CHEM 325: ELECTROCHEMISTRY EXAM APRIL 2023

CHUKA UNIVERISTY

UNIVERSITY EXAMINATIONS

THIRD YEAR EXAMINATIONS FOR THE AWARD OF BACHELOR OF SCIENCE AND BACHELOR OF EDUCATION (SCIENCE)

CHEM 325: ELECTROCHEMISTRY Time 2Hours

INSTRUCTIONS: ANSWER QUESTION *ONE* AND ANY OTHER T*WO* QUESTIONS

[*Constants: F = 96500 C mol^{-1} 2.0303RT/F = 0.0592V]*

QUESTION ONE [30marks]

a) (i) Discuss what constitutes the study of electrochemistry and illustrate with examples the importance of electrochemistry **[5marks]**

(ii). Define an electrical current and show what constitutes the flow of current in a conductor? **[3marks]**

b) (i) Give an account of the differences in conduction process of a metallic conductor, semiconductor and an insulator (illustrate with a sketch) **[3marks]**

(ii). Discuss briefly the mechanism for conduction of an electrolytic conductor. How does it differ from that of a metallic conductor? **[3marks]**

c). Distinguish between the following pairs. Show how they are related and give their units of measurement **[3marks]**

(i). Resistivity and Cell Constant

(ii) Conductance and Conductivity

d). Calculate the ionic strength and the mean activity of the following electrolytes **[5marks]**

(i) 0.05M $MgCl_2$ (mean activity coefficient ($\gamma_{\mp}$) of $MgCl_2$= 0.044)

(ii) 0.05M Na_3PO_4 (mean activity coefficient ($\gamma_{\mp}$) of Na_3PO_4 =0.066)

e). A conductivity cell was calibrated by filling it with 0.02M solution of KCl whose conductivity is $0.0278\Omega^{-1}\ cm^{-1}$. The resistance was found to be 457.3Ω. The cell was filled with $CaCl_2$ solution containing 0.555g of $CaCl_2$ per litre. The measured resistance was 1050 Ω. Calculate

(i). The cell constant for the cell **[2marks]**

(ii). The conductivity of $CaCl_2$ solution **[3marks]**

(iii). The molar conductance of $CaCl_2$ at this concentration **[3marks]**

[Atomic mass: Ca = 40.08 Cl = 35,45]

QUESTION TWO [20marks]

a) Give suitable explanations to the following observations.

(i) Experimental determination of conductance of an electrolyte employs use of an AC current rather than a DC current. **[2marks]**

(ii) When the concentration of an electrolyte is increased its conductivity

increases but it its molar conductance decreases.**[2marks]**

b). The molar conductance of a weak electrolyte at infinite dilution (Λ^0_m) cannot be determined by extrapolation of the plot of (Λ_m) against concentration. However, that of a strong electrolyte can. Explain with the help of a diagram.**[3marks]**

c)(i).State Kohrausch's law of independent ion migration **[2marks]**

(ii). Mention and briefly explain applications of Kohlrausch's law of independent migration of ion migration **[4marks]**

(iii).The molar conductance at infinite dilution of HCl, CH_3COONa and NaCl are 426.16, 910.0 and 126.45$\Omega^{-1}cm^2mol^{-1}$ respectively. If the molar conductance of a given acetic acid solution is 48.15 $\Omega^{-1}cm^2mol^{-1}$. Calculate

(i). The molar conductance of CH_3COOH at infinite dilution **[3marks]**

(ii). Degree of dissociation of CH_3COOH **[2 marks]**

d). At 18 ^oC the specific conductance of a saturated solution of AgCl in water was $2.40x10^{-6}$ Ω^{-1} cm^{-1}. Given that the molar conductance at infinite dilution of $AgNO_3$ = 116.5 Ω^{-1} cm^2mol^{-1} of NaCl = 110.3 Ω^{-1} cm^2mol^{-1} and $NaNO_3$ = 105 Ω^{-1} $cm^2mol^{-1}$and on assumption that AgCl is completely dissociated in solution, calculate

(i). The solubility of AgCl **[3marks]**

(ii) The solubility product of AgCl **[2marks]**

QUESTION THREE [20marks]

a) Conductometric measurements are used to determine the end points of acid base titrations. Sketch and discuss the conductometric titrations curves of the following acid-base reactions : (i) HCl and NaOH (ii) CH_3COOH and NaOH **[4marks]**

b).(i) Explain the meaning of the term transport number of an ion. **[2marks]**

(ii) In a moving boundary experiment to determine transport number of K^+ and Cl^-, 0.2M KCl was floated in 0.65M LiCl indicator solution in a tube of diameter 4.15mm. A steady current of 1.82mA was passed and the formed boundary was observed to have moved a distance of 6.4mm in 20 minutes.

Calculate the transport number of K^+ and Cl^- **[4marks]**

c)(i). With reference to change in oxidation number, standard reduction potential and gain/loss of electrons distinguish between the following pairs.**[3marks]**

(I). Reduction and Oxidation

(II). Oxidizing agent and reducing agent.

(ii) Given the following standard half reactions and their standard reduction potentials

Half reaction	E^o(V)
(i). $Ag^+ + e \longrightarrow Ag(s)$	0.8
(ii) $NO_3^- + 4H^+ + 3e \longrightarrow NO(g) + H_2O$	0.96
(iii) $Al^{3+} + 3e \longrightarrow Al(s)$	-1.67
(iv) $I_2(s) + 2e \longrightarrow 2I^-$	0.54
(v) $Br_2(l) + 2e \longrightarrow 2Br^-$	1.07
(vi) $Fe^{3+}(aq) + e \longrightarrow Fe^{2+}(aq)$	0.77
(vii) $Fe^{2+}(aq) + 2e \longrightarrow Fe(s)$	-0.44

(I) classify the species as either an oxidizing agent or a reducing agent or both. Explain **[2marks]**

(II)Arrange the oxidizing agents in order of increasing strength **[2marks]**

(III) Arrange the reducing agents in order of increasing strength**[2marks]**

(IV). Will Ag^+ ions oxidize Al to Al^{3+} ions or will Al^{3+} ions oxidize Ag(s) to Ag^+ ions . Justify your answer **[3marks]**

QUESTION FOUR [20marks]

a) (i). Distinguish between a galvanic (voltaic) cell and electrolytic cell **[2marks]**

(ii) Explain why is it necessary to use a salt bridge or a porous disc in a galvanic cell?. Give suitable electrolytes that are used as salt bridge and their characteristics **[2marks]**

(iii).The electrodes of commercial galvanic cells(batteries) are generally

labelled with plus (+) and minus (–). Which electrode is positive and which is negative? Explain the processes that take place at the positive and the negative electrodes **[2marks]**

b) (i). How are the Gibb's free energy change and cell electromotive force related? **[1mark]**

(ii). Explain what happens to E_{cell} when a battery is charged and as it discharges in relation to changes in Gibb's free energy **[2marks]**

c) Write the anode and cathode half reactions and the respective standard shorthand notation for the galvanic cells that use the following reactions **[3marks]**

(i). $Cd(s) + Sn^{2+}(aq) \rightarrow Cd^{2+}(aq) + Sn(s)$

(ii).$2Al(s) + 3Cd2+(aq) \rightarrow 2Al^{3+}(aq) + 3Cd(s)$

(d) A galvanic cell is to be designed at standard –state conditions using the following two half reactions

$Mn^{2+} + 2e \rightarrow Mn(s)$ $E^0(red) = -1.18V$

$Cr^{3+}(aq) + 3e \rightarrow Cr(s)$ $E^0(red) = -0.74V$

(i). write a balanced chemical equation describing the spontaneous cell reaction **[2marks]**

(ii). calculate the E^0_{cell} and ΔG^o of the above cell **3marks]**

(iii) Sketch a diagram showing the above galvanic cell based on the overall cell reaction Label all the components and indicate the direction of the electron flow and the direction of ion migration. Identify the cathode and the anode **[3marks]**

QUESTION FIVE

(a). A galvanic cell is constructed that uses the following reaction and operates at 298K

$$Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$$

(i) Write individual cell reactions **[2marks]**

(ii) What is the emf of this cell at standard conditions**[2marks]**

(iii) What is the emf of the cell $[Ni^{2+}] = 3.00M$ and $[Zn^{2+}] = 0.100M$ **[3marks]**

(iv) What is the equilibrium constant for the cell at 298K.**[3marks]**

b) The emf of the cell

$$(Al(s) \mid Al^{3+}(aq) \parallel Cd^{2+}(aq) \mid Cd(s)$$

is 0.663V at 20^0C and 0.07048V at 30^0C

(i). Write the individual half-cell reactions **[2marks]**

(ii) Write the overall cell reaction **[2marks]**

(iii) Calculate $\triangle G$, $\triangle H$, and $\triangle S$ at 30^0C **[6marks]**

Given: $Al^{3+}(aq)/Al(s)$ $E^o = -1.66V$

$Cd^{2+}(aq)/Cd(s)$ $E^o = -0.403V$