NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATIONS - APRIL/MAY 1999
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} = 0.0821 L atm K^{-1} mol^{-1}
Avogadro's Number = 6.022×10^{23} mol^{-1}
Charge on the electron e = 1.602×10^{-19} C
Faraday's constant F = 9.648×10^{4} C
1 atm = 1.013×10^{5} Pa 0^0 C = 273.15 K

SECTION A

1. At 298 K, the limiting molar conductances of KCl, KNO_3 and $AgNO_3$ are 149.9 S cm^2 mol^{-1}, 145.0 S cm^2 mol^{-1}, , and 133.4 S cm^2 mol^{-1} respectively. What is the limiting molar conductance of AgCl at this temperature? (5 marks)

2. When a hydrogen electrode and a calomel electrode (electrode potential 0.2415 V), are immersed in a certain solution at 298 K, a potential of 0.664 V is obtained. What is the pH of the solution? (6 marks)

3. The limiting current density for the reaction

$$I_3^- + 2\,e^- \rightarrow 3\,I^-$$

at a platinum electrode is 28.9 μA cm^{-3} when the concentration of KI is 6.6×10^{-4} M and the temperature 298 K. The diffusion coefficient of I_3^- is 1.14×10^{-5} cm s^{-1} . What is the thickness of the Nernst diffusion layer? (6 marks)

4. Calculate the thermodynamic limit at 298 K to the e.m.f. of a fuel cell operating on methane and air (partial pressure of O_2 = 0.2 atm), from the following data:-

ΔG^0_{298} (formation, CH_4) = -50.72 kJ mol^{-1}

(8 marks)

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5. A first-order reaction

$$A \rightarrow \text{Products}$$

was studied. Some time after the reaction began the first measurement was made and the clock started. The following measurements of the extent of reaction were then made:-

t/min	0	5	10
Percentage A reacted	19.8	34.2	46.7

(a) Calculate the rate constant. (6 marks)

(b) Estimate the time that elapsed between the start of the reaction and t = 0. (6 marks)

6. Explain what experiments you would conduct, and how you would analyse them, in order to determine the rate law for a reaction

$$A + B \rightarrow \text{Products}$$

using the Ostwald isolation and integrated rate law methods together. (12 marks)

7. At -195^0 C a certain catalyst absorbs 10 cm^3 of nitrogen gas (calculated at STP), per gram, in order to form a monolayer. If the effective area of a single nitrogen molecule is 1.62×10^{-19} m^3 at this temperature, calculate the surface area of the catalyst. (6 marks)

SECTION B

8. (a) Calculate the activity of 0.10 M HBr at 298 K, given that the formula

$$\log \gamma_{\pm} = -0.509 \, |z_+ z_-| \, I^{1/2}$$

applies. (5 marks)

(b) If the e.m.f. of the cell

$$\text{Pt} \mid H_2 \text{ (1 atm)} \mid \text{HBr (0.10 M)} \mid \text{AgBr(s)} \mid \text{Ag}$$

is 0.2005 V at 298 K, use the Nernst equation and your answer from (a) to calculate the corresponding standard e.m.f. (10 marks)

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9. The electromotive force of the cell

$$Pb(s) \mid PbSO_4(s) \mid Na_2SO_4 .10H_2O\ (sat) \mid Hg_2SO_4(s) \mid Hg(l)$$

is 0.9647 V at 298 K. The temperature coefficient is 1.74×10^{-4} V K^{-1} .

(a) What is the cell reaction? (3 marks)

(b) For the cell reaction, what are the values of ΔG^0, ΔH^0, ΔS^0, and the equilibrium constant K? (12 marks)

10. The formation of phosgene, $COCl_2$, by the reaction

$$CO + Cl_2 \rightarrow COCl_2$$

appears to follow the mechanism:-

$$Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\,Cl$$

$$Cl + CO \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} COCl$$

$$COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$$

Assuming the intermediates Cl and COCl are in a steady state, what is the rate law for this reaction. (15 marks)

11. Suppose a substance X decomposes according to first order kinetics into A or B by parallel paths. The Arrhenius parameters for the two reactions are:-

	Pre-exponential Factor A	Activation Energy (kJ mol^{-1})
k_A	10^{15}	126
k_B	10^{13}	84

(a) Explain which reaction will be dominant at high temperatures, and which at low temperatures. (5 marks)

(b) Calculate the temperature at which both products will be formed at the same rate. (10 marks)

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12. (a) Give an expression for the Langmuir adsorption isotherm, and explain the assumptions made in its derivation. (3 marks)

(b) The following table gives the volume of nitrogen (reduced to 1 atmosphere at 0^0 C), adsorbed per gram of active carbon at 0^0 C and a series of pressures:-

P/Pa	524	1731	3058	4534	7497
$v/cm^3\ g^{-1}$	0.987	3.04	5.08	7.04	10.31

Plot the data according to the Langmuir isotherm, and determine the constants.
(12 marks)

END OF QUESTION PAPER!!!!