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THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme - Level 5
Final Examination 2009/2010
CHU 3124 - Physical Chemistry

(2.5 hours)

22-06- 2010 **9.30 p.m - 12.00 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)	= 1.602×10^{-19} C
ln (X)	= $2.303 \log_{10}$ (X)

Part A

1. (a) $$\text{cis} - Cr(en)_2(OH)_2^{+} \rightleftharpoons \text{trans} - Cr(en)_2(OH)_2^{+}$$
(A) (B)

The cis and trans forms of the complex $Cr(en)_2(OH)_2^{+}$ are said to exist in equilibrium as shown by the above reversible equation. The values for the rate constants, k_1 and k_2, (the respective rate constants in the forward and backward directions), reported at 25 °C, are $k_1 = 3.2 \times 10^{-4}\ s^{-1}$ and $k_2 = 2.0 \times 10^{-3}\ s^{-1}$
Given that this is first order in both directions, and commencing an experiment with the cis form (initial concentration is 0.05 mol dm^{-3})

(i) derive an expression for $\frac{k_1}{k_2}$ in terms of the **equilibrium concentrations** of **A** and **B**

(ii) determine the equilibrium concentration of the trans isomer.

(iii) calculate the time taken for half of the equilibrium amount of the trans isomer to be formed.

(40 marks)

(b) A reaction of the form **A ----> P** is said to be 25 % complete in 25 minutes. If it follows first order kinetics, what would be the concentration of A at the end of another 50 minutes given that the initial concentration of A is 2.0 mol dm^{-3}.

(20 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 $k_1 \neq k_2 \neq 0$)

(i) Write down the rate expression (differential form) for the disappearance of A and the corresponding integrated form given that the initial concentration of A is $[A_0]$

(ii) The concentration of B at any time, t, can be expressed as

$$[B] = \frac{k_1[A_0]}{(k_2 - k_1)}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

Derive an expression for t_{max}, the time taken for the concentration of B to reach its maximum.

(iii) Sketch the curve showing the variation of the concentrations of A, B and C with time in the case where k_1 is approximately equal to k_2 and highlight the maxima you obtained in (iii) above.

(40 marks)

Part B

2. (a) A particular metal, A, forms divalent ions in ethyl alcohol, $A^{2+}(\text{ethyl alcohol})$. A student dipped a wire of A into a dilute solution of $A^{2+}(\text{ethyl alcohol})$. He observed the creation of a constant potential difference across the metal/solution interface. Giving necessary chemical reactions, briefly describe how this constant interfacial potential difference is created.

(20 marks)

(b) (i) Define the term "electrode potential of an electrode".

(ii) A student prepared a $Pb(s)|PbSO_4|SO_4^{2-}(aq)$ electrode. He found out the electric potential of this electrode to be -3.415 V at 25^0C.. He also found out the electric potential of the standard hydrogen electrode at the same temperature to be -3.100 V. Deduce the electrode potential of the $Pb(s)|PbSO_4|SO_4^{2-}(aq)$ electrode prepared by the student at 25^0C.

(15 marks)

(c) (i) Write down a relationship between the ionic strength of a solution and concentration of its constituent ions and identify all the parameters in it.

(ii) Calculate the ionic strength of an aqueous solution of $AlCl_3$ and NaCl where $[AlCl_3] = 0.01 \text{ mol dm}^{-3}$ and $[NaCl] = 0.05 \text{ mol dm}^{-3}$.

(15 marks)

(d) A student was given two aqueous solutions of $CuSO_4$, A and B at 25^0C. The concentration of $CuSO_4$ in A was $0.100 \text{ mol dm}^{-3}$. He was requested to estimate the concentration of $CuSO_4$ using potentiometry. He prepared an electrochemical cell by placing samples of A and B in two beakers, inserting two copper wires in them and electrically connecting the solutions in the two beakers using a salt bridge. Then he measured the emf of this cell, at 25^0C, using a potentiometer and found it to be 0.059 V. The electrode with solution A was found to be positive terminal of the cell.

(i) Write down a cell diagram for the electrochemical cell prepared by the student.

(ii) Write down the anode reaction, cathode reaction and the cell reaction assigned to the cell diagram you have drawn.

(iii) Giving reasons assign an emf to the cell reaction written above.

(iv) What is the charge number of the cell reaction written above?

(v) Write down the Nernst equation for the cell reaction written above and identify all the parameters in it.

(vi) What is the standard emf assigned to the cell diagram you have drawn?

(vii) Calculate the concentration of copper sulphate in solution B assuming activity coefficients of copper ions in both A and B to be unity.

(50 marks)

3. (a) Define the following as applied in electrochemistry.

(i) Electromotive force

(ii) Positive terminal of a Galvanic cell

(iii)Capacity of a battery

(15 marks)

(b) The reaction $A^{2+}(aq) + B^{3+}(aq) \rightarrow A^{3+}(aq) + B^{2+}(aq)$ could be used to determine the concentration of $A^{2+}(aq)$, titrimetrically, using a standard solution of $B^{3+}(aq)$. A student performed a potentiometric titration using a solution of $A^{2+}(aq)$ as the titrand and solution of $B^{3+}(aq)$ as the titrant. A platinum wire dipped in the titrand was used as the redox electrode. The standard electrode potential of the possible redox couples, at the temperature the experiment was performed, are given by $E^0_{A^{2+}|A^{3+}} = 0.230\ V$ and $E^0_{B^{2+}|B^{3+}} = 1.340\ V$. Sketch the graph of the electrode potential of the redox electrode formed at the platinum wire as a function of the volume of titant added. Clearly indicate 0.230 V and 1.340 V on the electrode potential axis and the end point on the x-axis.

(15 marks)

(c) The reaction $4\,NH_3(g) + 3\,O_2(g) \rightarrow 2\,N_2(g) + 6\,H_2O(l)$ is used in the ammonia fuel cell. The ionic medium of the fuel cell is alkaline. A battery where 100 such fuel cells, connected in series, is used in powering a motor vehicle. A current of 110.00 A was drawn from the battery when the vehicle was run at a constant speed of $40\ \text{km hour}^{-1}$. Under the operating conditions in the motor vehicle, $\Delta G = -1400.000\ \text{kJ mol}^{-1}$ for this reaction and the density of water formed is $1000.000\ \text{g dm}^{-3}$. The relative molar mass of H_2O is 18.000.

(i) Write down the spontaneous anode and cathode reactions in the fuel cell.

(ii) What is the charge number of the spontaneous cell reaction given above?

(iii) Calculate the emf of the battery under the operating conditions.

(iv) Calculate the power generated by the battery when the vehicle is run at $40\ \text{km hour}^{-1}$ assuming the voltage of the fuel cell to be equal to its emf.

(v) Calculate the rate of consumption of ammonia in the battery when the vehicle is run at $40\ \text{km hour}^{-1}$ in mol s^{-1}.

(vi) Calculate the total volume of water formed in the battery when the vehicle is run at a constant speed of $40\ \text{km hour}^{-1}$ for an hour.

(70 marks)

Part C

4. (a) Indicate **briefly** what you understand by

(i) angle of contact

(ii) surface pressure

(iii) **mobile** adsorption

(15 marks)

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

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

(15 marks)

(c) Indicating **briefly** the reasons for your choice, write down the names of **five** of the substances listed below whose molecular area can be determined using the **Langmuir** Trough Method

lauryl alcohol	$CH_3(CH_2)_{11}OH$
propionic acid	C_2H_5 COOH
cetyl alcohol	$CH_3(CH_2)_{15}OH$
iso - butanol	C_4H_9OH
N - hexanol	$C_6H_{13}OH$
palmitic acid	$CH_3(CH_2)_{14}COOH$
octo decanoic acid	$CH_3(CH_2)_{16}COOH$
ethyl palmitate	$CH_3(CH_2)_{14}COO\ C_2H_5$
acetic acid	CH_3COOH
N – pentanoic acid	C_4H_9 COOH
octanoic acid	$C_7H_{15}COOH$

(15 marks)

(d) (i) What is the **most principal** deduction that can be made from the Kelvin equation

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

(ii) **Deduce** from the Kelvin equation whether the vapour pressure outside a spherical droplet will always be greater than, equal to or less than the vapour pressure outside a planar surface.

(20 marks)

(e) (i) 25.0 cm^3 of olive oil formed an unimolecular film in an area of 8000 m^2. Assuming that olive oil (density = 0.8 g cm^{-3} at 25 °C) consists of an ester with a relative molecular mass of 1000, calculate

(α) the thickness of the film

(β) the area occupied by each olive oil molecule.

(ii) **List** THREE principal uses of unimolecular films

(35 marks)

5. (a) (i) Define "sticking probability" of a gas on a solid surface.

(ii) **List** FIVE factors on which the value of the sticking probability depends upon.

(20 marks)

(b) Indicate how a set of adsorption isosteres can be constructed from a set of adsorption isotherms that have been obtained experimentally.

(15 marks)

(c) **Sketch** the five different types of adsorption isotherms that are experimentally observed in adsorption studies(description not required).

(15 marks)

(d) How can the temperature range for adsorption be used as a criterion to distinguish chemisorption from physical adsorption?

(15 marks)

(e) The following data represents the conditions required to maintain adsorption of 20.5 cm^3 of nitrogen at STP on 25.0 g of a solid adsorbent.

T °C	33	21	13	-1.5
P/torr	3.00	1.60	1.00	0.50

Making use of a graphical plot, calculate the isosteric enthalpy of adsorption for this system.
Indicate the principal assumptions that have to be made to enable your calculation.

(35 marks)

6. (a) What is the principal characteristic feature of a colloidal solution that identifies it from a true solution and a suspension?

(15 marks)

(b) Write down the **general** name given to each of the following colloidal systems.
(i) cloud. (ii) soap lather (iii) butter
(iv) pearls (v) ruby glass

In each case, indicate the state of matter that corresponds to the dispersed phase

(20 marks)

(c) Compare the principal factors that determine the stabilities of lyophilic and lyophobic colloids.

(15 marks)

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

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

(i) Identify the terms in this equation.

(ii) Transform the above equation into a linear form which will enable the value of b to be obtained.

(20 marks)

(e) The monolayer volume(V_m) for the adsorption of argon gas on 0.264 g of a silica sample at 225 K is found to be 56 cm^3(reduced to STP). Given that the molecular area of argon is 16.0 x 10^{-20} m^2, calculate the specific surface area of the silica sample.

(30 marks)