

## CHEM 263 – Physical Chemistry

Class Test

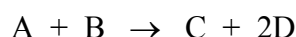
Thursday 30 June 2005

Time Allowed: 90 minutes

Instructions: Answer **all three questions**, each of which carries one third of the total marks.

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1. (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 an electronic pressure transducer.

The following results were obtained for an experiment in which the **initial partial pressures** of A and B were:  $P_A = 1.000 \text{ kPa}$  and  $P_B = 2.000 \text{ kPa}$  and the temperature =  $25^\circ\text{C}$ .

time / <b>ms</b>	0	2.0	5.0	10.0	$\infty$
total pressure / <b>kPa</b>	3.000	3.365	3.638	3.835	4.000

Show that the reaction is **second order** and calculate the rate constant **in units of  $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$** .

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

- (c) If the experiment is repeated at  $40^\circ\text{C}$  the rate constant is found to increase by a factor of 2.25. Determine the **activation energy** for the given reaction.

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

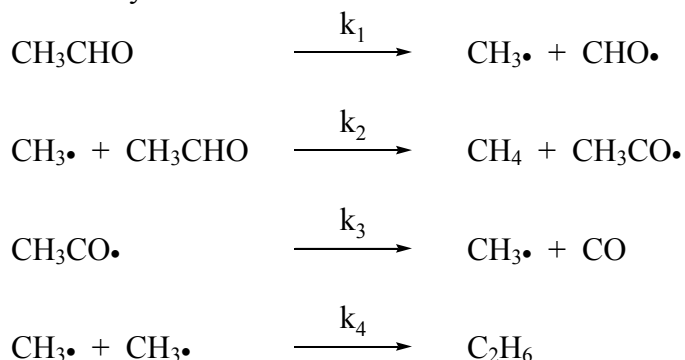
See Table for question 1 on the following page

**Table 25.3** Integrated rate laws

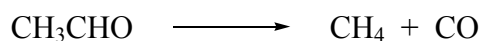
Order	Reaction	Rate law*	$t_{1/2}$
0	$A \rightarrow P$	$v = k$ $kt = x$ for $0 \leq x \leq [A]_0$	$\frac{[A]_0}{2k}$
1	$A \rightarrow P$	$v = k[A]$ $kt = \ln \frac{[A]_0}{[A]_0 - x}$	$\frac{\ln 2}{k}$
2	$A \rightarrow P$	$v = k[A]^2$ $kt = \frac{x}{[A]_0([A]_0 - x)}$	$\frac{1}{k[A]_0}$
	$A + B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
	$A \rightarrow P$ 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  $v = dx/dt$ .

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) The mechanism for the pyrolysis of acetaldehyde ( $\text{CH}_3\text{CHO}$ ) at temperatures around 800 K is mainly



The  $\text{CHO}\cdot$  radicals generate **small traces** only of  $\text{H}_2$  and additional  $\text{CO}$ , while the final step produces **tiny** amounts of  $\text{C}_2\text{H}_6$ . The observed overall reaction stoichiometry is thus closely approximated by



- Write steady state expressions for the concentrations of the radicals  $\text{CH}_3\cdot$  and  $\text{CH}_3\text{CO}\cdot$ .
- Find an **exact** expression for the overall rate of removal of acetaldehyde, as predicted by the above mechanism, in terms of  $[\text{CH}_3\text{CHO}]$  and the various elementary rate constants ( $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$ ) involved.
- What does the observed overall reaction stoichiometry (given above) tell you about the relative rates of the four steps in the mechanism?
- If the overall stoichiometry is taken into account, what is the observed order of the decomposition process?
- Calculate the observed activation energy for the reaction given that the activation energies for the steps in the above mechanism (in  $\text{kJ mol}^{-1}$ ) are:

$$E_1 = 318; \quad E_2 = 33; \quad E_3 = 43 \quad \text{and} \quad E_4 = 0$$

3. (a) (i) Derive the **Langmuir** adsorption isotherm in the form

$$\theta = \frac{V}{V_{\text{mon}}} = \frac{KP}{1 + KP}$$

using a simple model of adsorption. State clearly any assumptions which are made, and the nature of any parameters you introduce.

(V is the volume of gas adsorbed on a surface;  $V_{\text{mon}}$  is the volume corresponding to monolayer coverage; P is the pressure of gas in contact with the surface.)

- (ii) The **BET** isotherm may be expressed as

$$\frac{V}{V_{\text{mon}}} = \frac{cz}{(1 - z)\{1 - (1 - c)z\}}$$

**Briefly outline** the **additional** assumptions which are made in the derivation of this expression i.e. how is the Langmuir model extended? ( $z = P/P^*$  where  $P^*$  is the vapour pressure of a macroscopic layer of liquid (liquefied gas) on the surface; c is a constant.)

**Note: No derivation is required in this part.**

- (b) The adsorption of nitrogen on to a solid surface is known to follow the **Langmuir** isotherm. A series of measurements are made of the volumes of nitrogen gas being adsorbed on a particular solid sample using a gas burette. All gas volume measurements are corrected to equivalent volumes in  $\text{mm}^3$  at  $20^\circ\text{C}$  and  $101.3 \text{ kPa}$ . The solid sample adsorbs  $100 \text{ mm}^3$  when the pressure of nitrogen in contact with the solid is  $300 \text{ kPa}$ . The effective surface area of the solid sample is  $3.86 \text{ m}^2$  and one nitrogen molecule occupies an area of  $1.62 \times 10^{-19} \text{ m}^2$  when adsorbed.

**Calculate:**

- (i)  $V_{\text{mon}}$   
(ii) The volume of nitrogen adsorbed by the solid when the pressure is  $150 \text{ kPa}$ .

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

**Answers:**

- Q1: (b)  $k = 126.3 \text{ kPa}^{-1} \text{ s}^{-1} = 5.20 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
- (c)  $E_a = 41.9 \text{ kJ mol}^{-1}$
- Q2: (i)  $d[\text{CH}_3\cdot]/dt = r_1 - r_2 + r_3 - 2r_4 = 0$
- $d[\text{CH}_3\text{CO}\cdot]/dt = r_2 - r_3 = 0$
- (ii)  $d[\text{CH}_3\text{CHO}]/dt = k_1[\text{CH}_3\text{CHO}] + k_2(k_1/2k_4)^{1/2}[\text{CH}_3\text{CHO}]^{3/2}$
- (iii)  $r_2 \text{ and } r_3 \gg r_1 \text{ and } r_4$
- (iv) Observed rate =  $d[\text{CH}_3\text{CHO}]/dt \approx k_2(k_1/2k_4)^{1/2}[\text{CH}_3\text{CHO}]^{3/2}$
- (v)  $E_{\text{obs}} = 192 \text{ kJ mol}^{-1}$
- Q3: (b) (i)  $V_{\text{mon}} = 951.5 \text{ mm}^3$  (of nitrogen gas at 20°C and 101.3 kPa)
- (b) (ii)  $V = 52.8 \text{ mm}^3$  (of nitrogen gas at 20°C and 101.3 kPa)