A. M. E. C. E. A

MAIN EXAMINATION
JANUARY - APRIL 2017 TRIMESTER
FACULTY OF SCIENCE
DEPARTMENT OF CHEMISTRY
SCHOOL FOCUSED PROGRAMME
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CHEM 309: ELECTROCHEMISTRY

## Date: APRIL 2017

Duration: 2 Hours
INSTRUCTIONS: Answer Question ONE and any other Two Questions

Useful Information
$I F=96490 \mathrm{Cmol}^{-1}$
$R=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$
$0^{0} C=273 K$
$\operatorname{In} x=2.303 \log x$
At $25^{\circ} \mathrm{C} \frac{2.303 R T}{n F}=\frac{0.0591}{n}$

Q1. a) (i) Using the Debye-Huckel limiting equation, calculate the mean
activity coefficient of 0.002M Zinc Sulphate.

$$
\left(A=0.51 \mathrm{~mol}^{-1 / 2} \mathrm{dm}^{3 / 2} \text { at } 250 \text { for aqueous solutions }\right)
$$

(ii) Calculate the activity of 0.002 m zinc sulphate.
b) The conductivity of $1.25 \times 10^{-1} \mathrm{~mol} \mathrm{dm}{ }^{-3}$ solution of a monobasic acid is $2.39 \times 10^{-2} \Omega^{-1} \mathrm{~cm}^{-1}$. Its molar conductivity of infinite dilution is $400 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$. 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

$$
\begin{aligned}
& E^{0}\left(\mathrm{Co}^{2+} \mid \mathrm{Co}\right)=-0.2770 \mathrm{~V} \\
& E^{0}\left(C c^{4+} \mid C c^{3+}\right)=1.610 \mathrm{~V}
\end{aligned}
$$

(i) Represent the above information by a cell diagram.
(ii) Determine E0 for the cell
(1 mark)
(iii) Write the overall cell reaction and the Nernst expression for the cell.
e) Discuss the principle involved in conductimetric titrations.

Q2. a) Given the following electrochemical cell
(4 marks)
$\mathrm{Pb}\left|\mathrm{PbCl}_{2}\right| \mathrm{HCl}(\mathrm{IM}) \mathrm{AgCl} \mid \mathrm{Ag}$. The emf at 298 K is 0.490 V . If the rate of change of emf with temperature is $1.8 \times 10^{-4} \mathrm{~V} \mid$ deg. calculate;
(i) $\Delta G$ of the cell

## (2 marks)

(ii) $\Delta H$ of the cell
(2 marks)
(iii) $\Delta S$ of the cell
(2 marks)
b) A hydrogen electrode and normal calomel (reference electrode) electrode, gives an emf of 0.435 V when placed in a certain solution of $25^{\circ} \mathrm{C}$.
(i) what is the pH of the solution?
(ii) what is the value of $a_{H^{+}}$?
c) For the following cell with transference

$$
A g|A g C l|\left|H c l_{a \pm(1)} \equiv H c l_{a \pm(2)}\right| A g C l \mid A g
$$

given emf the emf with transference at 298 K is 0.0289 V and that of corresponding cell without transference is 0.0169 V . Calculate;
(i) The transference number of $\mathrm{H}^{+}$and Cl -ims
(ii) The liquid function potential
(iii) By considering individual electrode reaction, write the overall cell reaction.

Q3. a) The specific conductivity of a saturated sparingly soluble salt $\mathrm{MSO}_{4}$ at $25^{\circ} \mathrm{C}$ was found to be $4.63 \times 10^{-6} \mathrm{ohm}^{-1} \mathrm{~cm}^{-1}$. That of pure water was $1.11 \times 10^{-6} \mathrm{ohm}^{-1} \mathrm{~cm}^{-1}$, calculate
(i) The solubility of $\mathrm{MSO}_{4}$
(ii) The solubility product of $\mathrm{MSO}_{4}$

$$
\wedge_{{ }_{M S O_{4}}}^{0}=287 \mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}
$$

b) Briefly describe how the emf of an electrochemical cell can be determined.
(5 marks)
c) Calculate the equilibrium constant of the cell $\mathrm{Zn}\left|z n^{2+} \| F e^{3+}, \mathrm{Fe}^{2+}\right| \mathrm{pt}$ at 298 K given $\mathrm{Zn}\left|\mathrm{Zn}=-0.762 v, F e^{3+}, F e^{2+}\right| p t=0.771 V$
(3 marks)
d) Briefly discuss the factors that affect the rate of which ions of an electrolyte carry charge.

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 Kohrlansih 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.
(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.
b) A one liter solution of sea water was analysed and found to have the following ionic components.
29.31 g of $\mathrm{NaCl}, 1.83 \mathrm{~g}$ of $\mathrm{MgSO}_{4}, 3.99 \mathrm{~g}$ of $\mathrm{MgCl}_{2}, 1.34 \mathrm{~g}$ of $\mathrm{CaSO}_{4}$ and 0.85 g of $\mathrm{K}_{2} \mathrm{SO}_{4}$.

Calculate the ionic strength of this solution.
$\mathrm{Na}=23, \mathrm{Mg}=24, \mathrm{Ca}=40, \mathrm{~K}=39, \mathrm{Cl}=35.5, \mathrm{~S}=32$ and $\mathrm{O}=16$.
c) Define Over-potential.
(2 marks)

## *END*

