

NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATIONS - MAY 2003
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 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday's Constant $F = 9.6485 \times 10^4 \text{ C mol}^{-1}$ Avogadro's Number $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
1 atm = 760 torr $0^\circ \text{C} = 273.15 \text{ K}$

SECTION A

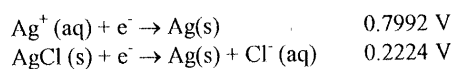
1. (a) The mean activity coefficient of 0.1 M HCl (aq) at 25°C is 0.796. What is the activity of HCl in this solution? (3 marks)
- (b) The mean activity coefficient of 0.1 M H₂SO₄ (aq) is 0.265. What is the activity of H₂SO₄ in this solution? (4 marks)
2. A solution of NaCl has an ionic strength of 0.24 mol kg⁻¹. LIBRARY USE ONLY
- (a) What is its molality? (3 marks)
- (b) What molality of MgSO₄ would have the same ionic strength? (5 marks)
3. The following table gives the emf at 25°C for the cell Pt | H₂ (1 bar) | HBr (m) | AgBr | Ag.
- | | | | | |
|------------|--------|--------|--------|--------|
| Molarity m | 0.01 | 0.02 | 0.05 | 0.10 |
| E (V) | 0.3127 | 0.2786 | 0.2340 | 0.2005 |
- (a) Determine E° by means of a suitable plot. (6 marks)
- (b) Calculate the mean activity coefficient for a 0.10 m solution of HBr. (6 marks)
4. Given that the standard electrode potential for Pt | H₂(g) | OH⁻ is -0.8279 V, devise a cell in which the cell reaction is
- $$\text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_3\text{O}^+ (\text{aq}) + \text{OH}^- (\text{aq}).$$
- Calculate its emf, and hence the ionic product for water at 298 K. (10 marks)

5. The gas-phase decomposition of HI to H₂ + I₂ at 781 K has a half-life of 135 min when the initial pressure of HI is 0.1 atm, and 13.5 min when the pressure is 1 atm.
- (a) Show that this proves the reaction is second order. (5 marks)
- (b) Assuming an ideal gas, what is the value of the rate constant in L mol⁻¹ s⁻¹? (6 marks)
6. If a first-order reaction has an activation energy of 104.6 kJ mol⁻¹ and a pre-exponential factor of 5 × 10¹³ s⁻¹, at what temperature will it have a half-life of 1 min? (7 marks)

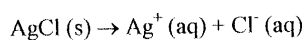
SECTION B

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7. (a) Given the following standard reduction potentials:



give the schematic diagram for a cell for which the cell reaction is:



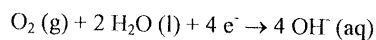
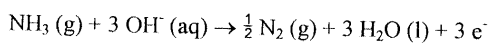
Determine its emf, and hence the solubility product of AgCl. (7 marks)

- (b) Given the following standard entropies, determine the temperature coefficient of the emf of the cell in (a).

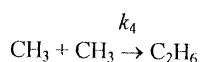
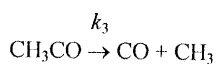
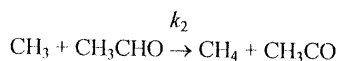
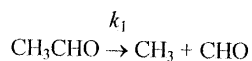
| | | | |
|---|----------|----------------------|----------------------|
| | AgCl (s) | Ag ⁺ (aq) | Cl ⁻ (aq) |
| S ⁰ (J K ⁻¹ mol ⁻¹) | 96.2 | 72.7 | 56.5 |

Does the solubility of AgCl increase with temperature? (8 marks)

8. In a fuel cell using ammonia as the anodic reactant, the electrode processes are:



- (a) State the overall cell reaction and the corresponding value of n , the number of electrons transferred. (3 marks)
- (b) Calculate the emf of this fuel cell at 298 K, when the gases are in their standard states, given that at temperature, the ΔG^\ominus (formation) is $-16.45 \text{ kJ mol}^{-1}$ for NH_3 , and $-237.13 \text{ kJ mol}^{-1}$ for H_2O . (9 marks)
- (c) Write an expression for the emf of this cell which takes into account variations in the pressures of the gases involved in the reaction. (3 marks)
9. The pyrolysis of acetaldehyde CH_3CHO at 793 K and 0.2 atm proceeds by a free-radical chain mechanism, which is, in a simplified form which ignores the relatively unimportant subsequent reactions of CHO , as follows:



- (a) Classify each elementary step shown as initiation, propagation, etc., identify the intermediates to which the Steady State Approximation may be applied, and state the overall reaction. (7 marks)
- (b) Apply the Steady State Approximation, and derive the rate law. (8 marks)
10. The hydroxyacid $\text{HO}(\text{CH}_2)_5\text{COOH}$, molar mass 132 g mol^{-1} , is polymerised, and it is found that the product has a number-average molar mass of $20\,000 \text{ g mol}^{-1}$.
- (a) What is the extent of reaction, p ? (6 marks)
- (b) What is the degree of polymerisation? (3 marks)
- (c) What is the mass-average molar mass? (6 marks)

11. (a) Describe the essential difference in the models used to derive the Langmuir and Brunauer-Emmett-Teller (BET) adsorption isotherms. Which of these would be more likely to apply to the adsorption of nitrogen gas on ZnO(s) at 77 K (the boiling point of nitrogen), and gas pressures approaching atmospheric? Explain. (5 marks)

(b) The following data apply to the system described in (a). The volumes v are corrected to STP. Plot it according to the relevant adsorption isotherm, find the volume of the monolayer, and the value of the other constant.

| | | | | | | | | | |
|---------------------------|-------|-------|-------|------|------|------|------|------|------|
| P/torr | 56 | 95 | 145 | 183 | 223 | 287 | 442 | 533 | 609 |
| $v(\text{cm}^3/\text{g})$ | 0.798 | 0.871 | 0.978 | 1.06 | 1.16 | 1.33 | 1.71 | 2.08 | 2.48 |

(10 marks)

END OF QUESTION PAPER!!!!

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