26. Reaction kinetics

26.1 Simple rate equations, orders of reaction and rate constants

Paper 4

Question Paper

1 **(a)** In aqueous solution, persulfate ions, $S_2O_8^{2-}$, react with iodide ions, as shown in reaction 1.

reaction 1 $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

The rate of reaction 1 is investigated.

A sample of $S_2O_8^{2-}$ is mixed with a large excess of iodide ions of known concentration. The graph in Fig. 5.1 shows the results obtained.

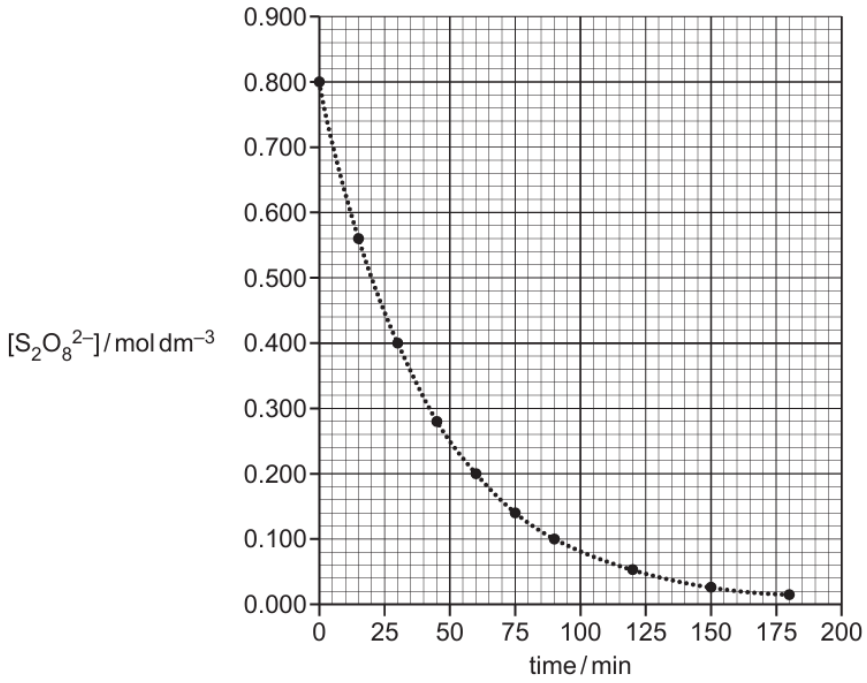


Fig. 5.1

(i) Use Fig. 5.1 to determine the initial rate of reaction 1. Show your working.

rate = ... $mol\,dm^{-3}\,min^{-1}$ [1]

(ii) The rate equation for reaction 1 is rate = $k\,[S_2O_8^{2-}]\,[I^-]$.

Suggest why a large excess of iodide ions allows the rate constant to be determined from the half-life in this investigation.

.....

.....

..... [1]

(c) Describe the effect of an increase in temperature on the rate constant and the rate of reaction 1.

.....

..... [1]

(d) In aqueous solution, thiosulfate ions, $S_2O_3^{2-}$, react with hydrogen ions, as shown in reaction 2.

reaction 2 $S_2O_3^{2-} + 2H^+ \rightarrow SO_2 + S + H_2O$

The rate of reaction is first order with respect to $[S_2O_3^{2-}]$ and zero order with respect to $[H^+]$ under certain conditions.

The rate constant, k, for this reaction is $1.58 \times 10^{-2}\,s^{-1}$.

Calculate the half-life, $t_{\frac{1}{2}}$, for reaction 2.

$t_{\frac{1}{2}}$ = ... s [1]

(e) The compound nitrosyl bromide, NOBr, can be formed as shown in reaction 3.

reaction 3 $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$

The rate is first order with respect to [NO] and first order with respect to $[Br_2]$.

The reaction mechanism has two steps.

Suggest equations for the **two** steps of this mechanism. State which is the rate-determining step.

step 1 .....

step 2 .....

rate-determining step = ...

[2]

2 **(a)** Nitrosyl chloride, NOCl, can be formed by the reaction between nitrogen monoxide and chlorine, as shown.

$$2NO + Cl_2 \rightarrow 2NOCl$$

The initial rate of this reaction is investigated, starting with different concentrations of NO and Cl_2. The results obtained are shown in Table 5.1.

Table 5.1

experiment	[NO] / mol dm^{-3}	[Cl_2] / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1	0.0250	0.0150	3.68×10^{-2}
2	0.0750	0.0150	3.32×10^{-1}
3	0.0500	0.0600	5.89×10^{-1}

(i) Use the data in Table 5.1 to deduce the rate equation for this reaction.

Explain your reasoning.

.....

.....

.....

.....

.....

..... [3]

(ii) Use your rate equation from **(a)(i)** and the data from experiment 1 to calculate the rate constant, *k*, for this reaction. Include the units of *k*.

k = ... units .....

[2]

(b) NO_2Cl is another compound containing nitrogen, oxygen and chlorine.

In sunlight, NO_2Cl can undergo homolytic fission to release chlorine radicals which can catalyse the conversion of ozone, O_3, into oxygen.

Complete the mechanism for this process.

initiation (homolytic fission) $NO_2Cl \rightarrow$ ..... + ...

propagation step 1 ..... + $O_3 \rightarrow$ ..... + ...

propagation step 2 ..... + ... $\rightarrow$ ..... + ...

[2]

(c) Ozone reacts with nitrogen dioxide, as shown.

$$O_3 + 2NO_2 \rightarrow N_2O_5 + O_2$$

The rate of reaction is first order with respect to O_3 and first order with respect to NO_2.

Suggest equations for a two-step mechanism for this reaction.

step 1 .....

step 2 .....

[2]

3 **(a)** The equation for reaction 1 is shown.

reaction 1 $X \rightarrow 2Y$

Reaction 1 is first order with respect to the concentration of X. The half-life of the reaction, $t_{\frac{1}{2}}$, is 900 s at 20 °C.

(i) A solution of X with a concentration of 0.180 mol dm^{-3} is prepared at 20 °C. Calculate the average rate of reaction 1 over the first 1800 s.

average rate of reaction 1 = ... [2]

(ii) Complete the rate equation for reaction 1.

rate = ... [1]

(iii) Show that the rate constant, k, is 7.70×10^{-4} s^{-1} at 20 °C.

[1]

(iv) Calculate the initial rate of reaction 1 when the concentration of X is 0.150 mol dm^{-3}.

Include units.

rate = ... units ..... [2]

4 **(a)** Aqueous acidified iodate(V) ions, IO_3^-, react with iodide ions, as shown.

$$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O$$

The initial rate of this reaction is investigated. Table 3.1 shows the results obtained.

Table 3.1

experiment	$[IO_3^-]$/mol dm^{-3}	$[H^+]$/mol dm^{-3}	$[I^-]$/mol dm^{-3}	initial rate/mol dm^{-3} min^{-1}
1	0.0400	0.0150	0.0250	4.20×10^{-2}
2	0.120	to be calculated	0.0125	7.09×10^{-2}

The rate equation for this reaction is rate = $k[IO_3^-][H^+]^2[I^-]^2$.

(i) Explain what is meant by order of reaction.

.....

.....

..... [1]

(ii) Complete Table 3.2.

Table 3.2

the order of reaction with respect to $[IO_3^-]$	
the order of reaction with respect to $[H^+]$	
the order of reaction with respect to $[I^-]$	
the overall order of reaction	

[1]

(iii) Use your answer to **(a)(ii)** to sketch lines in Fig. 3.1 to show the relationship between the initial rates and the concentrations of $[IO_3^-]$ and $[I^-]$.

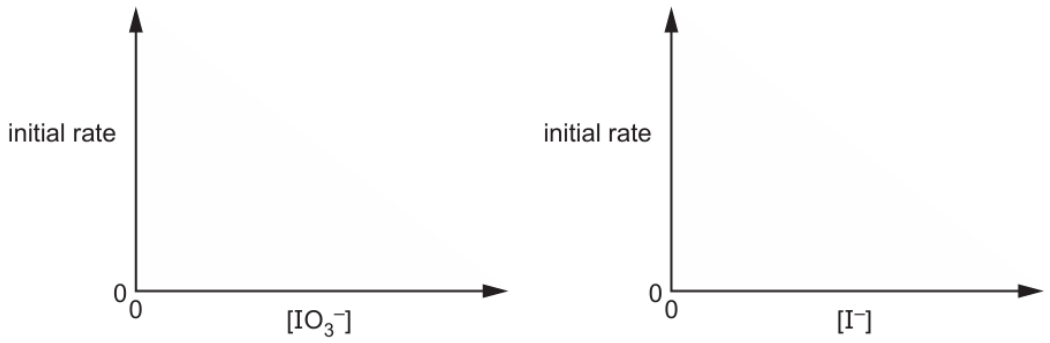


Fig. 3.1

[1]

(iv) Use data from Table 3.1 to calculate the rate constant, k, for this reaction.

Include the units of k.

k = ... units ..... [2]

(v) Use data from Table 3.1 to calculate the concentration of hydrogen ions, $[H^+]$, in experiment 2.

$[H^+]$ = ... $mol\,dm^{-3}$ [1]

(vi) This reaction is repeated in two separate experiments.

The experiments are carried out at the same temperature and with the same concentrations of I^- and IO_3^-.

One experiment takes place at pH 1.0 and the other experiment takes place at pH 2.0.

Calculate the value of $\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$.

value of $\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$ = ... [1]

(b) In aqueous solution, iron(III) ions react with iodide ions, as shown.

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

The initial rate of reaction is first order with respect to Fe^{3+} and second order with respect to I^-.

The mechanism for this reaction has three steps.

Each step involves only **two** ions reacting together.

Suggest equations for the **three** steps of this mechanism. Identify the rate-determining step.

step 1 .....

step 2 .....

step 3 .....

rate-determining step = ...

[3]

5 **(a)** In aqueous solution, iron(III) ions react with iodide ions, as shown.

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

A series of experiments is carried out using different concentrations of Fe^{3+} and I^-, as shown in Table 4.1.

Table 4.1

experiment	$[Fe^{3+}]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.0400	0.0200	2.64×10^{-4}
2	0.1200	0.0200	7.92×10^{-4}
3	0.0800	0.0400	2.11×10^{-3}

(i) Explain what is meant by overall order of reaction.

.....

.....

..... [1]

(ii) Use the data in Table 4.1 to deduce the order of reaction with respect to Fe^{3+} and with respect to I^-.

Explain your reasoning.

.....

.....

.....

..... [2]

(iii) Use your answer to **(a)(ii)** to construct the rate equation for this reaction.

rate = [1]

(iv) Use your answer to **(a)(iii)** and the data from experiment 1 to calculate the rate constant, *k*, for this reaction. Include the units of *k*.

k = ... units ..... [2]

(v) Describe qualitatively the effect of an increase in temperature on the rate constant and on the rate of this reaction.

.....

..... [1]

(b) In aqueous solution, iodide ions react with acidified hydrogen peroxide, as shown.

$$2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$$

The initial rate of reaction is found to be first order with respect to I^-, first order with respect to H_2O_2 and zero order with respect to H^+.

Fig. 4.1 shows a possible four-step mechanism for this reaction.

step 1	$H_2O_2 + I^- \rightarrow IO^- + H_2O$
step 2	$H^+ + IO^- \rightarrow HIO$
step 3	$HIO + I^- \rightarrow I_2 + OH^-$
step 4	$OH^- + H^+ \rightarrow H_2O$

Fig. 4.1

(i) Suggest which of the steps, 1, 2, 3 or 4, in this mechanism is the rate-determining step.

Explain your answer.

.....

.....

..... [1]

(ii) Identify a step in Fig. 4.1 that involves a redox reaction.

Explain your answer in terms of oxidation numbers.

.....

.....

..... [1]

(iii) Suggest the role of HIO in this mechanism.

Explain your reasoning.

.....

.....

..... [1]

6 Fluorine reacts with chlorine dioxide, ClO_2, as shown.

$$F_2(g) + 2ClO_2(g) \rightarrow 2FClO_2(g)$$

The rate of the reaction is first order with respect to the concentration of F_2 and first order with respect to the concentration of ClO_2. No catalyst is involved.

(a) (i) Suggest a two-step mechanism for this reaction.

step 1 →

step 2 →

[2]

(ii) Identify the rate-determining step in this mechanism. Explain your answer.

.....

..... [1]

(b) When the rate of the reaction is measured in $mol\,dm^{-3}\,s^{-1}$ the numerical value of the rate constant, *k*, is 1.22 under certain conditions.

(i) Complete the rate equation for this reaction, stating the overall order of the reaction.

rate =

overall order of reaction =

[1]

(ii) Use your rate equation in **(i)** to calculate the rate of the reaction when the concentrations of F_2 and ClO_2 are both $2.00 \times 10^{-3}\,mol\,dm^{-3}$.

rate = ... $mol\,dm^{-3}\,s^{-1}$ [1]

(c) Under different conditions, and in the presence of a large excess of ClO_2, the rate equation is as shown.

$$\text{rate} = k_1[F_2]$$

The half-life, $t_{\frac{1}{2}}$, of the concentration of F_2 is 4.00 s under these conditions.

(i) Calculate the numerical value of k_1, giving its units.

Give your answer to **three** significant figures.

k_1 = ... units .....

[2]

(ii) An experiment is performed under these conditions in which the starting concentration of F_2 is 0.00200 mol dm^{-3}.

Draw a graph on the grid in Fig. 1.1 to show how the concentration of F_2 changes over the first 12 s of the reaction.

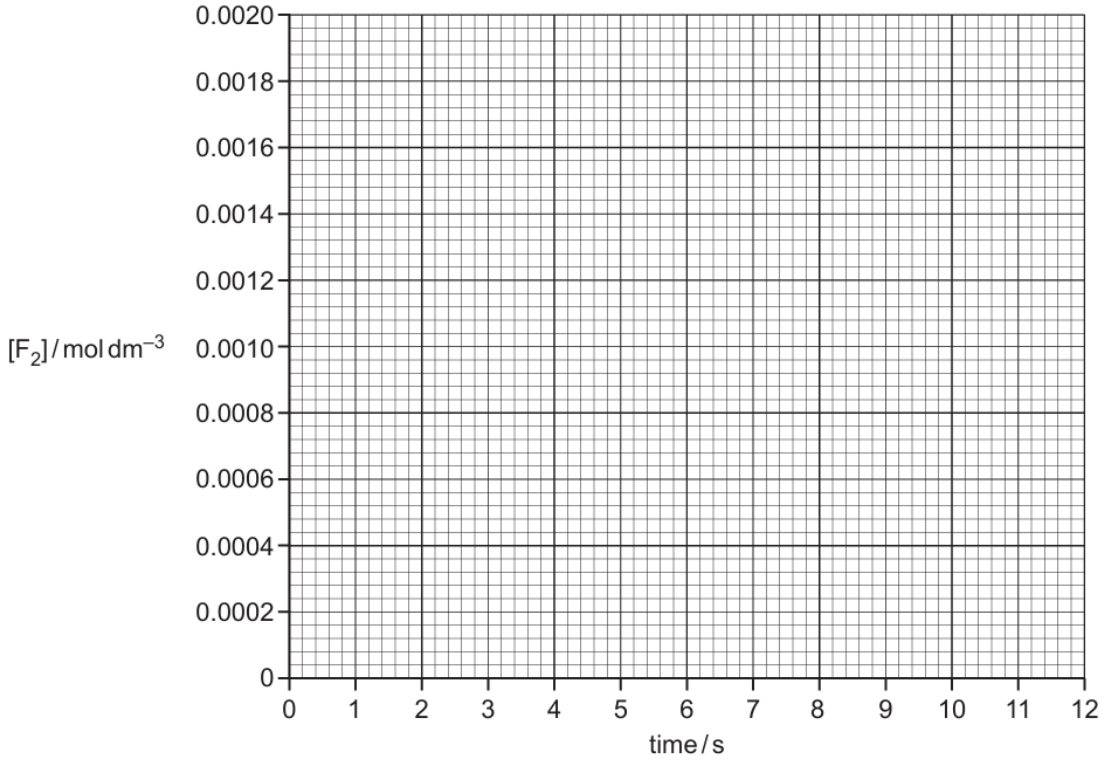


Fig. 1.1

[1]

(iii) Use your graph in Fig. 1.1 to find the rate of the reaction when the concentration of F_2 is 0.00100 mol dm^{-3}. Show your working on the graph.

rate = ... mol dm^{-3} s^{-1} [1]

7 Propanone, CH_3COCH_3, reacts with iodine, I_2, in the presence of an acid catalyst.

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$$

The rate equation for this reaction is shown.

$$\text{rate} = k[CH_3COCH_3][H^+]$$

(a) Complete Table 1.1 to describe the order of the reaction.

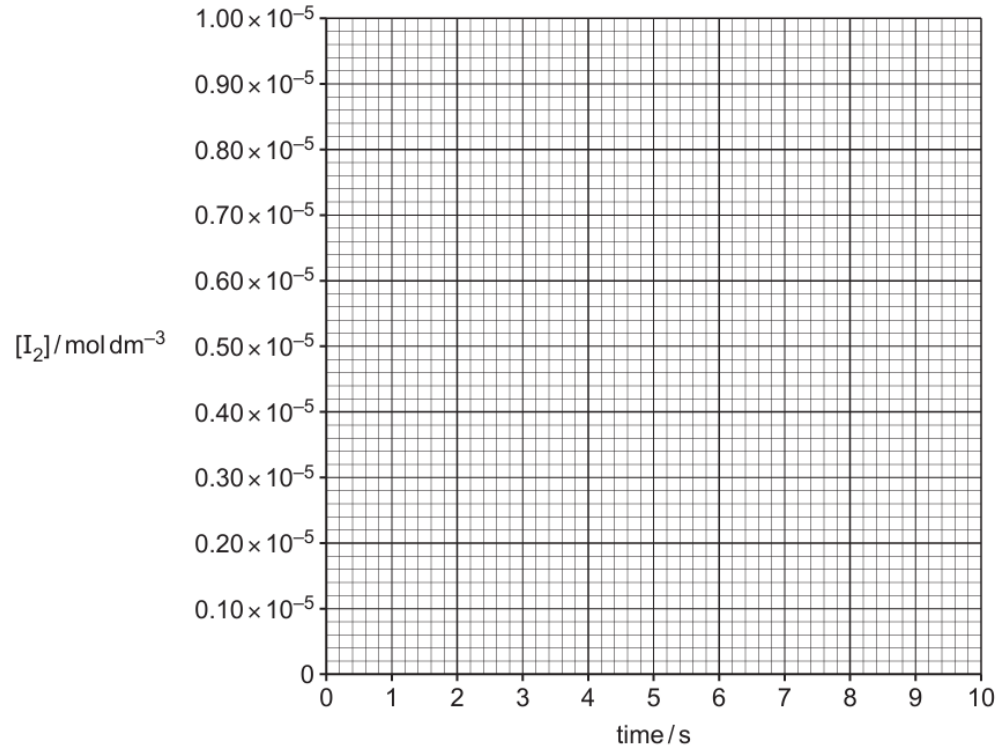
Table 1.1

order of the reaction with respect to $[CH_3COCH_3]$	
order of the reaction with respect to $[I_2]$	
order of the reaction with respect to $[H^+]$	
overall order of the reaction	

[2]

(b) An experiment is performed using a large excess of CH_3COCH_3 and a large excess of $H^+(aq)$. The initial concentration of I_2 is 1.00×10^{-5} mol dm^{-3}. The initial rate of decrease in the I_2 concentration is 2.27×10^{-7} mol dm^{-3} s^{-1}.

(i) Use the axes to draw a graph of $[I_2]$ against time for the first 10 seconds of the reaction.



[1]

(ii) State whether it is possible to calculate the numerical value of the rate constant, k, for this reaction from your graph. Explain your answer.

.....

..... [1]

(c) The experiment is repeated at a different temperature. The initial concentrations of H^+ ions, I_2 and CH_3COCH_3 are all $0.200\,mol\,dm^{-3}$.

The value of k at this temperature is $2.31 \times 10^{-5}\,mol^{-1}\,dm^3\,s^{-1}$.

Calculate the initial rate of this reaction.

rate = ... $mol\,dm^{-3}\,s^{-1}$ [1]

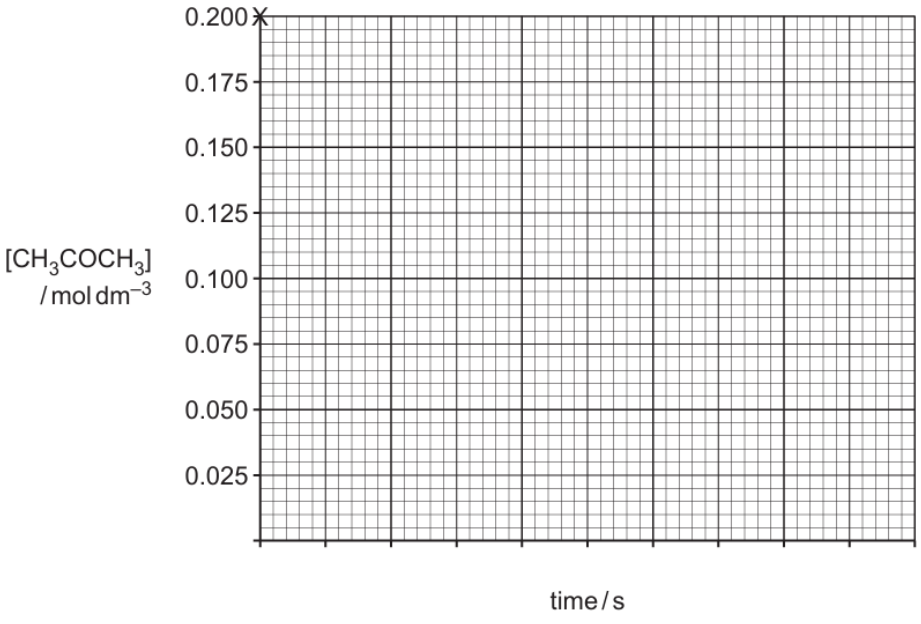
(d) The experiment is repeated using an excess of $H^+(aq)$. The new rate equation is shown.

$$rate = k_1[CH_3COCH_3]$$

(i) The value of k_1 is $1.1 \times 10^{-3}\,s^{-1}$. Calculate the value of the half-life, $t_{\frac{1}{2}}$.

$t_{\frac{1}{2}}$ = ... s [1]

(ii) Use your answer to **(i)** to draw a graph of $[CH_3COCH_3]$ against time for this reaction. The initial value of $[CH_3COCH_3]$ on your graph should be $0.200\,mol\,dm^{-3}$. The final value of $[CH_3COCH_3]$ on your graph should be $0.0250\,mol\,dm^{-3}$.



[1]

(e) A four-step mechanism is suggested for the overall reaction.

$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$ rate = $k[CH_3COCH_3][H^+]$

Part of this mechanism is shown.

step 1: $CH_3COCH_3 + H^+ \rightarrow CH_3C^+(OH)CH_3$

step 2: $CH_3C^+(OH)CH_3 \rightarrow CH_3C(OH)=CH_2 + H^+$

step 3: $\rightarrow$

step 4: $CH_3C^+(OH)CH_2I \rightarrow CH_3COCH_2I + H^+$

(i) Write an equation for step 3.

..... [1]

(ii) Suggest the slowest step of the mechanism. Explain your answer.

.....

..... [1]

(iii) Identify one conjugate acid-conjugate base pair in the mechanism.

conjugate acid ..... conjugate base ..... [1]

8 **(a)** The rate of reaction between 2-chloro-2-methylpropane, $(CH_3)_3CCl$, and methanol is investigated. When a large excess of methanol is used, the overall reaction is first order.

$$(CH_3)_3CCl + CH_3OH \rightarrow (CH_3)_3COCH_3 + HCl$$

Fig. 3.1 shows the results obtained.

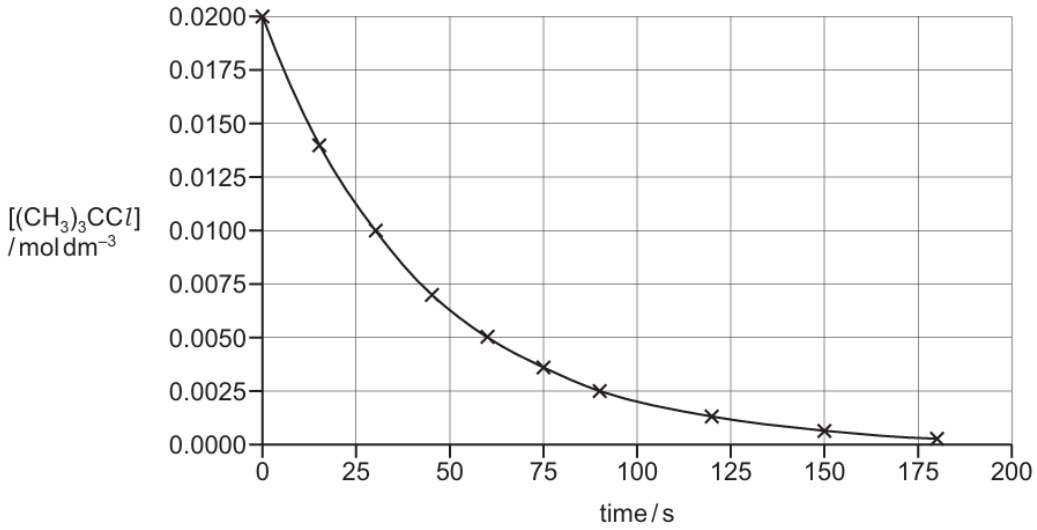


Fig. 3.1

(i) Use the graph to determine the rate of reaction at 40 s. Show all your working.

rate = ... mol dm^{-3} s^{-1} [1]

(ii) Use the graph to show that the overall reaction is first order. Explain your answer.

.....

.....

..... [2]

(b) In a different reaction, which is also a first order reaction, 75% of the reactant is consumed in 320 s.

Calculate the rate constant, *k*, for this reaction. State the units for *k*.

k = ... units = ... [2]

9 **(b)** Nitrogen monoxide reacts with oxygen.

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

This reaction is second order with respect to nitrogen monoxide and first order with respect to oxygen.

Under certain conditions the value of the rate constant, k, is $8.60 \times 10^6\,mol^{-2}\,dm^6\,s^{-1}$.

(i) Construct the rate equation for this reaction.

rate =

[1]

(ii) Calculate the initial rate of the reaction under these conditions when the initial concentration of nitrogen monoxide is $7.20 \times 10^{-4}\,mol\,dm^{-3}$ and the initial concentration of oxygen is $1.90 \times 10^{-3}\,mol\,dm^{-3}$.

rate of reaction = ... $mol\,dm^{-3}\,s^{-1}$ [1]

(c) The drug cisplatin, $Pt(NH_3)_2Cl_2$, hydrolyses in water.

$$Pt(NH_3)_2Cl_2 + H_2O \rightarrow [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$$

The rate equation is shown.

$$rate = k[Pt(NH_3)_2Cl_2]$$

The value of k is $2.50 \times 10^{-5}\,s^{-1}$ under certain conditions.

(i) This reaction has a constant half-life.

Explain why this is the case.

.....

..... [1]

(ii) Use the information in this question to show that the half-life of this reaction is 2.77×10^4 s.

[1]

(iii) 8.00×10^{-6} moles of $Pt(NH_3)_2Cl_2$ are added to $100\,cm^3$ of water.

Calculate the time taken for the concentration of $Pt(NH_3)_2Cl_2$ to fall to $2.50 \times 10^{-6}\,mol\,dm^{-3}$.

time taken = ... s [2]

10 Nitrogen monoxide, NO, reacts with ozone, O_3.

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

This reaction is first order with respect to both NO and O_3.
At 298 K, the rate constant $k = 11\,500\,mol^{-1}\,dm^3\,s^{-1}$.

(i) Complete the rate equation for this reaction.

rate = ...
[1]

(ii) A reaction is carried out in which the initial concentrations of NO and O_3 are both $1.20 \times 10^{-6}\,mol\,dm^{-3}$.

Calculate the initial rate of the reaction. State its units.

rate of reaction = ... units = ... [2]

(iii) The reaction described in **(a)(ii)** is monitored over a period of time.

Predict whether or not the graph of [NO] against time, under these conditions, shows that the reaction has a constant half-life. Explain your answer.

prediction .....

explanation .....

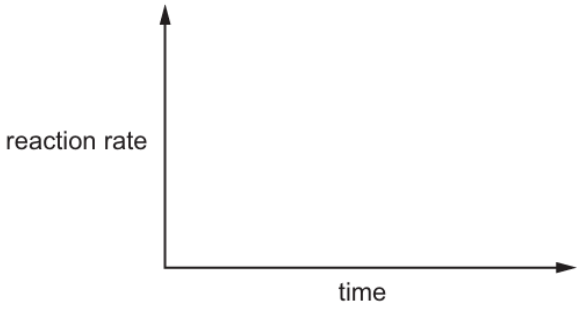
..... [1]

(b) Nitrous oxide, N_2O, decomposes into its elements.

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

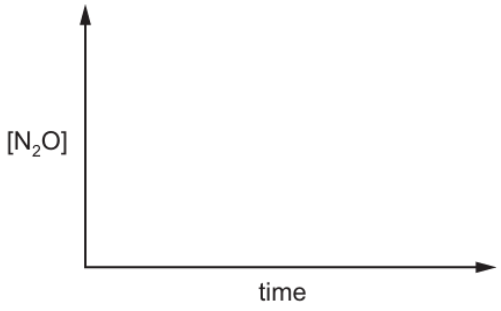
At a high temperature, a small amount of platinum wire is added to a large amount of nitrous oxide. The reaction follows zero order kinetics. The platinum wire behaves as a catalyst.

(i) Sketch a graph, on the axes below, of reaction rate against time for the catalysed decomposition of N_2O under these conditions.



[1]

(ii) Sketch a graph, on the axes below, of $[N_2O]$ against time for this reaction.



[1]

(iii) Platinum behaves as a heterogeneous catalyst in this reaction.

Describe the mode of action of a heterogeneous catalyst.

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.....

.....

..... [3]

(iv) Suggest a reason why this reaction has zero order kinetics when the amount of nitrous oxide is large and the amount of platinum is small.

.....

..... [1]

11 **(a)** In aqueous solution, chlorine dioxide, ClO_2, reacts with hydroxide ions as shown.

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$$

A series of experiments is carried out using different concentrations of ClO_2 and OH^-. The table shows the results obtained.

experiment	$[ClO_2]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1	0.020	0.030	7.20×10^{-4}
2	0.020	0.120	2.88×10^{-3}
3	0.050	0.030	4.50×10^{-3}

(i) Explain the term *order of reaction*.

.....

..... [1]

(ii) Use the data in the table to determine the order of reaction with respect to each reactant, ClO_2 and OH^-.

Explain your reasoning.

.....

.....

.....

.....

.....

..... [2]

(iii) Use your answer to **(a)(ii)** to construct the rate equation for this reaction.

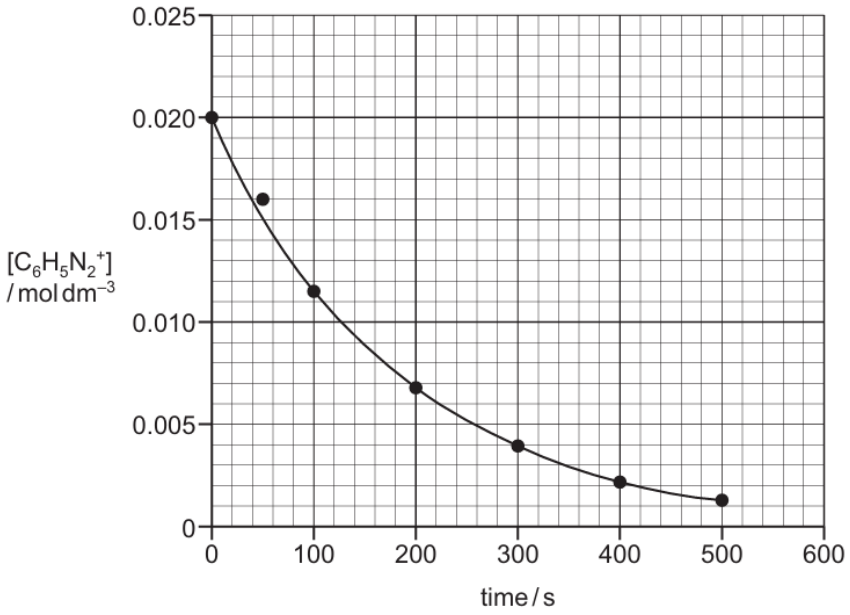
rate = ... [1]

(iv) Use your rate equation and the data from experiment 1 to calculate the rate constant, *k*, for this reaction.
Include the units of *k*.

k = ... units ..... [2]

(b) The decomposition of benzenediazonium ions, $C_6H_5N_2^+$, using a large excess of water, is a first-order reaction.

The graph shows the results obtained.



(i) Draw the structure of the organic product formed in this reaction.

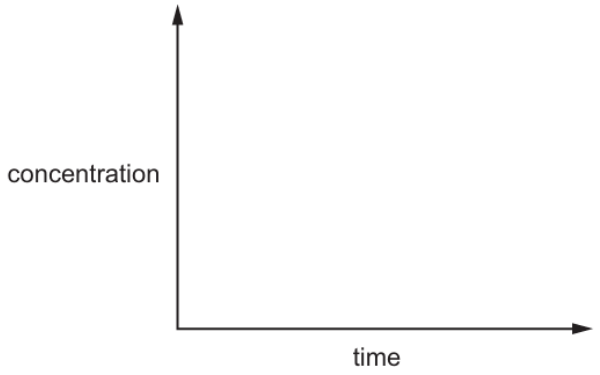
[1]

(ii) Use the graph to determine the rate of reaction at 100 s. Show your working.

rate = ... mol dm^{-3} s^{-1} [1]

(c) Sketch a concentration–time graph for a **zero-order** reaction.

Use your graph to suggest how successive half-lives for a zero-order reaction vary as the concentration of a reactant decreases. Indicate this by placing a tick (✓) in the appropriate box in the table.



successive half-lives decrease	no change in successive half-lives	successive half-lives increase

[1]

12 **(b)** The equation for the decomposition of hydrogen peroxide without a catalyst is shown.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Under certain conditions this reaction is found to be first order with respect to hydrogen peroxide, with a rate constant, k, of $2.0 \times 10^{-6}\,s^{-1}$ at 298 K.

Calculate the initial rate of decomposition of a $0.75\,mol\,dm^{-3}$ hydrogen peroxide solution at 298 K.

initial rate = ... $mol\,dm^{-3}\,s^{-1}$ [1]

(c) A four-step mechanism is suggested for the reaction between hydrogen peroxide and iodide ions in an acidic solution.

step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$

step 2 $H^+ + IO^- \rightarrow HIO$

step 3 $HIO + I^- \rightarrow I_2 + OH^-$

step 4 $OH^- + H^+ \rightarrow H_2O$

Step 1 is the rate-determining step.

(i) State what is meant by the term *rate-determining step*.

.....

..... [1]

(ii) Use this mechanism to construct a balanced equation for this reaction.

..... [1]

(iii) Deduce the order of reaction with respect to each of the following.

H_2O_2 = ... I^- = ... H^+ = ... [1]

13 Iodate(V) ions react with sulfite ions in acidic solution at pH 5.00 as shown.

$$IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-}$$

The initial rate of reaction was found to be first order with respect to IO_3^-, first order with respect to SO_3^{2-} and first order with respect to H^+.

(i) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ... $mol\,dm^{-3}\,s^{-1}$

units of *k* = ...
[2]

(ii) The rate of reaction depends on the pH of the solution. Assume all other concentrations remain the same.

Use the expression $x = \frac{\text{rate at pH 5.00}}{\text{rate at pH 4.00}}$ to calculate the value of x.

x = ... [1]

14 Nitrogen monoxide, NO, reacts with oxygen to form nitrogen dioxide, NO_2.

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

The rate equation for the forward reaction is shown.

$$\text{rate} = k[NO]^2[O_2]$$

(a) Complete the following table.

the order of reaction with respect to [NO]	
the order of reaction with respect to $[O_2]$	
the overall order of reaction	

[1]

(b) Two separate experiments are carried out at 30 °C to determine the rate of the forward reaction.

experiment	$[NO]$ / mol dm^{-3}	$[O_2]$ / mol dm^{-3}	rate / mol dm^{-3} s^{-1}
1	0.00300	0.00200	1.51×10^{-4}
2		0.00500	6.05×10^{-5}

(i) Use the data for experiment 1 to calculate the value of the rate constant, *k*. State the units of *k*.

k = ... units = ...

[2]

(ii) Calculate the value of [NO] in experiment 2.

[NO] = ... mol dm^{-3} [1]

(c) Define the term *rate-determining step*.

..... [1]

(d) Peroxodisulfate ions, $S_2O_8^{2-}$, react with iodide ions, I^-.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

The rate equation for the reaction in the absence of any catalyst is shown.

$$\text{rate} = k[S_2O_8^{2-}][I^-]$$

(i) Suggest equations for a two-step mechanism for this reaction, stating which of the two steps is the rate-determining step.

step 1 .....

step 2 .....

rate-determining step = ...

[2]

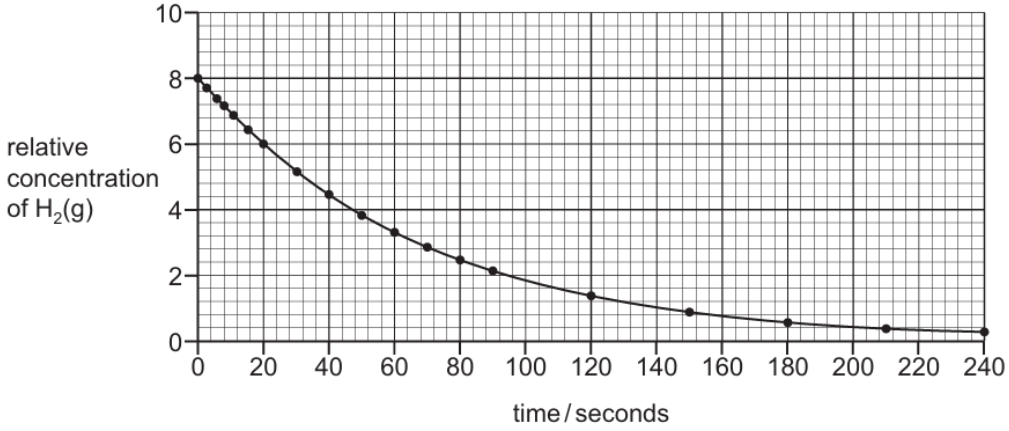
(ii) A large excess of peroxodisulfate ions is mixed with iodide ions. Immediately after mixing, $[I^-] = 0.00780\,\text{mol dm}^{-3}$. Under the conditions used, the half-life of $[I^-]$ is 48 seconds.

Calculate the iodide ion concentration 192 seconds after the peroxodisulfate and iodide ions are mixed.

iodide ion concentration = ... mol dm^{-3} [1]

15 The rate of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is studied.

(a) A small amount of $H_2(g)$ is mixed with a large excess of $I_2(g)$ at a temperature of 400 K and the reaction is monitored. The graph obtained is shown.



(i) Suggest why a large excess of $I_2(g)$ is used in this experiment.

..... [1]

(ii) The reaction is first order with respect to $H_2(g)$.

Use data from the graph to confirm this statement.

.....

.....

.....

..... [2]

(b) Three separate experiments were carried out at 400 K with different starting concentrations of $H_2(g)$ and $I_2(g)$. The results are shown in the table.

experiment	$[H_2(g)]$ / mol dm^{-3}	$[I_2(g)]$ / mol dm^{-3}	rate of reaction / mol dm^{-3} s^{-1}
1	1.0×10^{-2}	1.0×10^{-2}	2.0×10^{-17}
2	1.0×10^{-1}	1.0×10^{-1}	2.0×10^{-15}
3	5.0×10^{-1}	5.0×10^{-1}	5.0×10^{-14}

(i) Use the data, and the order of reaction with respect to $H_2(g)$ given in **(a)(ii)**, to deduce the order of reaction with respect to $I_2(g)$.

Explain your answer, giving data in support of your explanation.

.....

.....

.....

..... [3]

(ii) Use information from **(a)(ii)** and your answer to **(b)(i)** to write the rate equation for the forward reaction.

rate = ... [1]

(iii) Use your rate equation and data from experiment 1 to calculate the value of the rate constant, *k*, for the forward reaction at 400 K. Include units for *k*.

k = ... units = ...
[2]

(c) At 400 K the rate constant for the forward reaction is approximately 1000 times greater than the rate constant for the backward reaction. The overall orders of the forward and backward reactions are the same.

forward reaction	$H_2(g) + I_2(g) \rightarrow 2HI(g)$
backward reaction	$2HI(g) \rightarrow H_2(g) + I_2(g)$

(i) Use this information to explain what will happen if equal concentrations of $HI(g)$, $H_2(g)$ and $I_2(g)$ are mixed at 400 K.

You should comment on:
- the relative initial rates of the forward and backward reactions
- the position of the equilibrium reached.

.....

.....

..... [1]

(ii) At 700 K the rate constant for the forward reaction is approximately 50 times greater than the rate constant for the backward reaction.

Use this information and the information in **(c)(i)** to deduce the signs of the ΔH values of the forward and backward reactions. Explain your answer.

.....

.....

.....

..... [2]

16 **(a)** Chlorate(I) ions undergo the following reaction under aqueous conditions.

$$2NH_3 + Cl O^- \rightarrow N_2H_4 + Cl^- + H_2O$$

A series of experiments was carried out at different concentrations of $Cl O^-$ and NH_3.

The table shows the results obtained.

experiment	$[Cl O^-]$ / mol dm^{-3}	$[NH_3]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.200	0.100	0.256
2	0.400	0.200	2.05
3	0.400	0.400	8.20

(i) Use the data in the table to determine the order with respect to each reactant, $Cl O^-$ and NH_3.

Show your reasoning.

.....

.....

.....

.....

.....

..... [2]

(ii) Write the rate equation for this reaction.

rate = ... [1]

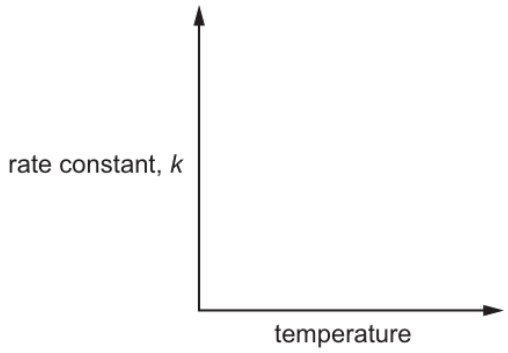
(iii) Use the results of experiment 1 to calculate the rate constant, *k*, for this reaction. Include the units of *k*.

k = ...

units = ...

[2]

(iv) On the axes sketch a graph to show how the value of k changes as temperature is increased.



[1]

A solution of iodide ions in aqueous alkali was added to a large excess of chlorate(I) ions and $[I^-]$ was measured at regular intervals.

(i) Describe how the results of this experiment can be used to confirm that the reaction is first-order with respect to $[I^-]$.

.....

.....

..... [2]

A three-step mechanism for this reaction is shown.

step 1 $Cl O^- + H_2O \rightarrow HCl O + OH^-$

step 2 $I^- + HCl O \rightarrow HIO + Cl^-$

step 3 $HIO + OH^- \rightarrow H_2O + IO^-$

(ii) Use this mechanism to deduce the overall equation for this reaction.

..... [1]

(iii) Identify a step that involves a redox reaction. Explain your answer.

.....

..... [1]

17 The initial rate of reaction for propanone and iodine in acid solution is measured in a series of experiments at a constant temperature.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+ \text{ catalyst}} CH_3COCH_2I + HI$$

The rate equation was determined experimentally to be as shown.

$$\text{rate} = k[CH_3COCH_3][H^+]$$

(a) State the order of reaction with respect to

- CH_3COCH_3 .....
- I_2 .....
- H^+ .....

and state the overall order of this reaction. .....

[2]

(b) The rate of this reaction is 5.40×10^{-3} mol dm^{-3} s^{-1} when

- the concentration of CH_3COCH_3 is 1.50×10^{-2} mol dm^{-3}
- the concentration of I_2 is 1.25×10^{-2} mol dm^{-3}
- the concentration of H^+ is 7.75×10^{-1} mol dm^{-3}.

(i) Calculate the rate constant, k, for this reaction. State the units of k.

k = ...

units = ...

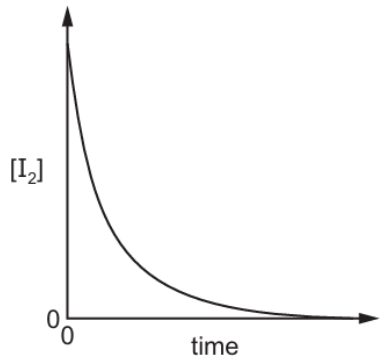
[2]

(ii) Complete the table by placing **one** tick (✓) in each row to describe the effect of **decreasing** the temperature on the rate constant and on the rate of reaction.

	decreases	no change	increases
rate constant			
rate of reaction			

[1]

(c) From the results, a graph is produced which shows how the concentration of I_2 changes during the reaction.



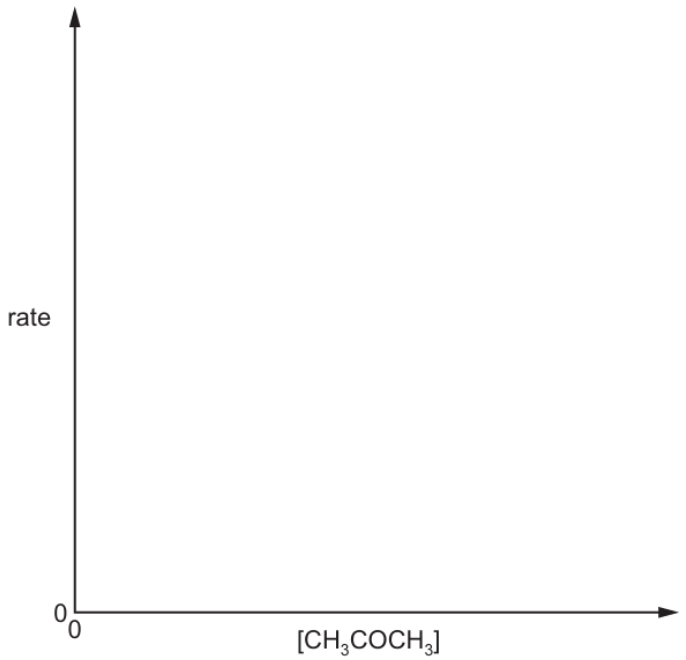
Describe how this graph could be used to determine the initial rate of the reaction.

.....

.....

..... [2]

(d) On the axes below, sketch a graph to show how the initial rate changes with different initial concentrations of CH_3COCH_3 in this reaction.



[1]

(e) The rate of a reaction between metal ions was studied. The following three-step mechanism has been suggested for this reaction. Step 1 is the rate-determining step.

step 1 $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$

step 2 $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$

step 3 $Mn^{4+} + Tl^{+} \rightarrow Tl^{3+} + Mn^{2+}$

(i) Explain the meaning of the term *rate-determining step*.

.....

..... [1]

(ii) Use this mechanism to

- determine the overall equation for this reaction

.....

- suggest the role of Mn^{2+} ions in this mechanism. Explain your answer.

.....

.....

.....

[2]

18 When $ClNO_2$ reacts with NO an equilibrium is established.

$$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$$

In each $ClNO_2$ molecule the nitrogen atom is bonded to the chlorine atom and bonded to each of the oxygen atoms separately.

(a) Draw a 'dot-and-cross' diagram for the $ClNO_2$ molecule.

[2]

(b) The reaction between $ClNO_2$ and NO is first order with respect to each reactant.

(i) Write the rate equation for this reaction.

rate = ... [1]

(ii) Deduce the units of the rate constant, k, when the concentrations of both gases are measured in mol dm^{-3} and the rate is measured in mol dm^{-3} s^{-1}.

..... [1]

(iii) State and explain whether or not the reaction **could** take place in a single step.

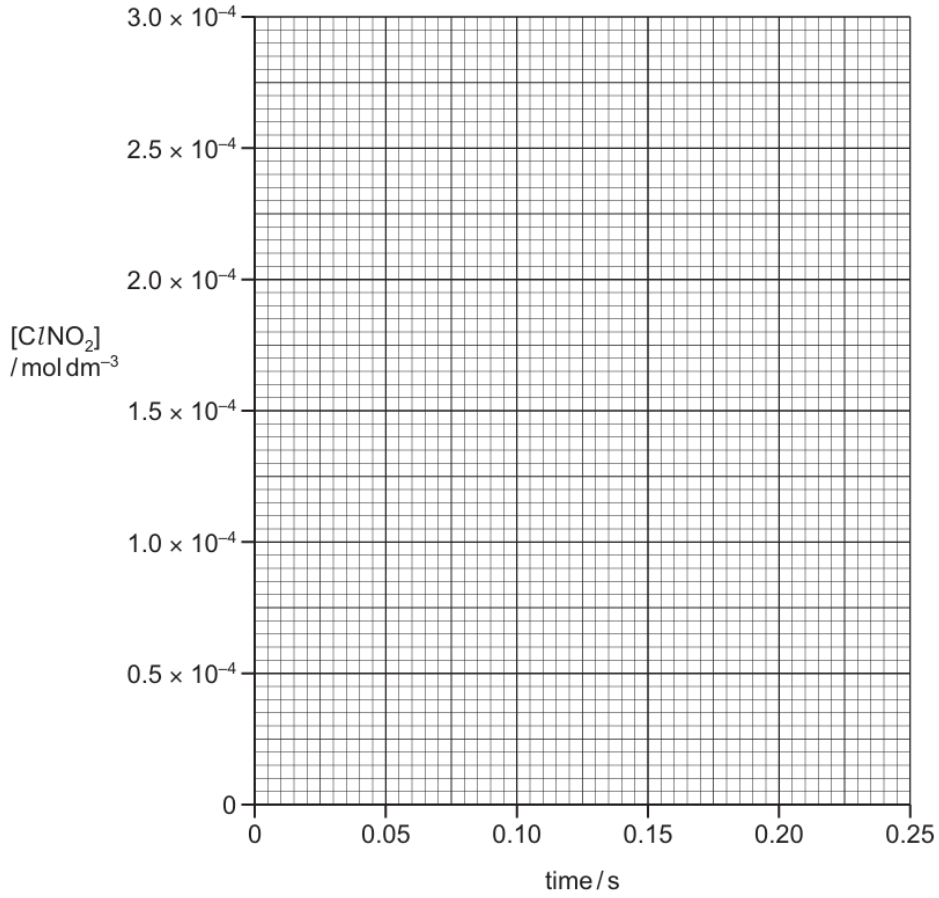
.....

.....

..... [1]

(c) An experiment is carried out in which the initial [$ClNO_2$] is 2.0×10^{-4} mol dm^{-3}. A large excess of NO is used. The initial rate of reaction is 1.0×10^{-4} mol dm^{-3} s^{-1}. The rate of the reaction is assumed to be constant for the first 0.20 seconds.

(i) Draw a graph on the grid to show how the concentration of $ClNO_2$ varies for the first 0.20 seconds.



[2]

(ii) Deduce the concentration of the NO_2 product at 0.20 seconds.

..... [1]

(iii) After 20 seconds the concentration of $ClNO_2$ remains constant.

Explain this observation.

..... [1]

19 **(a)** Explain what is meant by the following terms.

half-life of a reaction .....

.....

rate-determining step .....

.....

[2]

(b) The reaction between hydroxide ions and bromomethane is first order with respect to $[OH^-]$ and first order with respect to $[CH_3Br]$.

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

Suggest a practical method that would confirm that the reaction is first order with respect to $[OH^-]$.

- Your method should include details of measurements that would be taken in order to calculate the rate of the reaction.
- You should include a method of presenting the results to show that the reaction is first order with respect to $[OH^-]$.

.....

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.....

.....

..... [4]

(c) The hydrolysis of methyl ethanoate, $CH_3CO_2CH_3$, by hydroxide ions, OH^-, is first order with respect to $[CH_3CO_2CH_3]$ and also first order with respect to $[OH^-]$.

In a particular experiment,

- $[CH_3CO_2CH_3] = 0.100\,mol\,dm^{-3}$
- $[OH^-] = 0.100\,mol\,dm^{-3}$
- rate of reaction = $2.06 \times 10^{-3}\,mol\,dm^{-3}\,s^{-1}$.

Write a rate equation for this reaction and calculate the value of the rate constant, k, under these conditions. State the units of k.

rate = ...

k = ... units = ...

[3]

20 Nitrogen monoxide, NO(g), reacts with hydrogen, $H_2(g)$, under certain conditions.

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

(a) Define the term *rate of reaction*.

.....

..... [1]

(b) Identify a change in the reaction mixture that would enable the rate of this reaction to be studied.

..... [1]

The rate equation for this reaction is given.

$$\text{rate} = k[NO]^2[H_2]$$

The result of an experiment in which NO reacted with H_2 is shown in the table.

initial [NO] / mol dm^{-3}	initial [H_2] / mol dm^{-3}	initial rate of reaction / mol dm^{-3} s^{-1}
2.50×10^{-3}	2.50×10^{-3}	1.27×10^{-3}

(c) Use the data and the rate equation to calculate a value for the rate constant *k*.
Give the units of *k*.

k = ...

units = ...
[2]

(d) A second experiment is performed at the same temperature. The initial concentration of $H_2(g)$ is 4.60×10^{-3} mol dm^{-3}. The initial rate of the reaction is 2.31×10^{-3} mol dm^{-3} s^{-1}.

Calculate the initial concentration of NO(g).

initial concentration of NO(g) = ... mol dm^{-3} [1]

(e) State the order of the reaction with respect to NO(g) and with respect to H_2(g), and the overall order of the reaction.

[NO]	
[H_2]	
overall order	

[1]

(f) The reaction is believed to proceed in three steps.

1 $2NO \rightarrow N_2O_2$

2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$

3 $N_2O + H_2 \rightarrow N_2 + H_2O$

(i) Deduce which of the three steps is the rate-determining step.

..... [1]

(ii) Explain your answer to **(i)**.

.....

.....

..... [1]

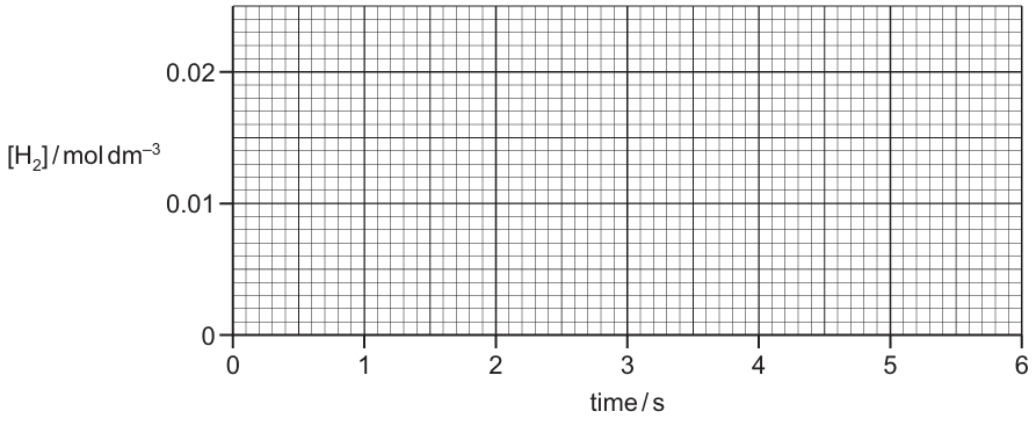
(g) A third experiment is performed under different conditions. A small amount of $H_2(g)$ of concentration $0.0200\,mol\,dm^{-3}$ is mixed with a large excess of NO(g). The concentration of $H_2(g)$ is found to have a constant half-life of 2.00 seconds under the conditions used.

(i) Define the term *half-life*.

.....

..... [1]

(ii) Use the axes below to construct a graph of the variation in the concentration of $H_2(g)$ during the first 6 seconds under the conditions used.



[2]

(h) NO(g) acts as a catalyst in the oxidation of atmospheric sulfur dioxide.

(i) Give two equations to describe how NO(g) acts as a catalyst in this process.

equation 1 .....

equation 2 .....

[1]

(ii) Explain why NO(g) can be described as a catalyst in this reaction.

.....

..... [1]

(iii) Describe, with the aid of an equation, an environmental consequence of the oxidation of atmospheric sulfur dioxide.

.....

..... [1]

21 Iodine monochloride, ICl, is a yellow-brown gas. It reacts with hydrogen gas under certain conditions as shown.

$$2ICl(g) + H_2(g) \rightarrow 2HCl(g) + I_2(g)$$

Experiments are performed using different starting concentrations of ICl and H_2. The initial rate of each reaction is measured. The following results are obtained.

experiment	[ICl] / mol dm^{-3}	[H_2] / mol dm^{-3}	relative rate of reaction
1	4.00×10^{-3}	4.00×10^{-3}	1.00
2	4.00×10^{-3}	7.00×10^{-3}	1.75
3	4.00×10^{-3}	1.00×10^{-2}	2.50
4	5.00×10^{-3}	8.00×10^{-3}	2.50
5	7.00×10^{-3}	8.00×10^{-3}	3.50

(a) Identify a change, taking place in the reaction mixture, that would enable measurements of the rate of this reaction to be made.

..... [1]

(b) Use the data in the table to show that the reaction is first order with respect to $H_2(g)$.

.....

.....

.....

..... [1]

(c) Use the data in the table to show that the reaction is first order with respect to ICl(g).

.....

.....

.....

..... [1]

(d) Complete the rate equation for the reaction between ICl(g) and $H_2(g)$.

rate = ... [1]

(e) Use experiment 3 to calculate a numerical value for the rate constant, *k*.

k = ... [1]

(f) The reaction $2IC\ell(g) + H_2(g) \rightarrow 2HC\ell(g) + I_2(g)$ is first order with respect to $IC\ell(g)$ and first order with respect to $H_2(g)$.

Suggest a mechanism for this reaction. You should assume

- the mechanism has two steps,
- the first step is much slower than the second step.

first step ..... → .....

second step ..... → .....
[2]

(g) An alternative method is used to show that the reaction is first order with respect to $H_2(g)$. This method uses a large excess of $IC\ell(g)$ and measures how the concentration of $H_2(g)$ varies with time.

(i) Describe two ways of using these results to show the reaction is first order with respect to $H_2(g)$ concentration.

.....

.....

.....

.....

.....

..... [3]

(ii) Explain the reason for using a large excess of $IC\ell(g)$.

.....

..... [1]