

### Question 1

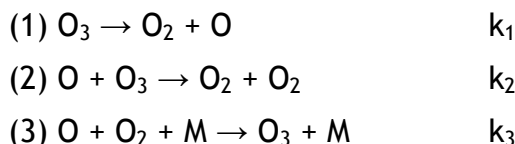
- a) Define the following terms which relate to the reaction  $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$
- the rate of reaction
  - the rate expression or rate law
  - the rate constant
- b) A gas phase reaction of the type  $2\text{A} \rightarrow \text{B}$  is monitored at 298 K by measuring the total pressure ( $P_t = P_A + P_B$ ). Note that at  $t=0$ , the pressure is due to A only.

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

- Derive an expression that 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 what is meant by the half-life of a chemical reaction. The reaction  $\text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5$  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