052

THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme - Level 5
Final Examination 2006/2007
CHU 3124 - Physical Chemistry

(2.5 hours)

5th May 2007 **10.00 p.m - 12.30 p.m**

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* 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

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 hypothetical reaction **B -------> Products** is said to be zero 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 seconds	80	120
[B] in mol dm^{-3}	2.0	1.5

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

(40 marks)

(b) Consider the following elementary reaction, A + A ------> Products:

(i) Write down the rate equation (differential form) for this reaction.

(ii) Show that the half- life ($t_{1/2}$) - time taken for the initial concentration of A, C_o, to become $C_o/2$ is inversely proportional to the initial concentration.

(20 marks)

(c) The table below contains kinetic data obtained for the reaction

X + Y ----> Z

(all concentration terms are expressed in **mol dm^{-3}** and data obtained at the same temperature)

[X]	[Y]	Initial Rate x 10^4 / mol dm^{-3} s^{-1}
2.0	2.0	2.0
4.0	2.0	8.0
2.0	4.0	16.0

(i) Determine the order of the reaction with respect to **X and Y**.

(ii) Hence, write down the expression for the rate law for this reaction.

(iii) Derive the units of the rate constant of this reaction in the given units and hence, obtain the corresponding SI unit of the rate constant.

(40 marks)

Part B

2. (a) Define the following as applied in electrochemistry.
   (i) Electromotive force of a cell
   (ii) Storage density of a battery
   (iii) Chemically reversible cell
   (iv) Electrode potential of an electrode

(20 marks)

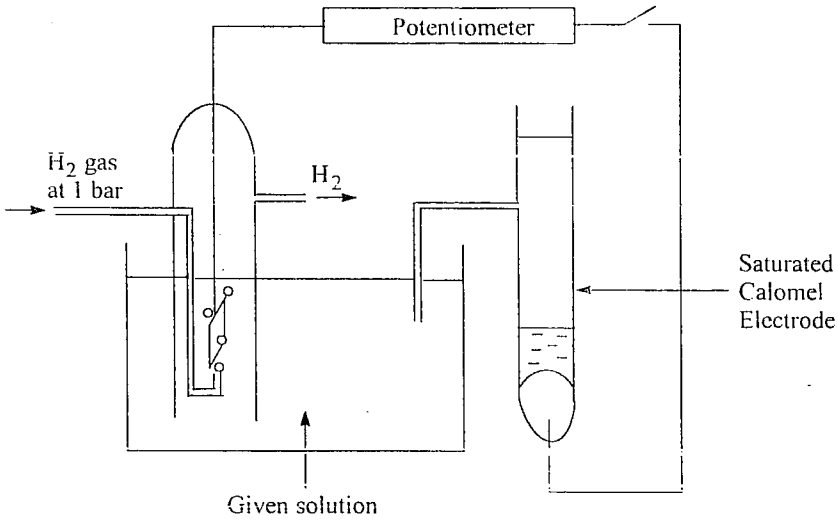
(b) Write down an indicator electrode (i.e. an electrode that could be used to determine the concentration) for each of the following ions.

(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 below and measured the emf of the electrochemical cell at 25^oC.



He found that the electric potential of the H_2 gas electrode to be 0.150 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 standard 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) (i) Write down the relationship between the ionic strength of a solution and the charge numbers of the ions and identify all the terms in it.

(ii) Calculate the ionic strength of 0.2 mol dm^{-3} solution of $MgCl_2$.

(iii) Write down the Debye–Huckel limiting law for the mean activity coefficient of an electrolyte and identify all the terms in it.

(iv) Calculate the mean activity coefficient of $MgCl_2$ in the above mentioned solution using Debye–Huckel limiting law. [$A = 0.509 \text{ dm}^{3/2} \text{ mol}^{-1/2}$]

(30 marks)

(b) $E^\circ = 1.03$ V for the cell diagram

$$Zn(s) \left| ZnCl_2(aq)\left(0.005 \text{ mol dm}^{-3}\right) \right| Hg_2Cl_2(s) \left| Hg(l) \right.$$

at 298 K. For the same cell diagram, $\left(\partial E^\circ / \partial T\right)_P = -4.52 \times 10^{-4} \text{ V K}^{-1}$ at 298 K.

(i) Write down the anode reaction, cathode reaction and the cell reaction for the above cell diagram.

(ii) Deduce the charge number of the above cell reaction.

(iii) Calculate, ΔG°, ΔS° and ΔH° for the above cell reaction at 298 K.

(70 marks)

Part C

4. (a) The surface tension (γ) of a liquid can be determined using the capillary rise method by using the expression

$$\gamma = \frac{h\rho gr}{2\cos\theta}$$

in which the various symbols have their customary meanings.
Use this expression to deduce that the level of a liquid such as mercury will be depressed within a capillary when immersed in the liquid.

(08 marks)

(b) An amount of work **A** has to be done on a surface aqueous system at a temperature **D** to extend its area by **E**. The molar concentration of this system is **C**. Pure Water has a surface tension, **T**; Gas constant is **X**.

Use the symbols given above but no other to write down , for the surface aqueous system, expressions for

(i) the surface tension, γ, of the solution.
(ii) the surface pressure, Π, of the solution.
(iii) the surface excess concentration, Γ, making use of the Gibbs Adsorption Isotherm.

(20 marks)

(c) What is the principal difference between a "surfactant" and a "capillary active substance" in respect of the variation of surface tension with increasing concentration of solutions containing these substances? Briefly provide reasons to explain this difference.

(18 marks)

(d) The molecular area of some substances can be determined using the Langmuir Trough Method. Which of the following substances will be suitable for this purpose?

acetic acid
lauryl alcohol [$CH_3(CH_2)_{12}OH$]
stearic acid [$CH_3(CH_2)_{16}OH$]
n-propyl acetate
ethyl palmitate [$CH_3(CH_2)_{14}COOC_2H_5$]
n – butanol
cholesterol

Briefly provide **general** reasons in support of your answer.

(19 marks)

(e) (i) Write down the equation of state for an ideal surface film.

(ii) What are the principal requirements for the existence of such an ideal surface film?

(iii) 0.50 mg of a protein when spread on 0.050 m^2 of the surface of dilute HCl in a Langmuir trough at 300 K has a surface pressure of 0.30 mN m^{-1}. Assuming that this protein forms an ideal surface film, calculate the relative molecular mass of the protein.

(35 marks)

5. Full marks will be given to candidates scoring about **100** out of the allotted **113** marks; pro- rata marks will be awarded to other candidates

(a) Define, in relation to surface phenomena,

(i) sticking probability (s)
(ii) monolayer volume (V_m)
(iii) multilayer adsorption

(18 marks)

(b) The monolayer volume (V_m) for the adsorption of krypton gas on 0.01 g of activated carbon at 78 K is 224 cm^3 (measured at STP). Molecular area of krypton = 16 x 10^{-20} m^2.

(i) How can a 78 K temperature be conveniently obtained?
(ii) Which company produces activated carbon in Sri Lanka?
(iii) Calculate the specific surface area of activated carbon.

(40 marks)

(c) Explain briefly how the temperature range of adsorption can be used to distinguish physical adsorption from chemisorption.

(15 marks)

(d) **Sketch** the five different types of adsorption isotherms that could be obtained for the adsorption at a solid/gas interface.

(15 marks)

(e) The equation

$$\theta = \frac{bP}{(1+bP)}$$ where b is a constant and P is the pressure.

is applicable for a number of gas/solid adsorption systems.

(i) Identify the symbol, θ, and define it.
(ii) By what name is this equation known.
(iii) State the **FOUR** most important assumptions on which this equation has been derived.

(25 marks)

6. (a) Use molecular size to distinguish between true solutions, suspensions and colloidal systems.

(12 marks)

(b) How does the charge possessed by colloidal particles effect the stability of lyophobic colloidal systems?

(10 marks)

(c) Name the principal factor that influences the stability of lyophilic colloidal systems.

(08 marks)

(d) The table below refers to colloidal dispersions. Identify the blanks in the table specified through capital alphabetical letters (A, B, C, -------I) by writing down the appropriate answers on your answer book.

Dispersion Medium	Dispersed Phase	General name given to the system	One typical example
A	B	C	Milk
Gas	Solid	D	E
F	G	Solid Foam	Polyurethane foam
Solid	Liquid	H	I

(27 marks)

(e) Show briefly how a given set of adsorption isotherms can be used to construct an equivalent set of isosteres.

The adsorption of nitrogen gas on charcoal amounted to 1.0 $cm^3\ g^{-1}$ of adsorbent under the following equilibrium conditions of pressure and temperature.

P/bar	12	36	X
T/^oC	-73	27	127

(i) Calculate the isosteric enthalpy of adsorption of nitrogen on charcoal indicating any two important assumptions you are compelled to make.

(ii) What is the name given to the equation that has to be used for the above calculation?

(iii) Calculate the value of **X**.

(43 marks)