

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

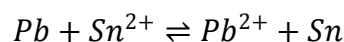
8.30 A.M. – 10.30 A.M.

INSTRUCTIONS: ANSWER QUESTION ONE AND ANY OTHER TWO QUESTIONS

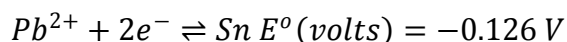
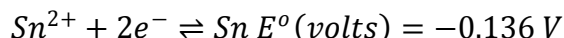
QUESTION ONE (30 MARKS)

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

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



Given:



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 $cd/cdCl_2, 2\frac{1}{2} H_2O / \text{satd sol}/AgCl/Ag$ is found to be 0.6753 volts at 25°C. Temperature coefficient of EMF in this case is -6.5×10^{-4} volt – degree⁻¹. Calculate ΔG , 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⁺(a₁), Quinhydrone/ PtE_{cell} at 25°C = 0.102 Volt

E°Quinhydrone at 25°C = 0.700 volt

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

CHEM 425

- (v) For the electrode concentration cell:
 $\text{Zn}(x_1) - \text{Hg}/\text{ZnSO}_4/\text{Zn}(x_2) - \text{Hg}$
E at 298 K is 0.0594V. x_1 and x_2 the mole fractions of Zn in Hg are 3×10^{-2} and 3×10^{-4} respectively. Calculate the ratio of the activity coefficient of Zn (on mole fraction basis) in the two amalgams. [1 mark]
- (c) (i) Discuss 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 $1.12 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ (after correction for the specific conductance of water). The $\lambda^\circ \text{Ag}^+$ and $\lambda^\circ \text{Cl}^-$ are 54.3 and $65.6 \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ respectively at this temperature. Find the solubility product of AgCl ($K_{sp} = 143.5$, 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 N KCl solution gave a resistance of 225.0 Ohms while a 0.01 N solution of HCl gave a resistance of $77.1 \Omega^{-1} \text{ cm}^{-1}$. Conductivity of KCl solution is $0.00141 \Omega^{-1} \text{ cm}^{-1}$. 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
 $\text{Ag}/\text{AgCl}/\text{HCl}(a_2): \text{HCl}(a_1)/\text{AgCl}/\text{Ag}$ $a_2 > a_1$, comment on the equation obtained. [12 marks]
- (b) The EMF of the cell with transference $\text{Ag}/\text{AgCl}/\text{HCl}(a_{\pm} = 0.01751)//\text{HCl}(a_{\pm} = 0.00904)/\text{AgCl}/\text{Ag}$ at 298K is 0.02807V.

CHEM 425

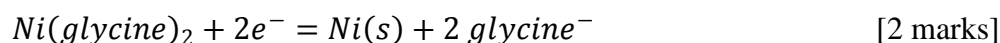
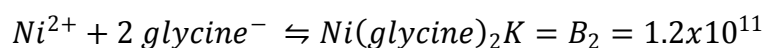
The corresponding cell without transference has an EMF of 0.01696v. Calculate the transference number of H^+ and the value of liquid junction potential.

$$\{F = 9.64853 \times 10^4 C \text{ mol}^{-1}, R = 8.31447 J K^{-1} \text{ Mol}^{-1}, \theta^\circ C = TK - 273.15\}.$$

[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. Calculate $K_S P$ for Calomel (Hg_2Cl_2), for 298K. [4 marks]

- (ii) From the formation constant of $Ni(\text{glycine})_2$ plus E° for the $Ni^{2+} + /Ni(s)$ couple



QUESTION THREE (20 MARKS)

- (a) (i) Discuss the principle involved in the titration of silver nitrate solution with sodium chloride solution using potentiometric technique. [6 marks]
- (ii) A 100 ml solution containing 0.1 M NaCl 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]

CHEM 425

- (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 $\text{K}_3\text{Fe}(\text{CN})_6$ 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]

CHEM 425

- (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 coulometric titrimetry. [1 mark]
- (ii) Briefly discuss the working principle of chronopotentiometry. [8 marks]
- (b) Differentiate between controlled potential (Potentiostatic) 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/cd²⁺ (0.01 M) // Cu²⁺ (0.01M) /Cu
 $Cu^{2+} + 2e \rightleftharpoons Cu(s) \quad E^\circ \text{ at } 25^\circ C = +0.337$
 $Cd^{2+} + 2e^- \rightleftharpoons Cd(s) \quad E^\circ \text{ at } 25^\circ C = -0.403$ [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]
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