NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
END OF SECOND SEMESTER EXAMINATIONS – MAY 2011
PHYSICAL CHEMISTRY II – SCH 2204
TIME: (3) THREE HOURS

INSTRUCTIONS TO CANDIDATES

MATERIAL
Reduction potential tables, graph papers.

INSTRUCTIONS TO STUDENTS
Answer All questions in section A and All questions in Section B.
Answer each question on a FRESH page.

$R = 8.314\ JK^{-1}mol^{-1} = 0.08205\ dm^3\ atm^{-1}\ K^{-1}mol^{-1}$.
$F = eN_A = 96\ 485\ C\ mol^{-1}$
1 atm = 760 torr = 760mmHg = 101 325 Pa
lnx = 2.3026logx

SECTION A *Answer ALL questions. Each question carries 10 marks*

1 (a) Define the following terms used in kinetic studies:
- (i) Order
- (ii) Molecularity
- (iii) Opposing Reactions
- (iv) Parallel Reactions
- (v) Consecutive Reactions

[5 marks]

(b) Taking Z, the collision number, to be $4\times 10^{10}\ mol^{-1}\ dm^3\ s^{-1}$, calculate the rate of collision, *Z* for two reactants both at a concentration of 3×10^{-2} $moldm^{-3}$. Compare the result with an experimental rate of reaction of $1.5\times10^{-6}\ moldm^{-3}s^{-1}$. Suggest a reason for any discrepancy.

[5 marks]

2 (a) What are the ionic strengths of the following solutions:
- (i) 1.0 $molkg^{-1}$ of $AgNO_3$
- (ii) 0.5 $molkg^{-1}$ $Al(SO_4)_3$ plus 1.0 $molkg^{-1}$ Na_2SO_4.

[3 marks]

(b) Give an account of the Retardation effects in strong electrolytes.

[7 marks]

3 (a) Which other two isotherms, apart from the Langmuir and the BET, are mentioned for adsorption of a gas onto a solid?

[4 marks]

(b) A sample of human hemoglobin had a sedimentation constant of 4.48 svedbergs in water at 20^0C, and a diffusion coefficient of 6.9×10^{-11} m^2s^{-1}. The specific volume of human hemoglobin is $0.749cm^3g^{-1}$, and the density of water at 20^0C is $0.998gcm^{-3}$. Calculate the molecular weight of human hemoglobin. [6 marks]
[$M = RTs/D(1-\upsilon_1\rho)$, and $1J = 1kgm^2s^{-2}$]

4. (a) Write a concise definition of the electromotive force (emf).

[2 marks]

(b) Briefly discuss the three models of charge separation at the electrode-electrolyte solution interface.

[6 marks]

(c) What is polarization overpotential? [2 marks]

SECTION B

Answer ALL questions from this section.

5. (a) Silver iodide is a sparingly soluble salt. The salt dissolves to give the following equilibrium: $AgI \rightleftharpoons Ag^+ + I^-$. Form a cell that gives this net reaction and calculate its solubility product, K_{sp} at 298K. Evaluate also its ΔG^0. [8 marks]

(b) The e.m.f of the cell: $Zn \mid ZnCl_2(0.05moldm^{-3}) \mid AgCl\ (s) \mid Ag$ is 1.015V at 298K, the silver electrode being positive, whilst the temperature coefficient of its e.m.f is $-0.000492VK^{-1}$. Write down the equation for the reaction occurring when the cell is allowed to discharge and evaluate the following changes:

(a) ΔG^0_{rxn}
(b) ΔH^0_{rxn}
(c) ΔS^0_{rxn} 298K.

[$\Delta H = -zFE + zFT\left(\frac{\partial E}{\partial T}\right)_p$, $\Delta S = -zF\left(\frac{\partial E}{\partial T}\right)_p$] [8 marks]

(c) Write the cell reactions and half-reactions for the following cells:
(i) $Sn \mid SnCl_2(aq) \parallel MnCl_2(aq), HCl(aq) \mid MnO_2(s) \mid Pt$
(ii) $Pt \mid Fe^{3+}(aq), Fe^{2+}(aq) \parallel Sn^{4+}(aq) \mid Sn^{2+}(aq) \mid Pt$ [4 marks]

6. (a) Give a detailed description of the adsorption at the surfaces of liquids. In your account, present the two possible cases of adsorption and use the property *surface tension* as the bases. Also define the terms *adsorption* and *surfactant*. [10 marks]

(b) Compare and contrast *Chemisorption* and *Physisorption*. [6 marks]

(c) Show how you prove that certain experimental results of adsorption fit the Langmuir adsorption isotherm. Assume you are given various values of pressure, p, and the corresponding volumes, V, of the adsorbate at a fixed temperature, T. [4 marks]

7. (a) Outline the moving the Moving Boundary Method for evaluating transport numbers [8 marks]

(b) In the decomposition of azomethane at a pressure of 2.18×10^4Pa and a temperature of 576K, the following time dependent azomethane concentrations were recorded:

t/minutes	0	30	60	90	120	150	180
[azomethane]/10^{-3}moldm^{-3}	8.70	6.52	4.89	3.67	2.75	2.06	1.55

$CH_3N_2CH_3 \longrightarrow 2CH_3 + N_2$

Show that the reaction is first order in azomethane and determine the rate co-efficient at this temperature. [12 marks]

END OF QUESTION PAPER!!!