THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme - Level 5
Final Examination 2015/2016
CHU 3124 - Physical Chemistry

(2 hours)

19th January 2016 **9.30 a.m - 11.30 a.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 x 10^{-23} J K^{-1}
Avogadro constant (L)	= 6.023 × 10^{23} mol^{-1}
Faraday constant (F)	= 96,500 C mol^{-1}
Plancks constant (h)	= 6.63 × 10^{-34} J s
Velocity of light (c)	= 3.0 × 10^{8} m s^{-1}
Atmospheric pressure (π)	= 1 bar = 10^5 Pa (N m^{-2})
Charge of a proton (e)	= 1.602 x 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) 1st order with respect to A and B
(II) zero order with respect to B but 2nd order with respect to A.

Derive the SI units of k, the rate constant in (I) above

(20 marks)

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

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

(30 marks)

(c) Consider the following reaction

$I^-(aq) \quad + \quad OCl^-(aq) \dashrightarrow Cl^-(aq) \quad + \quad OI^-(aq)$

Initial rate x 10^{-3} (mol dm^{-3} s^{-1})	Initial Concentration of I^- x 10^4 (in mol dm^{-3})	Initial Concentration of OCl^- x 10^4 (in mol dm^{-3})
1.92	8.25	3.85
3.84	16.50	3.85
5.76	8.25	11.60

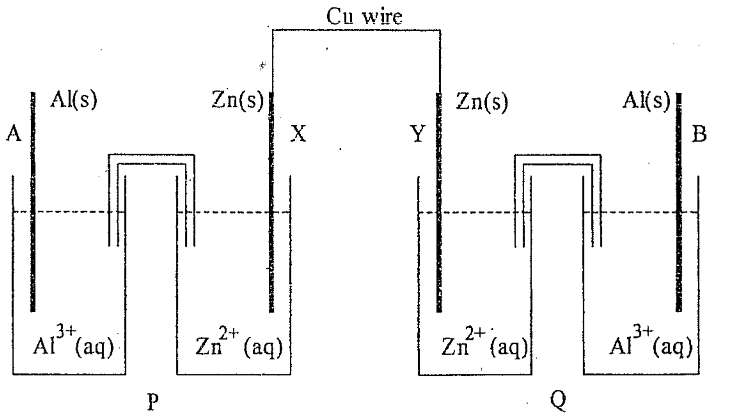
(all data are obtained at the same temperature)

(i) Determine the order of the reaction with respect to each of the reactants.
(ii) Hence, write down the general expression for the rate law for this reaction.
(iii) Determine the rate constant.

(50 marks)

Part B

2. (a) A student prepared a Galvanic cell, P, by placing an aluminium rod in an $Al^{3+}(aq)$ solution, a zinc rod in a $Zn^{2+}(aq)$ solution and bringing the electrical contact between the two solutions using a salt bridge. Using the same solutions and, aluminium and zinc rods, he prepared another Galvanic cell, Q, which is identical to P. He connected the two zinc rods of P and Q using a copper wire. The setup he prepared is sketched in the following figure.



(i) Using standard notation, draw a cell diagram for the electrochemical system shown in the above diagram.

(ii) What is the electric potential difference between the two aluminium rods (A and B) in the electrochemical system shown in the above diagram? Briefly explain your answer.

(30 marks)

(b) In a book of constants, a student noted that the standard electrode potential of a $Cu(s)|Cu^{2+}(aq)$ electrode at $25^{\circ}C$ is 0.340 V.

(i) Define the standard electrode potential of $Cu(s)|Cu^{2+}(aq)$ electrode.

(ii) Write down the half reaction (in standard form) of the above electrode.

(iii) Write down the Nernst equation for the electrode potential of the above electrode and identify all the parameters in it.

(iv) Calculate the electrode potential of the above electrode at $25^{\circ}C$ when the activity of $Cu^{2+}(aq)$ is 0.25

(35 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 sulphate ions in an aqueous solution of 0.02 mol dm^{-3} sodium sulphate at $25^{\circ}C$. $[A = 0.509]$

(35 marks)

3. (a) Define the following as applied to a battery.
   (i) Energy density
   (ii) Capacity
   (iii) Positive terminal

(21 marks)

(b) Ions of two compounds A and B react according to the following reaction.

$A^{3+}(aq) + B^{2-}(aq) \rightarrow A^{2+}(aq) + B^{-}(aq)$

The standard electrode potentials of the associated half reactions are as follows.

$A^{3+}(aq) + e^{-} \rightarrow A^{2+}(aq) \qquad E^{0}_{298} = 1.356 \text{ V}$

$B^{-}(aq) + e^{-} \rightarrow B^{2-}(aq) \qquad E^{0}_{298} = -0.870 \text{ V}$

A student performed a potentiometric titration using a solution of $A^{3+}(aq)$ as the titrand and a standard solution of $B^{2-}(aq)$ as the tritrant. A gold rod was used to construct the redox electrode and a saturated calomel electrode was used as the reference electrode.

(i) Draw the half-cell diagram for the redox electrode formed before the end point.

(ii) Draw the half-cell diagram for the redox electrode formed after the end point.

(iii) Sketch the variation of the electrode potential of the redox electrode, during the titration, versus the volume of titant added. Indicate the end point and the electrode potentials, of the two half reactions indicated above, on your sketch.

(30 marks)

(c) (i) State the major difference between a fuel cell and a primary or a secondary cell.

(ii) Ammonia could be oxidised in a fuel cell to generate electrical energy using the reaction, $4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(l)$ in an alkaline medium. For this reaction, $\Delta G = -1400.000 \text{ kJ mol}^{-1}$, under a certain set of experimental conditions. One hundred such fuel cells are connected in series in constructing a battery which is used to power a small carpentry workshop which draws a constant current of 10 A.

(α) Write down the spontaneous anode reaction and cathode reaction of the fuel cell.

(β) Deduce the charge number of the fuel cell reaction.

(γ) Calculate the emf of the battery.

(δ) Calculate the power delivered by the battery assuming that the potential difference across the battery remained at its emf when the current is drawn.

(λ) Calculate the rate of consumption of oxygen gas in the battery in mol s^{-1}.

(49 marks)

Part C

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

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

Clearly identify all the symbols on the right hand side of the above equation.

(10 marks)

(b) Write down the Gibbs Adsorption Isotherm indicating what the **principal** symbols contained in it refer to.

(14 marks)

(c) An amount of work **A** has to be done on a surface of an 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**.

Using 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.

(28 marks)

(d) What is the principal difference between a "surfactant" and a "capillary active substance" in terms of the variation of surface tension with increasing concentration of solutions containing these substances?

(18 marks)

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

(ii) 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.

(30 marks)

5 (a) Define, in relation to surface phenomena, the following

(i) sticking probability (s)

(ii) monolayer volume (V_m)

(16 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). Assuming that the molecular area of krypton is 15 x 10^{-20} m^2, calculate the specific surface area of activated carbon.

(30 marks)

(c) Calculate the rate of adsorption of oxygen gas molecules (assumed to behave ideally) at a temperature of 1000 K and a pressure of 10^5 Pa on a 100 m^2 surface given that the sticking probability = 0.1 (relative molecular mass of oxygen = 32)

(24 marks)

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

(30 marks)

6 (a) Derive the equation $\theta = \dfrac{bP}{(1+bP)}$ [applicable to gas/solid adsorption systems] that relates degree of surface coverage θ to pressure of gas P [where b is a constant]

State **FOUR** important assumptions based on which this equation has been derived.

(22 marks)

(b) Nitrogen gas adsorption on charcoal takes place to the extent of 0.990 cm^3 g^{-1} of charcoal under a pressure of 5.0 atm and at a temperature of 167 °C. However, at 327 °C, the same extent of adsorption was achieved only when the pressure was increased to 35 atm. With the aid of the equation given below, calculate the molar enthalpy of adsorption of nitrogen on charcoal.

$$\ln\frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

State clearly the assumptions you make.

(24 marks)

(c) Distinguish clearly between

(i) lyophilic colloids and lyophobic colloids

(ii) true solutions and colloidal solutions

(30 marks)

(d) What is the dispersed phase and the dispersing medium of the following dispersion systems? Give two examples in each case.

(i) liquid aerosol (ii) Emulsion (iii) Sol

(24 marks)