH, ΔS for cell reaction.

Where
ΔG = free energy change
ΔS = change in entropy
ΔH = change in enthalpy
$\{F = 96500\ C$ [3 marks]

(iii) List the advantages and disadvantages of Quinhydrone electrode. [2 marks]

(iv) Calculate the pH of the solution from the following potential data

Cell SCE//$H^{+}(a_1)$, Quinhydrone/ Pt

E_{cell} at 25˚C = 0.102 Volt

E˚Quinhydron at 25˚C = 0.700 volt

{F = 96500 C} ESCE at 25˚C = 0.242 volts [3 marks]

(v) For the electrode concentration cell:

$Zn(x_1) – Hg/ZnSO_4/Zn\ (x_2) – Hg$

E at 298 k is 0.0594V. x_1 and x_2 the mole fractions of Zn in Hg are $3x10^{-2}$ and $3x10^{-4}$ respectively. Calculate the ratio of the activity coefficient of Zn (on mole fraction basis) in the two a malgams. [1 mark]

(c) (i) Discus the principle underlying the conductometric titrations. [1½ marks]

(ii) Sketch schematically the titration curve for the titration of a weak acid by a strong base. [1½ marks]

(iii) State Kohlrausch law of independent migration of ions. [½ mark]

(iv) At a certain temperature the saturated solution of AgCl has a specific conductance of $1.12 \times 10^{-6}\Omega^{-1}$ cm^{-1} (after correction for the specific conductance of water). The $\lambda^{\circ}Ag^{+}$ and $\lambda^{\circ}cl^{-}$ are 54.3 and 65.6 Ω^{-1} cm^2 $equiv^{-1}$ respectively at this temperature. Find the solubility product of AgCl{$AgCl$ = 143.5, assume the degree of dissociation for the saturated solutions of precipitated salts is equal to unity). [2½ marks]

(v) Draw rough sketches to show how molar conductance vary during the progressive dilution of solution of:

(I) Strong electrolyte [½ marks]

(II) Weak electrolyte [½ marks]

(vi) Explain the graphs obtained in QV (I) and (II) [3 marks]

(vii) In conductivity cell 0.01 NKClsolutiongave a resistance of 225.0 Ohms while a 0.01N solution of HCl gave a resistance of 77.1 Ω^{-1}cm-1. Conductivity of Kcl solution is $0.00141\Omega^{-1}cm^{-1}$. . Calculate the conductance, equivalent conductance and molecular conductance of the Hcl solution. [2 marks]

QUESTION TWO

(a) Derive an equation for calculating the magnitude of liquid junction potential for the concentration cell with transference given below

$Ag/AgCl/HCl(a_2)$: Hcl (a_1)/Agcl/Ag $a_2 > a_1$, comment on the equation obtained. [12 marks]

(b) The EMF of the cell with transference Ag/Agcl/Hcl ($a_{\pm}$= 0.01751)//HCl ($a_{\pm}$=0.00904)/Agcl/Ag at 298K is 0.02807V.

The corresponding cell without transference has an EMF of 0.01696v. Calculate the transference number of H^+ and the value of liquid junction potential.
$\{F = 9.64853x10^4 C\ mol^{-1}, R = 8.31447\ J\ K^{-1}Mol^{-1}, \theta^{\circ}c = TK - 273.15\}$.

[2 marks]

(c) (i) Given that the standard potential of the Calomel electrode is 0.268 V and that of the Hg/Hg_2^{2+} electrode is 0.789V. CalculateK_SP for Calomel (Hg_2Cl_2), for 298K. [4 marks]

(ii) From the formation constant of $Ni(glycine)_2$ plus E° for the $Ni^{2+} + /Ni\ (s)$ couple
$Ni^{2+} + 2\ glycine^- \leftrightharpoons Ni(glycine)_2 K = B_2 = 1.2x10^{11}$
$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)\ E = -0.236V$deduce the value of E° for the reaction.
$Ni(glycine)_2 + 2e^- = Ni(s) + 2\ glycine^-$ [2 marks]

QUESTION THREE (20 MARKS)

(a) (i) Discuss the principle involved in the titration of silver nitrate solution with sodium chloride solution usingpotentiometric technique. [6 marks]

(ii) A 100 ml solution containing 0.1 MNaCl was titrated with 0.1 M $AgNO_3$ and the voltage of cell shown in figure below was monitored. The equivalence volume is V_c = 100 ml. calculate the voltage after the addition of:

(I) 65.0ml of $AgNO_3$ [3 marks]

(II) 135.0ml of $AgNO_3$ [2 marks]

(b) (i) Explain how the contribution of the analyte to the migration current and convection current is made negligible during experimental involving polarography. [3 marks]

(ii) Figure below shows cyclic voltammogram for a solution that is 6.0 mM in $K_3Fe(CN)_6$ and 1.0 M in KNO_3 using polished stationary platinum electrode as working electrode and SCE as reference electrode.

(I) Explain why a tiny anodic current was observed at the initial potential of +0.8V which immediately decreased to zero as the scan continued. [½ mark]

(II) Explain why the current was not observed between a potential of +0.7 and +0.4 V. [½ mark]

(III) Give reason to why when the potential became less positive than +0.4 V, a cathodic current started to develop. [1 mark]

(IV) Discuss various process occurring in region B D, DF and FJ.[4 marks]

QUESTION FOUR (20 MARKS)

(a) (i) Explain how chronopotentiometry can be distinguished from constant – current coulometric analysis and coulometrictitrimetry. [1 mark]

(ii) Briefly discuss the working principle of chronopotentiometry. [8 marks]

(b) Differentiate between controlled potential (Potentiostic) coulometry and controlled current (amperostatic) coulometry. [2½ marks]

(c) Explain briefly how chlorine can be detected using amperometry. [3½ marks]

(d) State five characteristics of overvoltage caused by charge transfer polarization. [2½ marks]

(e) (i) The following cell has a resistance of 4.00Ω. Calculate the potential when 1E is producing a current of 0.100 A

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

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

$Cd^{2+} + 2e^{-} \rightleftharpoons Cd(s)$ $\quad E^{\circ} at\ 25^{\circ}C = -0.403$ [1½ marks]

(ii) Calculate the potential required to generate a current of 0.1 A in the reverse direction in the cell shown in question e(i). [1 mark]
