

University of Canterbury

Mid Year Examination and Test Period 2009

Prescription Number(s):	CHEM 233
Paper Title:	Introduction to Physical Chemistry

Time Allowed: TWO HOURS

Number of pages: EIGHT

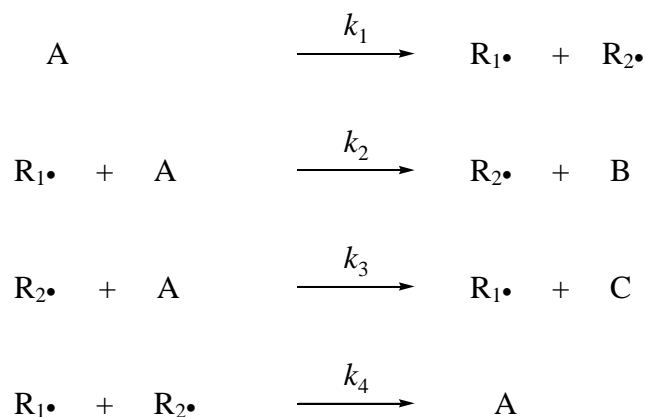
This paper is divided into **TWO** sections. Each section is worth 60 marks.

Answer **ALL** questions

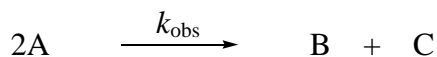
SECTION A

(Worth 60 marks; Answer both questions in this section.)

1. (a) Outline the assumptions made in using the steady-state method for the analysis of the kinetics of a complex reaction mechanism.
- (b) The mechanism for the decomposition of an organic compound, A, at elevated temperatures is described by:



The observed overall reaction stoichiometry is given by:



- (i) Write steady-state expressions for each of the two radical species involved: ($\text{R}_1\cdot$ and $\text{R}_2\cdot$).
- (ii) Find expressions for each of the steady-state radical concentrations, $[\text{R}_1\cdot]$ and $[\text{R}_2\cdot]$, in terms of $[\text{A}]$ and the various elementary rate constants (k_1 , k_2 , k_3 and k_4) involved in the mechanism.
- (iii) Show that the observed rate of reaction is given by

$$\frac{d[\text{B}]}{dt} = \frac{d[\text{C}]}{dt} = \left(\frac{k_1 k_2 k_3}{k_4} \right)^{1/2} [\text{A}]^{3/2}$$

- (iv) Calculate the observed activation energy for the reaction given that the activation energies for the steps in the above mechanism (in kJ mol^{-1}) are:

$$E_1 = 384; \quad E_2 = 74; \quad E_3 = 58 \quad \text{and} \quad E_4 = 4$$

TURN OVER

2. (a) Define the following terms that refer to the properties of ionic solutions:

- (i) conductance;
- (ii) conductivity;
- (iii) molar conductivity;
- (iv) transport number;
- (v) ion mobility.

(b) The resistance (R) of a series of aqueous solutions of the salt MX, formed by successive dilutions of a sample, was measured at 25 °C in a conductivity cell having a cell constant equal to 16.91 m⁻¹.

$c/\text{mol L}^{-1}$	0.00050	0.0010	0.0050	0.0100	0.020
R/Ω	2574	1296	265.9	135.6	69.64

Using the graph paper provided, verify that the molar conductivity follows the Kohlrausch law. Determine the limiting molar conductivity of MX (in units of mS m² mol⁻¹) and the Kohlrausch constant, K at 25 °C.

- (c) If the limiting (molar) ionic conductivity (λ_+) for M⁺ is 6.40 mS m² mol⁻¹ at 25°C, use your answer to part (b) to calculate the transport number for M⁺ in the solution of MX.
- (d) Briefly explain why the value of the limiting (molar) ionic conductivity (λ_+) for H⁺(aq) is so much larger than those given below for other “small” monovalent cations in aqueous solution.

[Data: Values for λ_+ in mS m² mol⁻¹: H⁺ 34.96; Li⁺ 3.87; Na⁺ 5.01; K⁺ 7.35]

SECTION B

(Worth 60 marks; Answer the one question in this section.)

3. All symbols have their usual thermodynamic meaning.

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

- (a) A useful equation for this question is $w = -nRT \ln(V_f/V_i)$.

2.5 mol of $\text{O}_2(\text{g})$ at 400 K has a volume of 300 L. It expands **isothermally** until it has a volume of 816 L.

- (i) What is the **minimum** amount of work that can be done by this process, and when is this situation realized?
- (ii) What is the **maximum** amount of work that can be done by this process?
- (iii) Give your understanding of how this maximum amount of work may be obtained.
- (iv) Calculate q for the situation of maximum work being done.

Question 3 continued on following page

Question 3 continued

- (b) The equipartition theorem of classical physics states, roughly, that the average energy of each different mode of motion of a molecule is $\frac{1}{2}RT$. The linear molecule $\text{N}_2(\text{g})$ has three translational modes of motion and two rotational modes of motion at room temperature.
- (i) Show that $C_{V,m}(\text{N}_2, \text{g}) = \frac{5}{2}R$ at room temperature. ($C_{V,m}$ is the molar heat capacity at constant volume.)
 - (ii) What is the value of $C_{p,m}(\text{N}_2, \text{g})$ at room temperature? ($C_{p,m}$ is the molar heat capacity at constant pressure.)
 - (iii) Calculate the heat required to increase the temperature of 2.4 mol of $\text{N}_2(\text{g})$ from 15 °C to 35 °C at constant **volume**.
 - (iv) Calculate the heat required to increase the temperature of 2.4 mol of $\text{N}_2(\text{g})$ from 15 °C to 35 °C at constant **pressure**.
 - (v) Give the physical reason for the differences between your answers in (iii) and (iv).
 - (vi) Estimate the value of $C_{V,m}$ at room temperature for the non-linear molecule $\text{NH}_3(\text{g})$. Explain your answer.

Question 3 continued on following page

Question 3 continued

- (c) This question is about the sublimation of H₂O at 0 °C.
- (i) Using only the following data, estimate the $\Delta_{\text{sub}}H(\text{H}_2\text{O}, 0\text{ °C})$, the enthalpy of sublimation of H₂O at 0 °C.

Data: $\Delta_{\text{freezing}}H(\text{H}_2\text{O}, 0\text{ °C}) = -6.01\text{ kJ mol}^{-1}$

$$\Delta_{\text{vaporization}}H(\text{H}_2\text{O}, 100\text{ °C}) = 40.7\text{ kJ mol}^{-1}$$

- (ii) Now use the following additional data to obtain a better estimate of $\Delta_{\text{sub}}H(\text{H}_2\text{O}, 0\text{ °C})$.

Data: $C_{p,m}(\text{H}_2\text{O}, \text{s}) = 37\text{ J K}^{-1}\text{ mol}^{-1}$

$$C_{p,m}(\text{H}_2\text{O}, \text{l}) = 75.29\text{ J K}^{-1}\text{ mol}^{-1}$$

$$C_{p,m}(\text{H}_2\text{O}, \text{g}) = 33.58\text{ J K}^{-1}\text{ mol}^{-1}$$

- (iii) What approximation is inherent in your method in (ii)?

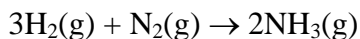
How could this approximation be dispensed with and an even more accurate value of $\Delta_{\text{sub}}H(\text{H}_2\text{O}, 0\text{ °C})$ be obtained?

- (iv) Using your answer from (ii), calculate $\Delta_{\text{sub}}U(\text{H}_2\text{O}, 0\text{ °C})$, the internal energy change of sublimation of H₂O at 0 °C.

Question 3 continued on following page

Question 3 continued

- (d) This question is about the reaction



Here are some thermodynamic data for the compounds in this reaction
(note that some entries have been deliberately left blank):

	$S^\ominus / (\text{J K}^{-1} \text{mol}^{-1})$	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$
H ₂ (g)	130.7	
N ₂ (g)	191.6	
NH ₃ (g)	192.5	-46.11

- (i) Calculate ΔS^\ominus , the standard entropy change for the reaction (at 298 K).
- (ii) Is the sign of your answer in (i) in accord with chemical intuition? Explain.
- (iii) Calculate the standard entropy change for the **surroundings** when the above reaction is carried out (at 298 K).
- (iv) Is the reaction spontaneous under standard conditions? Explain.
- (v) Calculate ΔG^\ominus , the standard Gibbs free energy change for the reaction (at 298 K).
- (vi) What is the maximum amount of useful (or non-expansion) work this reaction can do when carried out under standard conditions?

END OF PAPER