Q1.

A and B react together in the presence of an acid catalyst.

$$A(aq) + 2\,B(aq) \rightarrow C(aq) + D(aq)$$

The rate equation for this reaction is

$$rate = k[B]^2[H^+]$$

The table below shows how the values of the relative initial rate vary with different concentrations of each reagent at the same temperature.

Experiment	**[A] / mol dm^{-3}**	**[B] / mol dm^{-3}**	**[H$^+$] / mol dm^{-3}**	**Relative initial rate**
1	0.40	0.20	0.10	1.00
2	0.50	0.20	0.10	
3	0.40		0.10	0.64
4	0.50	0.30	0.06	

(a) Complete the table by calculating the missing values.

(3)

(b) A suggested mechanism for the reaction is shown.

Step 1 $B + H^+ \rightarrow BH^+$

Step 2 $BH^+ + B \rightarrow B_2H^+$

Step 3 $B_2H^+ + A \rightarrow C + D$

Deduce the rate-determining step for this reaction.

Give a reason for your answer.

Rate-determining step ____

Reason ____

____

____

(2)

(Total 5 marks)

Q2.

Hydrogen peroxide solution decomposes to form water and oxygen.

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

The reaction is catalysed by manganese(IV) oxide.

A student determines the order of this reaction with respect to hydrogen peroxide. The student uses a continuous monitoring method in the experiment.

The student places hydrogen peroxide solution in a conical flask with the catalyst and uses a gas syringe to collect the oxygen formed. The student records the volume of oxygen every 10 seconds for 100 seconds.

(a) Explain why the reaction is fastest at the start.

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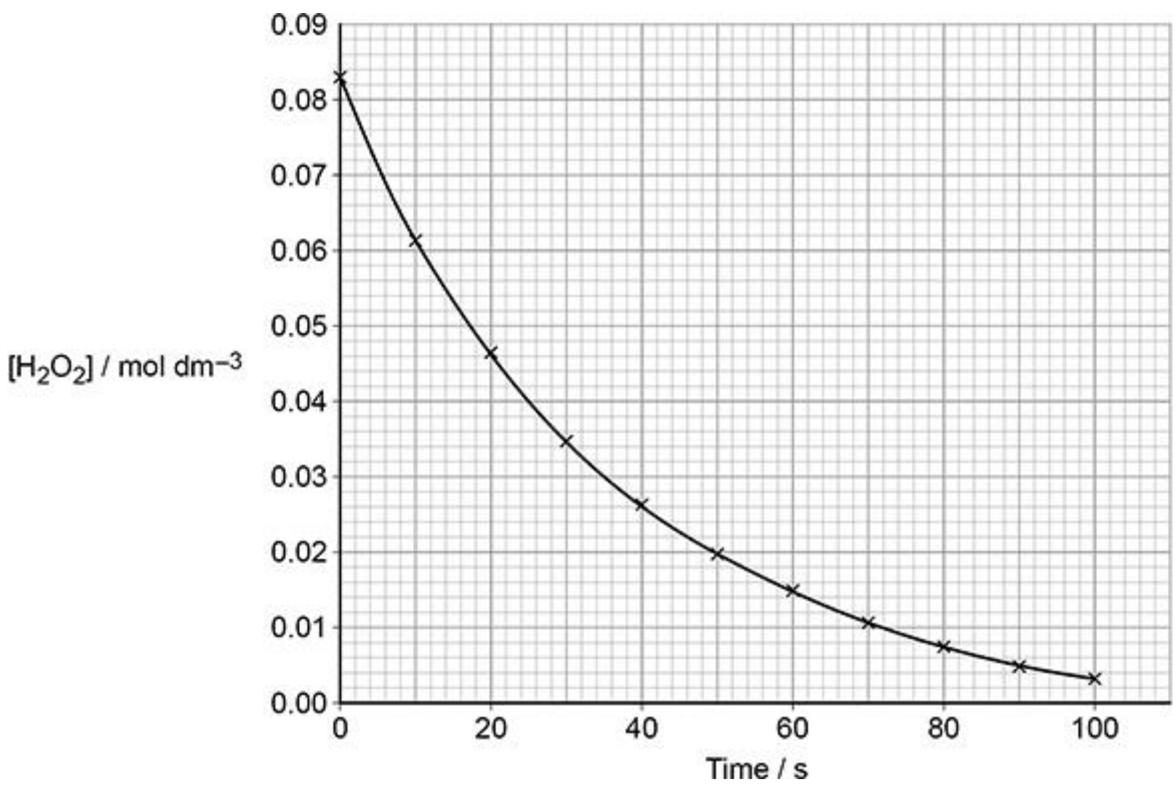
(2)

(b) The graph in **Figure 1** shows how the concentration of hydrogen peroxide changes with time in this experiment.

Figure 1



Tangents to the curve in **Figure 1** can be used to determine rates of reaction.

Draw a tangent to the curve when the concentration of hydrogen peroxide solution is 0.05 mol dm^{-3}

Use your tangent to calculate the gradient of the curve at this point.

Gradient ________________ mol dm^{-3} s^{-1}

(2)

(c) The concentration of hydrogen peroxide solution at time *t* during the experiment can be calculated using this expression.

$$[H_2O_2]_t = [H_2O_2]_{initial}\left(\frac{V_{max} - V_t}{V_{max}}\right)$$

$[H_2O_2]_t$ = concentration of hydrogen peroxide solution at time *t* / mol dm^{-3}

$[H_2O_2]_{initial}$ = concentration of hydrogen peroxide solution at the start / mol dm^{-3}

V_{max} = total volume of oxygen gas collected during the whole experiment / cm^3

V_t = volume of oxygen gas collected at time *t* / cm^3

In this experiment, V_{max} = 100 cm^3

Use **Figure 1** and the expression to calculate $[H_2O_2]_t$ when 20 cm^3 of oxygen has been collected.

$[H_2O_2]_t$ ________________ mol dm^{-3}

(2)

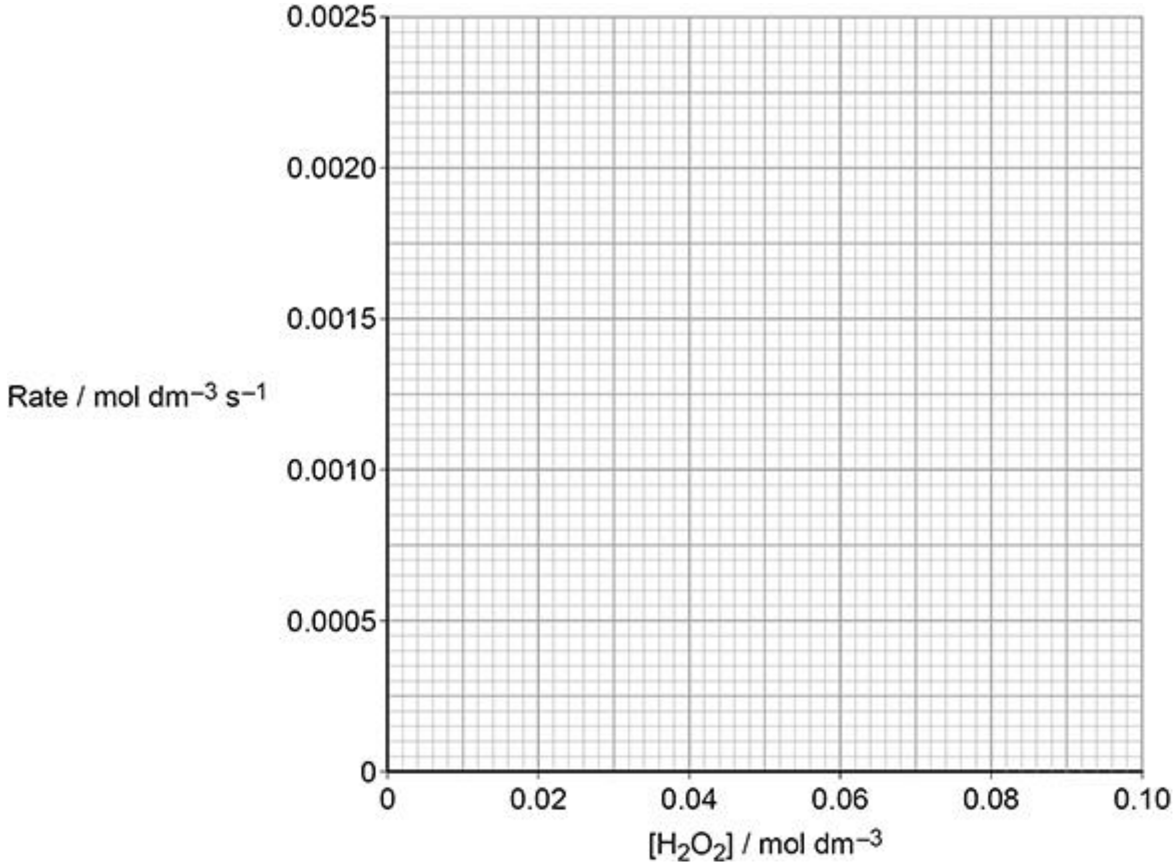
The table below shows data from a similar experiment.

$[H_2O_2]$ / mol dm^{-3}	0.02	0.03	0.05	0.07	0.09
Rate / mol dm^{-3} s^{-1}	0.00049	0.00073	0.00124	0.00168	0.00219

(d) Plot the data from the table above on the grid in **Figure 2**.

Draw a line of best fit.

Figure 2



(2)

(e) Use **Figure 2** to determine the order of reaction with respect to H_2O_2

State how the graph shows this order.

Order ____

How the graph shows this order ______________________________

____

____

(2)

(Total 10 marks)

Q3.

This question is about rates of reaction.

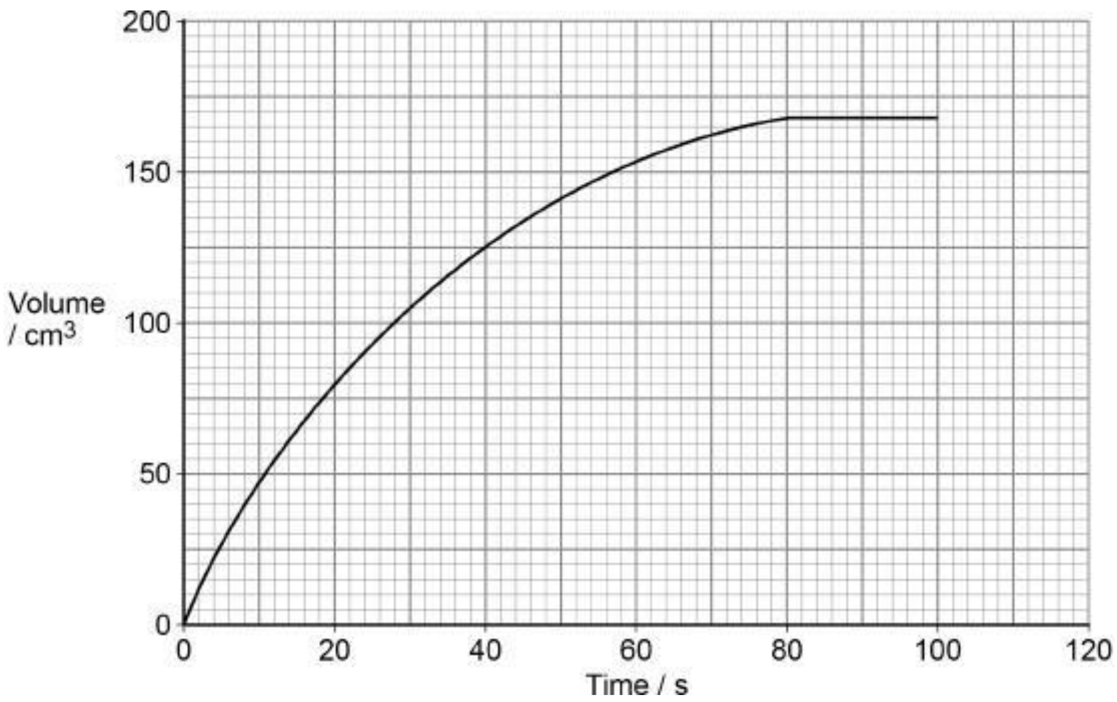
Phosphinate ions ($H_2PO_2^-$) react with hydroxide ions to produce hydrogen gas as shown.

$$H_2PO_2^- + OH^- \rightarrow HPO_3^{2-} + H_2$$

A student completed an experiment to determine the initial rate of this reaction.
The student used a solution containing phosphinate ions and measured the volume of hydrogen gas collected every 20 seconds at a constant temperature.

Figure 1 shows a graph of the student's results.

Figure 1



(a) Use the graph in **Figure 1** to determine the initial rate of reaction for this experiment. State its units. Show your working on the graph.

Rate ________________ Units ________________

(3)

(b) Another student reacted different initial concentrations of phosphinate ions with an excess of hydroxide ions. The student measured the time (t) taken to collect 15 cm^3 of hydrogen gas. Each experiment was carried out at the same temperature. The table shows the results.

Initial $[H_2PO_2^-]$ / mol dm^{-3}	***t* / s**
0.25	64
0.35	32
0.50	16
1.00	4

State the relationship between the initial concentration of phosphinate and time (t).

Deduce the order of the reaction with respect to phosphinate.

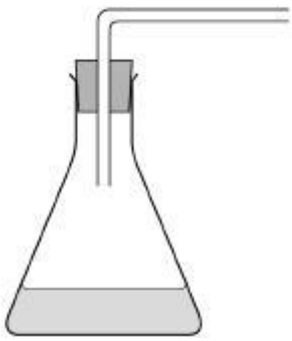
Relationship ____

Order ____

(2)

(c) Complete the diagram in **Figure 2** to show how the hydrogen gas could be collected and measured in the experiments in part (a) and (b).

Figure 2



The rate equation for a different reaction is

$$rate = k\,[L]\,[M]^2$$

(1)

(d) Deduce the overall effect on the rate of reaction when the concentrations of both **L** and **M** are halved.

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(1)

(e) The rate of reaction is 0.0250 mol dm^{-3} s^{-1} when the concentration of **L** is 0.0155 mol dm^{-3}

Calculate the concentration of **M** if the rate constant is 21.3 mol^{-2} dm^{6} s^{-1}

Concentration of **M** _______________ mol dm^{-3}

(3)

(f) Define the term overall order of reaction.

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(1)

(Total 11 marks)

Q4.

Cisplatin, $[Pt(NH_3)_2Cl_2]$, is used as an anti-cancer drug.

(a) Cisplatin works by causing the death of rapidly dividing cells.

Name the process that is prevented by cisplatin during cell division.

___

(1)

After cisplatin enters a cell, one of the chloride ligands is replaced by a water molecule to form a complex ion, **B**.

(b) Give the equation for this reaction.

___

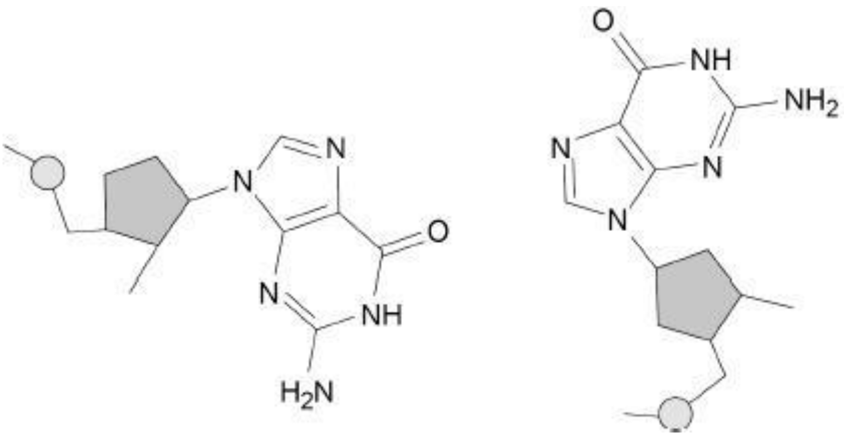
(2)

(c) When the complex ion **B** reacts with DNA, the water molecule is replaced as a bond forms between platinum and a nitrogen atom in a guanine nucleotide.
The remaining chloride ligand is also replaced as a bond forms between platinum and a nitrogen atom in another guanine nucleotide.

Figure 1 represents two adjacent guanine nucleotides in DNA.

Complete **figure 1** to show how the platinum complex forms a cross-link between the guanine nucleotides.

Figure 1



(2)

An experiment is done to investigate the rate of reaction in part (b).

(d) During the experiment the concentration of cisplatin is measured at one-minute intervals.

Explain how graphical methods can be used to process the measured results, to confirm that the reaction is first order.

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(3)

In another experiment, the effect of temperature on the rate of the reaction in part (b) is investigated.

The table shows the results.

Temperature T **/ K**	$\frac{1}{T}$ / K^{-1}	**Rate constant** k **/** s^{-1}	**ln** k
293	0.00341	1.97×10^{-8}	−17.7
303	0.00330	8.61×10^{-8}	−16.3
313	0.00319	3.43×10^{-7}	−14.9
318		6.63×10^{-7}	
323	0.00310	1.26×10^{-6}	−13.6

(e) Complete the table above.

(2)

(f) The Arrhenius equation can be written in the form

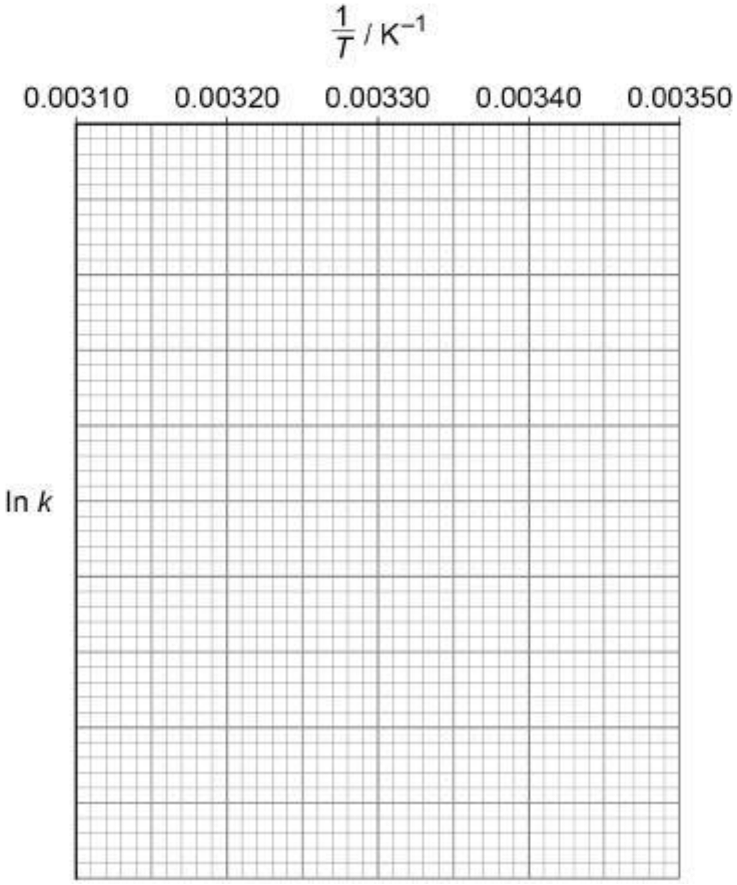
$$\ln k = \frac{-E_a}{RT} + \ln A$$

Use the data in the table above to plot a graph of ln k against $\frac{1}{T}$ on the grid in **Figure 2**.

Calculate the activation energy, E_a, in kJ mol^{-1}

The gas constant, $R = 8.31$ J K^{-1} mol^{-1}

Figure 2



E_a ______________ kJ mol^{-1}

(5)

(Total 15 marks)

Q5.

The rate expression for the reaction between **X** and **Y** is

$$rate = k\,[\mathbf{X}]^2\,[\mathbf{Y}]$$

Which statement is correct?

A The rate constant has units $mol^{-1}\ dm^3\ s^{-1}$

B The rate of the reaction is halved if the concentration of **X** is halved and the concentration of **Y** is doubled.

C The rate increases by a factor of 16 if the concentration of **X** is tripled and the concentration of **Y** is doubled.

D The rate constant is independent of temperature.

(Total 1 mark)

Q6.

Substances **P** and **Q** react in solution at a constant temperature.
The initial rate of reaction was studied in three experiments by measuring the change in concentration of **P** over the first five seconds of the reaction.
The data obtained are shown in **Table 1**.

Table 1

Experiment	**Time after mixing / s**	**Concentration / mol dm³**	
		P	**Q**
1	0	1.00×10^{-2}	1.25×10^{-2}
	5.0	0.92×10^{-2}	not measured
2	0	2.00×10^{-2}	1.25×10^{-2}
	5.0	1.84×10^{-2}	not measured
3	0	0.50×10^{-2}	2.50×10^{-2}
	5.0	0.34×10^{-2}	not measured

(a) Complete **Table 2** to show the initial rate of reaction of **P** in each experiment.

Table 2

Experiment	Initial rate / mol dm^{3} s^{-1}
1	1.6×10^{-4}
2	
3	

(1)

(b) Determine the order of reaction with respect to **P** and the order of reaction with respect to **Q**.

Order with respect to **P** ____________________________

Order with respect to **Q** ____________________________

(2)

(c) A reaction between substances **R** and **S** was second order with respect to **R** and second order with respect to **S**.
At a given temperature, the initial rate of reaction was 1.20×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of **R** was 1.00×10^{-2} mol dm^{-3} and the initial concentration of **S** was 2.45×10^{-2} mol dm^{-3}

Calculate a value for the rate constant, *k*, for the reaction at this temperature.
Give the units for *k*

k ____________________________ Units ____________________________

(3)

(Total 6 marks)

Q7.

Iodide ions are oxidised to iodine by hydrogen peroxide in acidic conditions.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

The rate equation for this reaction can be written as

$$rate = k\,[H_2O_2]^a\,[I^-]^b\,[H^+]^c$$

In an experiment to determine the order with respect to $H^+(aq)$, a reaction mixture is made containing $H^+(aq)$ with a concentration of 0.500 mol dm^{-3}

A large excess of both H_2O_2 and I^- is used in this reaction mixture so that the rate equation can be simplified to

$$rate = k_1\,[H^+]^c$$

(a) Explain why the use of a large excess of H_2O_2 and I^- means that the rate of reaction at a fixed temperature depends only on the concentration of $H^+(aq)$.

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(2)

(b) Samples of the reaction mixture are removed at timed intervals and titrated with alkali to determine the concentration of $H^+(aq)$.

State and explain what must be done to each sample before it is titrated with alkali.

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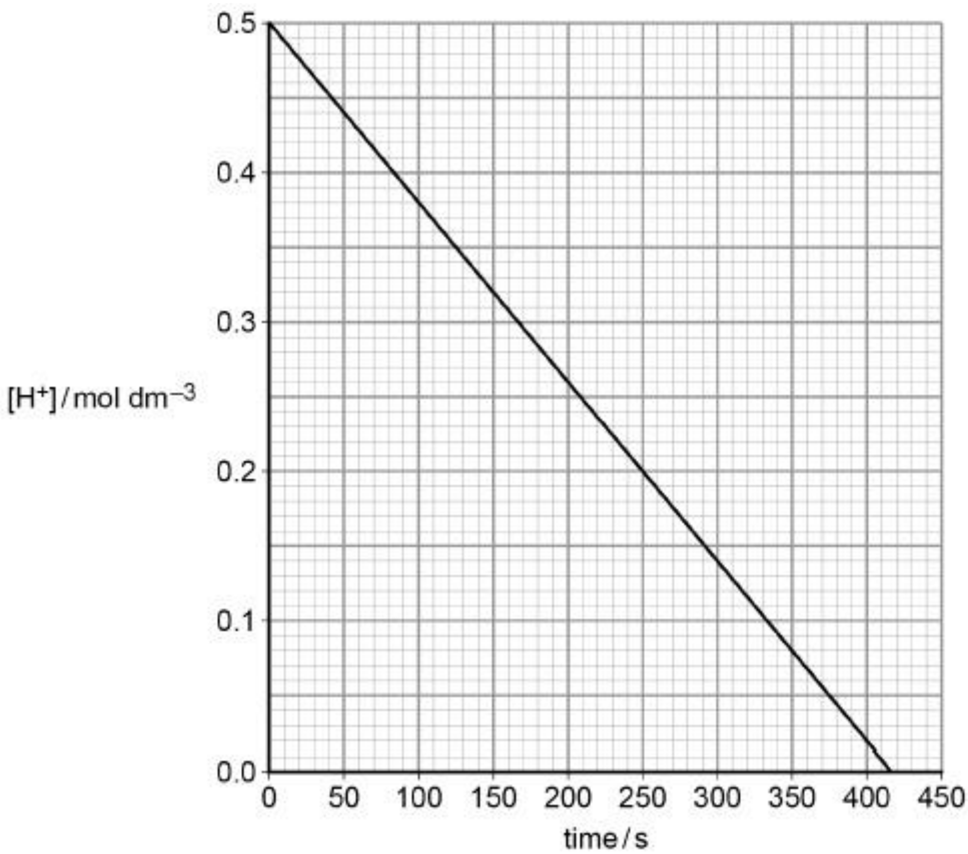
(2)

(c) A graph of the results is shown in **Figure 1**.

Figure 1



Explain how the graph shows that the order with respect to H^+(aq) is zero.

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(2)

(d) Use the graph in **Figure 1** to calculate the value of k_1

Give the units of k_1

k_1 ______________________

Units ______________________

(3)

(e) A second reaction mixture is made at the same temperature. The initial concentrations of $H^+(aq)$ and $I^-(aq)$ in this mixture are both 0.500 mol dm^{-3}

There is a large excess of H_2O_2

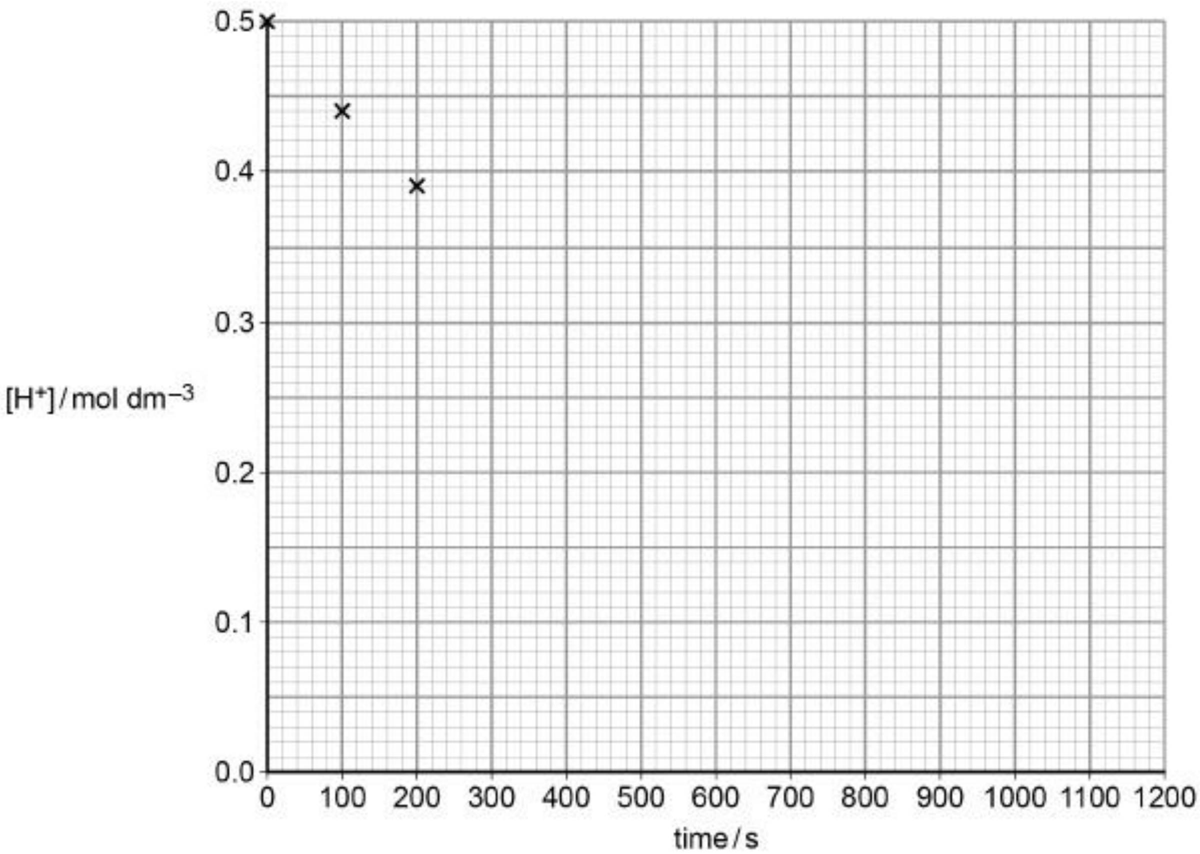
In this reaction mixture, the rate depends only on the concentration of $I^-(aq)$.

The results are shown in the table.

Time / s	0	100	200	400	600	800	1000	1200
$[H^+]$ / mol dm^{-3}	0.50	0.44	0.39	0.31	0.24	0.19	0.15	0.12

Plot these results on the grid in **Figure 2**. The first three points have been plotted.

Figure 2



(1)

(f) Draw a line of best fit on the grid in **Figure 2**.

(1)

(g) Calculate the rate of reaction when $[H^+]$ = 0.35 mol dm^{-3}
Show your working using a suitable construction on the graph in **Figure 2**.

Rate ______________________ mol dm^{-3} s^{-1}

(2)

(h) A general equation for a reaction is shown.

A(aq) + **B**(aq) + **C**(aq) → **D**(aq) + **E**(aq)

In aqueous solution, **A**, **B**, **C** and **D** are all colourless but **E** is dark blue.

A reagent (**X**) is available that reacts rapidly with **E**. This means that, if a small amount of **X** is included in the initial reaction mixture, it will react with any **E** produced until all of the **X** has been used up.

Explain, giving brief experimental details, how you could use a series of experiments to determine the order of this reaction with respect to **A**. In each experiment you should obtain a measure of the initial rate of reaction.

(6)
(Total 19 marks)

Mark Scheme

Q1.

A and B react together in the presence of an acid catalyst.

$$A(aq) + 2\ B(aq) \rightarrow C(aq) + D(aq)$$

The rate equation for this reaction is

$$rate = k[B]^2[H^+]$$

The table below shows how the values of the relative initial rate vary with different concentrations of each reagent at the same temperature.

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	[H$^+$] / mol dm^{-3}	Relative initial rate
1	0.40	0.20	0.10	1.00
2	0.50	0.20	0.10	
3	0.40		0.10	0.64
4	0.50	0.30	0.06	

(a) Complete the table by calculating the missing values.

(3)

(b) A suggested mechanism for the reaction is shown.

Step 1 $B + H^+ \rightarrow BH^+$

Step 2 $BH^+ + B \rightarrow B_2H^+$

Step 3 $B_2H^+ + A \rightarrow C + D$

Deduce the rate-determining step for this reaction.

Give a reason for your answer.

(2)

(Total 5 marks)

Q2.

Hydrogen peroxide solution decomposes to form water and oxygen.

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

The reaction is catalysed by manganese(IV) oxide.

A student determines the order of this reaction with respect to hydrogen peroxide. The student uses a continuous monitoring method in the experiment.

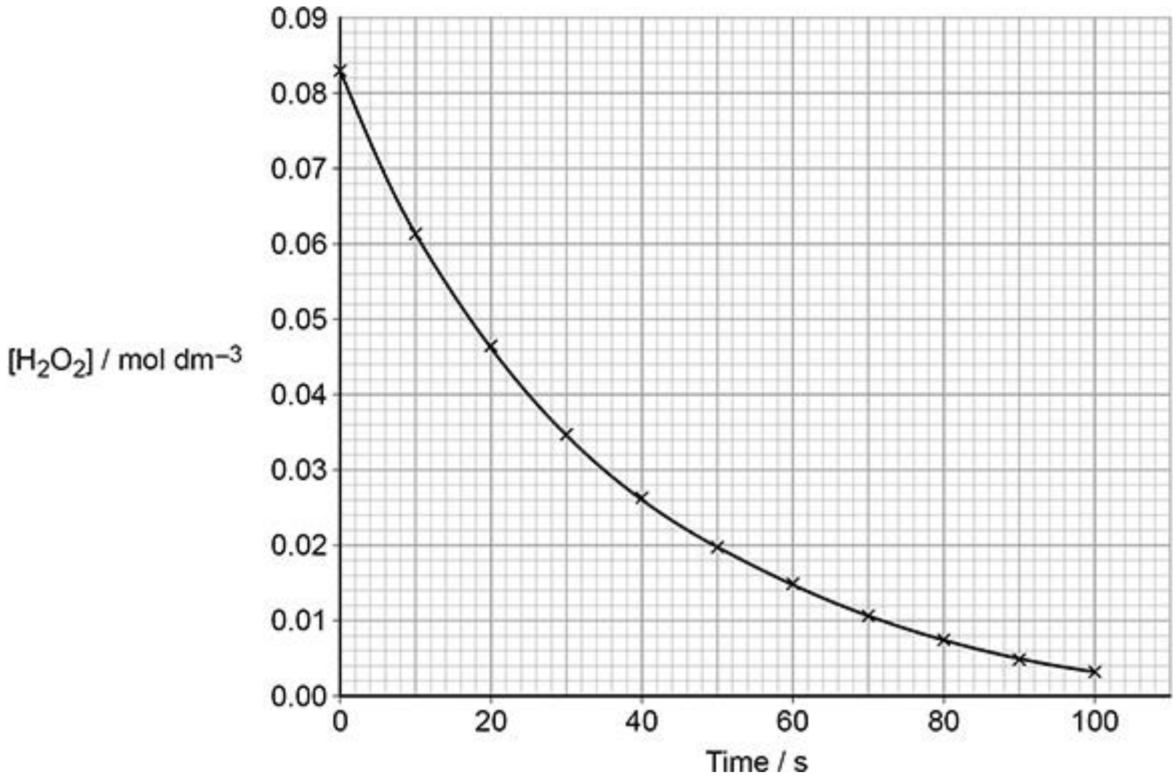
The student places hydrogen peroxide solution in a conical flask with the catalyst and uses a gas syringe to collect the oxygen formed. The student records the volume of oxygen every 10 seconds for 100 seconds.

(a) Explain why the reaction is fastest at the start.

(2)

(b) The graph in **Figure 1** shows how the concentration of hydrogen peroxide changes with time in this experiment.

Figure 1



Tangents to the curve in **Figure 1** can be used to determine rates of reaction.

Draw a tangent to the curve when the concentration of hydrogen peroxide solution is 0.05 mol dm^{-3}

Use your tangent to calculate the gradient of the curve at this point.

(2)

(c) The concentration of hydrogen peroxide solution at time *t* during the experiment can be calculated using this expression.

$$[H_2O_2]_t = [H_2O_2]_{initial}\left(\frac{V_{max} - V_t}{V_{max}}\right)$$

$[H_2O_2]_t$ = concentration of hydrogen peroxide solution at time *t* / mol dm^{-3}

$[H_2O_2]_{initial}$ = concentration of hydrogen peroxide solution at the start / mol dm^{-3}

V_{max} = total volume of oxygen gas collected during the whole experiment / cm^3

V_t = volume of oxygen gas collected at time *t* / cm^3

In this experiment, V_{max} = 100 cm^3

Use **Figure 1** and the expression to calculate $[H_2O_2]_t$ when 20 cm^3 of oxygen has been collected.

(2)

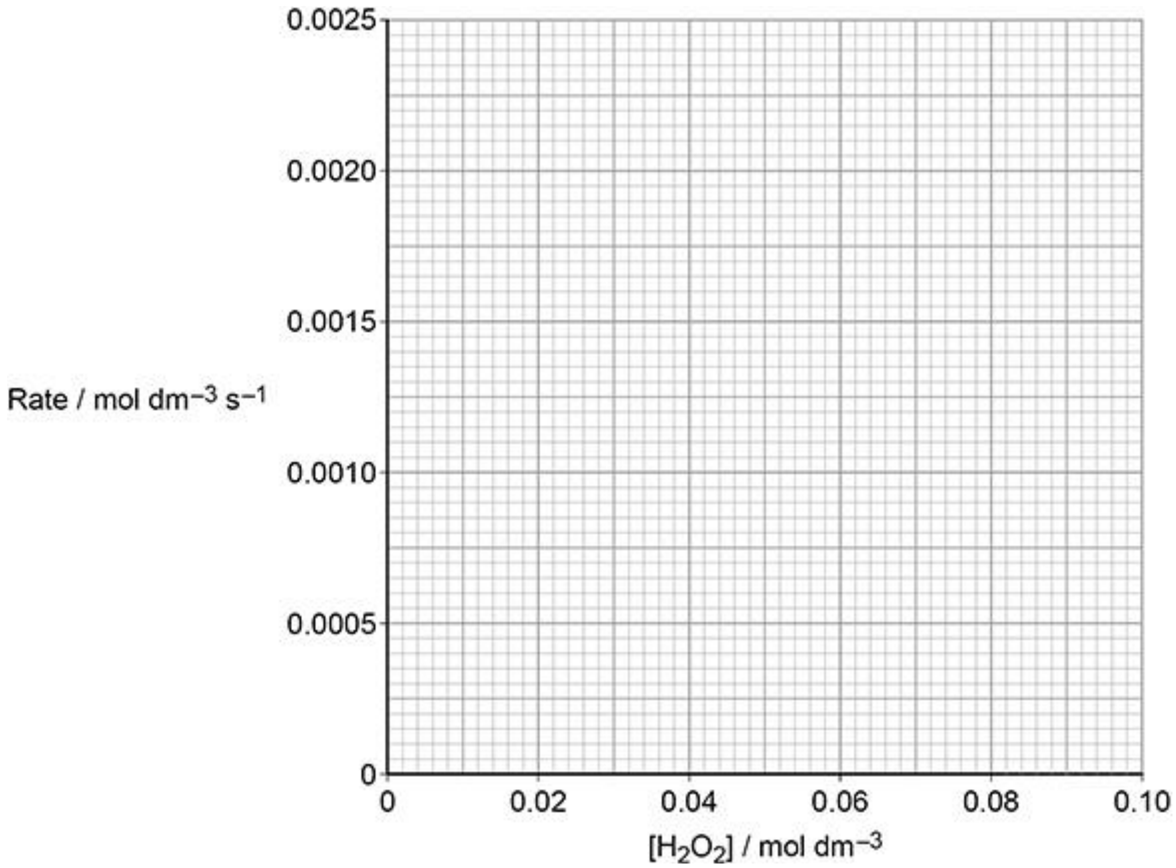
The table below shows data from a similar experiment.

$[H_2O_2]$ / mol dm^{-3}	0.02	0.03	0.05	0.07	0.09
Rate / mol dm^{-3} s^{-1}	0.00049	0.00073	0.00124	0.00168	0.00219

(d) Plot the data from the table above on the grid in **Figure 2**.

Draw a line of best fit.

Figure 2



(2)

(e) Use **Figure 2** to determine the order of reaction with respect to H_2O_2

State how the graph shows this order.

(2)
(Total 10 marks)

Q3.

This question is about rates of reaction.

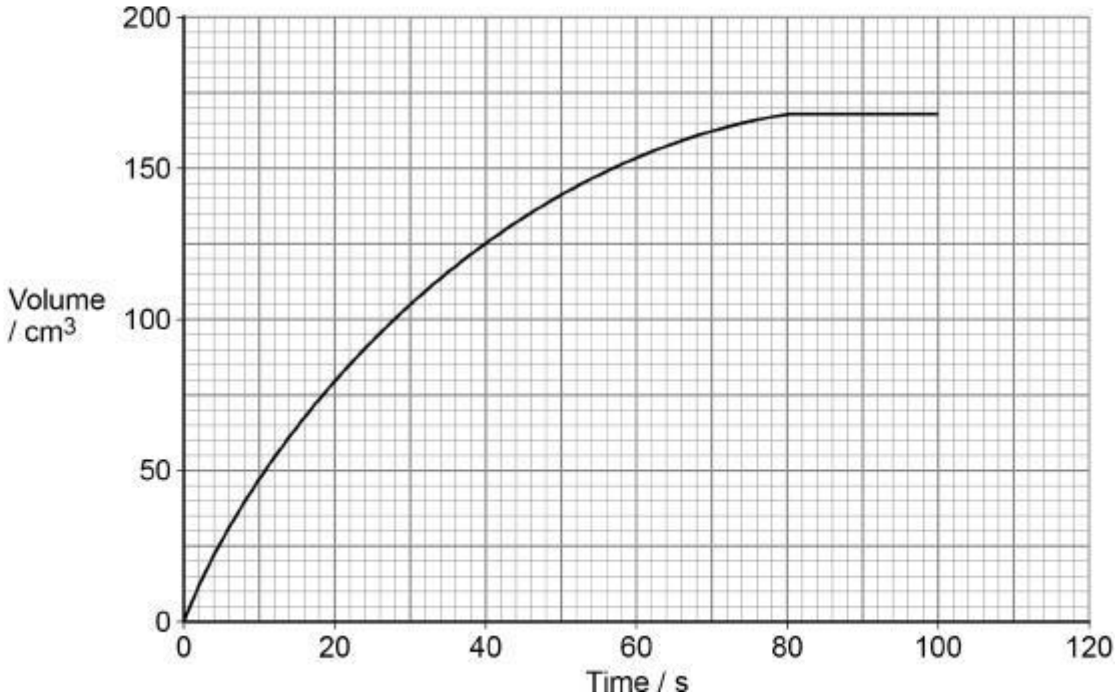
Phosphinate ions ($H_2PO_2^-$) react with hydroxide ions to produce hydrogen gas as shown.

$$H_2PO_2^- + OH^- \rightarrow HPO_3^{2-} + H_2$$

A student completed an experiment to determine the initial rate of this reaction.
The student used a solution containing phosphinate ions and measured the volume of hydrogen gas collected every 20 seconds at a constant temperature.

Figure 1 shows a graph of the student's results.

Figure 1



(a) Use the graph in **Figure 1** to determine the initial rate of reaction for this experiment. State its units. Show your working on the graph.

(3)

(b) Another student reacted different initial concentrations of phosphinate ions with an excess of hydroxide ions. The student measured the time (t) taken to collect 15 cm^3 of hydrogen gas. Each experiment was carried out at the same temperature. The table shows the results.

Initial [$H_2PO_2^-$] / mol dm^{-3}	***t* / s**
0.25	64
0.35	32
0.50	16
1.00	4

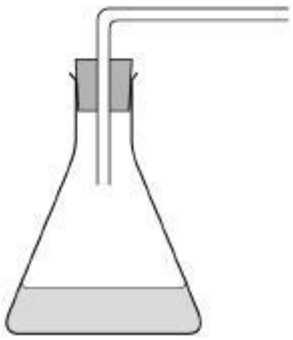
State the relationship between the initial concentration of phosphinate and time (t).

Deduce the order of the reaction with respect to phosphinate.

(2)

(c) Complete the diagram in **Figure 2** to show how the hydrogen gas could be collected and measured in the experiments in part (a) and (b).

Figure 2



The rate equation for a different reaction is

$$rate = k\,[L]\,[M]^2$$

(1)

(d) Deduce the overall effect on the rate of reaction when the concentrations of both **L** and **M** are halved.

(1)

(e) The rate of reaction is 0.0250 mol dm^{-3} s^{-1} when the concentration of **L** is 0.0155 mol dm^{-3}

Calculate the concentration of **M** if the rate constant is 21.3 mol^{-2} dm^{6} s^{-1}

(3)

(f) Define the term overall order of reaction.

(1)
(Total 11 marks)

Q4.

Cisplatin, $[Pt(NH_3)_2Cl_2]$, is used as an anti-cancer drug.

(a) Cisplatin works by causing the death of rapidly dividing cells.

Name the process that is prevented by cisplatin during cell division.

(1)

After cisplatin enters a cell, one of the chloride ligands is replaced by a water molecule to form a complex ion, **B**.

(b) Give the equation for this reaction.

(2)

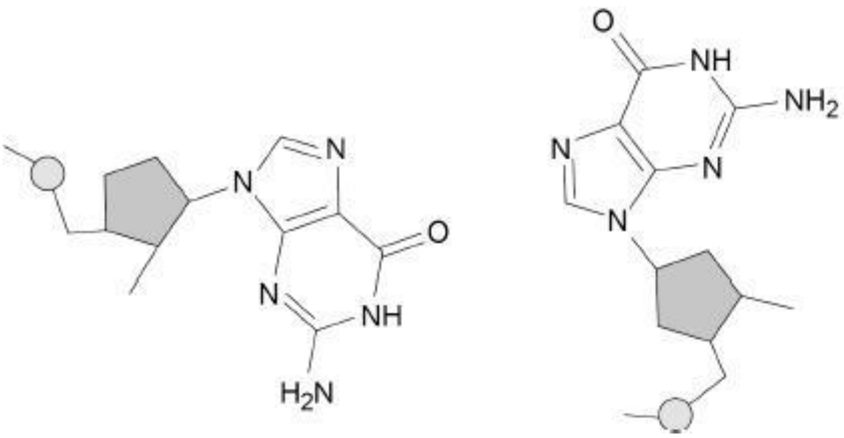
(c) When the complex ion **B** reacts with DNA, the water molecule is replaced as a bond forms

between platinum and a nitrogen atom in a guanine nucleotide.
The remaining chloride ligand is also replaced as a bond forms between platinum and a nitrogen atom in another guanine nucleotide.

Figure 1 represents two adjacent guanine nucleotides in DNA.

Complete **figure 1** to show how the platinum complex forms a cross-link between the guanine nucleotides.

Figure 1



(2)

An experiment is done to investigate the rate of reaction in part (b).

(d) During the experiment the concentration of cisplatin is measured at one-minute intervals.

Explain how graphical methods can be used to process the measured results, to confirm that the reaction is first order.

(3)

In another experiment, the effect of temperature on the rate of the reaction in part (b) is investigated.

The table shows the results.

Temperature ***T* / K**	$\frac{1}{T}$ / K^{-1}	**Rate constant** ***k* / s** $^{-1}$	**ln *k***
293	0.00341	1.97×10^{-8}	−17.7
303	0.00330	8.61×10^{-8}	−16.3
313	0.00319	3.43×10^{-7}	−14.9
318		6.63×10^{-7}	
323	0.00310	1.26×10^{-6}	−13.6

(e) Complete the table above.

(2)

(f) The Arrhenius equation can be written in the form

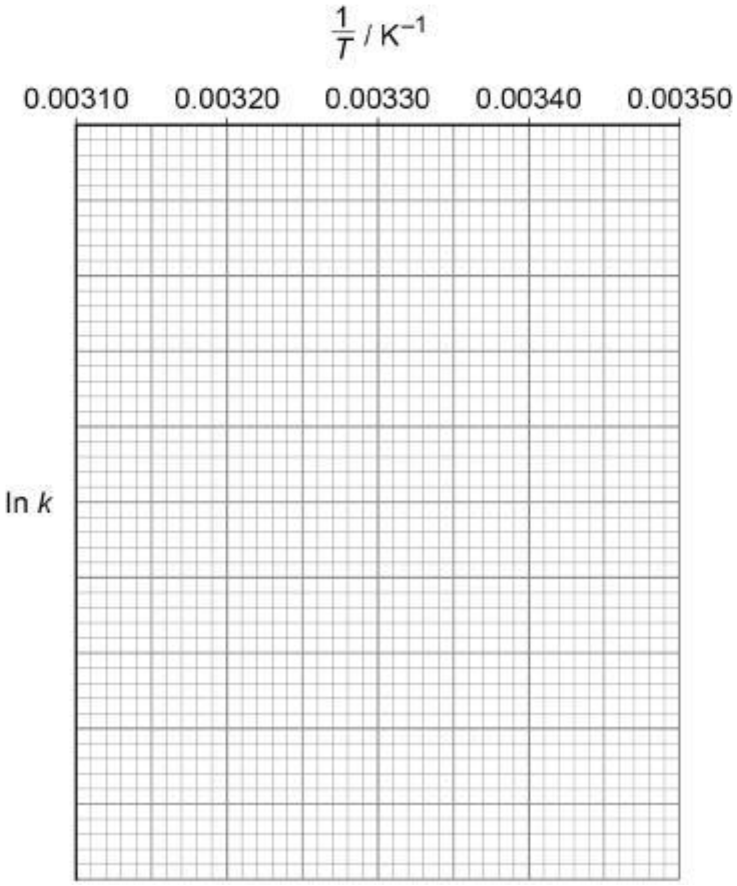
$$\ln k = \frac{-E_a}{RT} + \ln A$$

Use the data in the table above to plot a graph of ln k against $\frac{1}{T}$ on the grid in **Figure 2**.

Calculate the activation energy, E_a, in kJ mol^{-1}

The gas constant, R = 8.31 J K^{-1} mol^{-1}

Figure 2



(5)
(Total 15 marks)

Q5.

The rate expression for the reaction between **X** and **Y** is

$$rate = k\,[\mathbf{X}]^2\,[\mathbf{Y}]$$

Which statement is correct?

A The rate constant has units mol^{-1} dm^3 s^{-1}

B The rate of the reaction is halved if the concentration of **X** is halved and the concentration of **Y** is doubled.

C The rate increases by a factor of 16 if the concentration of **X** is tripled and the concentration of **Y** is doubled.

D The rate constant is independent of temperature.

(Total 1 mark)

Q6.

Substances **P** and **Q** react in solution at a constant temperature.
The initial rate of reaction was studied in three experiments by measuring the change in concentration of **P** over the first five seconds of the reaction.
The data obtained are shown in **Table 1**.

Table 1

Experiment	Time after mixing / s	Concentration / mol dm^3	
		P	Q
1	0	1.00×10^{-2}	1.25×10^{-2}
	5.0	0.92×10^{-2}	not measured
2	0	2.00×10^{-2}	1.25×10^{-2}
	5.0	1.84×10^{-2}	not measured
3	0	0.50×10^{-2}	2.50×10^{-2}
	5.0	0.34×10^{-2}	not measured

(a) Complete **Table 2** to show the initial rate of reaction of **P** in each experiment.

Table 2

Experiment	Initial rate / mol dm^3 s^{-1}
1	1.6×10^{-4}
2	
3	

(1)

(b) Determine the order of reaction with respect to **P** and the order of reaction with respect to **Q**.

(2)

(c) A reaction between substances **R** and **S** was second order with respect to **R** and second order with respect to **S**.
At a given temperature, the initial rate of reaction was 1.20×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of **R** was 1.00×10^{-2} mol dm^{-3} and the initial concentration of **S** was 2.45×10^{-2} mol dm^{-3}

Calculate a value for the rate constant, *k*, for the reaction at this temperature.
Give the units for *k*

(3)
(Total 6 marks)

Q7.

Iodide ions are oxidised to iodine by hydrogen peroxide in acidic conditions.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

The rate equation for this reaction can be written as

$$rate = k\,[H_2O_2]^a\,[I^-]^b\,[H^+]^c$$

In an experiment to determine the order with respect to $H^+(aq)$, a reaction mixture is made containing $H^+(aq)$ with a concentration of 0.500 mol dm^{-3}

A large excess of both H_2O_2 and I^- is used in this reaction mixture so that the rate equation can be simplified to

$$rate = k_1\,[H^+]^c$$

(a) Explain why the use of a large excess of H_2O_2 and I^- means that the rate of reaction at a fixed temperature depends only on the concentration of $H^+(aq)$.

(2)

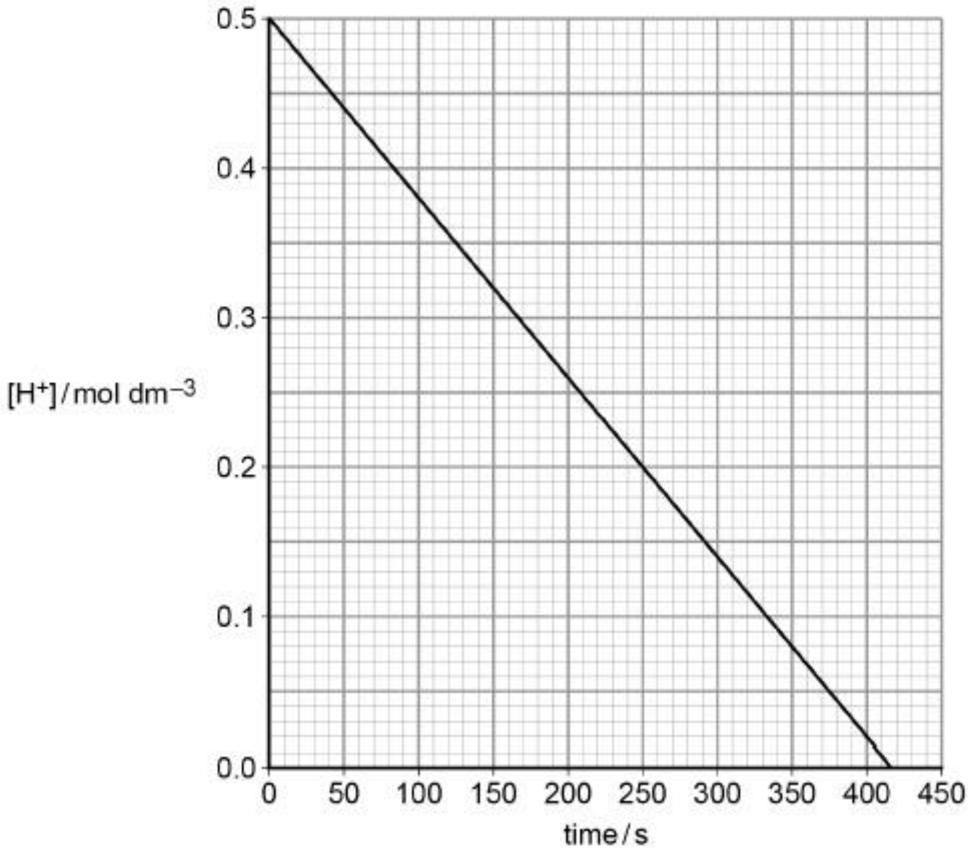
(b) Samples of the reaction mixture are removed at timed intervals and titrated with alkali to determine the concentration of $H^+(aq)$.

State and explain what must be done to each sample before it is titrated with alkali.

(2)

(c) A graph of the results is shown in **Figure 1**.

Figure 1



Explain how the graph shows that the order with respect to H^+(aq) is zero.

(2)

(d) Use the graph in **Figure 1** to calculate the value of k_1

Give the units of k_1

(3)

(e) A second reaction mixture is made at the same temperature. The initial concentrations of H^+(aq) and I^-(aq) in this mixture are both 0.500 mol dm^{-3}

There is a large excess of H_2O_2

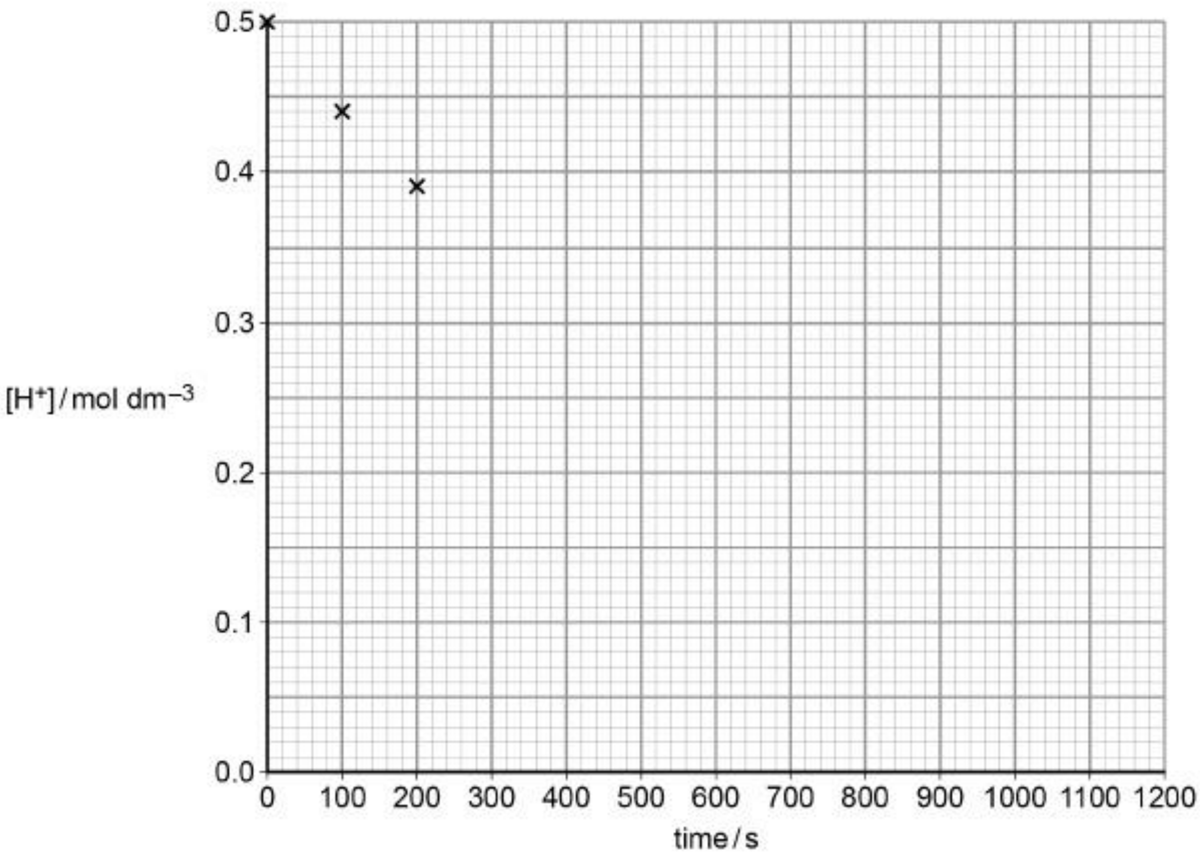
In this reaction mixture, the rate depends only on the concentration of I^-(aq).

The results are shown in the table.

Time / s	0	100	200	400	600	800	1000	1200
[H^+] / mol dm^{-3}	0.50	0.44	0.39	0.31	0.24	0.19	0.15	0.12

Plot these results on the grid in **Figure 2**. The first three points have been plotted.

Figure 2



(1)

(f) Draw a line of best fit on the grid in **Figure 2**.

(1)

(g) Calculate the rate of reaction when $[H^+] = 0.35$ mol dm^{-3}
Show your working using a suitable construction on the graph in **Figure 2**.

(2)

(h) A general equation for a reaction is shown.

$$\mathbf{A}(aq) + \mathbf{B}(aq) + \mathbf{C}(aq) \rightarrow \mathbf{D}(aq) + \mathbf{E}(aq)$$

In aqueous solution, **A**, **B**, **C** and **D** are all colourless but **E** is dark blue.

A reagent (**X**) is available that reacts rapidly with **E**. This means that, if a small amount of **X** is included in the initial reaction mixture, it will react with any **E** produced until all of the **X** has been used up.

Explain, giving brief experimental details, how you could use a series of experiments to determine the order of this reaction with respect to **A**. In each experiment you should obtain a measure of the initial rate of reaction.

(6)

(Total 19 marks)