PEARSON EDEXCEL A-LEVEL CHEMISTRY · 9CH0

CHEMISTRY



EXAM QUESTION PACK

TOPIC 16: KINETICS II

SCORE	PERCENTAGE
/277	%

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Q1.

For a given initial reactant pressure, the half-life for a first order gaseous reaction was found to be 30 minutes.

If the experiment were repeated at half the initial reactant pressure, the half-life would be

☒ **A** 15 minutes.

☒ **B** 30 minutes.

☒ **C** 45 minutes.

☒ **D** 60 minutes.

(Total for question = 1 mark)

Q2.

To determine the activation energy (E_a) for a reaction, the variation of reaction rate with temperature is investigated.

The rate constant, *k*, for the reaction is related to the absolute temperature, T, by the expression

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

where *R* is the gas constant.

The activation energy for the reaction could be obtained by plotting a graph of

	vertical axis	horizontal axis
☒ **A**	k	T
☒ **B**	k	$\frac{1}{T}$
☒ **C**	$\ln k$	T
☒ **D**	$\ln k$	$\frac{1}{T}$

(Total for question = 1 mark)

Q3.

This question is about carbon monoxide, CO, which is a toxic and colourless gas used widely in the chemical industry.

Carbon monoxide can also be made by the thermal decomposition of ethanal, CH_3CHO, in the gas phase.

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$$

This reaction was carried out at two different temperatures, and all other variables were kept constant.

Temperature / K	Rate / mol dm^{-3} s^{-1}	1/Temperature (1/T) / K^{-1}	ln rate
700	0.0108	1.43×10^{-3}	
850	4.90		1.59

(i) Complete the data in the table.

(1)

(ii) Calculate the activation energy, E_a, for the reaction without plotting a graph. Include a sign and units in your answer.

The Arrhenius equation may be written as

$$\ln \text{ rate} = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad [R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}]$$

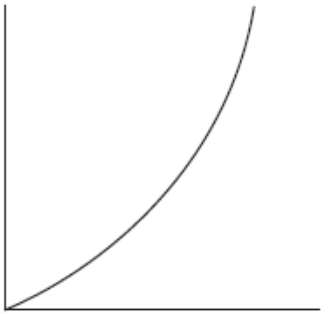
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(Total for question = 4 marks)

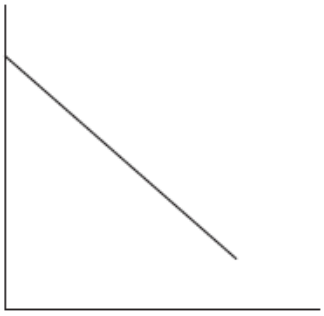
Q4.

Four sketch graphs are shown below.

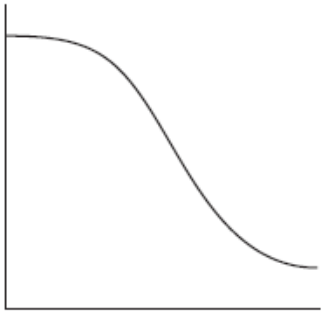
A



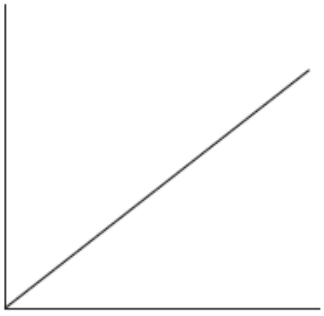
B



C



D



(a) Which could be a graph of the concentration of a reactant, on the vertical axis, against time for a **zero** order reaction?

(1)

- ☒ **A**
- ☒ **B**
- ☒ **C**
- ☒ **D**

(b) Which could be a graph of rate of reaction, on the vertical axis, against the concentration of a reactant for a **first** order reaction?

(1)

- ☒ **A**
- ☒ **B**
- ☒ **C**
- ☒ **D**

(c) Which could be a graph of rate of reaction, on the vertical axis, against the square of the concentration of a reactant for a **second** order reaction?

(1)

- ☒ **A**
- ☒ **B**

☒ **C**

☒ **D**

(d) Which could be a graph of the concentration of a reactant, on the vertical axis, against time for a reaction which is catalysed by a product?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for question = 4 marks)

Q5.

This question is about reaction kinetics.

Compound **A** decomposes in a first order reaction.

Calculate the time it takes for the mass of **A** to decrease from 600 g to 37.5 g if the decomposition has a constant half-life of 14 minutes.

(1)

(Total for question = 1 mark)

Q6.

The rate constant for this reaction was determined at various temperatures.
The data from these experiments are shown in the table.

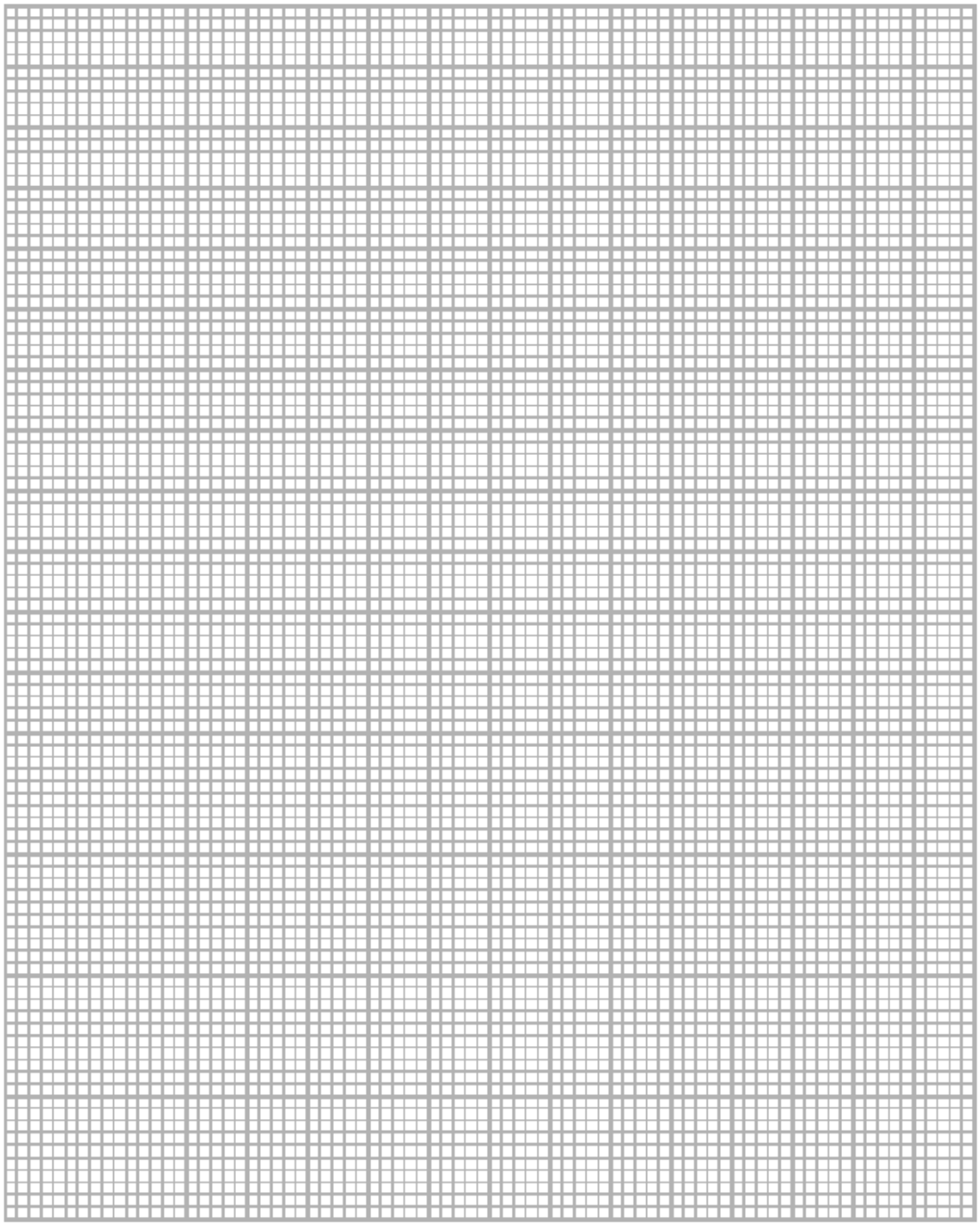
Temperature T / K	Rate constant k / $dm^3 mol^{-1} s^{-1}$	ln k	1/T /K^{-1}
556	7.04×10^{-7}	–14.17	0.00180
575	2.44×10^{-6}	–12.92	0.00174
629	6.04×10^{-5}	–9.71	0.00159
666	4.38×10^{-4}	–7.73	0.00150
700	2.32×10^{-3}	–6.07	0.00143

Use the data in the table to plot a graph and use it to calculate the activation energy, E_a, of the reaction, giving your answer to an appropriate number of significant figures and stating the units.

The rate constant of a reaction, k, is related to the temperature, **T**, by the expression

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{a constant}$$

(5)



Activation energy = ...

Q7.

This question is about transition metals and their ions.

Tungsten wire catalyses the decomposition of ammonia.

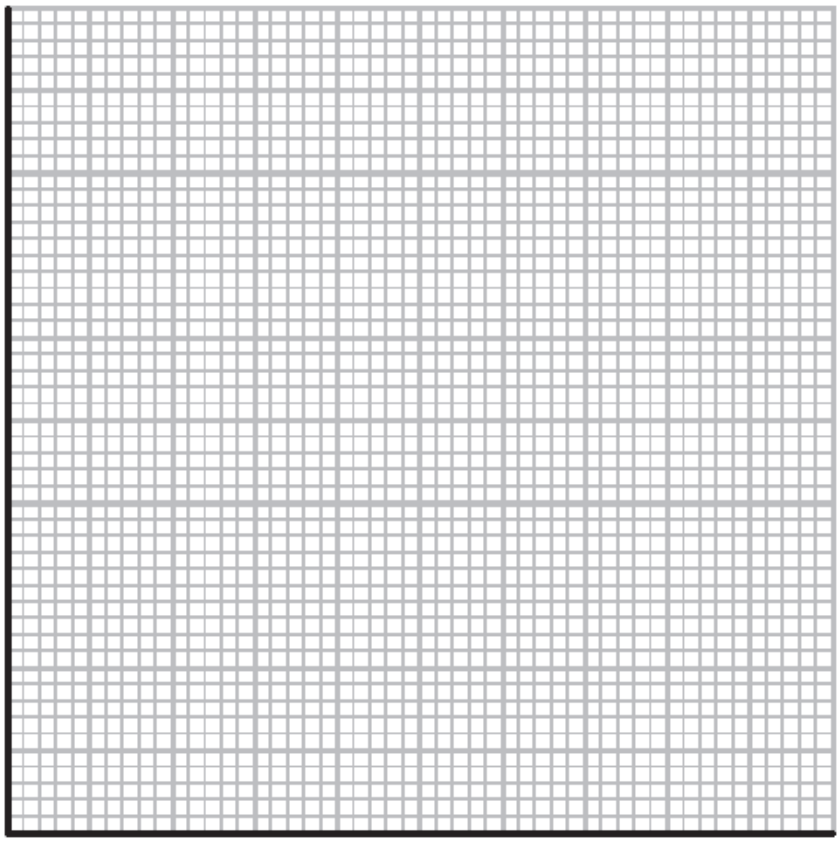
$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

In an experiment, the following results were obtained.

Time /s	Partial pressure of ammonia / kPa
0	0.350
100	0.335
200	0.319
300	0.303
400	0.287
500	0.271

(i) Plot a graph of partial pressure of ammonia against time.

(2)



(ii) Deduce the rate equation for this reaction by using your graph in (i).

Justify your answer.

(2)

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(iii) Use the graph to calculate the rate constant. Include units in your answer.

(2)

(iv) Describe the stages in the catalytic decomposition of ammonia by tungsten.

(3)

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(Total for question = 9 marks)

Q8.

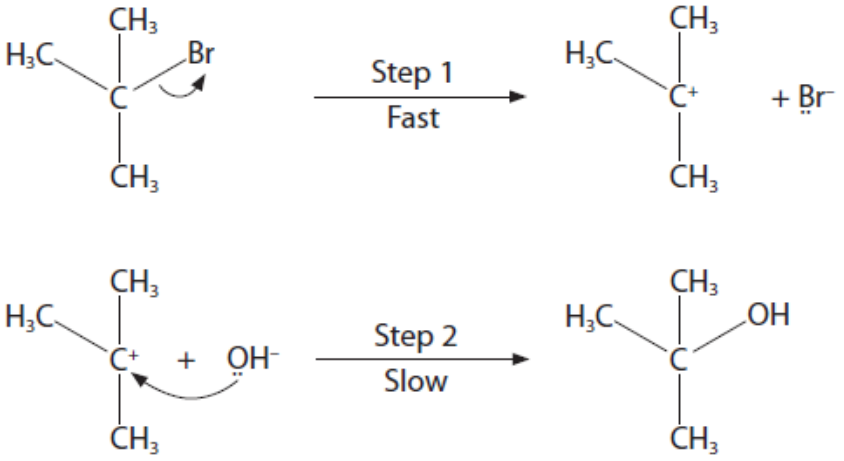
A student carried out a similar investigation into the kinetics of the reaction between 2-bromomethylpropane and hydroxide ions. A summary of the student's findings is shown below.

Kinetics Investigation - Summary of Key Findings

Reaction is first order with respect to 2-bromomethylpropane

Suggested Mechanism

S_N2 - as two steps in process



Use your knowledge of the mechanism of nucleophilic substitution reactions to suggest one feature of the summary, including the student's mechanism, that you agree with and two features you think are incorrect.

(3)

One feature you agree with.

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Two features you think are incorrect.

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Q9.

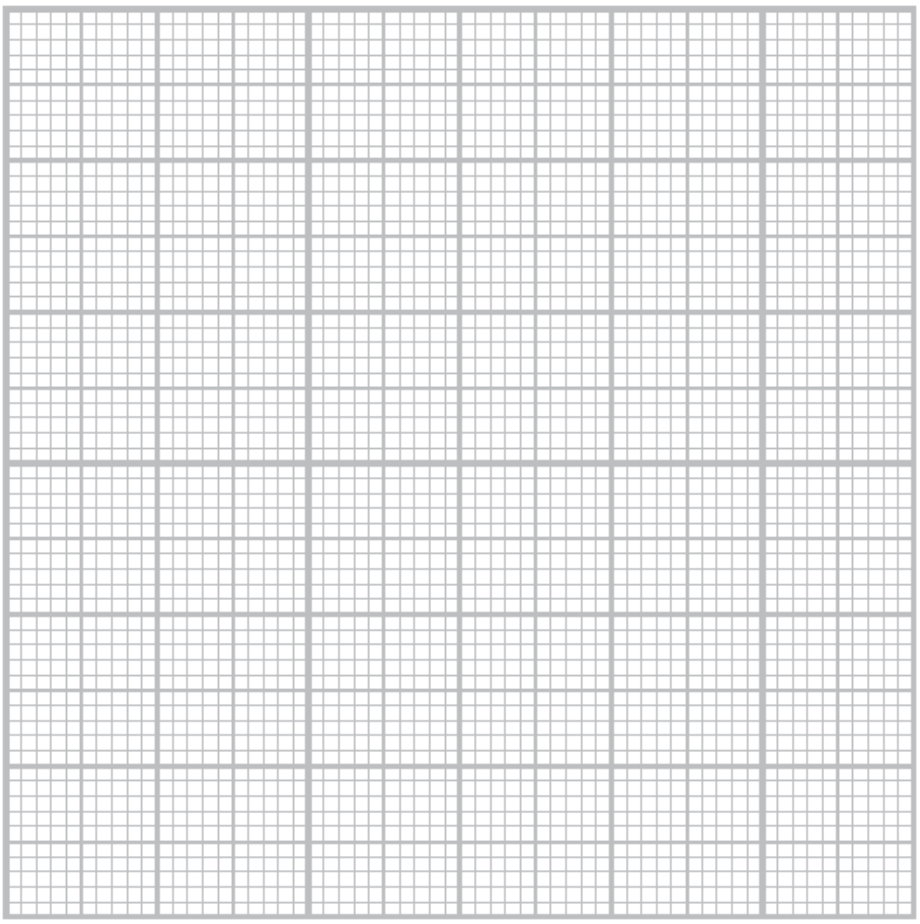
A series of experiments was carried out to determine the kinetics of the reaction between a chloroalkane, RCl, and potassium hydroxide in aqueous solution.
A large excess of the chloroalkane was used.

The data obtained are shown.

$[OH^-]$ / mol dm^{-3}	Time / s
0.00100	39
0.00200	31
0.00300	23
0.00400	16
0.00500	8

(a) Plot a graph of the concentration of the hydroxide ions against time.

(2)



(b) State the order with respect to hydroxide ions.
Justify your answer by reference to your graph in (a).

(2)

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(c) Deduce the type of mechanism occurring.
Justify your answer.

(2)

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(d) Give the classification of the chloroalkane in this reaction.

(1)

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(Total for question = 7 marks)

Q10.

This question is about the reaction kinetics of an 'iodine clock' reaction.

One example of an 'iodine clock' reaction that involves the iodate(V) ions and iodide ions in acidic solution is

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

A series of experiments was carried out by a student to determine the order of reaction with respect to iodate(V) ions. The concentrations of the iodide ions and the acid were in large excess and the volume of the iodate(V) solution was varied. The total volume of the reaction mixture was kept constant by the addition of suitable volumes of deionised water.
The following results were obtained:

Experiment Number	1	2	3	4	5	6
Volume of iodate(V) solution / cm^3	10.0	7.0	5.0	3.0	2.0	1.0
Time (t) / s	180	260	357	606	900	800
(1000/t) / s^{-1}	5.56				1.11	1.25

(i) In experiment 6, the student forgot to add deionised water to keep the total volume the same for each experiment.

State why the total volume should be kept the same.

(1)

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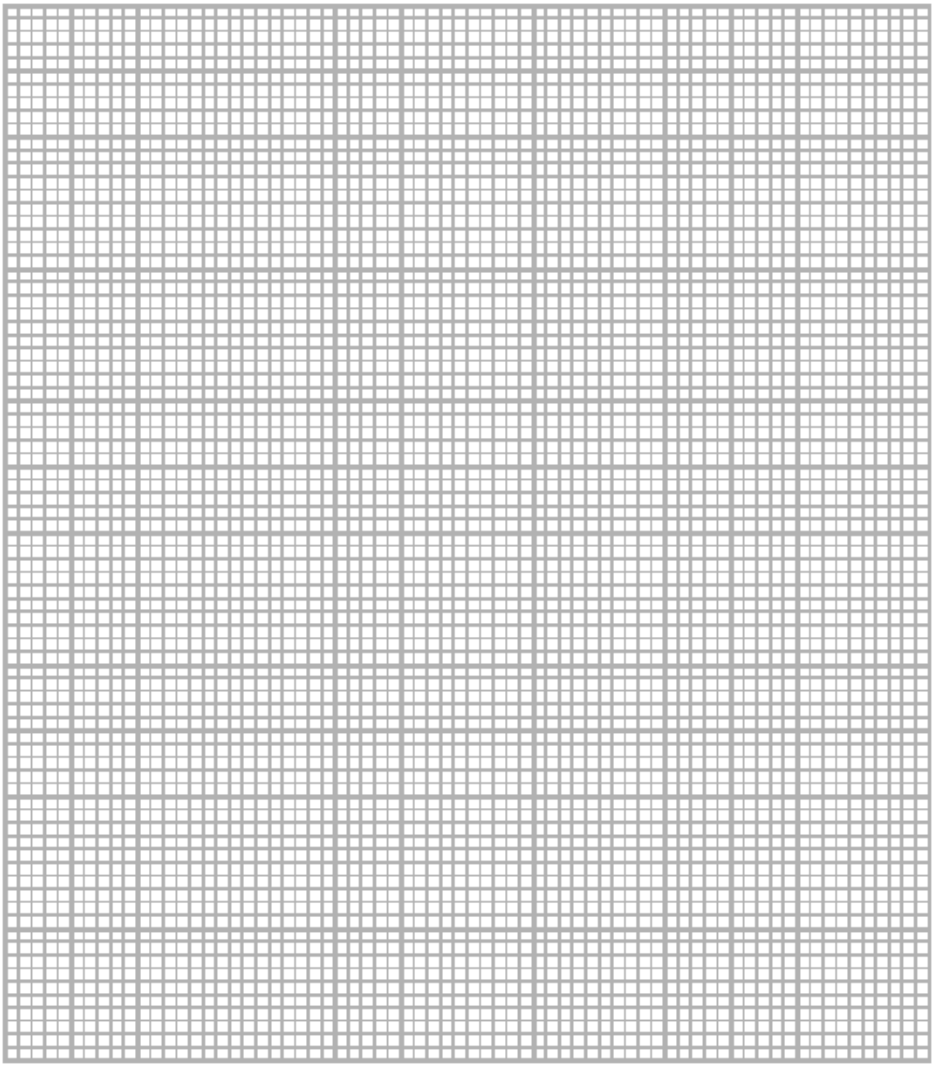
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(ii) Complete the table and use the results from experiments 1, 2, 3, 4 and 5 to plot a graph of 1000/t against volume of iodate(V) ions.

(4)



(iii) Deduce the order of reaction with respect to the iodate(V) ions. Justify your answer.

(2)

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(Total for question = 7 marks)

Q11.

At 556 K, hydrogen iodide decomposes without a catalyst.

The following data were obtained.

Initial concentration of hydrogen iodide / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
0.100	7.040×10^{-9}
0.300	6.336×10^{-8}

(i) Deduce the order of reaction with respect to hydrogen iodide when there is no catalyst present. Justify your answer.

(2)

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(ii) Write the rate equation for the reaction without a catalyst and calculate the rate of reaction when the initial concentration of hydrogen iodide is 0.500mol dm^{-3}.

(2)

Q12.

The halogenoalkane, 2-chloro-2-methylpropane, is prepared from 2-methylpropan-2-ol.

Step 1	Concentrated hydrochloric acid (in excess) and 2-methylpropan-2-ol (0.20 mol) are placed into a large conical flask. The flask is stoppered and then gently swirled for about 20 minutes.
Step 2	The mixture is transferred to a separating funnel and the lower aqueous layer is discarded.
Step 3	Sodium hydrogencarbonate solution is added to the separating funnel. The funnel is swirled carefully. The tap is opened frequently to release any build up of pressure. The lower aqueous layer is discarded.
Step 4	**Step 3** is repeated until there is no evidence of a build up of pressure.
Step 5	The product is transferred to a conical flask and anhydrous sodium sulfate is added, whilst swirling the flask.
Step 6	The product is filtered to remove the anhydrous sodium sulfate and then distilled, collecting the fraction that boils between 50 and 52 °C.

(a) Explain what causes the 'build up of pressure' in **Step 3**.
Write an equation for the reaction that takes place. State symbols are not required.

(2)

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(b) State the role of the anhydrous sodium sulfate in **Step 5** and describe how to tell when a sufficient amount has been added.

(2)

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(c) Explain the effect of **Steps 3** and **4** on the percentage yield for the preparation.

(2)

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(d) Complete the mechanism for the reaction between concentrated HCl and 2-methylpropan-2-ol by showing the formation of the intermediate, its formula and its reaction to produce the product. Show appropriate lone pairs.

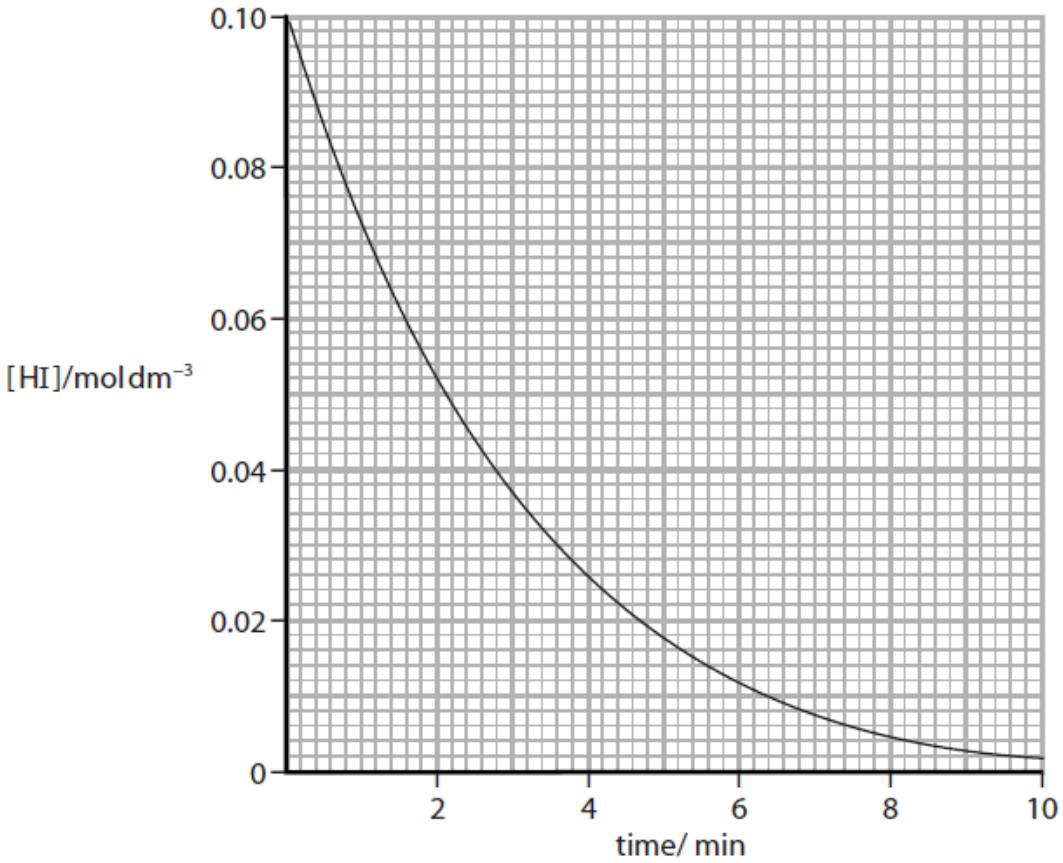
(4)



(Total for question = 10 marks)

Q13.

The graph shows how the concentration of hydrogen iodide changes with time when a platinum catalyst is present.



Measure two successive half-lives from the graph, showing your working, and deduce the order

of reaction with respect to hydrogen iodide. Justify your answer.

(2)

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Q14.

The equation for the reaction between iodine and propanone is:

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The kinetics of this reaction were studied.

(a) The order of the reaction with respect to iodine was determined by preparing a mixture of solutions of iodine and sulfuric acid in a conical flask. A solution of propanone was then added and a timer started. After one minute, a 10.0 cm^3 sample of the reaction mixture was removed. Further 10.0 cm^3 samples of the reaction mixture were removed at regular time intervals during the experiment.

After removal, each sample was immediately added to sodium hydrogencarbonate solution and then titrated with sodium thiosulfate solution to determine the concentration of iodine.

The table shows the volumes and initial concentrations of the substances in one experiment.

Substance	Volume / cm^3	Concentration / mol dm^{-3}
iodine	50	0.020
sulfuric acid	20	2.5
propanone	25	2.0

(i) Deduce, by calculation of the amounts used, whether propanone or iodine was in excess.

(2)

(ii) Name the piece of apparatus which is most suitable for measuring the volume of sulfuric acid.

(1)

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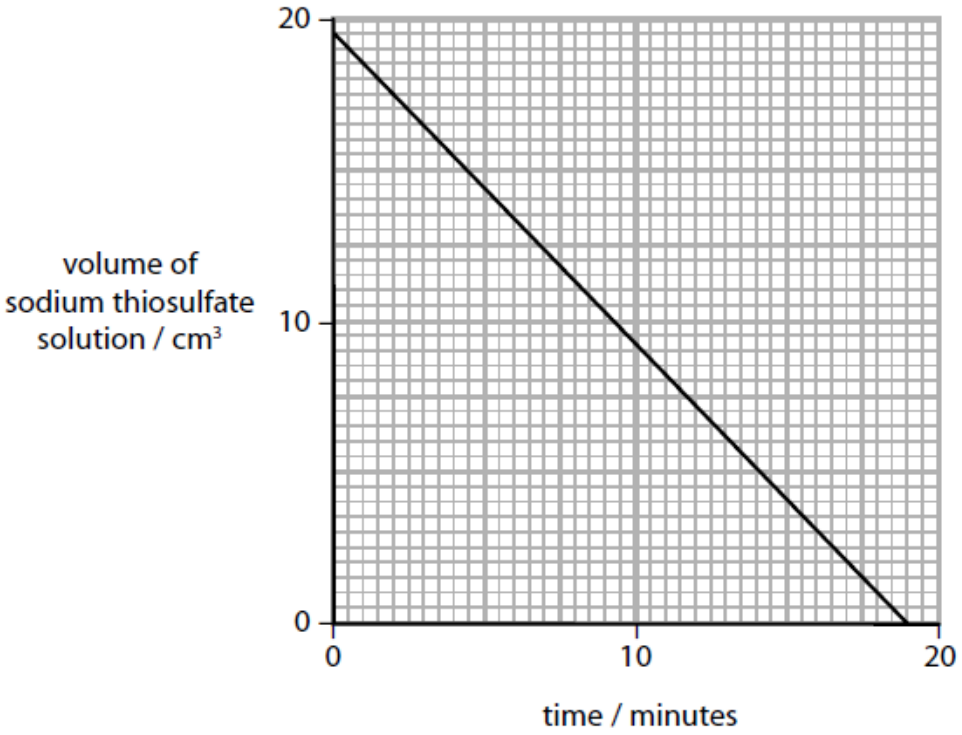
(iii) Name the piece of apparatus which is most suitable for removing the sample from the reaction mixture.

(1)

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(b) The graph shows the results of titrating the samples of the reaction mixture.



Explain how you can deduce the order of reaction with respect to iodine from this graph.

(2)

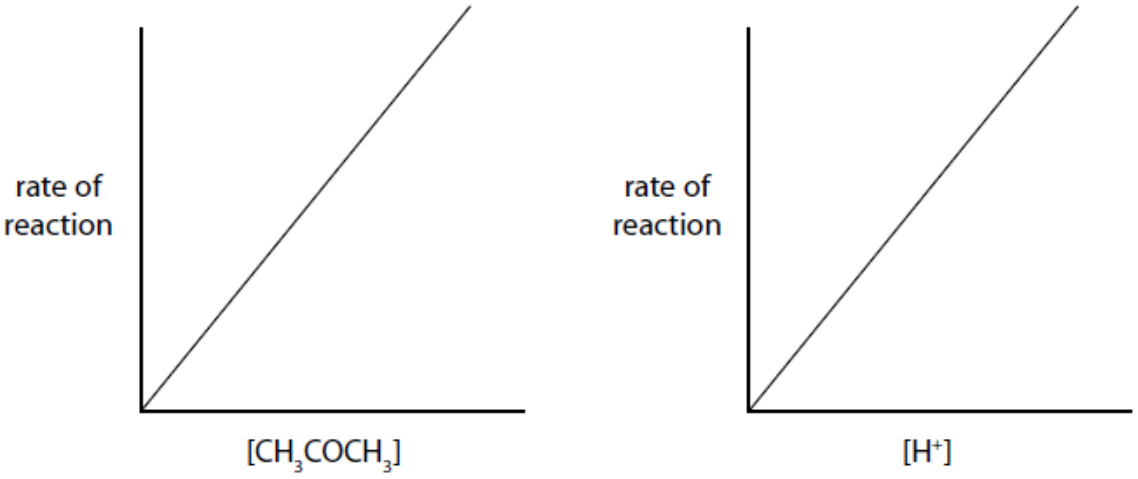
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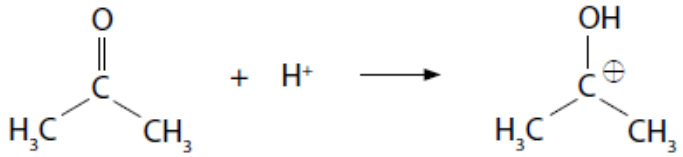
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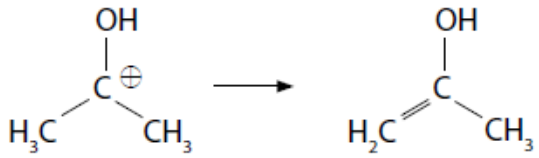
(c) These graphs were obtained in other experiments to determine the order of reaction with respect to propanone and to sulfuric acid.

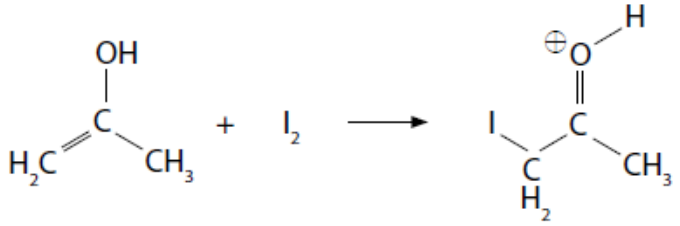


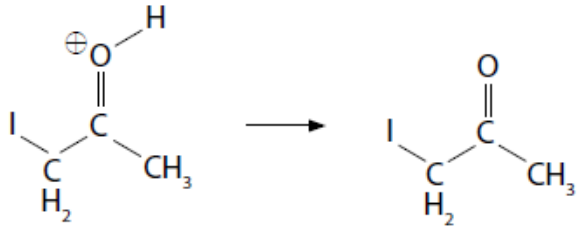
Use these graphs and your answer from part (b) to comment on whether this proposed mechanism for the reaction is correct.

(3)

step 1  fast

step 2  slow

step 3  fast

step 4  fast

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Q15.

This question is about reaction kinetics.

The rate constant for the reaction between bromoethane and aqueous hydroxide ions was determined at five different temperatures.

The results are given in the table.

Temperature (T) / K	1 / Temperature (1 / T) / K^{-1}	Rate constant, k / $dm^3\,mol^{-1}\,s^{-1}$	ln k
293	3.41×10^{-3}	5.83×10^{-5}	–9.75
303		1.67×10^{-4}	
313		5.26×10^{-4}	
323		1.36×10^{-3}	
333	3.00×10^{-3}	3.77×10^{-3}	–5.58

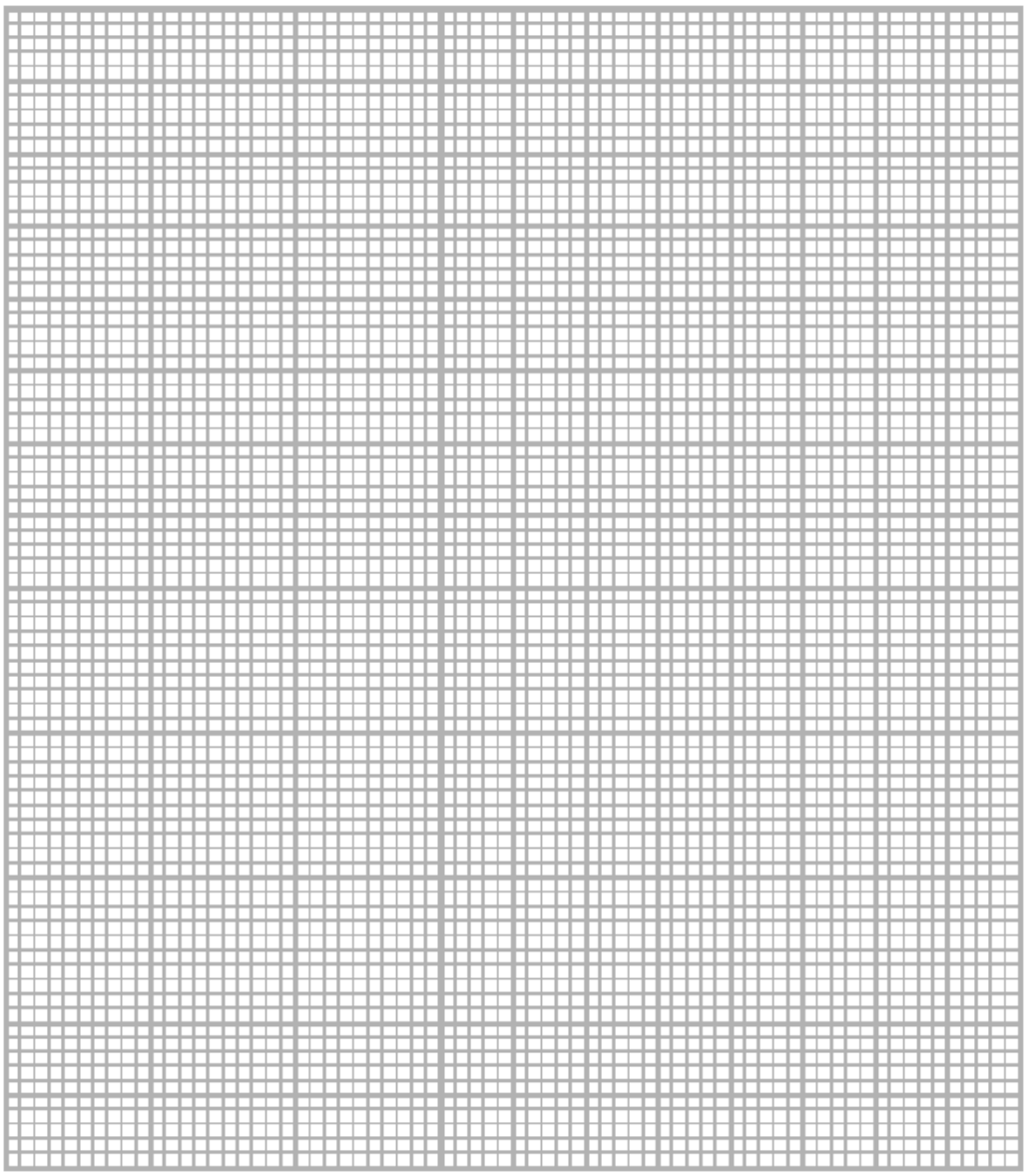
Complete the data in the table and use them to plot a graph of ln k against 1 / T and hence determine the activation energy, E_a, in kJ mol^{-1}.

You should include the value and units of the gradient of the line.

The Arrhenius equation can be expressed as

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$$

(7)



(Total for question = 7 marks)

Q16.

Persulfate ions, $S_2O_8^{2-}$, oxidize iodide ions in aqueous solution to form iodine and sulfate ions, SO_4^{2-}.

(a) Write the ionic equation for this reaction. State symbols are not required.

(1)

(b) The effect of persulfate ion concentration on the rate of this reaction was measured.

A few drops of starch solution and a small measured volume of sodium thiosulfate solution were added to the potassium persulfate solution.

Potassium iodide solution was then added and the time taken for the mixture to change colour was measured.

The reaction was repeated using different concentrations of potassium persulfate, but the same volumes and concentrations of sodium thiosulfate solution and potassium iodide solution.

The rates of the reaction were compared using the reciprocal of the time (1/time) for the mixture to change colour as a measure of the initial rate.

(i) What is the final colour of the reaction mixture?

(1)

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(ii) What would happen if the reaction was carried out without the addition of sodium thiosulfate?

(1)

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(iii) Explain why the concentration of iodide ions remains constant until the mixture changes colour.

(1)

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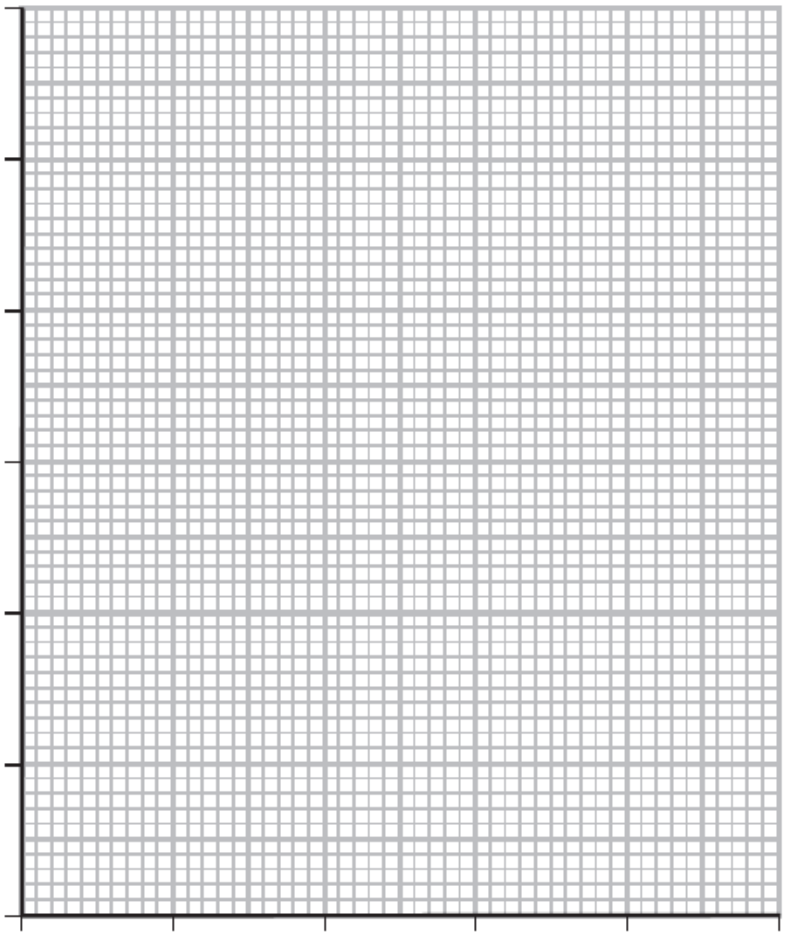
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(c) The results obtained from the experiment in part (b) were tabulated as follows.

$[S_2O_8^{2-}]$ /mol dm^{-3}	Time /s	1/time /s^{-1}
0.0100	40.0	0.0250
0.0090	44.4	0.0225
0.0075	53.3	0.0188
0.0060	66.7	0.0150

(i) Plot a graph of 1/time on the vertical axis against the concentration of the persulfate ions.

(2)



(ii) 1/time is a measure of the initial rate of the reaction.

Deduce the order of the reaction with respect to persulfate ions.

Justify your answer.

(2)

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(iii) The reaction is first order with respect to iodide ions. Write the overall rate equation for the reaction and deduce the units for the rate constant.

(2)

Rate =

Units for the rate constant .....

(Total for question = 10 marks)

Q17.

The compound sulfuryl chloride is a colourless liquid with the formula SO_2Cl_2.

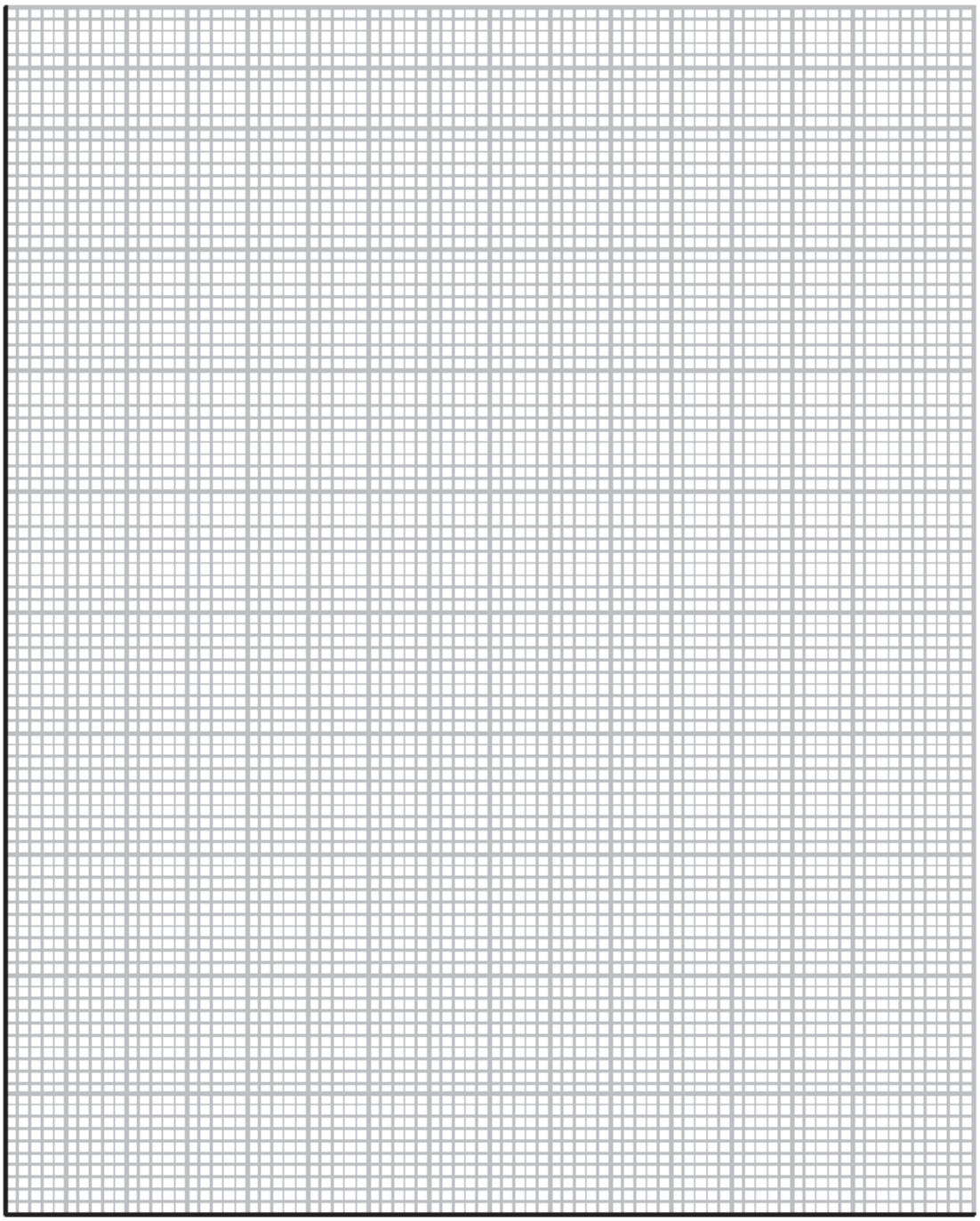
It decomposes at room temperature to form sulfur dioxide and chlorine.

The rate of the decomposition of SO_2Cl_2 can be investigated by monitoring the concentration of SO_2Cl_2 as the reaction proceeds. The data in the table were collected from such a reaction.

Time / s	$[SO_2Cl_2]$ / mol dm^{-3}
0	0.500
1000	0.370
2000	0.290
3000	0.200
4000	0.150
5000	0.110
6000	0.090
7000	0.060
8000	0.040

(i) Plot a graph of these results.

(3)



(ii) Determine the order of reaction with respect to SO_2Cl_2 and hence write the rate equation for the reaction.
Show on your graph how you arrived at your answer.

(3)

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(iii) Use your graph to find the rate of reaction when the concentration of SO_2Cl_2 is 0.200 mol dm^{-3}.

Hence calculate the rate constant, *k*, to an appropriate number of significant figures. Include units in your answer.

(4)

(b) Write a possible two-step mechanism for the reaction that is consistent with your rate equation and clearly identify the rate-determining step.

(2)

(Total for question = 12 marks)

Q18.

This question is about the effect of temperature on the rate of decomposition of nitrogen(V) oxide.

$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

The rate constant for the decomposition of nitrogen(V) oxide was determined at two temperatures.

Temperature / K	Rate constant / s^{-1}
328	1.50×10^{-3}
338	4.87×10^{-3}

Calculate the activation energy for this reaction.

Include units and give your answer to an appropriate number of significant figures.

You should **not** attempt to use any graphical method to answer this question.

The Arrhenius equation relating two rate constants, k_1 and k_2, at two different temperatures, T_1 and T_2, can be
expressed as

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(5)

(Total for question = 5 marks)

Q19.

This question is about the effect of changes in temperature on reactions.

An experiment to determine the activation energy for the reaction between magnesium and hydrochloric acid was carried out. The time taken for 0.100 g of magnesium to react completely when added to 20.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid was recorded at different temperatures. A summary of the processed data is shown.

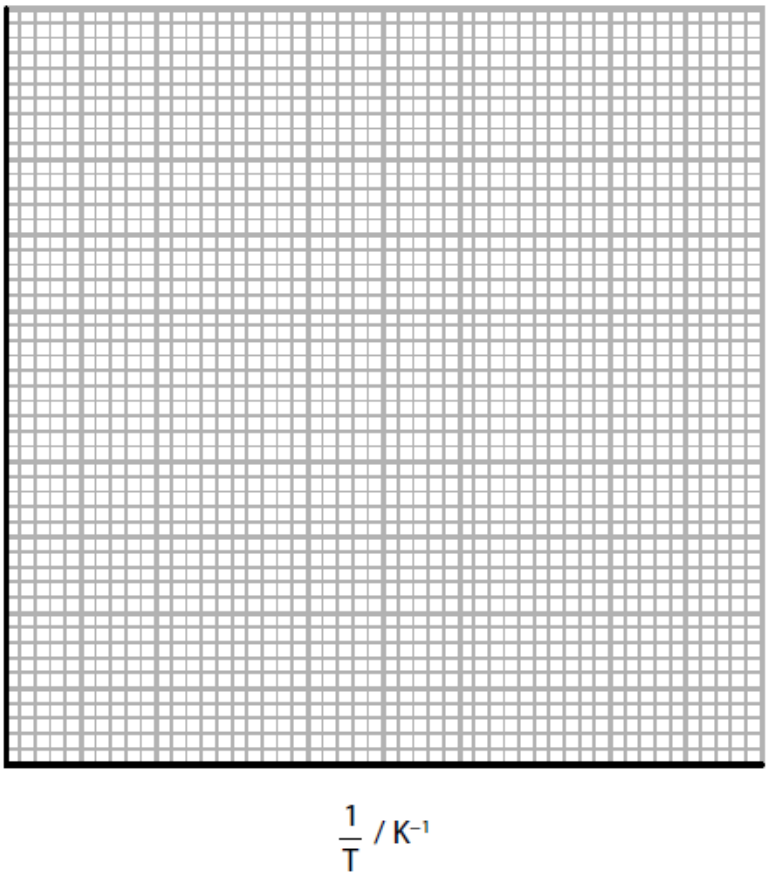
Temperature / K	$\frac{1}{T}$ / K^{-1}	ln *k*
283	3.53×10^{-3}	−4.80
299	3.34×10^{-3}	−3.56
311	3.22×10^{-3}	−3.00
322	3.11×10^{-3}	−2.25
329	3.04×10^{-3}	−1.79

The activation energy, E_a, of the reaction can be found using the equation:

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

Use this data to plot a graph of ln *k* against $\frac{1}{T}$ and hence determine the activation energy in kJ mol^{-1}.

(4)



Activation energy = ... kJ mol^{-1}

Q20.

A bromoalkane, RBr, reacts with aqueous hydroxide ions in a nucleophilic substitution reaction.

$$RBr + OH^- \rightarrow R—OH + Br^-$$

This reaction is first order with respect to the bromoalkane and the rate equation is

$$rate = k[RBr]^1[OH^-]^x$$

where x is the order of the reaction with respect to hydroxide ions.

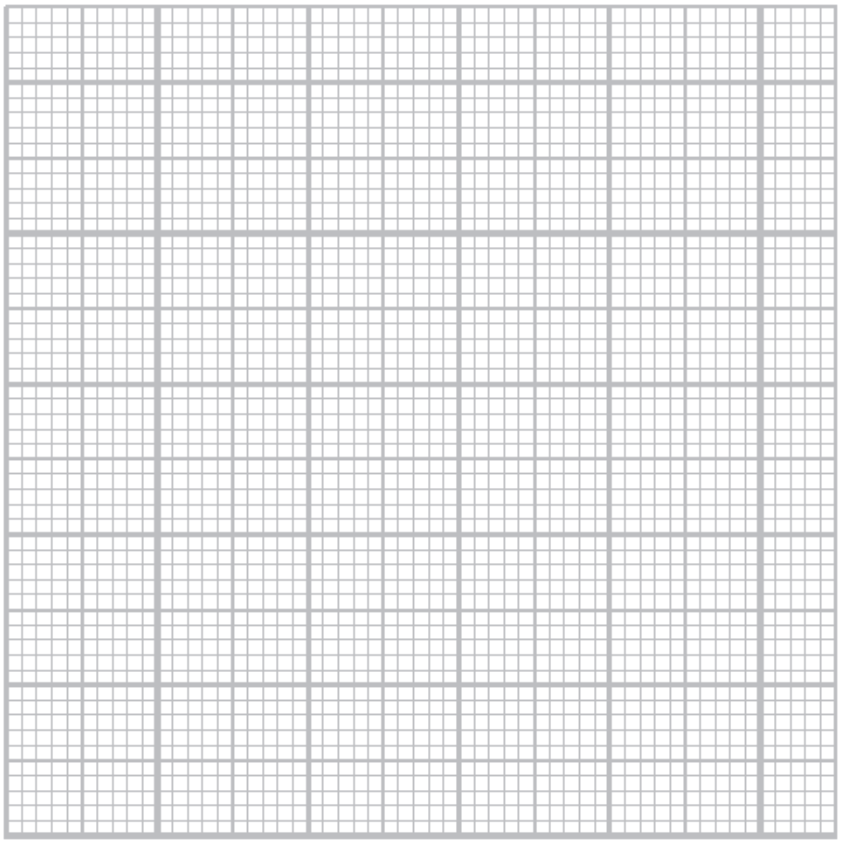
In an experiment, a sample of the bromoalkane was added to a large excess of aqueous sodium hydroxide and the concentration of the bromoalkane was determined at regular time intervals.

Results

Time / s	[RBr] / mol dm^{-3}
0	0.100
30	0.065
60	0.042
90	0.028
120	0.019
150	0.014

(i) Plot a graph of [RBr] against time.

(3)



(ii) Explain how the graph shows that the reaction is first order with respect to RBr.
Include the values of two consecutive half-lives.

You **must** show your working for the half-lives on the graph.

(2)

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(Total for question = 5 marks)

Q21.

This question is about reaction kinetics.

The 'initial rates' method was used to investigate the orders of reaction with respect to reactants **X**, **Y** and **Z**. The table shows the results obtained.

Run	Initial concentration / mol dm^{-3}			Initial rate / mol dm^{-3} s^{-1}
	X	Y	Z	
1	0.00100	0.00300	0.00600	2.17×10^{-6}
2	0.00100	0.00600	0.00600	8.68×10^{-6}
3	0.00050	0.00600	0.00600	4.34×10^{-6}
4	0.00300	0.00300	0.00300	6.51×10^{-6}

(i) Calculate the orders with respect to **X**, **Y** and **Z**.

X .....

Y .....

Z .....

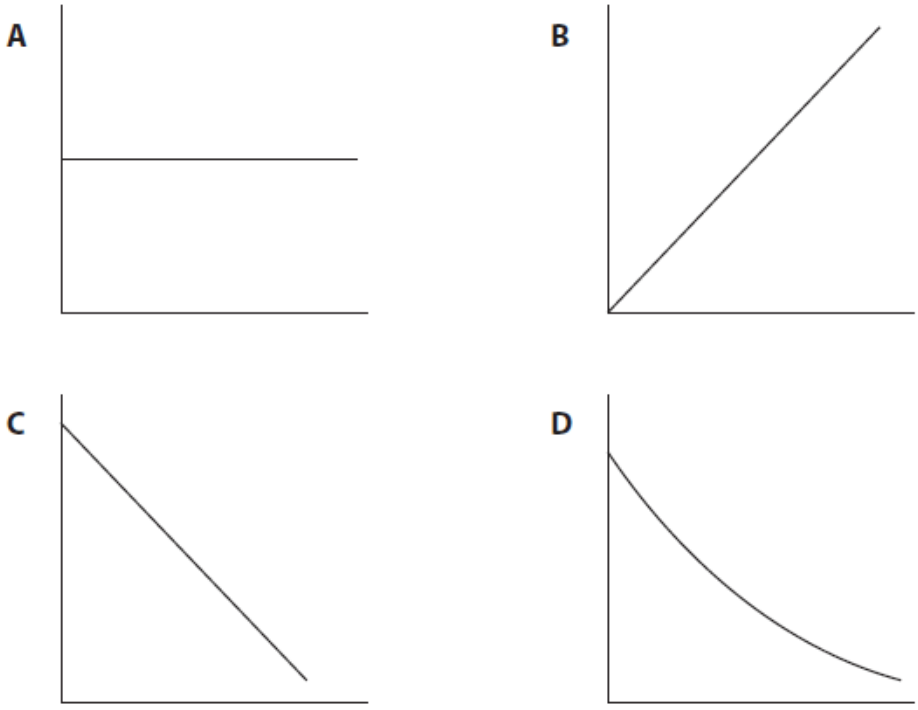
(ii) Give the rate equation for the reaction and hence calculate the rate constant, *k*, to an appropriate number of significant figures. Include units in your answer.

(4)

(Total for question = 4 marks)

Q22.

Four sketch graphs are shown below.



(a) Which could be a graph of rate of reaction, on the vertical axis, against the concentration of a reactant for a zero order reaction?

(1)

- ☒ **A**
- ☒ **B**
- ☒ **C**
- ☒ **D**

(b) Which could be a graph of rate of reaction, on the vertical axis, against the square of the concentration of a reactant for a second order reaction?

(1)

- ☒ **A**
- ☒ **B**
- ☒ **C**
- ☒ **D**

(c) Which could be a graph of the concentration of a reactant, on the vertical axis, against time for a first order reaction?

(1)

- ☒ **A**

☒ **B**

☒ **C**

☒ **D**

(d) Which could be a graph of ln(rate), on the vertical axis, against reciprocal of temperature, 1/T, for a reaction?

You may use the equation ln(rate) = $-\frac{E_a}{R} \times \frac{1}{T}$ + constant

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for question = 4 marks)

Q23.

Persulfate ions, $S_2O_8^{2-}$, oxidize iodide ions in aqueous solution to form iodine and sulfate ions, SO_4^{2-}.

(a) Write the ionic equation for this reaction. State symbols are not required.

(1)

(b) The effect of iodide ion concentration on the rate of this reaction was measured.

A few drops of starch solution and a small measured volume of sodium thiosulfate solution were added to a known volume of potassium persulfate solution.

Potassium iodide solution was then added and the time taken for the mixture to change colour was measured.

The reaction was repeated using different concentrations of potassium iodide, but the same volumes and concentrations of sodium thiosulfate solution and potassium persulfate solution.

The rates of the reaction were compared using the reciprocal of the time (1/time) for the mixture to change colour as a measure of the initial rate.

(i) What is the final colour of the reaction mixture?

(1)

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(ii) What would be observed if the reaction was carried out without the addition of sodium thiosulfate?

(1)

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(iii) Explain why the concentration of iodide ions remains constant until the mixture changes colour.

(1)

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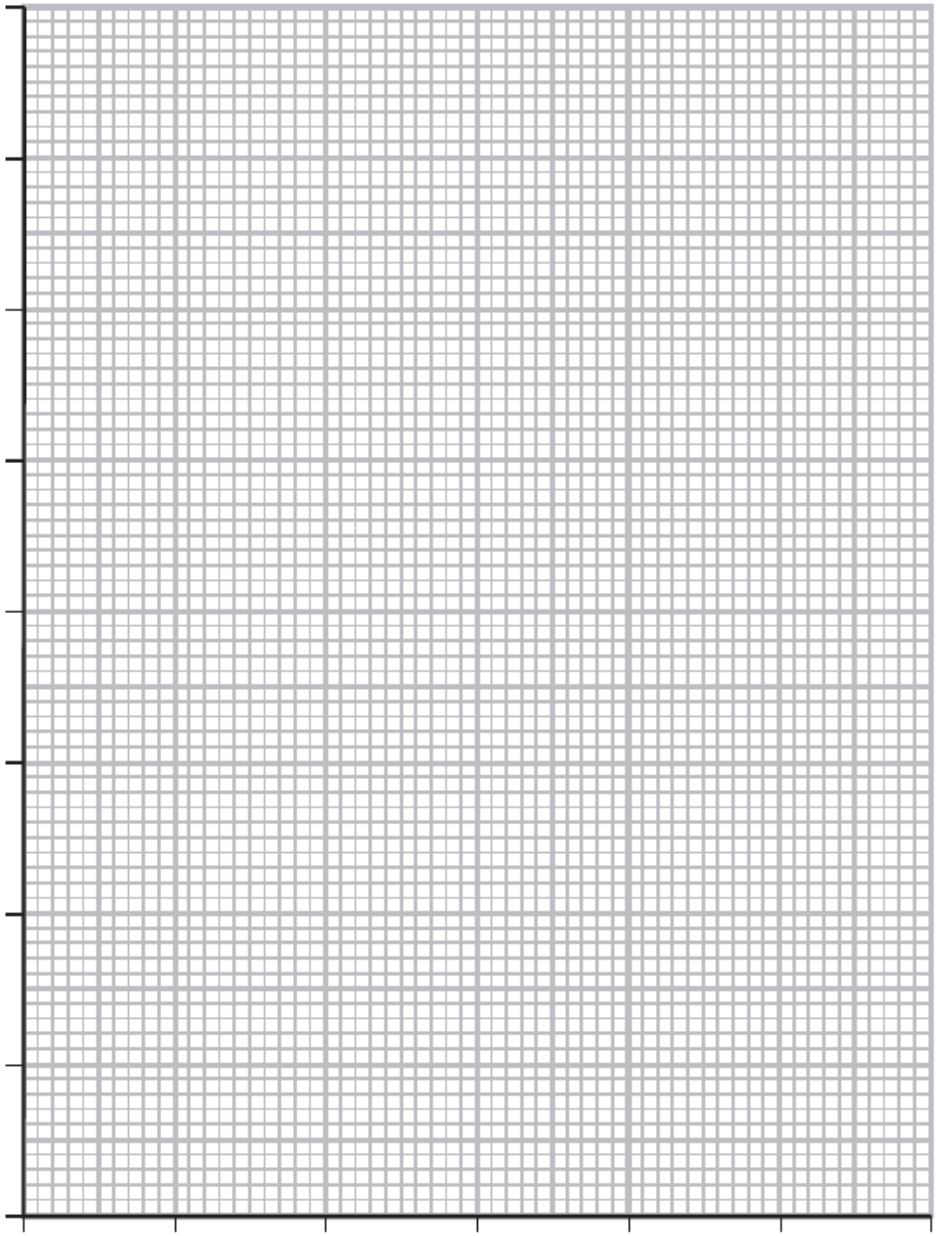
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(c) The results obtained were tabulated as follows.

$[I^-]$ /mol dm^{-3}	Time /s	1/time /s^{-1}
0.0100	40.0	0.0250
0.0075	53.3	0.0188
0.0050	80.0	0.0125
0.0040	100.0	0.0100

(i) Plot a graph of 1/time on the vertical axis against concentration of iodide ions.

(2)



(ii) 1/time is a measure of the initial rate of the reaction.

Deduce the order of reaction with respect to iodide ions.

Justify your answer.

(2)

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(iii) The reaction is first order with respect to persulfate ions. Write the overall rate equation for the reaction and deduce the units for the rate constant.

(2)

Rate =

Units for the rate constant .....

(Total for question = 10 marks)

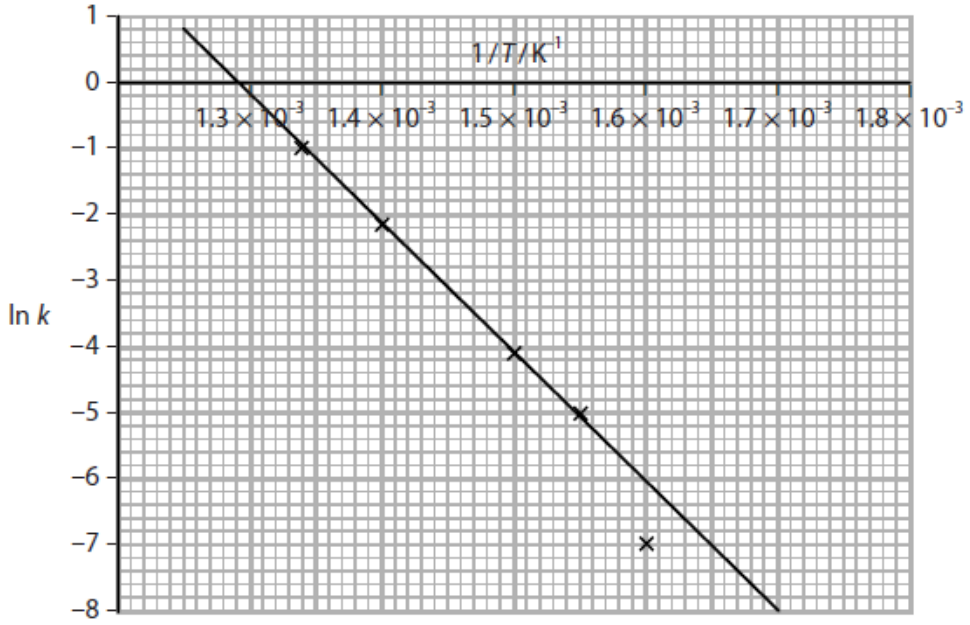
Q24.

This question is about the reaction kinetics of an 'iodine clock' reaction.

One example of an 'iodine clock' reaction that involves the iodate(V) ions and iodide ions in acidic solution is

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

Another 'iodine clock' reaction produced data that enabled the following graph of ln k against $1/T$ to be drawn.



(i) The Arrhenius equation can be expressed as

$$\ln k = -\frac{E_a}{R} \times \left[\frac{1}{T}\right] + \text{constant}$$

From the gradient of the graph, determine the activation energy, E_a , for this reaction.

Include a sign and units in your answer.

(3)

(ii) Give a reason for the point at ln $k = -7$ **not** being included in the line drawn on the graph.

(1)

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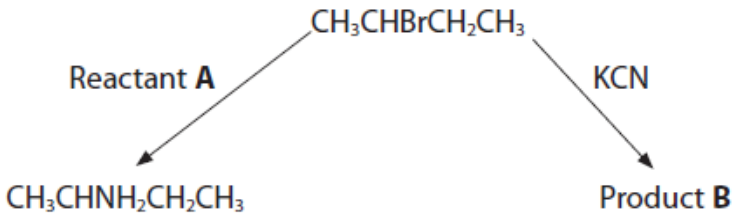
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(Total for question = 4 marks)

Q25.

This question is about halogenoalkanes.

(a) Some reactions of 2-bromobutane are:



(i) Give the **formula** for Reactant **A**.

(1)

.....

(ii) Give the **displayed** formula of the organic Product **B**.

(1)

(b) Which of these statements best explains why 2-chlorobutane reacts with potassium cyanide at a slower rate than 2-bromobutane?

(1)

☒ **A** the C-Cl bond has a higher bond enthalpy than the C-Br bond

☒ **B** the C-Cl bond has a lower bond enthalpy than the C-Br bond

☒ **C** the C-Cl bond is less polar than the C-Br bond

☒ **D** the C-Cl bond is more polar than the C-Br bond

(c) Halogenoalkanes are hydrolysed by hydroxide ions to form alcohols.

(i) Give reasons why these reactions are classified as nucleophilic substitution.

(2)

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(ii) Which of the following shows the relative rate of hydrolysis of 1-bromobutane, 2-bromobutane and 2-bromo-2-methylpropane?

(1)

		Fastest rate →		Slowest rate
☒	**A**	1-bromobutane	2-bromobutane	2-bromo-2-methylpropane
☒	**B**	1-bromobutane	2-bromo-2-methylpropane	2-bromobutane
☒	**C**	2-bromo-2-methylpropane	1-bromobutane	2-bromobutane
☒	**D**	2-bromo-2-methylpropane	2-bromobutane	1-bromobutane

(iii) The reaction between 2-bromo-2-methylpropane and hydroxide ions takes place in two steps.

$$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^- \qquad \text{slow}$$

$$(CH_3)_3C+ + OH^- \rightarrow (CH_3)_3COH \qquad \text{fast}$$

Give the rate equation for the reaction of 2-bromo-2-methylpropane with hydroxide ions. Justify your answer.

(2)

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(Total for question = 8 marks)

Q26.

This question is about transition metals.

Manganate(VII) ions, MnO_4^-, react with ethanedioate ions in acid solution.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

The reaction starts slowly, the rate of reaction then increases, before it decreases again.

Explain this sequence.

(3)

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(Total for question = 3 marks)

Q27.

This is a question about the hydrolysis of halogenoalkanes.

* Compare and contrast the mechanism of hydrolysis, using aqueous potassium hydroxide, of the primary halogenoalkane, RCH_2X, with that of the tertiary halogenoalkane, R_3CX.
Include diagrams of any intermediate or transition state.

Curly arrows are not required.

(6)

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(Total for question = 6 marks)

Q28.

This question is about the reaction kinetics of an 'iodine clock' reaction.

One example of an 'iodine clock' reaction that involves the iodate(V) ions and iodide ions in acidic solution is

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

A different version of the 'iodine clock' reaction involves mixing hydrogen peroxide with aqueous solutions of potassium iodide, sodium thiosulfate and starch.

The main reaction is

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

The reaction is first order with respect to hydrogen peroxide and iodide ions but zero order with respect to hydrogen ions.

(i) In one experiment, the following data were obtained:

Reactants	Initial concentration / mol dm^{-3}
$H_2O_2(aq)$	1.50×10^{-3}
$I^-(aq)$	2.10×10^{-3}
$H^+(aq)$	2.10×10^{-3}

Initial rate = 1.24×10^{-3} mol dm^{-3} s^{-1}

Write the rate equation and hence deduce the value of the rate constant, *k*, from these data. Include units and give your answer to an appropriate number of significant figures.

(2)

(ii) Explain the purpose of the starch present in the reaction mixture when starch is neither in the rate equation, nor in the reaction equation.

(2)

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(Total for question = 4 marks)

Q29.

Nitrogen monoxide and chlorine react together to form nitrosyl chloride.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

The rate equation for the formation of nitrosyl chloride is

Rate = $k[NO]^2[Cl_2]$

(i) Complete the table by adding the missing values.

Experiment	[NO] / mol dm^{-3}	[Cl_2] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.122	0.241	1.09×10^{-2}
2		0.482	8.72×10^{-2}
3	0.366		4.91×10^{-2}

(2)

(ii) Calculate the rate constant, *k*, using data from Experiment 1.

Include units with your answer.

(3)

(iii) Explain how using a catalyst increases the rate constant, *k*.

(2)

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(iv) The heterogeneous catalyst palladium was suggested for use in this reaction.

Explain how impurities in the gaseous reactants could make the catalyst less effective.

(3)

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(Total for question = 10 marks)

Q30.

This question is about the kinetics of chemical reactions.

A reaction between iodine and propanone, in the presence of hydrogen ions, has the rate equation:

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

(i) Give the overall order of the reaction.

(1)

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(ii) Explain, in terms of collision theory, why increasing the concentration of propanone changes the rate of reaction.

(2)

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Q31.

This question is about carbon monoxide, CO, which is a toxic and colourless gas used widely in the chemical industry.

Haemoglobin (Hb) found in red blood cells reacts almost irreversibly with carbon monoxide. Initial rate experiments were carried out to investigate the effect of the concentrations of Hb and CO on the rate of this reaction.

Experiment	[Hb] / mol dm^{-3}	[CO] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	2.09×10^{-6}	1.40×10^{-6}	8.20×10^{-7}
2	4.18×10^{-6}	1.40×10^{-6}	1.64×10^{-6}
3	3.26×10^{-6}	2.80×10^{-6}	2.56×10^{-6}

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

(1)

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(ii) Determine the order with respect to carbon monoxide using your answer to (i) and the data in the table.
Justify your answer.

(2)

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(iii) Write the rate equation for this reaction using your answers to (i) and (ii).

(1)

(iv) Calculate the rate constant, *k*, for the reaction, using the data from Experiment 1 and the rate equation from (iii).
Include units in your answer.

(3)

(Total for question = 7 marks)

Q32.

This question is about the reaction kinetics of an 'iodine clock' reaction.

One example of an 'iodine clock' reaction that involves the iodate(V) ions and iodide ions in acidic solution is

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

State why the order of reaction with respect to iodide ions cannot be five, even though 5 mol of iodide ions are shown in the equation.

(1)

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(Total for question = 1 mark)

Q33.

This question is about the kinetics of chemical reactions.

(a) The rate equation for the reaction between hydrogen and nitrogen monoxide is:

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

By what factor does the rate increase when the concentration of hydrogen is tripled and that of nitrogen monoxide is doubled?

(1)

☒ **A** 5

☒ **B** 6

☒ **C** 12

☒ **D** 18

(b) The 'initial rates' method is used to investigate the orders of reaction with respect to reactants **A**, **B** and **C**. The table shows the results obtained.

Run	Initial concentration / mol dm^{-3}			Initial rate / mol dm^{-3} s^{-1}
	A	B	C	
1	0.32	0.080	0.16	2.4×10^{-3}
2	0.64	0.080	0.16	4.8×10^{-3}
3	0.32	0.16	0.16	9.6×10^{-3}
4	0.64	0.32	0.48	0.23

(i) Deduce the orders with respect to **A** and **B**.

(2)

A .....

B .....

(ii) Deduce the order with respect to **C** and justify your answer.

(2)

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(iii) Give the rate equation for the reaction.

(1)

(iv) Calculate the rate constant, *k*, to an appropriate number of significant figures. Give units for your answer.

(3)

Q34.

This question is about reaction kinetics.

The kinetics of the 'bromine clock' were investigated and the rate equation was found to be

$$\text{Rate} = k[BrO_3^-][Br^-][H^+]^2$$

(i) What is the overall reaction order?

(1)

☒ **A** First

☒ **B** Second

☒ **C** Third

☒ **D** Fourth

(ii) Calculate the concentration of bromide ions required to produce a reaction rate of 4.08×10^{-3} mol dm^{-3} s^{-1} at 298 K given that

$k = 8.00\ dm^9\ mol^{-3}\ s^{-1}$

$[BrO_3^-] = 0.200\ mol\ dm^{-3}$

$[H^+] = 0.100\ mol\ dm^{-3}$

(2)

(Total for question = 3 marks)

Q35.

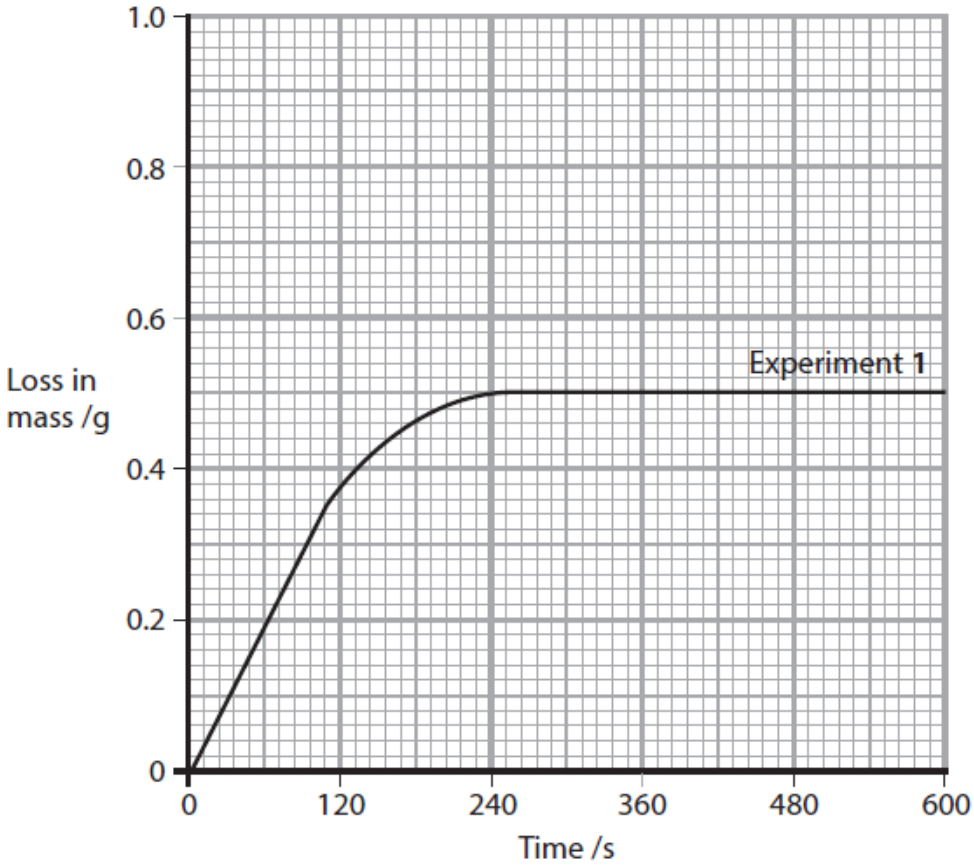
A series of experiments was carried out to investigate the factors which affect the rate of reaction between calcium carbonate and dilute hydrochloric acid.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

- 50.0 cm^3 of hydrochloric acid was added to 10 g of calcium carbonate (an excess) in a conical flask placed on an electronic balance.
- The loss in mass of the flask and its contents was recorded every 30 seconds for 10 minutes.
- The experiment was repeated using different sized pieces of calcium carbonate, a different concentration of hydrochloric acid or a different temperature.

Experiment	Size of calcium carbonate	Concentration of hydrochloric acid / mol dm^{-3}	Temperature /°C
1	small pieces	0.50	20
2	small pieces	0.50	60
3	one large piece	0.50	20
4	small pieces	1.00	20

The results of Experiment **1** are shown on the graph.



Draw curves on the graph to show the results you would expect for Experiments **2**, **3** and **4**.
Label the curves **2**, **3** and **4**.

(3)

(Total for question = 3 marks)

Q36.

Gentian violet is a purple crystalline solid used as an antifungal treatment.

It can be synthesised from dimethylphenylamine, $C_6H_5N(CH_3)_2$.

The rate constant for the reaction between a solution of gentian violet and aqueous sodium hydroxide was determined at different temperatures.

Temperature (T) / K	1 / Temperature ($1/T$) / K^{-1}	Rate constant, k / $dm^3 mol^{-1} s^{-1}$	ln k
283.5	3.53×10^{-3}	2.71×10^{-3}	−5.91
287.5	3.48×10^{-3}	3.55×10^{-3}	
291.5		4.75×10^{-3}	−5.35
295.0	3.39×10^{-3}	6.10×10^{-3}	−5.10
298.5	3.35×10^{-3}	7.60×10^{-3}	−4.88

(i) Complete the data in the table.

(1)

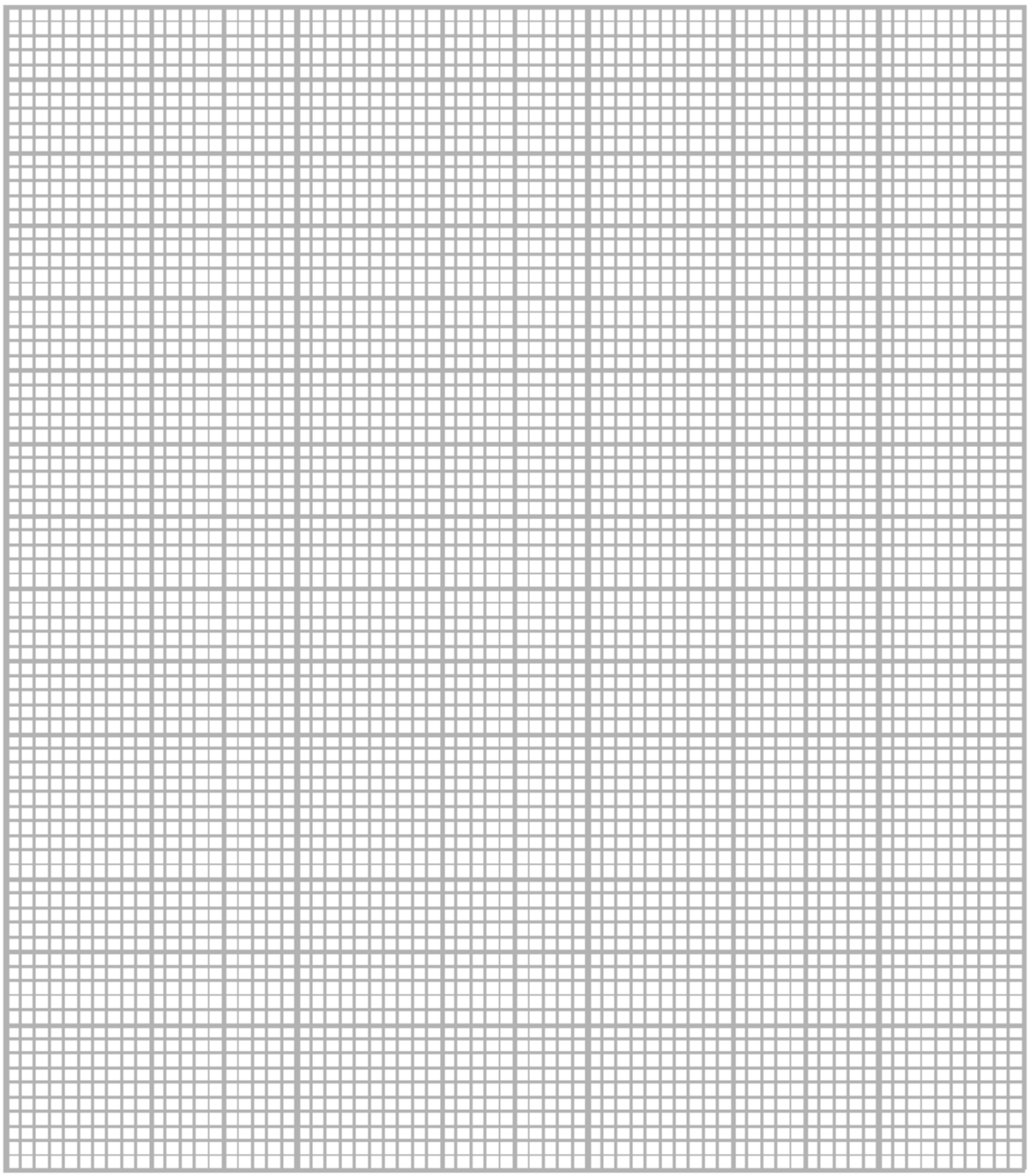
(ii) Plot a graph and use it to determine the activation energy for the reaction in kJ mol^{-1}.

You should include the value and units of the gradient of the line.

The Arrhenius equation can be shown as

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$$

(6)



Gradient

.....

Activation energy

.....

(Total for question = 7 marks)

Q37.

Methods for investigating reaction rates include

A colorimetry

B collecting and measuring the volume of a gas

C quenching, followed by titration with acid

D quenching, followed by titration with iodine solution.

Which method would be most suitable to investigate the rate of the following reactions?

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

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) $C_4H_9Br(l) + OH^-(aq) \rightarrow C_4H_9OH(l) + Br^-(aq)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for question = 2 marks)

Q38.

Bromate(V) ions, BrO_3^-, oxidize bromide ions, Br^-, in the presence of dilute acid, H^+, as shown in the equation below.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Three experiments were carried out using different initial concentrations of the three reactants.

The initial rate of reaction was calculated for each experiment.

The results are shown in the table below.

Experiment number	$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.050	0.25	0.30	1.68×10^{-5}
2	0.050	0.25	0.60	6.72×10^{-5}
3	0.15	0.50	0.30	1.01×10^{-4}

*(a) (i) This reaction is first order with respect to $BrO_3^-(aq)$. State, with reasons, including appropriate experiment numbers, the order of reaction with respect to

(5)

$H^+(aq)$

.....

.....

.....

$Br^-(aq)$

.....

.....

.....

.....

(ii) Write the rate equation for the reaction.

(1)

(iii) Use the data from experiment 1 and your answer to (a)(ii) to calculate the value of the rate constant. Include units in your answer.

(3)

(b) What evidence suggests that this reaction proceeds by more than one step?

(1)

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(c) The initial rate of reaction was obtained from measurements of the concentration of bromine at regular time intervals. How is the **initial** rate of formation of bromine calculated from a concentration-time graph?

(2)

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(Total for question = 12 marks)

Q39. The overall equation for a reaction between two chemicals, M and N, is

$$M + 2N \rightarrow P + Q$$

(a) This reaction occurs spontaneously at room temperature. Which of the following **must** be true?

(1)

⊖total **A** $\Delta H^{\ominus}_{reaction}$ is positive.

⊖total **B** $\Delta H^{\ominus}_{reaction}$ is negative.

⊖total **C** $\Delta S^{\ominus}_{total}$ is positive.

⊖total **D** $\Delta S^{\ominus}_{total}$ is negative.

(b) The reaction above occurs in two stages via an intermediate, T.

$$M + N \rightarrow T \qquad \text{slow}$$

$$N + T \rightarrow P + Q \qquad \text{fast}$$

From this it can be deduced that the rate equation for the reaction between M and N is

(1)

⊖total **A** rate = k[M][N]

⊖total **B** rate = $k[M][N]^2$

⊖total **C** rate = k[M][T]

⊖total **D** rate = k[N][T]

(Total for Question = 2 marks)

Q40. The ionic equation for the reaction of ammonium peroxodisulfate (persulfate), $(NH_4)_2S_2O_8$, with potassium iodide, KI, is

$$S^2O^{82-}(aq) + 2I^-(aq) \rightarrow 2SO_4{}^{2-}(aq) + I_2(aq)$$

(a) In a series of experiments to determine the rate equation for this reaction, 10 cm^3 of 0.0050 mol dm^{-3} sodium thiosulfate was mixed with 20 cm^3 of $(NH_4)_2S_2O_8$ solution and 5 drops of starch solution. 20 cm^3 of KI solution was added with mixing and the time taken for the solution to darken was noted. The initial concentrations of the $(NH_4)_2S_2O_8$ and KI solutions and the times for the mixture to darken are shown below.

Experiment Number	Initial concentration / mol dm^{-3}		Time for solution to darken / s
	$S_2O_8{}^{2-}$	I^-	
1	0.10	0.20	35
2	0.05	0.20	69
3	0.10	0.10	70

(i) Explain the purpose of the sodium thiosulfate solution.

(2)

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(ii) Use the data in the table to deduce the rate equation for the reaction between $S_2O_8{}^{2-}$ and I^- ions. Explain, by referring to the data, how you arrived at your answer.

(3)

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(b) A further experiment was carried out to confirm the order of the reaction with respect to iodide ions. $(NH_4)_2S_2O_8$ was mixed with KI to form a solution in which the initial concentration of $(NH_4)_2S_2O_8$ was 2.0 mol dm^{-3} and that of KI was 0.025 mol dm^{-3}. The concentration of iodine was measured at various times until the reaction was complete.

(i) Outline a method, **not** involving sampling the mixture, which would be suitable for measuring

the iodine concentrations in this experiment. Experimental details are not required but you should state how you would use your measurements to obtain iodine concentrations.

(3)

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(ii) Explain why the initial concentration of $(NH_4)_2S_2O_8$ is much higher than that of KI.

(1)

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(iii) State how the initial rate of reaction may be obtained from the results of this type of experiment.

(2)

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(iv) In such an experiment a student calculated the initial rate of reaction to be 8.75×10^{-5} mol dm^{-3} s^{-1}. Use this value, the initial concentrations in (b) and the rate equation that you obtained in (a)(ii), to calculate the rate constant for this reaction. Include units in your answer.

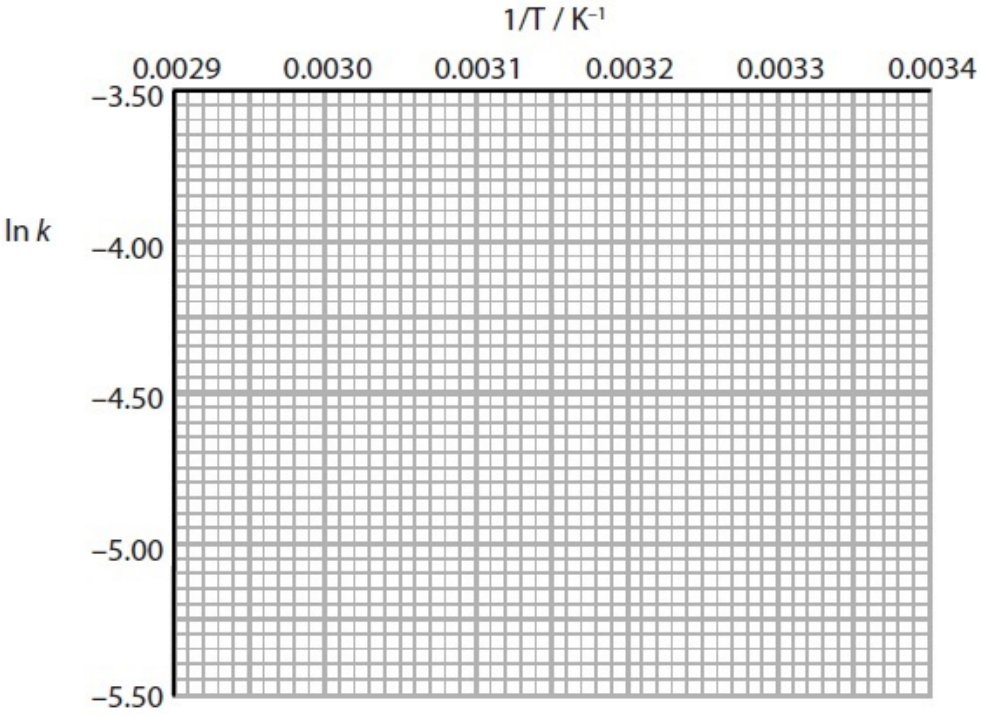
(2)

(c) Using the method outlined in (b), the rate constant for this reaction was determined at various temperatures. The data from these experiments are shown in the table below. Note that none of the temperatures corresponds to that used in (b) and that the rate constant is given in appropriate units.

Temperature T / K	Rate constant k	ln k	1/T / K^{-1}
300	0.00513	–5.27	0.00333
310	0.00833	–4.79	0.00323
320	0.0128	–4.36	0.00313
330	0.0201	–3.91	0.00303
340	0.0301	–3.50	0.00294

(i) Use the data in the table to plot a graph of ln k (on the y axis) against 1/T (on the x axis) and draw a best fit line through the points.

(2)



(ii) Determine the gradient of the best fit line in (c)(i) and use this value to calculate the activation energy, E_a, of the reaction, stating the units.

(4)

The rate constant of a reaction, k, is related to the temperature, T, by the expression

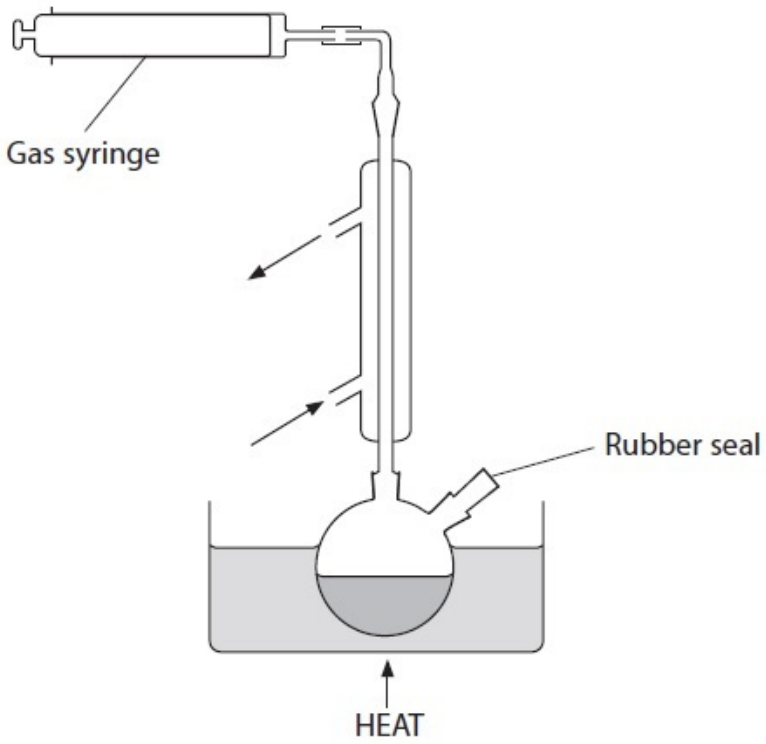
$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

(Total for Question = 19 marks)

Q41. This question is about the elimination of hydrogen bromide from bromoalkanes by reaction with alcoholic potassium hydroxide.

$$C_4H_9Br + KOH \rightarrow C_4H_8 + KBr + H_2O$$

To investigate the kinetics of this reaction the following apparatus was used:



A solution of concentrated potassium hydroxide in ethanol was refluxed and the gas syringe connected as shown.

0.6 cm^3 of 1-bromobutane was added to the solution with a hypodermic syringe through a rubber seal.

A stop clock was started and the volume of gas, V_t, measured at 2 minute intervals, for 12 minutes. When there was no further evolution of gas the volume of gas, V_{final}, was 76.5 cm^3.

(a) (i) Calculate the number of moles of 1-bromobutane used. You will need the values of the density and molar mass of 1-bromobutane from your Data booklet.

(2)

(ii) Calculate the maximum volume of gaseous but-1-ene, in cm^3, that could form.

[Molar volume of a gas 24 000 cm^3 under reaction conditions]

Suggest **two** reasons why this volume is unlikely to form.

(3)

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(b) The results obtained are shown in the table below.

Time t/min	Volume of but-1-ene V_t/cm^3	$(V_{final} - V_t)$/cm^3
0	0	76.5
2	31.5	45.0
4	51.0	25.5
6	62.5	14.0
8	68.5	8.0
10	72.0	4.5
12	74.0	2.5

(i) Explain why a large excess of potassium hydroxide is used in this experiment.

(1)

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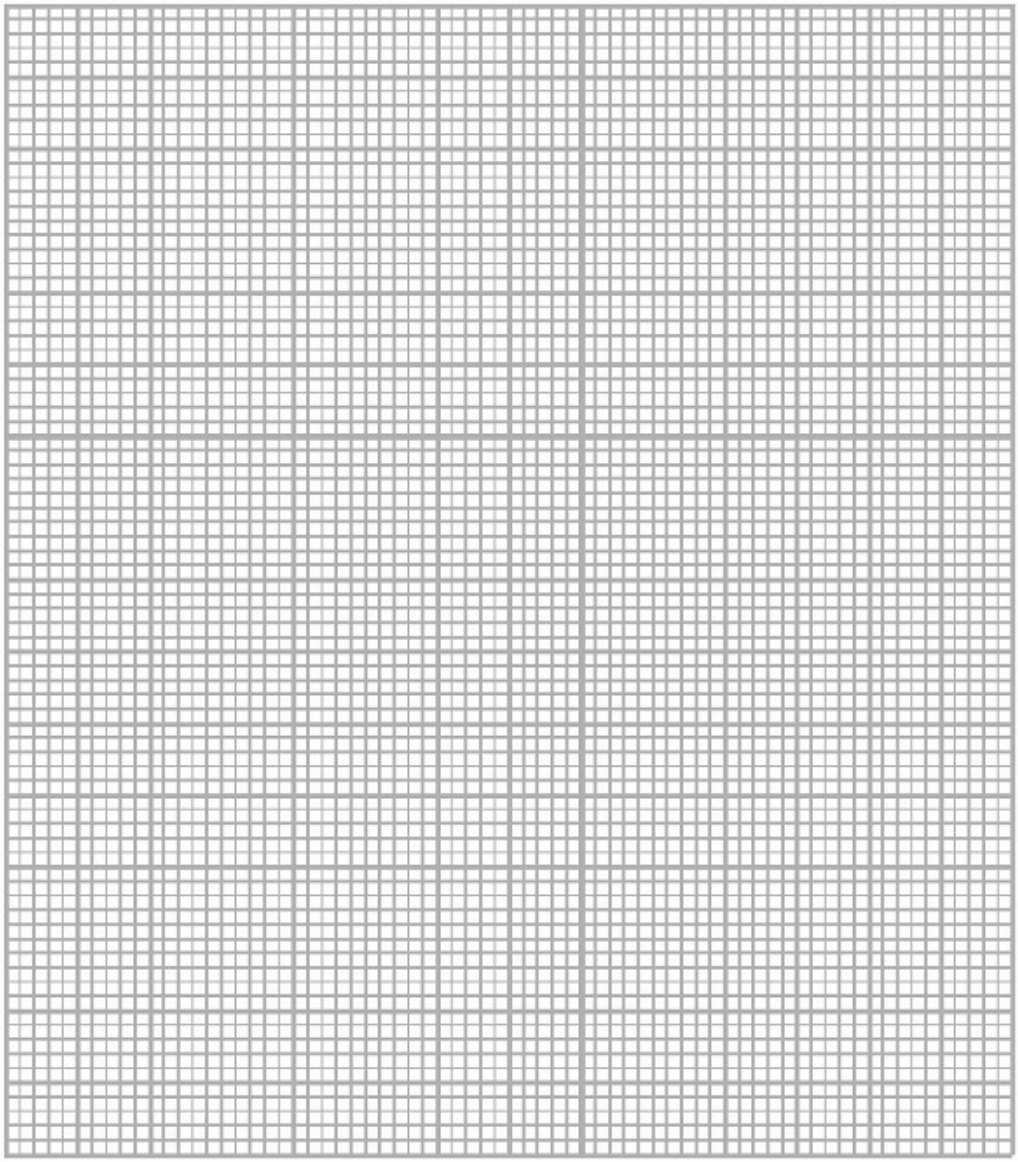
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(ii) Plot a graph of $(V_{final} - V_t)$/cm^3 against t/min.

(3)



(iii) Suggest why the value of ($V_{final} - V_t$) was plotted on your graph.

(1)

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(iv) Measure two successive half lives from your graph.

(2)

First half life
..... min

Second half life
..... min

(v) Deduce the order of reaction with respect to 1-bromobutane.

Justify your answer.

(2)

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(c) In another experiment, an excess of 1-bromobutane is reacted with varying concentrations of hydroxide ions. The results for the initial rate of the reaction are shown in the table below.

Experiment Number	$[C_4H_9Br]$ /10^{-2} mol dm^{-3}	$[OH^-]$ /10^{-3} mol dm^{-3}	Initial rate /10^{-5} mol dm^{-3} min^{-1}
1	2.50	2.50	5.00
2	2.50	1.25	2.50
3	2.50	0.50	1.00

(i) Deduce the order of reaction with respect to hydroxide ions. Justify your answer using the data in the table.

(2)

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(ii) Write the rate equation for the reaction using your answers to parts (b)(v) and (c)(i).

(1)

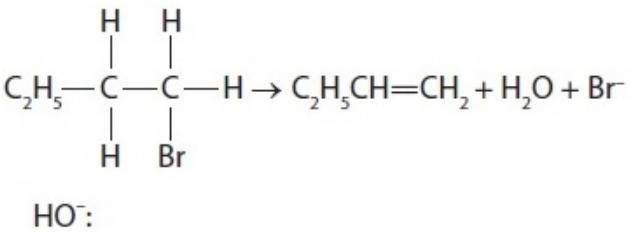
(iii) Give the units of the rate constant.

(1)

*(iv) It is suggested that the reaction begins with the slow attack by a hydroxide ion on a hydrogen atom in the 1-bromobutane, as shown below.

Complete the electron pair movement for this reaction using curly arrows and explain why this step is consistent with the rate equation for the reaction you have given in (c)(ii).

(3)



HO^-:

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(Total for Question = 21 marks)

Q42.

A bromoalkane, RBr, reacts with aqueous hydroxide ions in a nucleophilic substitution reaction.

$$RBr + OH^- \rightarrow R{-}OH + Br^-$$

This reaction is first order with respect to the bromoalkane and the rate equation is

$$\text{rate} = k[RBr]^1[OH^-]^x$$

where x is the order of the reaction with respect to hydroxide ions.

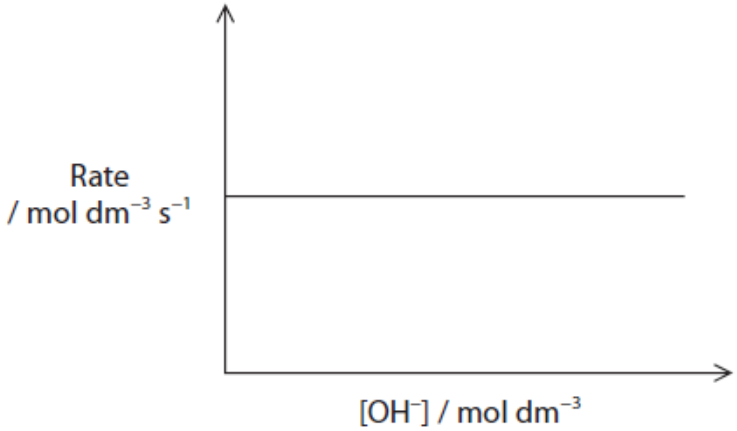
In an experiment, a sample of the bromoalkane was added to a large excess of aqueous sodium hydroxide and the concentration of the bromoalkane was determined at regular time intervals.

Results

Time / s	[RBr] / mol dm^{-3}
0	0.100
30	0.065
60	0.042
90	0.028
120	0.019
150	0.014

The experiment was repeated using equal concentrations of RBr and varying the concentration of hydroxide ions.

A graph was plotted of the results.



(i) Deduce the value of x in the rate equation.

$$\text{rate} = k[\text{RBr}]^1[\text{OH}^-]^x$$

(1)

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(ii) Give the mechanism for the reaction that is consistent with the orders of reaction with respect to R—Br and hydroxide ions.

Include curly arrows and relevant lone pairs.

(3)

(Total for question = 4 marks)

Q43.

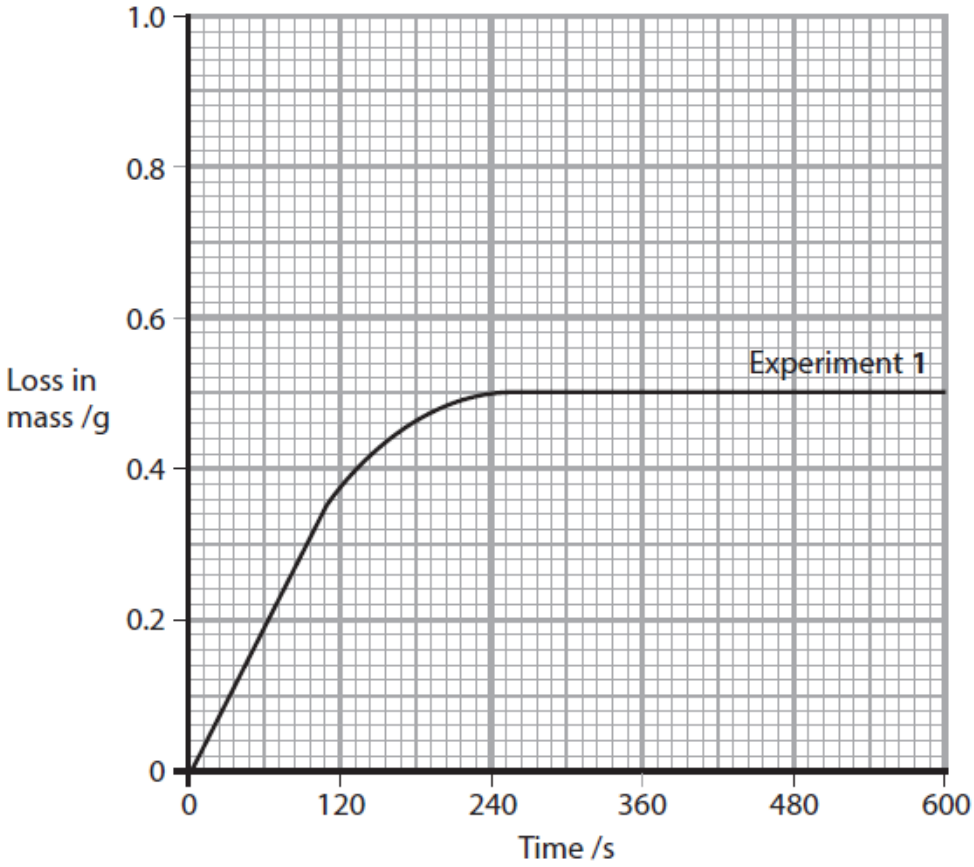
A series of experiments was carried out to investigate the factors which affect the rate of reaction between calcium carbonate and dilute hydrochloric acid.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

- 50.0 cm^3 of hydrochloric acid was added to 10 g of calcium carbonate (an excess) in a conical flask placed on an electronic balance.
- The loss in mass of the flask and its contents was recorded every 30 seconds for 10 minutes.
- The experiment was repeated using different sized pieces of calcium carbonate, a different concentration of hydrochloric acid or a different temperature.

Experiment	Size of calcium carbonate	Concentration of hydrochloric acid / mol dm^{-3}	Temperature /°C
1	small pieces	0.50	20
2	small pieces	0.50	60
3	one large piece	0.50	20
4	small pieces	1.00	20

The results of Experiment **1** are shown on the graph.



A student was required to devise an alternative method of carrying out this experiment that involved collecting the gas produced.

Outline the procedure that the student could use, including a diagram and the measurements needed.

(4)

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(Total for question = 4 marks)

Q44.

2-bromobutane can react with aqueous hydroxide ions by an S_N1 mechanism.

Explain why the butan-2-ol produced from a single optical isomer of 2-bromobutane, using this mechanism, is **not** optically active.

(3)

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(Total for question = 3 marks)

Q45.

The kinetics of the fast reaction below were investigated in a series of experiments.

$$A + B \xrightarrow{\text{catalyst } X} C + D \qquad \Delta H \text{ is negative}$$

(a) Outline a titrimetric method that could be used to measure the change in concentration of compound **A** with time. Compound **A** is an alkali, whereas compounds **B**, **C** and **D** are neutral.

(3)

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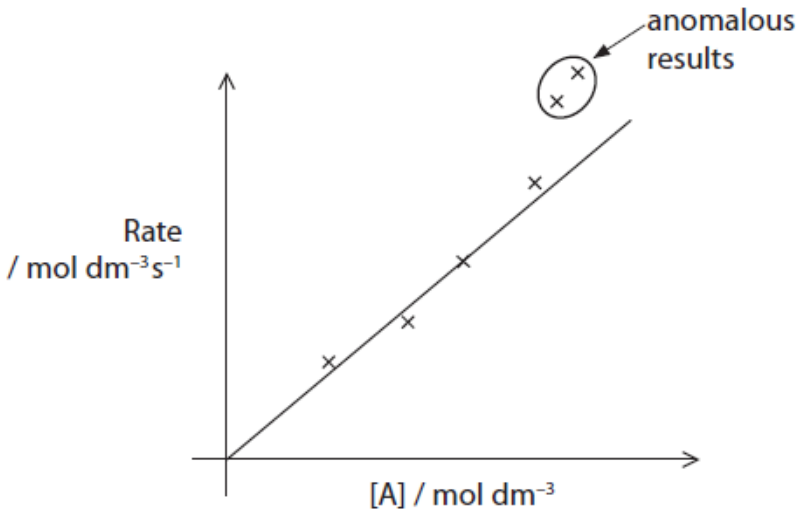
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(b) The rate of the reaction was measured at several different concentrations of **A**, in the presence of a large excess of compound **B** and a constant amount of catalyst **X**, to find the order of reaction with respect to **A**. The results are shown on the graph below.



(i) Explain how the graph confirms that the reaction is first order with respect to **A**.

(1)

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(ii) Suggest an explanation, other than human error, for the two anomalous results circled on the graph.

(3)

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(c) In a second series of experiments, further data were collected using an initial rates method. These results are summarised in the table below.

Experiment	Initial concentration / mol dm^{-3}			Initial rate / mol dm^{-3} s^{-1}
	A	**B**	**X**	
1	0.020	0.005	0.500	2.1×10^{-3}
2	0.040	0.005	0.500	4.2×10^{-3}
3	0.060	0.010	0.500	6.3×10^{-3}
4	0.080	0.010	0.250	4.2×10^{-3}

(i) Give **one** reason why obtaining these further data may be considered useful.

(1)

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(ii) Deduce the rate equation for this reaction, explaining how you arrived at your answer.

(5)

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(iii) Use your answer from (c)(ii), and appropriate data from **Experiment 4**, to calculate the value of the rate constant, *k*. Include units in your answer.

(2)

(Total for question = 15 marks)

Q46.

This is a question about halogenoalkanes and related compounds.

In aqueous sodium hydroxide, 1-bromoethane reacts to produce ethanol.

(i) Write the mechanism for this reaction, including all relevant curly arrows, lone pairs and dipoles. Include the transition state.

(4)

(ii) Give the reagents that are used to test that bromide ions are formed in this reaction mixture. Include the result of the test.

(2)

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(Total for question = 6 marks)

Q47.

A bromoalkane, RBr, reacts with aqueous hydroxide ions in a nucleophilic substitution reaction.

$$RBr + OH^- \rightarrow R—OH + Br^-$$

This reaction is first order with respect to the bromoalkane and the rate equation is

$$\text{rate} = k[RBr]^1[OH^-]^x$$

where x is the order of the reaction with respect to hydroxide ions.

In an experiment, a sample of the bromoalkane was added to a large excess of aqueous sodium hydroxide and the concentration of the bromoalkane was determined at regular time intervals.