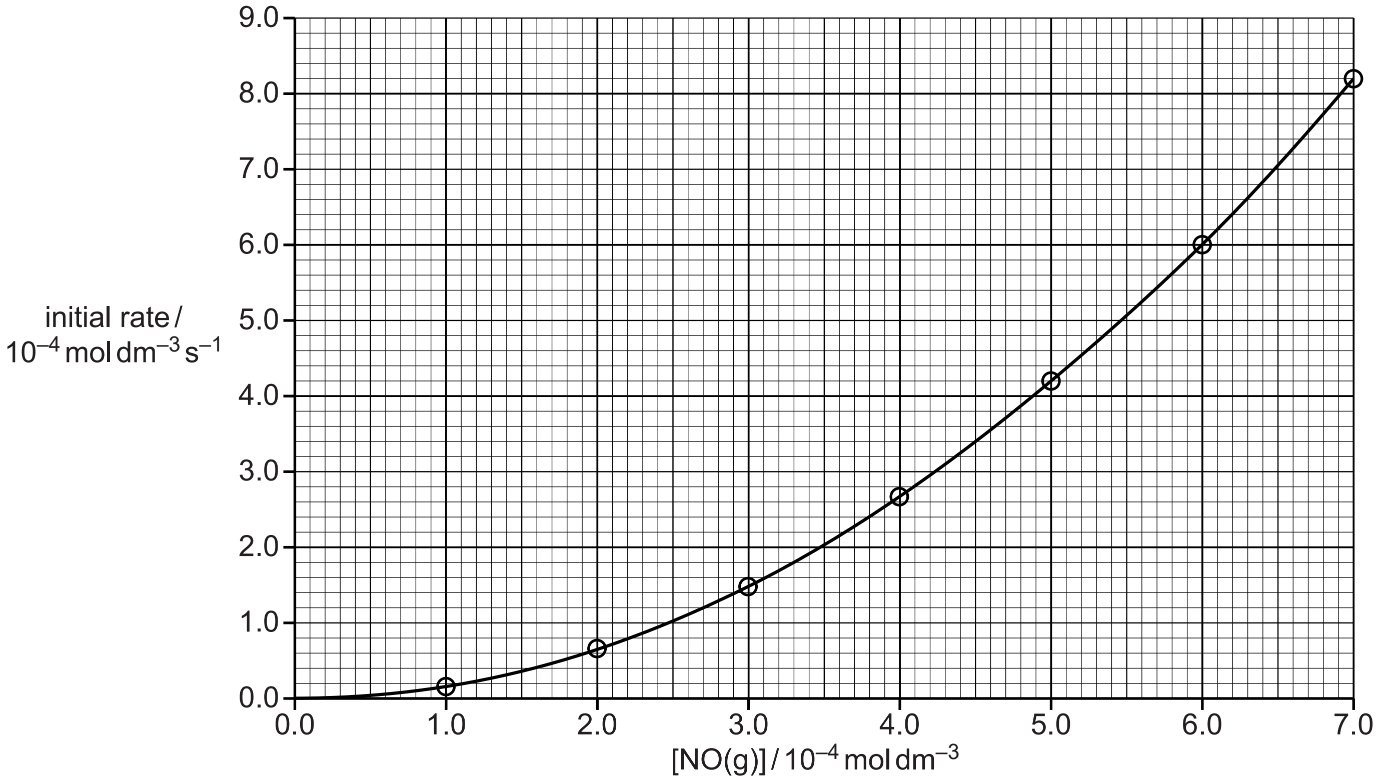
1 Hydrogen, H_2, reacts with nitrogen monoxide, NO, as shown below:

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

(a) The rate equation for this reaction is:

$rate = k[H_2(g)][NO(g)]^2$

The concentration of NO(g) is changed and a rate–concentration graph is plotted.



The chemist uses H_2(g) of concentration 2.0×10^{-2} mol dm^{-3}.

Using values from the graph, calculate the rate constant, k, for this reaction.

Give your answer to **two** significant figures and in **standard form**.

Show your working.

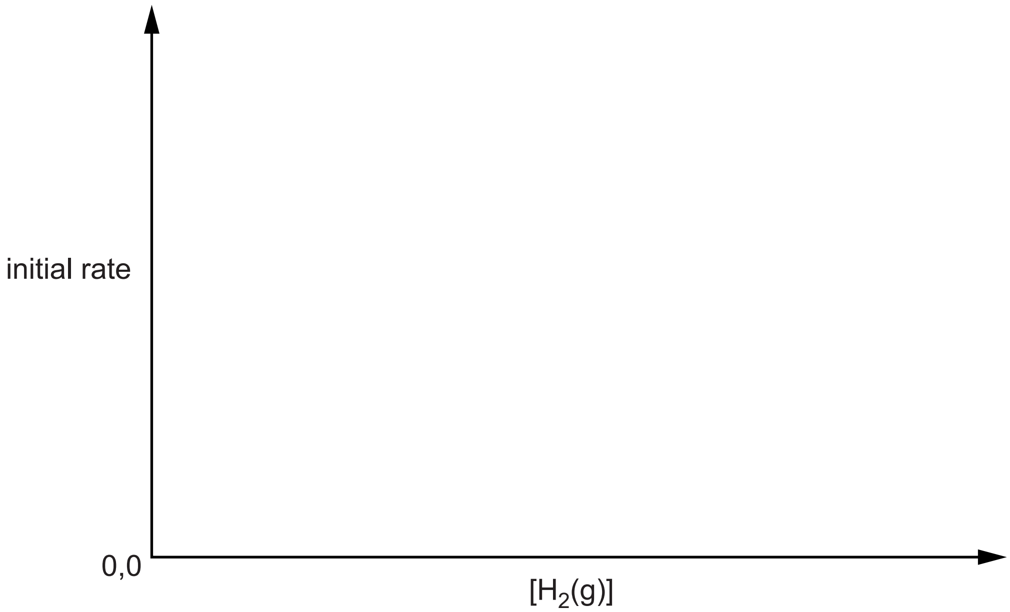
k = ... units .... **[4]**

(b) A chemist investigates the effect of changing the concentration of $H_2(g)$ on the initial reaction rate at two different temperatures.

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

(i) Using the axes below, sketch **two** graphs of the results.

Label the graphs as follows:
- **L** for the lower temperature
- **H** for the higher temperature.



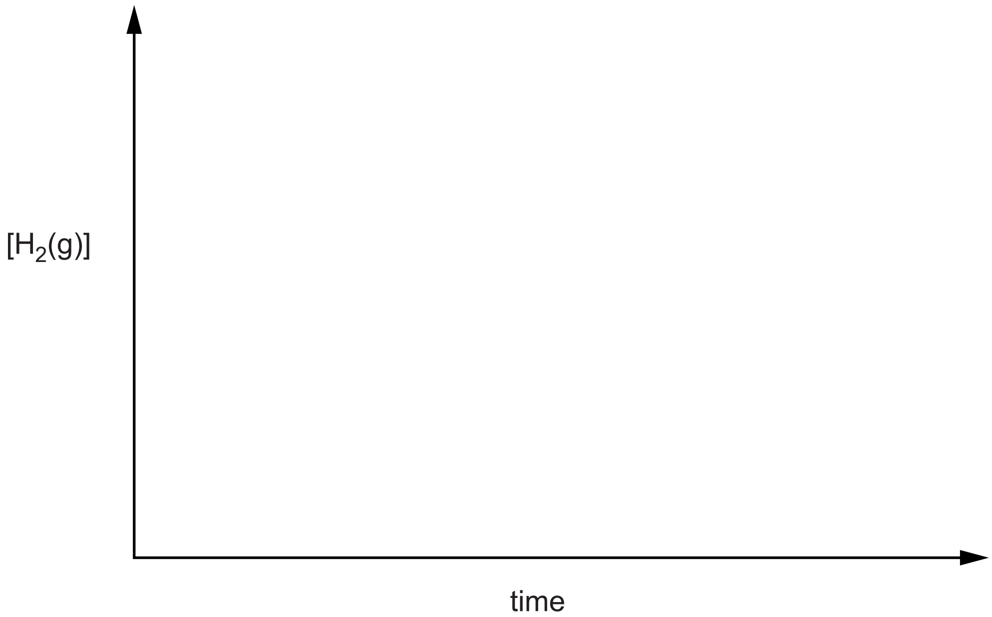
[2]

(ii) State the effect of the higher temperature on the rate constant, *k*.

.... **[1]**

(c) The reaction can also be shown as being first order with respect to H_2(g) by continuous monitoring of [H_2(g)] during the course of the reaction.

- Using the axes below, sketch a graph to show the results.
- State how you would use the graph to show this first order relationship for H_2(g).



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.... **[2]**

(d) The chemist proposes a three-step mechanism for the reaction:

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

(i) On the dotted line below, write the equation for step 3.

step 1:	$2NO \rightarrow N_2O_2$	fast
step 2:	$H_2 + N_2O_2 \rightarrow N_2O + H_2O$	slow
step 3:	....	fast

[1]

(ii) Explain why this mechanism is consistent with the rate equation *rate* = $k[H_2(g)][NO(g)]^2$.

....

....

.... **[1]**

[Total: 11]

2 A student carries out an initial rates investigation on the reaction below.

$$5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$$

From the results, the student determines the rate equation for this reaction:

$$\text{rate} = k\,[I^-(aq)]^2\,[IO_3^-(aq)]\,[H^+(aq)]^2$$

(a) **(i)** What is the overall order of reaction?

.... **[1]**

(ii) A proposed mechanism for this reaction takes place in several steps.

Suggest **two** reasons why it is unlikely that this reaction could take place in one step.

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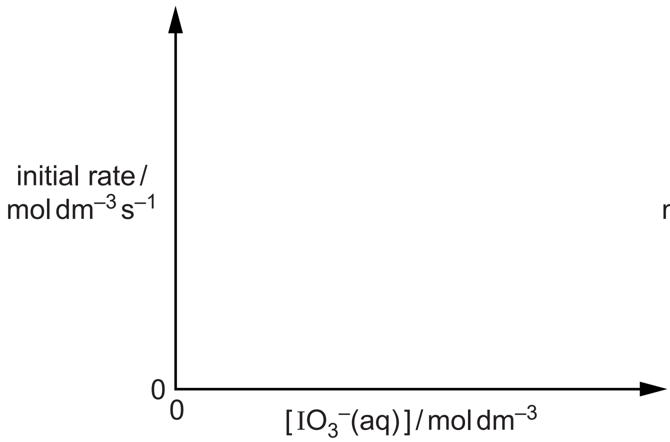
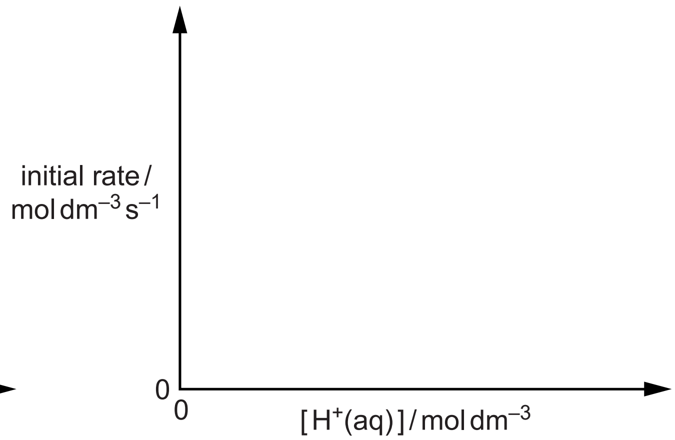
.... **[2]**

(b) On the rate–concentration graphs below, sketch lines to show the relationship between initial rate and concentration for $IO_3^-(aq)$ and $H^+(aq)$.





[2]

(c) The table below shows some of the student's results.

(i) Complete the table by adding the missing initial rates in the boxes.

	[I^-(aq)] / mol dm^{-3}	**[IO_3^-(aq)] / mol dm^{-3}**	**[H^+(aq)] / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
Experiment 1	0.015	0.010	0.020	0.60
Experiment 2	0.045	0.010	0.020	
Experiment 3	0.060	0.040	0.080	

[2]

(ii) Calculate the rate constant, *k*, for this reaction. Include units.

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

k = ... units ....**[3]**

(iii) The student repeats Experiment 1 using 0.020 mol dm^{-3} methanoic acid, HCOOH(aq) (pK_a = 3.75), instead of 0.020 mol dm^{-3} HCl(aq) as a source of H^+(aq).

Determine the initial rate in this experiment. Show your working.

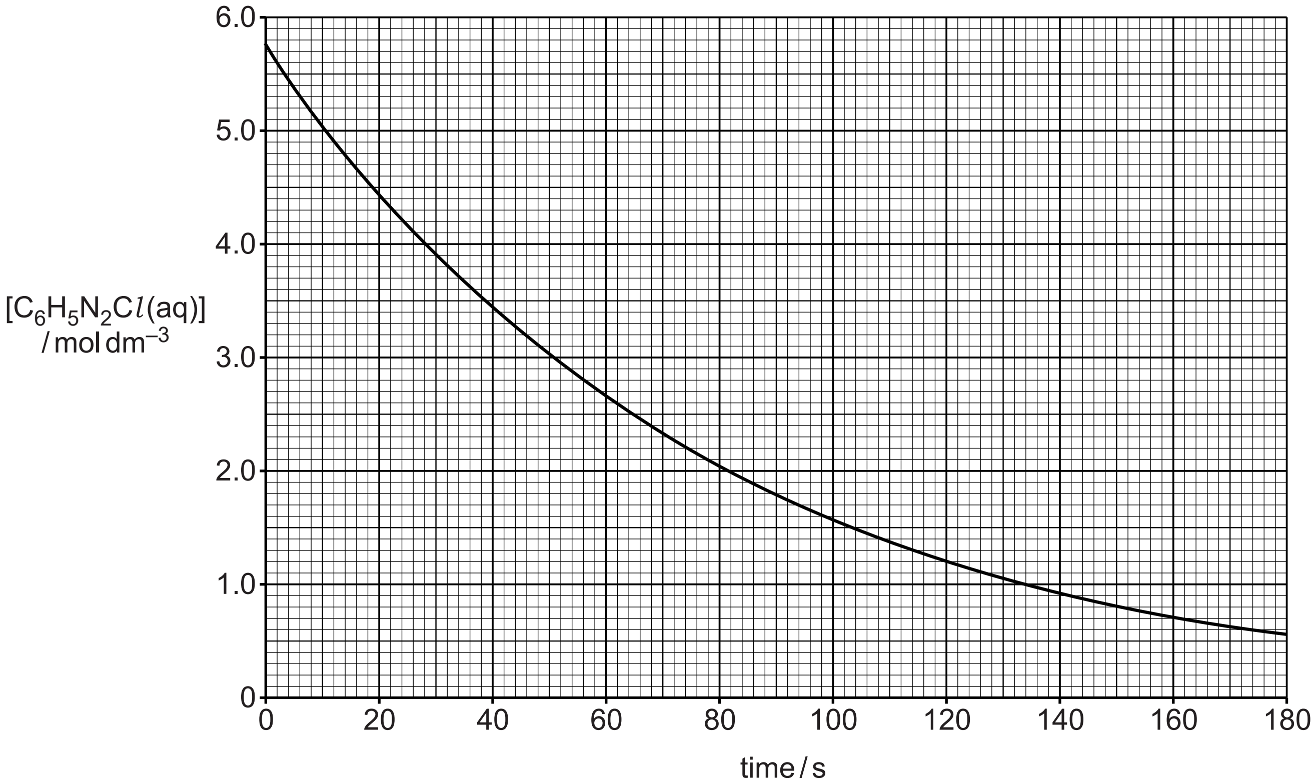
initial rate = ... mol dm^{-3} s^{-1} **[3]**

[Total: 13]

3 In aqueous solution, benzenediazonium chloride, $C_6H_5N_2Cl$, decomposes above 10 °

$$C_6H_5N_2Cl(aq) + H_2O(l) \xrightarrow{\text{C}} C_6H_5OH(aq) + N_2(g) + HCl(aq)$$

A student investigates the rate of this reaction using an excess of water at 50 °C. The student takes measurements at intervals during the reaction and then plots his experimental results to give the graph shown below.



(a) The student uses half-life to suggest the order of reaction with respect to $C_6H_5N_2Cl$.

(i) What is meant by the *half-life* of a reaction?

....

....

.... **[1]**

(ii) Confirm the order of reaction with respect to $C_6H_5N_2Cl$.

Show your working on the graph.

....

....

....

.... **[2]**

(iii) What would be the effect, if any, on the half-life of this reaction of doubling the initial concentration of $C_6H_5N_2Cl$?

.... **[1]**

(b) The student predicts that the rate equation is: rate = $k[C_6H_5N_2Cl]$.

(i) Using the graph and this rate equation, determine the rate of reaction after 40 s.

Show your working on the graph.

rate = ... units .... **[3]**

(ii) Calculate the rate constant, k, for this reaction and give its units.

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

(c) The order of this reaction with respect to H_2O is effectively zero.

Explain why.

....

....

.... **[1]**

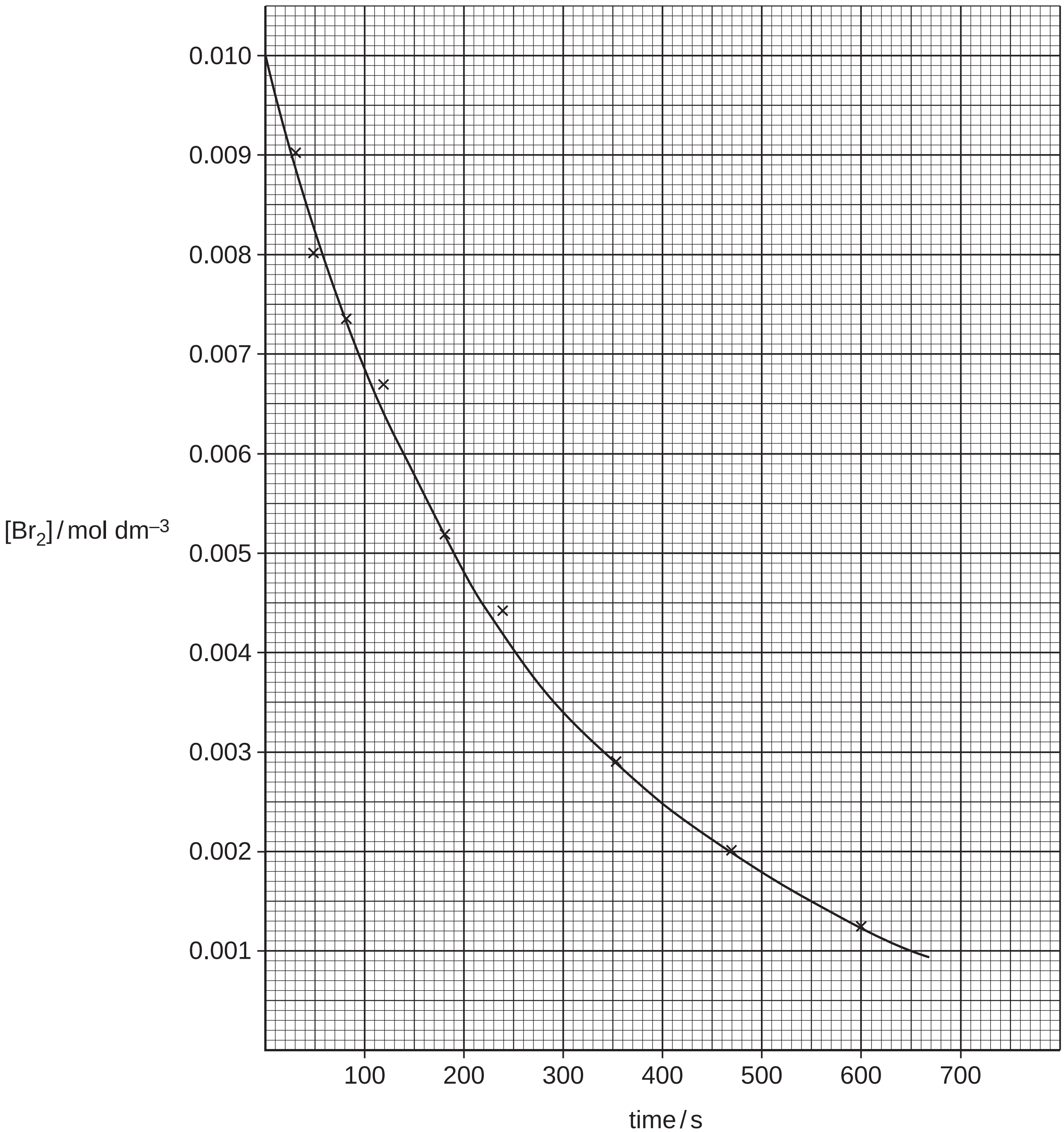
[Total: 10]

4 In aqueous solution, methanoic acid, HCOOH, reacts with bromine, Br_2.

$$HCOOH(aq) + Br_2(aq) \longrightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$$

A student carried out an investigation on the rate of this reaction. The student used a large excess of methanoic acid which ensured that its concentration was effectively constant throughout. During the reaction, bromine is used up and its orange colour becomes less intense. The intensity of the bromine colour can be measured with a colorimeter to give the bromine concentration.

The graph below was plotted from the experimental results.



In this investigation, a large excess of methanoic acid was used. Under these conditions, the reaction is effectively zero-order with respect to methanoic acid.

- Using the graph, determine the order of reaction with respect to bromine.
- Using the graph, determine the initial rate of the reaction.
- Calculate the rate constant, *k*, for the reaction between methanoic acid and bromine under these conditions.

In your answer you should make clear how your conclusions fit with the experimental results, including working shown on the graph and units where appropriate.

[9]

5 In the presence of acid, $H^+(aq)$, aqueous bromate(V) ions, $BrO_3^-(aq)$, react with aqueous bromide ions, $Br^-(aq)$, to produce bromine, $Br_2(aq)$.

A student carried out an investigation into the kinetics of this reaction.

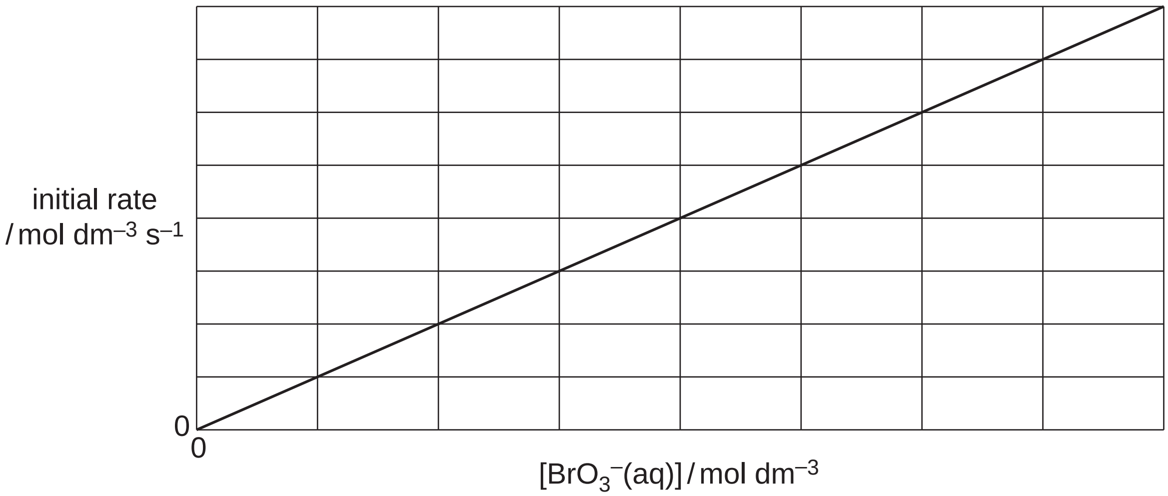
(a) Balance the ionic equation for this reaction.

$$BrO_3^- + \dots\dots\dots Br^- + \dots\dots\dots H^+ \longrightarrow \dots\dots\dots Br_2 + \dots\dots\dots H_2O$$

[1]

(b) The student investigated how different concentrations of $BrO_3^-(aq)$ affect the initial rate of the reaction.

A graph of initial rate against $[BrO_3^-(aq)]$ is shown below.



The student then investigated how different concentrations of $Br^-(aq)$ and $H^+(aq)$ affect the initial rate of the reaction.

The results are shown below.

$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
5.0×10^{-2}	1.5×10^{-1}	3.1×10^{-1}	1.19×10^{-5}
5.0×10^{-2}	3.0×10^{-1}	3.1×10^{-1}	2.38×10^{-5}
5.0×10^{-2}	1.5×10^{-1}	6.2×10^{-1}	4.76×10^{-5}

- Using the results from the student's experiments, what conclusions can be drawn about the kinetics of this reaction? Justify your reasoning.

- Calculate the rate constant for this reaction, including the units.

In your answer you should make clear how your conclusions fit with the experimental results.

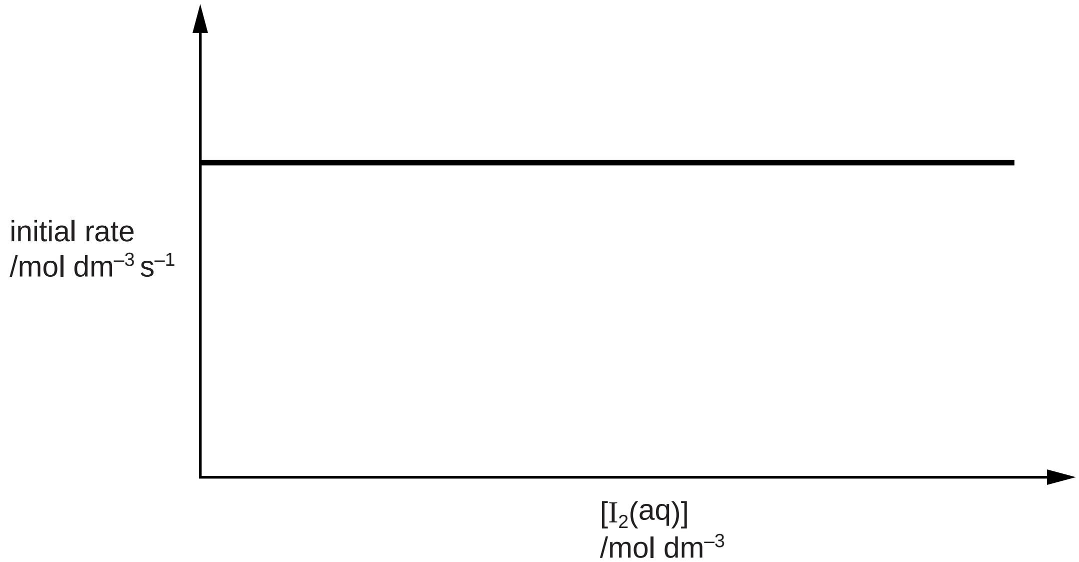
.... [9]

[Total: 10]

6 A student investigates the reaction between iodine, I_2, and propanone, $(CH_3)_2CO$, in the presence
of aqueous hydrochloric acid, $HCl(aq)$.

The results of the investigation are shown below.

Rate–concentration graph



Results of initial rates experiments

experiment	$[(CH_3)_2CO(aq)]$ / mol dm^{-3}	$[HCl(aq)]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.50×10^{-3}	2.00×10^{-2}	2.10×10^{-9}
2	3.00×10^{-3}	2.00×10^{-2}	4.20×10^{-9}
3	3.00×10^{-3}	5.00×10^{-2}	1.05×10^{-8}

(a) Determine the orders with respect to I_2, $(CH_3)_2CO$ and HCl, the rate equation and the rate constant for the reaction.

Explain all of your reasoning.

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.... **[9]**

(b) The student then investigates the reaction of hydrogen, H_2, and iodine monochloride, ICl.

The equation for this reaction is shown below.

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

The rate equation for this reaction is shown below.

$$\text{rate} = k[H_2(g)]\,[ICl(g)]$$

Predict a possible two-step mechanism for this reaction. The first step should be the rate-determining step.

step 1 ....

step 2 .... **[2]**

[Total: 11]

7 Hydrogen, H_2, reacts with nitrogen monoxide, NO, as shown in the equation below.

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

A chemist carries out a series of experiments and determines the rate equation for this reaction:

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

(a) In one of the experiments, the chemist reacts together:

- $1.2 \times 10^{-2}\,mol\,dm^{-3}\,H_2(g)$
- $6.0 \times 10^{-3}\,mol\,dm^{-3}\,NO(g)$

The initial rate of this reaction is $3.6 \times 10^{-2}\,mol\,dm^{-3}\,s^{-1}$.

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

k = ………………………. units ………………………. **[3]**

(b) Predict what would happen to the initial rate of reaction for the following changes in concentrations.

(i) The concentration of $H_2(g)$ is doubled.

.... **[1]**

(ii) The concentration of NO(g) is halved.

.... **[1]**

(iii) The concentrations of $H_2(g)$ and NO(g) are **both** increased by four times.

....

.... **[1]**

(c) The chemist carries out the reaction between hydrogen and nitrogen monoxide at a higher pressure.

(i) Explain, with a reason, what happens to the initial rate of reaction.

....

....

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.... **[1]**

(ii) State what happens to the rate constant.

.... **[1]**

(d) This overall reaction between hydrogen and nitrogen monoxide takes place by a two-step mechanism. The first step is much slower than the second step.

Suggest a possible two-step mechanism for the overall reaction.

step 1: ....

step 2: .... **[2]**

[Total: 10]