THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme - Level 5
Final Examination 2014/2015
CHU 3124 - Physical Chemistry

(2.0 hours)

31st Oct 2015 **2.00 p.m to 4.00 p.m**

- 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
- Mobile Phones are not allowed; switch 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) (i) Considering a reaction of the form A + B -------> Products, write down the expressions for the rate of disappearance of A if this reaction is

(I) 1st order with respect to each A and B

(II) zero order with respect to B but of order "half" with respect to A.

(ii) In each of the cases (I) and (II) above, **derive** the SI units of k, the rate constant.

(24 marks)

(b) The hypothetical reaction **B ------> Products** is said to be first order with respect to B.

(i) Write down the differential form of the rate equation and hence, derive the integrated form of the rate equation using the standard symbols.

(ii) Commencing with a known concentration of **B**, the decrease in concentration of B with time was studied and two readings taken as follows.

Time in minutes	8.0	12.0
[B] in mol dm^{-3}	0.25	0.15

Determine the initial concentration of B and the rate constant of this reaction.

(46 marks)

(c) (i) Name the **three (3) main** steps in a chain reaction. Considering the chain reaction involving H_2 and Cl_2 in the presence of light and its proposed mechanism, identify these three steps.

(ii) Illustrate the meaning of the term "steady state assumption (SSA) as applied to the kinetic study of chain reactions with reference to the above example.

(30 marks)

Part B

2. (a) **Define** the following as applied in electrochemistry.
   (i) Electromotive force of a cell
   (ii) Negative terminal
   (iii) Electrode potential of an electrode

(20 marks)

(b) **Write down** an indicator electrode (i.e. an electrode that could be used to determine the concentration) for each of the following ions.

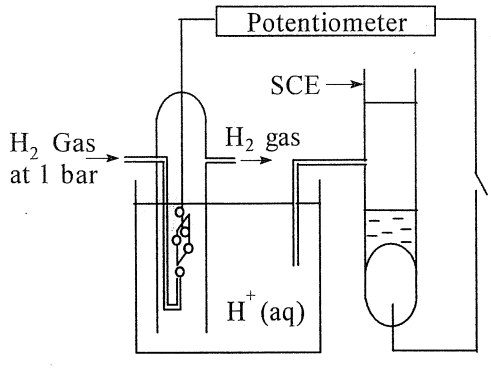
(i) $Cl^-(aq)$

(ii) $SO_4^{2-}(aq)$

(10 marks)

(c) A student was asked to experimentally measure the pH of a solution using a hydrogen gas electrode. He prepared the electrochemical system schematically represented in the figure and measured the emf of the electrochemical cell at $25^\circ C$.

He found that the electric potential of the H_2 gas electrode to be 0.560 V below the electric potential of the Saturated Calomel Electrode (SCE).



(i) Calculate the electrode potential of the H_2 gas electrode at $25^\circ C$ if the electrode potential of the SCE is 0.242 V at the same temperature.

(ii) Write down the Nernst equation corresponding to the electrode potential of the H_2 gas electrode and identify all the terms in it.

(iii) What is the <u>standard</u> electrode potential of the H_2 gas electrode?

(iv) Calculate the pH of the solution at $25^{\circ}C$ assuming the activity coefficient of any ionic species to be unity.

(70 marks)

3. (a) A student was asked to estimate the solubility product of $PbSO_4$ at $25^{\circ}C$ using the standard electrode potentials of electrodes listed in a book of constants.

(i) Write down the chemical reaction of $PbSO_4$ whose concentration equilibrium constant is equal to the solubility product of $PbSO_4$.

(ii) Write down a cell diagram whose cell reaction is the same as the reaction you have written above.

(iii) What are the electrodes the student has to find the standard electrode potentials of?

(iv) Write down the relationship between the thermodynamic equilibrium constant and the standard emf assigned to the above reaction and identify all the parameters in it.

(v) Write down the relationship between the above mentioned thermodynamic equilibrium constant and the solubility product of $PbSO_4$ and identify all the parameters in it.

(vi) The student found the standard emf assigned to the above reaction at $25^{\circ}C$ to be $-0.226\ V$. Estimate the solubility product of $PbSO_4$ at $25^{\circ}C$.
State any assumptions you make.

(50 marks)

(b) A battery is constructed by connecting two <u>identical</u> cells in series. The cell reaction is $Zn(s)+Cl_2(g) \longrightarrow ZnCl_2(s)$ with $\Delta G^0_{298} = -409.1\ kJ\ mol^{-1}$. Each cell in the battery contains 1 kg of Zn(s) and 1.5 kg of $Cl_2(g)$. In each cell, the other parts including the water, has a mass of 3 kg.

(i) What is the capacity of this battery?

(ii) Calculate the maximum electrical energy that can be derived from the battery (operated under) standard conditions at 298 K.

(iii) What is the maximum energy density of the battery under standard conditions at 298 K?
[Relative atomic masses: Zn = 65, Cl = 35.5]

(50 marks)

4 (a) (i) A spherical droplet of liquid (relative molecular mass =**B**, Density = **C**) with radius **X** at temperature **D** exhibits a vapour pressure **M** outside the droplet. The Vapour pressure outside a plane surface of the liquid equals **N**, Gas constant equals **R**, surface tension of liquid equals **T.**

Using the symbols given in the above passage but **no other,** complete the Kelvin equation given below.

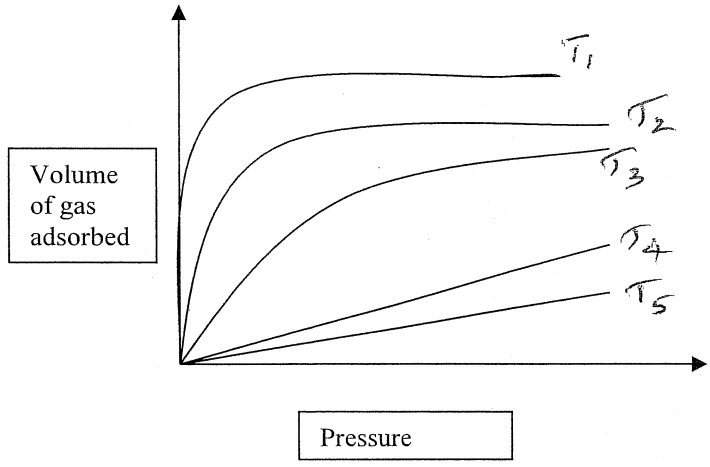
$$\ln\frac{M}{N} =$$

(16 marks)

(ii) The Kelvin equation expresses how the ration $\left(\frac{M}{N}\right)$ changes with radius, **X**. What is the most important conclusion that you can make from the Kelvin equation?

(10 marks)

(b) Typical adsorption isotherms obtained for a certain system at various temperatures, T_1, T_2, T_3, T_4 , T_5 , are given below.



(i) Is the adsorption more likely to be chemisorption OR physical adsorption?

(ii) Is $T_1 > T_2 > T_3 > T_4 > T_5$?

(iii) Briefly give adequate reasons in support of your answers to the questions in (i) above.

(24 marks)

(c) An amount of work, **W**, has to be done on a surface system at temperature **D** to extend its area by an amount **E**. The molar concentration of this aqueous system is **C**. Gas constant = **R**; surface tension of pure water = **T**

Using the symbols given but **no other,** write down for the system an expression for

(i) the surface tension

(ii) the surface pressure

(iii) the surface excess concentration using the Gibbs adsorption isotherm

(30 marks)

(d). The monolayer volume(V_m) for the adsorption of gaseous krypton on 1 kg carbon measured at 27 °C and 1 standard atmospheric pressure is 500 cm^3. A single krypton molecule has a molecular area of 22 x 10^{-20} m^2. Calculate the specific surface area of the carbon adsorbent.

(20 marks)

5 (a) 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	11.2	35.8
T/K	196	273

(i) Write down the mathematical expression that governs Clausius – Clapeyron equation

(ii) Calculate the temperature at which the same quantity of gas would be adsorbed under an equilibrium pressure of 25 bar.

(iii) Give two important assumptions that you are making in using this equation.

(32 marks)

(b) (i) State the assumptions made by Langmuir in formulating the Langmuir adsorption model.

(ii) Derive the Langmuir adsorption equation and express it in a linear form.

(40 marks)

(c) Distinguish between

(i) adsorption and absorption.

(ii) capillary active and capillary inactive substances

(28 marks)

6.(a) (i) Compare a true solution with a colloidal system.

(ii) What do you understand by the following two terms?

- dispersed phase
- dispersed medium

(40 marks)

(b) Define a surfactant and explain the term "**critical micelle concentration** " with reference to the action of a surfactant.

(30 marks)

(c) The table below refers to colloidal dispersions. Complete it by filling the blank boxes appropriately.

Dispersion Medium	Dispersed Phase	General Name given to dispersion system	One typical example	A second example
Solid	Gas			
		Solid emulsion		
	Solid		AgCl in Colloidal Dimension	

(30 marks)