NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
END OF SECOND SEMESTER EXAMINATIONS – AUGUST 2009
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 Any Three 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 = 3.303logx

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

1. (a) The limiting molar conductivities of aqueous ammonium chloride, sodium chloride and sodium hydroxide are $1.497x10^{-2}$ S cm^2 mol^{-1}, $1.2645x10^{-2}$ S cm^2 mol^{-1}, and $2.478x10^{-2}$ S cm^2 mol^{-1}, respectively, at 25 ^{0}C. Calculate the limiting molar conductivity of aqueous ammonia at this temperature? [4 marks]

(b) Estimate the mean activity coefficient of 0.005 $molkg^{-1}$ KCl (aq) at 25 ^{0}C given that the constant A =$0.509/(molkg^{-1})^{1/2}$ [4 marks]

(c) State two applications of conductometric methods. [2 marks]

2 .(a) Consider an electrode that responds to the equilibrium between nitrogen gas, water, hydrogen ions and Nitrate ions, according to the following reaction:
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longleftrightarrow NO(g) + 2H_2O(l)$
Derive an expression for the potential difference across the electrode interface. How does the potential depend on the concentration of Nitrate ions? How does the interfacial difference charge when the pressure of nitrogen oxide is increased? [4 marks]

(b) The standard potentials at 298K for Sn^{2+}/Sn and Pb^{2+}/Pb are -0.140V and – 0.126V, respectively. Calculate the ratio of Sn^{2+} to Pb^{2+} ion concentration when equilibrium is established at 298K in the reaction.
$Sn(s) + Pb^{2+} \longleftrightarrow Sn^{2+} + Pb(s)$

What is ΔG^{Θ}_{298K} for the reaction? [4 marks]

(c) Write the cell reaction and half-reaction for the following cells:
Ag | AgCl(s) | HCl(aq) || HBr(aq) | AgBr(s) | Ag [2 marks]

3. (a) State the conditions of temperature and pressure in which the Langmuir isotherm is strongly obeyed [2 marks]

(b) Write the three forms that the Langmuir isotherm reduces to and state the extent of absorption at which each form holds [6 marks]

(c) What is an isostere? [2 marks]

4. (a) State two major differences between a solution and a colloidal dispersion [2 marks]

(b) State the three major techniques that are used in characterization of colloidal systems. Highlight the principle for each technique and briefly explain its application. [6 marks]

(b) What is an emulsion? Give an example? [2 marks]

SECTION B

Answer ONLY THREE questions from this section.

5. (a) With the aid of diagrams, describe the three models of the electric double layer at the electrode/electrolyte interface [12 marks]

(b) For the cell Sn | $SnCl_2$(aq) || $MnCl_2$(aq), HCl(aq) | MnO_2(s) | Pt
(i)write the cell reaction and the half-reactions [4 marks]

(ii) Calculate the e.m.f of the cell at standard conditions [2 marks]

(iii) Calculate the equilibrium constant for the cell reaction. [2 marks]

6. (a) What is:
(i) the Kohlrausch's law for strong electrolytes
(ii) the Kohlrausch's law of independent migration of ions.
[4 marks]

(b) The molar conductivities, Λ, of aqueous sodium chloride at 25 ^{0}C and at various concentrations, c, are given in the following table:

c/ mol dm^{-3}	Λ/ S m^2 mol^{-1}
0.0005	0.012450
0.001	0.012374
0.002	0.012270
0.005	0.012065
0.01	0.011851

Plot a graph of Λ against $\sqrt{c}$ and determine the limiting molar conductivity at infinite dilution, Λ_0. Compare the graph with the theoretical plot given by the Onsager equation. At 25 ^{0}C the dielectric constant, D, of water is 78.5 and the viscosity of water is 8.9x 10^{-4} kgm^{-1}s^{-1}.
The Onsager limiting equation for a 1-1 electrolyte is:

$$\Lambda = \Lambda_{\infty} - \left[\frac{8.24\times10^{-4}}{\eta(DT)^{1/2}} + \frac{8.204\times10^{5}}{(DT)^{3/2}}\Lambda_0 \right]\sqrt{c}$$

where D is the dielectric constant, η the viscosity (in kgm^{-1}s^{-1}) and T the thermodynamic temperature [12 marks]

(c) State and explain the two effects on ions collectively known as the retardation effects in strong electrolytes [4 marks]

7. (a) Discuss the stability of colloids. In your discussion use the kinetics and the thermodynamics of the colloidal particles. [12 marks]

(b) What do you understand by the terms : (i) sol, (ii) suspension, (iii) lyophilic, (iv) jelly, (v) gel, and (vi) foam [6 marks]

(c) State the size range of colloidal particles [2 marks]

8. The volume of butane adsorbed on a gram sample of activated carbon at 0 ^{0}C varies with pressure as follows:

P/kPa	14.0	28.6	42.6	57.2	73.1	94.4
V/cm^3(s.t.p)	15.4	19.6	21.0	21.9	22.7	23.2

Show that the data fit langmuir equation and evaluate the constants
The Langmuir's isotherm: $\theta = \dfrac{Kp}{1+Kp}$ [20 marks]

9. The data below relates to the adsorption of ammonia on barium fluoride are reported below. Confirm that they fit the BET isotherm in the range of pressure reported, and find V_{mon} and c.

P/Torr	39.5	62.7	108	219	466	555	601	765
V/cm^3	9.2	9.8	10.3	11.3	12.9	13.1	13.4	14.1

At T =18.6 ^{0}C P_o = 6148 Torr

$$\frac{p}{V_{ads}(p_0 - p)} = \frac{1}{cV_m} + \frac{(c-1)p}{cV_m p_0}$$. [20 marks]

END OF QUESTION PAPER!!!