THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme - Level 5
Final Examination 2007/2008 065
CHU 3124 - Physical Chemistry
(2.5 hours)

13th June 2008 **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) (i) Considering a reaction of the form A + B -------> Products, write down the expressions for the rate of disappearance of A in terms of the concentrations of A and/or B if this reaction is

(I) 2nd order with respect to A and 2nd order with respect to B
(II) of order "half" with respect to A and "half" with respect to B.

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

(25 marks)

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

(i) A kinetic experiment, to study the variation in concentration of X, **[X],** with time,**t**, was carried out starting with a known concentration of X. The following readings were reported.

Time, **t** /s	80	120
[**X**] / mol dm^{-3}	2.0	1.5

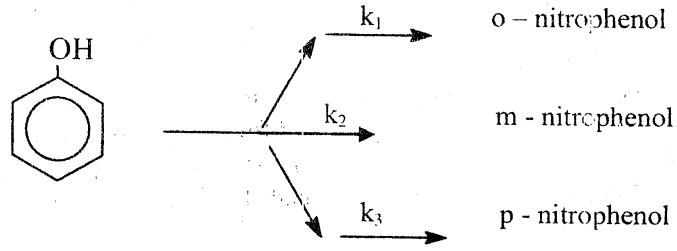
Determine the initial concentration of **X** and the rate constant of this reaction.

(ii) Consider the following elementary reaction, 2A ------> Products:
Show that the half- life ($t_{1/2}$) - time taken for the initial concentration of A, C_o, to become $C_o/2$ - is given by

$$t_{1/2} = \frac{1}{kC_o}$$ (where k is the rate constant)

(30 marks)

(c)



Nitration of Phenol produces the ortho- , meta- and para- products, simultaneously, but at different rates (k_1, k_2, k_3 are the respective rate constants) as shown above.

Write down the expression for the rate of disappearance of phenol and hence, show that

$$\ln\frac{a}{a-x} = (k_1 + k_2 + k_3)t$$

given that '**a**' is the initial concentration of phenol and that, the concentration of phenol, on nitration, reduces by '**x**' after a time, **t**,

(20 marks)

(d) (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) What is meant by "steady state assumption (SSA) as applied to the kinetic study of chain reactions?

(iii) Write down the expression(s) that correspond to SSA based on the proposed mechanism for the above chain reaction.

(25 marks)

Part B

2. (a) Define the following as applied in electrochemistry.
(i) emf
(ii) Electrode potential of an electrode
(iii) activity coefficient of an ionic species in a solution.

(21 marks)

(b) You are given that E^o_{298}/V for Fe^{3+} (aq) + e ----> Fe^{2+} (aq) and Fe^{2+} (aq) + e ----> Fe (s) are +0.771 and -0.447 respectively. Determine E^o_{298} for the half reaction Fe^{3+} (aq) + 3e ----> Fe (s)

(29 marks)

(c) (i) Write down the relationship between ionic strength of a solution and the concentration of ionic species; identify all the terms in it.

(ii) Calculate the ionic strength of a solution of KCNS and KOH in alcohol where the concentrations of them, in units of mol dm^{-3}, are 0.010 and 0.015 respectively. Assume that KCNS and KOH are weak electrolytes in alcohol and, the degree of dissociation of them in the above solution are 0.6 and 0.8 respectively.

(50 marks)

3. (a) Define the following as applied to batteries
   (i) Capacity
   (ii) Storage Density
   (iii) Energy Density

(21 marks)

(b) The half cell reactions of the Edison storage cell and their standard electrode potentials at 298 K are

$$Ni_2O_3(s) + H_2O(l) + 2e \text{ -------> } 2\,NiO(s) + 2OH^-(aq) \qquad E^o_{298} = 0.40\ V$$

$$FeO(s) + H_2O(l) + 2e \text{ ------> } Fe(s) + 2OH^-(aq) \qquad E^o_{298} = -0.87$$

(i) Write down the reaction that occurs in the cell when a current is drawn under standard conditions. Briefly explain your answer.

(ii) Write down a cell diagram for the Edison cell whose cell reaction is equal to the reaction you have given in part (i) above. Briefly explain your answer.

(iii) What is the magnitude of the standard emf of the Edison cell?

(iv) Giving reasons, indicate the difference between the emfs of two Edison cells, A and B, with activities of hydroxyl ions at 1.0 and 0.5 respectively.

(v) Calculate the maximum electrical work that can be obtained from an Edison cell per kilogram of Fe(s).
[Relative atomic mass of Fe = 56]

(79 marks)

Part C

4. (a) Define sticking probability (s); **list** the five factors on which the value of the sticking probability depends on (description of the factors are **not** required)

(16 marks)

(b) "Gaseous nitrogen and hydrogen react very slowly to give ammonia. However, the presence of a solid catalyst **enhances the reaction rate** in an industrially acceptable manner"

(i) Name this industrial process.

(ii) Use surface chemistry principles to explain briefly how the phenomenon takes place.

(iii) Name the German(surface) Chemist who was awarded the Nobel Prize for Chemistry in 2007 for his work in clarifying the mechanism for this phenomenon.

(20 marks)

(c) The Langmuir adsorption theory (1918) was **extended** in 1938 in a significant manner by the deduction of a more complete adsorption isotherm.
(i) Who were the three scientists responsible for this extension?
(ii) What was the significant extension?

(15 marks)

(d) Write down the general name given to the colloidal system of margarine. Identify the state of matter corresponding to the dispersed phase and to the dispersion medium in the system.

(15 marks)

(e) Distinguish, with the aid of a diagram, between a capillary active substance and a surfactant.

(12 marks)

(f) The Langmuir Trough Method can be used to determine the molecular surface area of certain substances using the principles of surface chemistry.
(i) What is the determining factor that will decide whether the Langmuir Trough Method can be used?
(ii) Identify **four** substances (from those listed below) that can be so used to determine their molecular areas.

acetic acid	-	CH_3COOH
lauric acid	-	$CH_3(CH_2)_{11}COOH$
propionic acid	-	C_2H_5COOH
isobutanol	-	C_4H_9OH
n- heptanol	-	$C_7H_{15}OH$
cetyl alcohol	-	$CH_3(CH_2)_{15}OH$
octa decanoic acid	-	$CH_3(CH_2)_{16}COOH$
myristic acid	-	$CH_3(CH_2)_{12}COOH$

(Note that 4 marks will be given for each correct answer while 2 marks will be deducted for each incorrect answer)

(22 marks)

5. (a) (i) Define angle of contact.
(ii) The surface tension of mercury is 0.50 N m^{-1} and its density is 13.6 g cm^{-3}. Given that the angle of contact for mercury is 137 °, calculate the lowering of the surface of mercury that will occur when a glass tube of internal radius 0.5 mm is inserted into the liquid.
(acceleration due to gravity = 9.8 m s^{-2})

(30 marks)

(b) **Write down** (no proof required) the Gibbs adsorption isotherm equation relevant to a solution of bulk concentration **A** with surface tension **B** at a temperature **C**. Surface excess concentration was found to be **D**
(Gas constant = **E**)
(**Note**: Your answer should NOT include any symbol not given above)

(15 marks)

(c) (i) **Write down** TWO practical uses of unimolecular films.
(ii) **Write down** the equation relevant to an ideal surface film comprising n moles occupying an area **F** at a temperature **C** when the surface pressure = $\prod$
(Gas constant = **E**)

(iii) Franklin found that 5.0 cm^3 of olive oil formed an unimolecular film of area 5000 m^2. Olive oil can be considered to consist mainly of glycerol trioleate which has to relative molecular mass of 1000 with a density at room temperature of 0.90 g cm^{-3}.
Calculate

(A) the film thickness of, and

(B) the area occupied by each olive oil molecule

in Franklin's olive oil film.

(55 marks)

6. (a) Give the **most important** criterion to distinguish between a true solution, a colloidal solution and a suspension.

(10 marks)

(b) Write a short account on the stability of lyophilic colloidal solutions.

(15 marks)

(c) Studies on the adsorption of nitrogen on charcoal revealed that to adsorb 10^5 moles of nitrogen on the surface of charcoal, the pressure required is 10 kPa at 300 K and 200 kPa at 500 K.
Calculate the pressure required to adsorb 10^5 moles of nitrogen on the surface of charcoal at 400 K.
State any essential assumption(s) that you make.

(45 marks)

(d) What do you understand by "monolayer volume (V_m) in respect of the adsorption of a gas on a solid surface?
Indicate what additional information/data is required and how you would use such information/data to calculate the specific surface area of a solid adsorbent, starting from the monolayer volume.

(30 marks)