NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY
SUPPLEMENTARY EXAMINATIONS - JULY 2001
PHYSICAL CHEMISTRY II - SCH 2204
TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

Answer **ALL** questions from Section A and **ANY THREE** from Section B.

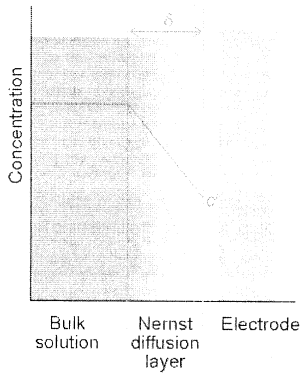
Gas Constant $R = 8.314\ J\ K^{-1}\ mol^{-1}$ $0^{o}\ C = 273.15\ K$
Faraday's Constant $F = 9.6485 \times 10^{4}\ C\ mol^{-1}$ Avogadro's Number $N_A = 6.022 \times 10^{23}\ mol^{-1}$

SECTION A

1. With the aid of the diagram below, explain the terms and derive expressions for

(a) concentration overpotential, (6 marks)

(b) limiting current. (6 marks)



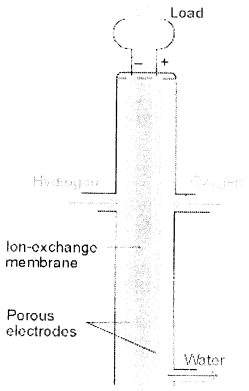
odd no's

At 298 K, the limiting molar conductances of $AgNO_3$, KNO_3 and KCl are 133.4, 145.0 and 149.9 S cm^2 mol^{-1} respectively. What is the limiting molar conductance of AgCl at this temperature? (4 marks)

3. (a) What is the ionic strength and mean activity coefficient of a 0.01 M solution of $LaCl_3$? (Debye-Hückel A = 0.509) (10 marks)

(b) What is the activity of Cl^- in this solution? (3 marks)

4. The diagram below represents a hydrogen/oxygen fuel cell.



(a) What are the electrode reactions and the overall cell reaction? (3 marks)

(b) Give two advantages of the fuel cell over a conventional galvanic cell. (2 marks)

(c) What is the purpose of the porous electrodes? Of the ion-exchange membrane? (2 marks)

(d) What would be the effect on the cell operation of using pure oxygen rather than air? (3 marks)

even no's

A solution of A is mixed with a solution of B containing the same number of moles, and the reaction A + B → C occurs. At the end of one hour, 50% of A has reacted. How much A will remain unreacted after 2 h if the reaction is:

(a) First order in A and zeroth order in B (3 marks)

(b) Zeroth order in both A and B (3 marks)

(c) First order in both A and B. (4 marks)

6. Define the symbols used in the BET isotherm

$$\frac{P}{V_a}\cdot\frac{P^0}{P^0-P}=\frac{1}{V_a^0 K}+\frac{P}{V_a^0}$$

and show that it reduces to the Langmuir isotherm when $p^0 >> p$. (6 marks)

SECTION B

7. Consider the cell $Pt\,|\,H_2(g)\,|\,HCl\ (aq)\,|\,AgCl(s)\,|\,Ag$

(a) What is the cell reaction? (2 marks)

(b) What is the Nernst equation for the cell? (2 marks)

(c) At 298 K, when the hydrogen gas is at standard pressure, and the HCl solution is 0.010 M, the emf is +0.4658 V. Calculate ΔG for the reaction under these conditions. (4 marks)

(d) Use your answers from (b) and (c), and assuming the Debye-Huckel limiting law, calculate E^0 for the $Ag(s)\,|\,AgCl\ (s)\,|\,Cl^-(aq)$ electrode. (Debye-Hückel A = 0.509) (7 marks)

8. The following are the molar conductivities of chloroacetic acid in aqueous solution at 298 K.

Concentration (10^{-4} M)	625	39.1	9.0
Λ(S cm^{-2} mol^{-1})	53.1	164	249

(a) If Λ_o = 362 S cm^{-2} mol^{-1}, find a value, ignoring activity coefficients, of the dissociation constant for chloroacetic acid based on each set of measurements. (12 marks)

(b) Which of the above results is likely to be closest to the true dissociation constant? Explain. (3 marks)

9. The emf of the cell

$$Pb(s) \mid PbSO_4(s) \mid Na_2SO_4.10H_2O\ (sat) \mid HgSO_4(s) \mid Hg(l)$$

is 0.9647 V at 298 K, and the temperature coefficient $\partial E^0/\partial T = 1.74 \times 10^{-4}$ V K^{-1}. What is the cell reaction, and what are the values of ΔG^0, ΔH^0 and ΔS^0, and the equilibrium constant K? (15 marks)

10. A certain gas phase reaction A → Products takes place in a reaction vessel of constatant volume and temperature. Initially the vessel contains pure A at 1 atm pressure. The total pressure in the vessel was found to vary with time in the following manner:

t (min)	0	2	4	6	8
p (atm)	1.00	0.67	0.60	0.57	0.55

(a) Show graphically that the reaction is a dimerisation of A (i.e $2A \rightarrow A_2$) (5 marks)

(b) Show that the reaction is second order in A. (5 marks)

(c) Calculate the half-life of the reaction. (5 marks)

11. The interconversion of ortho- and para-H_2 at temperatures around 750 °C involves the following elemental steps:

(1) $H_2 \rightarrow 2\ H$

(2) $H + o\text{-}H_2 \rightarrow p\text{-}H_2 + H$

(3) $H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$

(4) $2\ H \rightarrow H_2$

In the case where **initially pure p-H_2** reacts to form an equilibrium mixture of o-H_2 and p-H_2:

(a) State the overall reaction and classify each of the species as reactant, product or intermediate. (4 marks)

(b) Classify each of the elemental steps as initiation, propagation, etc. (4 marks)

(c) By applying the Steady State Approximation, show that the overall reaction is $\frac{3}{2}$ order. (7 marks)

END OF QUESTION PAPER!!!!

even no's