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EDEXCEL A LEVEL CHEMISTRY: QUESTIONS BY TOPIC

Kinetics II (16)

A Level Chemistry Topic 16

8 questions · 112 marks · Mark schemes included

Pearson Edexcel A Level Chemistry (9CH0), June 2017 - June 2025

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HOW TO USE THIS BOOKLET

Questions are grouped by specification sub-topic; within each sub-topic they run from the lowest mark tariff to the highest.

Click any sub-topic heading or question row below to jump straight to it.

On every question page, click ANSWER in the top-right corner to jump to its mark scheme.

Diagrams, graphs, tables and data are printed exactly as they appeared in the original papers.

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QUESTIONS

8 questions · 112 marks · grouped by sub-topic



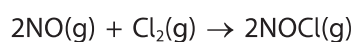
SUB-TOPIC 16(a)

RATE EQUATIONS AND ORDERS OF REACTION

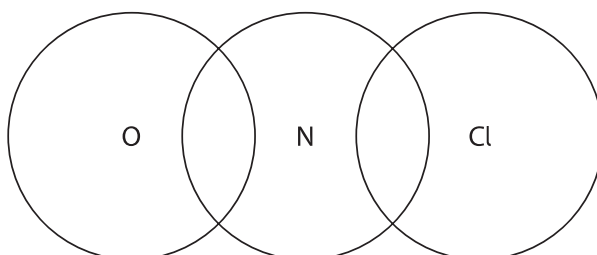
6 questions in this sub-topic · 86 marks · lowest tariff first



7 Nitrogen monoxide and chlorine react together to form nitrosyl chloride.



(a) Draw a dot-and-cross diagram for nitrosyl chloride, showing only the outer shell electrons.



(2)

(b) The rate equation for the formation of nitrosyl chloride is

$$\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]$$

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

Experiment	$[\text{NO}] / \text{mol dm}^{-3}$	$[\text{Cl}_2] / \text{mol dm}^{-3}$	Rate / $\text{mol dm}^{-3} \text{s}^{-1}$
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 7 = 12 marks)



6 Iodine reacts with propanone in acidic conditions.



A student was asked to investigate the kinetics of this reaction.

The student predicted that the rate equation for the reaction would be

$$\text{rate} = k[\text{I}_2(\text{aq})][\text{CH}_3\text{COCH}_3(\text{aq})][\text{H}^+(\text{aq})]^0$$

because the balanced equation shows that one molecule of iodine reacts with one molecule of propanone and the acid is a catalyst.

(a) The student first determined the order of reaction with respect to iodine by keeping the concentrations of propanone and acid constant.

The student used the outline procedure shown.

- mix 25 cm³ of aqueous propanone with 25 cm³ of dilute sulfuric acid in a conical flask
- add 25 cm³ of aqueous iodine, immediately start a stopwatch and swirl the mixture in the conical flask
- use a pipette to remove a 10.0 cm³ sample of the solution and place it in a clean conical flask
- add a spatula measure of sodium hydrogencarbonate and note the exact time it is added
- take four more 10.0 cm³ samples of the mixture and add sodium hydrogencarbonate to each of them at regular time intervals
- titrate the unreacted iodine in the samples with sodium thiosulfate solution using starch indicator.

(i) State how the student could ensure that the concentrations of propanone and acid are effectively constant throughout the experiment.

(1)

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(ii) Explain why sodium hydrogencarbonate is added.

(2)

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(b) The student obtained these results.

Time / min	5	10	15	20	25
Volume of thiosulfate / cm ³	15.0	13.8	12.6	11.4	10.2

- (i) Give a reason why it is not necessary to calculate the concentration of iodine at each time to work out the order of reaction with respect to iodine.

(1)

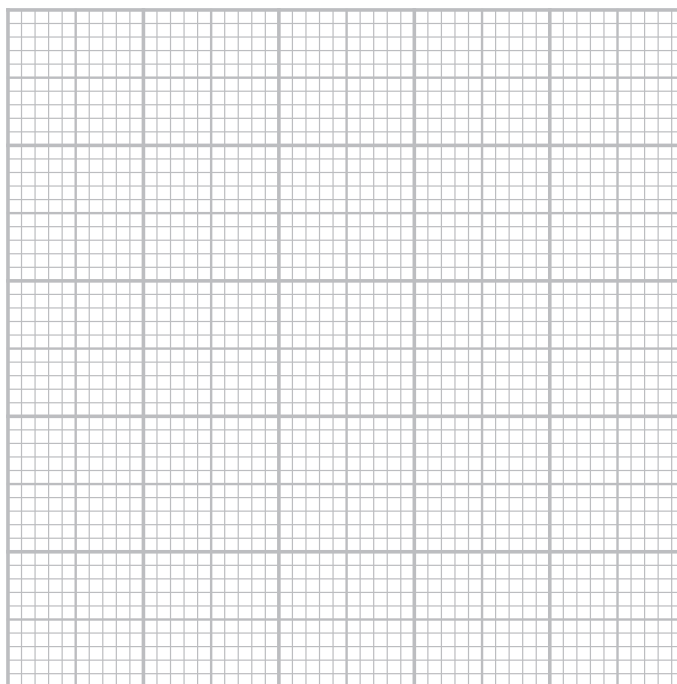
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- (ii) Plot a graph to show that the order of reaction with respect to iodine is zero.

(2)



- (iii) Give a reason why the graph shows that the order of reaction with respect to iodine is zero.

(1)

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(c) Further experiments showed that the correct overall rate equation is

$$\text{rate} = k[\text{CH}_3\text{COCH}_3(\text{aq})][\text{H}^+(\text{aq})][\text{I}_2(\text{aq})]^0$$

- (i) Deduce a possible rate determining step in the mechanism of this reaction. Curly arrows are not required.

(2)

(ii) Data from two experiments carried out at the same temperature are shown.

Experiment	$[\text{CH}_3\text{COCH}_3(\text{aq})] / \text{mol dm}^{-3}$	$[\text{H}^+(\text{aq})] / \text{mol dm}^{-3}$	$[\text{I}_2(\text{aq})] / \text{mol dm}^{-3}$	Rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	3.0	0.4	0.02	3.36×10^{-5}
2	4.0	0.2	0.04	

What is the rate, in $\text{mol dm}^{-3} \text{s}^{-1}$, in Experiment 2?

(1)

- ☐ A 2.24×10^{-5}
- ☐ B 3.36×10^{-5}
- ☐ C 4.48×10^{-5}
- ☐ D 8.96×10^{-5}

- (iii) The experiment in (a) is repeated but using aqueous bromine instead of aqueous iodine. All other conditions are kept the same.

Explain how you would expect the rate of reaction of bromination of propanone to compare with the rate of iodination of propanone.

Assume that the reaction between bromine and propanone in acidic conditions has the same rate equation as that between iodine and propanone in acidic conditions.

(2)

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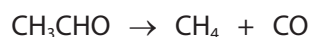
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(Total for Question 6 = 12 marks)



- 9 At high temperatures, ethanal decomposes to form methane and carbon monoxide. The reaction is second order with respect to ethanal and second order overall.



- (a) Write the rate equation for this reaction.

(1)

- (b) Deduce the units of the rate constant given that the units of rate are $\text{mol dm}^{-3} \text{s}^{-1}$.

(1)

- (c) The table shows the concentration of ethanal in a sample at different times.

Time / s	Concentration of ethanal / mol dm^{-3}
0	0.72
420	0.36
1260	0.18

Calculate average values for the rate of reaction between 0 and 420 seconds and between 420 and 1260 seconds.

Give your answers to an appropriate number of significant figures.

(2)

0 s – 420 s

420 s – 1260 s



- (d) Explain why the data given and your answers in (c) show that the reaction is **neither** zero order **nor** first order.

(2)

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- (e) The rate constant for the reaction was determined at five temperatures. The results are given in the table.

Temperature (<i>T</i>) / K	1/ Temperature (1/ <i>T</i>) / K ⁻¹	Rate constant (<i>k</i>) / units in (b)	ln <i>k</i>
700	1.43×10^{-3}	0.011	-4.51
730	1.37×10^{-3}	0.035	-3.35
760	1.32×10^{-3}	0.105	-2.25
790		0.343	
810	1.23×10^{-3}	0.787	-0.24

Determine the activation energy, E_a , in kJ mol⁻¹, by completing the data in the table and plotting a graph of ln *k* against 1/*T*.

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

The Arrhenius equation can be expressed as $\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$

(7)



A large grid of graph paper, consisting of 20 columns and 20 rows of small squares, intended for drawing or calculations.

Total for Question 9 = 13 marks)

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

(a) Draw a dot-and-cross diagram of a molecule of carbon monoxide.

Use dots (•) for the carbon electrons and crosses (x) for the oxygen electrons.

(2)

(b) Carbon monoxide can be made by the thermal decomposition of sodium ethanedioate.

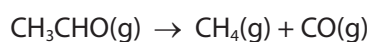


Calculate the atom economy, by mass, for the production of carbon monoxide in this reaction.

(2)



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



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

Temperature / K	Rate / $\text{mol dm}^{-3} \text{s}^{-1}$	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

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

(3)



- (d) 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)

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

(2)

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

(1)



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

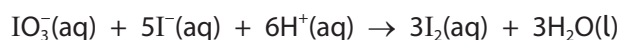
(3)

(Total for Question 6 = 15 marks)



9 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



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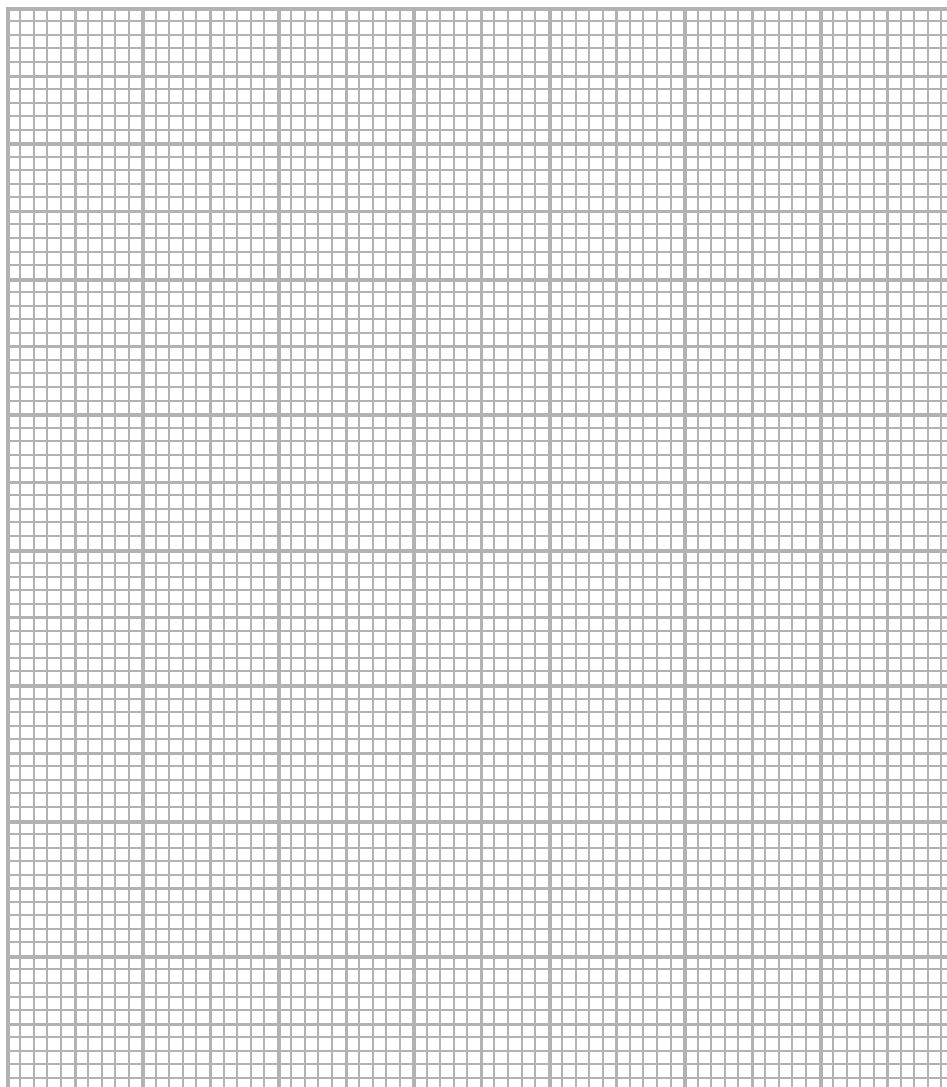
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- (ii) Complete the table and use the results from experiments 1, 2, 3, 4 and 5 to plot a graph of $1000/t$ against volume of iodate(V) ions.

(4)



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

(2)

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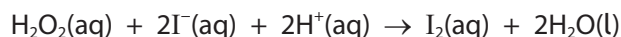
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- (c) A different version of the 'iodine clock' reaction involves mixing hydrogen peroxide with aqueous solutions of potassium iodide, sodium thiosulfate and starch.

The main reaction is



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 ₂ O ₂ (aq)	1.50 × 10 ⁻³
I ⁻ (aq)	2.10 × 10 ⁻³
H ⁺ (aq)	2.10 × 10 ⁻³

$$\text{Initial rate} = 1.24 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$$

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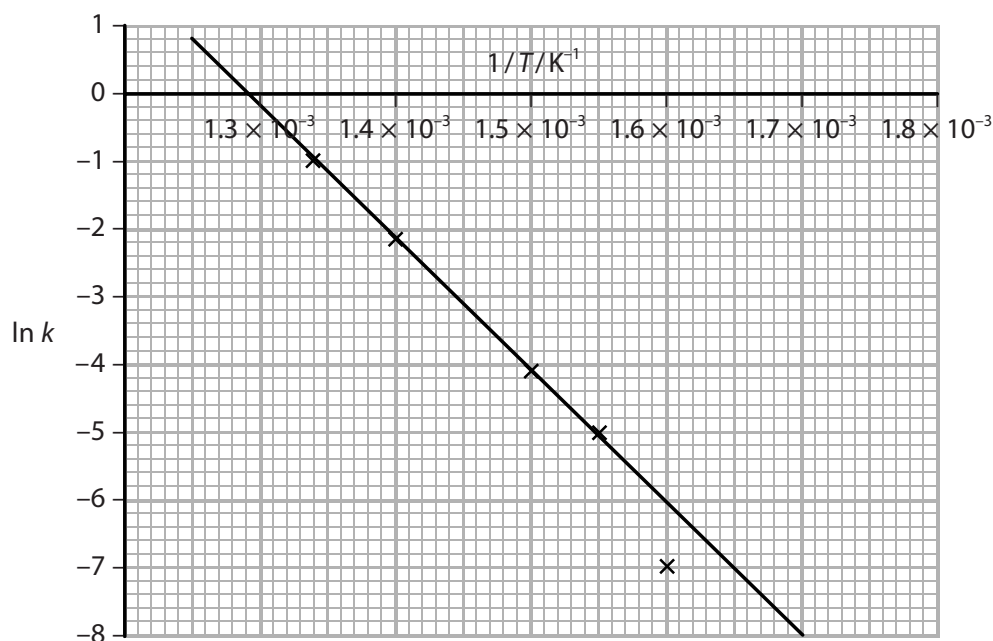
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- (d) Another 'iodine clock' reaction produced data that enabled the following graph of $\ln k$ against $1/T$ to be drawn.



- (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)

(Total for Question 9 = 16 marks)



9 This question is about reaction kinetics.

(a) 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)

(b) 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**.

(3)

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)



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

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

- (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 $4.08 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ at 298 K given that

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

$$[\text{BrO}_3^-] = 0.200 \text{ mol dm}^{-3}$$

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

(2)

- (d) 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.

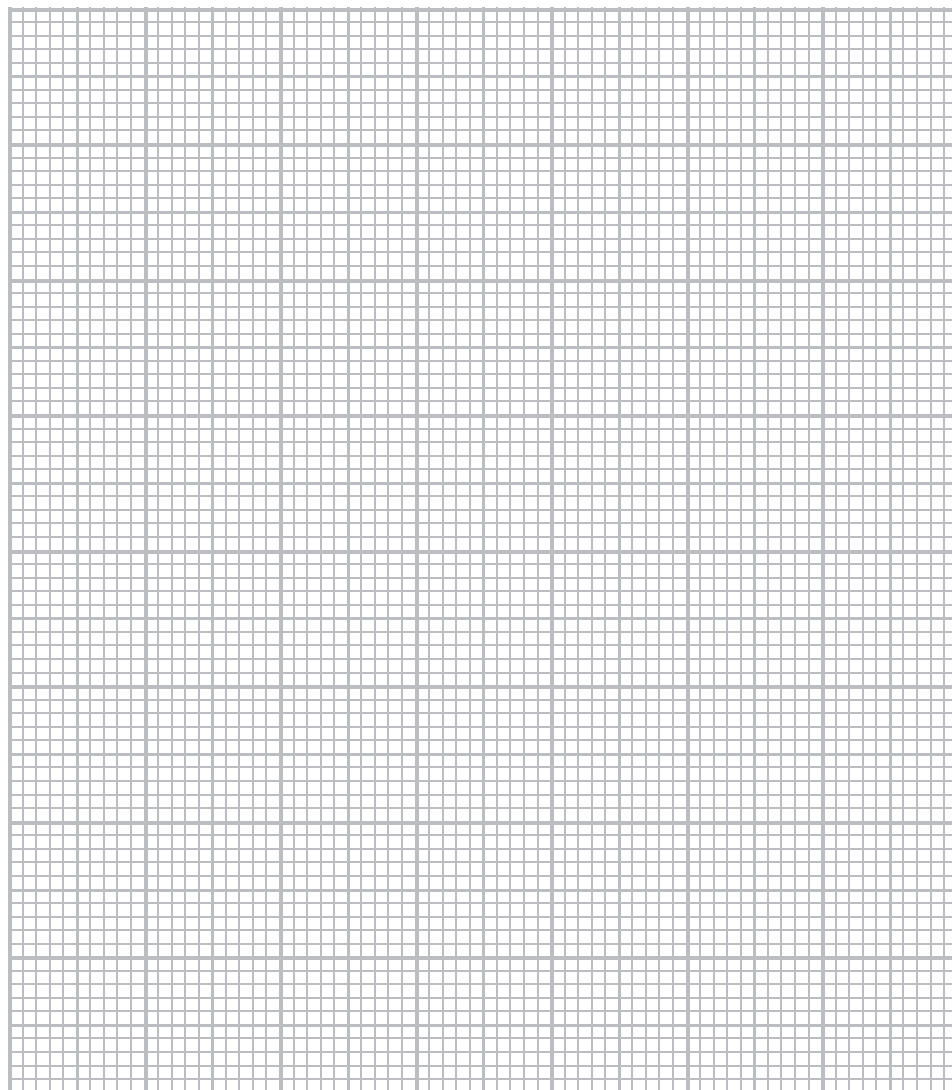
Temperature (T) / K	1 / Temperature (1 / T) / K ⁻¹	Rate constant, <i>k</i> / dm ³ mol ⁻¹ s ⁻¹	ln <i>k</i>
293	3.41 × 10 ⁻³	5.83 × 10 ⁻⁵	-9.75
303		1.67 × 10 ⁻⁴	
313		5.26 × 10 ⁻⁴	
323		1.36 × 10 ⁻³	
333	3.00 × 10 ⁻³	3.77 × 10 ⁻³	-5.58

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

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \quad (7)$$



(Total for Question 9 = 18 marks)



SUB-TOPIC 16(c)

ACTIVATION ENERGY AND THE ARRHENIUS EQUATION

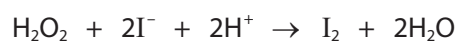
2 questions in this sub-topic · 26 marks · lowest tariff first



8 This question is about reaction kinetics and the Arrhenius equation.

(a) Different iodine clock reactions are often used to investigate reaction kinetics.

- (i) The iodine clock reaction with hydrogen peroxide involves the reaction shown.



Deduce **two** possible experimental techniques which could be used to monitor the progress of this reaction.

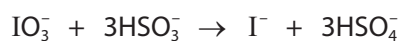
(2)

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- (ii) The iodate(V) reaction has the rate determining step



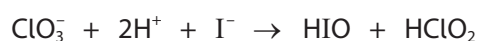
Give a possible reason why this is the slowest step.

(1)

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- (iii) The chlorate(V) reaction has the rate determining step

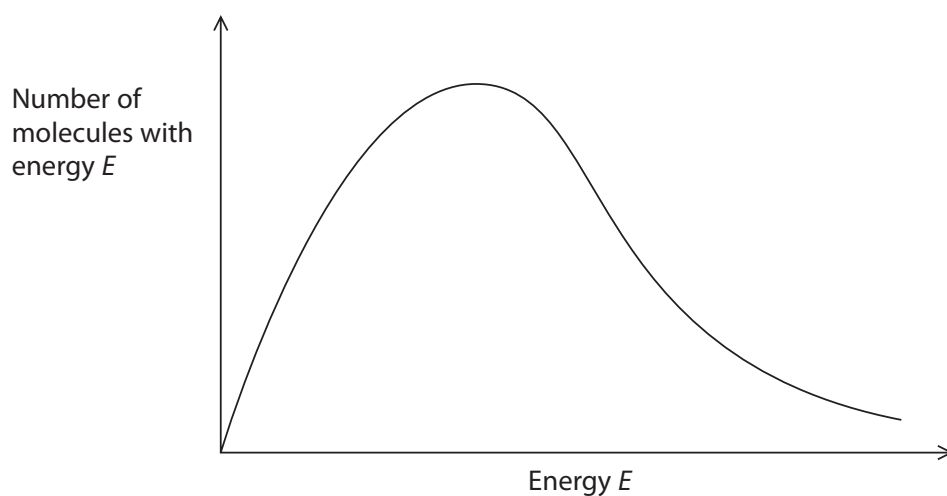


Deduce the rate equation for this iodine clock reaction.

(1)



- (b) The diagram shows a sketch of the Maxwell-Boltzmann curve for the distribution of molecular energies of a reaction mixture at temperature 298 K.



- (i) Add a curve to show the distribution at a temperature of 308 K.

(1)

- (ii) Explain why a temperature rise from 298 K to 308 K results in a large increase in the rate of reaction.

Refer to the Maxwell-Boltzmann distribution in your answer.

(2)

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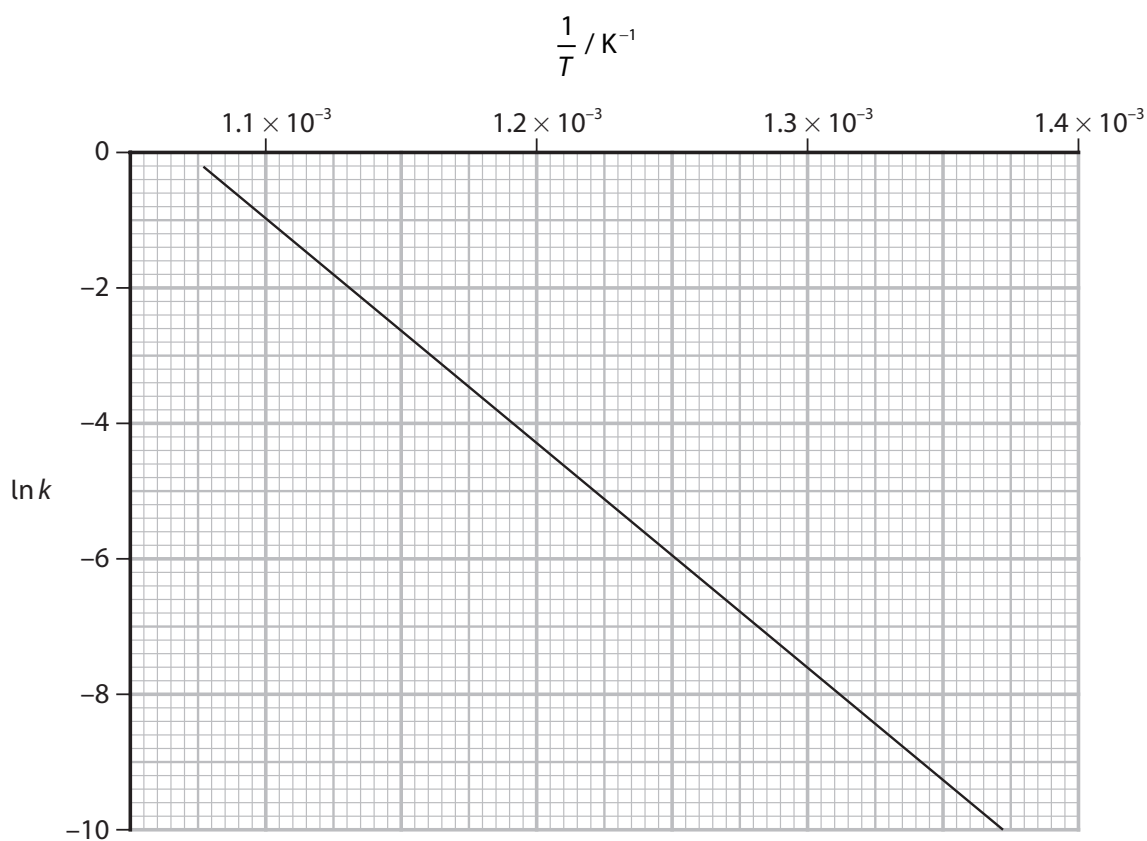
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(c) The Arrhenius equation may be written in a logarithmic or an exponential form.

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

A is a constant.

- (i) The rate constant, k , for the isomerisation of cyclopropane to propene was measured at various temperatures. The data obtained were used to draw the graph shown.



Determine the activation energy, E_a , from the gradient of the graph. Include units in your answer.

(3)

- (ii) At a temperature T , the fraction of molecules with energy equal to or greater than the activation energy is given by the expression

$$\text{fraction of molecules} = e^{-\frac{E_a}{RT}}$$

When a catalyst is added, the activation energy for a reaction is lowered.

Explain, using calculations, why lowering the activation energy from $50\,000\text{ J mol}^{-1}$ to $25\,000\text{ J mol}^{-1}$ at 298 K results in a large increase in the rate of reaction.

(3)

(Total for Question 8 = 13 marks)



9 Halogenoalkanes are hydrolysed to form alcohols.

- (a) The rate constant for the reaction of 1-bromopropane with aqueous sodium hydroxide was determined at five temperatures. Some of the results are given in the table.

Temperature (T) / K	1/Temperature ($1/T$) / K^{-1}	Rate constant (k) / $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$\ln k$
298	3.36×10^{-3}	1.36×10^{-4}	-8.9
	3.29×10^{-3}		-8.4
308	3.25×10^{-3}	3.04×10^{-4}	-8.1
318	3.14×10^{-3}	6.76×10^{-4}	-7.3
328	3.06×10^{-3}	1.23×10^{-3}	-6.7

- (i) Complete the table of data.

(2)

- (ii) Plot a graph of $\ln k$ against $1/T$ and use it to determine the activation energy, E_a , for this reaction in kJ mol^{-1} .

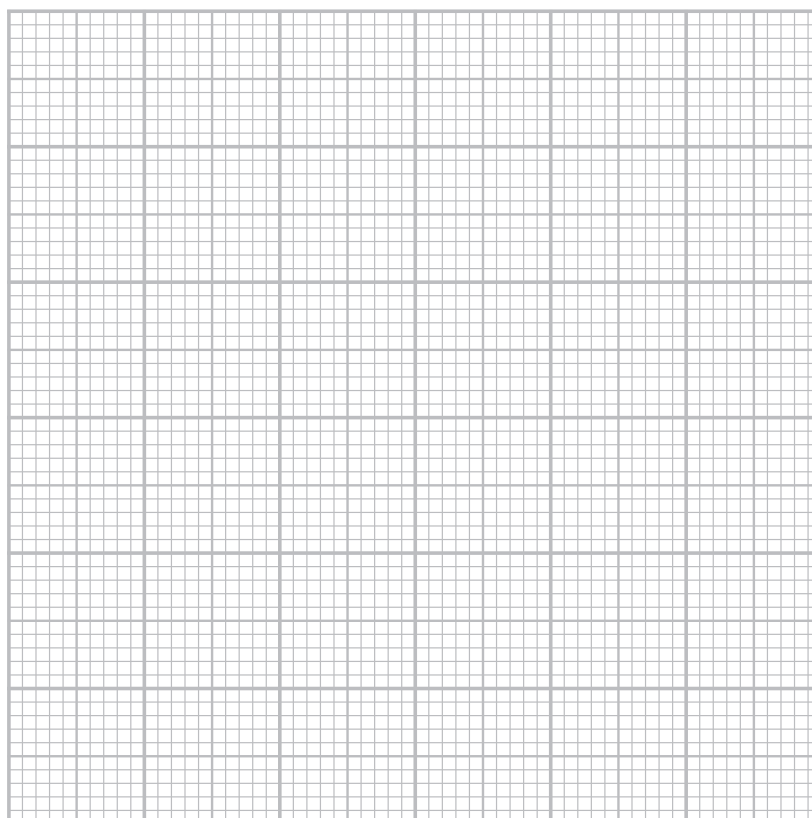
You must show your working on the graph and include the value of the gradient of the line and its units.

The Arrhenius equation can be expressed as

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

(5)





Gradient

Activation energy



- (iii) The rate constant for the reaction of 1-bromopropane with aqueous potassium hydroxide has the units of $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

Explain why it can be deduced that the reaction is second order overall.
Assume that the units of the rate of reaction are $\text{mol dm}^{-3} \text{s}^{-1}$.

(2)

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(b) The rate of reaction for the hydrolysis of 2-bromo-2-methylpropane by aqueous hydroxide ions is independent of the concentration of hydroxide ions.

- (i) Draw the S_N1 reaction mechanism for this hydrolysis.
Include curly arrows and any relevant dipoles and lone pairs of electrons.

(3)

- (ii) State how your mechanism is consistent with the rate of reaction being independent of hydroxide ion concentration.

(1)

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(Total for Question 9 = 13 marks)



MARK SCHEMES

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Question Number	Answer	Additional Guidance	Mark
7(a)	- electrons for double bond, single bond and lone pair around N (1) - rest of electrons on Cl and O (1)	<u>Example of dot-and-cross diagram</u> Allow any combination of dots/crosses/triangles for electrons Allow bond pairs in double bond shown horizontally Ignore lines drawn between atoms to show covalent bonds	(2)

Question Number	Answer	Additional Guidance	Mark
7(b)(i)	- concentration of NO in experiment 2 (1) - concentration of Cl₂ in experiment 3 (1)	<u>Example of calculation</u> 0.244 0.121 Do not award 0.1205 Both values must be to 3SF	(2)



Question Number	Answer	Additional Guidance	Mark
7(b)(ii)	M1 rearrangement of rate equation to find k (1) M2 calculation of k (1) M3 correct units for k (1)	<u>Example of calculation</u> $k = \frac{\text{rate}}{[\text{NO}]^2[\text{Cl}_2]}$ $\frac{1.09 \times 10^{-2}}{(0.122 \times 0.122 \times 0.241)}$ $= 3.03871 = 3.04$ Ignore SF Correct numerical answer for k scores both M1 and M2 $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$ Allow units in any order M3 stand alone mark	(3)

Question Number	Answer	Additional Guidance	Mark
7(b)(iii)	An explanation that makes reference to the following points: k increases because - the catalyst provides an alternative pathway of lower activation energy (1) - so a greater proportion of molecules / more molecules have energy greater than the activation energy (so faster reaction) (1)	Award 'particles' instead of 'molecules' Do not award "atoms" instead of 'molecules'	(2)



Question Number	Answer	Additional Guidance	Mark
7(b)(iv)	An explanation that makes reference to the following points: Catalysts will be less effective because • M1 impurities adsorb onto (catalyst) surface or impurities occupy active sites or impurities bond / bind to (catalyst) surface (1) • M2 impurities prevent bond weakening in the reactants or less surface area (of catalyst) / fewer active sites available for reaction (1) • M3 impurities form strong bonds (to surface) or impurities less likely to desorb (from surface) (1)	Do not award “absorb” for M1 Ignore impurities “react” Allow ‘no active sites available’ Allow ‘impurities remain on surface’	(3)

(Total Question 7 = 12 marks)



Question Number	Answer	Additional Guidance	Mark
6(a)(i)	An answer that makes reference to the following point: use (a much) higher concentration (of propanone and acid (than iodine) (1)	Allow use a high concentration (of propanone and acid) Allow use a (large) excess (of propanone and acid) Ignore use a higher volume of propanone and acid	(1)

Question Number	Answer	Additional Guidance	Mark
6(a)(ii)	An explanation that makes reference to the following point: - to neutralise the acid / H^+ (1) - so that the reactions is quenched / stopped (1)	Allow to remove / react with the acid / catalyst Allow to freeze the reaction Ignore 'slow down'	(2)

Question Number	Answer	Additional Guidance	Mark
6(b)(i)	An answer that makes reference to the following point: $[I_2]$ / concentration (of iodine) is (directly) proportional to the volume of (sodium) thiosulfate / $Na_2S_2O_3$ / $S_2O_3^{2-}$	Allow reverse argument Allow they react in a specific ratio / quoted ratio / 2:1 Do not award equal to or inversely proportional to Do not award I^- / iodide (ions)	(1)



Question Number	Answer	Additional Guidance	Mark
6(b)(ii)	- axes with time on x axis and labelled, including units and suitable scale so that points cover at least half the axes in both directions (1) - points plotted correctly to ($\pm\frac{1}{2}$ square) and straight line through points (1)	Example of graph Allow x axis to start at 5 Allow M2 if axes wrong way around in M1	(2)

Question Number	Answer	Additional Guidance	Mark
6(b)(iii)	(zero order) because graph is a straight line / linear or rate is constant	Allow the gradient is constant Do not award if their graph is a straight horizontal line Ignore through the origin This mark is dependent on the graph being a straight line with a constant gradient	(1)

Question Number	Answer	Additional Guidance	Mark
6(c)(i)	- an equation that has only H^+ and CH_3COCH_3 on the left (1) - correct product (1)	<u>Example of equation</u> $\text{CH}_3\text{COCH}_3 + \text{H}^+ \rightarrow \text{CH}_3\text{C}(\text{O}^+\text{H})\text{CH}_3$ or $\text{CH}_3\text{COCH}_3 + \text{H}^+ \rightarrow \text{CH}_3\text{C}^+(\text{OH})\text{CH}_3$ Allow structural / skeletal formulae e.g. product shown as $\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{O}^+ \\ \text{H} \end{array} \quad \text{or} \quad \begin{array}{c} \text{CH}_3-\text{C}^+-\text{CH}_3 \\ \\ \text{OH} \end{array}$ Allow $\text{C}_3\text{H}_7\text{O}^+$ Do not award $\text{CH}_3\text{COCH}_4^+$	(2)

Question number	Answer	Mark
6(c)(ii)	The only correct answer is A (2.24×10^{-5}) B is incorrect because 3.36×10^{-5} would be the rate if the reaction was zero order with respect to CH_3COCH_3 and first order with respect to H^+ and I_2 C is incorrect because 4.48×10^{-5} would be the rate if the reaction was first order with respect to CH_3COCH_3, H^+ and I_2 D is incorrect because 8.96×10^{-5} would be the rate if the reaction was first order with respect to CH_3COCH_3 and I_2 and zero order with respect to H^+	(1)



Question Number	Answer	Additional Guidance	Mark
6(c)(iii)	An explanation that makes reference to the following points: - rate will be the same (1) - because rate equation only involves propanone and acid / rate equation does not involve iodine / bromine (1)	Do not allow the rate would be constant. Allow the order with respect to bromine would be 0 / bromine would not be in the rate determining step M2 depends on correct M1	(2)

(Total for Question 6 = 12 marks)



Question Number	Answer	Additional Guidance	Mark
9(a)	rate equation	Rate = $k[\text{CH}_3\text{CHO}]^2$ Allow K for k Allow r or R for Rate Allow displayed, semi-structural or skeletal formula for ethanal Do not allow rounded brackets Do not allow missing rate Do not allow "rate equation = "	(1)

Question Number	Answer	Additional Guidance	Mark
9(b)	rate constant units	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ Allow units in any order Do not penalise use of $\text{mol}^- / \text{s}^-$ No TE on incorrect equation in (a)	(1)

Question Number	Answer	Additional Guidance	Mark
9(c)	- calculation of average rate between 0 – 420 s to 1/2 SF (1) - calculation of average rate between 420 – 1260 s to 1/2 SF (1)	<u>Example of calculation</u> Rate = $((0.72 - 0.36) \div (420 - 0)) = 8.5714 \times 10^{-4}$ $= 9 \times 10^{-4} / 8.6 \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$ Rate = $((0.36 - 0.18) \div (1260 - 420)) = 2.1429 \times 10^{-4}$ $= 2 \times 10^{-4} / 2.1 \times 10^{-4} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$ Penalise lack of 1/2 SF once only Ignore units even if incorrect Ignore negative sign in front of rate	(2)

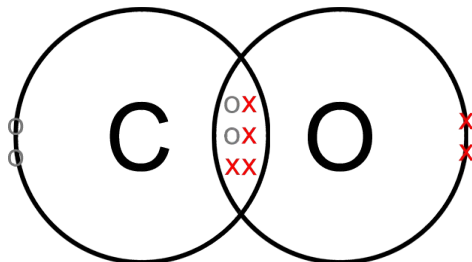
Question Number	Answer	Additional Guidance	Mark
9(d)	An explanation that makes reference to - not zero order because the rate is not constant (1) - not first order because the time taken for the concentration to halve is not equal/ half lives are not constant or not first order because the rate change is not (directly) proportional to the concentration change (1)	Allow the rates calculated in (c) are not the same Allow different times are taken for the concentration to halve Allow the concentration is halved but the rate decreases by a quarter If no other mark awarded allow (1) for reference to justification of second order due to concentration decreasing by $\frac{1}{2}$ but rate decreasing by $\frac{1}{4}$ or due to rate change proportional to concentration squared/ exponential change	(2)

Question Number	Answer	Additional Guidance	Mark
9(e)		Example of suitable graph: Gradient = $\frac{-4.25}{2.00 \times 10^{-4} \text{ K}^{-1}} = -21,250 \text{ K}$ $\frac{-E_a}{R} = -21,250$ so $E_a = 21,250 \times R = 176587.5 \text{ J mol}^{-1}$ $= \textcircled{+} 177 \text{ kJ mol}^{-1}$	(7)

	• calculation of $1/T$ value (1) • calculation of $\ln k$ value (1) • axes: correct way round and in the correct direction, labelled with units, suitable scale (1) • all points plotted correctly, with best-fit straight line (1) • calculation of gradient (1) • sign and units of gradient (1) • use of gradient to calculate activation energy (1)	1.27×10^{-3} -1.07 Penalise values not to 3 SF once only in M1 and M2 Accept use of 1×10^3 or 1×10^{-3} on x axis Do not award 1/t for 1/T Plotted points must cover at least $\frac{1}{2}$ the graph paper on each axis Allow ± 1 square Gradient = (-) 21250 Allow ± 900 - and K $E_a = -(-21250 \times 8.31) / 1000$ = (+) 177 (kJ mol⁻¹) Allow ± 7 Allow 177000 J mol⁻¹ ± 7000 Ignore SF except 1 SF Do not penalise mol⁻¹ TE on numerical value of gradient Final answer must be positive	
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(Total Question 9 = 13 marks)



Question Number	Answer	Additional Guidance	Mark
6(a)	3 bond pairs showing triple bond, one of which must be a dative bond (1) - both lone pairs on C and O (1)	<u>Example of dot and cross diagram:</u>  Allow 1 mark if correct number of electrons shown, but all as crosses or all as dots Ignore lines showing covalent bonds	(2)

Question Number	Answer	Additional Guidance	Mark
6(b)	- Expression of numerator and denominator for atom economy (1) - evaluation (1)	<u>Example of calculation</u> $28 \div [28 + 106] (\times 100) / [28 \div 134] (\times 100)$ $20.896 = 20.9\%$ Ignore SF except 1 SF Allow TE for M2 for 1 M_r error in M1 Allow 1 mark for $(106 \div 134) \times 100 = 79.1\%$	(2)

Question Number	Answer	Additional Guidance	Mark												
6(c)(i)	<table border="1"> <thead> <tr> <th>Temperature / K</th><th>Rate / mol dm⁻³ s⁻¹</th><th>1/Temperature</th><th>ln rate</th></tr> </thead> <tbody> <tr> <td>700</td><td>0.0108</td><td>1.43×10^{-3}</td><td>-4.53</td></tr> <tr> <td>850</td><td>4.90</td><td>1.18×10^{-3}</td><td>1.59</td></tr> </tbody> </table>	Temperature / K	Rate / mol dm ⁻³ s ⁻¹	1/Temperature	ln rate	700	0.0108	1.43×10^{-3}	-4.53	850	4.90	1.18×10^{-3}	1.59	values must be to at least 3SF Allow -4.5282 1.1765×10^{-3}	(1)
Temperature / K	Rate / mol dm ⁻³ s ⁻¹	1/Temperature	ln rate												
700	0.0108	1.43×10^{-3}	-4.53												
850	4.90	1.18×10^{-3}	1.59												

Question Number	Answer	Additional Guidance	Mark
6(c)(ii)	- recognition that (difference in ln rate) / (difference in $1/T$) = $-E_a / R$ (1) - calculation of $-E_a / R$ (1) - calculation of E_a with correct units (1)	<u>Example of calculation</u> $-6.12 / 2.5 \times 10^{-4}$ Can be subsumed within M2 $= -24480 \text{ (K)}$ $24480 \times 8.31 = (+) 203428.8 \text{ J mol}^{-1}$ $= (+) 203000 \text{ J mol}^{-1}$ $= (+) 203 \text{ kJ mol}^{-1}$ Ignore SF final answer between 200 -204 kJ mol ⁻¹ with no working scores (3)	(3)



Question Number	Answer	Additional Guidance	Mark
6(d)(i)	order with respect to Hb = 1		(1)

Question Number	Answer	Additional Guidance	Mark
6(d)(ii)	- order with respect to CO = 1 - justification	(1) standalone mark (1) Either using experiments 1 and 3 the concentration of Hb goes up by a factor of 1.56 and the concentration of CO doubles and the rate goes up by a factor of 3.12 Or using experiments 2 and 3 the concentration of Hb goes down by a factor of 0.78 but the rate increases by a factor of 1.56 so doubling the concentration of CO means doubling the rate M2 dependent on M1	(2)

Question Number	Answer	Additional Guidance	Mark
6(d)(iii)	rate equation	<u>Example of rate equation</u> $\text{rate} = k[\text{Hb}][\text{CO}]$ allow e.g R / r for rate and K for k Allow expressed in terms of k Allow TE from 6(d)(i) and 6(d)(ii) Note – must be consistent with 6(d)(i) and 6(d)(ii)	(1)

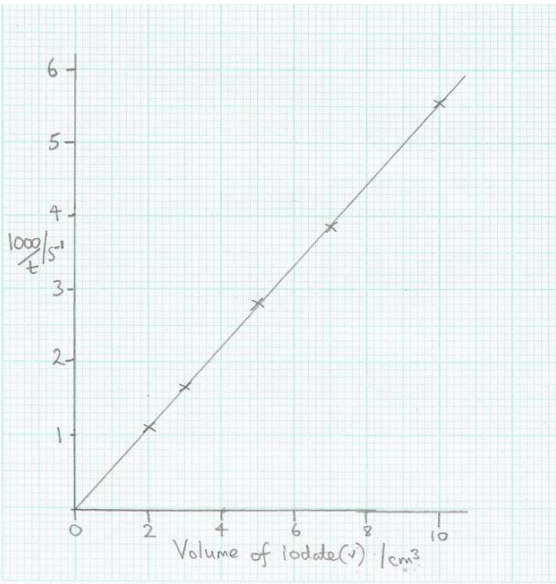
Question Number	Answer	Additional Guidance	Mark
6(d)(iv)	- rearrangement of rate equation to find k (1) - calculation of k (1) - correct units of k (1)	<u>Example of calculation</u> $k = \text{rate} / [\text{Hb}][\text{CO}]$ $8.20 \times 10^{-7} / (2.09 \times 10^{-6} \times 1.40 \times 10^{-6})$ $= 280246 = 280000$ Ignore SF except 1 SF $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ Allow units in any order Allow use of data from experiments 2 or 3 Correct answer including units with no working scores 3 marks Allow TE on rate equation from (d)(iii) No TE for mistake with rate equation within (d)(iv) e.g. rearrangement error	(3)

(Total Question 6 = 15 marks)



Question Number	Acceptable Answer	Additional Guidance	Mark
9(a)	A statement that makes reference to the following: The chance of five or more ions colliding in the rate determining step is negligible	Allow 'at the same time' for the RDS	(1)

Question Number	Acceptable Answer	Additional Guidance	Mark
9(b)(i)	A statement that makes reference to the following: So that the volume of iodate(V) ions is proportional to the concentration.	Allow the volume of iodate(V) ions can be used instead of the concentration in plotting the graph. Ignore reference to "fair tests".	(1)

Question Number	Acceptable Answer	Additional Guidance	Mark
9(b)(ii)	- calculation of all three $1000/t$ values (1) - axes: correct way round, labelled and including units (1) - suitable scale (1) - all points plotted correctly, with best-fit straight line through the origin (1)	(5.56) 3.85, 2.80, 1.65, (1.11) Do not award 2.8 or ≥ 3SF Do not award use of T for t Plotted points must cover at least $\frac{1}{2}$ the graph paper on each axis Allow $\pm \frac{1}{2}$ square Ignore plotting of experiment 6 Exemplar graph 	(4)

Question Number	Acceptable Answer	Additional Guidance	Mark
9(b)(iii)	An answer that makes reference to the following: - first order (with respect to iodate(V) ions) (1) - because straight line goes through the origin / rate is (directly) proportional to concentration (1)	Mark independently Allow "volume" for "concentration" Do not award references of proportionality to time Ignore references to half life	(2)

Question Number	Acceptable Answer	Additional Guidance	Mark
9(c)(i)	- value of rate constant to 2 or 3 SF (1) - units of rate constant (1)	<u>Example of calculation:</u> (Rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$ so $k = \text{rate} \div ([\text{H}_2\text{O}_2][\text{I}^-])$ $= 1.24 \times 10^{-3} \div (1.50 \times 10^{-3} \times 2.10 \times 10^{-3})$ $= 393.65\dots$ $= 390/394$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ Accept units in any order No TE on incorrect rate equation	(2)

Question Number	Acceptable Answer	Additional Guidance	Mark
9(c)(ii)	An explanation that makes reference to - starch is an indicator (to react with the iodine) (1) - the time taken for the formation of the blue-black complex (can be used to calculate the reaction rate) (1)	Do not award references to iodide/I⁻ Allow Reacts with iodine/produces a blue-black colour when the reaction is complete. Allow Changes colour when all the thiosulfate is used up. Allow indication of 'time taken'	(2)



Question Number	Acceptable Answer	Additional Guidance	Mark
9(d)(i)	- calculation of gradient of straight line (1) - numerical value of E_a (1) - sign and units (1)	<u>Example of calculation</u> Gradient = -19500 Allow ± 500 $-E_a = -19500 \times 8.31 / 1000$ $= 162 \pm 5$ + and kJ mol^{-1} Accept $+162000 \text{ Jmol}^{-1}$ Final answer with or without working scores (3) Allow TE for incorrect gradient as long as the final value is not negative Ignore SF except 1SF	(3)

Question Number	Acceptable Answer	Additional Guidance	Mark
9(d)(ii)	An answer that makes reference to the following: (Reason) anomalous point	Allow description of Allow 'outlier'	(1)

(Total for Question 9 = 16 marks)



Question Number	Answer	Additional Guidance	Mark
9(a)	Correct answer to 2 SF	(Four half-lives to decrease 600 g to 37.5 g so 4×14 mins) = 56 (mins) Penalise wrong units, e.g. "m"	

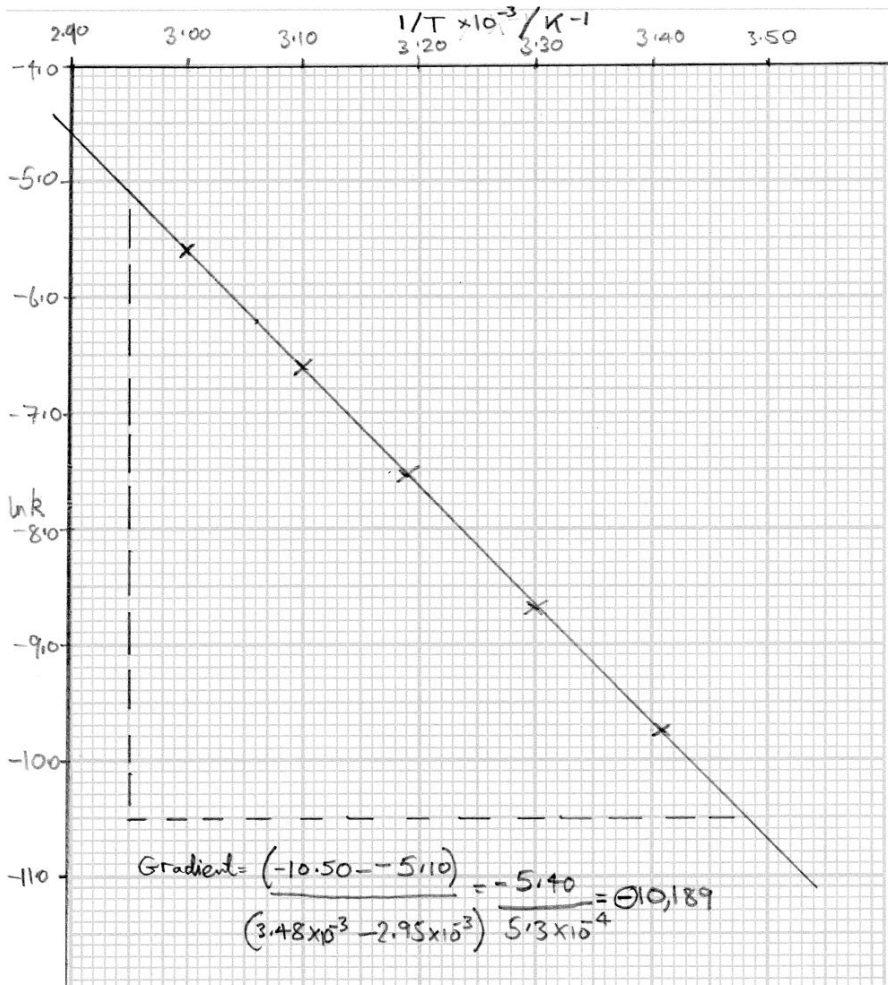
Question Number	Answer	Additional Guidance	Mark
9(b)(i)	Reaction Orders: • X First/1 (1) • Y Second/2 (1) • Z Zero/0 (1)	Allow "none"/"no order"	(3)



Question Number	Answer	Additional Guidance	Mark
9(b)(ii)	Marking point 1 - Rate = $k[X][Y]^2[Z]^0$ Marking point 2 - rearrangement of rate expression Marking point 3 - calculation of value for k to 2/3 SF Marking point 4 - units $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$	Reactants can be in any order Z does not have to be included in the rate equation TE from (b)(i) which will apply for all four marking points (1) (1) <u>Example of calculation:</u> $k = \text{rate} / [X][Y]^2$ (1) $k = \frac{2.17 \times 10^{-6}}{0.00100 \times 0.00300^2}$ = 241.11 = 241/240 Any 'run' can be used No TE on incorrect rearrangement (1) Allow units in any order Correct answer without working and with correct units to 2/3 SF scores marking points 2, 3 and 4	(4)

Question Number	Answer	Mark
9(c)(i)	The only correct answer is D (Fourth) A is not correct because this is the individual reaction order with respect to bromate(V) ions and with respect to bromide ions but is not the overall reaction order B is not correct because this is the reaction order with respect to hydrogen ions but is not the overall reaction order C is not correct because this is the number of species in the rate equation but is not the overall reaction order	(1)

Question Number	Answer	Additional Guidance	Mark
9(c)(ii)	- rearrange rate equation so $[\text{Br}^-] =$ (1) - calculation of value to 2/3 SF (1)	Example of calculation: $[\text{Br}^-] = \frac{\text{rate}}{k [\text{BrO}_3^-][\text{H}^+]^2}$ $= 0.255/0.26 \text{ (mol dm}^{-3}\text{)}$ Correct answer without working to 2/3 SF scores 2 marks If units given then must be correct No TE on incorrect rearrangement	(2)

Question Number	Answer	Additional Guidance	Mark
9(d)	Example of suitable graph  Gradient = $\frac{(-10.50 - -5.10)}{(3.48 \times 10^{-3} - 2.95 \times 10^{-3})} = -5.40 = -10,189$		(7)

	• calculation of all three $1/T$ values $\times 10^{-3}$ (1) • calculation of all three $\ln k$ values (1) • axes: correct way round, labelled, suitable scale (1) • all points plotted correctly, with best-fit straight line (1) • calculation of gradient with sign (1) • units of gradient (1) • use of gradient to calculate activation energy (1)	(3.41), 3.30, 3.19, 3.10, (3.00) (−9.75), −8.70, −7.55, −6.60, (−5.58) Allow omission of end zero Penalise more than 3SF once only Plotted points must cover at least $\frac{1}{2}$ the graph paper on each axis Do not award 1/t Allow $\pm \frac{1}{2}$ square Gradient = − 10200 Allow ± 500 Allow this mark if the value is seen in the E_a calculation K $E_a = 10200 \times 8.31 / 1000$ $= (+) 84.8 \text{ (kJ mol}^{-1}\text{)}$ Final answer must be positive and in the range (+) 80.6 – 88.9 (kJ mol^{−1}) Allow value given in J mol^{−1} but then these units are essential Ignore SF for gradient and activation energy values	
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(Total for Question 9 = 18 marks)

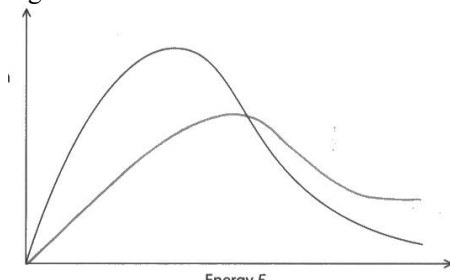
Question Number	Answer	Additional Guidance	Mark
8(a)(i)	An answer that makes reference to any two of the following points: • colorimetry (1) • (electrical) conductivity (1) • quenching and titration with thiosulfate (1) • quenching with excess carbonate and titration with acid (1) • add fixed amount of sodium thiosulfate and a few drops of starch solution and find the time until a blue-black colour is seen (1)	Ignore just colour change Do not award calorimetry Allow cooling for quenching COMMENT Allow cooling and titration with alkali Allow dilatometry Ignore pH	(2)

Question Number	Answer	Additional Guidance	Mark
8(a)(ii)	An answer that makes reference to following point: • negative species / ions will repel (each other) or unlikely that four species / ions will simultaneously combine		(1)



Question Number	Answer	Additional Guidance	Mark
8(a)(iii)	rate = $k[\text{ClO}_3^-][\text{H}^+]^2[\text{I}^-]$	Accept species in any order Allow rate = $k[\text{ClO}_3^-]^1[\text{H}^+]^2[\text{I}^-]^1$ Allow K for k Allow r/R for rate Ignore state symbols even if incorrect Do not award missing charges Do not award just $k[\text{ClO}_3^-][\text{H}^+]^2[\text{I}^-]$	(1)



Question Number	Answer	Additional Guidance	Mark
8(b)(i)	(increase in temperature) means peak shifts to the right and is lower	Do not award the line crossing the other line twice Do not award the curve crossing the x-axis Do not award a line which goes up on the right or that plateaus high above the x axis, e.g. 	(1)

Question Number	Answer	Additional Guidance	Mark
8(b)(ii)	An explanation that makes reference to the following points: - the area under the curve to the right of the E_a line has increased (substantially) (1) - so that a greater proportion of particles exceed the activation energy (1)	Allow answer/shading on the M-B sketch Allow more molecules/particles have energy greater than the activation energy Do not award M2 if there is any reference to the activation energy decreasing	(2)



Question Number	Answer	Additional Guidance	Mark
8(c)(i)	- gradient of slope expression (1) - calculation of gradient (1) - calculation of activation energy with units (1)	<u>An example of calculation</u> Allow gradient = $\Delta y \div \Delta x$ or equivalent expression with values Gradient = $((-8 - -2) \div (1.31 \times 10^{-3} - 1.13 \times 10^{-3}))$ $= (-) 33\,333 / (-) 33\,300 / (-) 33\,000 \text{ (K)}$ Allow range $(-) 32475$ to $(-) 34159$ $E_a = -(-33\,333 \times 8.31 =) (+)276\,997 \text{ J mol}^{-1} / (+)277\,000 \text{ J mol}^{-1} /$ $(+)276.997 \text{ kJ mol}^{-1} / (+)277 \text{ kJ mol}^{-1}$ Allow any answer in the range 270 to 284 Ignore SF except 1 SF Do not award M3 if E_a negative TE from M2 to M3	(3)



Question Number	Answer	Additional Guidance	Mark
8(c)(ii)	- calculation of expression with uncatalysed E_a - calculation of expression with catalysed E_a - about 24000 (times) increase and in the fraction of molecules now able to react	(1) $e^{-\frac{E_a}{RT}} = e^{-\frac{50000}{8.31 \times 298}} = 1.70 \times 10^{-9}$ (1) $e^{-\frac{E_a}{RT}} = e^{-\frac{25000}{8.31 \times 298}} = 4.13 \times 10^{-5}$ Increase = $(4.13 \times 10^{-5} \div 1.70 \times 10^{-9}) = 24276$ (1) Allow reference to $4.13 \times 10^{-5} \gg 1.70 \times 10^{-9}$ resulting in many more molecules able to react Ignore just more molecules or bigger fraction Allow a calculation involving the determination of the difference/ratio between the two values	(3)

(Total Question 8 = 13 marks)



Question Number	Answer	Additional Guidance	Mark
9(a)(i)	An answer that makes reference to the following points: • temperature value (1) • rate constant value (1)	304 (K) 2.25×10^{-4} Penalise non-3SF values once only 303.95 and 2.2487×10^{-4} scores (1)	(2)



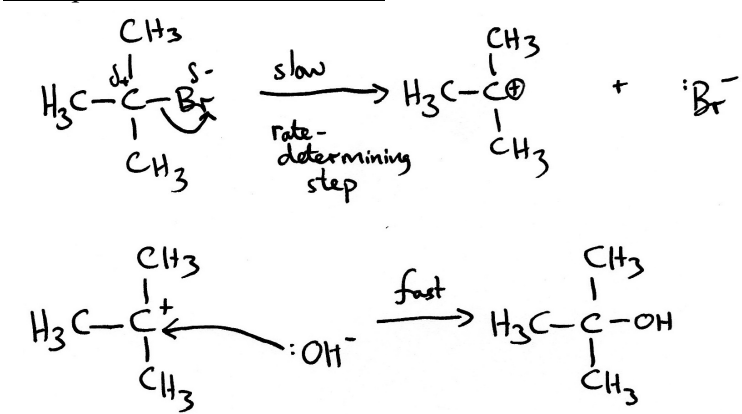
Question Number	Answer	Additional Guidance	Mark
9(a)(ii)		Example of suitable graph $\ln k$ $a = -9 - (-6.5) = -2.5$ $b = 3.37 \times 10^{-3} - 3.03 \times 10^{-3} = 3.4 \times 10^{-4}$ $\text{Gradient} = \frac{-2.5}{3.4 \times 10^{-4}} = -7353 \text{ K}$ $E_a = -7353 \times -8.31 = 61,103 \text{ J mol}^{-1}$ $\approx \underline{\underline{61.1 \text{ kJ mol}^{-1}}}$	(5)

	- axes: correct way round and in the correct direction, labelled with units (1) - all points plotted correctly, with best-fit straight line and suitable scale (1) - calculation of gradient (1) - sign and units of gradient (1) - use of gradient to calculate activation energy (1)	Do not award $1/t$ for $1/T$ Allow $\pm \frac{1}{2}$ square Plotted points must cover at least $\frac{1}{2}$ the graph paper on each axis Gradient = $(-)$ 7353 Allow ± 400 – and K Stand alone mark $E_a = -(-7353 \times 8.31) \div 1000$ $= (+) 61.1 \text{ (kJ mol}^{-1}\text{)}$ Allow ± 4 If no units, assume kJ mol^{-1}. Allow answer in J mol^{-1} providing units given Ignore SF except 1 SF TE on numerical value of gradient Do not award negative final value	
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Question Number	Answer	Additional Guidance	Mark
9(a)(iii)	An explanation that makes reference to the following points: - rate $\div k$ gives $\text{mol}^2 \text{dm}^{-6}$ (1) - which is units of concentration squared (meaning second order) (1) Alternative approach units of concentration squared (as a second order reaction) (1) - rate $\div [\text{mol}^1 \text{dm}^{-3}]^2 = k$ (1)		(2)



Question Number	Answer	Additional Guidance	Mark
9(b)(i)		<u>Example of suitable mechanism</u>  Allow structural/skeletal or combination (step 1) - dipole on C–Br bond and curly arrow from bond to, or just beyond the Br (1) - structure of carbocation intermediate and Br[–] (1) (step 2) - curly arrow from lone pair on oxygen of hydroxide ion to the positively charged carbon of the intermediate (1) If S_N2 given, award M1 only if correct dipole and curly arrow correct Ignore missing lone pair on Br[–] Br[–] can be shown in either the intermediate stage or the final products	(3)

Question Number	Answer	Additional Guidance	Mark
9(b)(ii) Clip with (b)(i)	An answer that makes reference to the following point: • step 1 identified as RDS and hydroxide ions do not appear in step 1	Note: Look at the mechanism in (b)(i) for evidence of the correct RDS, but must state hydroxide ions do not appear in step 1 Accept slow step	(1)

(Total for Question 9 = 13 marks)

