

CHEM 233 – Physical Chemistry

Class Test

Wednesday 21 May 2008

Time Allowed: TWO hours

Instructions: Answer ALL questions.

Question 1 is worth 36 marks and questions 2, 3 and 4 each carry 28 marks.

Total 120 marks.

1. [36 marks]

- (a) In New Zealand petrol stations and in the U.S.A., the most widely used units of pressure are pounds per square inch (lb in^{-2}). What is 29.4 lb in^{-2} in atm? [Useful information: $1 \text{ lb} = 453.6 \text{ g}$; $1 \text{ in} = 2.54 \text{ cm}$; $g = 9.81 \text{ m s}^{-2}$; $101\,325 \text{ Pa} = 1 \text{ atm}$.]
- (b) “Hot air rises.”
Use your knowledge of gases to give a (simple) scientific explanation of this common phrase.
- (c) In an experiment to measure the molar mass of a gas, 125 mL of the gas was confined in a glass vessel. The pressure was 76.0 mm Hg at 25°C and the mass of the gas was 16.3 mg.
Assuming perfect gas behaviour, what is the molar mass of the gas?
Suggest what the gas might be.
[Useful information: $1 \text{ atm} = 760 \text{ mm Hg}$; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.]
- (d) The van der Waals equation of state is

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

- (i) For C_2H_6 , $a = 5.507 \text{ atm dm}^6 \text{ mol}^{-2}$ and $b = 6.51 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$.
Calculate the pressure (in atm) exerted by 2.00 mol of ethane at 1 000 K in 400 cm^3 .
[Useful information: $R = 8.205\,74 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$.]
- (ii) Now calculate the pressure (in atm) exerted by 2.00 mol of a perfect gas at the same T and V .
- (iii) What do your answers to (i) and (ii) say about ethane under these conditions?

2. [28 marks]

(a) Distinguish clearly between the terms:

- (i) reaction **rate** and **rate constant**
- (ii) **differential rate law** and **integrated rate law**;
- (iii) **order** and **molecularity**.

(b) A chemical reaction which occurs in the gas phase is described by the stoichiometric equation



The progress of this reaction is monitored by measuring the **total pressure** in the reaction vessel using a rapidly-responding electronic pressure transducer.

The following results were obtained for an experiment in which the **initial partial pressures** of A and B were: $P_A^\circ = 1.500$ kPa and $P_B^\circ = 2.500$ kPa and the temperature = 20°C.

time / ms	0	4.0	8.0	12.0	∞
P_{total} (total pressure) / kPa	4.000	3.191	2.886	2.734	2.500

(i) Show that the respective partial pressures of A and B, as the reaction proceeds, are given by the expressions:

$$P_A = P_{total} - P_B^\circ$$

and

$$P_B = P_{total} - P_A^\circ$$

(ii) Prove that the reaction is **second order** overall (being first order with respect to each of A and B) and calculate the rate constant. Your final value should be expressed in units of **cm³ molecules⁻¹ s⁻¹**.

The Table from Atkins and de Paula (8th Edition) shown on the following page may prove useful.

(c) If the experiment is repeated at 34°C the rate constant is found to increase by a factor of 2.20. **Explain** how you would determine the **activation energy** for the given reaction (**no calculation required**).

Data: $R = 8.314$ J mol⁻¹ K⁻¹; 0°C = 273 K; $N_{Av} = 6.022 \times 10^{23}$ (molecules) mol⁻¹

See Table for question 1 on the following page

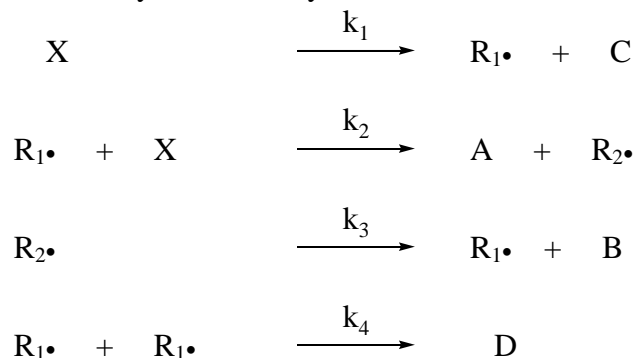
Table 25.3 Integrated rate laws

Order	Reaction	Rate law*	$t_{1/2}$
0	$A \rightarrow P$	$v = k$ $kt = x$ for $0 \leq x \leq [A]_0$	$\frac{[A]_0}{2k}$
1	$A \rightarrow P$	$v = k[A]$ $kt = \ln \frac{[A]_0}{[A]_0 - x}$	$\frac{\ln 2}{k}$
2	$A \rightarrow P$	$v = k[A]^2$ $kt = \frac{x}{[A]_0([A]_0 - x)}$	$\frac{1}{k[A]_0}$
	$A + B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
	$A \rightarrow P$ with autocatalysis	$v = k[A][P]$ $kt = \frac{1}{[A]_0 + [P]_0} \ln \frac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}$	
3	$A + 2B \rightarrow P$	$v = k[A][B]^2$ $kt = \frac{2x}{(2[A]_0 - [B]_0)([B]_0 - 2x)[B]_0} + \frac{1}{(2[A]_0 - [B]_0)^2} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
$n \geq 2$	$A \rightarrow P$	$v = k[A]^n$ $kt = \frac{1}{n-1} \left\{ \frac{1}{([A]_0 - x)^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$	$\frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$

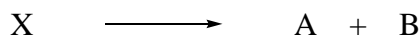
* $x = [P]$, and $v = dx/dt$.

3. [28 marks]

- (a) Outline the assumptions made when the steady state method is used for the analysis of the kinetics of a complex reaction mechanism.
- (b) The mechanism for the pyrolysis of an organic compound, X, at temperatures around 550°C is closely described by



The initial step above produces **small traces** only of the molecule C, while the final step produces **tiny** amounts of another “impurity” molecule, D. The observed overall reaction stoichiometry is thus closely approximated by



- (i) Write steady state expressions for the concentrations of the radicals $R_1\cdot$ and $R_2\cdot$.
- (ii) Find an **exact** expression for the **overall rate of removal of X**, as predicted by the above mechanism, in terms of $[X]$ and the various elementary rate constants (k_1 , k_2 , k_3 and k_4) involved.
- (iii) What does the observed overall reaction stoichiometry (given above) tell you about the relative rates of the four steps in the mechanism?
- (iv) If the overall stoichiometry is taken into account, show that the expression you obtained in part (ii) simplifies to

$$-\frac{d[X]}{dt} = k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} [X]^{3/2}$$

- (v) 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:

$$E_1 = 384; \quad E_2 = 65; \quad E_3 = 44 \quad \text{and} \quad E_4 = 2$$

4. [28 marks]

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

- (i) conductance;
- (ii) conductivity;
- (iii) molar conductivity;
- (iv) transport number;

(b) The resistance (R) of a series of aqueous KNO_3 solutions, formed by successive dilutions of a sample, were measured in a conductivity cell having a cell constant equal to 13.65 m^{-1} .

$c/\text{mol L}^{-1}$	0.00050	0.0010	0.0050	0.0100	0.020
R/Ω	1912	962.6	197.2	100.5	51.54

Using the graph paper provided, verify that the molar conductivity follows the Kohlrausch law and find the limiting molar conductivity of KNO_3 (in units of $\text{mS m}^2 \text{ mol}^{-1}$) and the Kohlrausch constant, K .

(c) **Briefly** explain why a solution of acetic acid does not follow the Kohlrausch law and describe how the acid dissociation constant, K_a , can be obtained from conductance measurements on acetic acid solutions.