16.1 Rate expression and reaction mechanism

The rate law for a reaction is derived from experimental data

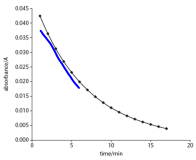
$$C_{60}O_3 \rightarrow C_{60}O + O_2$$

This reaction can be monitored by colorimetry (using a spectrophotometer) as the oxidised buckminsterfullerene absorbs.

$$\text{rate} = -\frac{\Delta[C_{60}O_3]}{\Delta t}$$

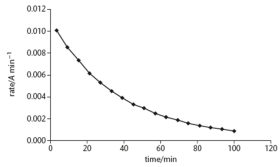
Time / minutes	$C_{60}O_3$ absorbance at 23 °C	Time / minutes	$C_{60}O_3$ absorbance at 23 °C
3	0.04241	57	0.01106
9	0.03634	63	0.00955
15	0.03121	69	0.00827
21	0.02680	75	0.00710
27	0.02311	81	0.00616
33	0.01992	87	0.00534
39	0.01721	93	0.00461
45	0.01484	99	0.00395
51	0.01286		

(concentration)



By calculating the rate at certain time intervals (using the gradient of the tangent at that point), we can plot a graph of rate against time:

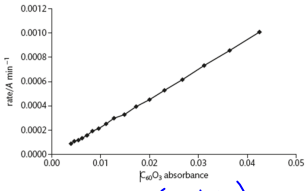
Rate



How is the rate related to the $[C_{60}O_3]$?

$[C_{60}O_3]$ is directly proportional to the rate of reaction.

We can confirm this by plotting the rate of the reaction against the absorbance of $C_{60}O_3$, as shown in Figure 6.24.



(concentration)

This shows that the $C_{60}O_3$ is a "1st order reactant"

The straight-line graph obtained in Figure 6.24 confirms that the rate of the reaction is directly proportional to the concentration of the reactant $C_{60}O_3$.

$$\text{reaction rate} \propto [C_{60}O_3]$$

$\propto \rightarrow = k$

This proportional relationship is converted into an equation by introducing a constant. So:

$$\text{reaction rate} = k\,[C_{60}O_3]$$

where k is the **rate constant**.

The rate constant k is a constant for a particular reaction at a specified temperature.

This format of expressing a rate is called the rate expression or rate law.

$$A + B \rightarrow \text{products}$$

$$\text{rate} \propto [A]^m\,[B]^n \text{ or rate} = k\,[A]^m\,[B]^n$$

The order of reaction with respect to a particular reactant is the power to which its concentration is raised in the rate equation. The overall order for the reaction is the sum of the individual orders for all reactants.

Worked example

The reaction:

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$

is shown to be second order with respect to NO and first order with respect to H_2.

Give the rate equation for this reaction and its overall order.

Rate $= k\,[H_2]^1[NO]^2$

Order $= 1+2 = 3$

Note that the rate constant is written with a lower case k. Do not confuse this with equilibrium constants which are written with an upper case K.

14 The rate expression for the reaction

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

is rate $= k\,[NO]\,[O_3]$. What is the order with respect to each reactant and what is the overall order?

15 The reaction

$$CH_3Cl(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Cl^-(aq)$$

is found to be second order overall. Give three possible rate expressions consistent with this finding.

(14) NO: first order
O_3: first order
Overall $= 2$

Rate $= k\,[CH_3Cl]\,[OH^-]$
Rate $= k\,[CH_3Cl]^2$
Rate $= k\,[OH^-]^2$

Units of k

$k = \frac{\text{Rate}}{[A][B]} = \frac{\text{mol dm}^{-3}\,s^{-1}}{\text{mol dm}^{-3}\,\text{mol dm}^{-3}}$

$k = \text{mol}^{-1}\,\text{dm}^3\,s^{-1}$

Rate $= k\,[A] \rightarrow s^{-1}$

Rate $= k\,[A][B]^3 \rightarrow \frac{\text{mol dm}^{-3}\,s^{-1}}{\text{mol}^4\,\text{dm}^{-12}} \rightarrow \text{mol}^{-3}\,\text{dm}^9\,s^{-1}$

Rate $= k\,[A][B]^2[D]^3 \rightarrow \frac{\text{mol dm}^{-3}\,s^{-1}}{\text{mol}^6\,\text{dm}^{-18}} \rightarrow \text{mol}^{-5}\,\text{dm}^{15}\,s^{-1}$

Units of *k* vary depending on the overall order of the reaction

Zero order	First order	Second order	Third order
rate = *k*	rate = *k* [A]	e.g. rate = *k* $[A]^2$	e.g. rate = *k* $[A]^3$

Worked example

A reaction has the rate expression rate = *k* $[A]^2$ [B].

Calculate the value of *k*, including units, for the reaction when the concentrations of both A and B are 2.50×10^{-2} mol dm^{-3} and the reaction rate is 7.75×10^{-5} mol dm^{-3} min^{-1}.

Solution

Substituting the values into the rate expression gives

$$7.75 \times 10^{-5}\ \text{mol dm}^{-3}\ \text{min}^{-1} = k\,(2.50 \times 10^{-2}\ \text{mol dm}^{-3})^2 \times (2.50 \times 10^{-2}\ \text{mol dm}^{-3})$$

$$\text{Therefore } k = \frac{7.75 \times 10^{-5}\ \text{mol dm}^{-3}\ \text{min}^{-1}}{(2.50 \times 10^{-2})^3\ (\text{mol dm}^{-3})^3}$$

$$= 4.96\ \text{mol}^{-2}\ \text{dm}^{6}\ \text{min}^{-1}$$

Reactions which are zero order overall are relatively uncommon. They occur when the rate of the reaction is independent of the concentration of the reactants. An example would be the decomposition of gaseous ammonia using a catalyst of heated platinum.

$$2NH_3(g) \xrightarrow{Pt(s)} N_2(g) + 3H_2(g)$$

The rate depends on the number of NH_3 molecules attached to the surface of the catalyst, which is very small relative to the total number of NH_3 molecules. So increasing the concentration of the reactant will not affect the rate.

Exercises

16 Give the units of *k* in each of the rate expressions below:

(a) rate = *k* $[NO_2]^2$ **(c)** rate = *k* $[NH_3]^0$ **(e)** rate = *k* $[H_2]$ $[I_2]$
(b) rate = *k* $[CH_3CH_2Br]$ **(d)** rate = *k* $[NO]^2$ $[Br_2]$

17 The reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ has a value of $k = 6.9 \times 10^{-4}\ s^{-1}$ at a certain temperature. Deduce the rate expression for this reaction.

18 A reaction involving A and B is found to be zero order with respect to A and second order with respect to B. When the initial concentrations of A and B are 1.0×10^{-3} mol dm^{-3} and 2.0×10^{-3} mol dm^{-3} respectively, the initial rate of the reaction is 4.5×10^{-4} mol dm^{-3} min^{-1}. Calculate the value of the rate constant for the reaction.

16 **(a)** $mol^{-1}\ dm^3\ s^{-1}$ **(b)** s^{-1}
(c) $mol\ dm^{-3}\ s^{-1}$ **(d)** $mol^{-2}\ dm^6\ s^{-1}$
(e) $mol^{-1}\ dm^3\ s^{-1}$

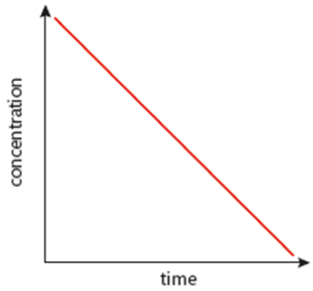
17 From the units of *k*, it must be 1st order.
Rate = $k[N_2O_5]$

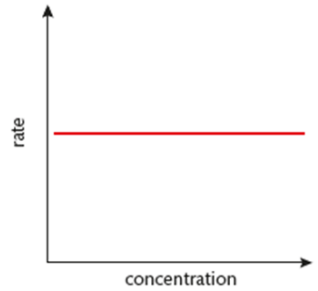
18 $k = 4.5 \times 10^{-4}/(2.0 \times 10^{-3})^2 = 1.1 \times 10^2\ mol^{-1}\ dm^3\ min^{-1}$

Zero-order reaction

Here the concentration of reactant A does not affect the rate of the reaction.

$$\text{rate} = k\,[A]^0 \text{ or rate} = k$$

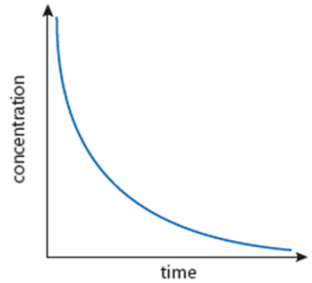


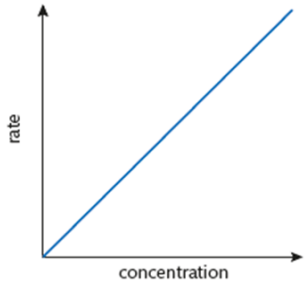


First-order reaction

Here the rate is directly proportional to the concentration of A.

$$\text{rate} = k\,[A]$$

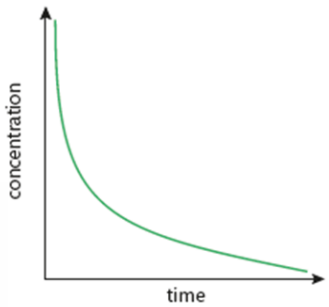


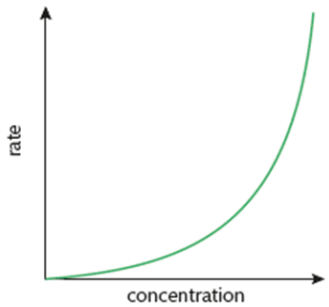


Second-order reaction

Here the rate is proportional to the square of the concentration of A.

$$\text{rate} = k\,[A]^2$$

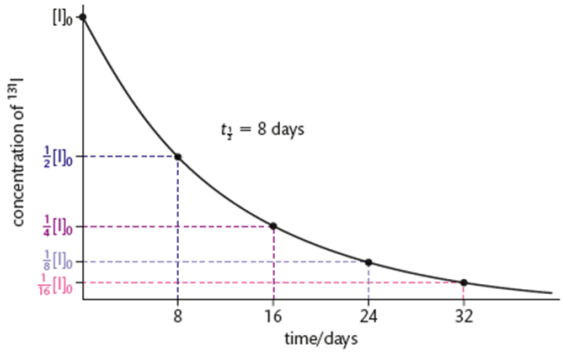




First-order reactions have a constant half-life

Half-life ($t_{1/2}$) - the time taken for the concentration of a reactant to decrease to half its original value.

For a first order reactions, we find that the $t_{1/2}$ is a constant and therefore independent of its starting concentration.

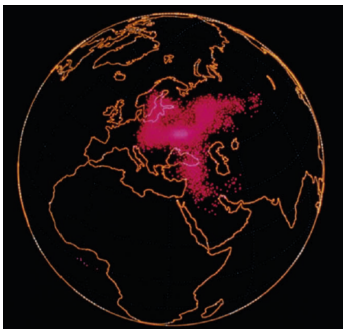


If a reactant has a constant half-life, then the reaction must be first order with respect to that reactant.

This graph shows the half-life of Iodine-131 which is used to treat thyroid cancer.

The term is most commonly used when describing radioactive elements but is applicable to all first order reactions.

The radioactiviity map below shows Europe 6 days after which event?



^{90}Sr has a $t_{1/2}$ of 29 years so will remain in the soil in some areas for up to 300 years.

Determination of the order of a reaction

Initial rates method

This involves carrying out a number of separate experiments with different starting concentrations of reactant A, and measuring the initial rate of each reaction. The concentrations of other reactants are held constant, so that the effect of [A] on reaction rate can be seen. The process can then be repeated for reactant B.

Worked example

Use the data in the table below to work out the order of reaction with respect to reactants A and B, and so write the rate expression for this reaction.

Experiment number	Initial concentrations / mol dm^{-3}		Initial rate of reaction / mol dm^{-3} s^{-1}
	[A]	[B]	
1	0.10	0.10	2.0×10^{-4}
2	0.20	0.10	4.0×10^{-4}
3	0.30	0.10	6.0×10^{-4}
4	0.30	0.20	2.4×10^{-3}
5	0.30	0.30	5.4×10^{-3}

Overall = 3rd order

Rate = $k[A][B]^2$

[A] = 1st order

[B] = 2nd order

[B] is doubled → $\times 2^2$ [B] is tripled → 3^2

20 The following data were obtained for the reaction of NO(g) with O_2(g) to form NO_2(g) at 25 °C.

Experiment	[NO] / mol dm^{-3}	[O_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.30	0.20	2.0×10^{-3}
2	0.30	0.40	4.0×10^{-3}
3	0.60	0.80	3.2×10^{-2}

Calculate the order with respect to the two reactants and write the rate expression for the reaction.

[NO] = 2

[O_2] = 1st

Rate = $k[O_2][NO]^2$

21 If a reaction A + 2B → products has the rate expression rate = k [A]^2, deduce the rates in experiments 2 and 3 in the table below.

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.01	~~0.01~~	3.8×10^{-3}
2	0.02	~~0.01~~	1.52×10^{-2}
3	0.02	~~0.02~~	

$\times 2^2$

0 order

Reaction mechanism

Most reactions involve a series of small steps

For example, in the reaction

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

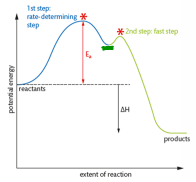
it has been shown that the mechanism involves the following elementary steps:

$$\text{step 1: } NO_2(g) + \cancel{NO_2(g)} \rightarrow NO(g) + \cancel{NO_3(g)}$$
$$\text{step 2: } \cancel{NO_3(g)} + CO(g) \rightarrow \cancel{NO_2(g)} + CO_2(g)$$
$$\text{overall reaction: } NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The overall reaction is obtained by cancelling molecules that appear on both sides.

NO_3 is an intermediate in this reaction, being produced and consumed in different steps, so it does not appear in the overall equation.

The rate-determining step is the slowest step in the reaction mechanism



The rate-determining step is the step in a reaction mechanism whose transition state has the highest energy.

For example, in the reaction

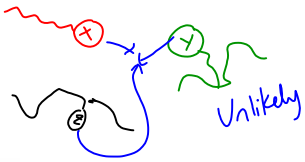
$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

it has been shown that the mechanism involves the following elementary steps:

$$\text{step 1: } NO_2(g) + \cancel{NO_2(g)} \rightarrow NO(g) + \cancel{NO_3(g)}$$
$$\text{step 2: } \cancel{NO_3(g)} + CO(g) \rightarrow \cancel{NO_2(g)} + CO_2(g)$$
$$\text{overall reaction: } NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The rate expression for an overall reaction is determined by the reaction mechanism

Equation for rate-determining step	Molecularity	Rate law
A → products	unimolecular	rate = k [A]
2A → products	bimolecular	rate = k [A]^2
A + B → products	bimolecular	rate = k [A] [B]



Rate = k[A][B][C]

Worked example

The reaction

$$2NO_2Cl(g) \rightarrow 2NO_2(g) + Cl_2(g)$$

is believed to have the following mechanism:

$$\text{step 1: } NO_2Cl(g) \rightarrow NO_2(g) + Cl(g) \quad \text{slow: the rate-determining step}$$
$$\text{step 2: } NO_2Cl(g) + Cl(g) \rightarrow NO_2(g) + Cl_2(g) \quad \text{fast}$$
$$\text{overall: } 2NO_2Cl(g) \rightarrow 2NO_2(g) + Cl_2(g)$$

Deduce the rate expression and the overall order of the reaction.

Rate = k [NO_2Cl] Overall → 1st order

Worked example

For the reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

the following reaction mechanism has been proposed.

$$\text{step 1: } NO(g) + NO(g) \rightarrow N_2O_2(g) \quad \text{fast}$$
$$\text{step 2: } N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g) \quad \text{slow: the rate-determining step}$$
$$\text{overall: } 2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Rate = k [N_2O_2][O_2] ✓ → [NO][NO] → $[NO]^2$

Rate = k $[NO]^2$ [O_2]

Overall → 3rd order

Reaction mechanisms can be supported by indirect evidence but cannot be observed. What

TOK

Exercises

22 If the reaction $NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$ occurs by a one-step collision process, what would be the expected rate expression for the reaction? rate = k [NO_2] [CO]

23 $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ is shown experimentally to be second order with respect to NO_2. Is this consistent with the following mechanism? Yes

$$NO_2 + NO_2 \rightarrow NO_3 + NO \quad \text{slow: the rate-determining step}$$
$$NO_3 + NO \rightarrow 2NO + O_2 \quad \text{fast}$$

rate = k $[NO_2]^2$

24 Which statement or statements about the following reaction at 450 °C is/are correct?

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

I The reaction must involve a collision between one O_2 and two SO_2 molecules. ✗
II Every collision between SO_2 and O_2 will produce SO_3. ✗
III The rate-determining step is the slowest step of the reaction. ✓

A I and III **C** III only
B II only **D** None of the statements is correct

25 If the mechanism of a reaction is:

$$AB_2 + AB_2 \rightarrow \cancel{A_2B_4} \quad \text{slow}$$
$$\cancel{A_2B_4} \rightarrow A_2 + 2B_2 \quad \text{fast}$$

(a) What is the overall equation for the reaction?
(b) What is the rate expression for this reaction?
(c) What units will the rate constant have in this expression?

$2AB_2 \rightarrow A_2 + 2B_2$

Rate = k $[AB_2]^2$

$mol^{-1}\ dm^3\ s^{-1}$

22 Rate = k[NO_2][CO]

23 Yes, it fits the kinetic data and the overall stoichiometry.

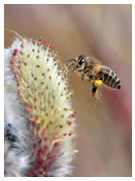
24 C

25 **(a)** $2AB_2 \rightarrow A_2 + 2B_2$
(b) Rate = k [AB_2]^2
(c) $mol^{-1}\ dm^3\ s^{-1}$

16.2 Activation energy

16.2	$k = Ae^{\frac{-E_a}{RT}}$
16.2	$\ln k = \frac{-E_a}{RT} + \ln A$
16.2	$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

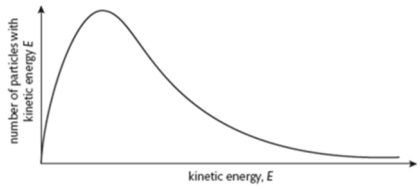
The rate constant *k* is temperature dependent



Why are bees only active during the summer months?

As we know temperature affects the rate of reaction but does not affect the concentration of reactants then it must affect k.

We also know that the temperature will have an effect on the number of particles with more kinetic energy than the E_a (particularly when the E_a is high for a reaction).



The Arrhenius equation (Svante Arrhenius) describes the relationship between them:

In data booklet

$$k \propto e^{\frac{-E_a}{RT}} \text{ or } \boxed{k = Ae^{\frac{-E_a}{RT}}}$$

A = Arrhenius constant, frequency factor or pre-exponential factor

We can use an Arrhenius plot to calculate E_a:

The equation of a straight line

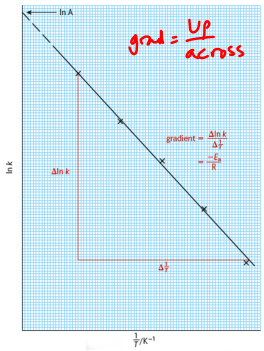
If we take the natural logarithm (logarithm to base e) of both sides of the equation above, we find that

$$\boxed{\ln k = -\frac{E_a}{RT} + \ln A}$$

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$$

$$y = mx + c$$

gradient y-intercept



ln k

1/T

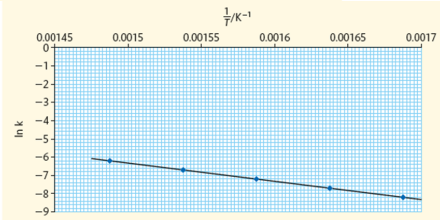
8.31 J K⁻¹ mol⁻¹

Worked example

The following data were collected for a reaction.

Rate constant / s^{-1}	Temperature / °C	Rate constant / s^{-1}	Temperature / °C
2.88×10^{-4}	320	1.26×10^{-3}	380
4.87×10^{-4}	340	1.94×10^{-3}	400
7.96×10^{-4}	360		

Determine the activation energy for the reaction in kJ mol^{-1} by a graphical method.



measured gradient = −9518.65 K

gradient = $-\frac{E_a}{R}$

E_a (J mol^{-1}) = 9518.65 (K) × 8.31 (J K^{-1} mol^{-1})

Therefore E_a = 79.1 kJ mol^{-1}

Solving simultaneous equations

Activation energy can also be calculated from values of the rate constant, k, at only two temperatures. The formula is derived as follows:

At temperature T_1 where the rate constant is k_1:

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A$$

At temperature T_2 where the rate constant is k_2:

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

By subtracting the second equation from the first, we can derive the following equation:

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This equation is also given in section 1 of the IB data booklet.

$$E_a = \frac{\left(\ln\frac{k_1}{k_2}\right)\cdot R}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Worked example

The table below shows data of rate constants for the gas-phase decomposition of hydrogen iodide at two different temperatures.

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

Temperature / °C	Rate constant / mol dm^{-3} s^{-1}
283	3.52×10^{-7}
508	3.95×10^{-2}

Calculate the activation energy for the reaction.

Solution

Convert temperatures in °C to K: $T_1 = 556$ K and $T_2 = 781$ K.

Substituting the values into the equation:

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{3.52\times10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{3.95\times10^{-2}\ \text{mol dm}^{-3}\ \text{s}^{-1}}\right) = \frac{E_a}{8.31\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{781\ \text{K}} - \frac{1}{556\ \text{K}}\right)$$

$$E_a = 1.87 \times 10^5\ \text{J mol}^{-1}$$

NATURE OF SCIENCE

The effect of increasing temperature on increasing the rate of reactions is widely observed in everyday examples such as puddles of water drying up more quickly when the weather is warmer. This temperature effect on rate can be broadly understood and explained in terms of the kinetic molecular theory and collision theory. But this approach is only qualitative. The significance of the Arrhenius equation is that it proposes a quantitative model to explain the effect of temperature change on reaction rate. Because this leads to testable predictions, it means that data can be generated which lend support to the theory.

11 **(a)** Nitrogen monoxide, NO, is involved in the decomposition of ozone according to the following mechanism.

$$O_3 \rightarrow O_2 + \cancel{O\bullet}$$
$$O_3 + \cancel{NO} \rightarrow \cancel{NO_2} + O_2$$
$$\cancel{NO_2} + \cancel{O\bullet} \rightarrow \cancel{NO} + O_2$$

Overall: $2O_3 \rightarrow 3O_2$

State and explain whether or not NO is acting as a catalyst. (2)

(b) The following is a proposed mechanism for the reaction of NO(g) with H_2(g).

Step 1: $2NO(g) \rightarrow N_2O_2(g)$

Step 2: $N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$

(i) Identify the intermediate in the reaction. (1)

(ii) The observed rate expression is rate $= k\,[NO]^2\,[H_2]$. Assuming that the proposed mechanism is correct, comment on the relative speeds of the two steps. (1)

(c) The following two-step mechanism has been suggested for the reaction of NO_2(g) with CO (g), where $k_2 \gg k_1$.

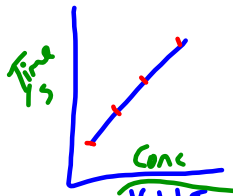
Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ k_1

Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ k_2

Overall: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

The experimental rate expression is rate $= k_1\,[NO_2]^2$. Explain why this mechanism produces a rate expression consistent with the experimentally observed one. (2)

Order of reaction with respect to KI



±0.01 s				Average
Times				7.02

% uncertainty

Average t	% uncert

	Vol KI	V_1 H_2O	V_2	V_3	V_4	Mol KI	Conc KI	% uncertainty
1	25		x	x	x			
2	20							
3	15							
4	10							
5	5							

C = 0.1M

5 cm^3

Qualitative KI was measured

$\frac{0.01}{7.02} \times 100 =$

0.1 cm^3

±0.05 cm^3

Conclusion

Describe correlation shown in graph. General comparison of graph with literature (reference). R^2 → Close to 1

Evaluation → Human reaction time → Random error

Decomposition of KI → I_2 in presence of light/air ↳ Systematic

End point subjectivity → Random

Measuring Parallax error → In this case random