1. 9701_s21_qp_43 Q5

5 Dinitrogen pentoxide, N_2O_5, is dissolved in an inert solvent (solv) and the rate of decomposition of N_2O_5 is investigated. This reaction produces nitrogen dioxide, which remains in solution, and oxygen gas.

$$N_2O_5(solv) \rightarrow 2NO_2(solv) + \tfrac{1}{2}O_2(g)$$

(a) Suggest what measurements could be used to follow the rate of this reaction from the given information.

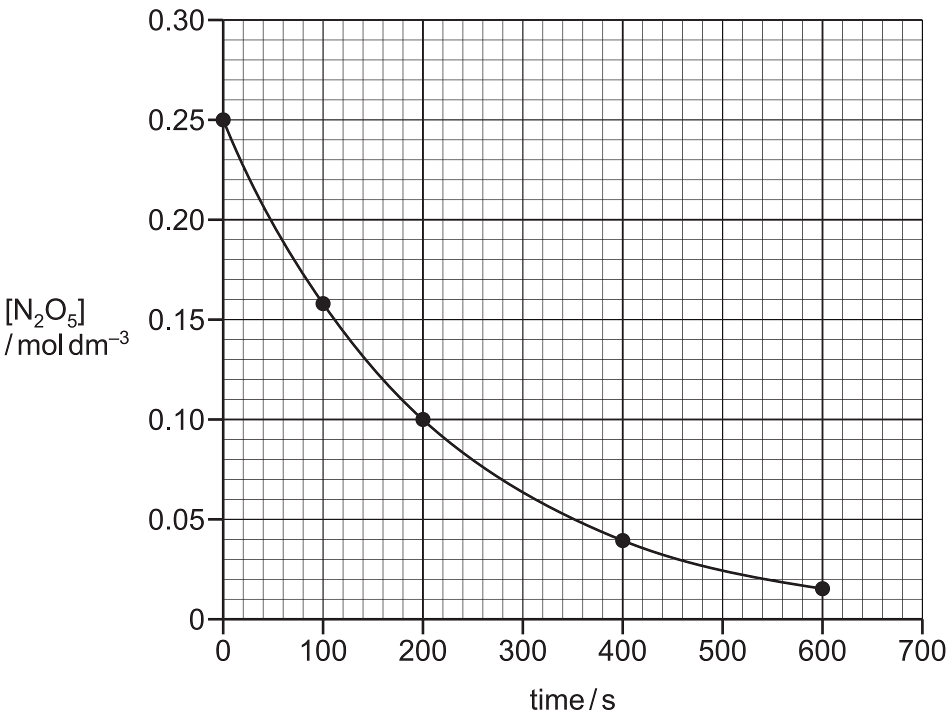
....

.... [1]

(b) In a separate experiment, the rate of the decomposition of $N_2O_5(g)$ is investigated.

$$N_2O_5(g) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

The graph shows the results obtained.



The reaction is first order with respect to N_2O_5. This can be confirmed from the graph using half-lives.

(i) Explain the term *half-life of a reaction*.

....

.... [1]

(ii) Determine the half-life of this reaction. Show your working on the graph.

half-life = ... s [1]

(iii) Suggest the effect on the half-life of this reaction if the initial concentration of N_2O_5 is halved.

.... [1]

(c) **(i)** Use the graph in **5(b)** to determine the rate of reaction at 200 s. Show your working.

rate = ...

units = ...
[2]

The rate equation for this reaction is shown.

$$\text{rate} = k[N_2O_5]$$

(ii) Use your answer to **(c)(i)** to calculate the value of the rate constant, k, for this reaction and state its units.

k = ... units .... [1]

(d) Nitrogen dioxide reacts with ozone, O_3, as shown.

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

The rate equation for this reaction is rate = $k[NO_2][O_3]$.

Suggest a possible two-step mechanism for this reaction.

....

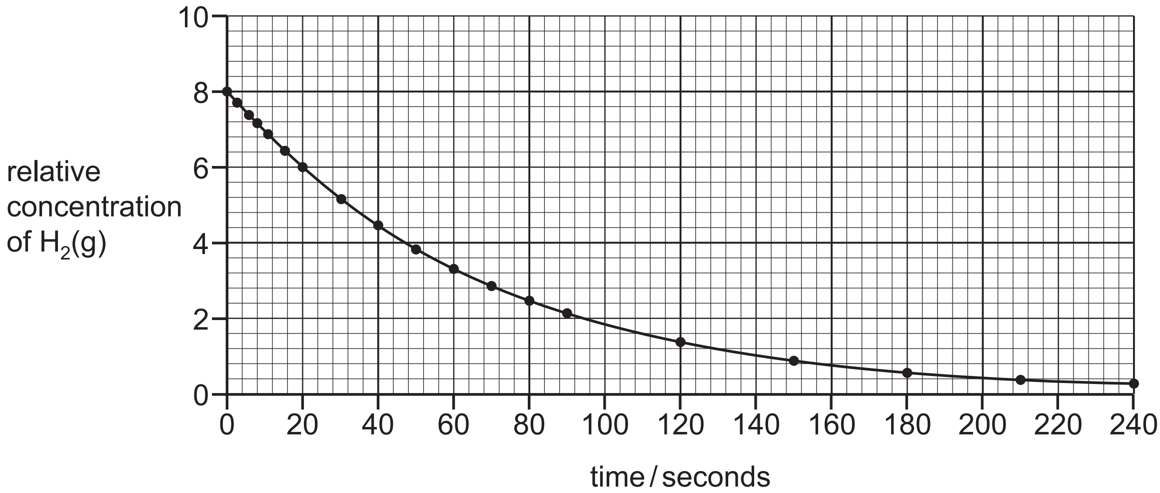
.... [2]

[Total: 9]

2. 9701_w20_qp_42 Q1

1 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]

[Total: 12]

3. 9701 s18 qp 42 Q2

2 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 $2ICl(g) + H_2(g) \rightarrow 2HCl(g) + I_2(g)$ is first order with respect to $ICl(g)$ 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 .... $\rightarrow$ ....

second step .... $\rightarrow$ ....
[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 $ICl(g)$ 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 $ICl(g)$.

....

.... [1]

(h) A chemical reaction may be speeded up by the presence of a catalyst.

Explain why a catalyst increases the rate of a chemical reaction.

....

.... [1]

[Total: 12]

4. 9701_s21_qp_42 Q7

7 **(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]

5. 9701_s18_qp_43 Q2

2 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]

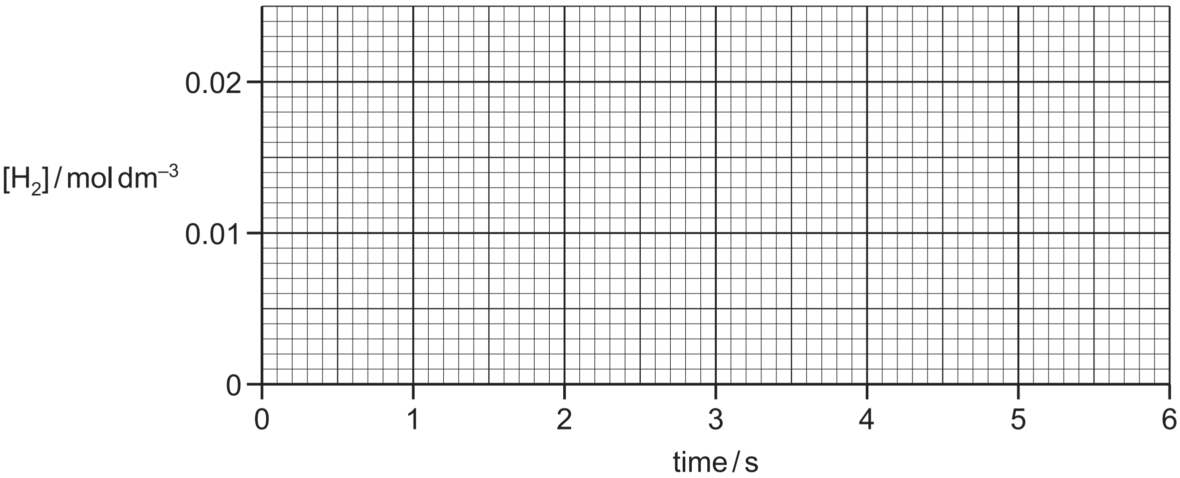
(g) A third experiment is performed under different conditions. A small amount of $H_2(g)$ of concentration $0.0200\,mol\,dm^{-3}$ is mixed with a large excess of NO(g). The concentration of $H_2(g)$ is found to have a constant half-life of 2.00 seconds under the conditions used.

(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]

[Total: 14]

6. 9701_w20_qp_43 Q1

1 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, $[I^-] = 0.00780\,mol\,dm^{-3}$. 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]

[Total: 8]

7. 9701_s19_qp_42 Q4

4 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 $5.40 \times 10^{-3}\,mol\,dm^{-3}\,s^{-1}$ when

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

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

k = ...

units = ...

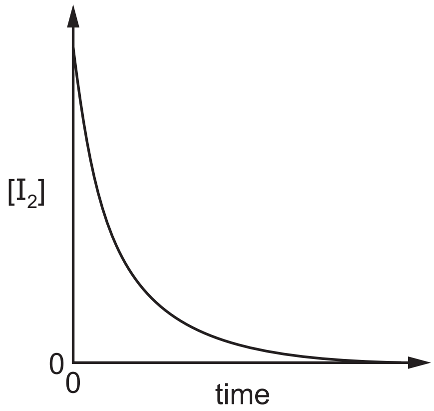
[2]

(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.



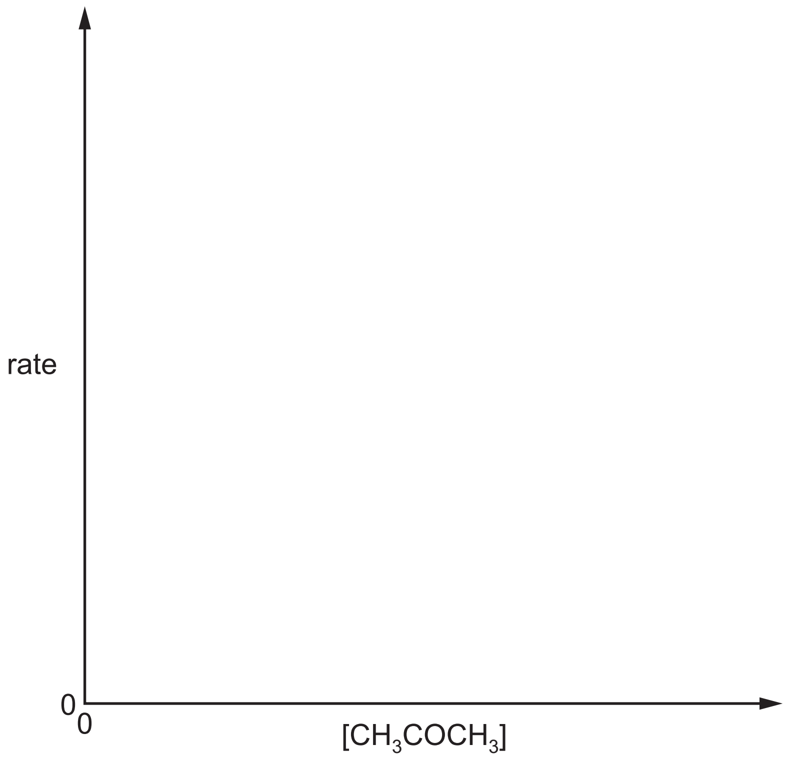
Describe how this graph could be used to determine the initial rate of the reaction.

....

....

.... [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]

[Total: 11]

8. 9701_m16_qp_42 Q4

4 (a) Ethanal, CH_3CHO, dimerises in alkaline solution according to the following equation.

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$

The initial rate of this reaction was measured, starting with different concentrations of CH_3CHO and OH^-. The following results were obtained.

$[CH_3CHO]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	initial rate of reaction (relative values)
0.10	0.015	1
0.20	0.015	2
0.40	0.030	8

(i) Deduce the order of the reaction with respect to CH_3CHO.

.... [1]

(ii) Deduce the order of the reaction with respect to OH^-.

.... [1]

(iii) State the overall rate equation for this reaction.

rate = ... [1]

(iv) State the units for the rate constant, *k*.

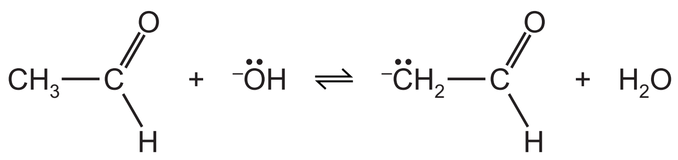
.... [1]

(v) Calculate the initial rate of reaction (relative value) for a reaction where the $[CH_3CHO]$ is 0.30 mol dm^{-3} and $[OH^-]$ is 0.030 mol dm^{-3}.

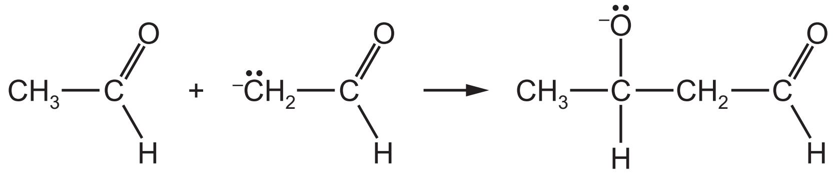
[1]

(b) **(i)** A three-step mechanism has been proposed for the reaction in **(a)**.

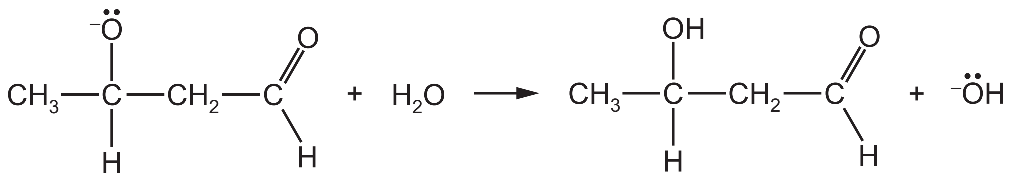
step 1



step 2



step 3



Using your rate equation in **(iii)**, predict which is the rate-determining step.
Explain your answer.

rate-determining step ....

explanation ....

.... [2]

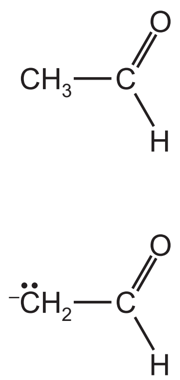
(ii) Describe the chemical behaviour of CH_3CHO in step 1.

.... [1]

(c) Name the mechanism occurring in steps 2 and 3.

.... [1]

(d) Using the diagram below, show the mechanism for step 2 showing the relevant curly arrows and dipoles.



[2]

[Total: 11]

9. 9701_s21_qp_41 Q5

5 Dinitrogen pentoxide, N_2O_5, is dissolved in an inert solvent (solv) and the rate of decomposition of N_2O_5 is investigated. This reaction produces nitrogen dioxide, which remains in solution, and oxygen gas.

$$N_2O_5(solv) \rightarrow 2NO_2(solv) + \tfrac{1}{2}O_2(g)$$

(a) Suggest what measurements could be used to follow the rate of this reaction from the given information.

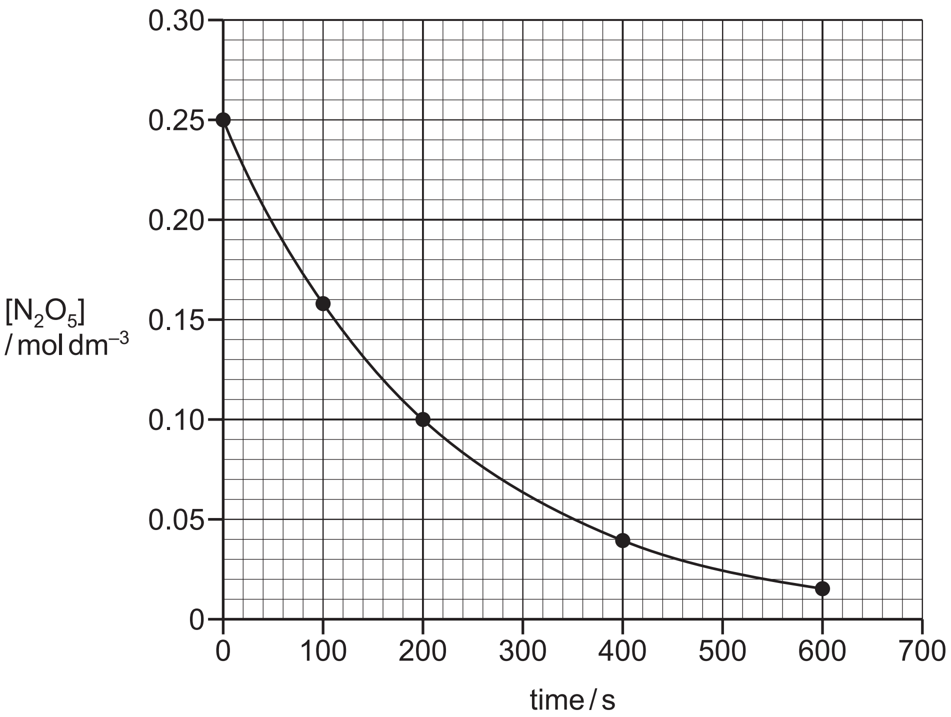
....

.... [1]

(b) In a separate experiment, the rate of the decomposition of $N_2O_5(g)$ is investigated.

$$N_2O_5(g) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

The graph shows the results obtained.



The reaction is first order with respect to N_2O_5. This can be confirmed from the graph using half-lives.

(i) Explain the term *half-life of a reaction*.

....

.... [1]

(ii) Determine the half-life of this reaction. Show your working on the graph.

half-life = ... s [1]

(iii) Suggest the effect on the half-life of this reaction if the initial concentration of N_2O_5 is halved.

.... [1]

(c) **(i)** Use the graph in **5(b)** to determine the rate of reaction at 200 s. Show your working.

rate = ...

units = ...
[2]

The rate equation for this reaction is shown.

$$\text{rate} = k[N_2O_5]$$

(ii) Use your answer to **(c)(i)** to calculate the value of the rate constant, k, for this reaction and state its units.

k = ... units .... [1]

(d) Nitrogen dioxide reacts with ozone, O_3, as shown.

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

The rate equation for this reaction is rate = $k[NO_2][O_3]$.

Suggest a possible two-step mechanism for this reaction.

....

.... [2]

[Total: 9]

10. 9701_w19_qp_41 Q2

2 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.

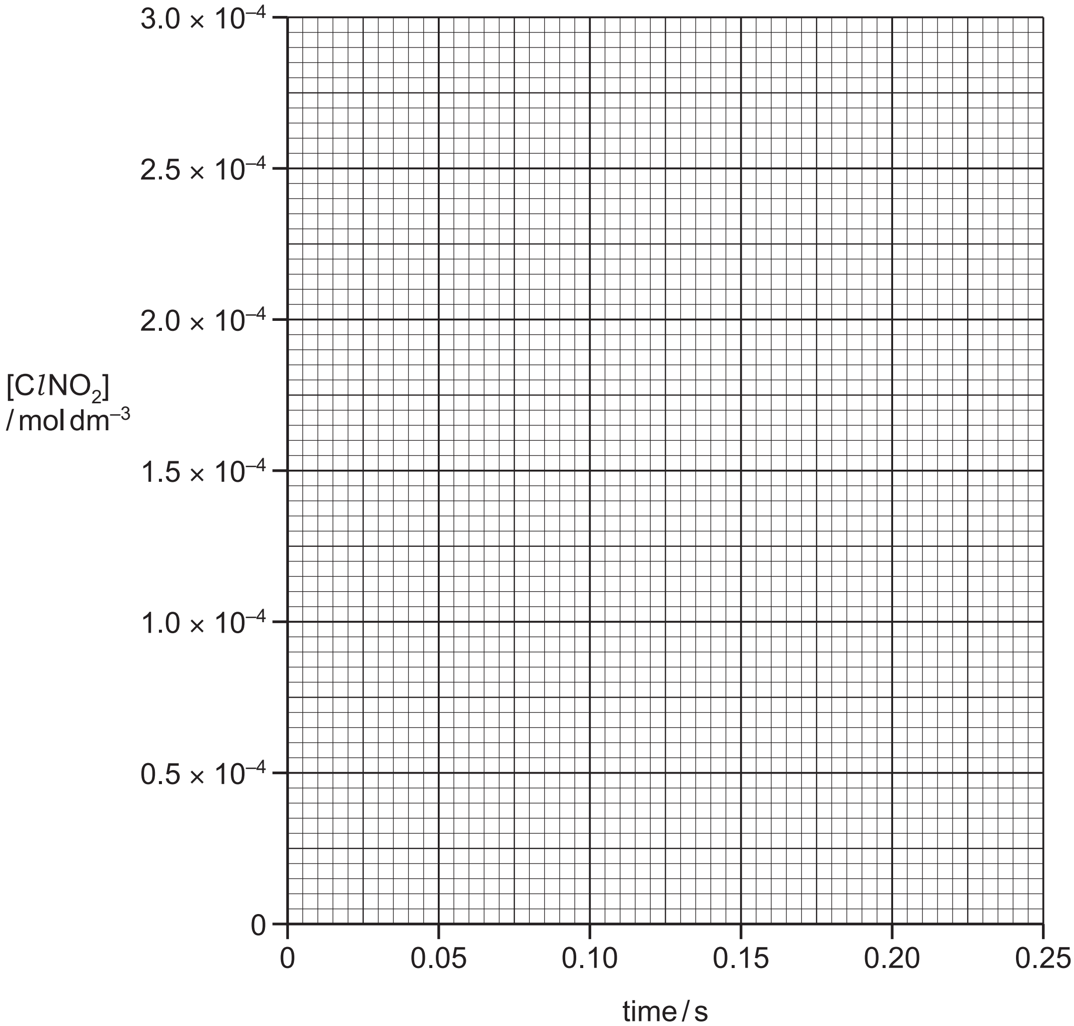
....

....

.... [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]

[Total: 9]