

University of Canterbury

Mid Year Examination and Test Period 2007

Prescription Number(s): CHEM 233

Paper Title: Introduction to Physical Chemistry

Time Allowed: TWO HOURS

Number of pages: SIX

Answer **ALL** questions

Question **ONE** is worth **50%** of the marks

Question **TWO** and **THREE** are each worth **25%** of the marks

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Some useful constants:

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

Faraday Constant $F = 96485 \text{ C mol}^{-1}$

Avogadro's Constant $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

(Question **ONE** is worth **50%** of the marks)

1. All **symbols** have their usual thermodynamic meaning.

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

- (a) Use the First Law of thermodynamics to show that:

(i) $\Delta U = q_V$

(ii) $\Delta H = q_p$

- (b) The heat capacity, C , of a material is defined by $C = dq/dT$.

- (i) Show that $C_{p,m} = C_{V,m} + R$ for a perfect gas, where the subscript 'm' denotes molar heat capacity. (Hint: Start with the definition of H , and use the results of question (a).)

- (ii) Explain the physical reason why $C_p > C_V$ for a gas.

- (c) 4.0 mol of Ar(g) at 250 K has a volume of 100 L. It expands **isothermally** and **reversibly** until it has a volume of 272 L.

- (i) Starting from the definition of work (in terms of p and V), show that $w = -nRT \ln(V_f/V_i)$ for this process.

- (ii) Calculate w for this process.

- (iii) Explain what a (mechanically) reversible process is.

Question 1 continued on following page

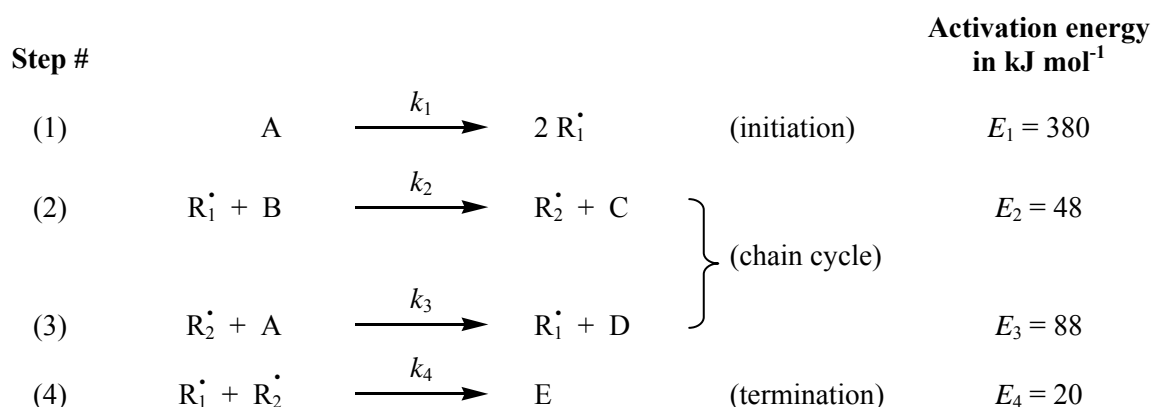
TURN OVER

Question 1 continued

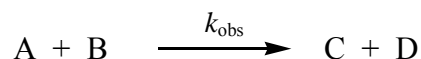
- (d) Trouton's rule is that $\Delta_{\text{vap}}S \approx 85 \text{ J K}^{-1} \text{ mol}^{-1}$ for a liquid at its normal boiling point, T_{b} , except where hydrogen bonding or some other kind of specific molecular interaction is present.
- Use your understanding of entropy and states of matter to explain why $\Delta_{\text{vap}}S(T_{\text{b}})$ is approximately the same for many liquids, with the exceptions to this rule being as stated above.
 - At atmospheric pressure, ethane boils at $-88.6 \text{ }^{\circ}\text{C}$. Estimate the enthalpy of vaporization for ethane at these conditions.
 - Explain whether $\Delta_{\text{vap}}S$ is less than, approximately equal to, or greater than $85 \text{ J K}^{-1} \text{ mol}^{-1}$ for evaporation of H_2O at $100 \text{ }^{\circ}\text{C}$ and 1 atm.
- (e) The Debye T^3 -law is that $C_{V,m} = aT^3$ for non-metallic substances at temperatures close to $T = 0$. For potassium chloride, $a = 9.6 \text{ } \mu\text{J K}^{-4} \text{ mol}^{-1}$.
- In an investigation into superconductivity, a sample of KCl(s) is heated from 1 K to 10 K. Determine the molar ΔU for this process.
[Hint and useful information: $\int kx^n dx = \frac{k}{n+1} x^{n+1} + \text{constant}$]
 - Estimate the molar ΔH for the process of (i).
 - Determine the molar entropy of KCl(s) at 5 K.
[Hint and useful information: $\int kx^n dx = \frac{k}{n+1} x^{n+1} + \text{constant}$]
 - Explain how the Third Law of thermodynamics enters into your calculation of (iii).

(Question **TWO** is worth **25%** of the marks)

2. (a) Outline the assumptions made when the steady state method is used for the analysis of the kinetics of a complex reaction mechanism.
- (b) A reaction has the following mechanism:



The “**chain length**” is **long**. This implies that r_2 and $r_3 \gg r_1$ and r_4 (where $r_1 = k_1[A]$, $r_2 = k_2[\text{R}_1^\bullet][\text{B}]$, etc). Under these conditions the overall reaction stoichiometry approximates to:



- (i) Write steady-state expressions for each of the two free radical species involved: R_1^\bullet and R_2^\bullet
- (ii) Find expressions for each of the steady-state radical concentrations, $[\text{R}_1^\bullet]$ and $[\text{R}_2^\bullet]$ in terms of $[\text{A}]$, $[\text{B}]$ and various k values.
- (iii) Show that the observed rate of reaction in the steady-state is given by:

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

- (iv) Calculate E_{obs} the **observed** activation energy for the overall reaction.

TURN OVER

(Question **THREE** is worth **25%** of the marks)

3. (a) Define the following terms which refer to the properties of ionic solutions.

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

(b) The resistance of a series of aqueous AgNO_3 solutions, formed by successive dilutions of a sample, were measured in a conductivity cell having a cell constant equal to 12.35 m^{-1} at 25°C .

$c/\text{mol L}^{-1}$	0.00050	0.0010	0.0050	0.0100	0.020	0.050
R/Ω	1880	946.3	194.2	99.00	50.86	21.43

Using the graph paper provided, verify that the molar conductivity follows the Kohlrausch law and find the limiting molar conductivity of AgNO_3 and the Kohlrausch constant, \mathbf{K} , at 25°C .

- (c) If the limiting (molar) ionic conductivity (λ_+) for Ag^+ is $6.19 \text{ mS m}^2 \text{ mol}^{-1}$ at 25°C , use your answer to part (b) to calculate the transport number for Ag^+ in AgNO_3 solution.
- (d) Briefly explain why the value of the limiting (molar) ionic conductivity (λ_+) for $\text{H}^+(\text{aq})$ is so much larger than those given (below) for other “small” monovalent cations in aqueous solution.

[Data: Values for λ_+ in $\text{mS m}^2 \text{ mol}^{-1}$: H^+ 34.96; Li^+ 3.87; Na^+ 5.01; K^+ 7.35]

END OF PAPER