THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme - Level 5
Final Examination 2010/2011
CHU 3124 - Physical Chemistry
(2.5 hours)

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12 -07- 2011 1.30 p.m - 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 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) In carrying out a kinetic experiment involving the hydrolysis of ethyl acetate with NaOH at 300 K (found to be first order with respect to each of the reactants), you have been asked to mix 5.00 cm^3 of the ester (density = 0.88 g cm^{-3} at 300 K) with a certain amount of distilled water (V_1) and 1.0 M NaOH (V_2) such that the total volume is 100.0 cm^3 and, that the concentration of NaOH is equal to that of the ester in the reaction mixture.

(i) Determine the initial concentration of ester in the reaction mixture.

(ii) Calculate V_1 and V_2.

(iii) With the aid of the expression $\frac{x}{b(b-x)} = kt$ (the symbols used have their usual meanings), the integrated form of the rate law for a second order reaction, determine the time taken for 75% of the ester to be hydrolysed under the above reaction conditions (Rate constant = 1.0 x 10^{-2} mol^{-1} dm^3 s^{-1} at 300 K).

(40 marks)

(b) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

The above **combination reaction between H_2 (g) and Br_2 (g) is said** to be a multi (five-) step reaction and the following reaction scheme (mechanism) has been proposed to explain the experimental observations in the kinetic studies of the above reaction.

$$Br_2 \xrightarrow{k_1} 2\,Br \quad ; \quad Br + H_2 \xrightarrow{k_2} HBr + H$$

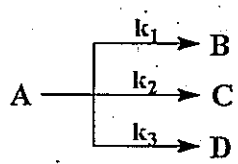
$$H + Br_2 \xrightarrow{k_3} HBr + Br \; ; \quad HBr + H \xrightarrow{k_4} Br + H_2 \quad ; \quad 2Br \xrightarrow{k_5} Br_2$$

Apply the steady state assumption to the two intermediates, Br and H, and, show that

$$[Br] = \sqrt{\frac{k_1[Br_2]}{k_5}}$$

(35 marks)

(c)



Consider the above parallel reaction scheme where the concentration of A reacted at time t is y and the corresponding concentration of B, C and D formed is y_1, y_2 and y_3 respectively. Assuming that these reactions follow first order kinetics and the initial concentration of A is 'b',

(i) write down the differential form of the rate equation in the usual form (the expression for $\frac{dy}{dt}$)

(ii) derive the overall rate expression (integrated form)

(25 marks)

Part B

2. (a) Define the following as applied in studying Galvanic cells.

(i) Electromotive force.

(ii) Capacity

(iii) Negative terminal

(iv) Electrode potential of an electrode

(16 marks)

(b) A student prepared two electrodes by dipping a rod of metal X in a solution of its ions, $X^{2+}(aq)$, a rod of metal Y in a solution of its ions, $Y^{3+}(aq)$ and bringing the electrical contact between the two solutions using a salt bridge. The temperature of the cell was maintained constant at $30^{\circ}C$. He found that the electric potential of the metal rod X is 2.867 V higher than the electric potential of the metal rod Y when there is no current through the cell.

(i) Write down a cell diagram for the above mentioned Galvanic cell.

(ii) Write down the anode, cathode and cell reactions for the cell diagram you have drawn above.

(iii) Assign an emf to the cell reaction you have written in part (ii) above under the experimental conditions the student prepared the cell.
Briefly explain your answer.

(30 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 copper ions in an aqueous solution of $0.01\ \text{mol dm}^{-3}$ copper sulphate solution at 25°C.
$[A = 0.509]$

(25 marks)

(d) At 30°C, the standard electrode potentials of half reactions $B^{4+}(aq) + 4e^{-} \rightarrow B(s)$ and $B^{4+}(aq) + e^{-} \rightarrow B^{3+}(aq)$ are $0.357\ \text{V}$ and $-0.506\ \text{V}$ respectively, where B is a metal.

(i) Write down the relationship between the Gibbs free energy and the electrode potential of a half reaction and identify all the parameters in it.

(ii) Calculate the standard electrode potential of electrode, $B(s)\left|B^{3+}(aq)\right.$ at 30°C.

(29 marks)

2. (a) A student was asked to estimate the solubility product of $PbSO_4$ at 25°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°C to be $-0.226\ \text{V}$. Estimate the solubility product of $PbSO_4$ at 25°C.
State any assumptions you make.

(50 marks)

(b) A battery is constructed by connecting two identical 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)**

Part C

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

(ii) Sketch the surface tension vs concentration of solute curves for the following types of solutes: capillary active, capillary inactive and surfactants.

(iii) Giving reasons, compare the shapes of the above curves.

(30 marks)

(b) This question refers to a glass capillary tube (internal radius = 0.5 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 5.0 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.

(20 marks)

(c) (i) Clearly identify all the symbols in the Kelvin equation given below.

$$\ln\left(\frac{P}{P^o}\right) = \frac{2M\gamma}{RT\rho r}$$

(ii) Consider a droplet of water of mass 10^{-16} kg. Calculate the ratio of its vapour pressure to that of the vapour pressure of water at 20 °C assuming that the surface tension of water at this temperature is 70.0 x 10^{-3} N m^{-1} and its density is 1.0 g cm^{-3}

(H = 1; O = 16)

(30 marks)

(d) The rate of adsorption of a certain gas (relative molar mass = 40) on 0.1 m^2 of a solid surface at 300 K and atmospheric pressure was found to be 8.5 x 10^{22} molecules cm^{-2} s^{-1} Calculate the sticking probability of this gas under the above conditions.

(20 marks)

5 (a) The Langmuir equation can be written in the form

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

(i) Identifying clearly all the symbols used, derive the above equation. State 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 tri atomic molecule which undergoes dissociation into three atoms on adsorption.

(45 marks)

(b) **Sketch** an (i) isotherm (ii) isobar (iii) isostere for the adsorption of a gas on solid surface (say, Ammonia on Charcoal) that are experimentally expected in adsorption studies. Briefly explain the shape of the curves you have drawn.

(30 marks)

(c) 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

(25 marks)

6. (a) A 0.02 M solution of octo decanoic acid (relative molar mass = 284) is prepared in benzene. On allowing a small amount of this solution to fall on a surface of water, the benzene evaporates, leaving a monomolecular (monolayer) film of acid. Calculate the volume of the acid that has to be used in order to cover an area of 400 cm^2 of the surface with a monolayer of the acid.[Assume that the area occupied by one molecule of the acid is 2.2 x 10^{-20} m^2]

(30 marks)

(b) Distinguish between

(i) dispersed phase and dispersion medium
(ii) Sol and Aerosol.
(iii) Lyophilic and Lyophobic Colloids

as applied to Colloidal Systems.

(30 marks)

(c) Write down the **general** name given to each of the following colloidal systems.

(i) fog (ii) smoke (iii) soap lather

In each case, identify the dispersed phase and the dispersion medium

(22 marks)

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

(i) Critical Micelle Concentration (CMC)
(ii) Micellar colloids

(18 marks)