

KINETICS II

QUESTION 1

a) Define the following terms which relate to the reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

- i) the rate of reaction
- ii) the rate expression or rate law
- iii) 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 ($P_{\text{T}} = P_{\text{A}} + P_{\text{B}}$).

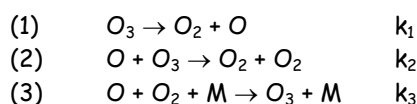
t / s	0	100	200	300	400
$P_{\text{T}} / \text{Torr}$	400	322	288	268	256

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

- i) Derive an expression which gives the pressure of A, P_{A} , in terms of the total pressure P_{T} .
- ii) Show that the data are consistent with a second order reaction.
- iii) Show that the rate constant at 298 K is $k_2 = 8.06 \times 10^{-6} \text{ Torr}^{-1}\text{s}^{-1}$
- iv) 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

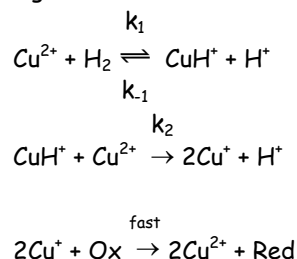
$$\frac{-d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]^2}{k_2[\text{O}_3] + k_3[\text{O}_2][\text{M}]}$$

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 H_2 in aqueous solution can be catalysed by Cu^{2+} 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 H_2 , is

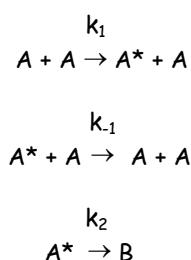
$$\text{rate} = \frac{k_1 k_2 [Cu^{2+}]^2 [H_2]}{k_{-1} [H^+] + k_2 [Cu^{2+}]}$$

Show that the rates given below for reaction at $100^\circ C$ with a fixed Cu^{2+} 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 H_2 solution under the conditions of the experiment is $7.14 \times 10^{-4} \text{ mol dm}^{-3} \text{ bar}^{-1}$.

$p(H_2) / \text{bar}$	5	10	20	20	20	20	20
$[H^+] / \text{mol dm}^{-3}$	0.01	0.01	0.01	0.1	0.2	0.4	0.5
rate / $\text{mol dm}^{-3} \text{ s}^{-1}$	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

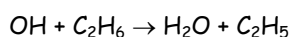
i) Show that the reaction kinetics, over the given concentration range, are consistent with the reaction scheme in a).

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 300K. 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
$t_{1/2}$ / 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.