KABARAK UNIVERSITY

UNIVERSITY EXAMINATIONS

2009/2010 ACADEMIC YEAR

FOR THE DEGREE OF BACHELOR OF EDUCATION SCIENCE

COURSE CODE: **CHEM 411**

COURSE TITLE: **ELECTROCHEMISTRY**

STREAM: **SESSION VII & VIII**

DAY: **SATURDAY**

TIME: **9.00 – 11.00 A.M.**

DATE: **28/11/2009**

INSTRUCTIONS:

- **F = 96500C/MOL**
- **Attempt ALL Questions**
- **Data 2.303RT/F =0.0592v at 25^{o}C, F=96500Cmol^{-1}, 0^{o}C= 273K, R=8.314Jmol^{-1}k^{-1}**

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Data $2.303RT/F = 0.0592v$ at 25^oC, $F=96500Cmol^{-1}$, $0^oC= 273K$, $R=8.314Jmol^{-1}k^{-1}$

1) a). Write down Kohlrausch law and define all the terms used (2 mks)

b). A conductivity cell has a resistance of 125 Ω when filled with 0.02M KCl at 298K and 5×10^4 Ω when filled with 6×10^{-5}M NH_4OH. The specific conductivity of 0.02M KCl is $2.77\times10^{-3}\Omega^{-1}cm^{-1}$ and the equivalent conductances of NH_4^+ and OH^- at an infinite dilution are 73.4 and $198\Omega^{-1}cm^2mol^{-1}$ respectively. Calculate,

i). the cell constant (2 mks)

ii). the degree of dissociation of NH_4OH in the 6×10^{-5}M solution (3 mks)

iii). the dissociation constant of NH_4OH at 298K (3 mks)

c). Define the term transport number of an ion and explain how it can be determined experimentally by moving boundary method (5 mks)

d). In a moving boundary experiment to determine the cation transport number in 0.01mol dm^{-3} KCl solution a current of 800μA caused the boundary to move a distance of 3.5cm in 1207s. Calculate the transport number of both ions. The radius of the tube was 0.191cm. (4 mks)

2. a) Describe the Debye – Huckel model for the structure of electrolyte solution. (2 mks)

b) In dilute solution, the Debye – Huckel theory reduces to the following expression for activity coefficient of ion; $\log\gamma_i = - QZ_i^2\sqrt{\mu}$ where;

$Q = 0.511$ for water at 25^oC

Z_i = formal charge on ion i

μ = ionic strength of the solution

i) Show that the general expression for the mean activity coefficient, $\gamma_\pm$, of the salt $A_{v+}B_{v-}$ is given by $\gamma_\pm = -Q|Z_+Z_-|\sqrt{\mu}$ (2 mks)

ii) Use the Debye – Huckel limiting law to calculate for 0.025 $PbBr_2$ aqueous solution at 25^oC,

I) The mean activity coefficient (4 mks)

II) The mean activity (3 mks)

III) The activity (3 mks)

iii) What effect will increase in concentration of a solution bring on the value of the activity coefficient? (1mk)

c) When current of 2A is passed through a column of solution of 0.2M AgCl, the velocity of Ag^+ ion was found to be $7x10^{-3}$cm/sec. The ionic mobility of Li^+ and Ag^+ ions are $4.01x10^{-8}M^2V^{-1}S^{-1}$ and $6.41x10^{-8}M^2V^{-1}S^{-1}$ respectively. Using the same apparatus and the same applied potential, calculate the velocity, in cm/sec of Li^+ ions in a 0.2M $LiNO_3$. (3 mks)

3. a) Define the term reference electrode. (1mk)

b) Write down the electrode reactions and the overall cell reaction. Calculate the cell potential for the cell Ni/Ni^{2+}(0.1M)/1M Ag^+/Ag given that E^o Ag^+,Ag = 0.8V and $E^o Ni^{2+}$,Ni =-0.23V. (4 mks)

c) The standard emf of the cell Ag/AgBr/AgBr/Ag is -0.726V at 298K. Use this information to calculate the solubility product of silver bromide in water. (3 mks)

d) The following cell was set up:

$Hg_{(l)}$ /$Hg_2Br_{2(s)}$/KBr (0.001M): KBr (0.01M)/$Hg_2Br_{2(s)}$/$Hg_{(l)}$

i) Write the equations for all the processes taking place and net cell reaction. (2 mks)

ii) Derive an equation for emf of this cell at 25°C (3 mks)

iii) Calculate the emf of this cell at 25°C, if t_+ is 0.4 for the KBr solution and the mean activity coefficient is 0.6 and 1 for 0.01M and 0.001M KBr solution respectively. (3 mks)

iv) Calculate the emf of this cell if there was no liquid junction potential. (2 mks)

v) Determine the value of the liquid junction potential. (1 mk)

4. a) The emf (E) and the derivative $(\delta E/\delta T)_p$ of the cell Pb/$PbBr_{2(s)}$, KBr(aq),$AgBr_{(s)}$/Ag are 0.492 V and - 0.000186 VK^{-1} respectively.

i) Write down the cell reaction for the above cell. (1 mk)

ii) Calculate ΔG, ΔH and ΔS at 27 °C (7 mks)

b) Briefly outline the principle underlying polarography and its applications (6 mks)