

NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

**DEPARTMENT OF APPLIED CHEMISTRY**  
**END OF SEMESTER EXAMINATIONS - MAY 2002**  
**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  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$        $0^\circ \text{C} = 273.15 \text{ K}$   
Faraday's Constant  $F = 9.6485 \times 10^4 \text{ C mol}^{-1}$       Avogadro's Number  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$   
Debye-Hückel  $A = 0.509$  in water at  $25^\circ \text{C}$

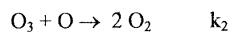
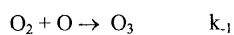
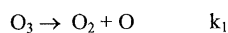
**SECTION A**

1. (a) What is the zero-current potential of a fuel cell which uses hydrogen and oxygen?  
[For  $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$      $\Delta G^0 = -237.13 \text{ kJ mol}^{-1}$ ] (4 marks)
- (b) Estimate the effect on the zero current potential in (a) when air is used instead of pure oxygen. (4 marks)
2. The  $\text{Sb} \mid \text{Sb}_2\text{O}_3 (\text{s}) \mid \text{OH}^- (\text{aq})$  electrode is reversible with respect to  $\text{OH}^-$  ions. Derive an expression for its potential in terms of the
- (a) pOH (4 marks)
- (b) pH of the solution. [ $\text{pK}_w = 14$ ] (2 marks)
3. The transfer coefficient  $\alpha$  of a certain electrode in contact with  $\text{M}^{3+}$  and  $\text{M}^{4+}$  ions in aqueous solution at  $25^\circ \text{C}$  is 0.39. The current density is found to be  $55.0 \text{ mA cm}^{-2}$  when the overvoltage is  $125 \text{ mV}$ .
- (a) Estimate the exchange current density. (5 marks)
- (b) What is the overvoltage required for a current density of  $75 \text{ mA cm}^{-2}$ ?  
[Hint: Which term in the Butler-Volmer equation is negligible at high overvoltages?] (6 marks)
4. The reaction
- $$2 \text{A} \rightarrow \text{P}$$
- has a second order rate law with  $k = 3.50 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ . Calculate the time required for the concentration of A to change from  $0.077 \text{ mol L}^{-1}$  to  $0.021 \text{ mol L}^{-1}$ . (6 marks)

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5. The rate constant for the decomposition of a certain substance is  $2.80 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $30^\circ\text{C}$  and  $1.38 \times 10^{-2}$  at  $50^\circ\text{C}$ . What is the activation energy for the reaction? (4 marks)

6. The following mechanism has been proposed for the conversion of ozone into  $\text{O}_2$ .



Derive the corresponding rate law. (10 marks)

7. A surface is half-covered by a gas when the pressure is 1 atm. The simple Langmuir isotherm applies.

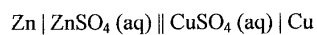
(a) What is  $K$  (in  $\text{atm}^{-1}$ )? (4 marks)

(b) What pressure will give 99% coverage? (3 marks)

(c) What coverage is given by a pressure of 0.1 atm? (3 marks)

### **SECTION B**

8. For the reaction in the Daniell cell



$\Delta G^\circ$  is  $-212.7 \text{ kJ mol}^{-1}$ . When the concentrations of the electrolytes are  $\text{CuSO}_4$  0.001 M and  $\text{ZnSO}_4$  0.003 M, calculate

(a) the ionic strengths of the solutions (4 marks)

(b) the mean activity coefficient in each compartment (3 marks)

(c) the reaction quotient (2 marks)

(d) the standard cell potential (3 marks)

(e) the actual cell potential (3 marks)

9. The resistances of a series of aqueous NaCl solutions, formed by successive dilution, were measured in a cell with cell constant  $0.2063 \text{ cm}^{-1}$ . The following values were found:

c (M)	0.00050	0.0010	0.0050	0.010	0.020
R (ohm)	3314	1669	342.1	174.1	89.08

Verify by means of a graph that the molar conductivity follows Kohlrausch's law, and determine the limiting molar conductance and the value of  $\kappa$ . (10 marks)

Given that  $\lambda^0(\text{Na}^+)$  is  $5.01 \text{ mS m}^2 \text{ mol}^{-1}$ , calculate the transport numbers of the two ions in NaCl solution at infinite dilution. (5 marks)

10. (a) After correction for the water conductance, the conductance of a saturated aqueous solution of AgCl at  $25^\circ\text{C}$  was found to be  $0.1887 \text{ mS m}^{-1}$ . What are the activities of the two ions in this solution? [ $\lambda^0(\text{Ag}^+)$  is  $6.18$ ;  $\lambda^0(\text{Cl}^-)$  =  $7.635 \text{ mS m}^2 \text{ mol}^{-1}$ ] (6 marks)

(b) Show that the solubility, S, of a sparingly soluble 1:1 salt is related to its solubility constant by

$$S = K_s^{1/2} e^{-1.172/S}$$

(5 marks)

(c) What is the solubility of AgCl at this temperature? (4 marks)

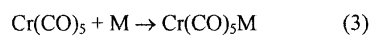
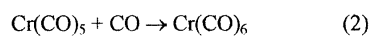
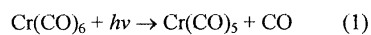
11. (a) Explain why the integrated rate law method is a convenient way to analyse kinetic data for the order of reaction. Derive the appropriate relationships for first and second order kinetics. (6 marks)

(b) The decomposition of a substance A gave the following data:

t (s)	0	2000	4000	6000	8000	10000	12000
[A] ( $\text{mol L}^{-1}$ )	1.10	0.86	0.67	0.52	0.41	0.32	0.25

Determine the order of reaction and the rate constant. (9 marks)

12. Photolysis of  $\text{Cr}(\text{CO})_6$  in the presence of certain molecules M, can give rise to the following reaction sequence:



Suppose that the light intensity is so weak that  $I \ll k_4 [\text{Cr}(\text{CO})_5\text{M}]$ .

(a) Find the factor  $f$  in the equation  $d[\text{Cr}(\text{CO})_5\text{M}]/dt = -fk_4 [\text{Cr}(\text{CO})_5\text{M}]$ . (9 marks)

(b) Show that a graph of  $1/f$  against  $[\text{M}]$  should be a straight line. (6 marks)

**END OF QUESTION PAPER!!!!**