NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

FACULTY OF APPLIED SCIENCES

DEPARTMENT OF APPLIED CHEMISTRY

PHYSICAL CHEMISTRY II

SCH 2204

END OF SEMESTER EXAMINATION PAPER

May 2017

This examination paper consists of 5 pages

Time Allowed: 3 hours

Total Marks: 100

Examiner's Name: Dr. Stephen Majoni

Useful information: R = 8.314J K^{-1} mol^{-1}; 1 *atm* = 101 325 Pa; 1 $bar = 1\times10^{5}\,Pa$

INSTRUCTIONS

1. Answer ALL questions in section A and any three (3) questions in section B
2. Each question in section A carries 10 marks and in section B carries 20 marks

MARK ALLOCATION

QUESTION	MARKS
A1.	**10**
A2.	**10**
A3.	**10**
A4.	**10**
B1	**20**
B2	**20**
B3	**20**
B4	**20**
TOTAL POSSIBLE MARKS	**100**

SECTION A

1) a) Model fitting procedures are used extensively in adsorption studies when evaluating the mechanism of adsorption. Using the Langmuir adsorption isotherm, discuss how this procedure is carried out. [7 Marks]

b) Thallium (I) is oxidized by cerium (IV) according to the following mechanism:

Step 1: $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$

Step 2: $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$

Step 3: $Tl^{+} + Mn^{4+} \rightarrow Tl^{3+} + Mn^{2+}$

i) What is the overall reaction for the oxidation of thallium? [1 Mark]

ii) Identify the catalyst and the type of catalysis (homogeneous or heterogeneous). [2 Marks]

2) a) The rate of decomposition of nitrogen pentoxide gas at constant temperature has been expressed as a function of the rate of production of O_2 as follows:

$$\frac{d[O_2]}{dt} = (3.25\times10^{-4}s^{-1})[N_2O_5]$$

The decomposition reaction equation is shown below:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

i) What is the order of the reaction? [2 Marks]

ii) What is the rate of transformation of N_2O_5? [2 Marks]

iii) What is the half-life of the reaction? [3 Marks]

b) The surface potential of a given colloid particle is a negative value, while the electrokinetic (zeta) potential is positive. What causes this phenomenon and what is the sign of the Stern potential in this system? [3 Marks]

3) Assuming standard-state conditions, determine whether the following cell reactions would occur spontaneously or not.

a) $Mg(s) + Sr^{2+}(aq) \rightarrow Mg^{2+}(aq) + Sr(s)$ [2 Marks]

b) $2In^{+}(aq) \rightarrow In^{2+}(aq) + In(s)$ [2 Marks]

c) $3Ag(s) + Au^{3+}(aq) \rightarrow 3Ag^{+}(aq) + Au(s)$ [2 Marks]

d) $2Br^{-}(aq) + Sn^{4+}(aq) \rightarrow Br_2(l) + Sn^{2+}(aq)$ [2 Marks]

e) $Cu^{+}(aq) + Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + Fe^{2+}(aq)$ [2 Marks]

4) a) Calculate the dissociation constant for ethanoic acid given that its conductivity $= 4.95\times10^{-5}Scm^{-1}$ for a concentration of 0.001 M , $\Lambda_m^0 = 390.5Scm^2mol^{-1}$

[6 Marks]

b) The gas phase decomposition of compound A at a given temperature proceeds by two parallel reactions as follows:

$A \rightarrow B \qquad k_1 = 5.23s^{-1}$

$A \rightarrow C \qquad k_2 = 13.23s^{-1}$

What is the maximum percentage yield for product C? [4 Marks]

SECTION B

1) The reaction in an electrochemical cell can be represented as follows:

$Fe(s) + 2Fe^{3+}(aq) \rightarrow 3Fe^{2+}(aq)$

a) Draw a line diagramme for the above cell. [2 Marks]

b) Given the following information:

Temperature coefficient $\left(\frac{\partial E^{\circ}}{\partial T}\right)_P = 1.14mV/K$ at 25°C and $\Delta_R S^{\circ} = nF\left(\frac{\partial E^{\circ}}{\partial T}\right)_P$,

calculate values for $\Delta_R S^{\circ}, \Delta_R G^{\circ}$, and $\Delta_R H^{\circ}$ for the cell at 25 °C. [8 Marks]

c) Calculate the cell potential at the following concentrations and 25 °C.

$Fe(s)|Fe^{2+}(aq, 0.02M)\|Fe^{3+}(aq, 0.3M)|Pt(s)$ [3 Marks]

d) The equilibrium constant for the reaction;

$Zn^{2+} + Cu(s) \rightarrow Zn(s) + Cu^{2+} = 1.62 \times 10^{37}$ at 25°C.

i) Write the equilibrium constant expression and the half reactions. [2 Marks]

ii) Calculate E°_{cell} and the maximum amount of work that the above cell can do under standard conditions. [5 Marks]

2) The solubility product of $Ag_2CrO_4(s)$ at $25^{o}C = 1.1 \times 10^{-12} M^3$

a) Using i) pure water, ii) a solution containing $0.0025m$ Na_2SO_4 and $0.0003m$ NaCl, and iii) a solution containing $0.025m$ Na_2SO_4 and $0.003m$ NaCl, discuss the effects of ionic strength on the solubility of $Ag_2CrO_4(s)$. [15 Marks]

b) Show that auto-ionization of water has negligible effect on the solubility of $Ag_2CrO_4(s)$. [5 Marks]

3) a) Using the eigen value solution for the particle in a 1-dimensional box given by the expression $E_n = \frac{h^2 n^2}{8ma^2}$, explain the colour transition observed by acid-base titration indicators during titrations. [5 Marks]

b) The decomposition of NO_2Cl occurs via the following mechanism:

Step 1: $NO_2Cl \xrightarrow{k_1} NO_2 + Cl$

Step 2: $NO_2Cl + Cl \xrightarrow{k_1} NO_2 + Cl_2$

Write the overall reaction and apply steady state approximation to show that the rate law can be obtained from any species in the reaction mixture. [15 Marks]

4) a) Kinetics data for the reaction $OCl^- + I^- \text{€} \quad OI^- + Cl^-$ in basic solution is given below:

$[OCl^-]$/M	$[I^-]$/M	$[OH^-]$/M	initial rate/Ms^{-1}
0.0015	0.0015	0.100	1.75×10^{-4}
0.0030	0.0015	0.100	3.50×10^{-4}
0.0015	0.0030	0.100	3.50×10^{-4}
0.0015	0.0015	0.050	3.50×10^{-4}

Evaluate the rate law for the reaction. [10 Marks]

b) The following data is for the kinetics of a decomposition process:

T/^oC	5	20	35	60
k /s^{-1}	2.46×10^{-5}	47.5×10^{-5}	576×10^{-5}	5480×10^{-5}

i) What is the order of the reaction? [1 Mark]

ii) What is the activation energy of the reaction? [9 Marks]

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END OF SEMESTER EXAMINATION PAPER SUPPLEMENTARY INFORMATION

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Useful information:

Reduction potential values

	E^o / V
$Ag^+(aq) + e^- \rightleftarrows Ag(s)$	+0.80
$Au^{3+}(aq) + 3e^- \rightleftarrows Au(s)$	+1.50
$Br_2(l) + 2e^- \rightleftarrows 2Br^-(aq)$	+1.08
$Cu^{2+}(aq) + 2e^- \rightleftarrows Cu(s)$	+0.34
$Cu^{2+}(aq) + e^- \rightleftarrows Cu^+(aq)$	+0.15
$Fe^{2+}(aq) + 2e^- \rightleftarrows Fe(s)$	-0.45
$Fe^{3+}(aq) + e^- \rightleftarrows Fe^{2+}(aq)$	+0.77
$In^{2+}(aq) + e^- \rightleftarrows In^+(aq)$	-0.40
$In^+(aq) + e^- \rightleftarrows In(s)$	-0.14
$Mg^{2+}(aq) + 2e^- \rightleftarrows Mg(s)$	-2.37
$Sn^{4+}(aq) + 2e^- \rightleftarrows Sn^{2+}(aq)$	+0.15
$Sr^{2+}(aq) + 2e^- \rightleftarrows Sr(s)$	-2.89
$Zn^{2+}(aq) + 2e^- \rightleftarrows Zn(s)$	+0.34

Formulae

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

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

$A = 0.509$ for aqueous solutions at 298 K