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MAIN EXAMINATION

SEPTEMBER –DECEMBER 2021

FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

REGULAR PROGRAMME

CHEM 309: ELECTROCHEMISTRY

Date: DECEMBER 2021	**Duration: 2 Hours**
INSTRUCTIONS: Answer Question ONE and any TWO Questions	

Useful Information

$IF = 96490 C mol^{-1}$

$R = 8.314 JK^{-1} mol^{-1}$

$0^0 C = 273 K$

$Inx = 2.303 \log x$

At 25^{0}C $\frac{2.303RT}{nF} = \frac{0.0591}{n}$

Q1. a) (i) Using the Debye-Huckel limiting equation, calculate the mean activity coefficient of 0.004M Zinc Sulphate. **(6 marks)**

($A = 0.51 mol^{-½} dm^{½}$ at 25°C for aqueous solutions)

(ii) Calculate the activity of 0.004M zinc sulphate. **(3 marks)**

b) The conductivity of $1.25 \times 10^{-1} mol\ dm^{-3}$ solution of a monobasic acid is $2.39 \times 10^{-2} \Omega^{-1} cm^{-1}$. Its molar conductivity of infinite dilution is

$400\Omega^{-1}cm^2mol^{-1}$. Calculate the degree of dissociation of the acid and its dissociation constant. **(6 marks)**

c) Briefly explain how the conductance of electrolytes can be measured. **(5 marks)**

d) Given

$$E^0\left(Co^{2+}\middle|Co\right) = -0.2770V$$
$$E^0\left(Cc^{4+}\middle|Cc^{3+}\right) = 1.610V$$

(i) Represent the above information by a cell diagram. **(1 mark)**
(ii) Determine E^0 for the cell **(2 marks)**
(iii) Write the overall cell reaction and the Nernst expression for the cell. **(3 marks)**

e) Discuss the principle involved in conductimetric titrations.

Q2. a) Given the following electrochemical cell **(4 marks)**

$Pb\left|PbCl_2\right|HCl(IM)\,AgCl\left|Ag\right.$. The emf at 298K is o.490V. If the rate of change of emf with temperature is $1.8\times10^{-4}V\left|\text{deg.}\right.$ calculate;

(i) ΔG of the cell **(2 marks)**
(ii) ΔH of the cell **(2 marks)**
(iii) ΔS of the cell **(2 marks)**

b) A hydrogen electrode and normal calomel (reference electrode) electrode, gives an emf of 0.435V when placed in a certain solution of 25^0c.

(i) what is the pH of the solution? **(2 marks)**
(ii) what is the value of a_{H^+}? **(2 marks)**

c) For the following cell with transference

$$Ag\left|AgCl\right|\left|Hcl_{a\pm(1)}\right. \equiv Hcl_{a\pm(2)}\left|AgCl\right|Ag$$

given emf the emf with transference at 298K is 0.0289V and that of corresponding cell without transference is 0.0169V. Calculate;

(i) The transference number of H^+ and Cl^- ions **(6 marks)**

(ii) The liquid function potential **(2 marks)**

(iii) By considering individual electrode reaction, write the overall cell reaction. **(2 marks)**

Q3. a) The specific conductivity of a saturated sparingly soluble salt MSO_4 at 25^0c was found to be $4.63\times10^{-6}ohm^{-1}cm^{-1}$. That of pure water was $1.11\times10^{-6}ohm^{-1}cm^{-1}$, calculate

(i) The solubility of MSO_4 **(2 marks)**

(ii) The solubility product of MSO_4 **(2 marks)**

$$\Lambda^0_{MSO_4} = 287 ohm^{-1}cm^2mol^{-1}$$

b) Briefly describe how the emf of an electrochemical cell can be determined. **(5 marks)**

c) Calculate the equilibrium constant of the cell $Zn\left|zn^{2+}\right\|Fe^{3+},Fe^{2+}\left|pt\right.$ at 298K given $Zn\left|Zn=-0.762v,Fe^{3+},Fe^{2+}\right|pt=0.771V$ **(3 marks)**

d) Briefly discuss the factors that affect the rate of which ions of an electrolyte carry charge. **(8 marks)**

Q4. a) The resistance R, of an electrical conductor is proportional to its length and inversely proportional to its cross-sectional are (A). Derive a relationship between the conductivity (K) with current density (j) and electric field intensity (E). **(6 marks)**

b) (i) State Kohrlausch law of independent ionic migration **(1 mark)**

(ii) Discuss briefly the Arrhenius theory of ionization. Considering acetic acid show that the molar conductivity and the limiting molar conductivity at infinite dilution are related in the Ostwald's dilution relationship. **(6 marks)**

c) Explain how a hydrogen electrode is used to measure pH. **(7 marks)**

Q5. a) (i) Briefly explain how the Hirtoff method is used to determine the transport numbers of ions in an electrolyte. **(6 marks)**

(ii) Perform the analysis of the anode and cathode compartments when IF of electricity is passed through a solution of copper (II) chloride using platinum electrodes. **(6 marks)**

b) A one liter solution of sea water was analysed and found to have the following ionic components.

29.31g of NaCl, 1.83g of $MgSO_4$, 3.99g of $MgCl_2$, 1.34g of $CaSO_4$ and 0.85g of K_2SO_4.

Calculate the ionic strength of this solution.

Na=23, Mg = 24, Ca=40, K=39, Cl=35.5, S=32 and O=16. **(6 marks)**

c) Define Over-potential. **(2 marks)**

END