THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme - Level 5
Final Examination 2012/2013
CHU 3124 - Physical Chemistry
2 h

21-12-2013 **9.30 a.m - 11.30 a.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 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 hydrolysis reaction between ethyl acetate and sodium hydroxide is found to be first order with respect to each of the reactants and, the rate constant for this reaction is reported to be 0.25 $mol^{-1}\ dm^3\ s^{-1}$ at 300 K.

(i) Write down the chemical equation for the above hydrolysis reaction.

(ii) Write down the general rate equation (differential form) for this reaction, assuming that the initial concentrations of both the reactants are same and equal to "**b**" mol dm^{-3} and that the concentration of the ester reacted at any time, t, is "**x**" mol dm^{-3}.

(iii) Hence, derive the integrated form of the above expression.

(36 marks)

(b) Consider a **second order** reaction of the form A ------> P. Given the following information, calculate the time required for the initial concentration to be reduced to one third of its initial value.

Initial concentration = 0.1 mol dm^{-3}
Half – life = 2.5×10^3 s

(28 marks)

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

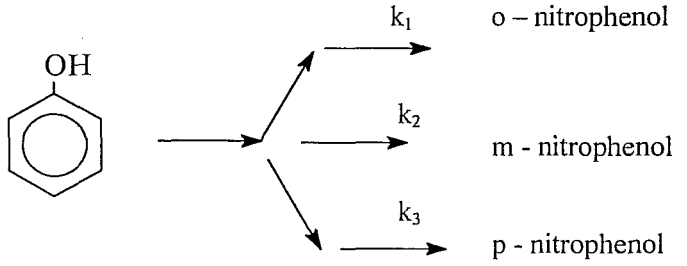
$$\mathbf{A} \xrightarrow{k_1} \mathbf{B} \xrightarrow{k_2} \mathbf{C}$$

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

Derive the integrated form of the rate equation, $[A] = [A_o]e^{-k_1 t}$ given that the initial concentration of A is $[A_o]$

(26 marks)

(c) Consider the following first order parallel reactions:



Write down the rate expression for the rate of disappearance of phenol in terms of the three rate constants.

(10 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.

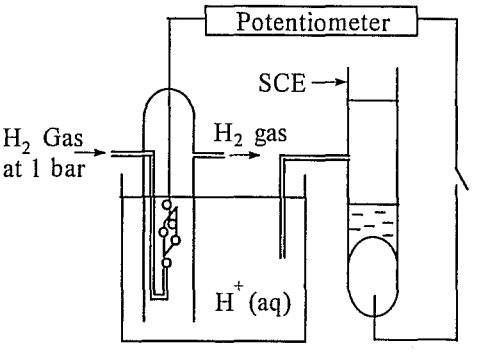
(i) $Cl^-(aq)$

(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 0.600 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) Define the following as applied to batteries.

(i) Capacity

(ii) Energy capacity

(iii) Cycle life

(21 marks)

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

$$Ni_2O_3(s) + H_2O(l) + 2e^- \rightarrow 2NiO(s) + 2OH^-(aq) \qquad E^0_{298} = 0.40\ V$$

$$FeO(s) + H_2O(l) + 2e^- \rightarrow Fe(s) + 2OH^-(aq) \qquad E^0_{298} = -0.87\ V$$

(i) Write down the cell reaction that occurs in the cell when a current is drawn.

(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.

(iii) What is the magnitude of the standard emf of the Edison cell at 298 K?

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

(iv) Calculate the maximum electrical work that can be obtained from an Edison cell per kilogram of Fe(s) at 298 K.

[Relative atomic mass of Fe = 56]

(79 marks)

Part C

4. (a) (i) Define surface tension and deduce its fundamental SI unit

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

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

This question refers to a glass capillary tube (internal radius = 1.0 mm) placed inside a certain liquid. The angle of contact of the liquid in the glass capillary is 120 °. The surface tension of this liquid is 6.0 mN cm^{-1} and its density is 3.0 g cm^{-3}. Calculate the depth to which the liquid level in the capillary tube will be depressed when placed in a pool of this liquid.
($g = 980\ cm\ s^{-2}$)

(30 marks)

(b) The Langmuir equation can be written in the form

$$bP = \frac{\theta}{(1-\theta)}$$

(i) Identifying clearly all the symbols used and derive the above equation, stating any assumptions made in the derivation.

(ii) Sketch the θ (y- axis) and P (x-axis) curve and explain its shape.

(iii) Write down the corresponding Langmuir equation for a di- atomic molecule which undergoes dissociation into two atoms on adsorption.

(45 marks)

c) The Langmuir adsorption (isotherm) may also be expressed in the following form, corresponding to adsorption from a solution

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

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

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

(25 marks)

5 (a) (i) What is meant by "adsorption"?

(ii) State a property that could be used to distinguish between physisorption and chemisorption

(18 marks)

(b) **Write down** (no proof required) the Gibbs Adsorption Isotherm equation relevant to a solution of bulk concentration Y having a surface tension β at a temperature X if its surface excess concentration is F (Gas constant = G)

(**NOTE**: Your answer should NOT include any symbol not given above)

(16 marks)

(c) (i) Define surface pressure (Π)

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

(iii) A certain amount 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 x 10^{-6} N cm^{-1}. This Langmuir Trough experiment was carried out at 300 K. Calculate the amount of protein used.

(30 marks)

(d) Nitrogen gas adsorption on charcoal takes place to the extent of 0.990 cm^3 g^{-1} of charcoal under a pressure of 10.0 atm and at a temperature of 175 °C. However at 275 °C, the same extent of adsorption was achieved only when the pressure was increased to 30 atm.

(i) Name the important assumptions made in using the equation $\ln \frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

(ii) Calculate the molar enthalpy of adsorption of nitrogen on charcoal.

(iii) Calculate the equilibrium pressure at which the same quantity of gas would be adsorbed at a temperature of 250 K

(36 marks)

6 (a) (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.

(28 marks)

(b) (i) Considering colloidal systems, explain the following terms

(α) the dispersed phase
(β) the dispersed medium
(λ) foams

(ii) Write down the **general** name given to each of the following colloidal systems. Identify the state of matter of the dispersed phase and the dispersion medium in each case.

(i) cloud.	(ii) soap lather	(iii) butter
(iv) pearls	(v) ruby glass	(vi) fog

(42 marks)

(c) (i) What is a "surfactant"?

(ii) Considering the action of Surfactants, explain the following terms:

(α) Critical Micelle Concentration (CMC)
(β) Micellar colloids

(30 marks)