

Kinetics II

Question 1

- a) Define the following terms which relate to the reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$
- the rate of reaction
 - the rate expression or rate law
 - the rate constant
- b) A gas phase reaction of the type $2\text{A} \rightarrow \text{B}$ is monitored at 298 K by measuring the total pressure ($P_t = P_A + P_B$).

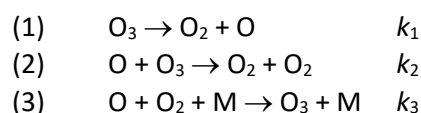
t / s	0	100	200	300	400
P_t / Torr	400	322	288	268	256

Note that at $t = 0$, the pressure is due to A only.

- Derive an expression which gives the pressure of A, P_A , in terms of the total pressure P_t .
- Show that the data are consistent with a second order reaction.
- Show that the rate constant at 298 K is $k_2 = 8.06 \times 10^{-6} \text{ Torr}^{-1} \text{ s}^{-1}$
- If the rate constant at 37°C is $k_2 = 1.73 \times 10^{-5} \text{ Torr}^{-1} \text{ s}^{-1}$, show how to calculate the activation energy of the reaction.

Question 2

The kinetics of the thermal decomposition of ozone can be accounted for by the following mechanism:



- a) Show that the steady state concentration of oxygen atoms is given by

$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_2[\text{O}_3] + k_3[\text{O}_2][\text{M}]}$$

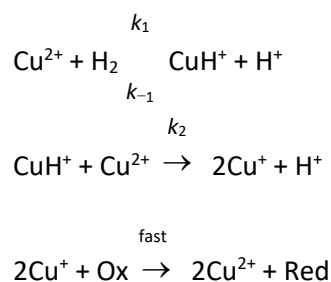
- b) Why is the species M included in both sides of reaction (3)?
- c) Show that the rate of disappearance of ozone according to the above mechanism is

$$-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]^2}{k_2[\text{O}_3] + k_3[\text{O}_2][\text{M}]}$$

- d) Outline the assumptions upon which the use of the steady-state approximation is based. Are these assumptions justified?

Question 3

- a) Explain, with examples, the meaning of the term *rate law* in chemical kinetics. Include in your answer an explanation of why the concept of overall order is not applicable to all, but only to some rate laws.
- b) Reductions by H₂ in aqueous solution can be catalysed by Cu²⁺ ions; the rates are independent of the concentration of the substrate being reduced. A mechanism proposed for these reactions is:



where Ox and Red represent oxidised and reduced forms of the substrate. By treating CuH⁺ as a reactive intermediate, show that the theoretical rate law for the consumption of H₂, is

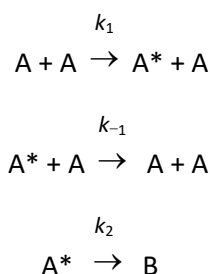
$$\text{rate} = \frac{k_1 k_2 [\text{Cu}^{2+}]^2 [\text{H}_2]}{k_{-1} [\text{H}^+] + k_2 [\text{Cu}^{2+}]}$$

Show that the rates given below for reaction at 100°C with a fixed Cu²⁺ concentration of 0.1 mol dm⁻³ are consistent with the mechanism, and determine the constant k_1 and the ratio k_{-1}/k_2 . The Henry's law constant (solution concentration / gas pressure) for H₂ solution under the conditions of the experiment is 7.14 x 10⁻⁴ mol dm⁻³ bar⁻¹.

p(H ₂) / bar	5	10	20	20	20	20	20
[H ⁺] / mol dm ⁻³	0.01	0.01	0.01	0.1	0.2	0.4	0.5
rate / mol dm ⁻³ s ⁻¹	3.5	7.0	14.0	11.48	9.57	7.18	6.38

Question 4

- a) Derive an equation for the rate of conversion of A into B according to the following reaction scheme.



- b) Explain why so-called unimolecular reactions that follow this scheme display a change in kinetics from first order to second order overall as the pressure is lowered and why the addition of inert gas can significantly influence the reaction rate.

- c) The cis-trans isomerisation of an alkene was studied as a function of pressure at constant temperature, and the following effective first-order rate constants were measured.

concentration $\times 10^6 / \text{mol dm}^{-3}$	4.0	7.0	14.0	65.0
rate constant $\times 10^5 / \text{s}^{-1}$	1.28	1.47	1.69	1.89

- i) Show that the reaction kinetics, over the given concentration range, are consistent with the reaction scheme in a).
- ii) Calculate k_1 and the limiting value of the effective first order rate constant at high pressures.
- iii) Explain why the reaction kinetics associated with many unimolecular reactions deviate significantly from the quantitative predictions of the reaction scheme in a).

Question 5

- a) Explain what is meant by the *half life* of a chemical reaction. The reaction



was studied at 300 K. For initial concentrations $[\text{OH}]_0 = [\text{C}_2\text{H}_6]_0 = a_0$, show that the half life of OH radicals is given by $(a_0 k_1)^{-1}$, where k_1 is the bimolecular rate constant for the reaction.

- b) For initial concentrations $[\text{OH}]_0 = [\text{C}_2\text{H}_6]_0 = 1.5 \times 10^{-10} \text{ mol dm}^{-3}$, the half life at 300 K was found to be 44 s. Determine the OH radical half life when $[\text{OH}]_0 = 1.5 \times 10^{-10} \text{ mol dm}^{-3}$ and $[\text{C}_2\text{H}_6]_0 = 1.5 \times 10^{-7} \text{ mol dm}^{-3}$ (i.e. in great excess over $[\text{OH}]_0$).
- c) For $[\text{OH}]_0 = [\text{C}_2\text{H}_6]_0 = 1.5 \times 10^{-10} \text{ mol dm}^{-3}$, the half life $t_{1/2}$ of OH varies with temperature as shown in the table below. Deduce what you can from these data.

T / K	300	450	900
$t_{1/2} / \text{s}$	44	12	1.85

- d) For the recombination reaction represented by the stoichiometric equation $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$, the half life of oxygen atoms increases with increasing temperature. Account for this behaviour.