THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme - Level 5
Final Examination 2011/2012
CHU 3124 - Physical Chemistry
2 h

08-12-2012 **9.30 a.m - 11.30 a.m**

NOTE: Duration of this paper is 2 h and **NOT** 2.5 h

- There are three (3) **parts A, B and C.**
- Answer **only four (4)** questions out of **six (6),** choosing **at least one question** from each part.
- If more than four questions are answered, only the **first four relevant answers** (those selected according to the specifications given above) in the order written, will be considered for marking
- **Indicate your choice of questions,** in order, in the space provided in the answer sheet
- The use of a non-programmable electronic calculator is permitted
- Logarithm tables and graph paper will be provided on request
- Mobile phones are **NOT** allowed; switch them off and leave them outside.

Gas constant (R)	$= 8.314\ J\ K^{-1}\ mol^{-1}$
Boltzmann Constant (k)	$= 1.380 \times 10^{-23}\ J\ K^{-1}$
Avogadro constant (L)	$= 6.023 \times 10^{23}\ mol^{-1}$
Faraday constant (F)	$= 96{,}500\ C\ mol^{-1}$
Plancks constant (h)	$= 6.63 \times 10^{-34}\ J\ s$
Velocity of light (c)	$= 3.0 \times 10^{8}\ m\ s^{-1}$
Atmospheric pressure (π)	$= 1\ bar = 10^{5}\ Pa\ (N\ m^{-2})$
Charge of a proton (e)	$= 1.602 \times 10^{-19}\ C$
$\log_e (X)$	$= 2.303 \log_{10} (X)$

Part A

1. (a) The data given below refers to the following chemical reaction.

$$I^-(aq) + OCl^-(aq) \text{ -----> } Cl^-(aq) + OI^-(aq)$$

Initial rate x 10^3 /(mol dm^{-3} s^{-1})	Initial Concentration of I^- x 10^4 /(mol dm^{-3})	Initial Concentration of OCl^- x 10^4 / mol dm^{-3}
1.92	8.25	3.85
3.84	16.50	3.85
5.76	8.25	11.55

(i) Determine the order with respect to each of the reactants and the rate constant for the reaction.
(ii) Hence, write down the rate equation.

(26 marks)

(b) 25.00 ml of a 0.05 M persulphate solution was allowed to react with 25.00 ml of 1 M KI (excess) in the presence of 20.00 ml of a 0.01 M thiosulphate solution, starch and 30.00 ml of water. The first order rate equation is $\ln \frac{a}{a-x} = kt$ (the symbols used have their usual meanings). Calculate

(i) the pseudo first order rate constant of this reaction given that the time taken for the first appearance of a blue color was 13 minutes and 20 seconds. in the above experiment

(ii) the half life of this reaction.

(26 marks)

(c) The reaction $2\,NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$ is second order in NO and first order in Cl_2.

4 moles of NO (g) and 2 moles of Cl_2 (g) were allowed to react in a volume of 2 dm^3 and the initial rate measured was 2.0×10^{-3} mol dm^{-3} s^{-1}.

(i) Determine the initial concentrations of NO and Cl_2

(ii) Calculate the **rate** at the instance when half of the initial amount of NO has reacted

(24 marks)

(d) Consider a consecutive, irreversible first order reaction of the form

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(where k_1 and k_2 are rate constants such that $k_1 \neq k_2 \neq 0$)

(i). Write down the rate expression (differential form) for the disappearance of A and hence, show that $\frac{[A]}{[A_o]} = e^{-k_1 t}$ given that the initial concentration of A is $[A_o]$

(ii) The concentration of B at any time, t is

$$[B] = \frac{k_1[A_o]}{(k_2 - k_1)}[e^{-k_1 t} - e^{-k_2 t}]$$

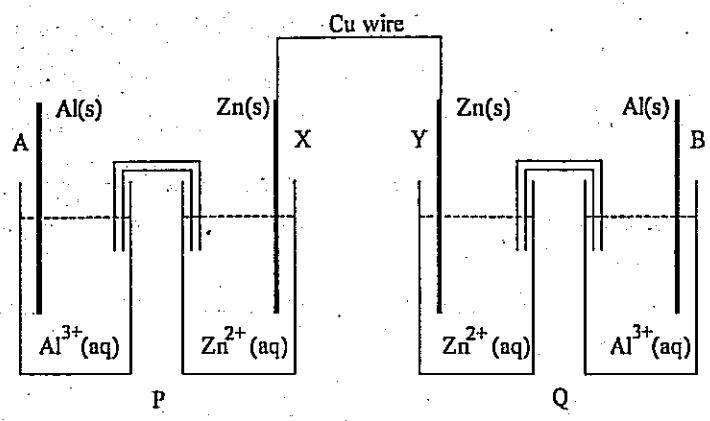
Show that the time taken, t, for the concentration of B to reach its maximum value is

$$t = \frac{1}{[k_1 - k_2]} \ln\left(\frac{k_1}{k_2}\right)$$

(24 marks)

Part B

2. (a) A student prepared a Galvanic cell, P, by placing an aluminium rod in an $Al^{3+}(aq)$ solution, a zinc rod in a $Zn^{2+}(aq)$ solution and bringing the electrical contact between the two solutions using a salt bridge. Using the same solutions and, aluminium and zinc rods, he prepared another Galvanic cell, Q, which is identical to P. He connected the two zinc rods of P and Q using a copper wire. The setup he prepared is sketched in the following figure.



(i) Using standard notation, draw a cell diagram for the electrochemical system shown in the above diagram.

(ii) What is the electric potential difference between the two aluminium rods (A and B) in the electrochemical system shown in the above diagram? Briefly explain your answer.

(30 marks)

(b) In a book of constants, a student noted that the standard electrode potential of a $Cu(s)\left|Cu^{2+}(aq)\right.$ electrode at $25^{\circ}C$ is 0.340 V.

(i) Define the standard electrode potential of $Cu(s)\left|Cu^{2+}(aq)\right.$ electrode.

(ii) Write down the half reaction (in standard form) of the above electrode.

(iii) Write down the Nernst equation for the electrode potential of the above electrode and identify all the parameters in it.

(iv) Calculate the electrode potential of the above electrode at $25^{\circ}C$ when the activity of $Cu^{2+}(aq)$ is 0.25

(35 marks)

(c) (i) Write down the Debye-Huckel limiting law for the activity coefficient of an ionic species in solution and identify all the terms in it.

(ii) Using the Debye-Huckel limiting law calculate the activity coefficient of sulphate ions in an aqueous solution of 0.02 mol dm^{-3} sodium sulphate at $25^{\circ}C$. $[A = 0.509]$

(35 marks)

3. (a) Define the following as applied in the study of galvanic cells.

(i) Electromotive force

(ii) Storage density

(iii) Energy density

(20 marks)

(b) The standard emf of $Ag(s)|AgBr(s)|HBr(aq)|H_2(g)|Pt(s)$ was measured over a range of temperatures and the data were fitted to the following equation:

$$E^0/V = -0.07131 + 4.99\times10^{-4}(T/K - 298) + 3.45\times10^{-6}(T/K - 298)^2$$

(i) Write down the relationship between the standard Gibbs free energy change of the cell reaction and the emf assigned to the above cell diagram and identify all the parameters in it.

(ii) Evaluate the standard Gibbs free energy change for the cell reaction assigned to the above cell diagram at 298K.

(iii) Write down the relationship between the standard entropy change of the cell reaction and the emf assigned to the above cell diagram and identify all the parameters in it.

(40 marks)

(c) A student was asked to determine the concentration of $Ti^{3+}(aq)$ in a solution using a potentiometric titration using a standard solution of $KMnO_4$ at 298 K. He was given the following information:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O \qquad E^0_{298} = 1.51\,V$$

$$Ti^{4+}(aq) + e^- \rightarrow Ti^{3+}(aq) \qquad E^0_{298} = 0.07\,V$$

(i) Briefly explain why the titrant has to be much more concentrated than the titrand in a potentiometric titration.

(ii) Sketch the electrode potential of the redox electrode constructed in the above mentioned titration as a function of the volume of $KMnO_4$ solution added. Clearly indicate the end point of the titration and the potentials 0.07 V and 1.51 V on the Y-axis of the sketch.

Briefly explain your answer. [Assume that the activity of $H^+(aq)$ is unity throughout the titration.]

(40 marks)

Part C

4. (a) Define (i) Surface Tension (ii) Surface Pressure (iii) Surface Excess

(18 marks)

(b) Write down the Clausius – Clapeyron (CC) equation
Give two important assumptions that you make in using this equation.

(16 marks)

(c) The adsorption of nitrogen gas on charcoal amounted to 0.925 $cm^3\ g^{-1}$ of adsorbent under the following equilibrium conditions of pressure and temperature.

P/bar	10.0	35.0
T/K	190	275

(i) With the aid of the CC equation, calculate the temperature at which the same quantity of gas would be adsorbed under an equilibrium pressure of 25 bar with the aid of the CC equation.

(ii) **Suppose** the data given above corresponds to a linear relationship between Pressure and Temperature such that P = kT +C for the same quantity of gas being adsorbed [k is the proportionality constant], calculate the temperature when the equilibrium pressure is 25 bar.

(38 marks)

(b) The expression for rate of collision of gas molecules on unit area of surface in unit time (u) is given by the expression $u = \frac{p}{\sqrt{2\pi m k T}}$

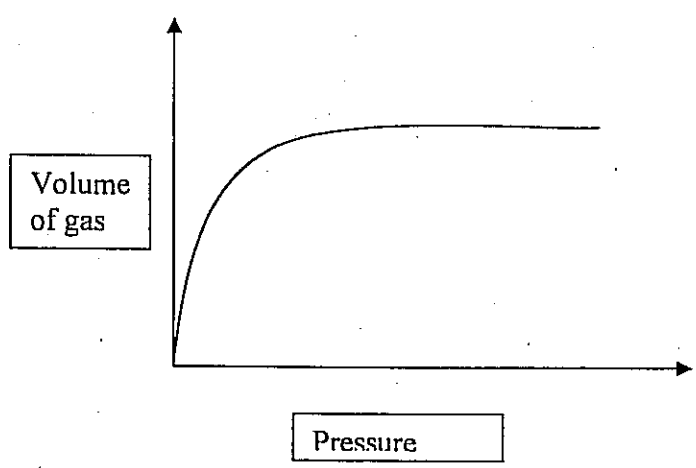
(i) Identify the rest of the symbols in the above equation.

(ii) Given that the rate of adsorption of nitrogen gas molecules (assumed to behave ideally) at a temperature of 227 °C and 1 standard atmospheric pressure on a 100 m^2 surface is 2.5 x 10^{22} molecules cm^{-2} s^{-1}, calculate the sticking probability.

(R.A.M of O = 16; N = 14)

(28 marks)

5. Given below is a typical adsorption isotherm obtained for a certain system at a temperature, T_1



(a) (i) Is the adsorption more likely to be chemisorption OR physical adsorption? Give reasons for your choice.
(ii) Copy the above isotherm at T_1 and sketch a second isotherm generated at a higher temperature, T_2 ($T_2 > T_1$) on the same diagram? Explain its shape in relation to the given isotherm.

(30 marks)

(b) Distinguish between an Isobar and an Isostere.

(12 marks)

(c) The Langmuir adsorption (isotherm) may also be expressed in the following form, corresponding to adsorption from a solution.[This is illustrated in the experiment involving the adsorption of acetic acid and charcoal which you carried out as part of the practical]

$$\frac{x}{m}=\frac{\alpha C}{1+\beta C}$$

(i) Identify, clearly, the symbols used in the above equation.

(ii) Show that $\lim_{c\to\infty}\left(\frac{x}{m}\right)=\frac{\alpha}{\beta}$

(30 marks)

(d)(i) Write down the equation of state for an ideal surface film using the standard symbols

(ii) A certain amount, 'x' g, of a protein of relative molar mass of 50,000 when spread on the surface of a solution [surface area 100 m^2] corresponded to a surface pressure of 2.5×10^{-3} mN cm^{-1}. This Langmuir Trough experiment was carried out at 300 K. Calculate 'x'.

(28 marks)

6. (a) A feature of a colloidal system is that it resembles both a suspension and true solution. Comment on this statement.

(14 marks)

(b) What is meant by

(i) the dispersed phase

(ii) the dispersed medium

(14 mark)

(c) Considering the three states of matter,s, l, g, classify all possible dispersion systems and tabulate them under the following titles

Dispersed Phase, Dispersion Medium, General Name of Dispersion System, One Example

(48 marks)

(d) (i) What is meant by a hydrophobic colloid?

(ii) Stability is conferred on lyophobic colloids due to the presence of charges.

Explain this statement and hence, explain what happens when an electrolyte is added to such systems.

(24 marks)