

AQA A-LEVEL CHEMISTRY • 7405

CHEMISTRY



EXAM QUESTION PACK

3.1.9 RATE EQUATIONS

SCORE

/412

PERCENTAGE

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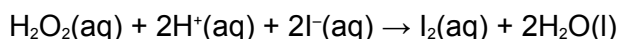
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Q1.

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



The rate equation for this reaction can be written as

$$\text{rate} = k [\text{H}_2\text{O}_2]^a [\text{I}^-]^b [\text{H}^+]^c$$

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

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

$$\text{rate} = k_1 [\text{H}^+]^c$$

- (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 $\text{H}^+(\text{aq})$.

(2)

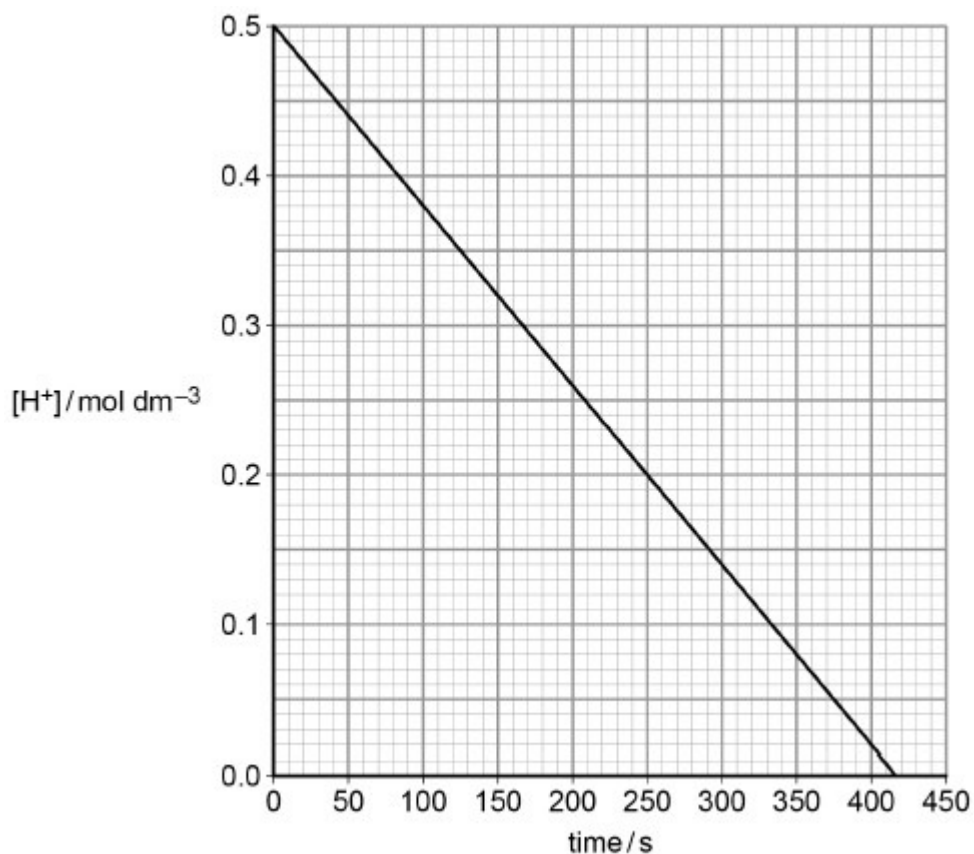
- (b) Samples of the reaction mixture are removed at timed intervals and titrated with alkali to determine the concentration of $\text{H}^+(\text{aq})$.

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 $\text{H}^+(\text{aq})$ is zero.

(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 $\text{H}^+(\text{aq})$ and $\text{I}^-(\text{aq})$ in this mixture are both $0.500 \text{ mol dm}^{-3}$

There is a large excess of H_2O_2

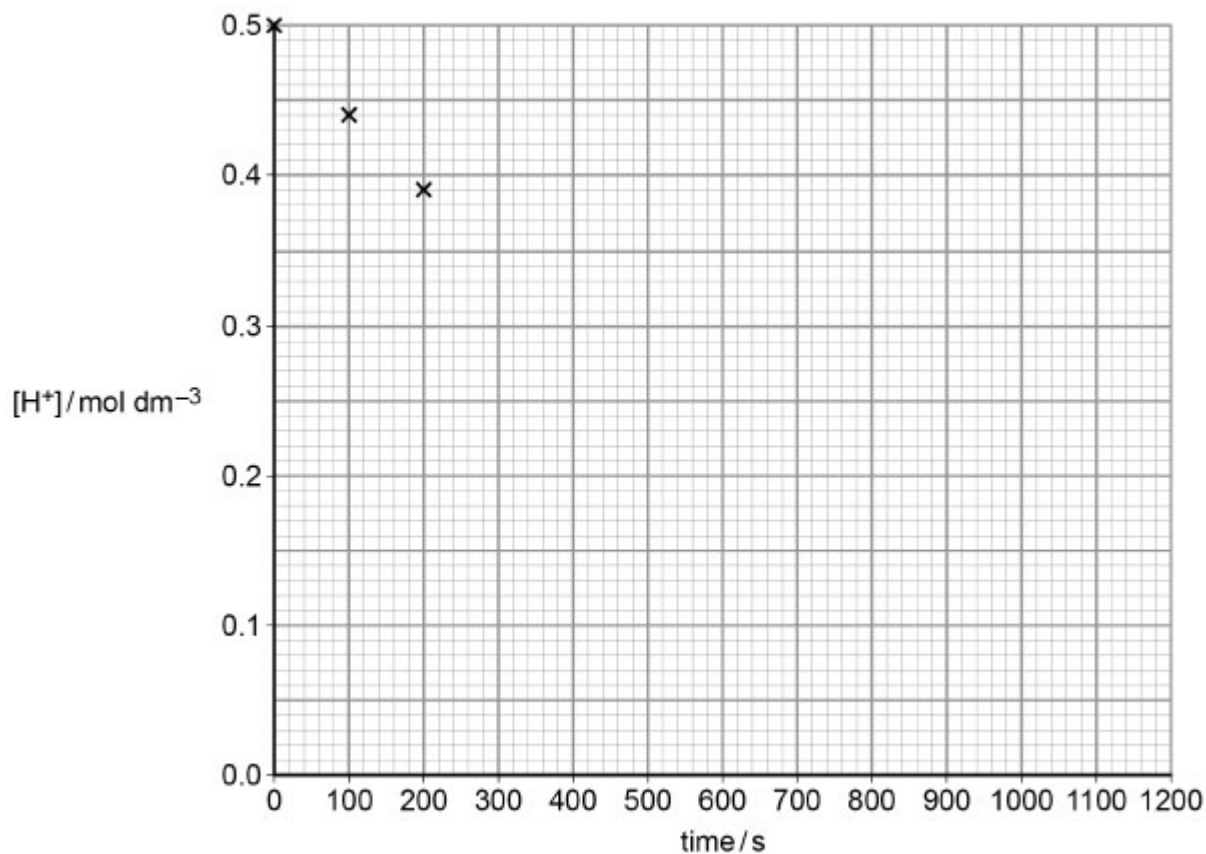
In this reaction mixture, the rate depends only on the concentration of $\text{I}^-(\text{aq})$.

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)

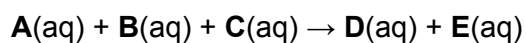
- (g) Calculate the rate of reaction when [H⁺] = 0.35 mol dm⁻³

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.



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

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.

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(Total 19 marks)

A series of experiments was carried out to find the order of reaction with respect to reactant **X**. In these experiments, only the concentration of **X** was changed.

B 

C ☐

D ☐

(Total 1 mark)

Q3.

The mechanisms of some reactions can be deduced from kinetic data.

The table shows the results of five experiments involving the reaction between benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) and potassium hydroxide solution.

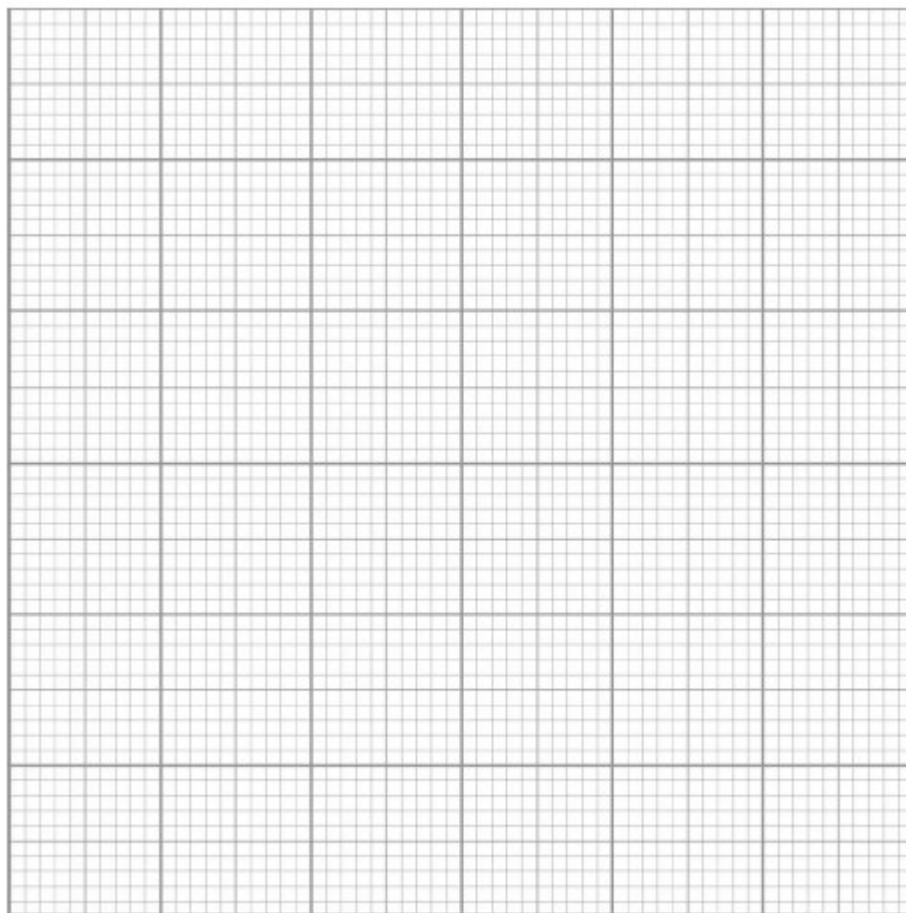
Experiment	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$	$[\text{C}_6\text{H}_5\text{CHO}]$ / mol dm^{-3}	$\text{C}_6\text{H}_5\text{CHO}]^2$	$[\text{KOH}]$ / mol dm^{-3}
1	0	0		0
2	2.90×10^{-6}	0.25		0.25
3	1.16×10^{-5}	0.50		0.25
4	2.61×10^{-5}	0.75		0.25
5	4.65×10^{-5}	1.00		0.25

(a) Calculate the value of $[\text{C}_6\text{H}_5\text{CHO}]^2$ for each experiment.

Write your answers in the table above.

Plot a graph of initial rate against $[\text{C}_6\text{H}_5\text{CHO}]^2$ on the grid below.

Label the axes with units.



(4)

- (b) Deduce the order of the reaction with respect to $\text{C}_6\text{H}_5\text{CHO}$ from the graph.

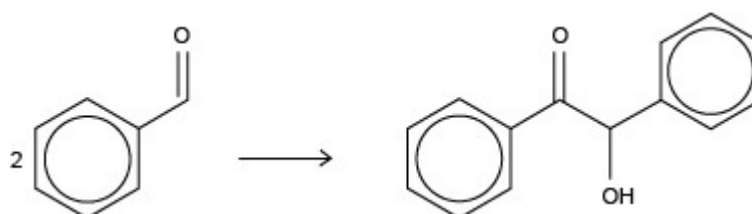
Explain your answer.

Order _____

Explanation _____

(2)

- (c) Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) undergoes a dimerisation reaction as shown:



The rate equation for the reaction is

$$\text{rate} = k [\text{C}_6\text{H}_5\text{CHO}] [\text{CN}^-]$$

Suggest the role of the cyanide ion in the reaction.

Explain your answer.

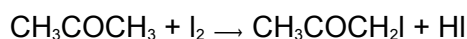
Role of CN^- _____

Explanation _____

(2)
(Total 8 marks)

Q4.

Iodine reacts slowly with propanone in the presence of an acid catalyst according to the equation



The rate of this reaction can be followed by preparing mixtures in which only the initial concentration of propanone is varied. At suitable time intervals, a small sample of the mixture is removed and titrated with sodium thiosulfate solution. This allows determination of the concentration of iodine remaining at that time. The rate of this reaction can be followed by preparing mixtures in which only the initial concentration of propanone is varied. At suitable time intervals, a small sample of the mixture is removed and titrated with sodium thiosulfate solution. This allows determination of the concentration of iodine remaining at that time.

Five mixtures, **A**, **B**, **C**, **D** and **E**, are prepared as shown in **Table 1**.

Table 1

Mixture	A	B	C	D	E
Volume of $0.0200 \text{ mol dm}^{-3} \text{ I}_2(\text{aq})/\text{cm}^3$	40.0	40.0	40.0	40.0	40.0
Volume of $0.100 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4(\text{aq})/\text{cm}^3$	25.0	25.0	25.0	25.0	25.0
Volume of $1.00 \text{ mol dm}^{-3} \text{ CH}_3\text{COCH}_3(\text{aq})/\text{cm}^3$	25.0	20.0	15.0	10.0	6.5
Volume of distilled water/ cm^3	0.0	5.0	10.0	15.0	18.5

- (a) Calculate the initial concentration, in mol dm^{-3} , of the propanone in mixture **A**.

Concentration = _____ mol dm^{-3}

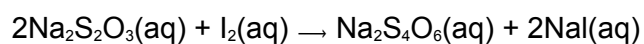
(2)

- (b) State and explain why different volumes of water are added to mixtures **B**, **C**, **D** and **E**.

(2)

- (c) Calculate the volume of $0.0100 \text{ mol dm}^{-3}$ sodium thiosulfate solution required to react with all of the iodine in a 10.0 cm^3 sample of mixture **E**, before the iodine reacts with propanone.

The equation for the reaction in the titration is



Volume = _____ cm^3

(4)

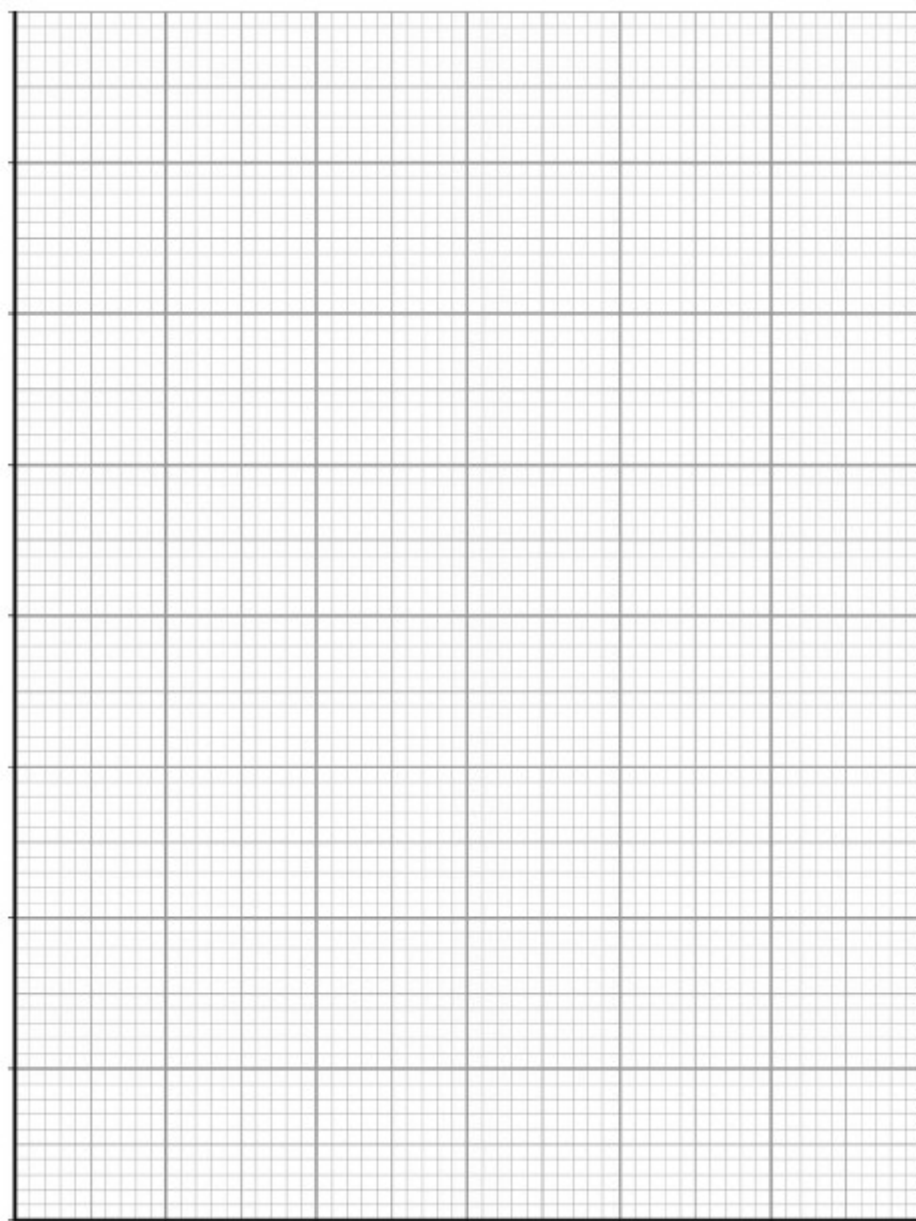
- (d) The results for mixture **E** are shown in **Table 2**.
V is the volume of $0.0100 \text{ mol dm}^{-3}$ sodium thiosulfate solution needed, at different times, **t**, to react with the iodine in a 10.0 cm^3 sample of **E**.

Table 2

t/min	5	10	20	30
V/cm³	17.5	17.2	16.6	16.0

Use these data and your answer to part (c) to plot a graph of **V** (*y*-axis) against **t** (*x*-axis) for mixture **E**.

Draw a best-fit straight line through your points and calculate the gradient of this line.



gradient = _____ $\text{cm}^3 \text{ min}^{-1}$

(5)

- (e) The gradients for similar graphs produced by mixtures **A**, **B**, **C** and **D** are shown in **Table 3**.
Each gradient is a measure of the rate of the reaction between iodine and propanone.

Table 3

Mixture	A	B	C	D
Gradient / $\text{cm}^3 \text{min}^{-1}$	-0.24	-0.20	-0.15	-0.10

Use information from **Table 1** and **Table 3** to deduce the order with respect to propanone. Explain your answer.

(2)

- (f) Each sample taken from the reaction mixtures is immediately added to an excess of sodium hydrogencarbonate solution before being titrated with sodium thiosulfate solution.

Suggest the purpose of this addition.
Explain your answer.

(2)

(Total 17 marks)

Q5.

The rate equation for the acid-catalysed reaction between iodine and propanone is:

$$\text{rate} = k [\text{H}^+] [\text{C}_3\text{H}_6\text{O}]$$

The rate of reaction was measured for a mixture of iodine, propanone and sulfuric acid at pH = 0.70

In a second mixture the concentration of the sulfuric acid was different but the concentrations of iodine and propanone were unchanged. The new rate of reaction was a quarter of the original rate.

What was the pH of the second mixture?

- A** 1.00 ☐
- B** 1.30 ☐
- C** 1.40 ☐
- D** 2.80 ☐

(Total 1 mark)

Q6.

A rate investigation was carried out on a reaction involving three reactants, **X**, **Y** and **Z**. The concentrations of the reactants were varied and the relative rate for each mixture determined.

Experiment	[X]/mol dm ⁻³	[Y]/mol dm ⁻³	[Z]/mol dm ⁻³	Relative rate
1	1 × 10 ⁻³	1 × 10 ⁻³	2 × 10 ⁻³	1
2	2 × 10 ⁻³	2 × 10 ⁻³	2 × 10 ⁻³	4
3	5 × 10 ⁻⁴	2 × 10 ⁻³	4 × 10 ⁻³	0.5

The reaction is zero order with respect to **Y**.

What is the overall order of reaction?

- A** 0 ☐
- B** 1 ☐
- C** 2 ☐
- D** 3 ☐

(Total 1 mark)

Q7.

This question involves the use of kinetic data to deduce the order of a reaction and calculate a value for a rate constant.

The data in **Table 1** were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Table 1

Experiment	Initial	Initial	Initial rate
------------	---------	---------	--------------

	concentration of A / mol dm ⁻³	concentration of B / mol dm ⁻³	/ mol dm ⁻³ s ⁻¹
1	0.12	0.26	2.10×10^{-4}
2	0.36	0.26	1.89×10^{-3}
3	0.72	0.13	3.78×10^{-3}

- (a) Show how these data can be used to deduce the rate expression for the reaction between **A** and **B**.

(3)

The data in **Table 2** were obtained in two experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature.

Table 2

Experiment	Initial concentration of C / mol dm ⁻³	Initial concentration of D / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
4	1.9×10^{-2}	3.5×10^{-2}	7.2×10^{-4}
5	3.6×10^{-2}	5.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{C}]^2[\text{D}]$$

- (b) Use the data from experiment **4** to calculate a value for the rate constant, k , at this temperature. Deduce the units of k .

$k =$ _____ Units = _____

(3)

- (c) Calculate a value for the initial rate in experiment 5.

Initial rate = _____ mol dm⁻³ s⁻¹

(1)

- (d) The rate equation for a reaction is

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

Explain qualitatively why doubling the temperature has a much greater effect on the rate of the reaction than doubling the concentration of **E**.

(3)

- (e) A slow reaction has a rate constant $k = 6.51 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3$ at 300 K.

Use the equation $\ln k = \ln A - E_a / RT$ to calculate a value, in kJ mol⁻¹, for the activation energy of this reaction.

The constant $A = 2.57 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3$.
The gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

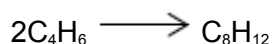
Activation energy = _____

(2)

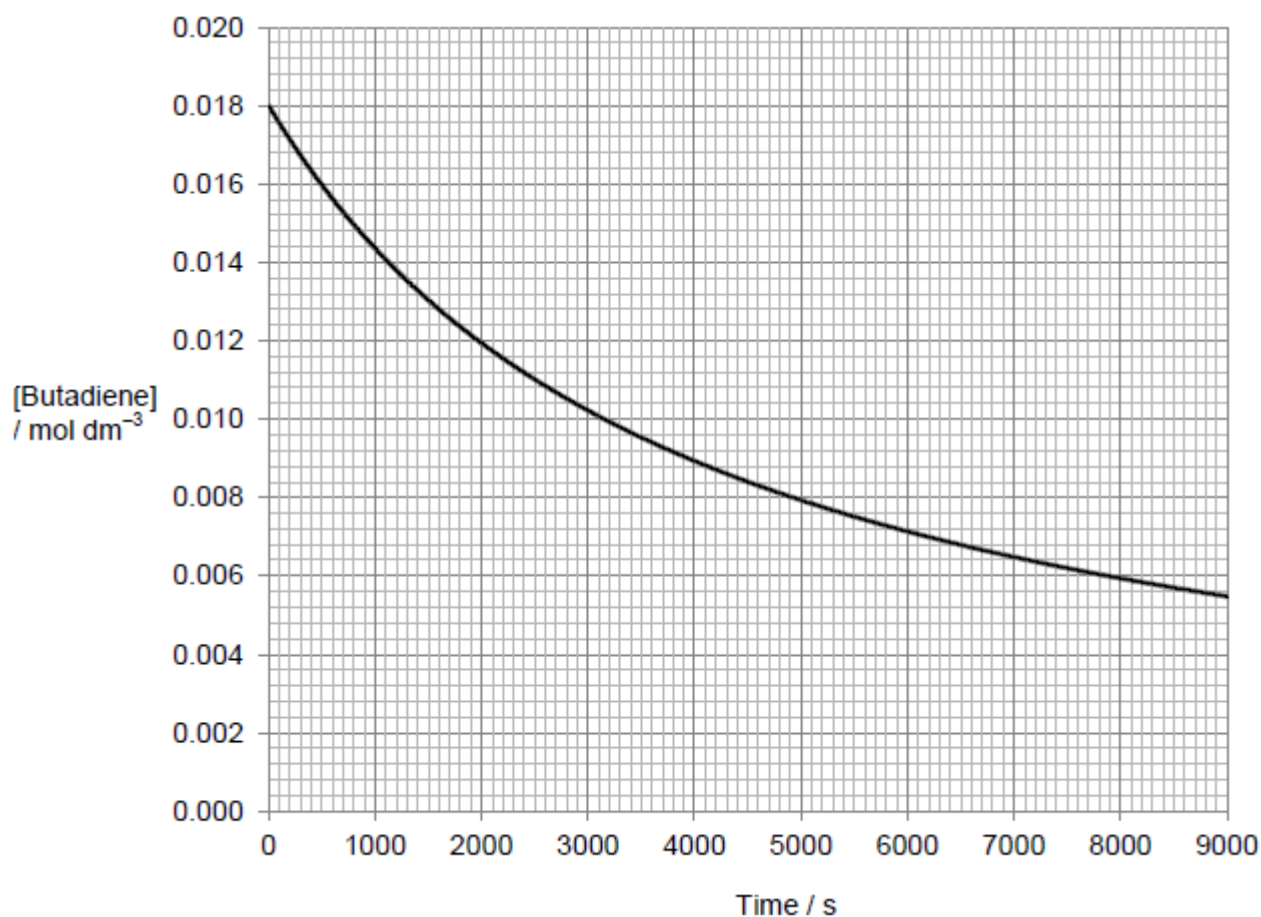
(Total 12 marks)

Q8.

Butadiene dimerises according to the equation



The kinetics of the dimerisation are studied and the graph of the concentration of a sample of butadiene is plotted against time. The graph is shown below.



- (a) Draw a tangent to the curve when the concentration of butadiene is 0.0120 mol dm⁻³.

(1)

- (b) The initial rate of reaction in this experiment has the value $4.57 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Use this value, together with a rate obtained from your tangent, to justify that the order of the reaction is 2 with respect to butadiene.

(5)

(Total 6 marks)

Q9.

The initial rate of the reaction between gases **D** and **E** was measured in a series of experiments at a constant temperature. The results are shown in the table.

Expt	Initial [D] / mol dm ⁻³	Initial [E] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	1.25×10^{-2}	5.81×10^{-1}	1.16×10^{-2}
2	1.88×10^{-2}	8.73×10^{-1}	3.92×10^{-2}
3	1.88×10^{-2}	1.75	1.57×10^{-1}

- (a) Deduce the order of reaction with respect to **D** and the order with respect to **E**.

Order with respect to **D** _____

Order with respect to **E** _____

Space for working _____

(2)

- (b) Suggest why initial rates of reaction are used to determine these orders rather than rates of reaction at other times during the experiments.

(1)

- (c) State how the initial rate is obtained from a graph of the concentration of the product against time.

(2)

(Total 5 marks)

Q10.

This question involves the use of kinetic data to calculate the order of a reaction and also a value for a rate constant.

- (a) The data in this table were obtained in a series of experiments on the rate of the reaction between compounds **E** and **F** at a constant temperature.

Experiment	Initial concentration of E / mol dm ⁻³	Initial concentration of F / mol dm ⁻³	Initial rate of reaction / mol dm ⁻³ s ⁻¹
1	0.15	0.24	0.42×10^{-3}
2	0.45	0.24	3.78×10^{-3}
3	0.90	0.12	7.56×10^{-3}

- (i) Deduce the order of reaction with respect to **E**.

(1)

- (ii) Deduce the order of reaction with respect to **F**.

(1)

- (b) The data in the following table were obtained in two experiments on the rate of the reaction between compounds **G** and **H** at a constant temperature.

Experiment	Initial concentration of G / mol dm ⁻³	Initial concentration of H / mol dm ⁻³	Initial rate of reaction / mol dm ⁻³ s ⁻¹
4	3.8×10^{-2}	2.6×10^{-2}	8.6×10^{-4}
5	6.3×10^{-2}	7.5×10^{-2}	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{G}]^2[\text{H}]$$

- (i) Use the data from Experiment 4 to calculate a value for the rate constant k at this temperature. Deduce the units of k .

Calculation _____

Units _____

(3)

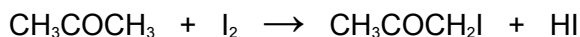
- (ii) Calculate a value for the initial rate of reaction in Experiment 5.

(1)

(Total 6 marks)

Q11.

The reaction between propanone and iodine in the presence of hydrochloric acid was studied at a constant temperature.



The following rate equation was deduced.

$$\text{rate} = k [\text{CH}_3\text{COCH}_3][\text{H}^+]$$

- (a) Suggest why the order with respect to iodine is zero.

(1)

- (b) In an experiment the initial concentrations of propanone, iodine and hydrochloric acid were as shown in the table. The initial rate of reaction in this experiment was $8.64 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$.

	Initial concentration / mol dm^{-3}
CH_3COCH_3	5.82×10^{-2}
I_2	1.78×10^{-3}
H^+	4.76×10^{-1}

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Use the data in the table and the rate equation to calculate a value for the rate constant at this temperature.
Give units with your answer.

(2)

- (c) A series of experiments was carried out using concentrations of propanone approximately 100 times the concentrations of iodine and hydrochloric acid.

Suggest the rate equation under these conditions.
Explain your answer.

(2)

(Total 5 marks)

Q12.

The initial rate of the reaction between two gases **P** and **Q** was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\text{P}]^2[\text{Q}]$$

- (a) Complete the table of data below for the reaction between **P** and **Q**.

Experiment	Initial [P] /mol dm ⁻³	Initial [Q] /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
1	0.20	0.30	1.8 = 10 ⁻³
2	0.40	0.60	
3	0.60		5.4 = 10 ⁻³

4		0.90	12.2×10^{-3}
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(Space for working) _____

(3)

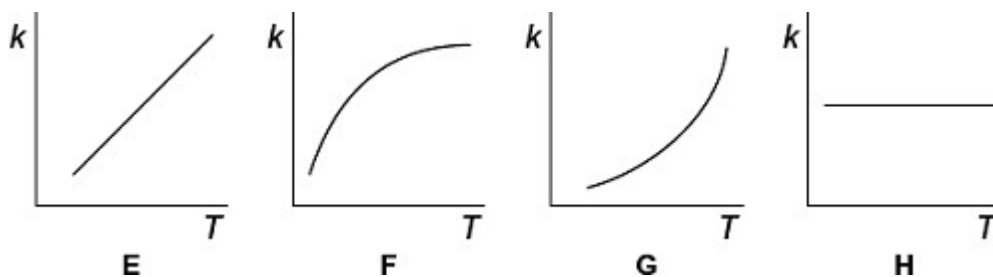
- (b) Use the data from Experiment 1 to calculate a value for the rate constant k and deduce its units.

Calculation _____

Units _____

(3)

- (c) Consider the graphs **E**, **F**, **G** and **H** below.



Write in the box below the letter of the graph that shows how the rate constant k varies with temperature.

(1)

(Total 7 marks)

Q13.

- (a) The data in the following table were obtained in two experiments about the rate of the reaction between substances **B** and **C** at a constant temperature.

Experiment	Initial concentration of B / mol dm ⁻³	Initial concentration of C / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	4.2×10^{-2}	2.6×10^{-2}	8.4×10^{-5}
2	6.3×10^{-2}	7.8×10^{-2}	To be calculated

The rate equation for this reaction is known to be

$$\text{rate} = k[\mathbf{B}]^2[\mathbf{C}]$$

- (i) Use the data from Experiment **1** to calculate a value for the rate constant k at this temperature and deduce its units.

Calculation _____

Units _____

(3)

- (ii) Calculate a value for the initial rate in Experiment **2**.

(1)

- (b) The data in the following table were obtained in a series of experiments about the rate of the reaction between substances **D** and **E** at a constant temperature.

Experiment	Initial concentration of D / mol dm ⁻³	Initial concentration of E / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
3	0.13	0.23	0.26×10^{-3}
4	0.39	0.23	2.34×10^{-3}
5	0.78	0.46	9.36×10^{-3}

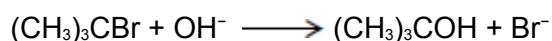
- (i) Deduce the order of reaction with respect to **D**.

(1)

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

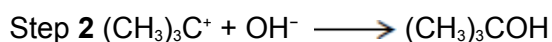
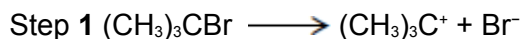
(1)

- (c) The compound $(\text{CH}_3)_3\text{CBr}$ reacts with aqueous sodium hydroxide as shown in the following equation.



This reaction was found to be first order with respect to $(\text{CH}_3)_3\text{CBr}$ but zero order with respect to hydroxide ions.

The following two-step process was suggested.



- (i) Deduce the rate-determining step in this two-step process.

(1)

- (ii) Outline a mechanism for this step using a curly arrow.

(1)
(Total 8 marks)

Q14.

- (a) In the presence of the catalyst rhodium, the reaction between NO and H_2 occurs according to the following equation.



The kinetics of the reaction were investigated and the rate equation was found to be

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

The initial rate of reaction was $6.2 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentration of NO was $2.9 \times 10^{-2} \text{ mol dm}^{-3}$ and the initial concentration of H_2 was $2.3 \times 10^{-2} \text{ mol dm}^{-3}$.

- (i) Calculate the value of the rate constant under these conditions and give its

units.

Calculation _____

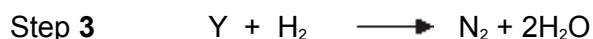
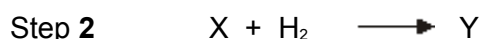
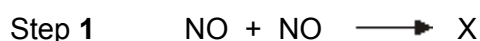
Units _____

(3)

- (ii) Calculate the initial rate of reaction if the experiment is repeated under the same conditions but with the concentrations of NO and of H₂ both doubled from their original values.

(1)

- (b) Using the rate equation and the overall equation, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.



Suggest which **one** of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step _____

Explanation _____

(2)

(Total 6 marks)

Q15.

The rate of hydrolysis of an ester **X** (HCOOCH₂CH₂CH₃) was studied in alkaline conditions at a given temperature. The rate was found to be first order with respect to the ester and first order with respect to hydroxide ions.

- (a) (i) Name ester **X**.

(1)

- (ii) Using **X** to represent the ester, write a rate equation for this hydrolysis reaction.

_____ (1)

- (iii) When the initial concentration of **X** was $0.024 \text{ mol dm}^{-3}$ and the initial concentration of hydroxide ions was $0.035 \text{ mol dm}^{-3}$, the initial rate of the reaction was $8.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$.
Calculate a value for the rate constant at this temperature and give its units.

Calculation _____

Units _____

_____ (3)

- (iv) In a second experiment at the same temperature, water was added to the original reaction mixture so that the total volume was doubled.
Calculate the initial rate of reaction in this second experiment.

(1)

- (v) In a third experiment at the same temperature, the concentration of **X** was half that used in the experiment in part (a) (iii) and the concentration of hydroxide ions was three times the original value.
Calculate the initial rate of reaction in this third experiment.

(1)

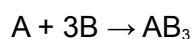
- (vi) State the effect, if any, on the value of the rate constant k when the temperature is lowered but all other conditions are kept constant. Explain your answer.

Effect _____

Explanation _____

(2)

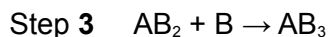
- (b) Compound **A** reacts with compound **B** as shown by the overall equation



The rate equation for the reaction is

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

A suggested mechanism for the reaction is



Deduce which one of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step _____

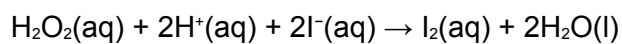
Explanation _____

(2)

(Total 11 marks)

Q16.

Hydrogen peroxide is a powerful oxidising agent. Acidified hydrogen peroxide reacts with iodide ions to form iodine according to the following equation.



The **initial rate** of this reaction is investigated by measuring the time taken to produce sufficient iodine to give a blue colour with starch solution.

A series of experiments was carried out, in which the concentration of iodide ions was varied, while keeping the concentrations of all of the other reagents the same. In each experiment the time taken (t) for the reaction mixture to turn blue was recorded.

The initial rate of the reaction can be represented as $\left(\frac{1}{t}\right)$, and the initial concentration of iodide ions can be represented by the volume of potassium iodide solution used.

A graph of $\log_{10} \left(\frac{1}{t}\right)$ on the y -axis against $\log_{10} (\text{volume of KI(aq)})$ is a straight line. The gradient of this straight line is equal to the order of the reaction with respect to iodide ions.

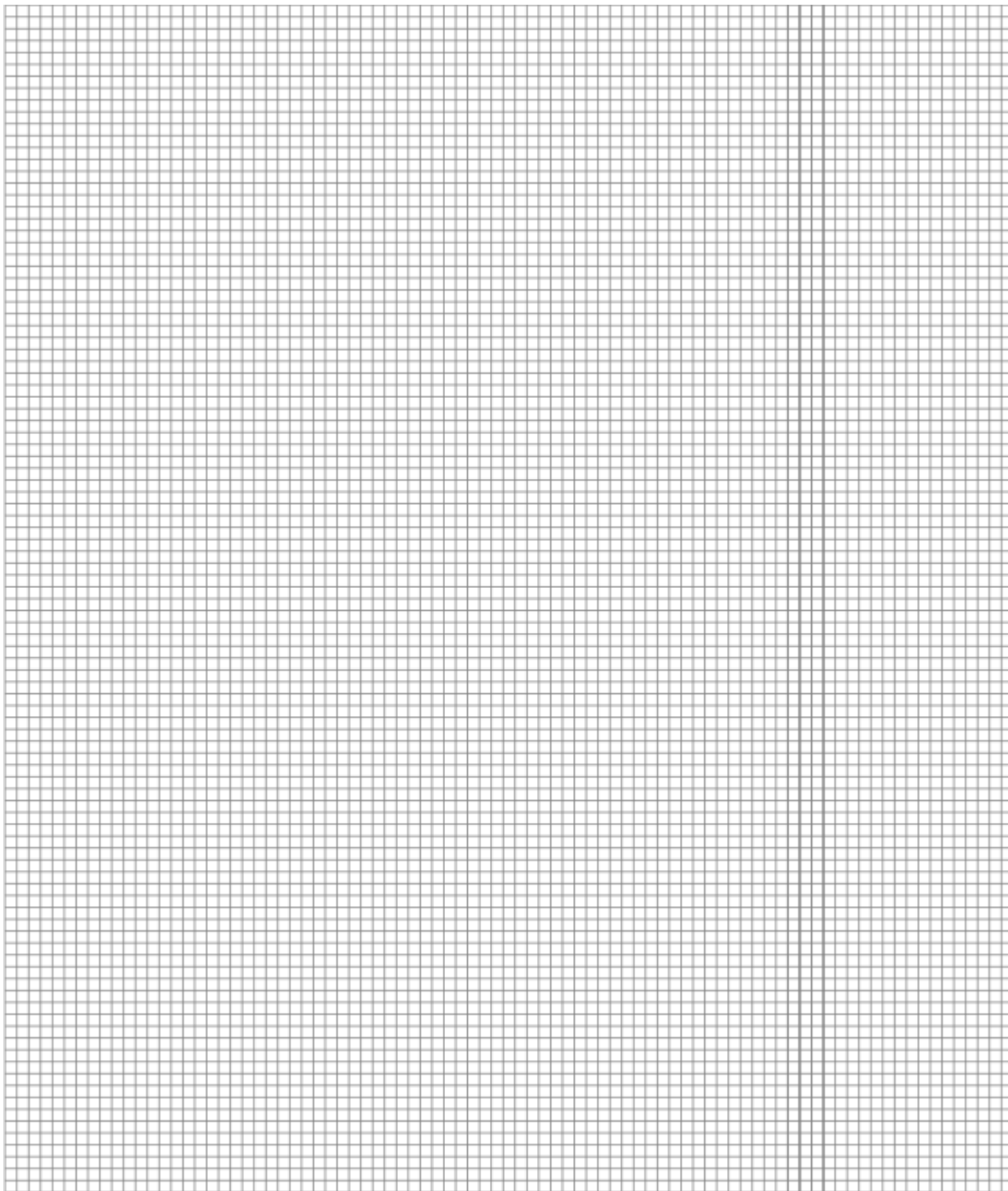
The results obtained are given in the table below. The time taken for each mixture to turn blue was recorded on a stopclock graduated in seconds.

Expt.	Volume of KI(aq) / cm ³	$\log_{10} (\text{volume of KI(aq)})$	Time / s	$\log_{10} \left(\frac{1}{t}\right)$
1	5	0.70	71	-1.85
2	8	0.90	46	-1.66

3	10	1.00	37	-1.57
4	15	1.18	25	-1.40
5	20	1.30	19	-1.28
6	25	1.40	14	-1.15

- (a) Use the results given in the table to plot a graph of $\log_{10} \left(\frac{1}{t} \right)$ on the y-axis against $\log_{10} (\text{volume of KI(aq)})$.

Draw a straight line of best fit on the graph, ignoring any anomalous points.



(5)

- (b) Determine the gradient of the line you have drawn. Give your answer to two decimal places. Show your working.

(3)

- (c) Deduce the order of reaction with respect to iodide ions.

(1)

- (d) A student carried out the experiment using a flask on the laboratory bench. The student recorded the time taken for the reaction mixture to turn blue. State **one** way this method could be improved, other than by repeating the experiment or by improving the precision of time or volume measurements. Explain why the accuracy of the experiment would be improved.

Improvement _____

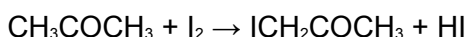
Explanation _____

(2)

(Total 11 marks)

Q17.

Propanone and iodine react in acidic conditions according to the following equation.



A student studied the kinetics of this reaction using hydrochloric acid and a solution containing propanone and iodine. From the results the following rate equation was deduced.

$$\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

- (a) Give the overall order for this reaction.

(1)

- (b) When the initial concentrations of the reactants were as shown in the table below, the initial rate of reaction was found to be $1.24 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$.

	initial concentration / mol dm^{-3}
CH_3COCH_3	4.40
I_2	5.00×10^{-3}
H^+	0.820

Use these data to calculate a value for the rate constant, k , for the reaction and give its units.

Calculation _____

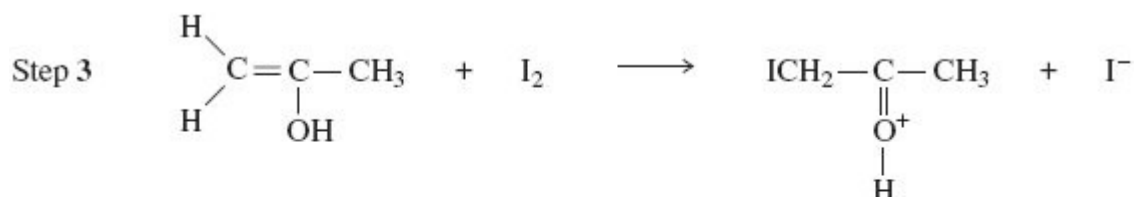
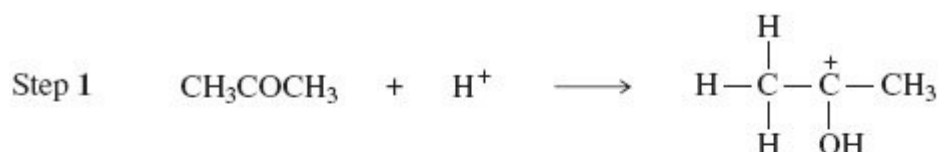
Units _____

(3)

- (c) Deduce how the initial rate of reaction changes when the concentration of iodine is doubled but the concentrations of propanone and of hydrochloric acid are unchanged.
-

(1)

- (d) The following mechanism for the overall reaction has been proposed.



Use the rate equation to suggest which of the four steps could be the rate-determining step. Explain your answer.

Rate-determining step _____

Explanation _____

(2)

- (e) Use your understanding of reaction mechanisms to predict a mechanism for Step 2 by adding one or more curly arrows as necessary to the structure of the carbocation below.



(1)

(Total 8 marks)

Q18.

Kinetic studies enable chemists to suggest mechanisms for reactions.

- (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
1	0.12	0.15	0.32×10^{-3}
2	0.36	0.15	2.88×10^{-3}
3	0.72	0.30	11.52×10^{-3}

- (i) Deduce the order of reaction with respect to **A**.

- (ii) Deduce the order of reaction with respect to **B**.

(2)

- (b) The following data were obtained in a series of experiments on the rate of the reaction between NO and O₂ at a constant temperature.

Experiment	Initial concentration of NO/mol dm ⁻³	Initial concentration of O ₂ /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	5.0×10^{-2}	2.0×10^{-2}	6.5×10^{-4}
5	6.5×10^{-2}	3.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

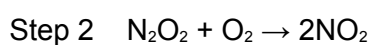
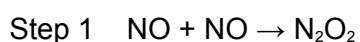
- (i) Use the data from Experiment **4** to calculate a value for the rate constant, *k*, at this temperature, and state its units.

Value of k _____

Units of k _____

- (ii) Calculate a value for the initial rate in Experiment 5.

- (iii) Using the rate equation, a scientist suggested a mechanism for the reaction which consisted of the two steps shown below.



Which did the scientist suggest was the rate-determining step?

(5)

(Total 7 marks)

Q19.

- (a) The following table shows the results of three experiments carried out at the same temperature to investigate the rate of the reaction between compounds **P** and **Q**.

	Experiment 1	Experiment 2	Experiment 3
Initial concentration of P /mol dm ⁻³	0.50	0.25	0.25
Initial concentration of Q /mol dm ⁻³	0.36	0.36	0.72
Initial rate/mol dm ⁻³ s ⁻¹	7.6×10^{-3}	1.9×10^{-3}	3.8×10^{-3}

Use the data in the table to deduce the order with respect to **P** and the order with respect to **Q**.

Order with respect to **P** _____

Order with respect to **Q** _____

(2)

- (b) In a reaction between **R** and **S**, the order of reaction with respect to **R** is one, the order of reaction with respect to **S** is two and the rate constant at temperature T_1 has a value of $4.2 \times 10^{-4} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$.
- (i) Write a rate equation for the reaction. Calculate a value for the initial rate of reaction when the initial concentration of **R** is 0.16 mol dm^{-3} and that of **S** is 0.84 mol dm^{-3} .

Rate equation _____

Calculation _____

- (ii) In a second experiment performed at a different temperature, T_2 , the initial rate of reaction is $8.1 \times 10^{-5} \text{ mol dm}^{-3}\text{s}^{-1}$ when the initial concentration of **R** is 0.76 mol dm^{-3} and that of **S** is 0.98 mol dm^{-3} . Calculate the value of the rate constant at temperature T_2 .

- (iii) Deduce which of T_1 and T_2 is the higher temperature.

(6)

(Total 8 marks)

Q20.

The rate of the reaction between substance **A** and substance **B** was studied in a series of experiments carried out at the same temperature. In each experiment the initial rate was measured using different concentrations of **A** and **B**. These results were used to deduce the order of reaction with respect to **A** and the order of reaction with respect to **B**.

- (a) What is meant by the term *order of reaction* with respect to **A**?

(1)

- (b) When the concentrations of **A** and **B** were both doubled, the initial rate increased by a factor of 4. Deduce the **overall** order of the reaction.

(1)

- (c) In another experiment, the concentration of **A** was increased by a factor of three and the concentration of **B** was halved. This caused the initial rate to increase by a factor of nine.

- (i) Deduce the order of reaction with respect to **A** and the order with respect to **B**.

Order with respect to **A** _____

Order with respect to **B** _____

- (ii) Using your answers from part (c)(i), write a rate equation for the reaction and suggest suitable units for the rate constant.

Rate equation _____

Units for the rate constant _____

Q21.

- (a) The initial rate of the reaction between substances **P** and **Q** was measured in a series of experiments and the following rate equation was deduced.

$$\text{rate} = k[\text{P}]^2[\text{Q}]$$

- (i) Complete the table of data below for the reaction between **P** and **Q**.

Experiment	Initial [P] / mol dm ⁻³	Initial [Q] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.20	0.30	4.8×10^{-3}
2	0.10	0.10	
3	0.40		9.6×10^{-3}
4		0.60	19.2×10^{-3}

- (ii) Using the data from experiment 1, calculate a value for the rate constant, k , and deduce its units.

(6)

- (b) What change in the reaction conditions would cause the value of the rate constant to change?

(1)

(Total 7 marks)

Q22.

- (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
1	0.15	0.24	0.45×10^{-5}
2	0.30	0.24	0.90×10^{-5}

3	0.60	0.48	7.20×10^{-5}

- (i) Show how the data in the table can be used to deduce that the reaction is first-order with respect to **A**.

- (ii) Deduce the order with respect to **B**.

(2)

- (b) The following data were obtained in a second series of experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature.

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	0.75	1.50	9.30×10^{-5}
5	0.20	0.10	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{C}]^2[\text{D}]$$

- (i) Use the data from Experiment 4 to calculate a value for the rate constant, k , at this temperature. State the units of k .

Value for k _____

Units of k _____

- (ii) Calculate the value of the initial rate in Experiment 5.

(4)

(Total 6 marks)

Mark schemes

Q1.

- (a) H_2O_2 and/or I^- concentration change is negligible /
 H_2O_2 and/or I^- concentration (effectively) constant

Only the concentration of H^+ changes.

so have a constant/no effect on the rate / so is zero order (w.r.t. H_2O_2 and I^-) / a and b are zero

Ignore references to H^+ is limiting reagent / rds / $\text{H}_2\text{O}_2/\text{I}^-$ not in rate equation

Do not allow reference to catalyst.

2

- (b) Stop the reaction / quench

By dilution / cooling / adding a reagent to react with $\text{H}_2\text{O}_2/\text{I}^-$

Allow valid suggestions about how to stop the reaction.

Do not allow reaction with acid/alkali / neutralisation for M2

Do not penalise other named reagents.

Ignore references to measuring volume and adding indicator

2

- (c) M1: constant gradient

OR

change/decrease in concentration is proportional to time

Allow constant rate / rate = k

Ignore reference to straight line

Not increase in concentration / concentration is inversely proportional / concentration (on its own) is proportional

M2: as $[\text{H}^+]$ changes/decreases

M2 dependent on correct M1

Allow rate v concentration graph would give horizontal straight line owtte

Allow so $[\text{H}^+]$ has no effect on the rate

2

- (d) evidence of attempt at calculation of gradient via $\Delta y/\Delta x$

allow construction lines on graph

$$k_1 = 0.0012 / 1.2 \times 10^{-3}$$

At least 2 sf (0.00118 – 0.00122)

Correct answer scores 2/2

No ecf from incorrect or inverted numbers in M1

$k_1 = - 0.0012$ scores 1/2

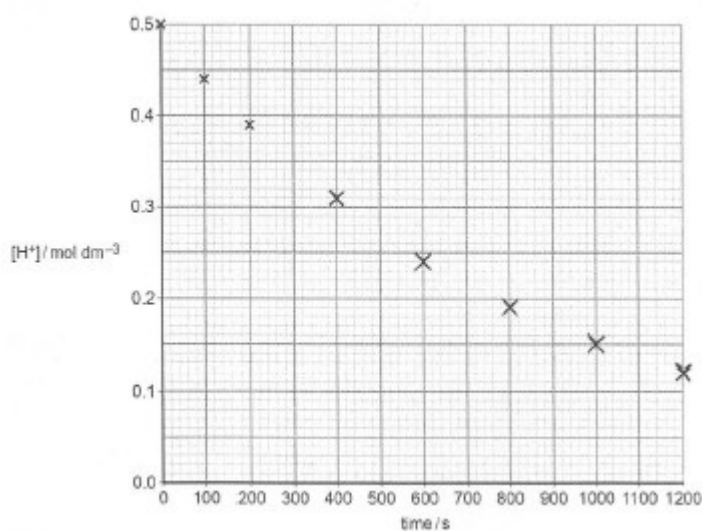
Additional processing of data such as including $[\text{H}^+]$ loses M2

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

M3 mark independently

3

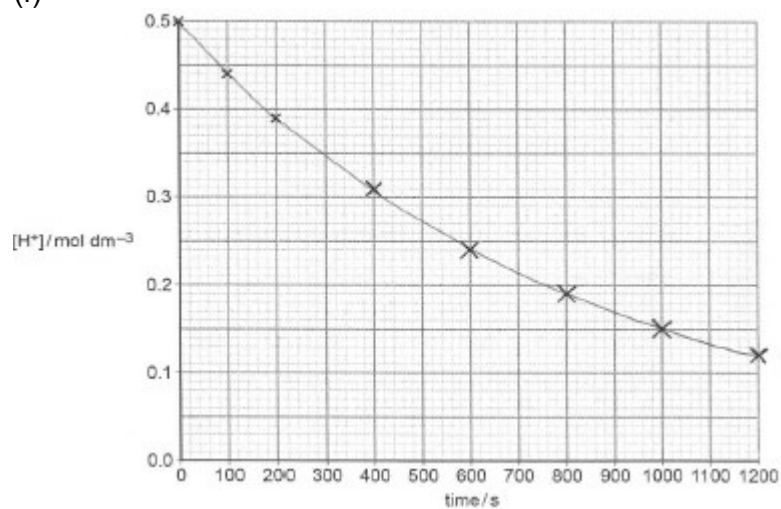
(e) 5 points correctly plotted



Allow $\pm$ half a small square for each point

1

(f)

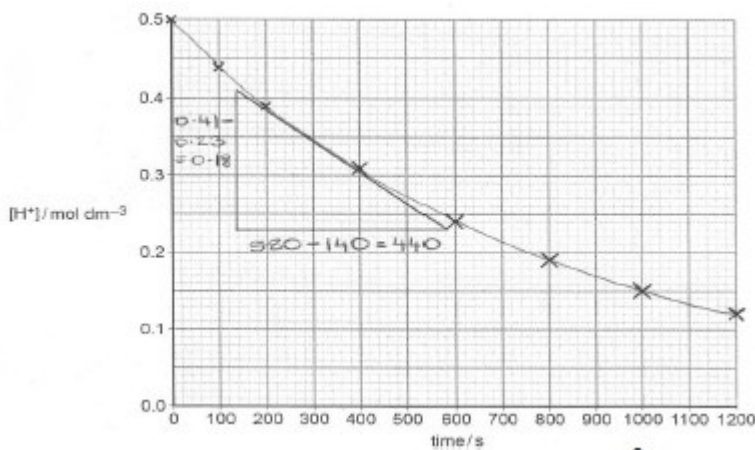


Smooth curve only within one small square of all points
(ecf on part (e))

Not a series of straight lines between points

1

(g)



M1: Tangent to curve drawn at $[\text{H}_3\text{O}^+] = 0.35 \text{ mol dm}^{-3}$

e.g. 0.18/440

M1 for a tangent / triangle / other suitable working

Allow ECF for both M1 and M2 following on from straight line drawn in 01.6, but must show suitable construction on graph for M1

M2: Rate = $4.09 \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1})$

Ignore negative signs

Allow value in range $3.70 \times 10^{-4} - 4.50 \times 10^{-4}$

At least 2sf

ecf from any straight line for correctly calculated gradient

2

- (h) This question is marked using levels of response. Refer to the Mark Scheme Instructions for examiners for guidance on how to mark this question

Level 3 5-6 marks	All stages are covered and the explanation of each stage is correct and virtually complete. Answer is coherent and shows progression through all three stages. A clear explanation of how the order is determined from the results is needed to show coherence.
Level 2 3-4 marks	All stages are covered (NB 'covered' means min 2 from stage 2) but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages covered and the explanations are generally correct and virtually complete Answer is coherent and shows some progression through all three stages. Some steps in each stage may be out of order and incomplete
Level 1 1-2 marks	Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR only one stage is covered but the explanation is

	generally correct and virtually complete Answer shows some progression between two stages
Level 0 0 marks	Insufficient correct Chemistry to warrant a mark

Indicative Chemistry content Method 1

Stage 1 Preparation

- 1a Measure (suitable/known volumes of) some reagents (ignore quoted values for volume)
- 1b Measure (known amount of) **X** / use a colorimeter
- 1c into separate container(s) – (allow up to two reagents and **X** measured together into one container); reference to **A**, **B** or **C** added last. NOT if **X** added last.

Stage 2 Procedure

- 2a Start clock/timer at the point of mixing (don't allow if only 2 reagents mixed) (allow even if **X** not added or added last)
- 2b Time recorded for appearance of blue colour/specific reading on colorimeter/disappearing cross
- 2c Use of same concentration of **B** and **C** / same total volume / same volume/amount of **X**
- 2d Same temperature/use water bath
- 2e Repeat with different concentrations of **A** (can be implied through different volumes of **A** and same total volume)

Stage 3 Use of Results

- 3a 1/time taken is a measure of the rate
- 3b plot of 1/time against volumes/concentrations of **A** or plot $\log(1/\text{time})$ vs $\log(\text{volume or concentration of A})$
- 3c description of interpreting order from shape of 1/time vs volume or concentration graph / gradient of log plot gives order / allow interpretation of time vs concentration graph / ratio between change in concentration and change in rate (e.g. $2 \times [\text{A}] = 2 \times \text{rate}$ so 1st order)

Indicative Chemistry content – Alternative Method Using Colorimetry and repeated Continuous Monitoring

Stage 1 Preparation

- 1a Measure (suitable/known volumes of) **A**, **B** and **C** (ignore quoted values for volume)
- 1b Use of colorimeter
- 1c into separate container(s) – (allow up to two reagents measured together into one container) – ignore use of **X**

Stage 2 Procedure

- 2a Start clock/timer at the point of mixing
- 2b Take series of colorimeter readings at regular time intervals
- 2c Use of same concentration of **B** and **C** / same total volume / (same

- volume/amount of **X**)
- 2d Same temperature
- 2e Repeat with different concentrations of **A** (can be implied through different volumes of **A** and same total volume)

Stage 3 Use of Results

- 3a Plot absorbance vs time and measure/calculate gradient at time=0
- 3b plot of gradient against volumes/concentrations of **A** or plot $\log(1/\text{time})$ vs $\log(\text{volume or concentration of A})$
- 3c description of interpreting order from shape of $1/\text{time}$ vs volume or concentration graph / gradient of log plot gives order

6

[19]

Q2.

D

[1]

Q3.

- (a) **Stage 1: Calculates value of $[\text{C}_6\text{H}_5\text{CHO}]^2$:**

M1 for the values (0, 0.0625; 0.25; 0.56 and 1) in the table.

Ignore precision.

1

Stage 2: Plots graph:

M2 for the graph labels with units and appropriate scales and using sensible proportion of graph (plotted points must cover at least half the printed grid).

$[\text{C}_6\text{H}_5\text{CHO}]^2$ on x-axis (with units) $\text{mol}^2 \text{dm}^{-6}$

Initial rate on y-axis (with units) $\text{mol dm}^{-3} \text{s}^{-1}$

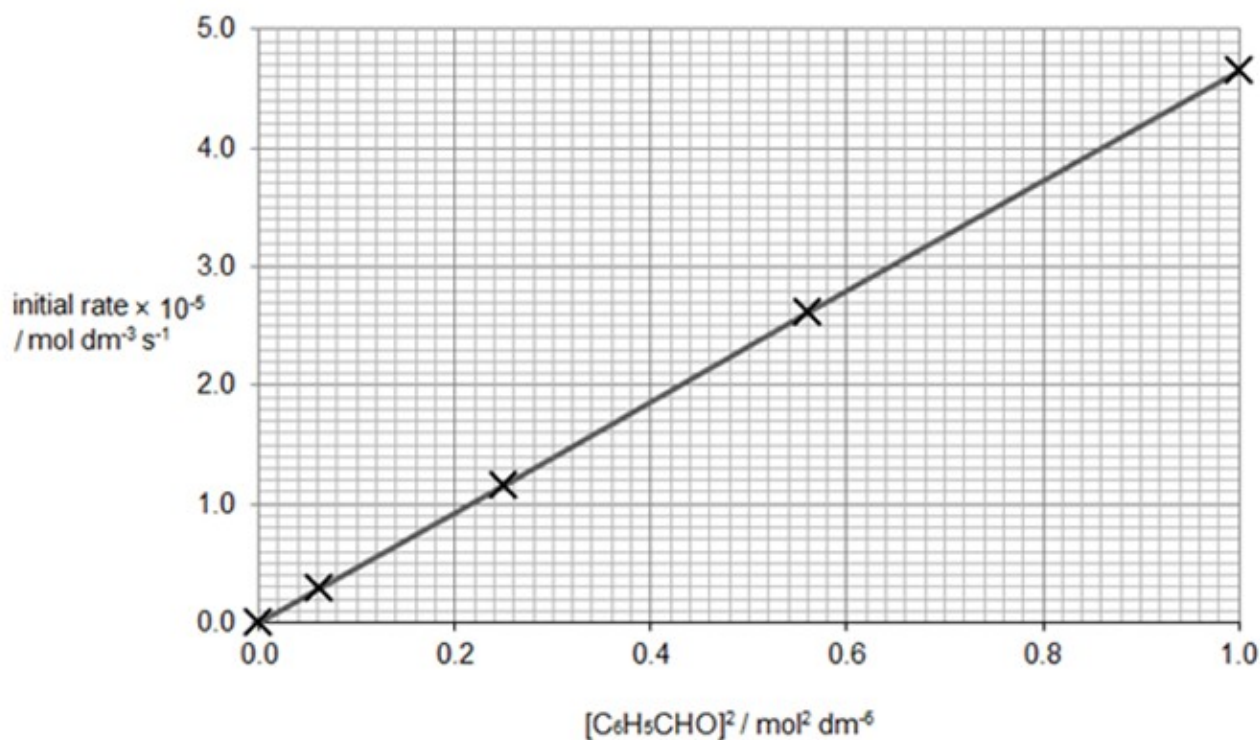
1

M3 for the plotting of 5 points.

1

Stage 3: Line of best fit:

M4 for the line of best fit.



(b) 2nd order

(since) $[C_6H_5CHO]^2$ plotted against rate is straight line / directly proportional.

(c) (Role of CN^-) catalyst

Ignore nucleophile.

CN^- appears in the rate equation but is not in the reaction equation.

[8]

Q4.

(a) Amount of propanone = $(25.0 \times 1) / 1000 = 0.025 \text{ mol}$

Concentration in mixture **A** = $0.025 / (90.0/1000) = 0.278 \text{ mol dm}^{-3}$

(b) To make volumes constant for all mixtures.

So that volume of propanone is proportional to concentration.

(c) Amount of iodine in mixture **E** = $(40.0 \times 0.02) / 1000 = 8.0 \times 10^{-4} \text{ mol}$

Amount of iodine in sample = $8.0 \times 10^{-4} \times (10 / 90) = 8.89 \times 10^{-5} \text{ mol}$

As 10 cm^3 sample taken from total volume of 90 cm^3

1

Amount of thio required = $2 \times 8.89 \times 10^{-5} = 1.78 \times 10^{-4}\text{ mol}$

1

Volume of thio = $(1.78 \times 10^{-4} / 0.01) \times 1000 = 17.8\text{ cm}^3$

1

(d) Scale

Graph must cover at least half the grid and axes must be plotted in correct orientation but ignore labeling.

1

Points

Must be correctly plotted to within $\pm$ half a small square.

1

Best-fit straight line

Must be the best-fit line possible if point(s) are plotted incorrectly.

Penalise doubled or kinked lines.

1

Gradient = y / x

1

= -0.060

Allow -0.059 to -0.061

Ignore any units given.

1

(e) Gradients / rates are proportional to volumes / concentrations of propanone **or** B to D show that gradient / rate halves when vol / concentration halves.

1

So first order with regard to propanone.

1

(f) To stop / quench the reaction at that time.

Ignore NaHCO_3 reacts with the HI produced.

1

By removing the acid catalyst for the reaction (by neutralisation).

1

[17]

Q5.

B

[1]

Q6.

D

[1]

Q7.

- (a) Consider experiments 1 and 2: [B constant]

[A] increases $\times 3$: rate increases by 3^2 therefore 2nd order with respect to A

1

Consider experiments 2 and 3:

[A] increases $\times 2$: rate should increase $\times 2^2$ but only increases $\times 2$

Therefore, halving [B] halves rate and so 1st order with respect to B

1

Rate equation: rate = $k[A]^2[B]$

1

- (b) rate =
- $k[C]^2[D]$
- therefore
- $k = \text{rate} / [C]^2[D]$

1

$$k = \frac{7.2 \times 10^{-4}}{(1.9 \times 10^{-2})^2 \times (3.5 \times 10^{-2})} = 57.0$$

Allow consequential marking on incorrect transcription

1

 $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$ *Any order*

1

- (c) rate =
- $57.0 \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2} = 3.99 \times 10^{-3} (\text{mol dm}^{-3} \text{s}^{-1})$

ORTheir $k \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2}$

1

- (d) Reaction occurs when molecules have
- $E \geq E_a$

1

Doubling T by 10°C causes many more molecules to have this E

1

Whereas doubling [E] only doubles the number with this E

1

- (e)
- $E_a = RT(\ln A - \ln k) / 1000$

Mark is for rearrangement of equation and factor of 1000 used correctly to convert J into kJ

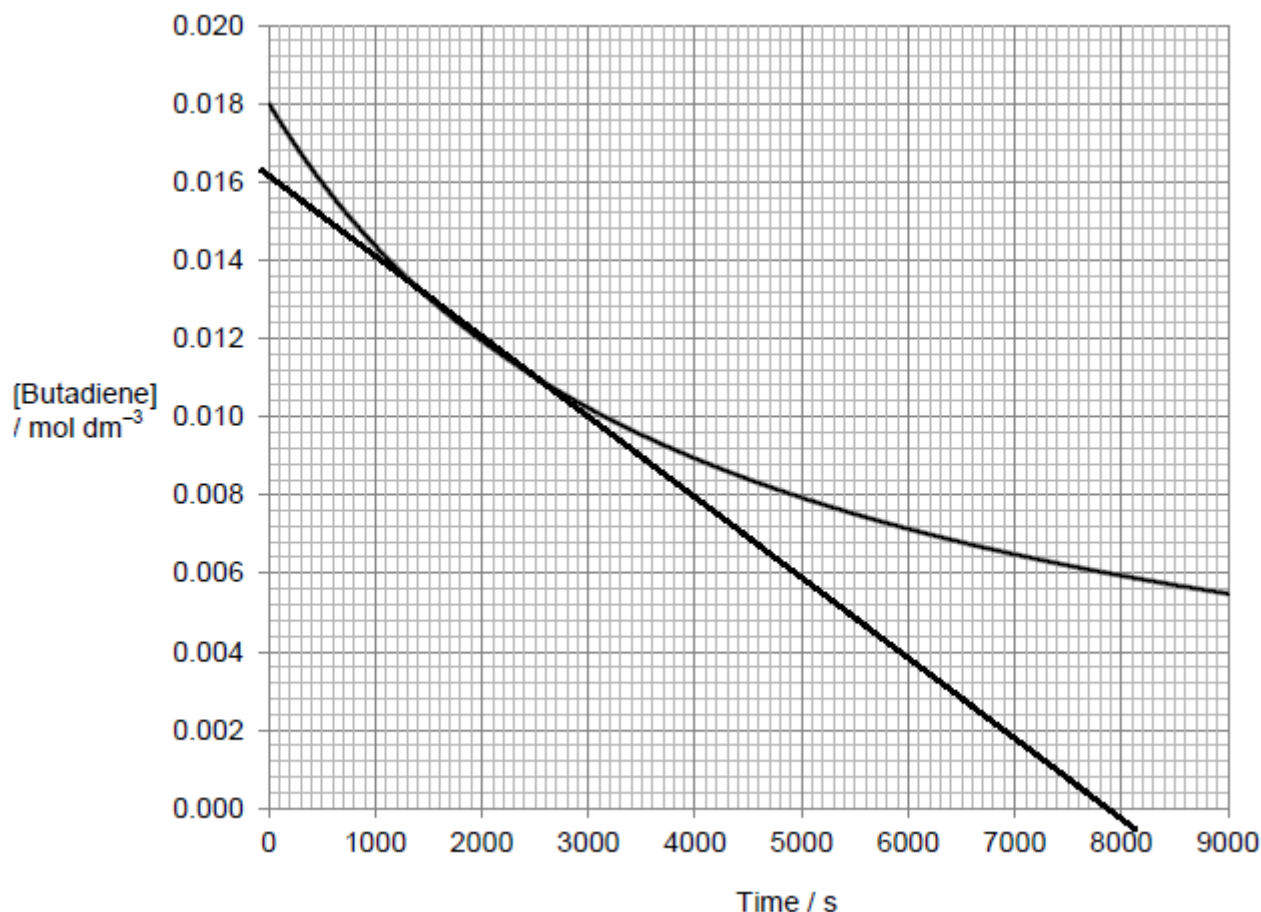
1

$$E_a = 8.31 \times 300 (23.97 - (-5.03)) / 1000 = 72.3 (\text{kJ mol}^{-1})$$

1

[12]**Q8.**

(a) Gradient drawn on graph



Line must touch the curve at 0.012 but must not cross the curve.

1

(b) Stage 1: Rate of reaction when concentration = 0.0120 mol dm⁻³

From the tangent

Change in [butadiene] = -0.0160 - 0 and change in time = 7800 - 0

Extended response

1

Gradient = $-(0.0160 - 0) / (7800 - 0) = -2.05 \times 10^{-6}$

Rate = 2.05×10^{-6} (mol dm⁻³ s⁻¹)

1

Stage 2: Comparison of rates and concentrations

Initial rate / rate at 0.0120 = $(4.57 \times 10^{-6}) / (2.05 \times 10^{-6}) = 2.23$

Marking points in stage 2 can be in either order

1

Initial concentration / concentration at point where tangent drawn = $0.018 / 0.012 = 1.5$

1

Stage 3: Deduction of order

If order is 2, rate should increase by factor of $(1.5)^2 = 2.25$ this is approximately equal to 2.23 therefore order is 2nd with respect to butadiene

1

[6]

Q9.

- (a) Order wrt **D** = 1 OR first OR [D] OR [D]¹

Ignore working

1

Order wrt **E** = 2 OR second OR [E]²

1

- (b) (At time zero/start) the concentrations are known

1

- (c) M1 (Calculate) gradient (of tangent/curve/graph)

Allow description of gradient calculation:

Change in conc / time

1

M2 at t=0 or at start of graph/curve

M2 scored only if M1 gained

Ignore the word initial

1

[5]

Q10.

- (a) (i) 2 or two or second or [E]²

1

- (ii) 1 or one or first or [F]¹ or [F]

1

- (b) (i) $k = \frac{8.6 \times 10^{-4}}{(3.8 \times 10^{-2})^2 \times (2.6 \times 10^{-2})}$

mark is for insertion of numbers into a correctly rearranged rate equ , k = etc.

AE (-1) for copying numbers wrongly or swapping two numbers.

1

= 22.9 (Allow 22.9 – 24 after correct rounding)

1

mol⁻²dm⁺⁶ s^{&8722;1}

Any order.

1

- (ii) $6.8(2) \times 10^{-3} \text{ (mol dm}^{\&8722;3}\text{s}^{-1}\text{)}$

OR if their k is wrong, award the mark consequentially

a quick check can be achieved by using

their answer = 2.9768×10^{-4} Allow 2.9 – 3.1×10^{-4} for the mark

their k

Allow 6.8×10^{-3} to 6.9×10^{-3}

Ignore units.

1

[6]

Q11.

- (a) Iodine is not involved in (or before) the rate determining / slow(est) / limiting step (in the mechanism)

Ignore, iodine does not appear in the rate equation or iodine concentration does not affect the rate

1

(b)
$$k = \left(\frac{8.64 \times 10^{-7}}{(5.82 \times 10^{-2}) \times (4.76 \times 10^{-1})} \right) = 3.1(2) \times 10^{-5}$$

Mark for answer

1

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

Mark units separately, i.e. only these units but can be in any order

1

- (c) Rate = $k [\text{H}^+]$

If wrong or missing CE = 0

1

(Large excess of propanone) so $[\text{CH}_3\text{COCH}_3]$ is (effectively) constant

1

[5]

Q12.

- (a) Exp 2 $14.(4) \times 10^{-3}$ **OR** $1.4(4) \times 10^{-2}$ or 0.014

Allow 2sf

1

Exp 3 0.1(0)

1

Exp 4 0.3(0)

If three wrong answers, check their value of k in 1(b).

They can score all 3 if they have used their (incorrect) value of k . see below.

Exp 2 rate = $0.096 \times k$

Exp 3 $[\text{Q}] = 0.015/k$

Exp 4 $[\text{P}] = 0.116/k$

1

(b)
$$K = \frac{1.8 \times 10^{-3}}{(0.20)^2 \times 0.30}$$

mark is for insertion of numbers into a correctly rearranged

rate equ , $k = \text{etc}$

1

$$= 0.15 \text{ (min 2sfs)} \quad \left(\text{allow } \frac{3}{20}\right)$$

if upside down, score only units mark

AE (-1) for copying numbers wrongly or swapping two numbers

1

$$\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

Any order

If k calculation wrong, allow units conseq to their k

1

(c) G

1

[7]

Q13.

$$(a) \quad (i) \quad k = \frac{8.4 \times 10^{-5}}{(4.2 \times 10^{-2})^2 \times 2.6 \times 10^{-2}} \quad \text{OR} \quad \frac{8.4 \times 10^{-5}}{(1.76 \times 10^{-3}) \times 2.6 \times 10^{-2}}$$

Mark is for insertion of numbers into a correctly rearranged rate equ , $k = \text{etc}$.

If upside down, score only units mark from their k

AE (-1) for copying numbers wrongly or swapping two numbers

1

$$= 1.8(3)$$

1

$$\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

Any order

If k calculation wrong, allow units consequential to their $k = \text{expression}$

1

$$(ii) \quad 5.67 \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1}) \quad \text{OR} \quad \text{their } k \times 3.1 \times 10^{-4}$$

Allow 5.57×10^{-4} to 5.7×10^{-4}

1

(b) (i) 2 or second or $[D]^2$

1

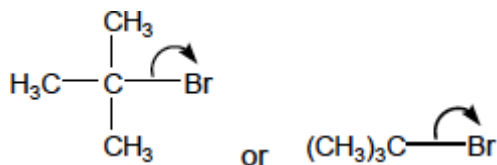
(ii) 0 or zero or $[E]^0$

1

- (c) (i) Step 1 or equation as shown
Penalise Step 2 but mark on

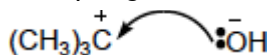
1

(ii)



Ignore correct partial charges, penalise full / incorrect partial charges

If Step 2 given above, can score the mark here for



allow: OH⁻ (must show lp)

If S_N2 mechanism shown then no mark (penalise involvement of :OH⁻ in step 1)

Ignore anything after correct step 1

1

[8]

Q14.

- (a) (i)

$$k = \frac{6.2 \times 10^{-6}}{(2.9 \times 10^{-2})^2 \times 2.3 \times 10^{-2}}$$

mark is for insertion of numbers into a correctly rearranged rate equ, k = etc

AE (-1) for copying numbers wrongly or swapping two numbers

1

$$= 0.32 \text{ (min 2 sfs)}$$

1

mol⁻² dm⁶ s⁻¹ Units must be conseq to their *k*

Any order

If k calculation wrong, allow units conseq to their k

1

- (ii) 4.95×10^{-5} to 4.97×10^{-5} or 5.0×10^{-5} (min 2 sfs)

(ignore units)

$$\text{rate} = \text{their } k \times 1.547 \times 10^{-4}$$

1

- (b) Step 2

If wrong no further mark

1

One H₂ (and two NO) (appear in rate equation)
 or species (in step 2) in ratio/proportion as in the rate equation

1

[6]

Q15.

- (a) (i) propyl methanoate

must be correct spelling

1

- (ii) rate =
- $k[X][OH^-]$

*allow $HCOOCH_2CH_2CH_3$ (or close) for X**allow () but penalise missing minus*

1

- (iii)
- $k = \frac{8.5 \times 10^{-5}}{(0.024)(0.035)}$

*In (a)(iii), if wrong orders allow**mark is for insertion of numbers in correct expression for k**If expression for k is upside down, only score units conseq to their expression*

1

$$= 0.10(12) \quad 2\text{sf minimum}$$

1 for conseq answer

1

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

*1 for conseq units**any order*

1

- (iv)
- $2.1(3) \times 10^{-5}$

*or $2.1(2) \times 10^{-5}$ ignore units**allow 2 sf****NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong k******See * below***

1

- (v)
- $1.3 \times 10^{-4} \quad (1.28 \times 10^{-4})$

*allow (1.26×10^{-4}) to (1.3×10^{-4}) ignore units**allow 2 sf****NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong k******See ** below***

1

For example, if orders given are 1st in X and second in OH^- **[The mark in a(ii) and also first mark in a(iii) have already been lost]****So allow mark * in (iv) for rate = their $k \times (0.012)(0.0175)^2 = \text{their } k \times (3.7 \times 10^{-6})$
(allow answer to 2sf)****** in (v) for rate = their $k \times (0.012)(0.105)^2 = \text{their } k \times (1.32 \times 10^{-4})$
(allow answer to 2sf)****The numbers will of course vary for different orders.**

(vi) Lowered

if wrong, no further mark

1

fewer particles/collisions have energy $> E_a$

OR

fewer have sufficient (activation) energy (to react)

not just fewer successful collisions

1

(b) Step 2

1

(this step with previous) involves one mol/molecule/particle
A and two Bs

or 1:2 ratio or same amounts (of reactants) as in rate equation

if wrong, no further mark

1

[11]

Q16.

(a) Log (1 / time) on the y -axis + log (vol) on x -axis

*If axes unlabelled use data to decide that log (1 / time) is on
the y -axis*

1

Sensible scales

*Lose this mark if the plotted points do not cover at least half
of the paper*

Lose this mark if the graph plot goes off the squared paper

Lose this mark if plots a non-linear / broken scale

*Lose this mark if uses an ascending y -axis of negative
numbers*

1

Plots points correctly $\pm$ one square

1

Line through the points is smooth

Lose this mark if the candidate's line is doubled

1

Line through the points is best fit – ignores last point

Must recognise that point at 25 cm^3 is an anomaly

*If wrong graph, mark consequentially on anomaly if correctly
plotted.*

*A kinked graph loses smooth **and** best fit marks*

1

(b) Uses appropriate x and y readings

Allow taken from table or taken or drawn on graph

Must show triangle on graph or such as $\frac{1.65 - 1.2}{1.4 - 0.9}$

1

Correctly calculates gradient 0.95 ± 0.02

Ignore positive or negative sign

Correct answer only with no working scores this mark

1

Answer given to 2 decimal places

1

- (c) First order or order is 1

Allow consequential answer from candidate's results

1

- (d) Thermostat the mixture / constant temperature / use a water bath
or Colorimeter / uv-visible spectrometer / light sensor to monitor colour change

1

Reaction / rate affected by temperature change

or Eliminates human error in timing / more accurate time of colour change

1

[11]

Q17.

- (a) 2 or two or second

1

(b) $k = \frac{1.24 \times 10^{-4}}{(4.40)(0.82)}$

*mark is for insertion of numbers into a correctly rearranged
rate equ, k = etc*

if upside down, (or use of I_2 data) score only units mark

1

$= 3.44 \times 10^{-5}$ (min 3sfs)

1

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

any order

1

- (c) no change or no effect or stays the same or 1.24×10^{-4}

1

- (d) 1 or 2 or 1 and 2

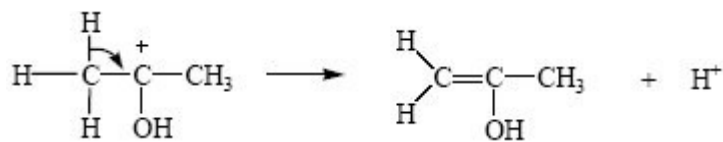
if wrong no further mark but mark on from no answer

1

rate equ doesn't involve I_2 or only step which includes 2
species in rate equ

1

(e)



any second arrow loses the mark

1

[8]

Q18.

(a) (i) 2

1

(ii) 0

1

(b) (i) $\text{rate}/[\text{NO}_2]^2[\text{O}_2]$

1

13

1

mol dm^{-3}

1

(ii) 1.9×10^{-3}

1

(iii) Step 2

1

[7]

Q19.

(a) order with respect to **P** is 2

1

order with respect to **Q** is 1

1

(b) (i) $\text{rate} = k[\text{R}][\text{S}]^2$

(if wrong expression, no further marks)

1

$\text{rate} = (4.2 \times 10^{-4}) \times 0.16 \times 0.84^2$

1

$= 4.7 \times 10^{-5} (\text{mol dm}^{-3} \text{ s}^{-1})$

ignore units even if wrong

1

(ii) $k = \frac{\text{rate}}{[\text{R}][\text{S}]^2} = \frac{8.1 \times 10^{-5}}{0.76 \times 0.98^2}$

$$= 1.1 \times 10^{-4}$$

(iii) T_1

**If calculated value for $k > 4.2 \times 10^{-4}$, then answer to (iii) is T_2*

[8]

Q20.

(a) Power (or index or shown as x in []^x) of concentration term (in rate equation) (1)

(b) 2 (1)

(c) (i) Order with respect to **A**: 2 (1)

Order with respect to **B**: 0 (1)

(ii) Rate equation: (rate =) $k [A]^2$ (1)

Allow conseq on c(i)

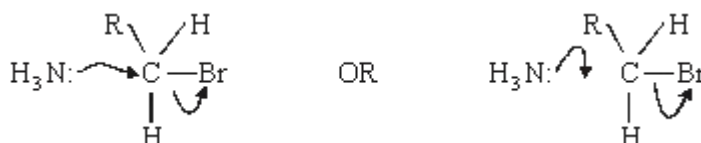
Units for rate constant: $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ (1)

conseq on rate equation

[6]

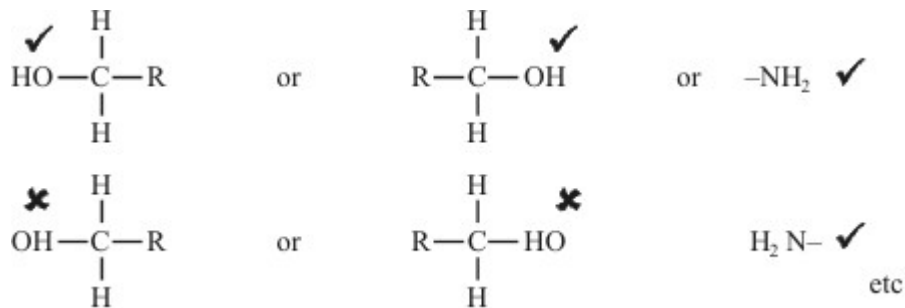
Organic points

(1) Curly arrows: must show movement of a pair of electrons, i.e. from bond to atom or from lp to atom / space e.g.



(2) Structures

penalise sticks (i.e.) once per paper



Penalise once per paper

allow CH_3- or $-\text{CH}_3$ or $\begin{array}{c} \text{CH}_3 \\ | \end{array}$ or CH_3
 or $\text{H}_3\text{C}-$

Q21.

- (a) (i) Experiment 2: $0.4(0) \times 10^{-3}$ **(1)**
 Experiment 3: 0.15 **(1)**
 Experiment 4: 0.28 **(1)**

(ii) $k = \frac{4.8 \times 10^{-3}}{(0.20)^2 \times (0.30)} = 0.4(0) \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

(1) (1) (1)

6

- (b) (change in) temperature **(1)**

1

[7]

Q22.

- (a) (i) (Experiment 1 $\rightarrow$ 2) [A] doubled, ([B] constant,) rate doubled **(1)**
stated or shown numerically

- (ii) 2 **(1)**
 or shown as ... $[\text{B}]^2$

2

(b) (i) $k = \frac{9.30 \times 10^{-5}}{(0.75)^2 \times (1.50)} = 1.1(0) \times 10^{-4}$

(1) (1)

units of k: $\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ **(1)**

(ii) $\text{rate} = (1.10 \times 10^{-4}) \times (0.20)^2 \times (0.10)$
 $= 4.4(1) \times 10^{-7} \text{ (mol dm}^{-3} \text{ s}^{-1})$
(1) for the answer

Ignore units
Conseq on (i)

Upside down expression for k scores zero in (i) for 9073
but rate = $9073 \times (0.2)^2 \times (0.1) = 36(.3)$
conseq scores (1) in (ii)

4

[6]

Examiner reports

Q1.

- (a) This proved to be a tougher starter question than anticipated (63.4% of students failed to score). In many cases, the question was repeated as an attempt at the answer with students suggesting that “the rate only depends on $[H^+]$ ”. Since this information had been given in the question, answers such as this could not be credited. The expected answer, that ‘a large excess makes the concentrations effectively constant so that they do not affect the rate’, was seldom seen.
- (b) As with part (a), not many students were able to achieve both marks (only 9.7%), with few suggesting ‘quenching’. Given how frequently quenching was, unnecessarily, suggested in answers to (h), this was surprising. In many cases, students described the process of titration itself rather than what should be done to the sample *before* titration. 74% of students failed to score here.
- (c) This question proved easier, with just over a third of students achieving both marks for appreciating that the line indicated a constant rate, showing that the falling concentration of hydrogen ions was having no effect.
- (d) A common error here was for students to start by (correctly) calculating the gradient of the line but then to divide it by a value for the $[H^+]$ (usually 0.5) or even by $[H^+]^2$ – despite having been told in part (c) that the order with respect to $H^+(aq)$ is zero. 36% of students, however, did gain all three marks.
- (e) 97.3% of students were able to plot the points correctly onto the given grid.
- (f) A significant number of students assumed that the instruction to ‘draw a line of best fit’ meant that the line must be straight. Students must learn that a best-fit line must be the best-fit to the points as plotted, so may be either straight or curved depending on the relationship between the plotted points; at A-level, students are expected to make this decision for themselves. Just under 40% of students did not gain this mark.
- (g) The idea of drawing a tangent (or, for award of ‘error carried forward’, simply constructing a ‘triangle’ on a straight line) proved tricky, with a significant minority of students simply dividing 0.35 by the corresponding time value from their line.
- (h) Fewer students than expected recognised the clue in the information given in the question that this was best done as a ‘clock’ reaction. Many students suggested answers that did not include ‘X’ in the initial mixture, as suggested, while many others used a variety of convoluted procedures involving what were essentially ‘continuous monitoring’ methods to generate concentration versus time graphs. In some cases, this was followed by a description of finding the gradient at $t = 0$, which addressed the requirement of the question to calculate an initial rate for each experiment. However, a direct measurement would have been much easier, both to do and to describe.

Credit was given for a wide variety of suggestions because, although a particular approach was hoped for, there are indeed several alternative approaches that would work. However, many students seemed to think that actual measurements of concentration (of what substance was often unclear from the descriptions) are needed, which led to suggestions that samples should be removed at timed intervals and titrated against X or placed into a colorimeter (the need to quench these samples was often over-looked). If a colorimeter was used, then the best approach

for continuous monitoring is simply to allow the reaction to proceed in the colorimeter and take a series of readings at timed intervals – much easier than sampling. The mean mark on this question was only 1.8 out of 6.

The extra answer space available this year meant that fewer students needed additional pages for this question, but many confused, badly ordered and muddled answers were seen that took up far more space than necessary through repetition and unnecessary elaboration.

Reading the question is always key, but here many students could have saved a lot of time and space by noticing that the question asked only about a method to determine the order of this reaction with respect to A. This would have avoided the need for them to repeat most of the procedure, looking at successively changing the concentrations of A, then B, then C, while keeping each of the other two constant. Levels-of-response questions are marked using 'levels' and the key to success is for students to concentrate first on the inclusion of as much correct Chemistry as possible to ensure access to Level 3 (worth 5 or 6 marks). This is probably best achieved using a 'bullet point' approach to structuring the answer. Within a level, the mark awarded depends on the clarity and coherence of an answer, together with there being a clear, logical progression through the description.

Appropriate apparatus and quantities should be mentioned as necessary. For example, rather than stating "add A, B and C to a container", a good start to the answer would be to write, "A measuring cylinder was used to measure known volumes, of known concentrations, of A, B and C into separate beakers". Unless specifically asked to suggest suitable volumes/concentrations, then it is sufficient for students to indicate that they would make a measurement without needing to state a value.

Q2.

A was the commonest incorrect response here, suggesting that those students thought it was a concentration v time graph rather than a rate v concentration graph. 76.5% of students were successful.

Q9.

Part (a) was answered well and two thirds of students scored both marks. By contrast, part (b) was a hard question with few correct answers. Many students spoke about the changing concentrations but few mentioned the importance of knowing the initial concentration. The first mark in part (c) for mentioning a gradient was often gained but the location of where to measure the gradient was only given by a third of students.

Q10.

This question was answered well. A few students lost marks through the incorrect use of calculators in the division necessary in part (b)(i) to find the rate constant, k , or by omitting s^{-1} from the units of the rate calculated in part (b)(ii).

Q11.

Part (a) was answered correctly by just over half of the students. The majority of incorrect answers were because students didn't answer the question and simply just repeated what the rate equation told them.

Calculation of a rate constant in part (b) was answered very well as usual but part (c)

proved to be very difficult. A large number of students could not deduce the correct rate equation. Those who did gain this mark were not often able to give a reason for their answer and the second mark was rarely seen.

Q12.

The kinetics question was, as usual, answered well with only Experiment 4 in part (a) causing much difficulty. However, in part (c) fewer than half of the students identified graph G as that correctly showing how the rate constant k varies with temperature.

Q13.

This question was answered well by most students and over 80% scored full marks in part (a). Part (c)(ii) was found slightly harder and, of those who correctly identified Step 1 as the slower step, most gained the mark for the curly arrow. Those who suggested Step 2 could also gain a mark for a correct arrow for that step. However, many gave a full S_N2 mechanism in both cases.

Q14.

Part (a) was well done with many candidates scoring full marks. Although most gave the correct answer to part (a)(ii), many did it by the long route, having failed to see that the answer was simply 8x the initial rate.

Candidates found part (b) more difficult. Many of those who correctly chose step 2 could not offer a full explanation.

Q15.

Most parts of this question were answered well. The ester was named correctly by over two thirds of the candidates but a surprising number attempted to write a stoichiometric equation in part (a)(ii) rather than a rate equation. Part (a)(iii) was answered very well but in part (a)(iv) the effect of dilution on the concentration of both reagents was missed by a large majority. However, when the exact concentrations were given in part (a)(v) most candidates were able to calculate the new rate of reaction correctly. The effect on the rate constant of lowering the temperature was well known in part (a)(vi), but few candidates were able to give a correct explanation and many offered a mathematical rather than a kinetic explanation. In part (b), the requirement to use the rate equation to identify the rate determining step proved difficult for the majority.

Q16.

In this Section, the graphs seen showed the usual range of mistakes seen in this type of question as mentioned in the marking scheme. The main difficulty was in ensuring that the **plotted** graph covered at least half the printed grid.

In part (b), most candidates were able to find an appropriate gradient and full marks were common. Allowance was made for consequential errors from the drawing of the graph but in part (c) the order quoted needed to be based on the final answer to part (b).

Candidates had some trouble with part (d), many thinking that a 'white tile' would improve the precision of time measurement.

Q17.

As usual for questions on kinetics, this was answered well. It was also pleasing that, in

part 3(d), over half of the candidates gained both marks on a question which required understanding of a new part of the specification. Application in part (e) of their understanding of the use of curly arrows in organic mechanisms was, however, less well done.

Q19.

As is normal, the use of rate equations is well understood and almost all candidates can answer these questions well. Very few failed to score the marks for deducing the orders with respect to **P** and **Q**. The calculation in part (b) using the given orders of reaction was well done by all except those candidates who could not rearrange the equation correctly. The same applied in part (b)(ii). In the few cases where the calculated value of the rate constant was incorrect, and greater than $4.2 \times 10^{-4} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ the usual answer of T_1 for part (b)(iii) was replaced by the answer T_2 consequential on their incorrect value of k .

Q20.

In part (a) few candidates were able to explain correctly what the term 'order of reaction' means. However, despite this most were able to use the idea itself and scored highly in the rest of the question. The fact that the rate of reaction increased by a factor of nine, 32, when the concentration of A increased by three times led some candidates to think that the order with respect to A was three rather than two.

Q21.

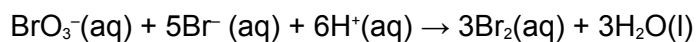
This question was generally answered well even by weaker candidates. Calculation of the concentration of P in part (a)(i) was the only part found difficult by many. Most answers to part (a)(ii) were correct, including the units. A change in temperature was the usual and correct answer in part (b).

Q22.

This question on rate equations was answered well by most candidates. Part (a)(i) required that the candidate stated or showed mathematically that the rate doubled when the concentration of A doubled when considering experiments 1 and 2. Part (a)(ii) was usually answered correctly. Problems arose in part (b) where some candidates had difficulty in rearranging the rate equation correctly. However the mark in part (b)(ii) could still be gained for correct working despite using a wrong rate constant calculated in part (b)(i).

Q1.

Bromate(V) ions and bromide ions react in acid conditions according to the equation



- (a) A series of experiments was carried out at a given temperature. The results were used to deduce the rate equation for the reaction.

$$\text{rate} = k [\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

Table 1 shows an incomplete set of results.

Table 1

Experiment	Initial $[\text{BrO}_3^-]$ / mol dm^{-3}	Initial $[\text{Br}^-]$ / mol dm^{-3}	Initial $[\text{H}^+]$ / mol dm^{-3}	Initial rate of reaction / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.10	0.20	0.30	2.4×10^{-2}
2		0.20	0.30	3.6×10^{-2}
3	0.20	0.40	0.50	
4	0.10	0.10		2.7×10^{-2}

Use the data from Experiment 1 to calculate a value for the rate constant, k , at this temperature and give its units.

Give your answer to an appropriate number of significant figures.

k _____ Units _____

(3)

- (b) Complete **Table 1**.

Space for working

(3)

- (c) A second series of experiments was carried out to investigate how the rate of the reaction varies with temperature.
The results were used to obtain a value for the activation energy of the reaction, E_a

Identical amounts of reagents were mixed at different temperatures.

The time taken, t , for a fixed amount of bromine to be formed was measured at different temperatures.

The results are shown in **Table 2**.

Table 2

Temperature, T / K	$\frac{1}{T} / \text{K}^{-1}$	Time, t / s	$\frac{1}{t} / \text{s}^{-1}$	$\ln \frac{1}{t}$
286	3.50×10^{-3}	54	1.85×10^{-2}	-3.99
295	3.39×10^{-3}	27	3.70×10^{-2}	
302		15	6.67×10^{-2}	-2.71
312	3.21×10^{-3}	8	1.25×10^{-1}	-2.08

Complete **Table 2**

(2)

- (d) The Arrhenius equation can be written as

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + C_1$$

In this experiment, the rate constant, k , is directly proportional to $\frac{1}{t}$

Therefore

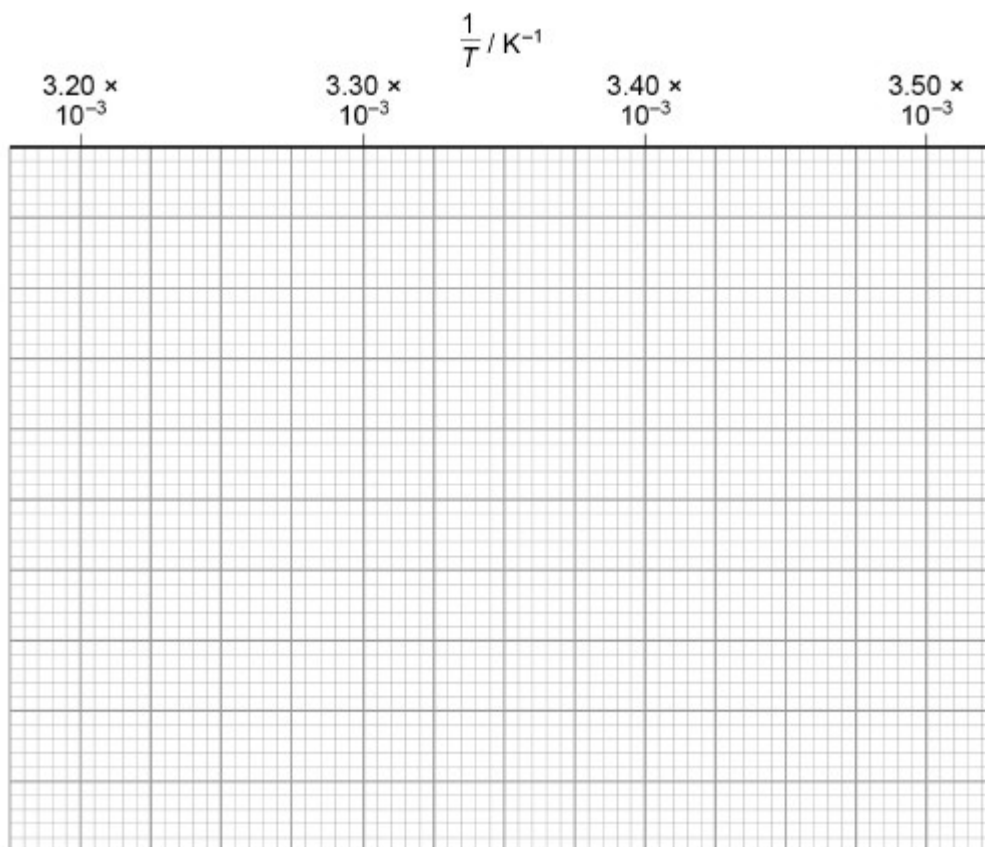
$$\ln \frac{1}{t} = -\frac{E_a}{R} \left(\frac{1}{T} \right) + C_2$$

where C_1 and C_2 are constants.

Use values from **Table 2** to plot a graph of $\ln \frac{1}{t}$ (y axis) against $\frac{1}{T}$ on the grid.

Use your graph to calculate a value for the activation energy, in kJ mol^{-1} , for this reaction.

The value of the gas constant, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$



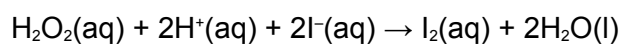
Activation energy _____ kJ mol⁻¹

(6)

(Total 14 marks)

Q2.

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



The rate equation for this reaction can be written as

$$\text{rate} = k [\text{H}_2\text{O}_2]^a [\text{I}^-]^b [\text{H}^+]^c$$

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

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

$$\text{rate} = k_1 [\text{H}^+]^c$$

- (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 $\text{H}^+(\text{aq})$.

(2)

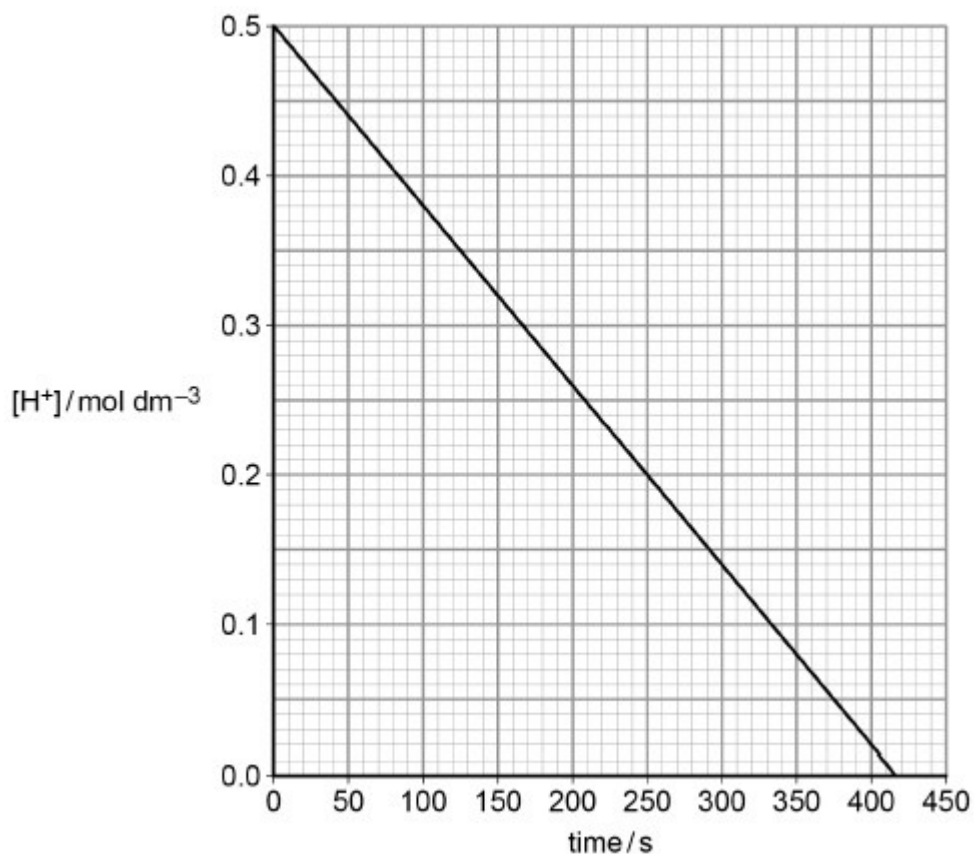
- (b) Samples of the reaction mixture are removed at timed intervals and titrated with alkali to determine the concentration of $\text{H}^+(\text{aq})$.

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 $\text{H}^+(\text{aq})$ is zero.

(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 $\text{H}^+(\text{aq})$ and $\text{I}^-(\text{aq})$ in this mixture are both $0.500 \text{ mol dm}^{-3}$

There is a large excess of H_2O_2

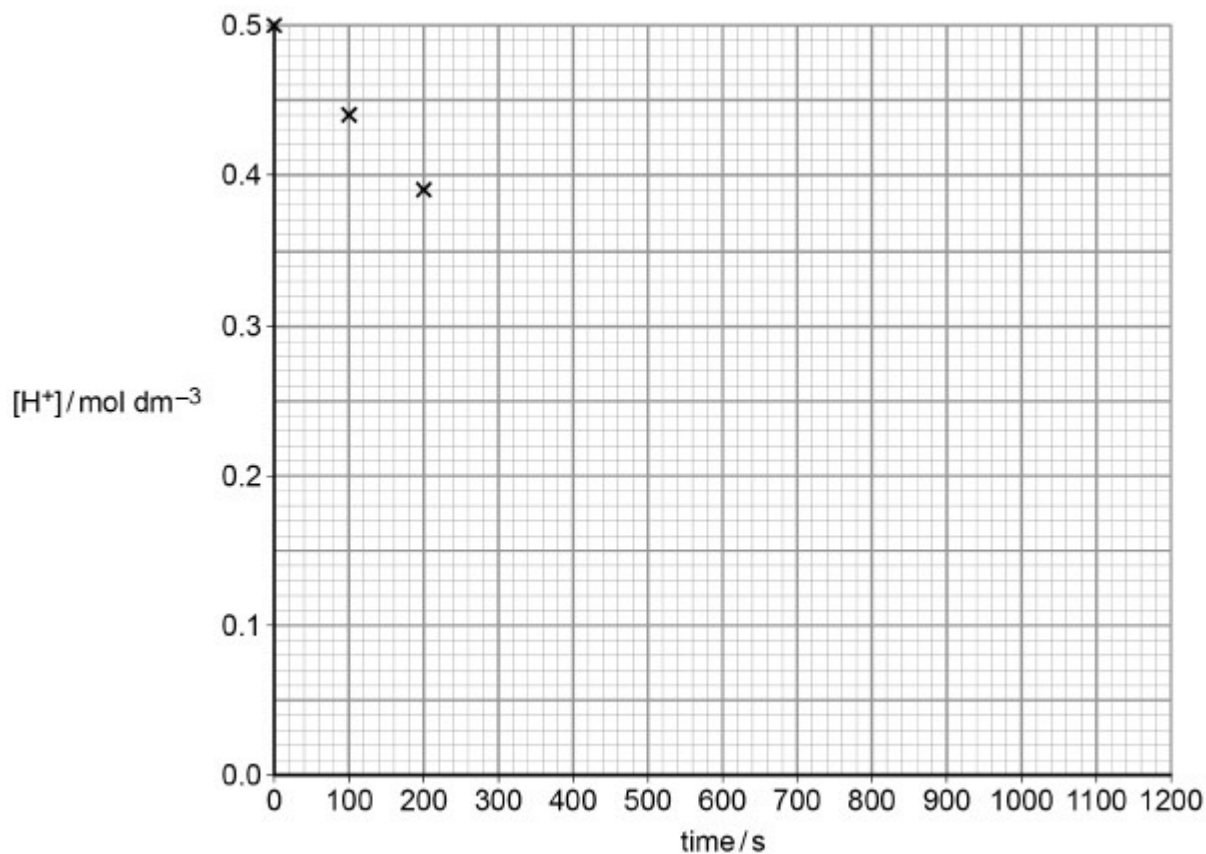
In this reaction mixture, the rate depends only on the concentration of $\text{I}^-(\text{aq})$.

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)

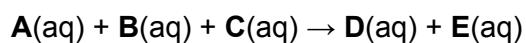
- (g) Calculate the rate of reaction when [H⁺] = 0.35 mol dm⁻³

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.



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.

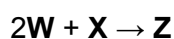
Explain, giving brief experimental details, how you could use a series of experiments to determine the order of this reaction with respect to **A**. In each experiment you should obtain a measure of the initial rate of reaction.

(6)

(Total 19 marks)

Q3.

Solutions of two compounds, **W** and **X**, react together in the presence of a soluble catalyst, **Y**, as shown in the equation



When the concentrations of **W**, **X** and **Y** are all doubled, the rate of reaction increases by a factor of four.

Which is a possible rate equation for this reaction?

- A** rate = $k [\text{W}]^2 [\text{X}]$ ☐
- B** rate = $k [\text{W}]^2 [\text{Y}]$ ☐
- C** rate = $k [\text{X}] [\text{Y}]$ ☐
- D** rate = $k [\text{X}] [\text{Z}]$ ☐

(Total 1 mark)

Q4.

A series of experiments is carried out with compounds **C** and **D**. Using the data obtained, the rate equation for the reaction between the two compounds is deduced to be

$$\text{rate} = k [\text{C}][\text{D}]$$

In one experiment at 25 °C, the initial rate of reaction is $3.1 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentration of C is 0.48 mol dm^{-3} and the initial concentration of D is 0.23 mol dm^{-3}

- (a) Calculate a value for the rate constant at this temperature and give its units.

Rate constant _____ Units _____

(3)

- (b) An equation that relates the rate constant, k , to the activation energy, E_a , and the temperature, T , is

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

Use this equation and your answer from part (a) to calculate a value, in kJ mol^{-1} , for the activation energy of this reaction at 25 °C.

For this reaction $\ln A = 16.9$

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

(If you were unable to complete part (a) you should use the value of 3.2×10^{-3} for the rate constant. This is not the correct value.)

Activation energy _____ kJ mol^{-1}

(4)

(Total 7 marks)

Q5.

The mechanisms of some reactions can be deduced from kinetic data.

The table shows the results of five experiments involving the reaction between benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) and potassium hydroxide solution.

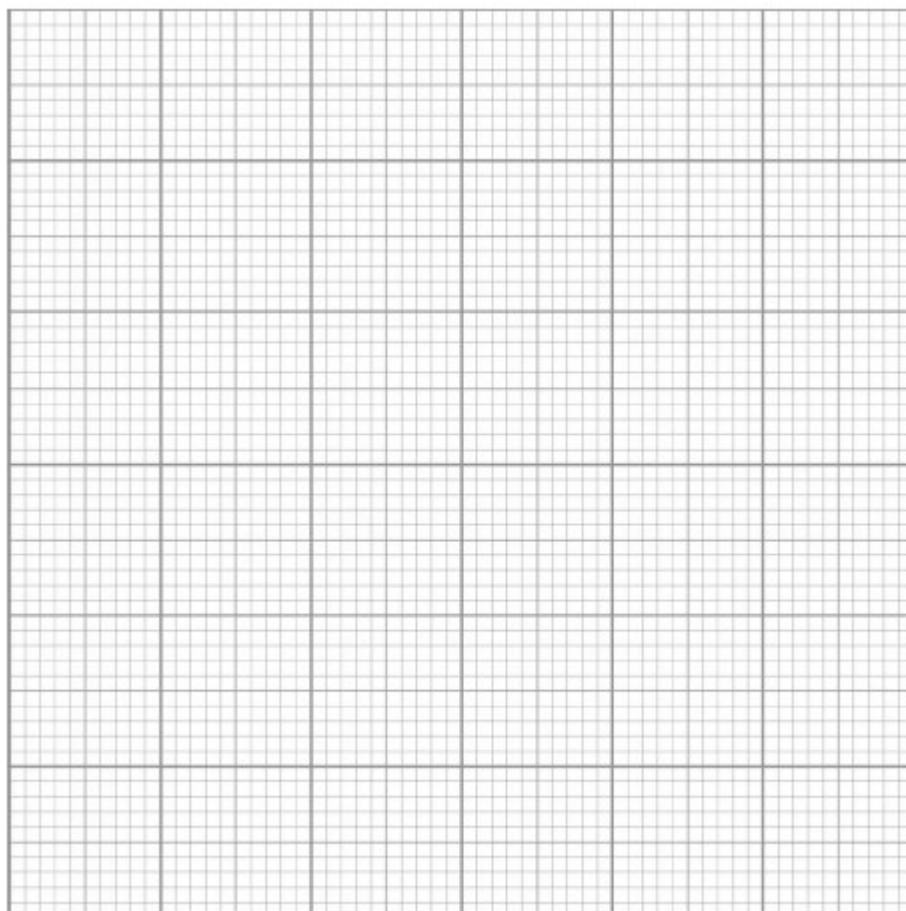
Experiment	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$	$[\text{C}_6\text{H}_5\text{CHO}]$ / mol dm^{-3}	$\text{C}_6\text{H}_5\text{CHO}]^2$	$[\text{KOH}]$ / mol dm^{-3}
1	0	0		0
2	2.90×10^{-6}	0.25		0.25
3	1.16×10^{-5}	0.50		0.25
4	2.61×10^{-5}	0.75		0.25
5	4.65×10^{-5}	1.00		0.25

- (a) Calculate the value of $[\text{C}_6\text{H}_5\text{CHO}]^2$ for each experiment.

Write your answers in the table above.

Plot a graph of initial rate against $[\text{C}_6\text{H}_5\text{CHO}]^2$ on the grid below.

Label the axes with units.



(4)

- (b) Deduce the order of the reaction with respect to $\text{C}_6\text{H}_5\text{CHO}$ from the graph.

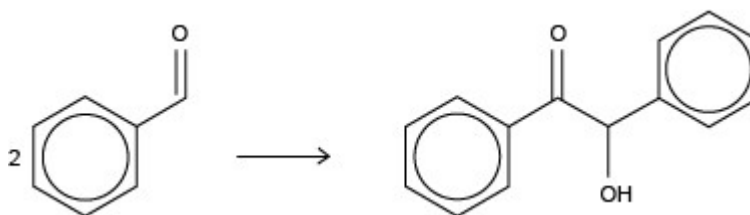
Explain your answer.

Order _____

Explanation _____

(2)

- (c) Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) undergoes a dimerisation reaction as shown:



The rate equation for the reaction is

$$\text{rate} = k [\text{C}_6\text{H}_5\text{CHO}] [\text{CN}^-]$$

Suggest the role of the cyanide ion in the reaction.

Explain your answer.

Role of CN^- _____

Explanation _____

(2)

(Total 8 marks)

Q6.

The Arrhenius equation can be written as:

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

The table below shows the value of the rate constant at different temperatures for a reaction.

Rate constant k/s^{-1}	$\ln k$	Temperature/K	$\frac{1}{T}$
6.13×10^{-5}		700	
2.75×10^{-4}		727	

8.25×10^{-4}		746	
8.23×10^{-3}		793	

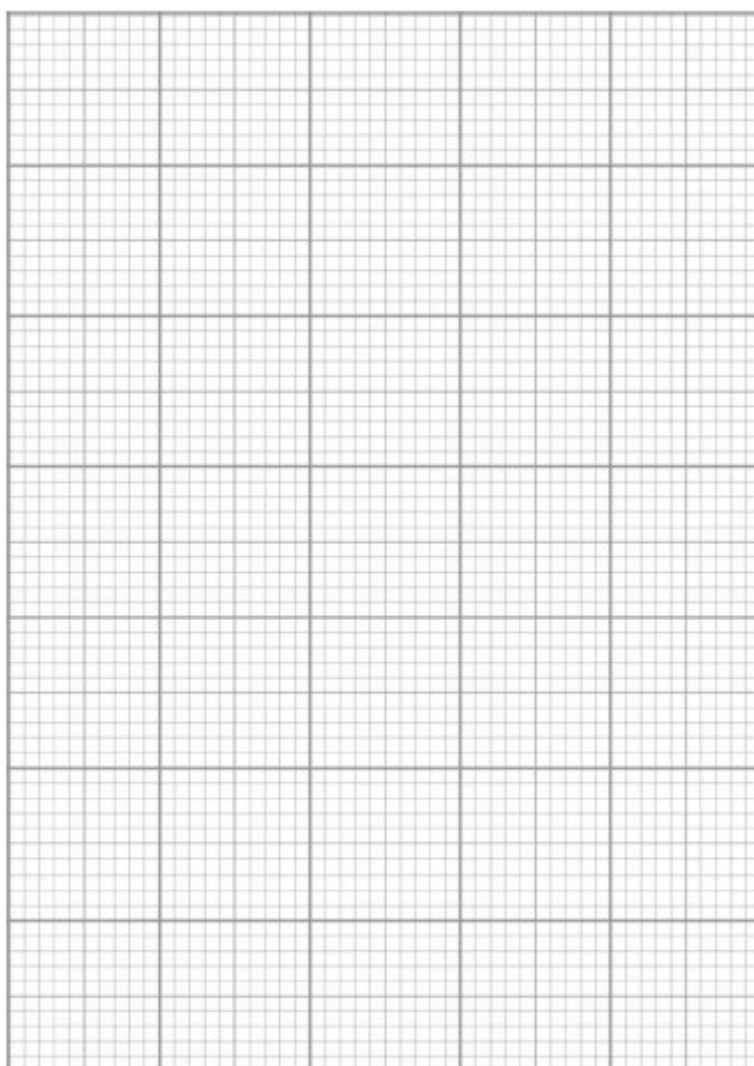
Complete the table by calculating the values of $\ln k$ and $\frac{1}{T}$ at each temperature.

Plot a graph of $\ln k$ against $\frac{1}{T}$ on the grid opposite.

Use your graph to calculate a value for the activation energy, in kJ mol^{-1} , for this reaction.

To gain full marks you must show all your working.

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



E_a _____ kJ mol^{-1}

(Total 8 marks)

Q7.

A rate investigation was carried out on a reaction involving three reactants, **X**, **Y** and **Z**. The concentrations of the reactants were varied and the relative rate for each mixture determined.

Experiment	[X]/mol dm ⁻³	[Y]/mol dm ⁻³	[Z]/mol dm ⁻³	Relative rate
1	1 × 10 ⁻³	1 × 10 ⁻³	2 × 10 ⁻³	1
2	2 × 10 ⁻³	2 × 10 ⁻³	2 × 10 ⁻³	4
3	5 × 10 ⁻⁴	2 × 10 ⁻³	4 × 10 ⁻³	0.5

The reaction is zero order with respect to **Y**.

What is the overall order of reaction?

- A** 0 ☐
- B** 1 ☐
- C** 2 ☐
- D** 3 ☐

(Total 1 mark)

Q8.

This question involves the use of kinetic data to deduce the order of a reaction and calculate a value for a rate constant.

The data in **Table 1** were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Table 1

Experiment	Initial concentration of A / mol dm ⁻³	Initial concentration of B / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.12	0.26	2.10 × 10 ⁻⁴
2	0.36	0.26	1.89 × 10 ⁻³
3	0.72	0.13	3.78 × 10 ⁻³

- (a) Show how these data can be used to deduce the rate expression for the reaction between **A** and **B**.

(3)

The data in **Table 2** were obtained in two experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature.

Table 2

Experiment	Initial concentration of C / mol dm ⁻³	Initial concentration of D / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
4	1.9×10^{-2}	3.5×10^{-2}	7.2×10^{-4}
5	3.6×10^{-2}	5.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{C}]^2[\text{D}]$$

- (b) Use the data from experiment **4** to calculate a value for the rate constant, k , at this temperature. Deduce the units of k .

$$k = \underline{\hspace{2cm}} \text{ Units} = \underline{\hspace{2cm}}$$

(3)

- (c) Calculate a value for the initial rate in experiment **5**.

Initial rate = _____ mol dm⁻³ s⁻¹

(1)

- (d) The rate equation for a reaction is

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

Explain qualitatively why doubling the temperature has a much greater effect on the rate of the reaction than doubling the concentration of **E**.

(3)

- (e) A slow reaction has a rate constant $k = 6.51 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3$ at 300 K.

Use the equation $\ln k = \ln A - E_a / RT$ to calculate a value, in kJ mol⁻¹, for the activation energy of this reaction.

The constant $A = 2.57 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3$.

The gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

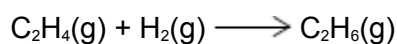
Activation energy = _____

(2)

(Total 12 marks)

Q9.

The rate equation for the hydrogenation of ethene



is $\text{Rate} = k[\text{C}_2\text{H}_4][\text{H}_2]$

At a fixed temperature, the reaction mixture is compressed to triple the original pressure.

What is the factor by which the rate of reaction changes?

A 6 ☐

B 9 ☐

C 12 ☐

D 27 ☐

(Total 1 mark)

Q10.

The initial rate of the reaction between gases **D** and **E** was measured in a series of experiments at a constant temperature. The results are shown in the table.

Expt	Initial [D] / mol dm ⁻³	Initial [E] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	1.25×10^{-2}	5.81×10^{-1}	1.16×10^{-2}
2	1.88×10^{-2}	8.73×10^{-1}	3.92×10^{-2}
3	1.88×10^{-2}	1.75	1.57×10^{-1}

- (a) Deduce the order of reaction with respect to **D** and the order with respect to **E**.

Order with respect to **D** _____

Order with respect to **E** _____

Space for working _____

(2)

- (b) Suggest why initial rates of reaction are used to determine these orders rather than rates of reaction at other times during the experiments.

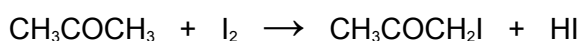
(1)

- (c) State how the initial rate is obtained from a graph of the concentration of the product against time.

(2)
(Total 5 marks)

Q11.

The reaction between propanone and iodine in the presence of hydrochloric acid was studied at a constant temperature.



The following rate equation was deduced.

$$\text{rate} = k [\text{CH}_3\text{COCH}_3][\text{H}^+]$$

- (a) Suggest why the order with respect to iodine is zero.

(1)

- (b) In an experiment the initial concentrations of propanone, iodine and hydrochloric acid were as shown in the table. The initial rate of reaction in this experiment was $8.64 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$.

	Initial concentration / mol dm^{-3}
CH_3COCH_3	5.82×10^{-2}
I_2	1.78×10^{-3}
H^+	4.76×10^{-1}

Use the data in the table and the rate equation to calculate a value for the rate constant at this temperature.
Give units with your answer.

(2)

- (c) A series of experiments was carried out using concentrations of propanone approximately 100 times the concentrations of iodine and hydrochloric acid.

Suggest the rate equation under these conditions.
Explain your answer.

(2)

(Total 5 marks)

Q12.

- (a) The table shows the results of three experiments to investigate the rate of reaction between compounds **A** and **B** dissolved in a given solvent.
All three experiments were carried out at the same temperature.

	Experiment 1	Experiment 2	Experiment 3
Initial concentration of A / mol dm ⁻³	1.60×10^{-2}	2.40×10^{-2}	3.60×10^{-2}
Initial concentration of B / mol dm ⁻³	4.20×10^{-2}	6.30×10^{-2}	6.30×10^{-2}
Initial rate / mol dm ⁻³ s ⁻¹	8.00×10^{-5}	1.80×10^{-4}	4.05×10^{-4}

- (i) Deduce the order of reaction with respect to **A**.
Tick (✓) **one** box.

Order of reaction with respect to A	Tick (✓)
0	
1	
2	

(1)

- (ii) Deduce the order of reaction with respect to **B**.
Tick (✓) **one** box.

Order of reaction with respect to B	Tick (✓)
0	
1	
2	

(1)

- (b) The reaction between two different compounds, **C** and **D**, is studied at a given temperature.

The rate equation for the reaction is found to be

$$\text{rate} = k[\text{C}][\text{D}]^2$$

- (i) When the initial concentration of **C** is $4.55 \times 10^{-2} \text{ mol dm}^{-3}$ and the initial concentration of **D** is $1.70 \times 10^{-2} \text{ mol dm}^{-3}$, the initial rate of reaction is $6.64 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Calculate the value of the rate constant at this temperature and deduce its units.

Calculation _____

Units of rate constant _____

(3)

- (ii) The experiment in part (i) is repeated at the same temperature but after the addition of extra solvent so that the total volume of the mixture is doubled.

Deduce the new initial rate of reaction.

(1)

(Total 6 marks)

Q13.

Gases **A** and **B** react as shown in the following equation.



The initial rate of the reaction was measured in a series of experiments at a constant temperature. The following rate equation was determined.

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

An incomplete table of data for the reaction between **A** and **B** is shown in the table.

Experiment	Initial [A] / mol dm ⁻³	Initial [B] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	4.2×10^{-3}	2.8×10^{-3}	3.3×10^{-5}
2	7.9×10^{-3}	2.8×10^{-3}	
3		5.6×10^{-3}	1.8×10^{-4}

- (a) Use the data from Experiment 1 to calculate a value for the rate constant, k , at this temperature.
Deduce the units of k .

Calculation _____

Units _____

(3)

- (b) Use your value of k from (a) to complete the table for the reaction between **A** and **B**.
(If you have been unable to calculate an answer for (a), you may assume a value of 2.3. This is **not** the correct answer.)

(2)

- (c) The reaction is zero order with respect to **B**.

State the significance of this zero order for the mechanism of the reaction.

(1)

(Total 6 marks)

Q14.

This question involves the use of kinetic data to calculate the order of a reaction and also a value for a rate constant.

- (a) The data in this table were obtained in a series of experiments on the rate of the reaction between compounds **E** and **F** at a constant temperature.

Experiment	Initial concentration of E / mol dm ⁻³	Initial concentration of F / mol dm ⁻³	Initial rate of reaction / mol dm ⁻³ s ⁻¹
1	0.15	0.24	0.42×10^{-3}
2	0.45	0.24	3.78×10^{-3}
3	0.90	0.12	7.56×10^{-3}

- (i) Deduce the order of reaction with respect to **E**.

_____ (1)

- (ii) Deduce the order of reaction with respect to **F**.

_____ (1)

- (b) The data in the following table were obtained in two experiments on the rate of the reaction between compounds **G** and **H** at a constant temperature.

Experiment	Initial concentration of G / mol dm ⁻³	Initial concentration of H / mol dm ⁻³	Initial rate of reaction / mol dm ⁻³ s ⁻¹
4	3.8×10^{-2}	2.6×10^{-2}	8.6×10^{-4}
5	6.3×10^{-2}	7.5×10^{-2}	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{G}]^2[\text{H}]$$

- (i) Use the data from Experiment **4** to calculate a value for the rate constant k at this temperature. Deduce the units of k .

Calculation _____

Units _____

_____ (3)

- (ii) Calculate a value for the initial rate of reaction in Experiment **5**.

Q15.

- (a) The data in the following table were obtained in two experiments about the rate of the reaction between substances **B** and **C** at a constant temperature.

Experiment	Initial concentration of B / mol dm ⁻³	Initial concentration of C / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	4.2×10^{-2}	2.6×10^{-2}	8.4×10^{-5}
2	6.3×10^{-2}	7.8×10^{-2}	To be calculated

The rate equation for this reaction is known to be

$$\text{rate} = k[\text{B}]^2[\text{C}]$$

- (i) Use the data from Experiment **1** to calculate a value for the rate constant k at this temperature and deduce its units.

Calculation _____

Units _____

(3)

- (ii) Calculate a value for the initial rate in Experiment **2**.

(1)

- (b) The data in the following table were obtained in a series of experiments about the rate of the reaction between substances **D** and **E** at a constant temperature.

Experiment	Initial concentration of D / mol dm ⁻³	Initial concentration of E / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
3	0.13	0.23	0.26×10^{-3}
4	0.39	0.23	2.34×10^{-3}

5	0.78	0.46	9.36×10^{-3}
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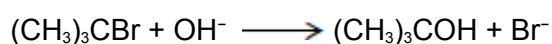
- (i) Deduce the order of reaction with respect to **D**.

(1)

- (ii) Deduce the order of reaction with respect to **E**.

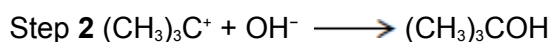
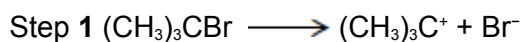
(1)

- (c) The compound $(\text{CH}_3)_3\text{CBr}$ reacts with aqueous sodium hydroxide as shown in the following equation.



This reaction was found to be first order with respect to $(\text{CH}_3)_3\text{CBr}$ but zero order with respect to hydroxide ions.

The following two-step process was suggested.



- (i) Deduce the rate-determining step in this two-step process.

(1)

- (ii) Outline a mechanism for this step using a curly arrow.

(1)

(Total 8 marks)

Q16.

Gases **P** and **Q** react as shown in the following equation.



The initial rate of the reaction was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\text{P}]^2[\text{Q}]$$

- (a) Complete the table of data for the reaction between **P** and **Q**.

Experiment	Initial [P] / mol dm ⁻³	Initial [Q] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	2.5×10^{-2}	1.8×10^{-2}	5.0×10^{-5}
2	7.5×10^{-2}	1.8×10^{-2}	
3	5.0×10^{-2}		5.0×10^{-5}
4		5.4×10^{-2}	4.5×10^{-4}

(Space for working) _____

(3)

- (b) Use the data from Experiment 1 to calculate a value for the rate constant (*k*) at this temperature. Deduce the units of *k*.

Calculation _____

 Units _____

(3)

(Total 6 marks)

Q17.

The initial rate of the reaction between two gases **P** and **Q** was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\text{P}]^2[\text{Q}]$$

- (a) Complete the table of data below for the reaction between **P** and **Q**.

Experiment	Initial [P] /mol dm ⁻³	Initial [Q] /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
------------	-----------------------------------	-----------------------------------	--

1	0.20	0.30	$1.8 = 10^{-3}$
2	0.40	0.60	
3	0.60		$5.4 = 10^{-3}$
4		0.90	$12.2 = 10^{-3}$

(Space for working) _____

(3)

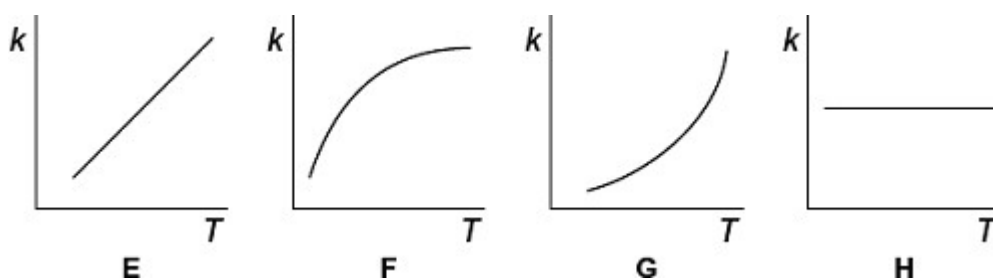
- (b) Use the data from Experiment 1 to calculate a value for the rate constant k and deduce its units.

Calculation _____

Units _____

(3)

- (c) Consider the graphs **E**, **F**, **G** and **H** below.



Write in the box below the letter of the graph that shows how the rate constant k varies with temperature.

(1)

(Total 7 marks)

Q18.

- (a) In the presence of the catalyst rhodium, the reaction between NO and H₂ occurs according to the following equation.



The kinetics of the reaction were investigated and the rate equation was found to be

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

The initial rate of reaction was $6.2 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentration of NO was $2.9 \times 10^{-2} \text{ mol dm}^{-3}$ and the initial concentration of H₂ was $2.3 \times 10^{-2} \text{ mol dm}^{-3}$.

- (i) Calculate the value of the rate constant under these conditions and give its units.

Calculation _____

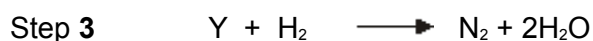
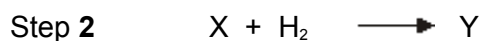
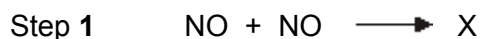
Units _____

(3)

- (ii) Calculate the initial rate of reaction if the experiment is repeated under the same conditions but with the concentrations of NO and of H₂ both doubled from their original values.

(1)

- (b) Using the rate equation and the overall equation, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.



Suggest which **one** of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step _____

Explanation _____

Q19.

The rate of hydrolysis of an ester **X** ($\text{HCOOCH}_2\text{CH}_2\text{CH}_3$) was studied in alkaline conditions at a given temperature. The rate was found to be first order with respect to the ester and first order with respect to hydroxide ions.

- (a) (i) Name ester **X**.

_____ (1)

- (ii) Using **X** to represent the ester, write a rate equation for this hydrolysis reaction.

_____ (1)

- (iii) When the initial concentration of **X** was $0.024 \text{ mol dm}^{-3}$ and the initial concentration of hydroxide ions was $0.035 \text{ mol dm}^{-3}$, the initial rate of the reaction was $8.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$.
Calculate a value for the rate constant at this temperature and give its units.

Calculation _____

Units _____

_____ (3)

- (iv) In a second experiment at the same temperature, water was added to the original reaction mixture so that the total volume was doubled.
Calculate the initial rate of reaction in this second experiment.

_____ (1)

- (v) In a third experiment at the same temperature, the concentration of **X** was half that used in the experiment in part (a) (iii) and the concentration of hydroxide ions was three times the original value.
Calculate the initial rate of reaction in this third experiment.

(1)

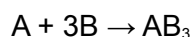
- (vi) State the effect, if any, on the value of the rate constant k when the temperature is lowered but all other conditions are kept constant. Explain your answer.

Effect _____

Explanation _____

(2)

- (b) Compound **A** reacts with compound **B** as shown by the overall equation



The rate equation for the reaction is

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

A suggested mechanism for the reaction is



Deduce which one of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step _____

Explanation _____

(2)

(Total 11 marks)

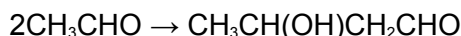
Q20.

A reaction mechanism is a series of steps by which an overall reaction may proceed.

The reactions occurring in these steps may be deduced from a study of reaction rates.

Experimental evidence about initial rates leads to a rate equation. A mechanism is then proposed which agrees with this rate equation.

Ethanal dimerises in dilute alkaline solution to form compound **X** as shown in the following equation.



X

A chemist studied the kinetics of the reaction at 298 K and then proposed the following rate equation.

$$\text{Rate} = k [\text{CH}_3\text{CHO}][\text{OH}^-]$$

- (a) Give the IUPAC name of compound **X**.

(1)

- (b) The initial rate of the reaction at 298K was found to be $2.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentration of ethanal was 0.10 mol dm^{-3} and the initial concentration of sodium hydroxide was $0.020 \text{ mol dm}^{-3}$. Calculate a value for the rate constant at this temperature and give its units.

Calculation _____

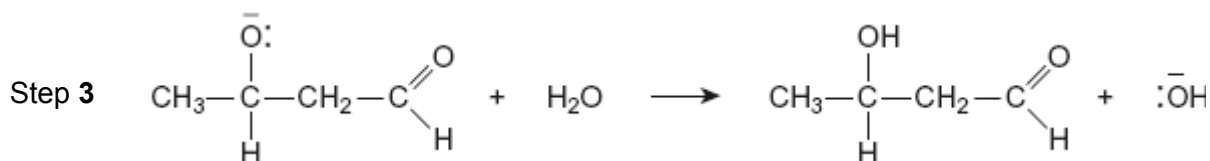
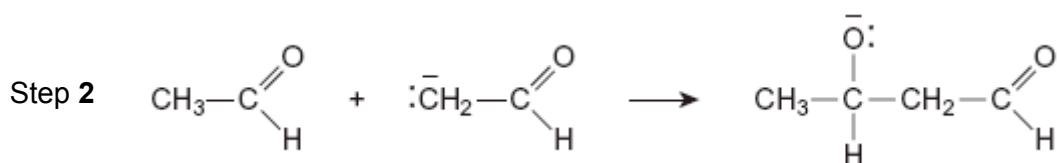
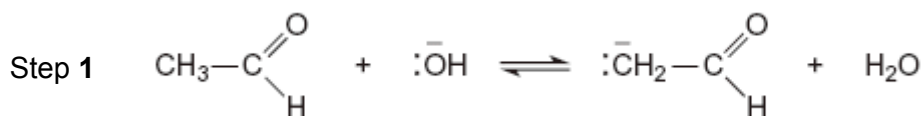
Units _____

(3)

- (c) The sample of **X** produced consists of a racemic mixture (racemate). Explain how this racemic mixture is formed.

(2)

- (d) A three-step mechanism has been proposed for this reaction according to the following equations.



- (i) Using the rate equation, predict which of the three steps is the rate-determining step. Explain your answer.

Rate-determining step _____

Explanation _____

(2)

- (ii) Deduce the role of ethanal in Step 1.

_____ (1)

- (iii) Use your knowledge of reaction mechanisms to deduce the type of reaction occurring in Step 2.

_____ (1)

- (iv) In the space below draw out the mechanism of Step 2 showing the relevant curly arrows.

(2)

- (e) In a similar three-step mechanism, one molecule of **X** reacts further with one molecule of ethanal. The product is a trimer containing six carbon atoms.

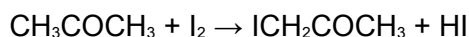
Deduce the structure of this trimer.

(1)

(Total 13 marks)

Q21.

Propanone and iodine react in acidic conditions according to the following equation.



A student studied the kinetics of this reaction using hydrochloric acid and a solution containing propanone and iodine. From the results the following rate equation was deduced.

$$\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

- (a) Give the overall order for this reaction.

(1)

- (b) When the initial concentrations of the reactants were as shown in the table below, the initial rate of reaction was found to be $1.24 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$.

	initial concentration / mol dm^{-3}
CH_3COCH_3	4.40
I_2	5.00×10^{-3}
H^+	0.820

Use these data to calculate a value for the rate constant, k , for the reaction and give its units.

Calculation _____

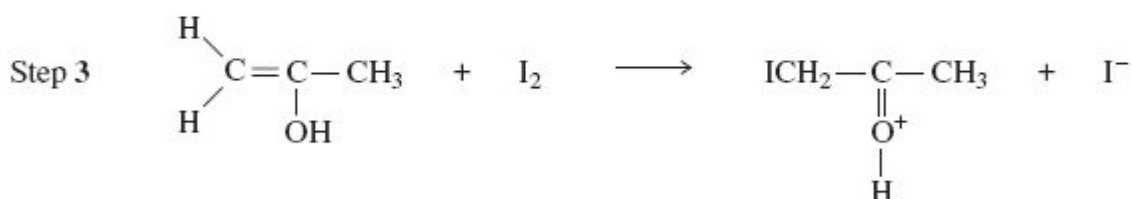
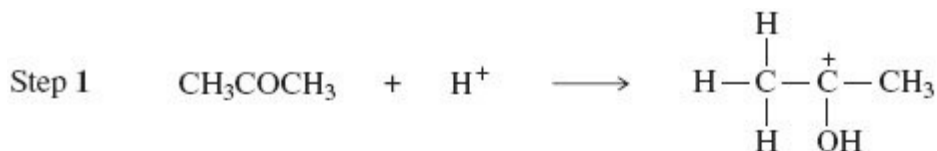
Units _____

(3)

- (c) Deduce how the initial rate of reaction changes when the concentration of iodine is doubled but the concentrations of propanone and of hydrochloric acid are unchanged.

(1)

- (d) The following mechanism for the overall reaction has been proposed.



Use the rate equation to suggest which of the four steps could be the rate-determining step. Explain your answer.

Rate-determining step _____

Explanation _____

(2)

- (e) Use your understanding of reaction mechanisms to predict a mechanism for Step 2 by adding one or more curly arrows as necessary to the structure of the carbocation below.



(1)

(Total 8 marks)

Q22.

Kinetic studies enable chemists to suggest mechanisms for reactions.

- (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Experiment	Initial concentration	Initial concentration	Initial rate/
------------	-----------------------	-----------------------	---------------

	of A /mol dm ⁻³	of B /mol dm ⁻³	mol dm ⁻³ s ⁻¹
1	0.12	0.15	0.32×10^{-3}
2	0.36	0.15	2.88×10^{-3}
3	0.72	0.30	11.52×10^{-3}

- (i) Deduce the order of reaction with respect to **A**.

- (ii) Deduce the order of reaction with respect to **B**.

(2)

- (b) The following data were obtained in a series of experiments on the rate of the reaction between NO and O₂ at a constant temperature.

Experiment	Initial concentration of NO/mol dm ⁻³	Initial concentration of O ₂ /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	5.0×10^{-2}	2.0×10^{-2}	6.5×10^{-4}
5	6.5×10^{-2}	3.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

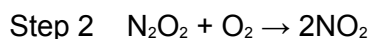
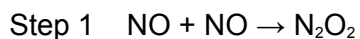
- (i) Use the data from Experiment **4** to calculate a value for the rate constant, *k*, at this temperature, and state its units.

Value of *k* _____

Units of *k* _____

- (ii) Calculate a value for the initial rate in Experiment **5**.

- (iii) Using the rate equation, a scientist suggested a mechanism for the reaction which consisted of the two steps shown below.



Which did the scientist suggest was the rate-determining step?

(5)

(Total 7 marks)

Q23.

The hydrolysis of methyl propanoate was studied in acidic conditions at 25°C and the rate equation was found to be

$$\text{rate} = k[\text{CH}_3\text{CH}_2\text{COOCH}_3][\text{H}^+]$$

- (a) Use the data below to calculate the value of the rate constant, k , at this temperature. Deduce its units.

Initial rate of reaction / $\text{mol dm}^{-3} \text{ s}^{-1}$	Initial concentration of methyl propanoate / mol dm^{-3}	Initial concentration of hydrochloric acid / mol dm^{-3}
1.15×10^{-4}	0.150	0.555

Rate constant _____

Units _____

(3)

- (b) The reaction in part (a) was repeated at the same temperature, but water was added so that the volume of the reaction mixture was doubled. Calculate the initial rate of reaction under these conditions.

(1)

- (c) A third experiment was carried out at a different temperature. Some data from this experiment are shown in the table below.

Initial rate of reaction / $\text{mol dm}^{-3} \text{ s}^{-1}$	Value of rate constant at this different temperature	Initial methyl propanoate / mol dm^{-3}
4.56×10^{-5}	8.94×10^{-4}	0.123

Calculate the initial pH of the reaction mixture. Give your answer to two decimal places.

(3)
(Total 7 marks)

Q24.

The initial rate of the reaction between the gases NO and H₂ was measured in a series of experiments at a constant temperature and the following rate equation was determined.

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

- (a) Complete the table of data below for the reaction between NO and H₂

Experiment	Initial [NO] / mol dm ⁻³	Initial [H ₂] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	3.0 × 10 ⁻³	1.0 × 10 ⁻³	1.8 × 10 ⁻⁵
2	3.0 × 10 ⁻³		7.2 × 10 ⁻⁵
3	1.5 × 10 ⁻³	1.0 × 10 ⁻³	
4		0.50 × 10 ⁻³	8.1 × 10 ⁻⁵

(3)

- (b) Using the data from experiment 1, calculate a value for the rate constant, *k*, and state its units.

(3)
(Total 6 marks)

Q25.

- (a) Compound **A**, HCOOCH₂CH₂CH₃, is an ester. Name this ester and write an equation for its reaction with aqueous sodium hydroxide.

Name _____

Equation _____

(2)

- (b) The initial rate of reaction between ester **A** and aqueous sodium hydroxide was measured in a series of experiments at a constant temperature. The data obtained are shown below.

Experiment	Initial concentration of NaOH / mol dm ⁻³	Initial concentration of A / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.040	0.030	4.0×10^{-4}
2	0.040	0.045	6.0×10^{-4}
3	0.060	0.045	9.0×10^{-4}
4	0.120	0.060	to be calculated

Use the data in the table to deduce the order of reaction with respect to **A** and the order of reaction with respect to NaOH. Hence calculate the initial rate of reaction in Experiment 4.

Order with respect to **A** _____

Order with respect to NaOH _____

Initial rate in Experiment 4 _____

(3)

- (c) In a further experiment at a different temperature, the initial rate of reaction was found to be 9.0×10^{-3} mol dm⁻³ s⁻¹ when the initial concentration of **A** was 0.020 mol dm⁻³ and the initial concentration of NaOH was 2.00 mol dm⁻³. Under these new conditions with the much higher concentration of sodium hydroxide, the reaction is first order with respect to **A** and appears to be zero order with respect to sodium hydroxide.

- (i) Write a rate equation for the reaction under these new conditions.

- (ii) Calculate a value for the rate constant under these new conditions and state its units.

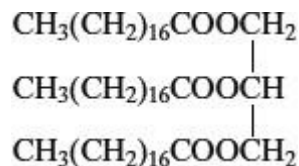
Calculation _____

Units _____

- (iii) Suggest why the order of reaction with respect to sodium hydroxide appears to be zero under these new conditions.

(6)

- (d) A naturally-occurring triester, shown below, was heated under reflux with an excess of aqueous sodium hydroxide and the mixture produced was then distilled. One of the products distilled off and the other was left in the distillation flask.



- (i) Draw the structure of the product distilled off and give its name.

Structure

Name _____

- (ii) Give the formula of the product left in the distillation flask and give a use for it.

Formula _____

Use _____

(4)

(Total 15 marks)

Q26.

- (a) The following table shows the results of three experiments carried out at the same temperature to investigate the rate of the reaction between compounds **P** and **Q**.

	Experiment 1	Experiment 2	Experiment 3
Initial concentration of P /mol dm ⁻³	0.50	0.25	0.25
Initial concentration of Q /mol dm ⁻³	0.36	0.36	0.72
Initial rate/mol dm ⁻³ s ⁻¹	7.6 × 10 ⁻³	1.9 × 10 ⁻³	3.8 × 10 ⁻³

Use the data in the table to deduce the order with respect to **P** and the order with respect to **Q**.

Order with respect to **P** _____

Order with respect to **Q** _____

(2)

- (b) In a reaction between **R** and **S**, the order of reaction with respect to **R** is one, the order of reaction with respect to **S** is two and the rate constant at temperature T_1 has a value of $4.2 \times 10^{-4} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$.

- (i) Write a rate equation for the reaction. Calculate a value for the initial rate of reaction when the initial concentration of **R** is 0.16 mol dm^{-3} and that of **S** is 0.84 mol dm^{-3} .

Rate equation _____

Calculation _____

- (ii) In a second experiment performed at a different temperature, T_2 , the initial rate of reaction is $8.1 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ when the initial concentration of **R** is 0.76 mol dm^{-3} and that of **S** is 0.98 mol dm^{-3} . Calculate the value of the rate constant at temperature T_2 .

- (iii) Deduce which of T_1 and T_2 is the higher temperature.

(6)

(Total 8 marks)

Q27.

- (a) The initial rate of the reaction between compounds **A** and **B** was measured in a series of experiments at a fixed temperature. The following rate equation was deduced.

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

- (i) Complete the table of data below for the reaction between **A** and **B**.

Expt	Initial [A] /mol dm ⁻³	Initial [B] /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
1	4.80×10^{-2}	6.60×10^{-2}	10.4×10^{-3}
2	4.80×10^{-2}	3.30×10^{-2}	
3		13.2×10^{-2}	5.20×10^{-3}
4	1.60×10^{-2}		10.4×10^{-3}

- (ii) Using the data for experiment 1, calculate a value for the rate constant, k , and state its units.

Calculation _____

Units _____

(6)

- (b) State how the value of the rate constant, k , would change, if at all, if the concentration of **A** were increased in a series of experiments.

(1)

(Total 7 marks)

Q28.

- (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
1	0.12	0.15	0.32×10^{-3}
2	0.36	0.15	2.88×10^{-3}
3	0.72	0.30	11.52×10^{-3}

- (i) Deduce the order of reaction with respect to **A**.

- (ii) Deduce the order of reaction with respect to **B**.

(2)

- (b) The following data were obtained in a series of experiments on the rate of the reaction between NO and O₂ at a constant temperature.

Experiment	Initial concentration of NO/mol dm ⁻³	Initial concentration of O ₂ /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	5.0×10^{-2}	2.0×10^{-2}	6.5×10^{-4}
5	6.5×10^{-2}	3.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

- (i) Use the data from experiment 4 to calculate a value for the rate constant, k , at this temperature, and state its units.

Value of k _____

Units of k _____

- (ii) Calculate a value for the initial rate in experiment 5.

(4)

(Total 6 marks)

Q29.

The rate of the reaction between substance **A** and substance **B** was studied in a series of experiments carried out at the same temperature. In each experiment the initial rate was measured using different concentrations of **A** and **B**. These results were used to deduce the order of reaction with respect to **A** and the order of reaction with respect to **B**.

- (a) What is meant by the term *order of reaction* with respect to **A**?

(1)

- (b) When the concentrations of **A** and **B** were both doubled, the initial rate increased by a factor of 4. Deduce the **overall** order of the reaction.

(1)

- (c) In another experiment, the concentration of **A** was increased by a factor of three and the concentration of **B** was halved. This caused the initial rate to increase by a factor of nine.

- (i) Deduce the order of reaction with respect to **A** and the order with respect to **B**.

Order with respect to **A** _____

Order with respect to **B** _____

- (ii) Using your answers from part (c)(i), write a rate equation for the reaction and suggest suitable units for the rate constant.

Rate equation _____

Units for the rate constant _____

(4)

(Total 6 marks)

Q30.

- (a) The initial rate of the reaction between substances **P** and **Q** was measured in a series of experiments and the following rate equation was deduced.

$$\text{rate} = k[\text{P}]^2[\text{Q}]$$

- (i) Complete the table of data below for the reaction between **P** and **Q**.

Experiment	Initial [P] / mol dm ⁻³	Initial [Q] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.20	0.30	4.8×10^{-3}
2	0.10	0.10	
3	0.40		9.6×10^{-3}
4		0.60	19.2×10^{-3}

- (ii) Using the data from experiment 1, calculate a value for the rate constant, k , and deduce its units.

(6)

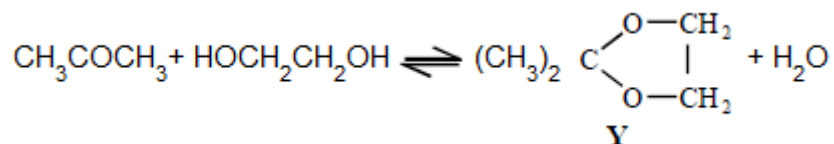
- (b) What change in the reaction conditions would cause the value of the rate constant to change?

(1)

(Total 7 marks)

Q31.

This question is about the reaction between propanone and an excess of ethane-1,2-diol, the equation for which is given below.



In a typical procedure, a mixture of 1.00 g of propanone, 5.00 g of ethane-1,2-diol and 0.100 g of benzenesulphonic acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, is heated under reflux in an inert solvent. Benzenesulphonic acid is a strong acid.

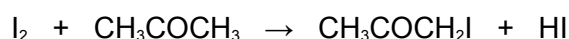
When the concentration of benzenesulphonic acid is doubled, the rate of the reaction doubles. It can be deduced that

- A the reaction is first order overall.
- B the reaction is third order overall.
- C the reaction is acid-catalysed.
- D units for the rate constant, k , are $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$.

(Total 1 mark)

Q32.

Iodine and propanone react in acid solution according to the equation



The rate equation for the reaction is found to be

$$\text{rate} = k [\text{CH}_3\text{COCH}_3][\text{H}^+]$$

- (a) Deduce the order of reaction with respect to iodine and the overall order of reaction.

Order with respect to iodine _____

Overall order _____

(2)

- (b) At the start of the experiment, the rate of reaction was found to be $2.00 \times 10^{-5} \text{ mol dm}^{-3} \text{s}^{-1}$ when the concentrations of the reactants were as shown below.

Reactant	Concentration / mol dm^{-3}
CH_3COCH_3	1.50
I_2	2.00×10^{-2}
H^+	3.00×10^{-2}

Use these data to calculate a value for the rate constant and deduce its units.

Rate constant _____

Units _____

(3)

- (c) How can you tell that H^+ acts as a catalyst in this reaction?

(2)

- (d) Calculate the initial rate of reaction if the experiment were to be repeated at the same temperature and with the same concentrations of iodine and propanone as in part (b) but at a pH of 1.25

(3)

(Total 10 marks)

Q33.

- (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
1	0.15	0.24	0.45×10^{-5}
2	0.30	0.24	0.90×10^{-5}
3	0.60	0.48	7.20×10^{-5}

- (i) Show how the data in the table can be used to deduce that the reaction is first-order with respect to **A**.

- (ii) Deduce the order with respect to **B**.

(2)

- (b) The following data were obtained in a second series of experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature.

Experiment	Initial concentration of A /mol dm ⁻³	Initial concentration of B /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
4	0.75	1.50	9.30×10^{-5}
5	0.20	0.10	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\text{C}]^2[\text{D}]$$

- (i) Use the data from Experiment 4 to calculate a value for the rate constant, k , at this temperature. State the units of k .

Value for k _____

Units of k _____

- (ii) Calculate the value of the initial rate in Experiment 5.

(4)

(Total 6 marks)

Q34.

$$\text{Rate} = k [\text{A}]^2 [\text{B}]$$

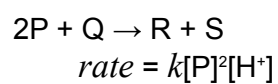
Correct units for the rate constant in the rate equation above are

- A** mol dm⁻³ s⁻¹
B mol⁻¹ dm⁻³ s⁻¹
C mol² dm⁻⁶ s⁻¹
D mol⁻² dm⁶ s⁻¹

(Total 1 mark)

Q35.

The equation and rate law for the reaction of substance P with substance Q are given below.



Under which one of the following conditions, all at the same temperature, would the rate of reaction be slowest?

	[P] / mol dm ⁻³	pH
A	0.1	0
B	1	2
C	3	3
D	10	4

(Total 1 mark)

Mark schemes

Q1.

- (a) $k = \frac{2.4 \times 10^{-2}}{0.10 \times 0.20 \times (0.30)^2}$
- Mark is for insertion of numbers into a correctly re-arranged equation.* 1
- = 13 (must be 2 sfs) 1
- Units $\text{mol}^{-3} \text{dm}^3 \text{s}^{-1}$
- Can be in any order* 1
- (b) Experiment 2 $[\text{BrO}_3^-] = 0.15$ 1
- Experiment 3 rate = 0.26 or 0.27 1
- Experiment 4 $[\text{H}^+] = 0.45$ or 0.46
- If k wrong in (a) : allow the expected answer OR values
conseq to their k (allow mix & match)*
- Ex 2 $[\text{BrO}_3^-] = 2/k$*
- Ext 3 rate = $0.02 \times k$*
- Ex 4 $[\text{H}^+] = \text{square root of } (2.7/k)$* 1
- (c) $1/T$ value $3.31(1) \times 10^{-3}$ or 0.00331(1)
- Must be 3 sig figs or more* 1
- $\ln(1/t)$ value -3.30 or -3.297
- Not allow -3.29* 1
- (d) **M1** y axis labelled with values (no units) and plotted points use over half of the axis 1
- M2** points plotted correctly (see graph below) 1
- M3** best fit straight line (minimum 3 points plotted)
+ - one small square for line of best fit 1
- M4** gradient = -6.64×10^3 (K) or -6640 (K)
Range - 6.5×10^3 to -6.8×10^3 or -6500 to -6800 1
- M5** $E_a = M4 \times 8.31$

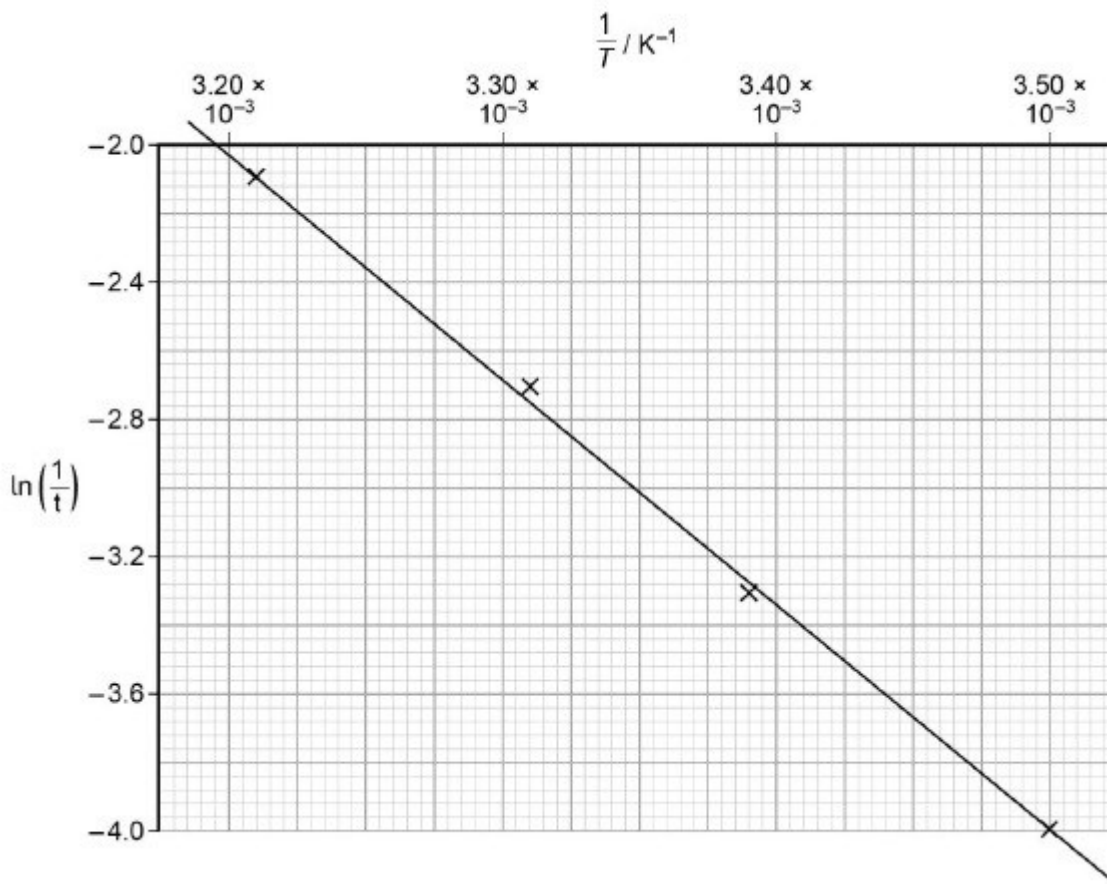
If gradient outside range then max 4 for M1, M2, M3 and M5

1

M6 = 55.2 kJ mol⁻¹

Range 54.0 - 56.5

1



[14]

Q2.

- (a) H₂O₂ and/or I⁻ concentration change is negligible /
H₂O₂ and/or I⁻ concentration (effectively) constant
Only the concentration of H⁺ changes.

so have a constant/no effect on the rate / so is zero order (w.r.t. H₂O₂ and I⁻) / a and b are zero

Ignore references to H⁺ is limiting reagent / rds / H₂O₂/I⁻ not in rate equation

Do not allow reference to catalyst.

2

- (b) Stop the reaction / quench

By dilution / cooling / adding a reagent to react with H₂O₂/I⁻

Allow valid suggestions about how to stop the reaction.

Do not allow reaction with acid/alkali / neutralisation for M2

*Do not penalise other named reagents.
Ignore references to measuring volume and adding indicator*

2

- (c) M1: constant gradient

OR

change/decrease in concentration is proportional to time

Allow constant rate / rate = k

Ignore reference to straight line

Not increase in concentration / concentration is inversely proportional / concentration (on its own) is proportional

M2: as $[H^+]$ changes/decreases

M2 dependent on correct M1

Allow rate v concentration graph would give horizontal straight line owtte

Allow so $[H^+]$ has no effect on the rate

2

- (d) evidence of attempt at calculation of gradient via $\Delta y/\Delta x$
allow construction lines on graph

$$k_1 = 0.0012 / 1.2 \times 10^{-3}$$

At least 2 sf (0.00118 – 0.00122)

Correct answer scores 2/2

No ecf from incorrect or inverted numbers in M1

$k_1 = - 0.0012$ scores 1/2

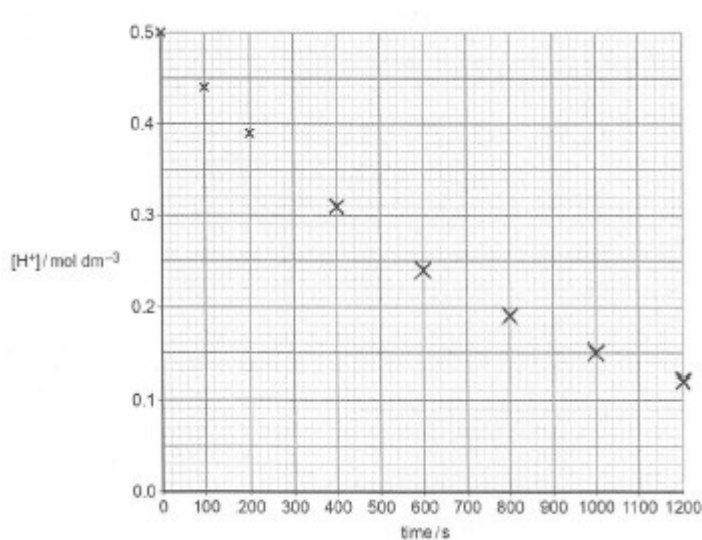
Additional processing of data such as including $[H^+]$ loses M2

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

M3 mark independently

3

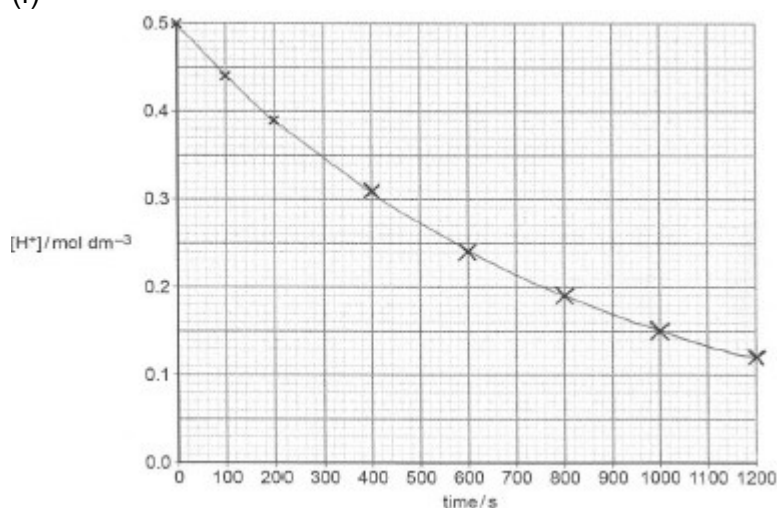
- (e) 5 points correctly plotted



Allow $\pm$ half a small square for each point

1

(f)

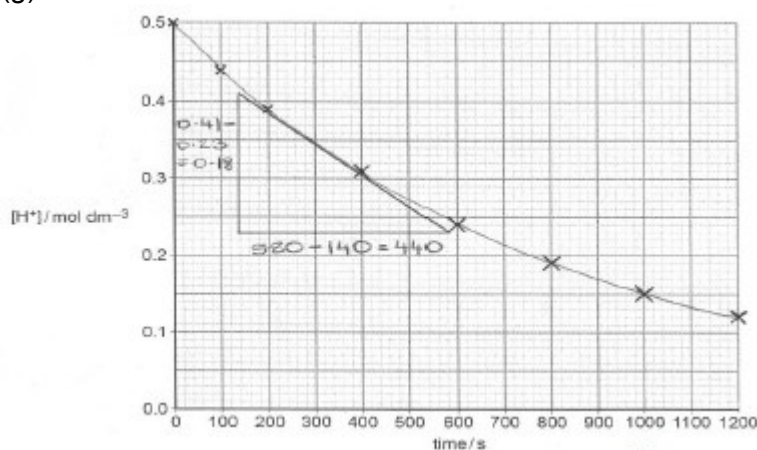


Smooth curve only within one small square of all points
(ecf on part (e))

Not a series of straight lines between points

1

(g)



M1: Tangent to curve drawn at $[\text{H}_3\text{O}^+] = 0.35 \text{ mol dm}^{-3}$

e.g. $0.18/440$

M1 for a tangent / triangle / other suitable working

Allow ECF for both M1 and M2 following on from straight line drawn in 01.6, but must show suitable construction on graph for M1

M2: Rate = $4.09 \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1})$

Ignore negative signs

Allow value in range $3.70 \times 10^{-4} - 4.50 \times 10^{-4}$

At least 2sf

ecf from any straight line for correctly calculated gradient

2

(h) This question is marked using levels of response. Refer to the Mark Scheme

Instructions for examiners for guidance on how to mark this question

Level 3 5-6 marks	All stages are covered and the explanation of each stage is correct and virtually complete. Answer is coherent and shows progression through all three stages. A clear explanation of how the order is determined from the results is needed to show coherence.
Level 2 3-4 marks	All stages are covered (NB 'covered' means min 2 from stage 2) but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages covered and the explanations are generally correct and virtually complete Answer is coherent and shows some progression through all three stages. Some steps in each stage may be out of order and incomplete
Level 1 1-2 marks	Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR only one stage is covered but the explanation is generally correct and virtually complete Answer shows some progression between two stages
Level 0 0 marks	Insufficient correct Chemistry to warrant a mark

Indicative Chemistry content Method 1

Stage 1 Preparation

- 1a Measure (suitable/known volumes of) some reagents (ignore quoted values for volume)
- 1b Measure (known amount of) **X** / use a colorimeter
- 1c into separate container(s) – (allow up to two reagents and **X** measured together into one container); reference to **A**, **B** or **C** added last. NOT if **X** added last.

Stage 2 Procedure

- 2a Start clock/timer at the point of mixing (don't allow if only 2 reagents mixed) (allow even if **X** not added or added last)
- 2b Time recorded for appearance of blue colour/specific reading on colorimeter/disappearing cross
- 2c Use of same concentration of **B** and **C** / same total volume / same volume/amount of **X**
- 2d Same temperature/use water bath
- 2e Repeat with different concentrations of A (can be implied through different volumes of A and same total volume)

Stage 3 Use of Results

- 3a 1/time taken is a measure of the rate
- 3b plot of 1/time against volumes/concentrations of **A** or plot $\log(1/\text{time})$ vs $\log(\text{volume or concentration of A})$
- 3c description of interpreting order from shape of 1/time vs volume or concentration graph / gradient of log plot gives order / allow interpretation of time vs concentration graph / ratio between change in concentration and change in rate (e.g, $2x[A] = 2 \times \text{rate}$ so 1st order)

Indicative Chemistry content – Alternative Method Using Colorimetry and repeated Continuous Monitoring

Stage 1 Preparation

- 1a Measure (suitable/known volumes of) **A**, **B** and **C** (ignore quoted values for volume)
- 1b Use of colorimeter
- 1c into separate container(s) – (allow up to two reagents measured together into one container) – ignore use of **X**

Stage 2 Procedure

- 2a Start clock/timer at the point of mixing
- 2b Take series of colorimeter readings at regular time intervals
- 2c Use of same concentration of **B** and **C** / same total volume / (same volume/amount of **X**)
- 2d Same temperature
- 2e Repeat with different concentrations of **A** (can be implied through different volumes of **A** and same total volume)

Stage 3 Use of Results

- 3a Plot absorbance vs time and measure/calculate gradient at time=0
- 3b plot of gradient against volumes/concentrations of **A** or plot $\log(1/\text{time})$ vs $\log(\text{volume or concentration of A})$
- 3c description of interpreting order from shape of 1/time vs volume or concentration graph / gradient of log plot gives order

6

[19]

Q3.

c

[1]

Q4.

(a)

$$k = (\text{rate}/[C][D]) = \frac{3.1 \times 10^{-3}}{(0.48) \times (0.23)}$$

Mark is for insertion of numbers into correctly rearranged rate equation

1

$$= 2.8 \times 10^{-2} \quad \text{min}^{-2}\text{sfs}$$

1

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

Mark units separately in any order.

1

(b) $\ln k = \ln 2.8 \times 10^{-2} (= -3.58)$

M1 = ln (their k)

If incorrect then award M2 and M3 only

Alternative value

$$\ln k = \ln 3.2 \times 10^{-3} = -5.74$$

M1

$$E_a = RT(\ln A - \ln k)$$

OR

$$-E_a = RT(\ln k - \ln A)$$

If ln 16.9 used max 3

If temp used 25 max 2

Incorrect rearrangement then M1 only

M2

$$E_a = 8.31 \times 298 (16.9 + 3.58) \quad (= 50716 \text{ J mol}^{-1})$$

Alternative value

$$E_a = 8.31 \times 298 (16.9 + 5.74)$$

$$(= 56076 \text{ J mol}^{-1})$$

M3

$$E_a = 51 \text{ kJ mol}^{-1}$$

– 50.7 or -51 scores max 2

Alternative value

$$E_a = 56 \text{ kJ mol}^{-1}$$

M4

[7]

Q5.

(a) **Stage 1: Calculates value of $[\text{C}_6\text{H}_5\text{CHO}]^2$:**

M1 for the values (0, 0.0625; 0.25; 0.56 and 1) in the table.

Ignore precision.

1

Stage 2: Plots graph:

M2 for the graph labels with units and appropriate scales and using sensible proportion of graph (plotted points must cover at least half the printed grid).

$[\text{C}_6\text{H}_5\text{CHO}]^2$ on x-axis (with units) $\text{mol}^2 \text{ dm}^{-6}$

Initial rate on y-axis (with units) $\text{mol dm}^{-3} \text{ s}^{-1}$

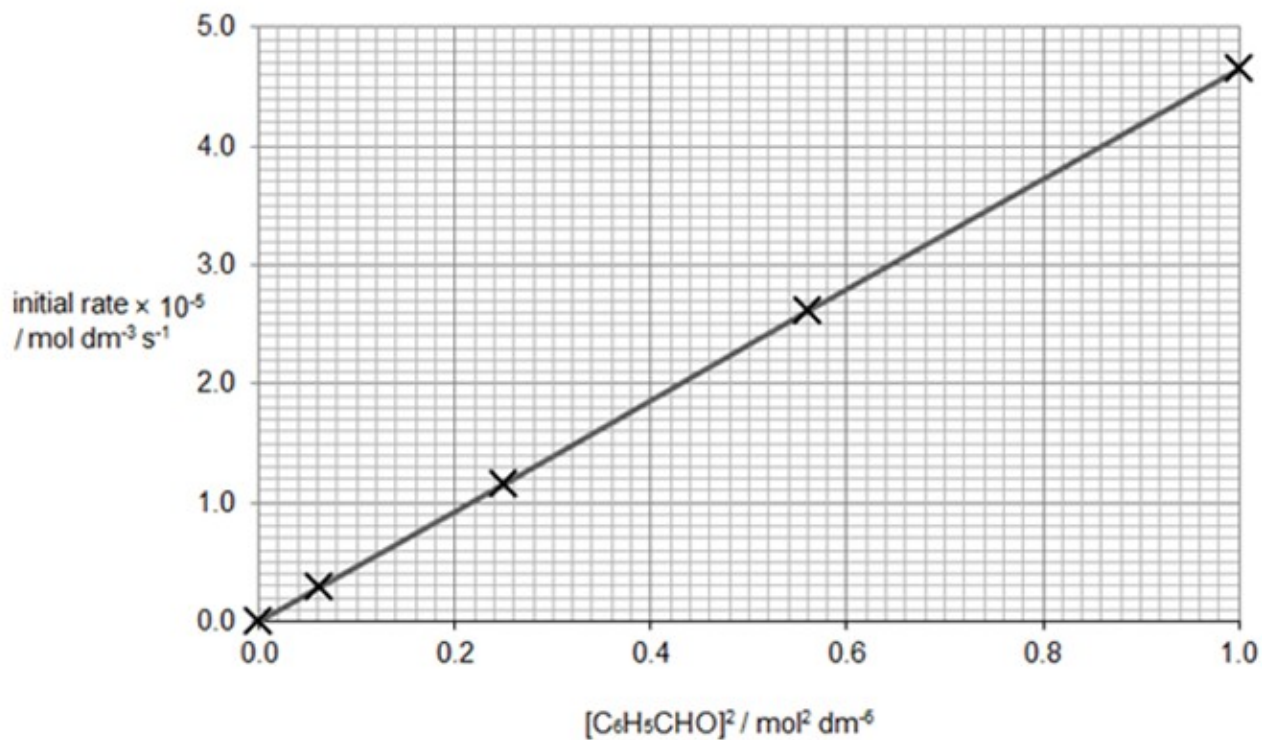
1

M3 for the plotting of 5 points.

1

Stage 3: Line of best fit:

M4 for the line of best fit.



1

(b) 2nd order

1

(since) $[C_6H_5CHO]^2$ plotted against rate is straight line / directly proportional.

1

(c) (Role of CN^-) catalyst

Ignore nucleophile.

1

CN^- appears in the rate equation but is not in the reaction equation.

1

[8]

Q6.

Stage 1: Complete table and draws graph:

Rate constant k/s^{-1}	$\ln k$	Temperature $/K$	$\frac{1}{T}$
6.13×10^{-5}	-9.7(0)	700	1.43×10^{-3}

2.75×10^{-4}	-8.2(0)	727	1.38×10^{-3}
8.25×10^{-4}	-7.1(0)	746	1.34×10^{-3}
8.23×10^{-3}	-4.8(0)	793	1.26×10^{-4}

Extended response question

M1 Calculates (four) values of $\frac{1}{T}$

1

M2 Calculates (four) values of $\ln k$

1

M3 Plots points on graph

1

M4 Draws line of best fit.

1

Stage 2: Calculates gradient:

M5 working = $\frac{\Delta y}{\Delta x}$ (such as $\frac{-6.9}{0.24 \div 1000}$ OR $\frac{-5.5}{0.19 \div 1000}$)

Stage 2 can only be accessed if the table has been completed correctly and a straight line graph is drawn.

1

M6 answer = -2.88×10^4

Correct answer with or without working scores M5 and M6.

1

Stage 3: Calculates E_a :

M7 (recognises that gradient = $-2.88 \times 10^4 \propto \frac{-E_a}{R}$)

$E_a = 2.88 \times 10^4 \times 8.314$

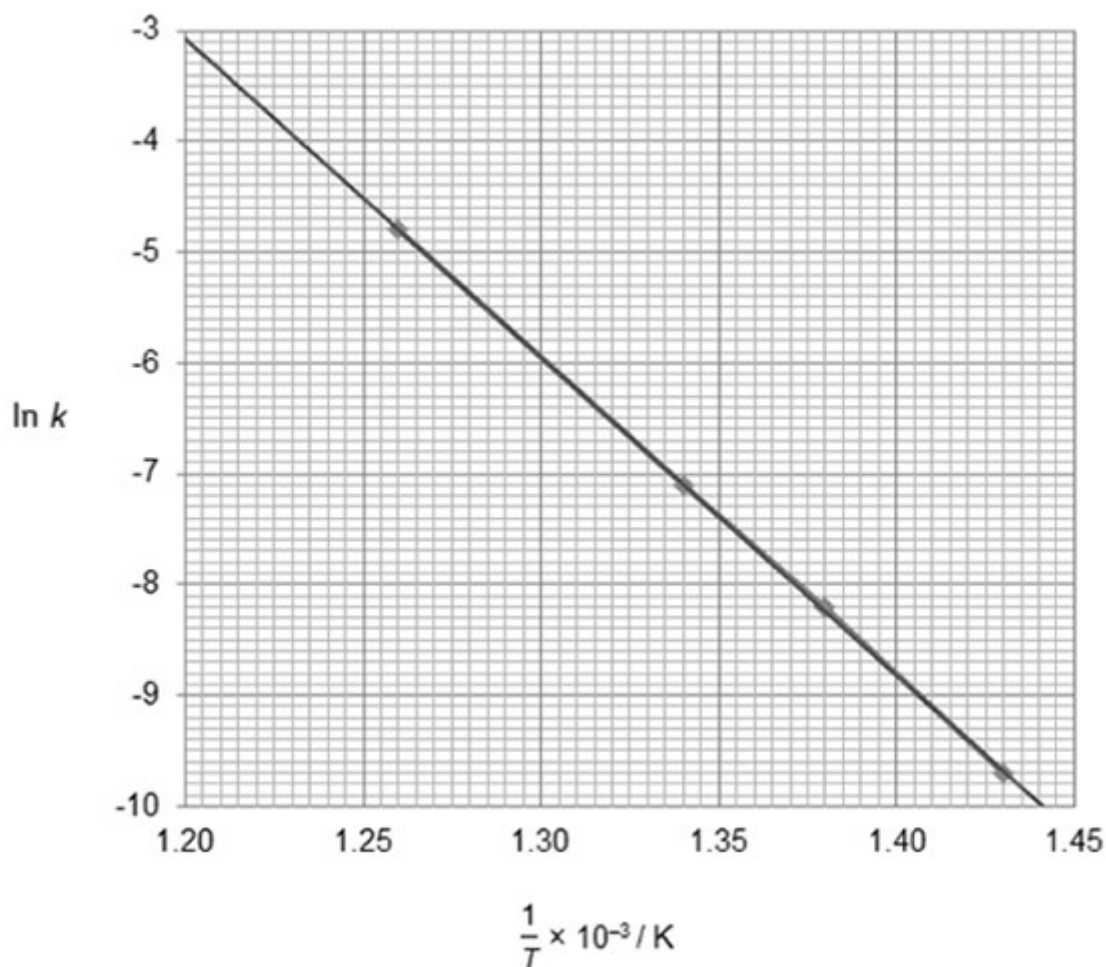
Stage 3 can only be accessed if the student has correctly calculated a gradient from their line graph.

1

M8 ($\div 1,000 =$) $E_a = 239 \text{ kJ mol}^{-1}$

*Correct answer with or without working scores M7 and M8.
Answer to correct number of significant figure (3 sf).*

1



[8]

Q7.

D

[1]

Q8.

(a) Consider experiments 1 and 2: [B constant]

[A] increases $\times 3$: rate increases by 3^2 therefore 2nd order with respect to A

1

Consider experiments 2 and 3:

[A] increases $\times 2$: rate should increase $\times 2^2$ but only increases $\times 2$

Therefore, halving [B] halves rate and so 1st order with respect to B

1

Rate equation: rate = $k[A]^2[B]$

1

(b) rate = $k[C]^2[D]$ therefore $k = \text{rate} / [C]^2[D]$

1

$$k = \frac{7.2 \times 10^{-4}}{(1.9 \times 10^{-2})^2 \times (3.5 \times 10^{-2})} = 57.0$$

Allow consequential marking on incorrect transcription

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

Any order

1

(c) $\text{rate} = 57.0 \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2} = 3.99 \times 10^{-3} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$

OR

Their $k \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2}$

1

(d) Reaction occurs when molecules have $E \geq E_a$

1

Doubling T by 10 °C causes many more molecules to have this E

1

Whereas doubling $[E]$ only doubles the number with this E

1

(e) $E_a = RT(\ln A - \ln k) / 1000$

Mark is for rearrangement of equation and factor of 1000 used correctly to convert J into kJ

1

$E_a = 8.31 \times 300 (23.97 - (-5.03)) / 1000 = 72.3 \text{ (kJ mol}^{-1}\text{)}$

1

[12]

Q9.

B

[1]

Q10.

(a) Order wrt **D** = 1 OR first OR $[D]$ OR $[D]^1$

Ignore working

1

Order wrt **E** = 2 OR second OR $[E]^2$

1

(b) (At time zero/start) the concentrations are known

1

(c) M1 (Calculate) gradient (of tangent/curve/graph)

Allow description of gradient calculation:

Change in conc / time

1

M2 at t=0 or at start of graph/curve
M2 scored only if M1 gained
Ignore the word initial

1

[5]

Q11.

- (a) Iodine is not involved in (or before) the rate determining / slow(est) / limiting step (in the mechanism)

Ignore, iodine does not appear in the rate equation or iodine concentration does not affect the rate

1

(b) $k = \left(\frac{8.64 \times 10^{-7}}{(5.82 \times 10^{-2}) \times (4.76 \times 10^{-1})} \right) = 3.1(2) \times 10^{-5}$

Mark for answer

1

mol⁻¹ dm⁺³ s⁻¹

Mark units separately, i.e. only these units but can be in any order

1

- (c) Rate = $k [H^+]$

If wrong or missing CE = 0

1

(Large excess of propanone) so [CH₃COCH₃] is (effectively) constant

1

[5]

Q12.

- (a) (i) 2

1

- (ii) 0

1

(b) (i) $K = \frac{6.64 \times 10^{-5}}{(4.55 \times 10^{-2}) \times (1.70 \times 10^{-2})^2}$

*Correct answer for k with or without working scores 2.
First mark is for insertion of numbers into a correctly rearranged rate equ, k = etc.*

1

= 5.05 (range allowed 5.03–5.07)

AE (-1) for copying numbers wrongly or swapping two numbers.

1

$$\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

Mark units separately, ie only these units but can be in any order.

1

(ii) $8.3 \times 10^{-6} \text{ (mol dm}^{-3} \text{ s}^{-1})$

Allow 0.83×10^{-5} .

Ignore units.

OR if not 8.3×10^{-6} , look at their k in part(i) and if not 5.05

Allow ecf for their (incorrect) $k \times (1.64 \times 10^{-6})$

1

[6]

Q13.

(a) $k = \text{rate} / [\text{A}]^2$ or $\frac{3.3 \times 10^{-5}}{(4.2 \times 10^{-3})^2}$

1

= 1.87 or 1.9

Answer scores 2

1.90 scores first mark only (incorrect rounding)

1

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

Any order and independent of calculation

1

(b) Expt 2 rate = $1.167 \times 10^{-4} - 1.2 \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1})$

If answers in table are not those given here, check their value of k in part (a) or use of alternative k .

1

Expt 3 $[\text{A}] = 9.7 \times 10^{-3} - 9.8(1) \times 10^{-3} \text{ (mol dm}^{-3})$

If their k is incorrect in part (a) mark this part consequentially e.g. if $k = 7.9 \times 10^{-3}$ due to lack of squaring in (a)

Using alternative value for k

expt 2 4.9×10^{-7}

Expt 2 rate = $1.4(4) \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1})$

expt 3 1.5×10^{-1}

Expt 3 $[\text{A}] = 8.85 \times 10^{-3} \text{ (mol dm}^{-3})$

(expt 2 $6.24 \times 10^{-5} \times \text{their } k$)

(expt 3 $0.0134 / \sqrt{k}$)

1

(c) Slow step or rds involves only A

OR

B does not appear in the slow step or the rds

OR

B only appears after the slow step or the rds

Not B has no effect on the rate or B is not in the rate equation

Allow "it" for B

1

[6]

Q14.

- (a) (i) 2 or two or second or $[E]^2$

1

- (ii) 1 or one or first or $[F]^1$ or $[F]$

1

(b) (i) $k = \frac{8.6 \times 10^{-4}}{(3.8 \times 10^{-2})^2 \times (2.6 \times 10^{-2})}$

mark is for insertion of numbers into a correctly rearranged rate equ, $k = \text{etc.}$

AE (-1) for copying numbers wrongly or swapping two numbers.

1

$= 22.9$ (Allow 22.9 – 24 after correct rounding)

1

$\text{mol}^{-2}\text{dm}^6 \text{ s}^{-1}$

Any order.

1

- (ii) $6.8(2) \times 10^{-3} (\text{mol dm}^{-3}\text{s}^{-1})$

OR if their k is wrong, award the mark consequentially

a quick check can be achieved by using

their answer $= 2.9768 \times 10^{-4}$ Allow 2.9 – 3.1×10^{-4} for the mark

their k

Allow 6.8×10^{-3} to 6.9×10^{-3}

Ignore units.

1

[6]

Q15.

(a) (i) $k = \frac{8.4 \times 10^{-5}}{(4.2 \times 10^{-2})^2 \times 2.6 \times 10^{-2}}$ **OR** $\frac{8.4 \times 10^{-5}}{(1.76 \times 10^{-3}) \times 2.6 \times 10^{-2}}$

Mark is for insertion of numbers into a correctly rearranged rate equ, $k = \text{etc.}$

If upside down, score only units mark from their k

AE (-1) for copying numbers wrongly or swapping two numbers

1

$= 1.8(3)$

1

$$\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

Any order

If k calculation wrong, allow units consequential to their $k = \text{expression}$

1

(ii) $5.67 \times 10^{-4} (\text{mol dm}^{-3} \text{ s}^{-1})$ **OR** their $k \times 3.1 \times 10^{-4}$

Allow 5.57×10^{-4} to 5.7×10^{-4}

1

(b) (i) 2 or second or $[\text{D}]^2$

1

(ii) 0 or zero or $[\text{E}]^0$

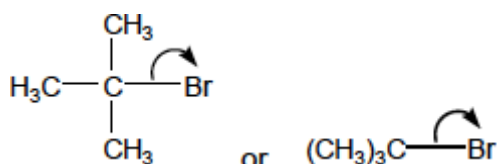
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(c) (i) Step 1 or equation as shown

Penalise Step 2 but mark on

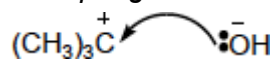
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(ii)



Ignore correct partial charges, penalise full / incorrect partial charges

If Step 2 given above, can score the mark here for



allow: OH^- (must show lp)

If $\text{S}_{\text{N}}2$ mechanism shown then no mark (penalise involvement of $:\text{OH}^-$ in step 1)

Ignore anything after correct step 1

1

[8]

Q16.

(a) Exp 2 4.5×10^{-4}
Min 2sf

1

Exp 3 4.5×10^{-3}

If three wrong answers, check their value of k in (b).

1

Exp 4 0.043 OR 4.3×10^{-2} OR 0.044 OR 4.4×10^{-2}

They can score all 3 if they have used their (incorrect) value of k . see below.

$$\text{Exp 2 rate} = k \times (1.0125 \times 10^{-4})$$

$$\text{Exp 3 } [Q] = 0.02/k$$

$$\text{Exp 4 } [P] = 0.0913/k$$

1

$$(b) \quad k = \frac{5.0 \times 10^{-5}}{(2.5 \times 10^{-2})^2 \times (1.8 \times 10^{-2})}$$

Mark is for insertion of numbers into a correctly rearranged rate equ, $k =$ etc

If upside down, score only units mark from their k

AE (-1) for copying numbers wrongly or swapping two numbers

1

$$= 4.4(4) \text{ (allow 40/9)}$$

1

$$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$$

Any order

If k calculation wrong, allow units conseq to their k expression

1

[6]

Q17.

(a) Exp 2 $14.(4) \times 10^{-3}$ **OR** $1.4(4) \times 10^{-2}$ or 0.014
Allow 2sf

1

Exp 3 0.1(0)

1

Exp 4 0.3(0)

If three wrong answers, check their value of k in 1(b).

They can score all 3 if they have used their (incorrect) value of k . see below.

$$\text{Exp 2 rate} = 0.096 \times k$$

$$\text{Exp 3 } [Q] = 0.015/k$$

$$\text{Exp 4 } [P] = 0.116/k$$

1

$$(b) \quad K = \frac{1.8 \times 10^{-3}}{(0.20)^2 \times 0.30}$$

mark is for insertion of numbers into a correctly rearranged rate equ, $k =$ etc

1

$$= 0.15 \text{ (min 2sfs)} \quad \left(\text{allow } \frac{3}{20} \right)$$

if upside down, score only units mark

AE (-1) for copying numbers wrongly or swapping two

numbers

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

Any order

If k calculation wrong, allow units conseq to their k

1

(c) G

1

[7]

Q18.

(a) (i)

$$k = \frac{6.2 \times 10^{-6}}{(2.9 \times 10^{-2})^2 \times 2.3 \times 10^{-2}}$$

mark is for insertion of numbers into a correctly rearranged rate equ, $k = \text{etc}$

AE (-1) for copying numbers wrongly or swapping two numbers

1

$$= 0.32 \text{ (min 2 sfs)}$$

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$ Units must be conseq to their k

Any order

If k calculation wrong, allow units conseq to their k

1

(ii) 4.95×10^{-5} to 4.97×10^{-5} or 5.0×10^{-5} (min 2 sfs)

(ignore units)

$$\text{rate} = \text{their } k \times 1.547 \times 10^{-4}$$

1

(b) Step 2

If wrong no further mark

1

One H_2 (and two NO) (appear in rate equation)
or species (in step 2) in ratio/proportion as in the rate equation

1

[6]

Q19.

(a) (i) propyl methanoate

must be correct spelling

1

(ii) $\text{rate} = k[\text{X}][\text{OH}^-]$

allow $\text{HCOOCH}_2\text{CH}_2\text{CH}_3$ (or close) for X

allow () but penalise missing minus

1

(iii) $k = \frac{8.5 \times 10^{-5}}{(0.024)(0.035)}$

In (a)(iii), if wrong orders allow

mark is for insertion of numbers in correct expression for k

If expression for k is upside down, only score units conseq to their expression

1

= 0.10(12) 2sf minimum

1 for conseq answer

1

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

1 for conseq units

any order

1

(iv) $2.1(3) \times 10^{-5}$

or $2.1(2) \times 10^{-5}$ ignore units

allow 2 sf

NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong k

See * below

1

(v) $1.3 \times 10^{-4} (1.28 \times 10^{-4})$

allow (1.26×10^{-4}) to (1.3×10^{-4}) ignore units

allow 2 sf

NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong k

See ** below

1

For example, if orders given are 1st in X and second in OH⁻

[The mark in a(ii) and also first mark in a(iii) have already been lost]

So allow mark * in (iv) for rate = their k $\times (0.012)(0.0175)^2$ = their k $\times (3.7 \times 10^{-6})$
(allow answer to 2sf)

** in (v) for rate = their k $\times (0.012)(0.105)^2$ = their k $\times (1.32 \times 10^{-4})$
(allow answer to 2sf)

The numbers will of course vary for different orders.

(vi) Lowered

if wrong, no further mark

1

fewer particles/collisions have energy $> E_a$

OR

fewer have sufficient (activation) energy (to react)

not just fewer successful collisions

1

(b) Step 2

1

(this step with previous) involves one mol/molecule/particle
A and two Bs

or 1:2 ratio or same amounts (of reactants) as in rate equation

if wrong, no further mark

1

[11]

Q20.

(a) 3-hydroxybutanal

ignore number 1 i.e. allow 3-hydroxybutan-1-al
not hydroxyl

1

(b)
$$k = \frac{2.2 \times 10^{-3}}{(0.10)(0.02)}$$

1

$$= 1.1$$

1

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

1

(c) planar or flat C=O or molecule

allow planar molecule

1

equal probability of attack from above or below

must be equal; not attack of OH⁻

1

(d) (i) Step 1 if wrong – no mark for explanation.

1

involves ethanal and OH⁻ or species/ “molecules”
in rate equation

1

(ii) (B-L) acid or proton donor

not Lewis acid

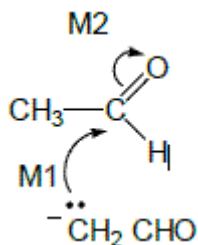
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(iii) nucleophilic addition

QOL

1

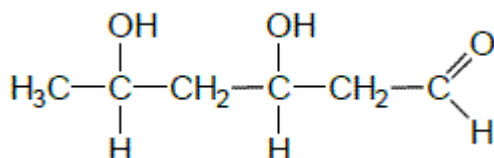
(iv)



not allow M2 before M1, but allow M1 attack on C+ after non-scoring carbonyl arrow
ignore error in product

2

(e)



1

[13]

Q21.

(a) 2 or two or second

1

(b) $k = \frac{1.24 \times 10^{-4}}{(4.40)(0.82)}$

mark is for insertion of numbers into a correctly rearranged rate equ, $k =$ etc
if upside down, (or use of I_2 data) score only units mark

1

$= 3.44 \times 10^{-5}$ (min 3sfs)

1

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

any order

1

(c) no change or no effect or stays the same or 1.24×10^{-4}

1

(d) 1 or 2 or 1 and 2

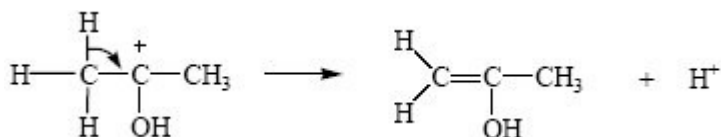
if wrong no further mark but mark on from no answer

1

rate equ doesn't involve I_2 or only step which includes 2 species in rate equ

1

(e)



any second arrow loses the mark

1

[8]

Q22.

(a) (i) 2

1

(ii) 0

1

(b) (i) $\text{rate}/[\text{NO}_2]^2[\text{O}_2]$

1

13

1

mol dm^{-3}

1

(ii) 1.9×10^{-3}

1

(iii) Step 2

1

[7]

Q23.

(a) $k = \text{rate}/[\text{CH}_3\text{CH}_2\text{COOCH}_3][\text{H}^+]$

1

or

$$= \frac{1.15 \times 10^{-4}}{(0.150)(0.555)}$$

$$= 1.38 \times 10^{-3} \text{ to } 1.4 \times 10^{-3}$$

1

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

1

(b) $\text{ans} = \text{rate constant} \times (\frac{1}{2} \times 0.150) \times (\frac{1}{2} \times 0.555)$

ignore units

$$= \text{rate constant} \times 0.0208$$

$$2.88 \times 10^{-5}$$

$$(1.38 \times 10^{-3} \text{ gives } 2.87 \times 10^{-5})$$

Allow $2.87 - 2.91 \times 10^{-5}$ (1.4×10^{-3} gives 2.91×10^{-5})

1

(c) $[H^+] = \text{rate} / k[\text{CH}_3\text{COOCH}_2\text{CH}_3]$

1

$$= \frac{4.56 \times 10^{-5}}{(8.94 \times 10^{-4})(0.123)}$$

$$= 0.415 \text{ (0.4146)}$$

1

pH = 0.38 mark independently

$$[H^+] = 0.41 \text{ gives } \text{pH} = 0.39$$

1

[7]

Q24.

(a) exp2 4.0×10^{-3}

1

exp3 0.45×10^{-5}

1

exp4 9.0×10^{-3}

1

(b) $\frac{1.8 \times 10^{-5}}{(3.0 \times 10^{-3})^2 (1.0 \times 10^{-3})}$

1

2000

1

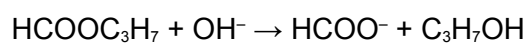
$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

1

[6]

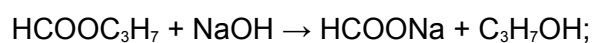
Q25.

(a) propyl methanoate;



1

OR



1

(b) order wrt A = 1;

1

order wrt NaOH = 1;

		1
	Initial rate in Exp 4 = 2.4×10^{-3} ;	1
(c)	(i) $r(\text{ate}) = k[A]$	
	OR	
	$r(\text{ate}) = k[A][\text{NaOH}]^0$; (penalise missing [] but mark on) (penalise missing [] once per paper) (if wrong order, allow only units mark conseq on their rate eqs) (penalise k_s or k_w etc)	1
(ii)	$k = \frac{9.0 \times 10^{-3}}{0.02}$;	1
	= 0.45;	1
	s^{-1} ;	1
(iii)	(large) excess of OH^- or $[\text{OH}^-]$ is large/high;	1
	$[\text{OH}^-]$ is (effectively) constant	
	OR	
	$[\text{A}]$ is the limiting factor (Q of L mark)	1
(d)	(i)	
	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHOH} \\ \\ \text{CH}_2\text{OH} \end{array}$	1
	propan(e)-1,2,3-triol	
	OR	
	1,2,3-propan(e)triol	
	OR	
	Glycerol;	1
(ii)	$\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$ or $\text{C}_{17}\text{H}_{35}\text{COONa}$ or $\text{C}_{18}\text{H}_{35}\text{O}_2\text{Na}$; (ignore 3 in front of formula but not if indicating trimer)	1

(not just anion and penalise Na shown as covalently bonded) soap -
allow with detergent but not detergent alone;

1

[15]

Q26.

(a) order with respect to **P** is 2

1

order with respect to **Q** is 1

1

(b) (i) rate = $k[\mathbf{R}][\mathbf{S}]^2$

(if wrong expression, no further marks)

1

$$\text{rate} = (4.2 \times 10^{-4}) \times 0.16 \times 0.84^2$$

1

$$= 4.7 \times 10^{-5} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$$

ignore units even if wrong

1

$$(ii) \quad k = \frac{\text{rate}}{[\mathbf{R}][\mathbf{S}]^2} = \frac{8.1 \times 10^{-5}}{0.76 \times 0.98^2}$$

1

$$= 1.1 \times 10^{-4}$$

1

(iii) T_1

**If calculated value for $k > 4.2 \times 10^{-4}$, then answer to (iii) is T_2*

1

[8]

Q27.

(a) (i) Experiment 2 2.60×10^{-3}

1

Experiment 3 0.60×10^{-2}

1

Experiment 4 11.4×10^{-2}

1

$$(ii) \quad k = \frac{10.4 \times 10^{-3}}{(4.80 \times 10^{-2})(6.60 \times 10^{-2})^2}$$

1

$$= 49.7$$

(Allow 49.8 and 50)

1

$$\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

1

(b) No change

1

[7]

Q28.

(a) (i) 2 (1)

(ii) 0 (1)

2

(b) (i) Value of k : $k = \frac{\text{rate}}{[\text{NO}]^2 [\text{O}_2]} = \frac{6.5 \times 10^{-4}}{(5.012 \times 10^{-2})^2 (2.0 \times 10^{-2})} = 13$

Units of k : $\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ (1)

(ii) $\text{rate} = 13 (6.5 \times 10^{-2})^2 (3.4 \times 10^{-2})$
 $= 1.9 \times 10^{-3} \text{ (mol dm}^{-3} \text{ s}^{-1})$ (1)

If k wrong, the mark in (ii) may be gained conseq for their
 $k \times 1.437 \times 10^{-4}$

4

[6]

Q29.

(a) Power (or index or shown as x in $[\]^x$) of concentration term
 (in rate equation) (1)

1

(b) 2 (1)

1

(c) (i) Order with respect to **A**: 2 (1)

Order with respect to **B**: 0 (1)

(ii) Rate equation: $(\text{rate} =) k [\text{A}]^2$ (1)

Allow conseq on c(i)

Units for rate constant: $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ (1)

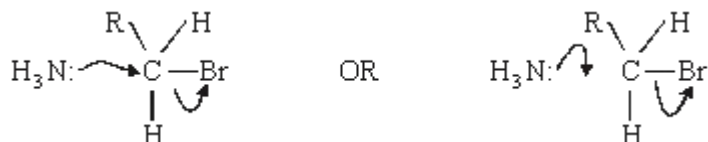
conseq on rate equation

4

[6]

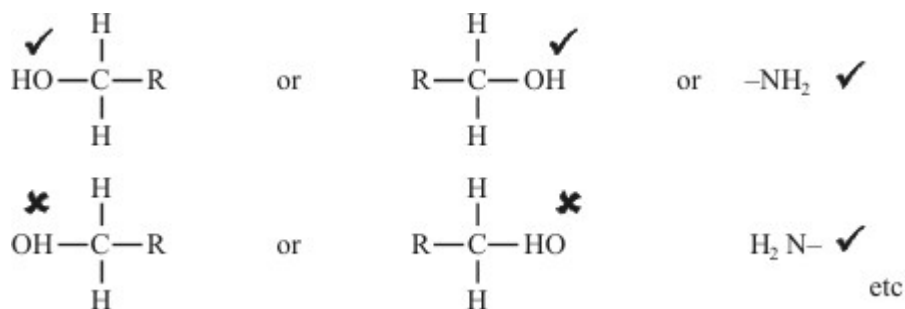
Organic points

(1) Curly arrows: must show movement of a pair of electrons,
 i.e. from bond to atom or from lp to atom / space
 e.g.



(2) Structures

penalise sticks (i.e. $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$) once per paper



Penalise once per paper

allow CH_3- or $-\text{CH}_3$ or $\begin{array}{c} \text{CH}_3 \\ | \end{array}$ or CH_3
 or $\text{H}_3\text{C}-$

Q30.

- (a) (i) Experiment 2: $0.4(0) \times 10^{-3}$ **(1)**
 Experiment 3: 0.15 **(1)**
 Experiment 4: 0.28 **(1)**

(ii) $k = \frac{4.8 \times 10^{-3}}{(0.20)^2 \times (0.30)} = 0.4(0) \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

(1) **(1)** **(1)**

6

- (b) (change in) temperature **(1)**

1

[7]

Q31.

C

[1]

Q32.

- (a) Order with respect to iodine: 0 **(1)**
 Overall order: 2 **(1)**

2

- (b) Rate constant: $k = \frac{2 \times 10^{-5}}{(1.5) \times (3 \times 10^{-2})} = 4.4(4) \times 10^{-4}$ (1)
 Units: $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ (1)
- (c) Appears in rate equation (1)
OR implied by mention of concentration or order
 does not appear in (stoichiometric / overall) equation (1)
- (d) $\text{pH} = -\log_{10} [\text{H}^+]$ (1)
 $= 1.25$
 $[\text{H}^+] = 0.056(2)$ (1)
 $\therefore \text{rate} = (4.44 \times 10^{-4}) \times (1.50) \times (0.0562)$
 $= 3.75 \times 10^{-5}$ (1) ($\text{mol dm}^3 \text{s}^{-1}$)
 (3.7 — 3.8)
Can score all 3 conseq on k from part (b)

3

2

3

[10]

Q33.

- (a) (i) (Experiment 1 $\rightarrow$ 2) [A] doubled, ([B] constant,) rate doubled (1)
stated or shown numerically
- (ii) 2 (1)
 or shown as ... $[\text{B}]^2$

2

- (b) (i) $k = \frac{9.30 \times 10^{-5}}{(0.75)^2 \times (1.50)} = 1.1(0) \times 10^{-4}$
 (1) (1)

units of k: $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$ (1)

- (ii) $\text{rate} = (1.10 \times 10^{-4}) \times (0.20)^2 \times (0.10)$
 $= 4.4(1) \times 10^{-7} (\text{mol dm}^{-3} \text{s}^{-1})$
 (1) for the answer

Ignore units

Conseq on (i)

Upside down expression for k scores zero in (i) for 9073

but rate = $9073 \times (0.2)^2 \times (0.1) = 36(.3)$

conseq scores (1) in (ii)

4

[6]

Q34.

D

[1]

Q35.

C

[1]

Examiner reports

Q1.

- (a) 28.5% of students scored full marks in this question, but others failed to gain marks either by giving the answer to three significant figures (or as the fraction 40/3), or for incorrect signs for the powers in the units.
- (b) Almost all students gave the correct answer to Experiment 2. Over 60% of students also scored the other two marks but some found these two other parts harder. There were also some who rounded their answer to one figure and failed to gain the mark.
- (c) The two values in **Table 2** were given correctly by 82% of students. Of the others, some gave values that were incorrectly rounded.
- (d) The best students scored full marks for answers which included carefully drawn graphs. However, there was a spread of marks down to those who were unable to plot the graph correctly or those few who made no attempt. An appreciable number of students chose a wrong scale for the y-axis and only used half of the grid provided. This small graph often led to an inaccurate gradient and so an activation energy that was outside the expected range.

Q2.

- (a) This proved to be a tougher starter question than anticipated (63.4% of students failed to score). In many cases, the question was repeated as an attempt at the answer with students suggesting that “the rate only depends on $[H^+]$ ”. Since this information had been given in the question, answers such as this could not be credited. The expected answer, that ‘a large excess makes the concentrations effectively constant so that they do not affect the rate’, was seldom seen.
- (b) As with part (a), not many students were able to achieve both marks (only 9.7%), with few suggesting ‘quenching’. Given how frequently quenching was, unnecessarily, suggested in answers to (h), this was surprising. In many cases, students described the process of titration itself rather than what should be done to the sample *before* titration. 74% of students failed to score here.
- (c) This question proved easier, with just over a third of students achieving both marks for appreciating that the line indicated a constant rate, showing that the falling concentration of hydrogen ions was having no effect.
- (d) A common error here was for students to start by (correctly) calculating the gradient of the line but then to divide it by a value for the $[H^+]$ (usually 0.5) or even by $[H^+]^2$ – despite having been told in part (c) that the order with respect to $H^+(aq)$ is zero. 36% of students, however, did gain all three marks.
- (e) 97.3% of students were able to plot the points correctly onto the given grid.
- (f) A significant number of students assumed that the instruction to ‘draw a line of best fit’ meant that the line must be straight. Students must learn that a best-fit line must be the best-fit to the points as plotted, so may be either straight or curved depending on the relationship between the plotted points; at A-level, students are expected to make this decision for themselves. Just under 40% of students did not gain this mark.

- (g) The idea of drawing a tangent (or, for award of 'error carried forward', simply constructing a 'triangle' on a straight line) proved tricky, with a significant minority of students simply dividing 0.35 by the corresponding time value from their line.
- (h) Fewer students than expected recognised the clue in the information given in the question that this was best done as a 'clock' reaction. Many students suggested answers that did not include 'X' in the initial mixture, as suggested, while many others used a variety of convoluted procedures involving what were essentially 'continuous monitoring' methods to generate concentration versus time graphs. In some cases, this was followed by a description of finding the gradient at $t = 0$, which addressed the requirement of the question to calculate an initial rate for each experiment. However, a direct measurement would have been much easier, both to do and to describe.

Credit was given for a wide variety of suggestions because, although a particular approach was hoped for, there are indeed several alternative approaches that would work. However, many students seemed to think that actual measurements of concentration (of what substance was often unclear from the descriptions) are needed, which led to suggestions that samples should be removed at timed intervals and titrated against X or placed into a colorimeter (the need to quench these samples was often over-looked). If a colorimeter was used, then the best approach for continuous monitoring is simply to allow the reaction to proceed in the colorimeter and take a series of readings at timed intervals – much easier than sampling. The mean mark on this question was only 1.8 out of 6.

The extra answer space available this year meant that fewer students needed additional pages for this question, but many confused, badly ordered and muddled answers were seen that took up far more space than necessary through repetition and unnecessary elaboration.

Reading the question is always key, but here many students could have saved a lot of time and space by noticing that the question asked only about a method to determine the order of this reaction with respect to A. This would have avoided the need for them to repeat most of the procedure, looking at successively changing the concentrations of A, then B, then C, while keeping each of the other two constant. Levels-of-response questions are marked using 'levels' and the key to success is for students to concentrate first on the inclusion of as much correct Chemistry as possible to ensure access to Level 3 (worth 5 or 6 marks). This is probably best achieved using a 'bullet point' approach to structuring the answer. Within a level, the mark awarded depends on the clarity and coherence of an answer, together with there being a clear, logical progression through the description.

Appropriate apparatus and quantities should be mentioned as necessary. For example, rather than stating "add A, B and C to a container", a good start to the answer would be to write, "A measuring cylinder was used to measure known volumes, of known concentrations, of A, B and C into separate beakers". Unless specifically asked to suggest suitable volumes/concentrations, then it is sufficient for students to indicate that they would make a measurement without needing to state a value.

Q3.

43% of students chose correctly. A was the commonest incorrect response, perhaps suggesting that those students were expecting the orders in the rate equation to match the balancing in the reaction equation instead of working out the orders from the rate data given.

Q4.

- (a) This kinetics question was answered well apart from occasional slips in deducing the units.
- (b) It was pleasing to see that 47% of students scored full marks in this topic which is new to the specification. The others made one or more errors in reading the given value of $\ln A$ as A , in wrongly rearranging the equation, or in using incorrect units.

Q10.

Part (a) was answered well and two thirds of students scored both marks. By contrast, part (b) was a hard question with few correct answers. Many students spoke about the changing concentrations but few mentioned the importance of knowing the initial concentration. The first mark in part (c) for mentioning a gradient was often gained but the location of where to measure the gradient was only given by a third of students.

Q11.

Part (a) was answered correctly by just over half of the students. The majority of incorrect answers were because students didn't answer the question and simply just repeated what the rate equation told them.

Calculation of a rate constant in part (b) was answered very well as usual but part (c) proved to be very difficult. A large number of students could not deduce the correct rate equation. Those who did gain this mark were not often able to give a reason for their answer and the second mark was rarely seen.

Q12.

Most students scored highly on this question. Only part (b)(ii) proved difficult for some who were unable to calculate the new initial rate in part (b)(ii) either by dividing the given rate by 8 or by using their rate constant to calculate the new rate.

Q13.

The calculation in part (a) was well answered and there were few errors although the units mark was occasionally lost. In part (b) the calculations were again well answered: experiment 3 involving a square root was the least well done. Marks were awarded consequentially on an incorrect value of k . Few students used the value of k of 2.3 supplied.

Here as elsewhere, students should be encouraged to keep their answer in their calculator as they work through a question and then write the final answer to the appropriate number of significant figures (usually 3).

The mark in part (c) proved elusive for many students, who referred to the rate of the reaction and not the mechanism as required by the question. It was well known that the concentration of **B** would not affect the rate, but how **B** was involved in the mechanism and the rate determining step was not well known.

Q14.

This question was answered well. A few students lost marks through the incorrect use of calculators in the division necessary in part (b)(i) to find the rate constant, k , or by omitting s^{-1} from the units of the rate calculated in part (b)(ii).

Q15.

This question was answered well by most students and over 80% scored full marks in part (a). Part (c)(ii) was found slightly harder and, of those who correctly identified Step 1 as the slower step, most gained the mark for the curly arrow. Those who suggested Step 2 could also gain a mark for a correct arrow for that step. However, many gave a full S_N2 mechanism in both cases.

Q16.

As is usual with kinetics questions, this produced some high marks, with many students scoring full marks. In part (a), the more tricky calculation for Expt 4 was least well done and in part (b) the most common mistake in calculating the value of k was to forget to square the concentration of **P**.

Q17.

The kinetics question was, as usual, answered well with only Experiment 4 in part (a) causing much difficulty. However, in part (c) fewer than half of the students identified graph G as that correctly showing how the rate constant k varies with temperature.

Q18.

Part (a) was well done with many candidates scoring full marks. Although most gave the correct answer to part (a)(ii), many did it by the long route, having failed to see that the answer was simply 8x the initial rate.

Candidates found part (b) more difficult. Many of those who correctly chose step 2 could not offer a full explanation.

Q19.

Most parts of this question were answered well. The ester was named correctly by over two thirds of the candidates but a surprising number attempted to write a stoichiometric equation in part (a)(ii) rather than a rate equation. Part (a)(iii) was answered very well but in part (a)(iv) the effect of dilution on the concentration of both reagents was missed by a large majority. However, when the exact concentrations were given in part (a)(v) most candidates were able to calculate the new rate of reaction correctly. The effect on the rate constant of lowering the temperature was well known in part (a)(vi), but few candidates were able to give a correct explanation and many offered a mathematical rather than a kinetic explanation. In part (b), the requirement to use the rate equation to identify the rate determining step proved difficult for the majority.

Q20.

This question was generally well done although in part (a), fewer candidates than expected could name compound **X** correctly. Part (b) was answered very well but in part (c) many candidates did not read the full question and described what a racemic mixture contains rather than how one is formed in this reaction. Part (d) was answered very well except for part (d)(ii) where fewer than 50% of candidates could deduce that ethanal was acting as a proton donor in the reaction. The deduction required in part (e) was also found difficult despite the hint given that the required product contained six carbon atoms.

Q21.

As usual for questions on kinetics, this was answered well. It was also pleasing that, in part 3(d), over half of the candidates gained both marks on a question which required

understanding of a new part of the specification. Application in part (e) of their understanding of the use of curly arrows in organic mechanisms was, however, less well done.

Q23.

As usual with questions involving rate equations, this question was answered well, particularly parts (a) and (c). Part (b) however was poorly answered and only the very best candidates gained this mark. Many of the rest only divided the original rate by 2 instead of by 4 as the concentrations of both the ester and of I^- ions were halved. Again it was disappointing to see the number of candidates who did not give the pH to two decimal places despite being asked to do so.

Q24.

This question was answered well by most candidates and full marks were often gained. The value of the concentration of NO in experiment 4 was the least well answered part of section (a). Only a few candidates failed to calculate the answer 2000 for the rate constant in part (b). The few errors seen usually involved a failure to square the NO concentration or problems with the powers of 10. The units were usually correctly given.

Q25.

The first three parts of this question were well answered. In part (a), most candidates were able to name the ester *propyl methanoate* correctly although the equation for its reaction with sodium hydroxide was less well answered. The orders and the initial rate in part (b) were correctly deduced by most candidates and many were able to deduce the correct rate equation in part (c) and to use it correctly to calculate the rate constant. Those who gave an incorrect rate equation were awarded a mark for units which were consistent with their rate equation. By comparison, few were able to answer part (c)(iii) correctly by stating that the large excess of sodium hydroxide meant that its concentration was effectively constant. Part (b) distinguished fairly well between those who recognised the alcohol formed by hydrolysis of the ester drawn and were able to deduce that it would distil easily. Either the systematic name, propane-1,2,3-triol, or its common name glycerol, were accepted. The formula of the sodium salt of the acid was accepted in several forms and its use as soap was well known by most, even those who gained no other marks in part (c).

Q26.

As is normal, the use of rate equations is well understood and almost all candidates can answer these questions well. Very few failed to score the marks for deducing the orders with respect to **P** and **Q**. The calculation in part (b) using the given orders of reaction was well done by all except those candidates who could not rearrange the equation correctly. The same applied in part (b)(ii). In the few cases where the calculated value of the rate constant was incorrect, and greater than $4.2 \times 10^{-4} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ the usual answer of T_1 for part (b)(iii) was replaced by the answer T_2 consequential on their incorrect value of k .

Q27.

This question was generally answered well as is usual in questions about rates of reaction. As expected, the value required in experiment 4 was the least well answered section in part (a)(i). In part (a)(ii), the major problem for some was to rearrange the rate equation to produce k as the subject of an equation. Disappointing numbers of candidates were unable to do this correctly. The units were usually correctly given as was the answer to part (b).

Q28.

As is usual in this type of question, high marks were obtained by most candidates. Part (a)(ii) caused the most problems with the answer 2 being common from the weaker candidates. Occasionally in part (b) the value of the concentration of NO was not squared in the calculation and the units were sometimes not given correctly. The value of the initial rate in part (b)(ii) was allowed consequential to an incorrect answer in part (b)(i).

Q29.

In part (a) few candidates were able to explain correctly what the term 'order of reaction' means. However, despite this most were able to use the idea itself and scored highly in the rest of the question. The fact that the rate of reaction increased by a factor of nine, 32, when the concentration of A increased by three times led some candidates to think that the order with respect to A was three rather than two.

Q30.

This question was generally answered well even by weaker candidates. Calculation of the concentration of P in part (a)(i) was the only part found difficult by many. Most answers to part (a)(ii) were correct, including the units. A change in temperature was the usual and correct answer in part (b).

Q32.

This question on rate equations was answered well by most candidates even those who scored less well elsewhere in the paper. In part (a) most candidates deduced the overall order correctly, but to deduce that the order with respect to iodine was zero proved more difficult. Part (b) was well answered by most students, but only the better candidates were able to gain both marks in part (c). Many gave a general description of the role of a catalyst rather than the evidence that hydrogen ions appear in the rate equation but not in the overall stoichiometric equation. The use of pH to show a change of hydrogen ion concentration was understood by most candidates although some were unable to convert a pH value into a hydrogen ion concentration. Full marks were available for correct use in part (d) of an incorrect rate constant calculated in part (b).

Q33.

This question on rate equations was answered well by most candidates. Part (a)(i) required that the candidate stated or showed mathematically that the rate doubled when the concentration of A doubled when considering experiments 1 and 2. Part (a)(ii) was usually answered correctly. Problems arose in part (b) where some candidates had difficulty in rearranging the rate equation correctly. However the mark in part (b)(ii) could still be gained for correct working despite using a wrong rate constant calculated in part (b)(i).