MATTAN SEMSESTER, 2024/2025 SESSION

CHM 403 - ELECTROCHEMISTRY

TIME ALLOWED - 1 HOUR

(CONSTANTS: F = 96500 C, R = 8.314 J mol^{-1} K^{-1})

1. The molar conductivity at 18°C at a certain concentration of NH_4OH is $1.31 \times 10^{-2} M^2\Omega^{-1}mol^{-1}$. Compute the molar conductivity at infinite dilution and the degree of dissociation of NH_4OH if the molar conductivities at infinite dilution at 18°C for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 2.88×10^{-2}, $1.20 \times 10^{-2} \times 10^{-2}$ and $1.29 \times 10^{-2}\Omega^{-1}mol^{-1}$ respectively.

2. A conductance cell containing 0.01 $moldm^{-3}$ KCl solution was found to have a resistance of 2573 ohm at 25 °, and a conductivity of 1.409 ohm^{-1} m^{-1}. The same cell when filled with a 0.200 $moldm^{-3}$ solution of CH_3COOH has a resistance of 5083 ohm. Calculate:
   i) The conductivity, k, of the CH_3COOH solution
   ii) The molar conductivity, Λ, of the solution of KCl
   iii) The molar conductivity of the CH_3COOH solution

3. a. Explain the following terms as related to electron transfer processes on surfaces:
   i. Chemical flux
   ii. Electron flux

   b. What are the necessary conditions for an ion or a neutral specie to be involved in charge transfer process(es) at the electrode?

4. When dilute sodium hydroxide was electrolysed using a nickel cathode, the overpotential was found to be 0.394 V to maintain a current density of 0.01 A cm^{-2} and 0.148 V to maintain a current density of 0.0001 A cm^{-2}. Calculate the transfer coefficient and exchange current density for the hydrogen/hydrogen ion equilibrium at a nickel cathode in the given medium.

Afinyelo Oluwafemi
CHM/2021/052

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree Examination Part IV

CHM 403: ELECTROCHEMISTRY

Harmattan Semester Examination (2024/2025 Session)

Time Allowed: 2 *hours* Date: 16th March 2026

INSTRUCTION: SECTION A: ANSWER ANY TWO (2) QUESTIONS
SECTION B: ANSWER QUESTION 4 AND ANY OTHER ONE

Constant: ($R = 8.314\ J\ mol^{-1}\ K^{-1}$, $F = 96500\ C\ mol^{-1}$)

$R = \frac{\rho L}{A}$ $\frac{RA}{L}$ ρ

SECTION A

1(a). (i) What is a conductometric titration?

(ii) Briefly state three common types of conductometric titration, illustrated with an equation each. $\alpha = \frac{\Lambda_c}{\Lambda_0}$

(b). For a particular weak acid, HA, the dissociation constant, K, is 1.42×10^{-4} at 298 K and the limiting molar conductivity at zero concentration of the H^+ and A^- ions are 3.50×10^{-2} and $0.48 \times 10^{-2}\ m^2\Omega^{-1}mol^{-1}$, respectively. Calculate the conductivity and resistivity of 0.01 mol dm^{-3} of the acid, HA. **(18 marks)**

2(a). The conductivity of a $\overset{K_{H_2O}}{\text{saturated}}$ solution of $\overset{Na_2SO_4}{\text{sodium sulphate}}$ at 25 °C is $\overset{K}{3.850 \times 10^{-4}}\ \Omega^{-1}m^{-1}$ and the conductivity of the water used is $0.626 \times 10^{-4}\ \Omega^{-1}m^{-1}$. The limiting molar conductivity at zero concentration for $\overset{\Lambda_{Na}}{Na^+}$ and ½ SO_4^{2-} are 12.142×10^{-3} and $8.201 \times 10^{-3}\ m^2\Omega^{-1}mol^{-1}$, respectively. Calculate the concentration of $\overset{Na_2SO_4}{\text{sodium sulphate}}$ at this temperature.

$dm \left(\frac{1dm}{10^{-1}}\right)^3$

(b). The electrolytic conductivity of 0.001 moldm^{-3} of Na_2SO_4, is $2.6 \times 10^{-2}\ \Omega^{-1}m^{-1}$. If the solution is saturated with $CaSO_4$, the conductivity rises to $7.0 \times 10^{-2}\ \Omega^{-1}m^{-1}$. Calculate the solubility product for $CaSO_4$ given the ionic molar conductivity, $\Lambda_{Na^+} = 5.00 \times 10^{-3}$ and $\Lambda_{\frac{1}{2}Ca^+} = 5.95 \times 10^{-3}\ m^2\Omega^{-1}mol^{-1}$ at this concentration. **(18 marks)**

3(a). The e.m.f. of the cell, $Cd - Hg/CdCl_2\ (0.01M), AgCl_{(s)}\ /\ Ag$ is 0.7580 V. The standard e.m.f. of the cell is 0.5732 V. Calculate the mean activity of cadmium chloride solution.

(b). Calculate the mean activity coefficient of the ions in Na_2SO_4 solution using the Debye-Huckel limiting law if the solution is made up of 0.005 moldm^{-3} Na_2SO_4 at 25°C. **(18 marks)**

SECTION B

4(a). Define electrolysis **(3 marks)**

(b). Write the electrode half-reactions, the overall cell reactions, and calculate the standard potential of each of the following cells:

$[Ca]\ [SO_4^{2-}$

$\Lambda = \frac{K}{C}$ $HCl + NH_4OH$ NH_4Cl

$C = \frac{K_{CaSO_4}}{\Lambda_{CaSO_4}}$

$\frac{}{m^3} \times \frac{10^{-3}\ m}{1dm^3}$

$Zn SO_4 \rightarrow Zn^{2+}_{(s)} + e^-$

2.

(i) Zn(s)|$ZnSO_4$(aq)||$AgNO_3$(aq)|Ag(s) (4 marks)

(ii) Cd(s)|$CdCl_2$(aq)||HNO_3(aq)|H_2(g)|Pt(s) (4 marks)

(iii) Determine the spontaneity (or otherwise) of each of the cells in i and ii above, given that the standard reduction potentials are: Zn/Zn^{2+}; E° = -0.76 V, Cd/Cd^{2+}; E° = -0.40 V, Ag/Ag^+; E° = +0.80 V, Cr/Cr^{3+}; E° = -0.74 V. (3 marks)

(c). One of the alternatives to the standard hydrogen electrode is the quinhydrone electrode (quinhydrone, $Q{\cdot}QH_2$, is a complex of quinone, $C_6H_4O_2$ = Q, and hydroquinone, $C_6H_4O_2H_2$ = QH_2), where the concentrations of Q and QH_2 are equal to each other. The electrode half-reaction is:

$$Q(aq) + 2\,H^+(aq) + 2\,e^- \rightarrow QH_2(aq),\ E^\ominus = +0.6994\ V.$$

$E = E^0 - \log$

$AgNO_3 \xrightarrow{+e^-} Ag_{(s)} + NO_3^-$

At what electrode potential will the pH of the cell reaction be 2.04? (4 marks)

$E^{qh} + \frac{RT}{nF} \ln \frac{ox}{red}$

$C_{cell} = C_{q \cdot qH_2} + C_Q + C_{QH_2}$

5(a). Give at least three important properties of a reference electrode (3 marks)

(b). For the hydrogen evolution reaction from a 0.1 M HCl solution on a lead electrode at 25 °C, the steady-state current density was measured at different overpotentials. At an overpotential (magnitude) of 0.50 V, the current density was 2.4×10^{-5} A cm^{-2}, and at an overpotential (magnitude) of 0.40 V, the current density was 3.1×10^{-6} A cm^{-2}.

(i) At which electrode is this reaction likely to take place? Give a simple reason for your answer (2 marks)

(ii) Calculate:

(1) The slope of the Tafel's plot for the process (9 marks)

(2) The transfer coefficient, α, for the reaction (2 marks)

(3) The exchange current density (2 marks)

6(a). The overvoltage of an individual electrode may be expressed as the sum of contributions from activation η_A, concentration η_C, and resistive film η_R over voltages.

Explain each of these overvoltages (3 marks)

(b). The exchange current density i_0 for the Ag^+/Ag redox couple on a platinum electrode is 5.0×10^{-2} A cm^{-2} at 25 °C. The reaction is:

$I_0 = 5 \times 10^{-2}$ A

$$Ag^+ + e^- \rightleftharpoons Ag$$ reduction_cathode $E = E^0 -$

with standard potential $E^\circ = +0.799$ V.

Calculate the current density when the overpotential $\eta = E - E^\circ$ is:

(i) +20 mV (5marks)

(ii) −150 mV (5 marks)

(iii) +500 mV (5 marks)

Given that the transfer coefficient, α = 0.50

$$E = E^0 - \frac{RT}{nF} \ln \frac{QH_2}{[Q][H^+]^2}$$

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree Examination Part IV
CHM 403: ELECTROCHEMISTRY

Harmattan Semester Examination (2023/2024 Session)

Time Allowed: 2 *hours* **Date: 1st March 2025**

INSTRUCTION: SECTION A: ANSWER ANY **TWO** (2) QUESTIONS
SECTION B: ANSWER ANY **TWO** (2) QUESTIONS

Constant: ($R = 8.314\ J\ mol^{-1}\ K^{-1}$, $F = 96500\ C\ mol^{-1}$)

SECTION A

$K_{solution}$ $3.850 \times 10^{-4}\ \Omega^{-1} m^{-1}$
$K_{solvent} = 0.626 \times 10^{-4}\ \Omega^{-1} m^{-1}$

1(a). What is transport number?

(b). The conductivity of a saturated solution of sodium sulphate at 25 °C is $3.850 \times 10^{-4}\ \Omega^{-1}m^{-1}$ and the conductivity of the water used is $0.626 \times 10^{-4}\ \Omega^{-1}m^{-1}$. The limiting molar conductivity at zero concentration for Na^+ and ½ SO_4 are 12.142×10^{-3} and $8.201 \times 10^{-3}\ m^2\Omega^{-1}mol^{-1}$ respectively. Calculate the concentration of sodium sulphate at this temperature.

(c). Calculate the mean activity coefficient of the ions in Na_2SO_4 solution using the Debye-Huckel limiting law if the solution is made up of 0.005 moldm^{-3} Na_2SO_4 at 25°C. $A = 0.509$ [19 marks]

$\log \gamma_\pm = -A|z^+z_-|\sqrt{I}$

2(a). The molar conductivity, Λ_c at 20 °C of a 0.01 moldm^{-3} aqueous solution of ammonia (NH_4OH) is $9.6\ cm^2\Omega^{-1}\ mol^{-1}$. For NH_4Cl, $\Lambda^o = 129.8\ cm^2\ \Omega^{-1}\ mol^{-1}$ and the ionic conductivities Λ_o of OH^- and Cl^- are 174 and $65.6\ cm^2\Omega^{-1}\ mol^{-1}$ respectively. Calculate;

$\alpha = \frac{\Lambda_c}{\Lambda_o}$

- (i). Λ^o for the ammonia solution and
- (ii). the degree of dissociation in 0.01 moldm^{-3} solution.

$\Lambda = \frac{k}{c}$

(b). A conductivity cell standardized with 0.01 mol.m^{-3} KCl was found to have a resistance of 189 ohms and molar conductivity $149.9\ m^2\ mol^{-1}\ \Omega^{-1}$. With 0.01 mol.m^{-3} ammonia solution (NH_4OH), the resistance was 2460 ohms. Given the molar conductivity at infinite dilution that; $\Lambda^o\ (NH_4^+) = 73.4$ and $\Lambda^o\ (OH^-) = 198.6\ m^2\ mol^{-1}\ \Omega^{-1}$, Calculate the;

$kR = \frac{L}{a}$

- (i). molar conductivity (Λ_c) of the ammonia solution
- (ii). the degree of dissociation (α) of the ammonia solution

(c). In **not more than five lines**, describe the three modes of interaction of ions used by the inter-ionic attraction theory to explain variations in molar conductivity with concentration.

[19 marks]

3(a). The electrolytic conductivity of 0.001 moldm^{-3} of Na_2SO_4, is $2.6 \times 10^{-2}\Omega^{-1}m^{-1}$. If the solution is saturated with $CaSO_4$, the conductivity rises to $7.0 \times 10^{-2}\ \Omega^{-1}m^{-1}$. Calculate the solubility product for $CaSO_4$ given the ionic molar conductivity, $\Lambda_{Na^+} = 5.00 \times 10^{-3}$ and $\Lambda_{\frac{1}{2}Ca^+} = 5.95 \times 10^{-3}\ m^2\Omega^{-1}mol^{-1}$ at this concentration.

$K_{sp} = 4c^3$

(b). In a moving boundary experiment to determine the cation transport number in 0.02 moldm^{-3} lithium chloride solution, a current of 1.6×10^{-3} ampere caused the boundary to move a distance of 7×10^{-2} m in 0.6705 hours. If the cross section of the transport tube is $1.115 \times 10^{-5}\ m^2$, calculate the transport numbers of the cation and anion. [19 marks]

SECTION B

$KR = \frac{l}{a}$ $t^+ = \frac{xaFcz^+}{Q}$

4(a). Define the following terms:

- (i). Electrode polarization
- (ii). Concentration polarization
- (iii). Reference electrodes

[6 marks]

(b). The transfer coefficient of a certain electrode in contact with M^{2+} and M^{3+} in aqueous solution at 25°C is 0.42. The current density is found to be 17.0 mA cm^{-2} when the overpotential is 105 mV. What is the overpotential required for a current density of 72 mA cm^{-2}? [12 marks]

5(a). Derive the Nernst equation from your knowledge of the change in Gibb's free energy. [4 marks]

(b). For the cell at 25°C and 1 bar

$$Pt|Ag|AgCl(s)|HCl(aq)|Hg_2Cl_2(s)|Hg|Pt$$

(i). write the cell reaction [2 marks]

(ii). find the emf if the HCl molality is 0.100 mol/kg [4 marks]

(iii). find the emf if the HCl molality is 1.00 mol/kg. [2 marks]

(iv). For this cell, $\left(\frac{\partial E}{\partial T}\right)_p = 0.338\ mV/K$ at 25 °C and 1 bar. Find ΔG°, ΔH°, and ΔS° for the cell reaction at 25°C. [10 marks]

Given that

$Ag|AgCl|Cl^-$ $E^\ominus = +0.2222V$ and

$Cl^-|Hg_2Cl_2|Hg$ $E^\ominus = +0.2680V$

6(a). The Tafel equation that relates the overpotential to the current density for processes at electrodes can be written in the form:

$|\eta| = a + b\log_{10}|i|$ where a and b are known as the Tafel's constants

What are the corresponding expressions for a and b in terms of measurable quantities for an anodic process [5 marks]

(b). When dilute sodium hydroxide was electrolysed using a nickel cathode, the overpotential was found to be 0.394 V to maintain a current density of 0.01 A cm^{-2} and 0.148 V to maintain a current density of 0.0001 A cm^{-2}. Calculate the transfer coefficient and exchange current density for the hydrogen/hydrogen ion equilibrium at a nickel cathode in the given medium. [13 marks]

$\eta_1 = 0.394V$
$i_1 = 0.01 A cm^{-2}$
$\eta_2 = 0.148V$
$i_2 = 0.0001 A cm^{-2}$
i_0 \$ α.

$\ln i_1 = \ln i_0 + (1-\alpha) f \eta_1$
$\ln i_2 = \ln i_0 + (1-\alpha) f \eta_2$
$\ln\left(\frac{i_2}{i_1}\right) ~~i~~ = (1-\alpha) f (\eta_2 - \eta_1)$

$\ln \frac{i_2}{i_1}$

$\ln\left(\frac{i}{i_0}\right) = \alpha f \eta_1$

$\frac{i}{i_0} = 0.48 \times 38.95 \times 0.394$ $i = i_0$

$i = i_0 e^{-\frac{\alpha f \eta}{RT}}$

$i_0 = \frac{i}{}$

$\frac{i}{i_0} = e^{7.37} = 1581$

$i_0 = \frac{0.01}{1581}$

$\ln \frac{i_2}{i_1} =$

$\ln i_1 = \ln i_0$

$\ln\left(\frac{i_2}{i_1}\right) = \alpha f(\eta_2 - \eta_1)$

$-4.605 = \alpha(38.95)(0.148 - 0.394)$

$\ln i_1 = \ln i_0 + \alpha f \eta_1$
$\ln i_0 = \ln(0.01) - (0.48 \times 38.95 \times 0.394)$
$\ln i_0 = -11.97$
$i_0 = 6.32 \times 10^{-6}$.

Department of Chemistry

***OBAFEMI AWOLOWO UNIVERSITY* ILE-IFE, NIGERIA**

MID – HARMATTAN SEMESTER EXAMINATION

CHM 403 – ELECTROCHEMISTRY

TIME ALLOWED - 1:00 HOUR

1. The limiting molar ionic conductivities at 25 °C for La^{3+} (aq) and SO_4^{2-}(aq) are 209.1 and 160.0 S cm^2 mol^{-1}. Find the limiting molar conductivities of lanthanum sulphate at 25 °C. Thence, find the transport numbers of lanthanum and sulphate ion in an aqueous solution of lanthanum sulphate $+3$
2. After correcting for the conductivity of the solvent, the conductivity of a saturated solution of silver bromide in water is 6.99×10^{-8} S cm^{-1} at 18 °C. If the molar ionic conductivities of Ag^+(aq) and Br^-(aq) are 53.5 and 68.0 S cm^2 mol^{-1} respectively, find the solubility of silver bromide in water. From this calculate the solubility product for silver bromide.
3.
   i. Briefly explain the following:
      a. difference between and ideal and a non-ideal solutions of electrolyte
      b. asymmetric effect of ionic atmosphere
   ii. Express the mean molality of an aqueous solution of lanthanum sulphate in terms of the molality m of the solution

$\Lambda = k/c$

$(100cm)^2 - 1(m)^2$

$898.2 cm^2$

0.05982

$100cm - 1m$

$(10cm)^3 - 1dm^3$

$1000cm^3 - 1dm^3$

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OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE

B.Sc. Chemistry Degree Examination

Part IV

MID RAIN SEMESTER EXAMINATION 2018/2019 SESSION

CHM 403 –Electrochemistry

July, 2019

Time: [illegible] hr

$\ell =$ $P_H =$ $= \log$ $\times H$

i.e $\phi = \phi_s - \phi_a$ $= 0$

$AH_2 \rightleftharpoons H^+$ → oxidation pH

$\to 2K^+ + SO_4^{2-}$ → acidic

1. At 25°C and pH 7, a solution containing compound **A** and its reduced form **AH_2** has a standard electrode potential of -0.60 V. A solution containing **B** and **BH_2** has a standard potential of -0.16 V. If a cell were constructed with these systems as half cells,

(a). Is **AH_2** oxidized by **B** or is **BH_2** oxidized by **A** under standard conditions?

$2H^+ + A^- \rightleftharpoons AH_2$

$\rightleftharpoons BH_2$

(b). What is the reversible emf of the cell?

(c). What would be the effect of pH on the equilibrium ratio **$[B][AH_2]/[A][BH_2]$**?

2 (a). What simple difference exists between a polarizable and a non-polarizable electrode surface?

$W = \frac{\sigma}{\varepsilon}$

(b). The zeta potential is 4.182×10^{-4} V and the charge density at the electrode surface is 3.52×10^{-8} C m^{-2}, find the thickness of the diffusion layer. (Relative permittivity of water = 78.54 and permittivity of free space = 8.854×10^{-12} C^2 J^{-1} m^{-1}).

$\rho = -$

3. Calculate the mean activity coefficient for Ba^{2+} and SO_4^{2-} ions in a saturated solution of $BaSO_4$ ($K_{sp} = 9.2 \times 10^{-11}$ mol^2 dm^{-6}) in 0.20 moldm^{-3} K_2SO_4 assuming the Debye-Hückel limiting law applies. (A = 0.51)

4. In **not more than five lines**, describe the three modes of interaction of ions used by the inter-ionic attraction theory to explain variations in molar conductivity with concentration.

Ion pa

Asym effe

$\alpha =$ 1:1

$\frac{\Lambda}{\Lambda^0}$ 1:1 $c+c$ $= 2c$ $2c$? $\frac{1}{\cancel{x}}$

[30 marks]

$\alpha =$

$SO_4 + K_2SO_4 \to K_2$

Oxidation.

$K_2SO_4 \to 2K + SO_4$ 95064 60×1

2 : 1

0.2

$\alpha =$

0.2

1:2

$\frac{3.52 \times 10^{-8}}{91 \times 10^{-25}} = 1.21 \times 10^{17}$

$K_{sp} = c^2$

$10^{-11} = c$

91×10

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Chemistry Degree Examination
CHM 403: ELECTROCHEMISTRY
2018/2019 Harmattan Semester Examination

Time Allowed: 2½ Hours

Date: 23rd July, 2019

Instructions: Answer ALL Questions in Section A and ANY TWO Questions in Section B

Useful Constants: Relative permittivity of water = 78.54, Faraday constant = 96,500 C
R = 8.314 $J.mol^{-1}.K^{-1}$, permittivity of free space = 8.854×10^{-12} C^2 J^{-1} m^{-1}, K_B = 1.38×10^{-23} $J.K^{-1}$.

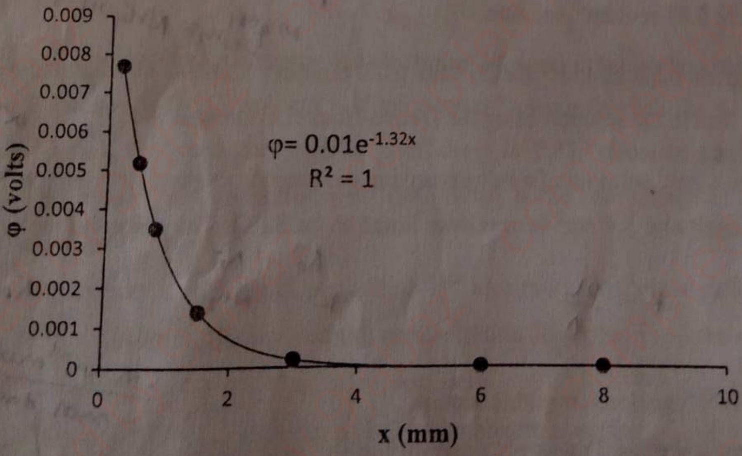
SECTION A: Answer **ALL** questions in this section

1. (a). What simple difference exists between a 'polarizable' and a 'non-polarizable' electrode surface?

(b). The solution provided by the Stern model to the problem of 'polarizable electrode surface' may be written as

$$\varphi = Ae^{-\chi x} + Be^{\chi x} \qquad (*);$$

where $1/\chi$ and x are the thickness of the diffused layer and the position of the electrolytic io from the electrode surface respectively. If the figure below is an experimental observation fro Dr. Sanusi's CHM 403 class,



i. Under what condition does equation (*) (theoretical solution) matches t experimental observation?

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ii. From the graph, what would be the value of $1/\chi$, the thickness of the diffused layer? 0.256

iii. What would be the measured charge density per unit area of the electrode (σ) in C m^{-2} at 25°C, if the edge of the outer Helmholtz plane is at 3 mm? 5.24×10^{-12}

iv. Using the charge density obtained in 1(b(iii)), calculate the potential at this point and provide its alternative name. 0.01

v. From the graph, determine the potential at the surface of the electrode, i.e. φ_0. 3.66×10^{-3}

(c). Given that the current density i produced by cell A and B are 0.25 A m^{-2} and 0.5 A m^{-2} respectively. (i) What would be the reaction rates in cells A and B if the valency of the charged ions are 1 and 3 respectively. (ii) In which of the cells would the electrochemical process be faster?

$\frac{C m^{-2}}{C^{2} J^{-1} m^{-1}} \times m$

A=0.051

[15 marks]

2. (a). The molar conductivity at 20□C of a 0.01 moldm^{-3} aqueous solution of ammonia is 9.6 cm$^{2}\Omega^{-1}$ mol^{-1}. For NH_4Cl, Λ_0 = 129.8 cm^{2} Ω^{-1} mol^{-1} and the ionic conductivities of OH^- and Cl^- are 174 and 65.6 cm^{2} Ω^{-1} mol^{-1} respectively. Calculate,

$r = \frac{i}{zF} = \Lambda = \frac{k}{C}$

(i) Λ_0 for the ammonia solution and NH_4OH NH_4 N $\Lambda = \frac{k}{2}$ Λ

(ii) the degree of ionization in 0.01 moldm^{-3} solution. α NH_4OH $2NH_3 = NH_4OH + NH_4Cl$

(b). A solution is made up of 0.02 moldm^{-3} $CdCl_2$ and 0.02 moldm^{-3} $CuSO_4$. Calculate the activity coefficient of Cu^{2+} ions in the solution using the Debye-Huckel limiting law. $\alpha = \frac{\Lambda_C}{\Lambda_0}$

(c). The resistance of 0.01mol dm^{-3} solution of a salt occupying a distance between two platinum electrodes placed 1.80 cm apart and 5.4 cm^{2} in area was found to be 32 Ω. Calculate the molar conductance of the solution.

$\Lambda_0^{+} + \Lambda_0^{-}$

$\alpha = \frac{\Lambda_C}{\Lambda_0}$ $R = \frac{\rho l}{A}$ $k =$ NH_3 $\Lambda_0 + \Lambda_0$

[15 marks]

$\frac{cm^{2}\Omega^{-1} mol^{-1}}{mol\ dm^{-3}}$

SECTION B: Answer any two questions from this section

3. Suppose **Figure Y (shown on page 3)** was obtained during the experiment conducted in Dr. Sanusi's CHM 403 class. If this experiment was aimed at determining the mechanism of the electronation reaction $2H^+ + 2e^- \rightarrow H_{2(g)}$ at 25°C, and given the following two-step processes as the proposed pathways for the reaction,

(i) $H^+ + e^- \rightarrow H_{ads}$ ....electronation step

(ii) $2H_{ads} \rightarrow H_{2(g)}$ ....combination step;

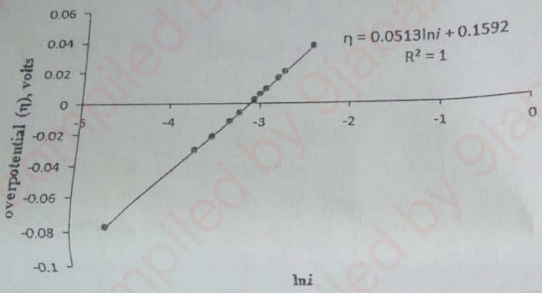
$NH_4 + NH_4 \rightarrow 2NH_3 + H_2$ mols

(a) calculate the value of β and determine which would be the slow step of the two steps (i) and (ii). $-\frac{RT}{\beta zF}\ln i_0$.

(b) determine the exchange current density.

(c) calculate the concentration of the adsorbed hydrogen atom (H_{ads}) on the cathode at 0.045 volts overpotential, assuming A to be equal to 1.00×10^{-3} mol.dm^{-3}. $[H_{ads}] = K\,A\,\frac{\eta F}{RT}$.

(d) At what current density would the amount of hydrogen calculated in 3(c) be deposited if the rate constant is 1.0×10^{-5} m^{-2} s^{-1}? $r = k_{ads}[H_{ads}]$.



$$\eta = \frac{RT\ln i}{\beta zF} - \frac{RT\ln i_0}{\beta zF}$$

Figure Y.

[20 marks]

④ (a). The exchange current at the electrodes of a cell in which two electrons are involved in the cell reaction is 0.311 mA cm^{-2}. If the current flowing through the surfaces of the electrodes is 0.612 mA cm^{-2} and the transfer coefficient is 0.43, calculate the cathodic and the anodic overpotentials of the electrodes at 25°C. What is the overvoltage of the cell and the electrode reaction rate?

$$-\eta = \frac{RT\ln i}{\beta zF} - \frac{RT\ln i_0}{\beta zF}$$

(b). If the current flowing through the B/B^{2+} electrode with Nernst diffusion layer of 2.5×10^{-3} m is 0.500 A. Assuming that the bulk concentration for B^{2+} ion and the coefficient of diffusion are 0.2 mol.dm^{-3} and 4.9×10^{-8} m^2 s^{-1} respectively, D_i

(i) determine the concentration of B^{2+} at the electrode surface. 0.199 $i = zFD_i\frac{(C_{bulk} - C_s)}{\delta}$

(ii) calculate the limiting current density (i_L). 0.75656

(iii) what is the concentration overpotential?

$$-\eta_c = \frac{RT}{F}\left(\ln 1 - \frac{i}{i_L}\right)$$

[20 marks]

$$r = \frac{i}{zif}$$

5 (a). (i) Define transport number of an ion

(ii) The molar conductivity of 0.02 mol.dm^{-3} $AgNO_3$ is 128.5 cm^2 mol^{-1} Ω^{-1}. If the transport number of Ag^+ = 0.477, calculate the mobilities of Ag^+ and NO_3^- ions in 0.02 mol.dm^{-3} $AgNO_3$ solution.

(b). Calculate the ionic strength of the solution obtained by mixing,

(i) 20 cm^3 of 0.10 moldm^{-3} KCl with 30 cm^3 of 0.01 moldm^{-3} $BaCl_2$;

(ii) 15 cm^3 of 0.02 moldm^{-3} NaOH with 20 cm^3 of 0.01 moldm^{-3} H_2SO_4.

(c). A conductivity cell standardized with 0.01 mol.dm^{-3} KCl was found to have a resistance of 189 Ω and molar conductivity 149.9 m^2 mol^{-1} Ω^{-1}. However, with 0.01 mol.dm^{-3} ammonia solution (NH_4OH), the resistance was 2460 Ω. Given the molar conductivity at infinite dilution as ($\Lambda^o_{NH_4^+}$) = 73.4 m^2 mol^{-1} Ω^{-1} and ($\Lambda^o_{OH^-}$) = 198.6 m^2 mol^{-1} Ω^{-1}. Calculate;

(i) the molar conductivity (Λ) and the degree of dissociation (α) of the ammonia solution

(ii) the base dissociation constant (K) of the ammonia solution.

[20 **marks**]

TessyB's Copy

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE
B.SC. (CHEMISTRY) DEGREE HARMATTAN SEMESTER, 2017/2018 SESSION

CHM 403: **Electrochemistry**

TIME ALLOWED: 1 Hour

INSTRUCTION: **Answer ALL questions**

(Given: Faraday's constant, F = 96500 C mol^{-1}, Universal Gas Constant, R = 8.314 J K^{-1} mol^{-1})

1. (a) Discuss with diagram the following standard secondary reference electrodes: (i) Glass electrode (ii) Silver-silver chloride electrode

(b) In a cyclic voltammetry experiment, the electron transport at a glassy carbon electrode (diameter = 3 mm) at 25 ^{0}C was determined in 5.0 mM $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox probe in 0.1 M pH 7.0 PBS (vs Ag|AgCl, sat'd KCl) (scan rate: 25 mV/s).
The number of electrons (n) due to the reversible process at the electode is related to the current (I) using Randles-Sevcik equation: $I = (2.69 \times 10^3)n^{3/2}CA(Dv)^{1/2}$
Where I = peak current (9.997×10^{-5} A) and D = diffusion coefficient of FeCN solution = 7.6×10^{-6} cm^2/s. Determine "n" and state the function of the sat'd KCl.

2. (a) State five (5) advantages of a dropping mercury electrode
Using the Llkovic equation id = $607nD^{1/2}Cm^{2/3}t^{1/6}$
Calculate the limiting diffusion current that would be expected from the reduction of 2×10^{-4} M Pb^{2+} using the DME characteristics (m = 2.0 mg/s, t = 4 sec, diffusion coefficient of Pb^{2+} = 1.01×10^{-5} cm^2/s).
(b) Consider the cell notation: $Zn/ZnCl_2//AgCl/Ag$
The e.m.f. of the cell represented above at 25 ^{0}C is 0.986 V and the temperature coefficient is -7.25×10^{-4} volt/kelvin. Calculate the values of the basic thermodynamic parameters.

$\Delta G = -nFE$
$= -nFE$
$= -190$

$E_0 = E + 0.05916 \log a_{Cl^-}$

$E = E_{cell} - 0.05916 \log a_{Cl^-}$
0.98

$(Zn^{2+})(Cl^-)^2$

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree (Chemistry) Examination Part IV
CHM 403: Electrochemistry
Harmattan Semester Examination 2017/2018 Session

Time Allowed: 2 Hours **Date: August 20, 2018**

Instructions: Answer **ANY THREE** (3) questions.
(Faraday's constant, F = 96500 C mol^{-1}, Universal Gas Constant, R = 8.314 J K^{-1} mol^{-1})

SECTION A

1. The values of Λ^{o} for NaOH(aq), NH_4Cl(aq) and NaCl(aq) in aqueous solutions at 18°C are 219.96, 129.54 and 108.40 S cm^2 mol^{-1} respectively. The molar conductivity of a 0.0010 M aqueous solution of NH_3 at 18°C is 29.03 S cm^2 mol^{-1}.
   a. Determine the degree of protonation and the equilibrium constant of ammonia in water. **(Note: At infinite dilution, weak electrolytes are considered to be fully ionised)**
   b. One of the applications of conductance measurements is conductimetric titrations, draw the form of the graph (conductivity vs volume of titrant) of such titration for
      i. Strong acid – strong base titration
      ii. Weak acid – strong base titration
      iii. Strong acid – weak base titration
      iv. Explain in not than **6 lines** the titration curve in b(i) above

[25 MARKS]

2. Using the equation $\log_{10}\gamma_i = -\frac{Az_i^2\sqrt{\mu}}{1+\sqrt{\mu}}$ where $A = 0.510$ mol$^{-1/2}$. dm$^{3/2}$ where μ is the ionic strength of the solution
   a. Calculate the individual activity coefficients for a 0.100 moldm^{-3} solution of magnesium chloride 0.435
   b. Use these to calculate the mean activity coefficient for the electrolyte. 0.574
   c. Use the Debye-Huckel expression for the mean activity coefficient to calculate the mean activity coefficient. 0.435
   d. Comment on the results

[25 MARKS]

SECTION B

3.
   a. Discuss the following electroanalytical techniques:
   (i) Polarography (ii) Cyclic voltammetry (iii) Square wave voltammetry and (iv) Galvanostatic Charge discharge
   b. In a cyclic voltammetry experiment, the electron transport at a glassy carbon electrode (diameter = 5 mm) at 25 ^{0}C was determined in 5.0 mM $[Fe(CN)_6]^{4-}$ /$[Fe(CN)_6]^{3-}$ redox probe in 0.1 M pH 7.0 PBS (vs Ag|AgCl, sat'd KCl) (scan rate: 50 mV/s).

a γ

The number of electrons (n) due to the reversible process at the electrode is related to the current (I) using Randles-Sevcik equation: $I = (2.69 \times 10^5)n^{3/2}CA(Dv)^{1/2}$ where I = peak current (9.997×10^{-5} A) and D = diffusion coefficient of FeCN solution = 7.6×10^{-6} cm^2/s. Determine "n" and state the function of the sat'd KCl.

[25 MARKS]

4.

a. (i) Define the term "Over potential" and discuss the different types that occur during electrochemical process.

(ii) State Tafel equation and define the terms in the equation. What electrode process does the equation describe?

(iii) Using the Ilkovic equation, $i_d = 607nD^{1/2}Cm^{2/3}t^{1/6}$ calculate the limiting diffusion current that would be expected from the reduction of 2×10^{-4} M Pb^{2+} using the DME characteristics (m = 2.0 mg/s, t = 4 sec, diffusion coefficient of $Pb^{2+} = 1.01 \times 10^{-5}$ cm^2/s).

b. (i) Using mathematical expressions, state the two limiting cases of Butler-Volmer

(ii) The exchange current of a Cu/Cu^{n+} electrode is 0.65 mAcm^{-2}. What amount of currents flows through the electrode of total area of 3.0 cm2 at 298 K when the potential difference across the electrode is 5.5 ~~k~~mV and the ion activity is unity?

[25 MARKS]

Resistance

E = E° − 0.059 log

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA

B.Sc (CHEMISTRY) DEGREE EXAMINATION, 2016/2017 Harmattan Semester

CHM 403: Electrochemistry

TIME: 1½ hours

NSTRUCTIONS: Answer Any Three Question in Sections A and B. Each question carries ual marks.

Section A

Question 1

$a_\pm = c_\pm \gamma_\pm$

(a) What is transport number of an ion?

(b) What are the charge carriers in (i) cobalt metal (ii) sodium sulphate solution (iii) helium gas and (iv) germanium doped with boron?

$\alpha = \frac{\Lambda_c}{\Lambda_o}$

(c) Explain briefly with equations why the conductivity of cadmium iodide solution decreases with increase in concentration.

CdI_2

(d) The molar conductivity of 0.001 mol dm^{-3} solutions of KCl, NaCl and ½K_2SO_4 are 149.9, 126.5 and 153.5 cm^2 Ω^{-1} mol^{-1} respectively. Calculate the molar conductivity for the same concentration of ½Na_2SO_4.

$\Lambda = \kappa / c$

Question 2

(a) Define the term activity coefficient. Arrange the following electrolytes in increasing order of activity coefficient, aqueous $NaIO_3$, Na_2SO_4 and Na_3PO_4.

(b) Why will the mobility of aqueous H$^+$ ions be more than double that of its close in size aqueous Li$^+$ ions?

(c) Outline two factors that relax after a while when an electric current is applied to an aqueous solution for which the terminology 'relaxation time' is commonly used.

(d) A solution of LiCl was electrolysed in a Hittorf cell. After a current of 0.79 ampere had been passed for two hours, the mass of LiCl in the anode had decreased by 0.793g. (i) Calculate the transport numbers of the Li$^+$ and Cl$^-$ ions. (ii) If the molar conductivity of LiCl is 1.15×10^{-2} m^2 Ω^{-1} mol^{-1}, what are the ionic conductivities of Li$^+$ and Cl$^-$ ions? [f = 96500 C mol^{-1} and molar weight of Li = 7.0g]

0.317

0.682

$\Lambda_c = \Lambda_o - b\sqrt{c}$

SECTION B

Question 3

a. What are the properties of an ideal reference electrode?

b. The Nernst equation for an organic redox electrode (quinhydrone) is:

$$E_{qh} = E^{o} + \frac{RT}{2F}\ln\frac{[Ox]}{C_{Red}} - \frac{RT}{2F}\ln K_1K_2 + \frac{RT}{2F}\ln\left([H^+]^2 + K_1[H^+] + K_1K_2\right).$$

Rewrite the above expression for this electrode

- i. In an acid medium
- ii. In a rather alkaline medium
- iii. How does each of the expressions in (i and ii) above shows the variation of the electrode potential with pH of the solution?

c. A 0.10 M $CdSO_4(aq)$ solution is electrolyzed between a cadmium cathode and a platinum anode with a current density of 1.00 mA cm^{-2}. The hydrogen overpotential is 0.60 V. What will be the concentration of Cd^{2+} ions when evolution of H_2 begins at the cathode? Assume all activity coefficients are unity (E^o for Cd/Cd^{2+} = -0.40 V)

$Cd^{2+} + 2e^- \rightleftharpoons Cd$

$Cd \rightarrow Cd^{2+} + 2e^-$

$E = E^o + \frac{RT}{2F}\ln\left(\frac{Cd^{2+}}{Cd}\right)$

Question 4

a. Define the following terms

- i. Electrode polarization
- ii. Exchange current
- iii. Activation over-potential

$J_o = Ne$

b. Distinguish between voltammetry and chronopotentiometry

$V = Aa$

c. How many electrons or protons are transported through the double layer in each second when the Cu, H_2/H^+ ($j_o = 1.0\times10^{-6}$ A cm^{-2}) and Pt/Ce^{4+}, Ce^{3+} ($j_o = 4.0 \times 10^{-5}$ A cm^{-2}) electrode are at equilibrium at 25 °C? Take the area as 1.0 cm^2 in each case. Estimate the frequency at which a single atom on the surface takes part in an electron transfer process, assuming an electrode atom occupies about $(260\ pm)^2$ of the surface

$Q = It$

$\Delta G = -nFE$

$Q = It$

$m^{-2}s^{-1}$

$f = cT_m$

$J =$

$f = c/T$

$= hc/\lambda$

$\rightarrow 4.2195 \times 10^{-3}$

Obafemi Awolowo University, Ile-Ife

Department of Chemistry

2014/2015 Harmattan Semester Test

CHM 403 -- Electrochemistry

$\gamma = a/c_i$ mol dm^{-3}

Time allowed: 1 hour

Question 1

(a) Give the S.I units of (i) activity and (ii) activity coefficient

(b) How and why does the conductance of (i) a metal and (ii) an electrolyte vary with the rise in temperature? (Answer in 10 lines or less)

(c) Outline two limitations of the use of conductance method for determining the equivalent point of acid-base titrations.

(d) Given a solution of 0.25 mol dm^{-3} ferric sulphate, calculate the ionic strength of the solution. If the ionic conductances at infinite dilution of the iron and sulphate ions are 2.85×10^{-2} and 1.25×10^{-2} m^2 Ω^{-1} mol^{-1} respectively at 298 K, find the mobility of the iron ion assuming the transport number of iron ion is 0.624. [F = 96500]

N

Question 2

a. For the following reference electrodes

i. Silver-silver chloride: Ag/AgCl

ii. Calomel: KCl (m)/Hg_2Cl_2/Hg

iii. Mercurous sulphate electrode: K_2SO_4/Hg_2SO_4/Hg

Write the half cell reaction and the corresponding Nernst equation for each of the electrodes

b. A cell is made up of hydrogen electrode in an unknown solution and a sliver electrode in 0.100 mol dm^{-3} Ag$^+$ solutions. The standard e.m.f of the cell is +1.24 V. What is the pH of the unknown solution, assuming that the hydrogen gas pressure is 1 atmosphere? (standard reduction potential for Ag/Ag$^+$ = 0.80 V).

1.24

$\lambda = \mu \alpha Z F$

$_2(SO_4)_3 \rightarrow 2Fe^{3+} + 3SO_4^{2-}$

2(0.25) 3(0.25

$\frac{1}{2}\Sigma(0.5(3)^2 + 0.75(2)^2)$

$\frac{1}{2}(4.5 + 3)$

1.24 = 0.05916 log a a-

0.8 - 0.05916 log

1.24 = 0

1.24

log

Section B

Answer only one question in this section

$\alpha = \frac{\lambda}{\lambda_0}$ $\lambda = \frac{\lambda}{c}$

$K = \alpha^2 c$

3 a. What is the flaw in the Helmholtz model of the electrical double layer at a solid-liquid interface? (5 marks)

b. The classical dissociation constant of methanoic acid is 1.85×10⁻⁴ at 298 K and the limiting ionic conductance at infinite dilution of the hydrogen and methanoate ions are 3.50×10⁻² and 3.50×10⁻³ m² Ω⁻¹ mol⁻¹ respectively. Calculate the resistivity of 0.25 mol dm⁻³ solution of methanoic acid. (10 marks)

$\alpha = \sqrt{\frac{K}{C}}$

$\alpha = \sqrt{K/c}$

$CH_3COOH \rightleftharpoons COO^- + H^+$

(Polarization) Reduction / fall in current supply

4 a. What is the major disadvantage and the consequence of the conductance measured using the direct current method? (5 marks)

$\rho = \frac{L}{\kappa R}$

Charge build up

b. The conductivity of 0.01 mol dm⁻³ of lead nitrate solution at 298 K is 0.2382 Ω⁻¹ m⁻¹. If the transport number of lead ions is 0.584, calculate the diffusion coefficient of lead ions in the solution. (10 marks)

$D = \frac{\mu kT}{e z}$

$\mu = \frac{t}{zF} = \frac{0.58}{2 \times 96}$

$D = 38$

Section C

Answer only one question from this section.

5 a. Define the terms in and limit the generality of the following expressions:

i. $j = j_0 f\eta$ (3 marks)

ii. $j = j_0 e^{(1-\alpha)f\eta}$ (3 marks)

iii. $j = -j_0 e^{-\alpha f\eta}$ (3 marks)

b. Given that the exchange current density and the transfer coefficient for the reaction

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

on platinum electrode at 25 °C are 2.5×10⁻³ A cm⁻² and 0.58 respectively. Determine what current density would be needed to obtain over-potential of 0.30 V as calculated from

i. Butler-Volmer equation (4 marks)

ii. The Tafel equation. (4 marks)

Is the validity of the Tafel approximation affected at higher over-potentials (of 0.4 V and more)? (3 marks)

6 a. Distinguish between voltammetry and chronopotentiometry (8 marks)

b. A 0.10 M FeSO₄ (aq) solution is electrolysed between a magnesium cathode and a platinum anode with a current density of 1.50 mA cm⁻². The hydrogen over-potential is 0.60 V. What will be concentration of Fe²⁺ when evolution of hydrogen gas just begins at the cathode? Assume all activity coefficients are unity (12 marks)

BAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
BSc (CHEMISTRY) DEGREE EXAMINATION
2014/2015 Harmattan Semester
CHM 403 -- Electrochemistry

Time allowed: 2 hours **Date: Sept. 2015**

INSTRUCTION: (i) Answer all the questions in section A and one question each from sections B and C

(ii) Leave a blank sheet between each section and answer each question on a fresh page.

CONSTANTS: Debye-Huchel constant = 0.50 $k = 1.385\times10^{-23}$ J K^{-1}

$F = 96500$ coul mol^{-1} electronic charge = 1.602×10^{-19} V

$\gamma_\pm = (\gamma_+^x\ \gamma_-^y)^{1/v}$

$\gamma_\pm$ $\gamma_\pm$ $(CrSO_4)$

Section A

Answer all the questions in this section

1. Two solutions A and B are each of concentration 0.10 mol dm^{-3} Solution A is sodium sulphate and solution B is chromium sulphate. Calculate the followings;

$CrSO_4 \rightarrow Cr^{2+} + SO_4^{2-}$

(i) The activity coefficients of the sodium and sulphate ions in solution A [Debye-~~Huchel limiting law is applicable to ions] (4 marks)~~ $\log \gamma_\pm$

(ii) The mean activity coefficient of solution A using the expression, $\sigma_\pm = (\sigma_+^{v+}\ \sigma_-^{v-})^{1/v}$ ~~and the Debye-Huchel limiting law. (4 marks)~~ $I = 0.3$ $(0.67 \cdot 0.3570)$

(iii) The concentration in mol dm^{-3} of the chromium ions in solution B (2 marks) 0.4761 · 0.35

(iv) The activity coefficients of the chromium and sulphate ions in solution B (4 marks)

(v) The mean activity coefficient of solution B using the two methods in (ii) above. (4 marks) = 0.55

(vi) Are the $\sigma_\pm$ obtained from the two methods the same in (ii)? Are they the same in (v)? Suggest a reason of less than two lines for each answer. (4 marks)

$$\begin{array}{r} 22 \\ 15 \\ \hline 37 \end{array}$$

[Note: Your answers must be labeled as the questions are itemized]

2 a. Explain the following

i. Electrode polarization (3 marks) — shift of electrode potential from the equilibrium potential which is due to uneven currents

ii. Activation over-potential (3 marks) $\eta = E - E^\circ$ 15

iii. Exchange current density (3 marks) J_0

b. Discuss the main structural features of the electric double layer (6 marks)

Electrode double … is the a layer … 2 parallel char… the 1st layer surf… charge cons of the c… Inverted 2nd layer …

$-Na^+$

$= SO_4^{2-}$

$$\log \gamma_+ = -A Z_+ \sqrt{I}$$
$$= -0.5\times1\sqrt{0.05}$$
$$= -0.5\times1\cdot0.2236$$
$$\log \gamma_+ = -0.111$$
$$\gamma_+ = 10^{-0.111}$$

$I = \frac{1}{2}\sum m_i z_i^2$

$I = \frac{1}{2}\cdot 0.1\ \text{mol dm}^{-3}\times1^2$

$I_{Na^+} = 0.05$

mol

$i = i_0 (e^{\frac{[illegible]}{RT}}$ [illegible]

(a) Discuss the following electrochemical terms: (i) Polarography (ii) Cyclic voltammetry (iii) Square wave voltammetry (iv) Irreversible process

(16 marks)

Electron transport at a glassy carbon electrode (diameter = 3 mm) was determined in 1.0 mM $K_3[Fe(CN)_6]$ in 1.0 M KCl solution (vs Ag|AgCl, sat'd KCl) at different scan rates (300 – 600 mV/s) using cyclic voltammetric techniques. The anodic peak potential was recorded against scan rate and the data obtained presented in the Table below. Using the Tafel equation: $E_p = \frac{b}{2}\log v + constant$

Determine the Tafel value b, (ii) Write the half-cell and the net cell reactions for the electrochemical cell. (iii) What is the function of the 1.0 M KCl electrolyte? (iv) State the function of the Ag|AgCl, sat'd KCl.

Scan rate v (mVs^{-1})	300	350	400	500	550	600
Ep (V)	0.33	0.34	0.36	0.39	0.41	0.42

(9 marks)

(a) Discuss the following: (i) Electrode Over potential (ii) Quinehydrone electrode
State the Fick's law and define all the terms in its mathematical expression.
Give two reasons (providing mathematical expression) why Butler-Volmer equation is considered as one of the most important equations for electrochemical kinetics at the electrodes surface. (16 marks)
The data below are for the cell: $Pt(s)|H_2(g,P^\theta)|HBr(aq, m)|AgBr_{(s)}|Ag_{(s)}$ at 25 °C. Determine the standard emf of the cell.

$m(10^{-4})/ molkg^{-1}$	4.042	8.444	37.19
E/V	0.47381	0.43636	0.36173

(9 marks)

$J \propto \frac{d[C]}{dx}$

$0.59m - b\sqrt{m}$

$J \propto \frac{\partial c}{\partial x}$

$J \propto \frac{\partial c}{\partial x}$

$J = D \cdot N \frac{\partial c}{\partial x}$

1-2

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA

BSc (CHEMISTRY) DEGREE EXAMINATION, 2014/2015

CHM 403: ELECTROCHEMISTRY

$D = \frac{uK_BT}{ez} = \frac{uRT}{zF}$.

TIME: 2:30 mins

INSTRUCTIONS: Answer <u>ANY THREE</u> questions

(Given: Faraday's constant, F = 96486 C mol^{-1}, Universal Gas Constant, R = 8.314 J K^{-1} mol^{-1})

$\frac{m^2}{Vs} \div \frac{V}{m}$

1. (a) Given that the molar conductivities of Cs$^+$, SO_4^{2-}, Mg^{2+} and $Mg(NO_3)_2$ are 0.772×10^{-2}, 1.600×10^{-2}, 1.060×10^{-2} and 2.488×10^{-2} S m^2 mol^{-1} respectively. Calculate the molar conductivity of (i) Cs_2SO_4 (ii) NO_3^- and $CsNO_3$

$V = \frac{m^2}{Vs} \times \frac{V}{m}$

0.0314 0.01428 0.02 $K =$

(6 marks)

(b) Explain Wien effects. What is the relationship between First Wien effect and Debye-Falkenhagen effect?

$K = \frac{\Lambda_c}{\Lambda_0}$ $\Lambda = 3.042\times10^{-6}$ S $x =$

(6 marks)

(c) The conductance of a saturated solution of AgCl was 3.042×10^{-6} S in a conductivity cell with a cell constant of 98.4 m^{-1}. The conductance of water in the cell was measured to be 1.171 μS. Calculate the K_{sp} of AgCl if the limiting molar conductivity of AgCl is 1.383×10^{-2} S m^2 mol^{-1}.

E = u

(7 marks)

d) Arrange K$^+$, H$^+$ and Na$^+$ ions in decreasing order of their mobility and explain why?

(6 marks)

(a) Why does the molar conductance of strong electrolytes increase with increase in dilution despite the fact that they are known to ionize completely in solution, even in very concentrated solutions?

$K^+ > Na^+ > H^+$ H^+ $K^+ < Na^+ < H$

(4 marks)

$H^+ <$

) List four factors that can cause the transport of ions in solution. (4 marks)

c) State the equation for the Debye-Huckel limiting law and the experimental condition under which this equation will hold. Arrange the following electrolytes in decreasing order in which the Debye-Huckel limiting law will accurately describe them: $Ca_3(PO_4)_2$, $MgCl_2$, $NaNO_3$ and K_3PO_4.

$Vs \times \frac{m^2}{Vs} \times \frac{V}{m}$ $V = \frac{V}{m} =$ $\frac{m^2}{V} = \frac{V}{m}$.

(4 marks)

(d) The mobility of the silver ion is 7.912×10^{-8} m^2 /(Vs).

(i) Calculate the drift speed of the silver ion in an electric field of 125 V/m

(ii) Estimate the hydrodynamic radius of the silver ion (note, $\eta_o = 0.890 \times 10^{-3}$ kg/ (ms)).

(iii) Calculate the molar conductivity of silver ion

(iv) Estimate the diffusion coefficient of the silver ion at 298 K. (note: 1 V = 1 J/C; 1 V = 1 AΩ; 1 S = 1/Ω).

$D = \frac{uRT}{zF} = \frac{uk_BT}{ez} =$ $u = z$ $V = E/u$

(13 marks)

$r = 21\times10^{-15}$ $\Lambda = zuF$ $u = \frac{\Lambda}{zF}$ $u = \frac{\partial E}{\partial x}$ 125

$u = zu'$

$\Lambda = zuF$

$D = \frac{uRT}{6\pi\eta a}$. $\partial x =$

$\Lambda = zuF$ 1.609×10^{-19} C =

0.05×10^{-3}

5×10^{-3} mol/cm^3

$CH_3CH_2COO^- + H^+$

$CH_3COOH \rightleftharpoons CH_3COO^-$

8 The conductivity of 0.05 mol dm^{-3} solution of ethanoic acid at 18°C is 4.4×10^{-4} Ω^{-1} cm^{-1}. The molar conductivities of the hydrogen and ethanoate ions at infinite dilution at the same temperature are 310 and 77 cm^2 Ω^{-1} mol^{-1} respectively. Calculate the dissociation constant of ethanoic acid.

$= \frac{4.4 \times 10^{-2}}{\Omega^{-1}}$

$= 310 \times 10^{-4}$ m^2

77×10^{-4} m^2

9 The molar conductivity at 18°C of a certain concentration of NH_4OH is 131.36 cm^2 Ω^{-1} mol^{-1}. Compute the molar conductivity at infinite dilution and the degree of dissociation of NH_4OH if the molar conductivities at infinite dilution at 18°C for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 288.8, 120.3 and 129.8 cm^2 Ω^{-1} mol^{-1} respectively.

4.4×10^{-2}

* 10 In a Hittorf experiment aqueous silver nitrate solution was electrolysed between the silver electrodes. The amount of silver nitrate in the anode compartment was 0.227g before electrolysis and 0.281g after electrolysis. During the electrolysis 0.0194g of copper was deposited on the cathode of a copper coulometer in series with the Hittorf cell. Calculate the transport numbers of Ag^+ and NO_3^- ions.

1 m =

1 cm =

1 cm^2 =

* 11 What are the mobilities of H^+ and SO_4^{2-} ions in aqueous solution at infinite dilution given the ionic conductance at infinite dilution at 298K of H^+ ions to be 3.49×10^{-2} and that of SO_4^{2-} ions to be 1.596×10^{-2} m^2 Ω^{-1} mol^{-1}.

12 The ionic conductivity of Li^+ ions at zero concentration is 3.864×10^{-3} m^2 Ω^{-1} mol^{-1}. Calculate the number of ionic diameter traversed in one second under a potential difference of 10 v m^{-1} if the radius of the solvated ion is 2.36×10^{-10} m.

13 Find the diffusion coefficient and the hydrodynamic radius in Å of the SO_4^{2-} ion in water at 298K given its mobility to be 8.27×10^{-8} m^2 v^{-1} s^{-1}. [Viscosity of water = 1.00×10^{-3} kg m^{-1} s^{-1}. Electronic charge = 1.602×10^{-19} coul.]

$D = \frac{\mu RT}{Fz}$

14. Calculate the activity ~~coefficients~~ coefficient of Na^+ and SO_4^{2-} ions ~~and the mean activity~~ and the mean activity coefficient of the ions ~~coefficients of the ions~~ in 0.005 mol dm^{-3} of sodium sulphate at 298K. ~~[illegible]~~

15 In a moving boundary experiment to determine the cation transport number in 0.02 mol dm^{-3} lithium chloride solution, a current of 1.60×10^{-3} amp caused the boundary to move a distance of 7.00×10^{-2} m in 0.6795 hours. If the cross-section of the transport tube is 1.115×10^{-5} m^2, calculate the transport numbers of the cation and anion.

$k = \frac{1}{R}\frac{l}{A}$

$AgNO_3$

(10) Loss = 0.281 − 0.227

~~= 0.2583~~ = 0.054

= 0.054 × ... = ~~1.0012×10^{-3}~~ eqmv

Obafemi Awolowo University, Ile-Ife
Department of Chemistry
2010/2011 Mid – Harmattan Semester Test

Time allowed: 1 hour

Constants : Debye-Huckel constant, A = 0.509, π = 3.142, F = 96500 coul mol^{-1}

CHM 403 – ELECTROCHEMISTRY

Instruction : Answer all questions

The inter ionic attraction lowers the free energy of [illegible] and from $\Delta G = kT \ln \gamma$, γ tends to decrease as ΔG decreases

1(a) A plot of log $\gamma_\pm$ against $\sqrt{I}$ shows a minimum, explain briefly the root of the observed minimum.

(b) 50.00 cm^3 of 0.10 mol dm^{-1} NaOH is added to 50.00 cm^3 of 0.05 mol dm^{-3} H_2SO_4. What is/are the

(i) ions in solution?

(ii) concentration of the solution?

(iii) ionic strength of the solution?

(iv) mean ionic activity coefficient of the solution? → $\log \gamma_\pm = -A z_+ z_- \sqrt{I}$

(v) mean ionic activity of the solution?

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

2(a) ~~Given the reaction $Ca(OH)_2 + 2HCN$~~ $\rightarrow Ca(CN)_2 + 2H_2O$,

(i) sketch the graph of the conductivimetric titration when $Ca(OH)_2$ is progressively added to HCN.

(ii) Explain coincisely the shape of your graph.

(b) The velocity of a boundary of HCl with LiCl is followed in aqueous solution. It moves 15.0 cm in a tube of 1 cm diameter in 22 minutes when the current is 11.54 mA. If the concentration of the HCl is 0.01065 mol dm^{-3}, what are the transport numbers of the hydrogen and chloride ions?

$t_-\Lambda$

S cm^2 mol^{-1}

πr

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

$2Na^+ \quad SO_4^{2-}$

$t_-\Lambda = z_- u_- F$

$u_- = \frac{t_-\Lambda}{z_- F}$

$\frac{0.005 \text{ mol}}{2}$

0.0025

$1 m^3 = 1000 dm^3$

$1 dm^3 = 1000 cm^3$

$\Lambda = \frac{\kappa}{c}$

$\delta = \kappa^{-1} = \left(\frac{\varepsilon_0 \varepsilon_r kT}{e^2 \sum n_i z_i^2}\right)^{1/2}$

$\log \gamma_\pm$

(0.2)

Obafemi Awolowo University, Ile-Ife, Nigeria
Department of Chemistry

TUTORIAL QUESTIONS 2

ELECTROCHEMISTRY (CHM 403)

Calculate the approximate thickness (δ) of the diffuse double layer which is established at a negatively charged plane solid surface in contact with a 0.01 mol dm^{-3} aqueous solution of sodium sulphate at 298K. The relative permittivity of water at this temperature may be taken to be 78.54.

Particles of the colloidal dispersion of a noble metal have an effective mean radius of 0.25mm in a 0.04 mol dm^{-3} aqueous solution of a 1:1 electrolyte and have an electrophoretic mobility of 3.50×10^{-8} m^2 V^{-1} at 298K. Calculate an approximate value for the zeta (ξ) potential. Viscosity of water at 298K is 8.94×10^{-4} kg m^{-1} s^{-1}. relative permittivity of water at 298K is 78.5.

A glass tube 15cm long and mean internal diameter 0.? mm is filled with aqueous static source while a potential difference of 250V is applied between its ends. A temperature of 298K is maintained throughout the time of imposition of the potential difference of 250V is applied between its ends. A temperature of 298K is maintained throughout the time of imposition of the potential difference. Calculate the rate of electro-osmotic flow of the water at 298K given that the zeta-potential (ξ) for a glass/water interface is -40mV, the viscosity of water is 8.9×10^{-4} kg m^{-1} s^{-1} and its relative permittivity is 78.54 at this temperature.

In an electrochemical reaction, the current density is 10 mA cm^{-2} where the valency, z. Calculate the rate of the reaction, v.

An electrochemical reaction was taking place at a large anodic overpotential. If the potential is made more positive by 0.2V, by how much would the reaction velocity change. T = 298K. β = 0.5. F = 96,500 C mol^{-1} and R = 8.314 J K^{-1} mol^{-1}

ξ ϕ z VA

$V = \frac{\xi}{L}$

aldehyde

N-Pyry alcohol → aldehyde → nitrile → α-hydroxynitrile → cyanogenic glucoside

R—C=N

Department of Chemistry

IM

write d dissociate for Na_2SO_4

CHM 403 – Electrochemistry Tutorial Questions

The conductivity of a saturated solution of barium suplate at 25°C is 3.590×10^{-4} ohm^{-1}m^{-1} and of the conductivity water used is 0.618×10^{-4} ohm^{-1} m^{-1}. The limiting molar conductance at zero concentration for 1/2Ba and 1/2 SO_4^{2-} are 6.364×10^{-3} and 8.000×10^{-3} ohm^{-1} m^{2} mol^{-1} respectively.
Calculate the solubility product of barium sulphate at this temperature, assuming complete dissociation of the salt. $K_{sp} = 1.061 \times 10^{-4}$.

2. The limiting molar conductance at zero concentration of tetraethylammonium picrate in ethanol (viscosity = 0.0101 poise) at 298K is 5.54×10^{-3} ohm^{-1}m^{2} mol^{-1}. Calculate the limiting ionic conductance of the tetraethylammonium cation in acetone at 298K, given that the limiting ionic conductance at zero concentration of the piccrate ion in acetone (viscosity = 0.00316 poise) at 298K is 8.242×10^{-3} ohm^{-1} m^{2} mol^{-1}.

3. The electrolytic conductivity of a 0.001 mol dm^{-3} of Na_2SO_4 is 2.6×10^{-2} ohm^{-1}m^{-1}. If the solution is saturated with $CaSO_4$, the conductivity becomes 7.0×10^{-2} ohm^{-1}m^{-1}; Calculate the solubility product for $CaSO_4$ given the ionic molar conductance, $\Lambda(Na^+) = 5.00 \times 10^{-3}$ and $\Lambda(1/2Ca^{2+}) = 5.95 \times 10^{-3}$ ohm^{-1}m^{2} mol^{-1} at these concentrations.

The resistance of a cell when filled with 0.01 mol dm^{-3} KCl was found to be 189 Ω, the cell was then filled with ammonia solution of 0.01 mol dm^{-3} and the resistance was 2460 Ω. Calculate the base dissociation constant of the ammonia solution given that the molar conductances at infinite dilution of K^+, Cl^-, NH_4^+ and OH^- are 7.64×10^{-3}, 7.35×10^{-3}, 7.34×10^{-3} and 19.86×10^{-3} ohm^{-1} m^{2} mol^{-1} respectively.

The classical dissociation constant of propanoic acid is 1.34×10^{-5} at 25°C and the limiting ionic conductances at infinite dilution of the hydrogen and propanoate ions are 3.498×10^{-2} and 3.58×10^{-3} ohm^{-1}m^{2} mol^{-1} respectively. Calculate the resistivity of a 0.10mol dm^{-3} solution of propanoic acid.

The degree of dissociation of an acid HA in 0.01 molar aqueous solution at 298K is 0.0810. Calculate the true dissociation constant of the acid. If to this solution is added an equal volume of 0.01 mol dm^{-3} aqueous sodium hydroxide containing sodium sulphate, at 0.003 mol dm^{-3}, what will be (a) the ionic strength and (b) the hydrogen ion concentration of the resulting solution?

A solution contining 10.850g silver nitrate per 1000g water was electrolysed between silver elctrodes. After elctrolysis the whole solution was removed and was found to weigh 54.900g. On analysis it was found to contain silver equivalent to 0.7217g silver nitrate. In a coulometer in series, 0.04672g copper was deposited. Calculate the transport number of the silver ion and the nitrate ion. 0.49 & 0.506

8 The conductivity of 0.05 mol dm^{-3} solution of ethanoic acid at 18^{0}C is 4.4x10^{-4} Ω^{-1} cm^{-1}. The molar conductivities of the hydrogen and ethanoate ions at infinite dilution at the same temperature are 310 and 77 cm^2 Ω^{-1} mol^{-1} respectively. Calculate the dissociation constant of ethanoic acid.

9 The molar conductivity at 18^{0}C of a certain concentration of NH_4OH is 131.36 cm^2 Ω^{-1} mol^{-1}. Compute the molar conductivity at infinite dilution and the degree of dissociation of NH_4OH if the molar conductivities at infinite dilution at 18^{0}C for $BaOH_2$, $BaCl_2$ and NH_4Cl are288.8, 120.3 and 129.8 cm^2 Ω^{-1} mol^{-1} respectively.

10 In a Hittorf experiment aqueous silver nitrate solution was electrolysed between the silver electrodes. The amount of silver nitrate in the anode compactment was 0.227g before electrolysis and 0,281g after electrolysis. During the electrolysis 0.0194g of copper was deposited on the cathode of a copper coulometer in series with the Hittorf cell. Calculate the transport numbers of Ag^+ and NO_3^- ions. 0.476 & 0.574

11 What are the mobilities of H^+ and SO_4^{2-} ions in aqueous solution at infinite dilution given the ionic conductance at infinite dilution at 298K of H^+ ions to be 3.49x 10^{-2} and that of SO_4^{2-} ions to be 1.596x10^{-2} m^2 Ω^{-1} mol^{-1}.

12 The ionic conductivity of Li^+ ions at zero concentration is 3.864x10^{-3} m^2 Ω^{-1} mol^{-1}. Calculate the number of ionic diameter traversed in one second under a potential difference of 10 v m^{-1} if the radius of the solvated ion is 2.36x10^{-10} m.

13 Find the diffusion coefficient and the hydrodynamic radius in A^0 of the SO_4^{2-} ion in water at 298K given its mobility to be 8.27x10^{-3} m^2 v^{-1} s^{-1}. [Viscosity of water = 1.00x10^{-3} kg m^{-1} s^{-1}. Electronic charge = 1.602x10^{-19} coul.]

14 Calculate the activity coefficients of Na^+ and SO_4^{2-} ions and the mean activity coefficient of the ions ~~and the mean activity coefficient of the ions~~ in 0.005 mol dm^{-3} of sodium sulphate at 298K. given the ionic activity to be [illegible]

15 In a moving boundary experiment to determine the cation transport number in 0.02 mol dm^{-3} lithium chloride solution, a current of 1.60x10^{-3} amp caused the boundary to move a distance of 7.00x10^{-2} m in 0.6705 hours. If the cross-section of the transport tube is 1.115x10^{-5} m^2, calculate the transport numbers of the cation and anion.

Increase in anode Compartment = 0.281g − 0.227g = 0.054g.

mole equivalent = $\frac{0.054g}{170 \text{ (mass of } AgNO_3)}$ = 3.17647×10^{-4} mol equi.

Total amount deposited = $\frac{0.0194g}{\text{molar mass}}$ = $\frac{0.0194}{63.6/2}$ = 6.1006×10^{-4}

$t = \frac{3.17647\times10^{-4}}{6.1006\times10^{-4}} = 0.521$

3

d) Using the charge density obtained in 3(c), calculate the potential at this point and provide its alternative name. From the graph, determine the potential at the surface of the electrode, i.e. φ_0.

$\varphi = 0.01e^{-0.5x}$

$x = \delta + 1/\chi = 3 \times 10^{-3} + 2 = 2.003$

$\varphi = 0.01\, e^{-0.5 \times 2}$

3.67×10^{-3}

4 (a). Calculate the current density i (in A m^{-2}) for a migrating ion A^+ if the migration rate is 0.025 mol. s^{-1}.

$i = zF$

(b). Given that the current density i produced by cell A and B are 0.25 A m^{-2} and 0.5 A m^{-2} respectively. What would be the reaction rate in cells A and B if the valency of the charged ions are 1 and 3 respectively. In which of the cells would the electrochemical process be faster? A will be faster.

higher rate will be faster

(c) What fraction of hydrated protons would populate an excited state at 25°C, if the energy of the state is 450 J and the transmission coefficient β is unity? $n(H_3O)^+ = n_{H_3O^+}\, e\left(\frac{-\Delta G^\circ}{k_bT}\right)$

5. Suppose the figure below is the result obtained to determine the mechanism of the electronation reaction $2H^+ + 2e^- \rightarrow H_{2(g)}$, conducted during Dr. Sanusi's CHM 403 class. If the following two-step processes are proposed for the reaction at 25°C,

(i) $H^+ + e^- \rightarrow H_{ads}$ ....electronation step

(ii) $2H_{ads} \rightarrow H_{2(g)}$ ....combination step,

a). determine which of the two steps (i) and (ii) is the slow step. 0.057

b). what is the value of β for this reaction? $\frac{1}{2}$

c). determine the exchange current density.

d). calculate the concentration of the hydrogen atom adsorbed on the cathode at 0.045 volts overpotential, assuming A to be equal to 1×10^{-3} mol.dm^{-3}. At what current density would this amount of hydrogen be deposited if the rate constant is given as 1×10^{-5} s^{-1}.

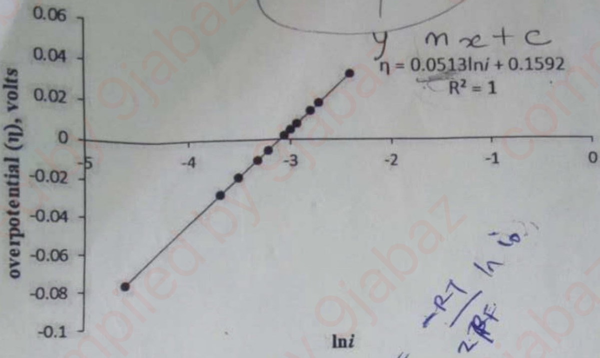
$[H_{ads}] = A\, e^{-\eta F/RT}$

rate = k × conc.

$r = k_{ads}[H]^2_{ads}$

$r = \frac{i}{2iF}$

4



$y = mx + c$

$r = k_{ads}[H_{ads}]^2$

$\eta = \frac{-RT}{2\alpha F}\ln(i)$

6 (a). State the difference between a charge transfer and concentration overpotential.

(b). If the current flowing through the B/B^{2+} electrode with Nernst diffusion layer of 2.5 × 10^{-3} mm is 0.500 mA. Assuming the bulk concentration for B^{2+} and the diffusion coefficient are 0.2 mol.dm^{-3} and 4.9 × 10^{-5} mol.dm^{-3} s^{-1} respectively,

(i) *determine the concentration of B^{2+} at the electrode surface.*

(ii) calculate the limiting current density (i_L). $i_L = zFD_i\left(\frac{C_{bulk}}{\delta}\right)$

(iii) what is the concentration overpotential?

Note generally that, R^2 is just a correlation coefficient that measures the degree of consistency/reliability of the experimental data. 0.9 < R^2 ≤ 1.0 indicates high consistency/reliability.

$-\eta_c = \left(\frac{kT}{t_L F}\right) i$

2

0.612 mA cm^{-2} and the transfer coefficient is 0.43, calculate the cathodic and the anodic overpotentials of the electrodes at 25°C. What is the overvoltage of the cell and the electrode reaction rate?

(c). What was the major modification carried out in the Stern model that made it better than the Gouy-Chapmans' in explaining the concept of 'polarizable electrode surface'?

3. The solution provided by the Stern model to the problem of 'polarizable electrode surface' may be written as

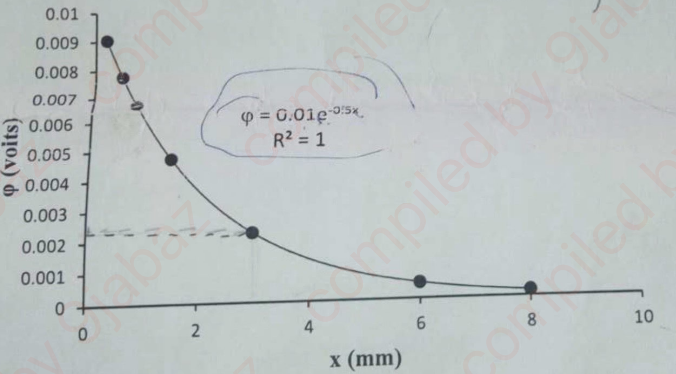
$$\varphi = Ae^{-\chi x} + Be^{\chi x} \qquad (**);$$

where $1/\chi$ and x are the thickness of the diffused layer and the position of the electrolytic ion from the electrode surface respectively. If the figure below is an experimental observation from Dr. Sanusi's CHM 403 class,

$\eta = E - E_{rev}$

$x = \delta + 1/\chi$.

$V = \frac{i}{zF}$



a) Under what condition does equation (**) (theoretical solution) matches the experimental observation?

b) From the graph, what would be the value of $1/\chi$, the thickness of the diffused layer?

c) What would be the measured charge density per unit area of the electrode (σ) in C m^{-2} at 25°C, if the edge of the outer Helmholtz plane is at 3 mm?

Obafemi Awolowo University, Ile-Ife
Department of Chemistry
2012/2013 Harmattan Semester Examination
CHM 403 – Eletrochemistry

Time allowed: 2 hours

Instruction: Answer All Questions in the same booklet but leave a Blank page between Sections A and B

Constants : R = 8.314 J mol^{-1}, F = 96500 coulomb mol^{-1}

Section A

Question 1

(a) Give the S.I. units of (i) concentration of a solution (ii) activity of a solution.

(b) Arrange and give reasons (5 to 6 lines) the order of increasing molar conductivity of the following electrolytes, potassium sulphate, lithium sulphate and tetraoxosulphate (VI) acid

(c) The molar conductivity of sodium fluoride in 0,10 mol dm^{-3} solution is 8,35 m^2 Ω^{-1} mol^{-1}. The salt may be taken as 92% dissociated. If the transport number of sodium ion is 0,45, calculate the mobilities of Na$^+$ and F$^-$ ions.

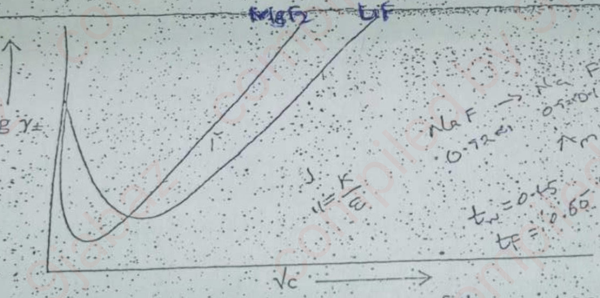
$F c_i z_i = \kappa$

Question 2

(a) Define the term activity coefficient. is d measure of d extent at which ions interact in solution

$Li_2SO_4 < K_2SO_4 < H_2SO_4$

(b)



$a = x^x y^y c^v \gamma^v$

$NaF \rightarrow Na \; F$ 0.92×0.1 0.92×0.1

$0.92 c$

$\Lambda_m \; NaF \; 8.35$

$c = 0.1$

$u = \frac{\kappa}{\varepsilon}$

$t_{+} = 0.45$

$t_F = 0.55$

$t_+ = \frac{J_i}{J} = \frac{F c_i z_i u_i}{F \Sigma c_i z_i u_i}$

Outline (6 lines or less) the salient features of the variation of activity coefficients with concentration shown in the diagram above.

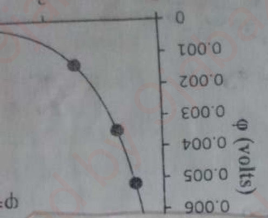
(c) The transference number of sodium ion in sodium cyanide is 0.384 and that of the sulphate ion in tetraoxosulphate (VI) acid is 0.212. The molar conductivities at infinite dilution of sodium cyanide and tetraoxosulphate (VI) acid are 2.45 and 10.68 m^2 Ω^{-1} mol^{-1} respectively, calculate,

(i) the transference number of the cyanide ion $1 - t_{Na^+}$

(ii) the molar conductivity at infinite dilution of hydrogen cyanide 4.925

CN^-

$t_+ = \alpha u z F$ $\Lambda^{\infty}_{m\,HCN} = (2.45 + 10$



$[Ox]$, $[Red]$
$v_{ox} = k_c[Ox]$
$v_{red} = k_a[Red]$
$j = F(k_a[\ldots$

Section B

[Question 5 is optional but earns bonus marks]

Question 3

Product flux in the charge transfer across the electrode-solution interface is given by:

Product flux = κ{species} where κ has units of $cm\,s^{-1}$

(a) Derive an expression for the net current density (j) from $j_a - j_c$. Under what condition(s) is the current anodic or cathodic?

(b) Using the activated rate theory, show that $j = FB_a[Red]e^{-\frac{\Delta G_a^{\ddagger}}{RT}} - FB_c[Ox]e^{-\frac{\Delta G_c^{\ddagger}}{RT}}$. Explain all the terms used and state any assumption(s).

Question 4

Using typical electrochemical cells, explain the origin of

(a) background limits at a working electrode

(b) when the faradaic and nonfaradaic processes are in operation under these conditions

(c) what a supporting electrolyte is.

Question 5

Describe fuel cells as one of the devices of electrochemical technology

$J = \frac{D(c_0 - c)}{\delta}$

Obafemi Awolowo University, Ile-Ife, Nigeria
Department of Chemistry

TUTORIAL QUESTIONS 2

$\phi = VA$

S – ME

ELECTROCHEMISTRY (CHM 403)

Calculate the approximate thickness (δ) of the diffuse double layer which is established at a negatively charged plane solid surface in contact with a 0.01 mol dm⁻³ aqueous solution of sodium sulphate at 298K. The relative permittivity of water at this temperature may be taken to be 78.54.

Particles of the colloidal dispersion of a noble metal have an effective mean radius of 0.25mm in a 0.04 mol dm^{-3} aqueous solution of a 1:1 electrolyte and have an electrophoretic mobility of 3.50 x 10^{-8} m^{2} V^{-1} at 298K. Calculate an approximate value for the zeta (ξ) potential. Viscosity of water at 298K is 8.94 x 10^{-4} kg m^{-1} s^{-1}. Relative permittivity of water at 298K is 78.5.

A glass tube 15cm long and mean internal diameter [illegible] mm is filled with [illegible] static source while a potential difference of 250V is applied between its ends. A temperature of 298K is maintained throughout the time of imposition of the potential difference of 250V is applied between its ends. A temperature of 298K is maintained throughout the time of imposition of the potential difference. Calculate the rate of electro-osmotic flow of the water at 298K given that the zeta-potential (ξ) for a glass/water interface is – 40mV, the viscosity of water is 8.9 x 10^{-4} kg m^{-1} s^{-1}, and its relative permittivity is 78.5 at this temperature.

In an electrochemical reaction, the current density is 10 mA cm^{-2} where the valency, 1.

1. Calculate the rate of the reaction, v.

An Electrochemical reaction was taking place at a large anodic overpotential. If the potential is made more positive by 0.2V, by how much would the reaction velocity change? T = 298K. β = 0.5, F = 96,500 C mol^{-1} and R = 8.314 J K^{-1} mol^{-1}

N-hydroxy acid → aldoxime → nitrile → α-hydroxynitrile → glc

Obafemi Awolowo University, Ile-Ife
Department of Chemistry
2010/2011 Mid – Harmattan Semester Test

Time allowed: 1 hour

Constants : Debye-Huchel constant, A = 0.509, π = 3.142, F = 96500 C mol⁻¹

CHM 403 – ELECTROCHEMISTRY.

Instruction : Answer all questions

The interionic attraction lowers the free energy of the ions in dilute soln and from $dG = kT\ln\gamma$, γ tends to decrease as dG decreases

1(a) A plot of log $\gamma_\pm$ against $\sqrt{I}$ shows a minimum, explain briefly the root of the observed minimum.

(b) 50.00 cm³ of 0.10 mol dm⁻¹ NaOH is added to 50.00 cm³ of 0.05 mol dm⁻³ H_2SO_4. What is/are the

(i) ions in solution?

(ii) concentration of the solution?

(iii) ionic strength of the solution?

(iv) mean ionic activity coefficient of the solution? $\Rightarrow \log\gamma_\pm = -A z^+ z^- \sqrt{I}$

(v) mean ionic activity of the solution?

Na_2SO_4 $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$ 0.075 SO_4^{2-}

2(a) ~~Given the reaction $Ca(OH)_2 + 2HCN$~~ $\rightarrow Ca(CN)_2 + 2H_2O$,

(i) sketch the graph of the conductivimetric titration when $Ca(OH)_2$ is progressively added to HCN.

(ii) Explain coincisely the shape of your graph.

(b) The velocity of a boundary of HCl with LiCl is followed in aqueous solution. It moves 15.0 cm in a tube of 1 cm diameter in 22 minutes when the current is 11.54 mA. If the concentration of the HCl is 0.01065 mol dm⁻³, what are the transport numbers of the hydrogen and chloride ions?

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

$2Na^+$ SO_4^{2-}

l = distance

a = cross-sectional area

πr^2

$t_-\Lambda = z^- u^- F$

$u^- = \frac{t_-\Lambda}{z^- F}$

0.005

Q = It

1 dm³ = 1000 cm³

$Cu(SO_4)_2$

$\frac{10.5}{\frac{2mol}{cm^3}(0.2)^2}$

Obafemi Awolowo University, Ile-Ife, Nigeria
Department of Chemistry

TUTORIAL QUESTIONS 2

ELECTROCHEMISTRY (CHM 403)

$\phi = \frac{\xi}{VA}$ $V = \frac{\xi}{L}$

1. Calculate the approximate thickness (δ) of the diffuse double layer which is established at a negatively charged plane solid surface in contact with a 0.01 mol dm^{-3} aqueous solution of sodium sulphate at 298K. The relative permittivity of water at this temperature may be taken to be 78.54.

2. Particles of the colloidal dispersion of a noble metal have an effective mean radius of 0.25mm in a 0.04 mol dm^{-3} aqueous solution of a 1:1 electrolyte and have an electrophoretic mobility of 3.50 x 10^{-8} m^2 V^{-1} s^{-1} at 298K. Calculate an approximate value for the zeta (ξ) potential. Viscosity of water at 298K is 8.94 x 10^{-4} kg m^{-1} s^{-1}. relative permittivity of water at 298k is 78.5.

πd^2

3. A glass tube 15cm long and mean internal diameter of 2mm is filled with water ... static source while a potential difference of 250V is applied between its ends. A temperature of 298K is maintained throughout the time of imposition of the potential ~~difference of 250V is applied between its ends.~~ A temperature of 298K is maintained throughout the time of imposition of the potential difference. Calculate the rate of electro-osmotic flow of the water at 298K given that the zeta-potential (ξ) for a glass/water interface is − 40mV, the viscosity of water is 8.9 x 10^{-4} kg m^{-1} s^{-1}, and its relative permittivity is 78.5 at this temperature.

$\Delta\phi = \frac{I}{KA}$

4. In an electrochemical reaction, the current density is 10 mA cm^{-2} where the valency, z

   1. Calculate the rate of the reaction, v.

5. An Electrochemical reaction was taking place at a large anodic overpotential. If the potential is made more positive by 0.2V, by how much would the reaction velocity change? T = 298K. β = 0.5. F = 96,500 C mol^{-1} and R = 8.314 J K^{-1} mol^{-1}

N-bromo... a.q.ti → aldoxime → nitrile → α-hydroxynitrile

DAH 0.005 mol will give ... mol of Na_2SO_4

Obafemi Awolowo University, Ile-Ife

Department of Chemistry

2010/2011 Mid – Harmattan Semester Test

Time allowed: 1 hour

Constants : Debye-Huchel constant, A = 0.509, $\pi = 3.142$, F = 96500 coul mol^{-1}

CHM 403 – ELECTROCHEMISTRY.

Instruction : Answer all questions

The interionic attraction lowers the free energy of $\frac{d}{dI}$, ... and from $dG = kT \ln \gamma$, γ tends to decrease as dG decreases

1 (a) A plot of log $\gamma_\pm$ against $\sqrt{I}$ shows a minimum, explain briefly the root of the observed minimum.

(b) 50.00 cm^3 of 0.10 mol dm^{-3} NaOH is added to 50.00 cm^3 of 0.05 mol ~~dm^{-3}~~ H_2SO_4. What is/are the

(i) ions in solution?

~~(ii) concentration of the solution?~~

(iii) ionic strength of the solution? Na_2SO_4 only

(iv) mean ionic activity coefficient of the solution? → $\log \gamma_\pm = -A z^+ z^- \sqrt{I}$

(v) mean ionic activity of the solution?

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

$2Na^+ \quad SO_4^{2-}$

~~2(a) Given the reaction, $Ca(OH)_2 + 2HCN \rightarrow Ca(CN)_2 + 2H_2O$,~~

(i) sketch the graph of the conductivimetric titration when $Ca(OH)_2$ is progressively added to HCN.

(ii) Explain coincisely the shape of your graph.

(b) The velocity of a boundary of HCl with LiCl is followed in aqueous solution. It moves 15.0 cm in a tube of 1 cm diameter in 22 minutes when the current is 11.54 mA. If the concentration of the HCl is 0.01065 mol dm^{-3}, what are the transport numbers of the hydrogen and chloride ions?

$t_- \lambda$

u.v. / visible ray x-ray

$\Omega cm^2 mol^{-1}$

πr^2

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

$2Na^+ \quad SO_4^{2-}$

$t_- \Lambda = z u F$ area

$\frac{t\, zFC}{Q}$

$u = \frac{t\, \Lambda}{zF}$

0.0025

$\frac{0.005\ mol}{2}$

0.0025

$\frac{2679\ mol}{m^3}$

$\frac{F C z^+ x a}{p}$

$1 m^3 = 1000 dm^3$

$1 dm^3 = 1000 cm^3$

0.010

$1 m^3 = 1000 dm^3$

$\Lambda = \frac{c}{}$

$\left(\varepsilon_0 \varepsilon_r k T \right)^{1/2}$

Department of Chemistry

TUTORIAL QUESTIONS 2

ELECTROCHEMISTRY (CHM 403)

ξ

$\phi = VA$

$V = \rho$

$\frac{\varepsilon}{L}$

1. Calculate the approximate thickness (δ) of the diffuse double layer which is established at a negatively charged plane solid surface in contact with a 0.01 mol dm^{-3} aqueous solution of sodium sulphate at 298K. The relative permittivity of water at this temperature may be taken to be 78.54.

Particles of the colloidal dispersion of a noble metal have an effective mean radius of 0.25mm in a 0.04 mol dm^{-3} aqueous solution of a 1:1 electrolyte and have an electrophoretic mobility of 3.50 x 10^{-8} m^2 V^{-1} at 298K. Calculate an approximate value for the zeta (ξ) potential. Viscosity of water at 298K is 8.94 x 10^{-4} kg m^{-1} s^{-1}. relative permittivity of water at 298k is 78.5.

$\frac{\pi d}{4}$

A glass tube 15cm long and mean internal diameter 1.2 mm is filled with water from a static source while a potential difference of 250V is applied between its ends. A temperature of 298K is maintained throughout the time of imposition of the potential difference of 250V is applied between its ends. A temperature of 298K is maintained throughout the time of imposition of the potential difference. Calculate the rate of electro-osmotic flow of the water at 298K given that the zeta-potential (ξ) for a glass/water interface is – 40mV, the viscosity of water is 8.9 x 10^{-4} kg m^{-1} s^{-1} and its relative permittivity is 78.54 at this temperature.

In an electrochemical reaction, the current density is 10 mA cm^{-2} where the valency, z

1. Calculate the rate of the reaction, v.

An Electrochemical reaction was taking place at a large anodic overpotential. If the potential is made more positive by 0.2V, by how much would the reaction velocity change? T = 298K. β = 0.5. F = 96,500 Cmol^{-1} and R = 8.314 J K^{-1} mol^{-1}.

N-Hydroxy a.a → aldoxime → nitrile → α-hydroxy nitrile

$\xi = \frac{\eta U_e}{\varepsilon_r \varepsilon}$

Obafemi Awolowo University
Ile-Ife, Nigeria

2010/2011 Session Harmattan Semester Examination
CHM 403 - Electrochemistry

Time Allowed: 2 Hours

[illegible]y, 2011 Constant: F = 96500 $Cmol^{-1}$

8:40
10:40

Instructions: Answer all questions. Answer Sections A and B in Separate Booklets.

SECTION A

$\frac{S^+ v^+ n^+ z^+ e C}{d} = \mu$ (21)

(1a). Give the S.I. units of (i) resistivity (ii) electrical field strength.

(b). What are responsible for the transportation of currents in (i) copper metal (ii) potassium iodate solution and (iii) argon gas?

(c). The ionic conductivity of Li^+ ions at zero concentration is 3.864×10^{-3} $m^2\Omega^{-1}mol^{-1}$. Calculate he number of ionic diameter traversed in one second under a potential difference of 10 V m^{-1}, if e radius of the solvated ion is 2.36×10^{-10} m. (Answer to be in whole number).

a). Which of the electrolytes, K_2SO_4 and H_2SO_4 will transport current faster in solution and

$t_+ = \mu \Lambda F$

$\Omega^{-1} m^{-1}$

Calculate the ionic strength of 0.20 mol dm^{-3} $K_2Cr_2O_7$ prepared in 0.40 mol dm^{-3} HCl.

The transference number of sodium ion in sodium cyanide is 0.384 and that of sulphate ion raoxosulphate(VI) acid is 0.212. The molar conductances at infinite dilution of sodium e and tetraoxosulphate(VI) acid are 2.45 and 10.68 $m^2 ohm^{-1} mol^{-1}$ respectively. Calculate ransference number of the cyanide ion.

$t_+ + d = S_+$

mobility of the sulphate ion

$\mu = \frac{velocity}{E}$

molar conductance at infinite dilution of hydrogen cyanide.

$\Lambda = \alpha = \frac{\Lambda}{\Lambda_0}$

$t_+ = \mu Z F$

$BaCl_2$

H_2SO_4

$\Lambda_0 = \mu \cdot Z F$

Obafemi Awolowo University, Ile-Ife
Department of Chemistry
2012/2013 Mid – Harmattan Semester Test
CHM 403 -- Electrochemistry

Time allowed: 1 hour

Constants : $R = 8.314\ J\ mol^{-1}$, $k = 1.385\times10^{-23}\ J\ K^{-1}$, $F = 96500$ Coul mol^{-1}
Electronic Charge $= 1.602\times10^{-19}$ coul.

Instruction : Answer all questions

Question 1

(a) What is Debye-Huchel length? (answer must not exceed 3 lines)

(b) $S = \mu E$. (i) What are S, μ and E in this equation? Give the S.I. units of E.

S → Drift speed

$E \rightarrow V m^{-1}$

$\mu = m^2 V^{-1}$

(c) A solution of HCl was electrolysed in a transport cell between platinum electrodes. The cathode compactment contained 0.196g of chloride ions before electrolysis and 0.182g afterwards. A silver coulometer in series with the cell had a deposit of 0.2499g of silver. Calculate the transport numbers of the H^+ and Cl^- ions.

Question 2

(a) Give an example of a metal-insoluble salt electrode. Write the electrode reaction equation in form of reduction.

(b) On what principle is the moving boundary method of measuring the transport number of ions predicated? (answer in maximum of 3 lines)

(c) If the mobility of the sulphate ion is $8.55\times10^{-6}\ m^2\ v^{-1}\ s^{-1}$ at 27°C, calculate and give the units of the diffusion coefficient of the ion at this temperature.

Pt|Ag|AgCl

Pt|H_2

Pt|H_2/

$D = \frac{\mu kT}{Fz} \rightarrow m^2 s^{-1}$

If 0.014

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$Ag \rightarrow Ag$

$\rightarrow Ag + Cl^-$

$\frac{\mu kT}{ez} = \frac{8.55\times10^{-6} \times 1.385\times10^{-23} \times 300}{1.602\times10^{-19} \times 2}$

$D = kT$

MBM is based on the observe rate of movement of a sha

$CH_3COO^- + H^+$

$\Lambda = \frac{K}{C}$ $\alpha = \frac{\Lambda_c}{\Lambda_0}$

8 The conductivity of 0.05 mol dm^{-3} solution of ethanoic acid at 18°C is 4.4×10^{-4} Ω^{-1} cm^{-1}. The molar conductivities of the hydrogen and ethanoate ions at infinite dilution at the same temperature are 310 and 77 $cm^2\ \Omega^{-1}\ mol^{-1}$ respectively. Calculate the dissociation constant of ethanoic acid.

$\alpha = \frac{K}{\Lambda_0 C}$

$K = \alpha^2 c$

9 The molar conductivity at 18^0C of a certain concentration of NH_4OH is 131.36 $cm^2\ \Omega^{-1}\ mol^{-1}$. Compute the molar conductivity at infinite dilution and the degree of dissociation of NH_4OH if the molar conductivities at infinite dilution at 18^0C for $BaOH_2$, $BaCl_2$ and NH_4Cl are288.8, 120.3 and 129.8 $cm^2\ \Omega^{-1}\ mol^{-1}$ respectively.

10 In a Hittorf experiment aqueous silver nitrate solution was electrolysed between the silver electrodes. The amount of silver nitrate in the anode compactment was 0.227g before electrolysis and 0,281g after electrolysis. During the electrolysis 0.0194g of copper was deposited on the cathode of a copper coulometer in series with the Hittorf cell. Calculate the transport numbers of Ag^+ and NO_3^- ions.

11 What are the mobilities of H^+ and SO_4^{2-} ions in aqueous solution at infinite dilution given the ionic conductance at infinite dilution at 298K of H^+ ions to be 3.49×10^{-2} and that of SO_4^{2-} ions to be $1.596\times10^{-2}\ m^2\ \Omega^{-1}\ mol^{-1}$.

12 The ionic conductivity of Li^+ ions at zero concentration is $3.864\times10^{-3}\ m^2\ \Omega^{-1}\ mol^{-1}$. Calculate the number of ionic diameter traversed in one second under a potential difference of 10 v m^{-1} if the radius of the solvated ion is 2.36×10^{-10} m.

$D = \frac{\mu kT}{e}$

13 Find the diffusion coefficient and the hydrodynamic radius in A^0 of the SO_4^{2-} ion in water at 298K given its mobility to be $8.27\times10^{-8}\ m^2\ v^{-1}\ s^{-1}$. [Viscosity of water = $1.00\times10^{-3}\ kg\ m^{-1}\ s^{-1}$. Electronic charge = 1.602×10^{-19} coul.]

$6\pi\eta r$

14. Calculate the activity coefficients of Na^+ and SO_4^{2-} ions ~~and the mean activity~~ and the mean activity ~~coefficient of the ions~~ coefficient of the ions in 0.005 mol dm^{-3} of sodium sulphate at 298K. [illegible]

15 In a moving boundary experiment to determine the cation transport number in 0.02 mol dm^{-3} lithium chloride solution, a current of 1.60×10^{-3} amp caused the boundary to move a distance of 7.00×10^{-2} m in 0.6705 hours. If the cross-section of the transport tube is $1.115\times10^{-5}\ m^2$, calculate the transport numbers of the cation and anion.

$- K_{[illegible]}$
$= 0.0207 mol m^{-3}$
$\frac{1}{\eta}$ - viscosity

③ $C_{Na_2SO_4} = 1 mol\ m^{-3}$

$\Lambda_{Na^+} = 5.00\times10^{-3}\ \Omega^{-1} mol^{-1} m^2$

$K_{soln} = K_{soln} - K_{solvent}$

$= 7.0\times10^{-2} - 2.6\times10^{-2}$

$= 4.4\times10^{-2}\ \Omega^{-1} m^{-1}$

$K_{Na_2SO_4} = 4.4\times10^{-2}\ \Omega^{-1} m^{-1}$

$(\Lambda_{Na^+} + \Lambda_{SO_4^{2-}}) = \frac{K_{Na_2SO_4}}{C_{Na_2SO_4}}$

$= \frac{2.6\times10^{-2}\ \Omega^{-1} m^{-1}}{1 mol\ m^{-3}}$

$= 2.6\times10^{-2}\ \Omega^{-1} mol^{-1} m^2$

$\Lambda_{SO_4^{2-}} = 2.6\times10^{-2} - 5.00\times10^{-3}$

$= 2.1\times10^{-2}$

$C = \frac{4.4\times10^{-1}}{0.01645}$

$C = 2.674 mol\ m^{-3}$

$= 0.00267 mol\ dm^{-3}$

$K_{sp} = (0.00267 mol\ dm^{-3})^2$

$= \underline{7.154\times10^{-6} mol^2 dm^{-6}}$

4.) $R_{KCl} = 139\ \Omega$ $C_{KCl} = 0.01 mol\ L^{-1}$

$R_{NH_4OH} = 2460\ \Omega$ $C_{NH_4OH} = 0.01 mol\ L^{-1}$

But KR = Constant and

$K = \Lambda C$; $\therefore \Lambda_1 C_1 R_1 = \Lambda_2 C_2 R_2$

$\frac{R_{KCl}}{R_{[illegible]}} = \frac{\Lambda_{NH_4OH} C_{NH_4OH}}{}$

$\alpha = \frac{\Lambda_c}{\Lambda_0} = \frac{189}{(7.34+19.88)\times10^{-3}} = \frac{189}{0.0272}$

$= \underline{6.95\times10^{3}}$

5.) $\alpha = \frac{\Lambda_c}{\Lambda^0} = \sqrt{K/c}$; $\Lambda_c = \frac{K}{c}$

$\rho = 1/k$

$\Lambda_c = ?$ $\Lambda_0 = 3.498\times10^{-2} + 3.58\times10^{-3}$

$\Lambda_0 = 0.03856\ ohm^{-1} m^2 mol^{-1}$

$K = 1.34\times10^{-5}$ $c = 0.10 mol\ dm^{-3}$

$C = 100 mol\ m^{-3}$

$\Lambda_c = \Lambda_0 \sqrt{K/c} = 0.03856\sqrt{\frac{1.34\times10^{-5}}{100}}$

$= 1.4115\times10^{-5}$

6.) $K_T = K_c \gamma_\pm^2$

$K_c = \frac{\alpha^2 c}{1-\alpha} = 7.139$

$\log K_T = \log K_c + 2$

$= \log K_c - 2A$

$= \log K_c - 2A$

$I = \frac{1}{2}\sum m_i z_i^2$

$= \frac{1}{2}[(0.01)(1)^2 +$

$= \frac{1}{2}(0.01 + 0.01)$

$A = 0.509$

$\log K_T = \log(7.139$

$= -4.248$

$K_T = 10^{-4.248}$

$= 5.647\times$

CHM 403 - Electrochemistry Tutorial Questions

The conductivity of a saturated solution of barium suplate at 25°C is 3.590×10^{-4} $ohm^{-1}m^{-1}$ and of the conductivity water used is 0.618×10^{-4} $ohm^{-1}m^{-1}$. The limiting molar conductance at zero concentration for 1/2Ba and 1/2 SO_4^{2-} are 6.364×10^{-3} and 8.000×10^{-3} $ohm^{-1} m^2 mol^{-1}$ respectively.
Calculate the solubility product of barium sulphate at this temperature, assuming complete dissociation of the salt.

The limiting molar conductance at zero concentration of tetraethylammonium pricrate in ethanol (viscosity = 0.0101 poise) at 298K is 5.54×10^{-3} $ohm^{-1}m^2 mol^{-1}$. Calculate the limiting ionic conductance of the tetraethylammonium cation in acetone at 298K, given that the limiting ionic conductance at zero concentration of the piccrate ion in acetone (viscosity = 0.00316 poise) at 298K is 8.242×10^{-3} $ohm^{-1} m^2 mol^{-1}$.

The electrolytic conductivity of a 0.001 mol dm^{-3} of Na_2SO_4 is 2.6×10^{-2} $ohm^{-1}m^{-1}$. If the solution is saturated with $CaSO_4$, the conductivity becomes 7.0×10^{-2} $ohm^{-1}m^{-1}$, Calculate the solubility product for $CaSO_4$ given the ionic molar conductance, $\Lambda(Na^+) = 5.00\times10^{-3}$ and $\Lambda(1/2Ca^{2+}) = 5.95\times10^{-3}$ $ohm^{-1}m^2 mol^{-1}$ at these concentrations.

The resistance of a cell when filled with 0.01 mol dm^{-3} KCl was found to be 189Ω, the cell was then filled with ammonia solution of 0.01 mol dm^{-3} and the resistance was 2460Ω, Calculate the base dissociation constant of the ammonia solution given that the molar conductances at infinite dilution of K^+, Cl^-, NH_4^+ and OH^- are 7.64×10^{-3}, 7.35×10^{-3}, 7.34×10^{-3} and 19.86×10^{-3} $ohm^{-1} m^2$ mol^{-1} respectively.

The classical dissociation constant of propanoic acid is 1.34×10^{-5} at 25°C and the limiting ionic conductances at infinite dilution of the hydrogen and propanoate ions are 3.498×10^{-2} and 3.58×10^{-3} $ohm^{-1}m^2 mol^{-1}$ respectively. Calculate the resistivity of a 0.10mol dm^{-3} solution of propanoic acid.

The degree of dissociation of an acid HA in 0.01 molar aqueous solution at 298K is 0.0810. Calculate the true dissociation constant of the acid. If to this solution is added an equal volume of 0.01 mol dm^{-3} aqueous sodium hydroxide containing sodium sulphate, at 0.003 mol dm^{-3}, what will be (a) the ionic strength and (b) the hydrogen ion concentration of the resulting solution?

A solution contining 10.850g silver nitrate per 1000g water was electrolysed between silver elctrodes. After elctrolysis the whole solution was removed and was found to weigh 54.900g. On analysis it was found to contain silver equivalent to 0.7217g silver nitrate. In a coulometer in series, 0.04672g copper was deposited. Calculate the transport number of the silver ion and the nitrate ion.

Obafemi Awolowo University, Ile-Ife
Department of Chemistry

CHM 403 – Electrochemistry Tutorial Questions

✓ The conductivity of a saturated solution of barium suplate at 25°C is 3.590×10^{-4} $ohm^{-1}m^{-1}$ and of the conductivity water used is 0.618×10^{-4} $ohm^{-1}m^{-1}$. The limiting molar conductance at zero concentration for 1/2Ba and 1/2 SO_4^{2-} are 6.364×10^{-3} and 8.008×10^{-3} $ohm^{-1}m^{2}mol^{-1}$ respectively.
Calculate the solubility product of barium sulphate at this temperature, assuming complete dissociation of the salt.

2. The limiting molar conductance at zero concentration of tetraethylammonium picrate in ethanol (viscosity = 0.0101 poise) at 298K is 5.54×10^{-3} $ohm^{-1}m^{2}mol^{-1}$. Calculate the limiting ionic conductance of the tetraethylammonium cation in acetone at 298K, given that the limiting ionic conductance at zero concentration of the picrate ion in acetone (viscosity = 0.00316 poise) at 298K is 8.242×10^{-3} $ohm^{-1}m^{2}mol^{-1}$.

∗ 3 ✓ The electrolytic conductivity of a 0.001 mol dm^{-3} of Na_2SO_4 is 2.6×10^{-2} $ohm^{-1}m^{-1}$. If the solution is saturated with $CaSO_4$, the conductivity becomes 7.0×10^{-2} $ohm^{-1}m^{-1}$. Calculate the solubility product for $CaSO_4$ given the ionic molar conductance. $\Lambda(Na^{+})=5.00\times10^{-3}$ and $\Lambda(1/2Ca^{2+})=5.95\times10^{-3}$ $ohm^{-1}m^{2}mol^{-1}$ at these concentrations.

$\lambda = \frac{k}{c}$

4 ✓ The resistance of a cell when filled with 0.01 mol dm^{-3} KCl was found to be 139 Ω, the cell was then filled with ammonia solution of 0.01 mol dm^{-3} and the resistance was 2460Ω, Calculate the base dissociation constant of the ammonia solution given that the molar conductances at infinite dilution of K^+, Cl^-, NH_4^+ and OH^- are 7.64×10^{-3}, 7.35×10^{-3}, 7.34×10^{-3} and 19.86×10^{-3} $ohm^{-1}m^{2}mol^{-1}$ respectively.

5 ✓ The classical dissociation constant of propanoic acid is 1.34×10^{-5} at 25°C and the limiting ionic conductances at infinite dilution of the hydrogen and propanoate ions are 3.498×10^{-2} and 3.58×10^{-3} $ohm^{-1}m^{2}mol^{-1}$ respectively. Calculate the resistivity of a 0.10mol dm^{-3} solution of propanoic acid.

∗ 6 The degree of dissociation of an acid HA in 0.01 molar aqueous solution at 298K is 0.0810. Calculate the true dissociation constant of the acid. If to this solution is added an equal volume of 0.01 mol dm^{-3} aqueous sodium hydroxide containing sodium sulphate, at 0.003 mol dm^{-3}, what will be (a) the ionic strength and (b) the hydrogen ion concentration of the resulting solution?

k, c

7. A solution contining 10.850g silver nitrate per 1000g water was electrolysed between silver elctrodes. After elctrolysis the whole solution was removed and was found to weighs 54.900g. On analysis it was found to contain silver equivalent to 0.7217g silver nitrate. In a coulometer in series, 0.04672g copper was deposited. Calculate transport number of the silver ion and the nitrate ion.

$HA \rightleftharpoons H^+ + A^-$

DEPARTMENT OF CHEMISTRY
OBAFEMI AWOLOWO UINVERSITY, ILE-IFE, NIGERIA
HARMATTAN SEMESTER EXAMINATION, 2013/2014 SESSION
CHM 403 – ELECTROCHEMISTRY
TIME ALLOWED - 2½ HOURS
Answer each section in separate booklet

SECTION A

$\Lambda = \frac{k}{c}$

QUESTION ONE

molar Conduct

a. State Kohlrausch law of independent migration of ions.

Λ^o_m NaI

12.69 9.10 18.78

b. The limiting molar conductivities of NaI, $NaCH_3CO_2$, and $Mg(CH_3CO_2)_2$ are 12.69 mS m² mol⁻¹, 9.10 mS m² mol⁻¹, and 18.78 mS m² mol⁻¹, respectively (all at 25 °C). What is the limiting molar conductivity of MgI_2?

$\Lambda_m MgI_2$ $\alpha = \Lambda_m / \Lambda^o_m$

$\Lambda_o = 434.78\ cm^2\ \Omega\ mol^{-1}$

c. The Oswald dilution law given as

$$K_a = \frac{\Lambda_m^2 c}{\Lambda^o_m\left(\Lambda^o_m - \Lambda_m\right)}$$

can be used to determine the dissociation constant of a weak acid. A chemist, in an attempt to determine the dissociation constant and the limiting molar conductivity of butanoic acid, plotted $\frac{1}{\Lambda_m}$ versus $\Lambda_m c$ and obtained a straight line graph with the slope being equal to 0.454 S⁻² cm⁻⁴ mol dm³ and the intercept on the $\frac{1}{\Lambda_m}$ axis equals to 0.0023 S⁻¹ cm⁻² mol. Process this information to determine K_a and Λ^o_m for butanoic acid

Ka

slope $= \frac{1}{K}$

$K_a =$

$\Lambda_m = \Lambda^o_m - b\sqrt{c}$

$\frac{1}{\Lambda_m} = \frac{1}{\Lambda^o_m} - \frac{b}{\Lambda}$

QUESTION TWO

(i) relaxation
(ii) electrophoretic

a. Discuss the factors that affect the mobility of an ion in solution in the presence of an applied electric field. relaxation & electro phoretic

$\frac{1}{\Lambda_m} = 0.0023$

b. Calculate I, $\gamma_\pm$, and $a_\pm$ for a $0.0250m$ solution of $AlCl_3$ at 298 K. Assume complete dissociation.

$\frac{1}{\Lambda_m} + 0.$

c. Chloroacetic acid has a dissociation constant of 1.38×10^{-3}. Calculate the degree of dissociation for a $0.0825m$ solution of this acid using the Debye-Huckel limiting law.

$K_a = \frac{\alpha^2 m}{1-\alpha}$

$K_a = \frac{a_- a_+}{a_{HX}}$ $\gamma_\pm^2 \left(\frac{m_- m_+}{m}\right)$

$B\sqrt{c}$ $(A+B)\sqrt{c}$ $\frac{\alpha^2 m}{(1-\alpha)} = \gamma_\pm^2$

$K_a = \gamma_\pm \alpha$ $\alpha = \frac{K_a}{m}$

C_2H_5

CH_3COOH

$ClCH_2COOH$

$K_a \to 1.38 \times 10^{-3}$

$= \gamma_\pm^2 \alpha^2 m$

$\alpha = \left(\frac{K_a}{m}\right)^{\frac{1}{2}}$

SECTION B

QUESTION ONE

a. Show how the quinhydrone electrode can be used to measure pH

b. Sketch the current versus potential profile for the cells i-iv below

i. $Pt|(H^+, Br^-)(1M)|AgBr(s)|Ag(s)$

ii. $Hg(l)|(H^+, Br^-)(1M)|AgBr(s)|Ag(s)$

iii. $Hg(l)|(H^+, Br^-)(1M), Cd^{2+}(10^{-3}M)|AgBr(s)|Ag(s)$

iv. $Pt(s)|(H^+, Br^-)(1M), Cd^{2+}(10^{-3}M)|AgBr(s)|Ag(s)$

c. What are the three characteristic features of current-potential profiles?

d. Write the half reaction and the overall cell reactions for cell b(iii)

QUESTION TWO

The Butler – Volmer equation cab be reduced to the form:

$$j = j_o\left[e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}\right]$$

i. Using the limiting form of this equation at large and negative over-potential, η, derive an expression for the value of α given j_1 at η_1 and j_2 at η_2

ii. Calculate the values of f at 298 K and 400 K. What effect, if any, will f have on the exchange current density at $\eta = 2$ volts?

$j_1 \approx -j_o e^{-\alpha f \eta_1}$

$\frac{j_1}{j_2} \approx e^{(\alpha f \eta_1 + \alpha f \eta_2)}$

QUESTION THREE (BONUS)

Discuss the application(s) of electrodes in Biosensors OR Fuel cells. (NB: Discussion without half-cell reactions will attract no marks)

$-\ln\left(\frac{j_1}{j_2}\right) = \alpha f \eta$

$f = \frac{nF}{RT}$

$t_+ = \frac{x a c z^+ F}{It}$

$j/j_o = e^{-\alpha f \eta}$

$-\alpha f \eta = \ln j/j_o$

$\alpha = -\frac{1}{f\eta} \ln j/j_o$

$= -\frac{RT}{nF\eta} \ln j/j_o$

2.303

0.5

$= RT$

DEPARTMENT OF CHEMISTRY
OBAFEMI AWOLOWO UINVERSITY, ILE-IFE, NIGERIA
HARMATTAN SEMESTER MID-SEMESTER EXAMINATION
CHM 403 – ELECTROCHEMISTRY
TIME ALLOWED – 40 minutes

QUESTION ONE

a. What do you understand by the term "transport number"

b. If the limiting molar conductivity, Λ^o, for KCl (aq) at 25°C is 149.8 S cm^2 mol^{-1} and the limiting molar ionic conductivity for K^+ (aq) is 73.5 S cm^2 mol^{-1}, calculate the transport number t_+ for the K^+ ion. What is t_- for Cl^- (aq)

QUESTION TWO

a. The solubility of a sparingly soluble salt MX is described by the following equilibrium

$$MX \rightleftharpoons M^+(aq) + X^-(aq)$$

Show that S, the solubility of MX depends on the solubility product of MX (K_S) and the ionic strength of the solution as follows (a is a positive constant)

$$\log_{10} S = \frac{1}{2}\log_{10} K_S + a\sqrt{I}$$

b. Calculate I, $\gamma_\pm$, and $a_\pm$ for a 0.0325m solution of $K_4Fe(CN)_6$ at 298 K

dissociatn eq $K_4Fe(CN)_6 \longrightarrow 4K^+ + [Fe(CN$

$a_\pm = \gamma_\pm m_\pm$

$-(3 \times 0.52]m$

$65m$

$= 0.325m \; I$

$0.509 |z_+z_-| \sqrt{I}$

16.07

-069

~~$K_4Fe(CN)_6$~~ $\longrightarrow$ ~~[illegible]~~ $+$ ~~[illegible]~~ $+$ ~~[illegible]~~

$+ (0.0325)(0.$ 6

$\gamma_\pm = 0.5092$

0.7286

$0.0325m$

$m_\pm$

$(\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}\, m$

$= (256)^{1/5} \times 0.0325$ molal

$t_+ = \frac{I^+}{I}$

$\Lambda_m = \frac{1000k}{c}$

0.995

S MX

Ksp MX

K_S K_S

$S = K_S \times \log$

$y = mx + c$

$a(a_+$

$c = \frac{1000k}{\Lambda}$

Obafemi Awolowo University, Ile-Ife
Department of Chemistry
2012/2013 Harmattan Semester Examination
CHM 403 – Eletrochemistry

Time allowed: 2 hours

nstruction: Answer All Questions in the same booklet but leave a Blank age between Sections A and B

onstants : R = 8.314 J mol^{-1}, F = 96500 coulomb mol^{-1}

Section A

Question 1

-mol dm⁻³ ~~H₂SO₄~~ LiSO₄ < d

(a) Give the S.I. units of (i) concentration of a solution (ii) activity of a solution.

(b) Arrange and give reasons (5 to 6 lines) the order of increasing molar conductivity of the following electrolytes, potassium sulphate, lithium sulphate and tetraoxosulphate (VI) acid.

(c) The molar conductivity of sodium fluoride in 0,10 mol dm^{-3} solution is 8,35 m^2 Ω^{-1} mol^{-1}. The salt may be taken as 92% dissociated. If the transport number of sodium ion is 0.45, calculate the mobilities of Na^+ and F^- ions.

LiSO₄ < K₂SO₄ < H₂SO₄

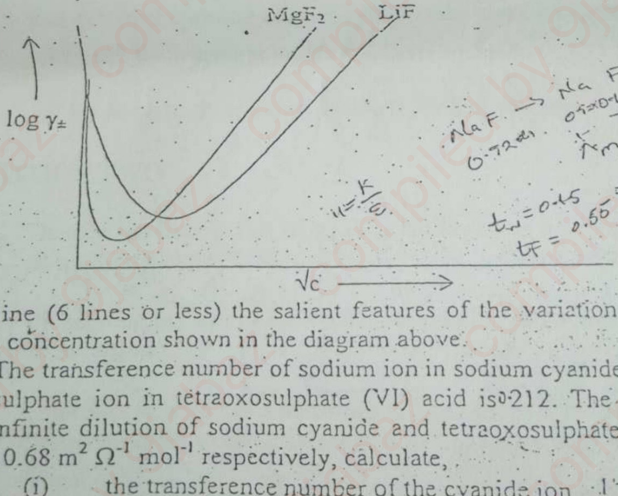
$F e_i z_i = k$

Question 2

(a) Define the term activity coefficient.

(b)

Lith -- < K₂SO₄ < H₂SO₄



$a = x^x y^y c^v \gamma^v$

$NaF \rightarrow Na + F$

0.92 × 0.1   0.92 × 0.1

Λ_m NaF 8.35

$c = 0.1$

$u = K/\varepsilon$

$t_{Na} = 0.45$

$t_F = 0.55$

$t_{Na} = \frac{j_i}{J} = \frac{F c_i z_i u_i}{F \Sigma c_i z_i u_i}$

Outline (6 lines or less) the salient features of the variation of activity coefficients with concentration shown in the diagram above.

(c) The transference number of sodium ion in sodium cyanide is 0.384 and that of the sulphate ion in tetraoxosulphate (VI) acid is 0.212. The molar conductivities at infinite dilution of sodium cyanide and tetraoxosulphate (VI) acid are 2.45 and 10.68 m^2 Ω^{-1} mol^{-1} respectively, calculate,

(i) the transference number of the cyanide ion $1 - t_{Na^+}$

(ii) the molar conductivity at infinite dilution of hydrogen cyanide

CN⁻

$t_+ \propto u z F$ $\Lambda_m^\infty = (2.45 + 10$

[Ox] , [Red]
$v_{ox} = k_c[Ox]$
$v_{red} = k_a[Red]$
$j_c = Fk_c[Ox]$

Section B

[Question 5 is optional but earns bonus marks]

Question 3

roduct flux in the charge transfer across the electrode-solution interface is given by,

Product flux = κ{species} where κ has units of cm s^{-1}

(a) Derive an expression for the net current density (j) from $j_a - j_c$. Under what condition(s) is the current anodic or cathodic?

(b) Using the activated rate theory, show that $j = FB_a[Red]e^{-\frac{\Delta G_a^{\ddagger}}{RT}} - FB_c[Ox]e^{-\frac{\Delta G_c^{\ddagger}}{RT}}$. Explain all the terms used and state any assumption(s).

j =

Question 4

Jsing typical electrochemical cells, explain the origin of

(a) background limits at a working electrode

(b) when ~~the~~ are faradaic and nonfaradaic processes ~~are~~ in operation under these conditions

(c) what a supporting electrolyte is.

Question 5

Describe fuel cells as one of the devices of electrochemical technology

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a

10 dm = 1 m
1 dm = $\frac{1}{10}$ m
1 dm^3 = $\left(\frac{1}{10}\right)^3$ m^3

$K_\gamma = \gamma_\pm^2 \cdot \frac{m_+ m_-}{m_{MX}}$
$\log K_\gamma = 2\log\gamma_\pm + \log K_m$
$= -0.509|z_+z_-| I^{1/2}$
$= -2A I^{1/2} + \log K_m$
$K_\gamma = \gamma_+^{\nu_+}\gamma_-^{\nu_-}$
$= \gamma_\pm^{\nu}$