THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme - Level 5
Final Examination 2013/2014
CHU 3124 - Physical Chemistry
2 h

04-12 -2014 **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) $= 8.314\ \text{J K}^{-1}\,\text{mol}^{-1}$
Boltzmann Constant (k) $= 1.380 \times 10^{-23}\ \text{J K}^{-1}$
Avogadro constant (L) $= 6.023 \times 10^{23}\ \text{mol}^{-1}$
Faraday constant (F) $= 96{,}500\ \text{C mol}^{-1}$
Plancks constant (h) $= 6.63 \times 10^{-34}\ \text{J s}$
Velocity of light (c) $= 3.0 \times 10^{8}\ \text{m s}^{-1}$
Atmospheric pressure (π) $= 1\ \text{bar} = 10^{5}\ \text{Pa (N m}^{-2})$
Charge of a proton (e) $= 1.602 \times 10^{-19}\ \text{C}$
$\log_e(X) = 2.303 \log_{10}(X)$

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) zero order with respect to B but second order with respect to A.

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

(ii) In each of the cases (I) and (II), **write down** the SI units of k, the rate constant.

(16 marks)

(b) A reaction of the form **A ----> P** is said to be 25 % complete in 40 minutes.

If it follows first order kinetics,

(i) derive the relationship between time (t) and concentration of amount reacted (x) with the aid of the rate equation assuming that the initial concentration of A is ***b.***

(ii) calculate the rate constant and hence, calculate the concentration of A at the end of another 60 minutes given that the initial concentration of A is $2.0 \times 10^{4}\ \text{mol m}^{-3}$.

(36 marks)

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

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

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

(i) **Write down** the differential form of the rate expression for the formation of B

(ii) Given that the concentration of B at any time t is $[B] = \dfrac{k_1[A_o]}{(k_2 - k_1)}[e^{-k_1 t} - e^{-k_2 t}]$

show that maximum value for the concentration of B is reached when

$$t = \frac{1}{[k_1 - k_2]} \ln\left(\frac{k_1}{k_2}\right)$$

(30 marks)

(d) What do you understand by the following terms as used in chemical kinetics.

(i) "steady state assumption" as applied in the kinetic study of chain reactions

(ii) Illustrate the meaning of the term "pseudo first order reaction" with reference to the rate expression $-\dfrac{d[A]}{dt} = k_1[A][B]$

(ii) a catalyst

(18 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 $30^{o}C$. 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 V and -0.506 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, $B(s)|B^{3+}(aq)$ at 30°C.

(29 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 <u>electrode potential</u> 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, $\Delta G = -1400\text{ kJ mol}^{-1}$ 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) Define (i) surface pressure (ii) surface tension

(12 marks)

(b) (i) Define monolayer volume (V_m)

(ii) The monolayer volume(V_m) for the adsorption of gaseous krypton on 500 g carbon measured at 37 °C and 1 standard atmospheric pressure is 300 cm^3. A single krypton molecule has a molecular area of 22×10^{-20} m^2. Calculate the specific surface area of the carbon adsorbent.

(21 marks)

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

(ii) 0.40 mg of a protein when spread on 0.1 m^2 of the surface of a solution of HCl in a Langmuir trough at 300 K gave a surface pressure of 5.0×10^{-3} mN cm^{-1}. Assuming that the protein forms an ideal surface film, calculate the molar mass of the protein.

(20 marks)

(d) An amount of work, **W**, has to be done on a surface system at temperature **Y** to extend its area by an amount **A**. The molar concentration of this aqueous system is **C**. Gas constant = **G**; surface tension of pure water = **T**

Using the symbols given but **no other,** write down for the system an expression for

(i) the surface tension (ii) the surface pressure

(iii) the surface excess concentration using the Gibbs adsorption isotherm.

(15 marks)

(e) (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 particle of mist of mass 10^{-16} kg. Calculate the ratio of its vapour pressure to that of the vapour pressure of water at 27 °C. Assume that the surface tension of water at this temperature is 70.0×10^{-3} N m^{-1} and its density is 1.0 g cm^{-3} (H = 1; O = 16)

(32 marks)

5. (a) (i) Define “sticking probability” and **list** (do not describe) the **five** factors on which its value depends.

(ii) Identify, clearly, the symbols in the expression $u = \frac{P}{\sqrt{2\pi mkT}}$

(iii) 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)

(44 marks)

(c) 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 177 °C. However at 277 °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 $\mathrm{In}\frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

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

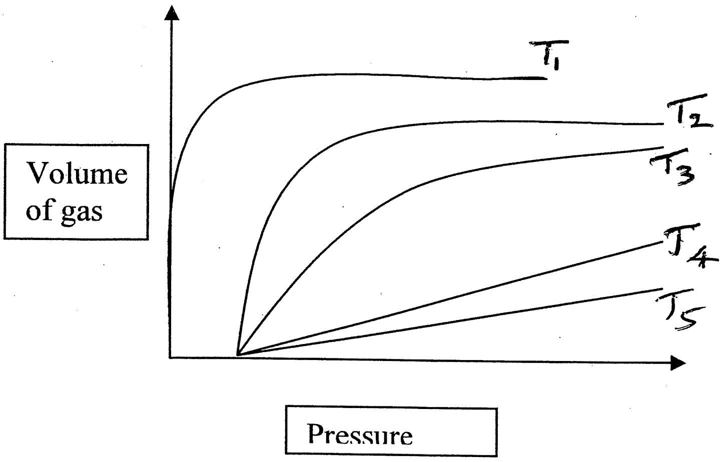
(36 marks)

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

$$\frac{x}{m} = \frac{\alpha C}{1+\beta C};\quad \text{Show that} \quad \lim_{C \to \infty}\left(\frac{x}{m}\right) = \frac{\alpha}{\beta}$$

(20 marks)

6 (a) Typical adsorption isotherms obtained for a certain system at various temperatures, T_1, T_2, T_3, T_4 ----- are given below.



(a) (i) Is the adsorption more likely to be chemisorption OR physical adsorption?

(ii) Is $T_1 > T_2 > T_3 > T_4 > T_5$?

(b) Briefly give adequate reasons in support of your answers to the questions in (a) above.

(26 marks)

(b) Distinguish clearly between
- (i) true solution and colloidal solution
- (ii) lyophilic colloids and lyophobic colloids

(24 marks)

(c) What do you understand by "**critical micelle concentration** "? Explain its significance in the action of surfactants.

(26 marks)

(d) **Write down** the general name given to each of the following colloidal systems and, in each case, identify the state of matter corresponding to the dispersed phase and the dispersion medium

(i) smoke (ii) cloud (iii) soap lather (iv) milk

(24 marks)