Question - 01

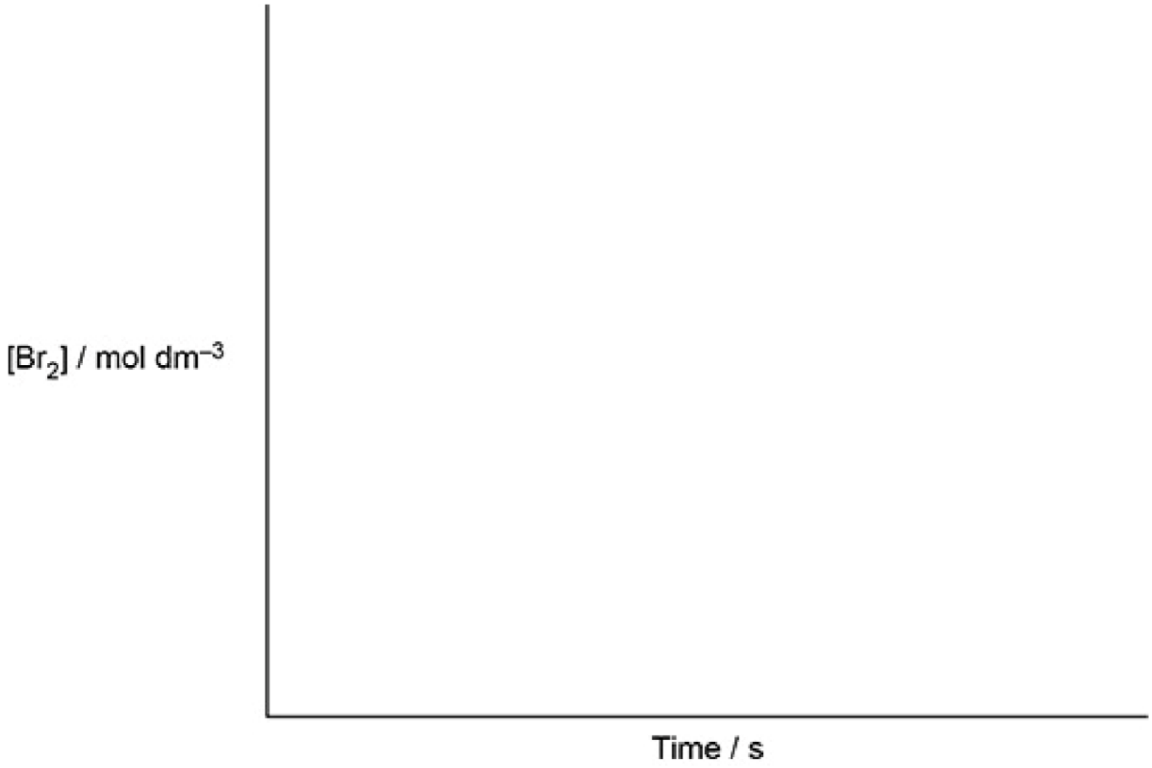
Propanone reacts with bromine in alkaline conditions.

$$CH_3COCH_3 + Br_2 + OH^- \rightarrow CH_3COCH_2Br + Br^- + H_2O$$

The rate equation for this reaction is

$$Rate = k\,[CH_3COCH_3]\,[OH^-]$$

(a) Sketch a graph on the axes provided to show how, at constant temperature, the concentration of bromine changes during this reaction.



(1)

(b) The table shows the initial rate of this reaction for experiments using different mixtures containing propanone, bromine and hydroxide ions.

Experiment	**$[CH_3COCH_3]$ / mol dm^{-3}**	**$[Br_2]$ / mol dm^{-3}**	**$[OH^-]$ / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
1	1.50×10^{-2}	2.50×10^{-2}	2.50×10^{-2}	2.75×10^{-11}
2	1.50×10^{-2}	2.50×10^{-2}		8.25×10^{-11}
3	3.75×10^{-3}	5.00×10^{-2}	1.00×10^{-1}	

Complete the table above.

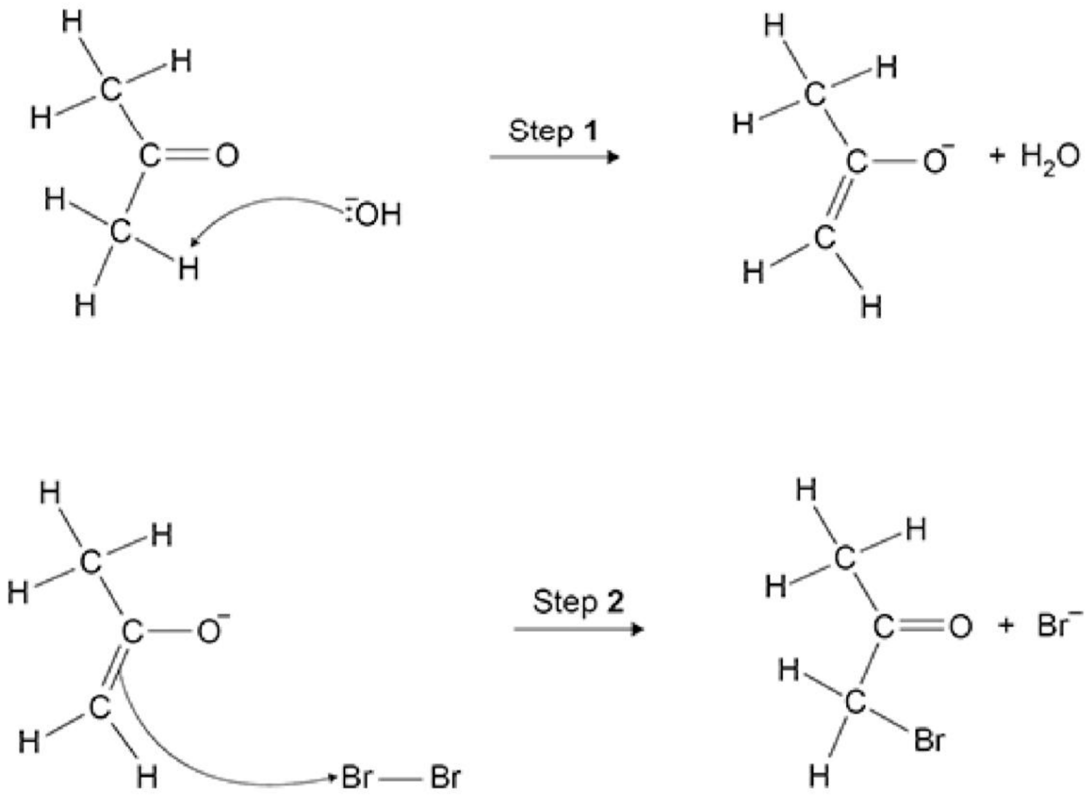
Use the data from experiment **1** to calculate the rate constant *k* for this reaction.

Give the units for the rate constant.

k ______________________ Units ______________________

(5)

(c) The figure below shows an incomplete mechanism for this reaction.



Complete the mechanism in the figure by adding four curly arrows and any relevant lone pair(s) of electrons.

(4)

(d) Use evidence from the rate equation to explain why Step **1** is the rate determining step.

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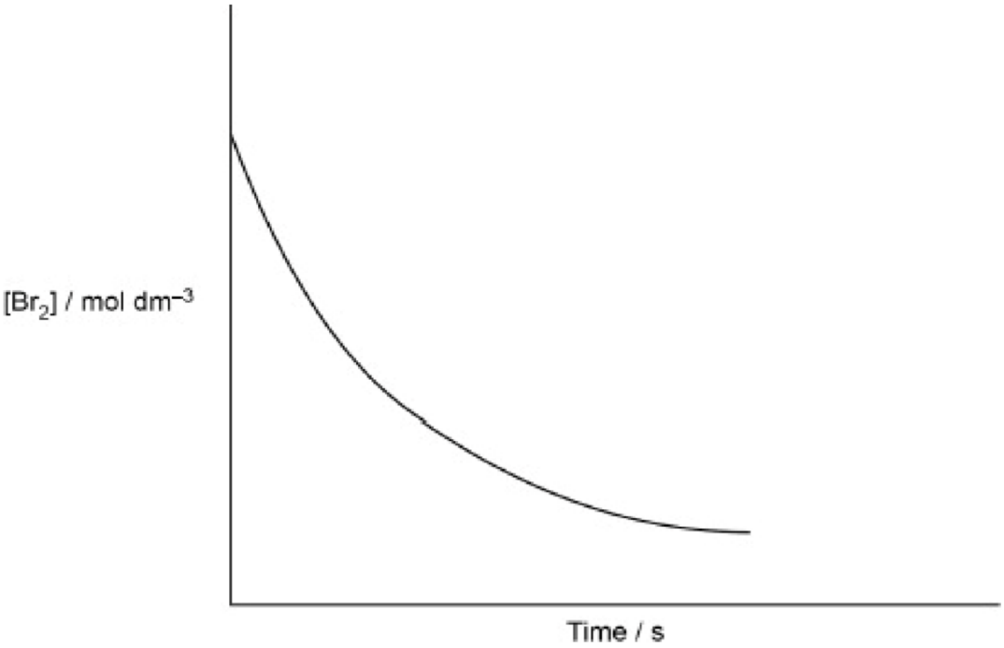
(1)

(a) Curve e.g.



Curve with decreasing gradient

1

(b) **M1** For [OH^-] = 7.50 × 10^{-2}

M2 For rate = 2.75 × 10^{-11}

M3 $k = \frac{\text{rate}}{[CH_3COCH_3][OH^-]}$

M3 For rearranging rate equation

OR

$$k = \frac{2.75 \times 10^{-11}}{(1.5 \times 10^{-2}) \times (2.5 \times 10^{-2})}$$

For inserting correct numbers in rearranged equation

M4 k = 7.3(3) × 10^{-8}

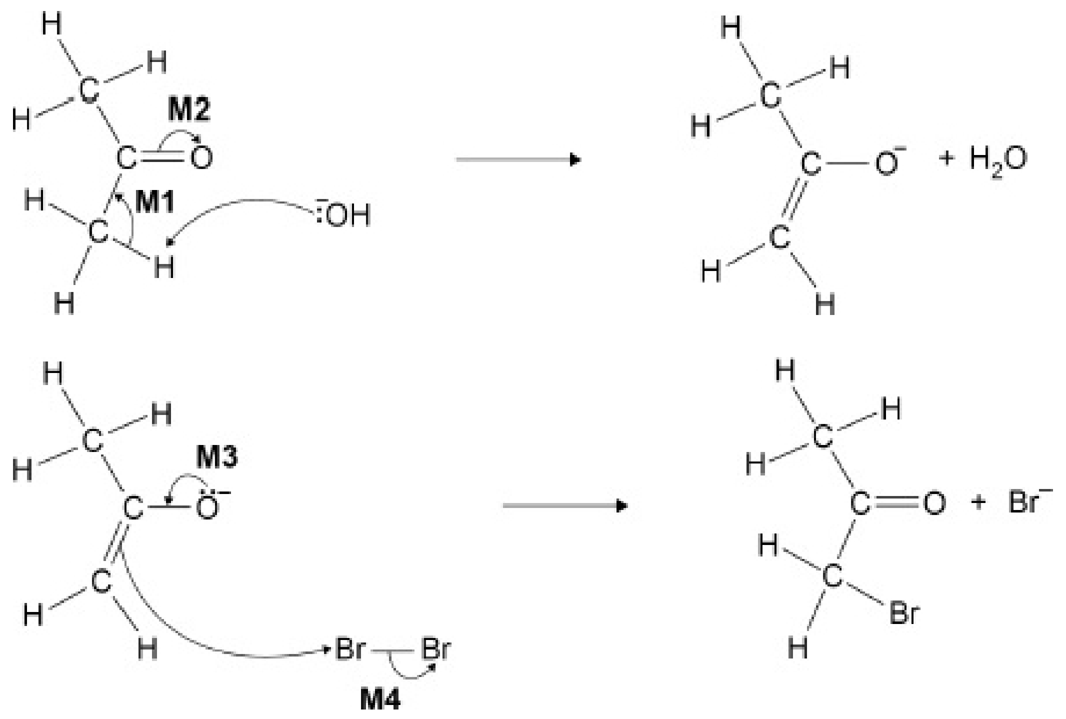
M5 Units = $mol^{-1}dm^3s^{-1}$

If rearrangement upside down lose M3 but can score M4 for 1.36 × 10^7 as ECF

M5 for mol dm^{-3} s as ECF

5

(c)



M1 Arrow from C-H bond to C-C

M2 Arrow from C=O bond to O

M3 Arrow from lone pair on O to C-O bond

M4 Arrow from Br-Br bond to Br

Dipoles must be correct if shown for M4

4

(d) Step 1 includes CH_3COCH_3 <u>and</u> OH^- and these are also in the rate equation

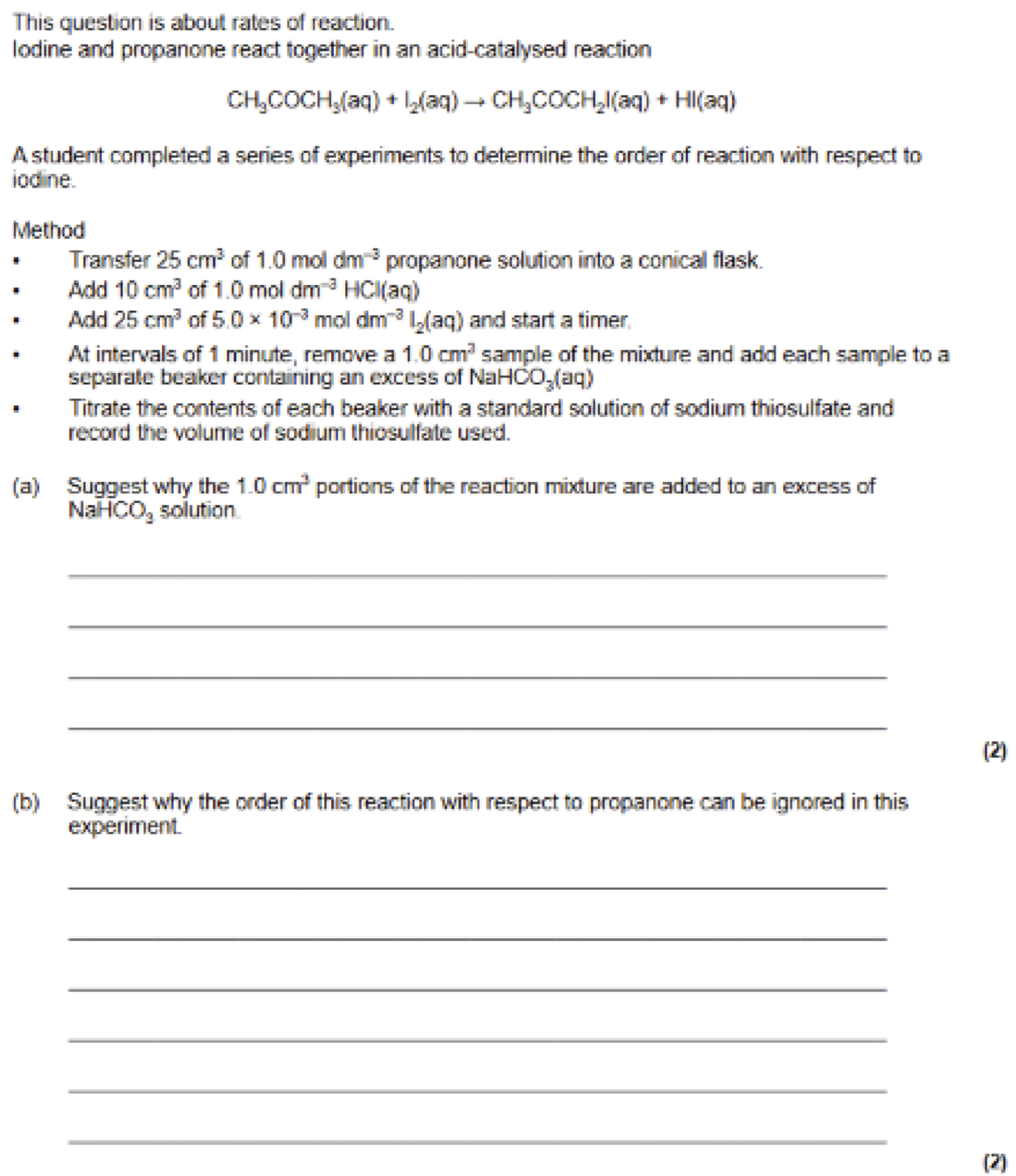
OR

Step 1 contains all the species in the rate equation

Br_2 not in step 1 <u>and</u> not in rate equation so it has to be step 1

1

Question - 02



This question is about rates of reaction.
Iodine and propanone react together in an acid-catalysed reaction

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

A student completed a series of experiments to determine the order of reaction with respect to iodine.

Method

- Transfer 25 cm^3 of 1.0 mol dm^{-3} propanone solution into a conical flask.
- Add 10 cm^3 of 1.0 mol dm^{-3} HCl(aq)
- Add 25 cm^3 of 5.0×10^{-3} mol dm^{-3} $I_2(aq)$ and start a timer.
- At intervals of 1 minute, remove a 1.0 cm^3 sample of the mixture and add each sample to a separate beaker containing an excess of $NaHCO_3(aq)$
- Titrate the contents of each beaker with a standard solution of sodium thiosulfate and record the volume of sodium thiosulfate used.

(a) Suggest why the 1.0 cm^3 portions of the reaction mixture are added to an excess of $NaHCO_3$ solution.

(2)

(b) Suggest why the order of this reaction with respect to propanone can be ignored in this experiment.

(2)

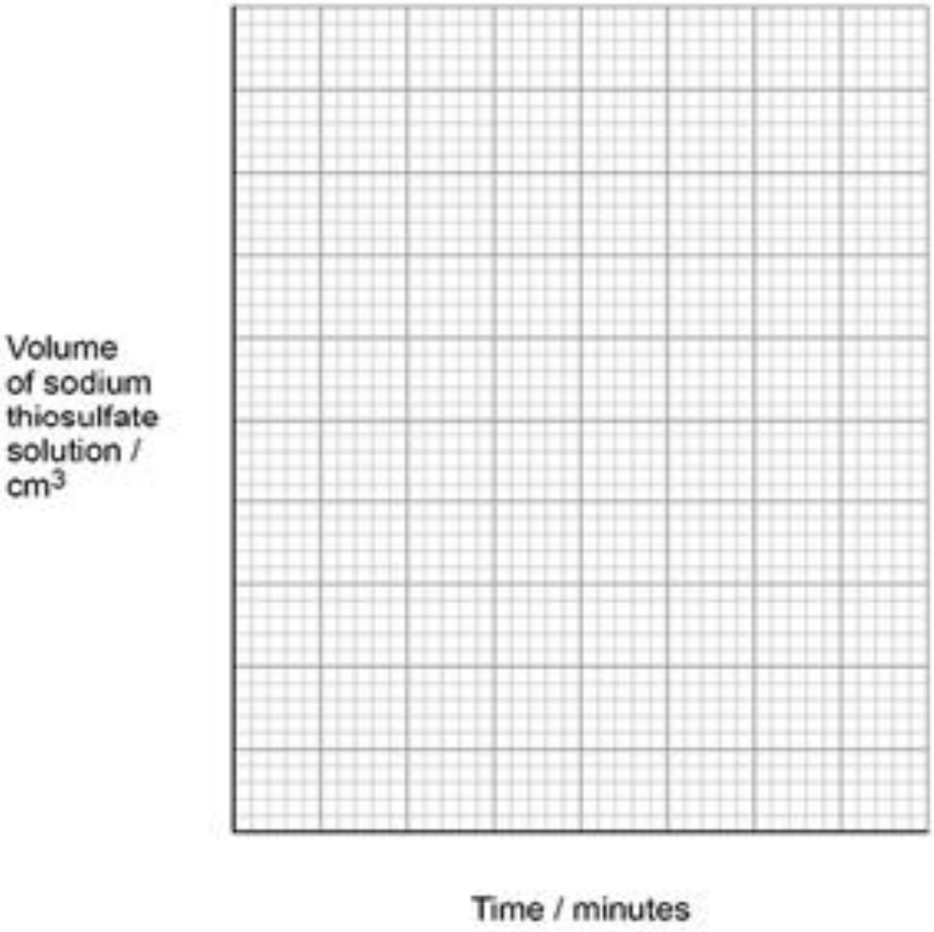
The volume of sodium thiosulfate solution used in each titration is proportional to the concentration of iodine in each beaker.

The table below shows the results of the experiment.

Time / minutes	**Volume of sodium thiosulfate solution / cm^3**
1	41
2	35
3	24
4	22
5	16
6	10

(c) Use the results in the table above to draw a graph of volume of sodium thiosulfate solution against time.

Draw a line of best fit.



(3)

(d) Explain how the graph shows that the reaction is zero-order with respect to iodine in the reaction between propanone and iodine.

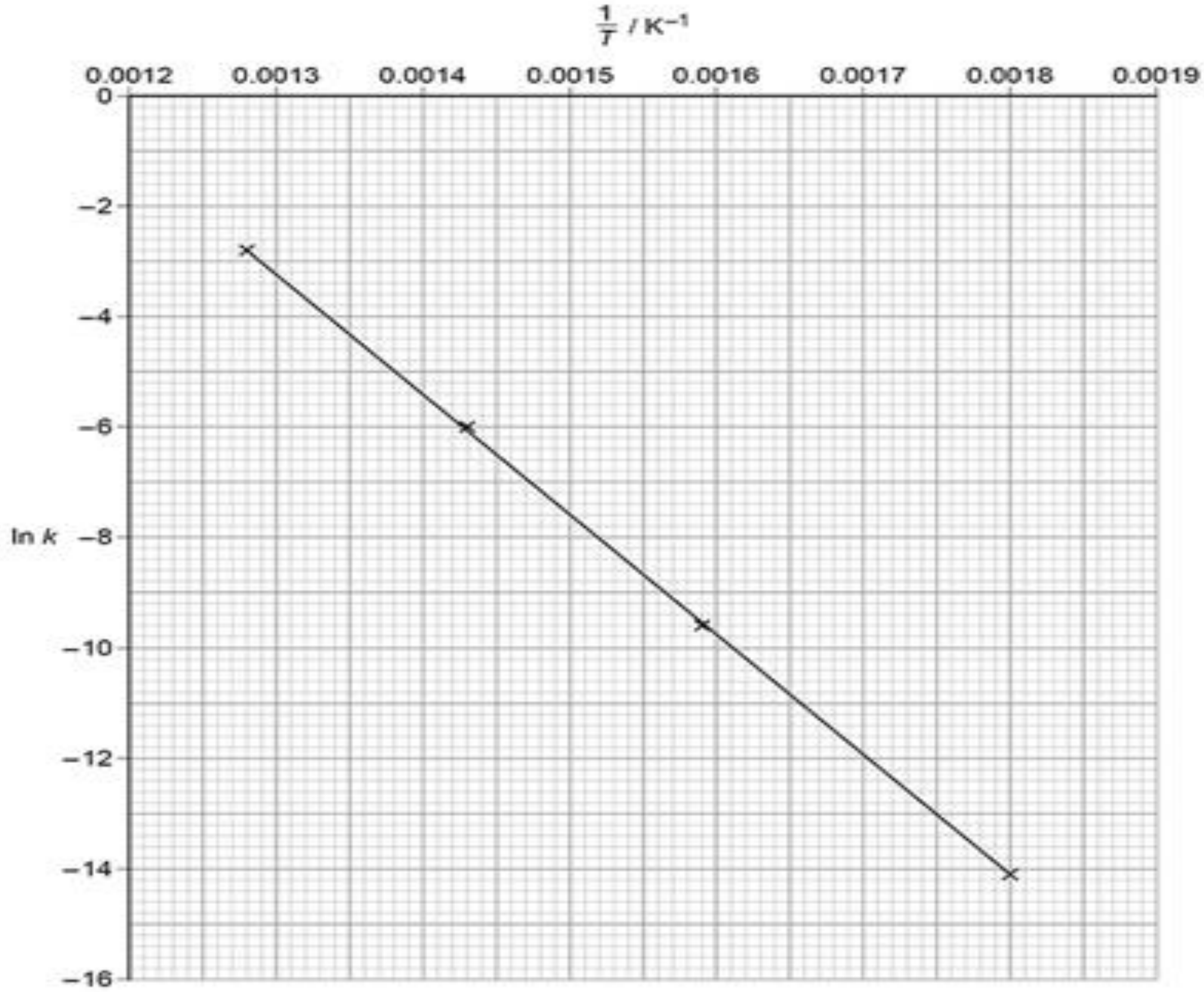
(2)

(e) The Arrhenius equation can be written as

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

The figure below shows a graph of ln k against $\frac{1}{T}$ for the reaction

$$2\,HI(g) \rightarrow H_2(g) + I_2(g)$$



Use the figure above to calculate a value for the activation energy (E_a), in kJ mol^{-1}, for this reaction.

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

(a) The sodium hydrogencarbonate solution neutralises the acid (catalyst)

M1

So stops the reaction

M2

(b) The concentration/amount of propanone is much larger than/200 times larger than the concentration/amount of iodine

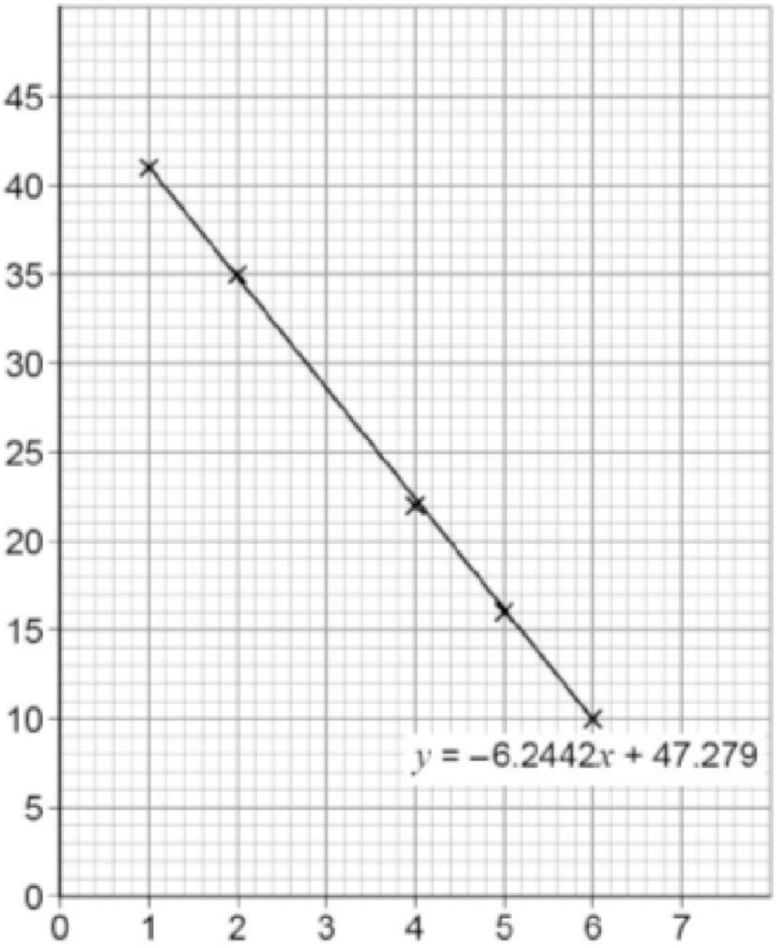
M1

<u>Concentration</u> of propanone is (almost) constant

The change in concentration in propanone is negligible

M2

(c)



M1

Suitable axes (plotted points must take up at least half of the grid)

M2

For all points correctly plotted to ± $^1/_2$ small square

For straight line of best fit which avoids the anomalous plot M1

M3

(d) The graph is a straight line / has a constant gradient

M1

So the rate of reaction does not change as the concentration (of iodine) changes / the iodine is being used up at a constant rate.

Correct rate vs conc graph scores M2

M2

(e) Gradient = (−14.1 − −2.8) / (0.00180 − 0.00128)
= −11.3 / 0.00052
= −21731

Allow -21330 to -22130

M1

Gradient = $-E_a / R$

$-E_a$ = their answer x 8.31 (= 180583 J mol^{-1})

M2

E_a = M2 ÷ 1000 (= 181 kJ mol^{-1})

M3

Hydrogen peroxide solution decomposes to form water and oxygen.

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

The reaction is catalysed by manganese(IV) oxide.

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

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

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

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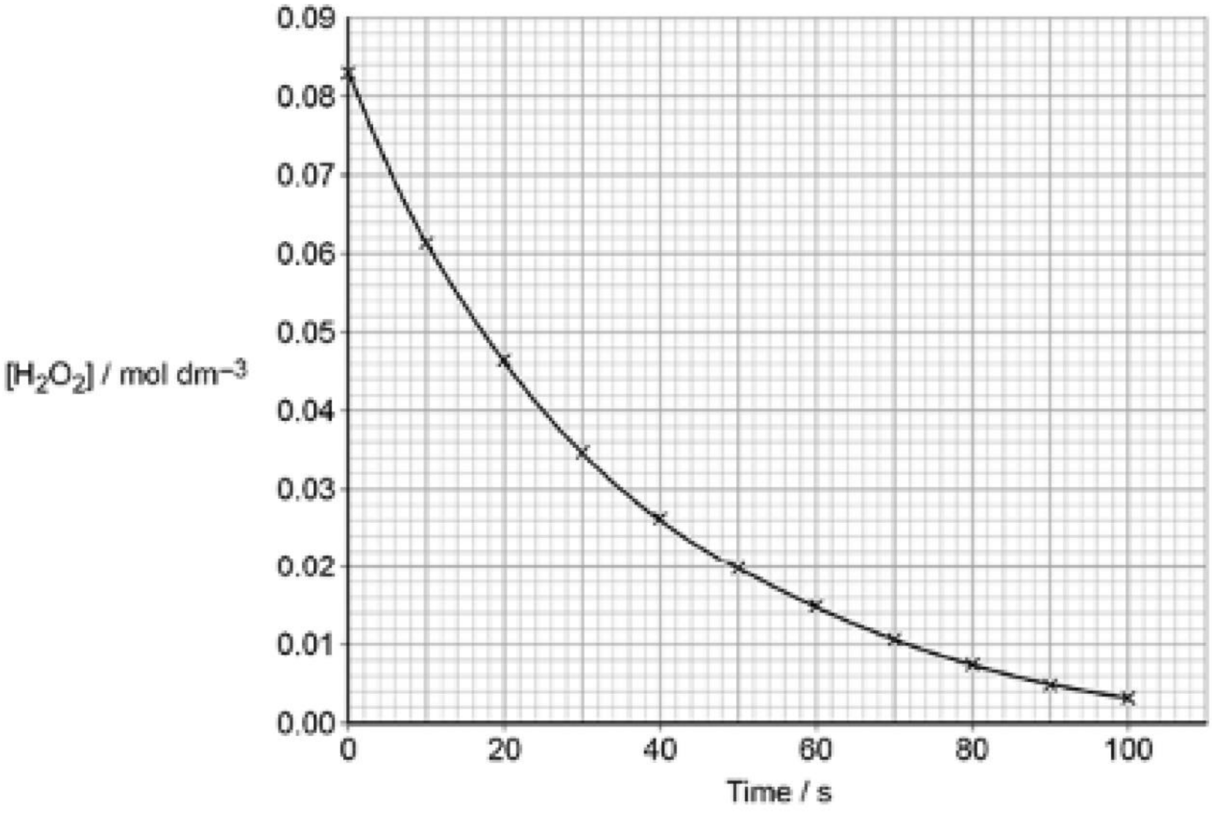
____

(2)

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

Figure 1



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

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

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

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

(2)

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

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

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

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

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

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

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

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

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

(2)

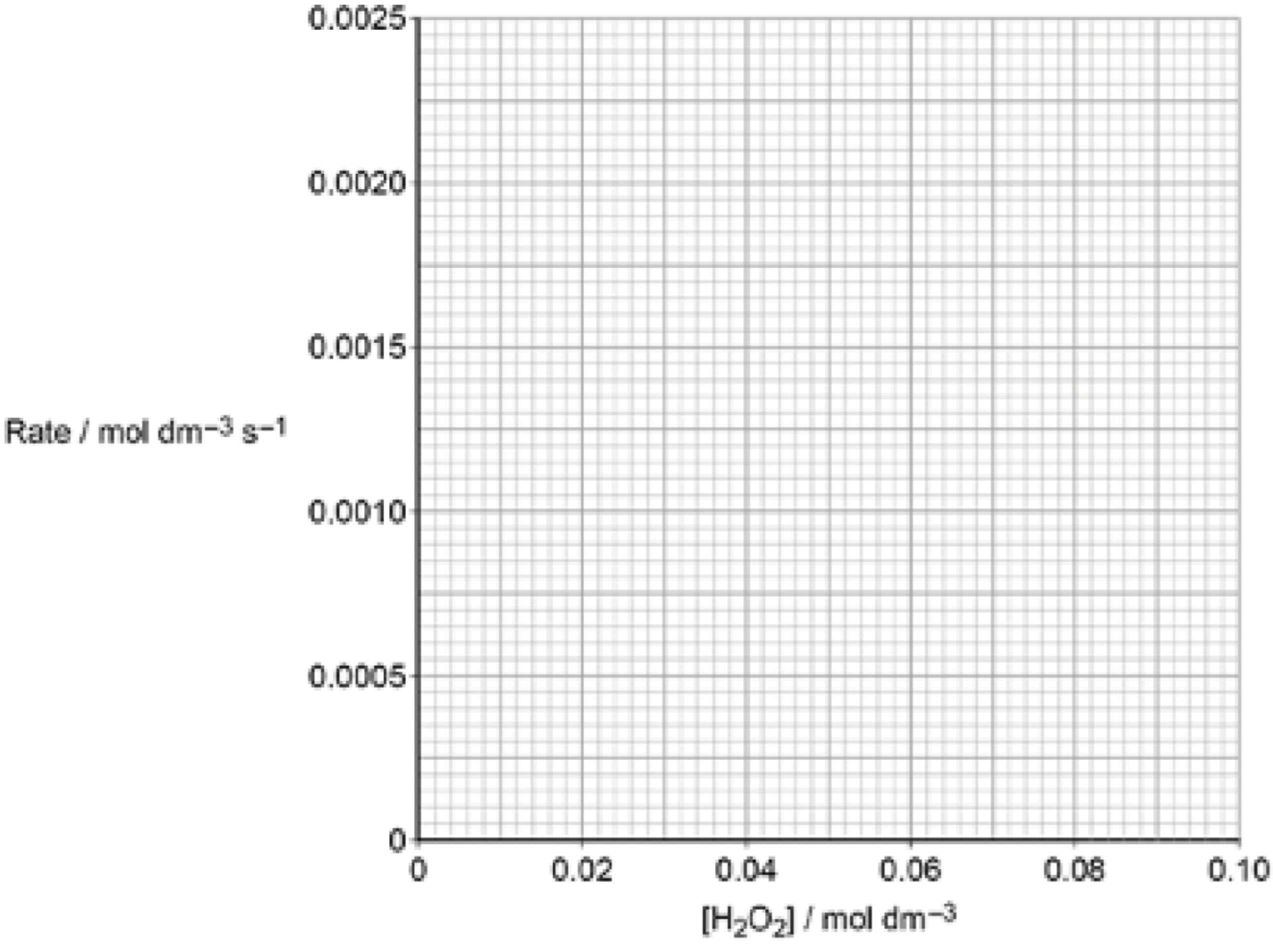
The table below shows data from a similar experiment.

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

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

Draw a line of best fit.

Figure 2



(2)

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

State how the graph shows this order.

Order ____

How the graph shows this order ______________________________

____

____

(2)

(a) **M1** High**er**/**est** concentration of / more H_2O_2 / particles / molecules / reactants

1

M2 More frequent successful collisions

1

Alternative approach

***M1** Lower/est concentration of / fewer particles / molecules / reactants as time goes on*

***M2** Less frequent successful collisions (look for both ideas even if separated)*

***Ignore** 'chance' / 'probability'*

(b) **M1** Suitable tangent drawn

***M1** Tangent must be drawn with ruler and touch line at 0.05 mol dm^{-3} (± 1 square) and not cross the curve (if white seen between lines it crosses)*

1

M2 −0.00120 to −0.00155 (mol dm^{-3} s^{-1})

***M2 Ignore** units*

***Allow** ecf from unsuitable tangent i.e if M1 not awarded*

***Ignore** sign of gradient*

1

(c) **M1** $[H_2O_2]_{initial}$ = 0.083 mol dm^{-3}

***Allow** 0.082 − 0.084*

1

M2 $[H_2O_2]_t$ = 0.0664 (mol dm^{-3})

***Allow** 0.0656 − 0.0672 (scores 2/2)*

2SF minimum

***Allow** ecf from **M1** (M2 = M1 × 0.8)*

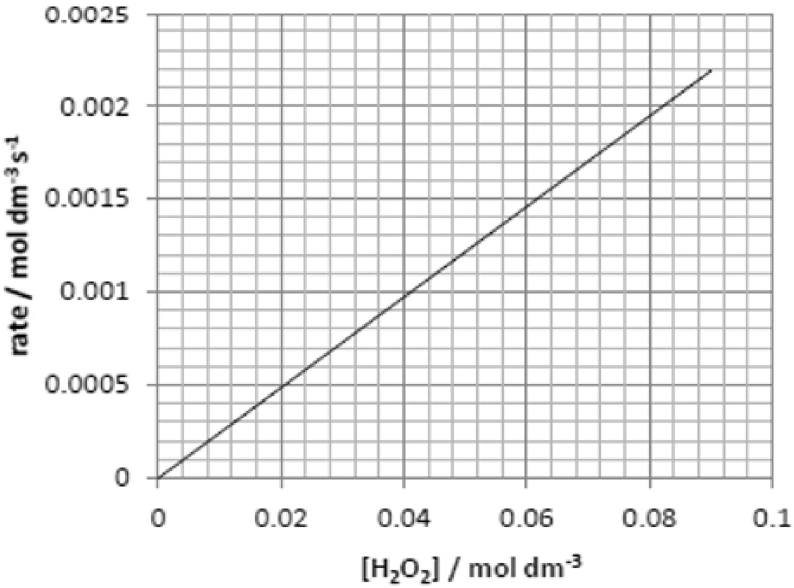
1

(d) **M1** Points plotted

__M1__ allow each point (± 1/2 square)

1

M2 best fit straight line drawn



__M2__ line should be drawn with a ruler and cover the five points given going within 1 square of each point, no doubles no kinks. The line does not need to be extended to the origin

__Allow__ reasonable best fit line if points plotted incorrectly

1

(e) **M1** 1st order

1

M2 straight line graph through the origin

__Ignore__ rate is (directly) proportional to [H_2O_2]

__Allow__ constant gradient line through the origin

__Allow__ use of data from line to show e.g. x2 conc = x2 rate

__Allow__ if M1 missing

__Not__ if M1 wrong

1

Question - 04

An acidified solution of butanone reacts with iodine as shown.

$$CH_3CH_2COCH_3 + I_2 \rightarrow CH_3CH_2COCH_2I + HI$$

(a) Draw the displayed formula for $CH_3CH_2COCH_2I$

Give the name of $CH_3CH_2COCH_2I$

Displayed formula

Name ____

(2)

(b) The rate equation for the reaction is

$$rate = k[CH_3CH_2COCH_3][H^+]$$

Table 1 shows the initial concentrations used in an experiment.

Table 1

	$CH_3CH_2COCH_3$	**I_2**	**H^+**
Initial concentration / mol dm^{-3}	4.35	0.00500	0.825

The initial rate of reaction in this experiment is 1.45×10^{-4} mol dm^{-3} s^{-1}

Calculate the value of the rate constant, k, for the reaction and give its units.

k ____________________

Units ____________________

(3)

(c) Calculate the initial rate of reaction when all of the initial concentrations are halved.

Initial rate of reaction ____________________ mol dm^{-3} s^{-1}

(1)

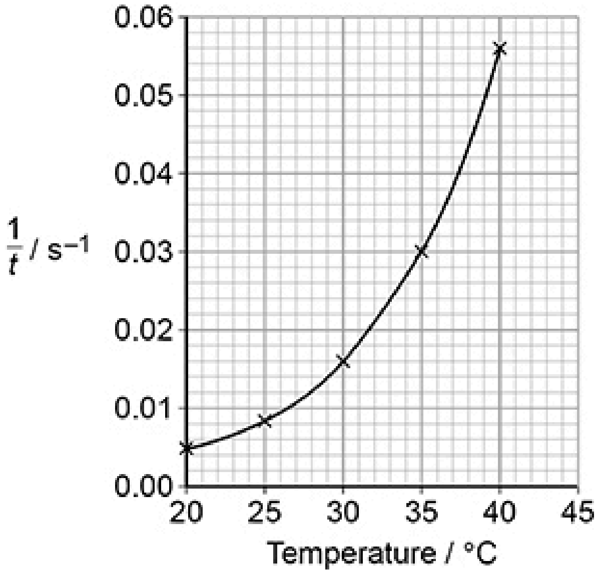
(d) An experiment was done to measure the time, *t*, taken for a solution of iodine to react completely when added to an excess of an acidified solution of butanone.

Suggest an observation used to judge when all the iodine had reacted.

____

____

The experiment was repeated at different temperatures.
The graph below shows how $\frac{1}{t}$ varied with temperature for these experiments.



(1)

(e) Describe and explain the shape of the graph above.

____

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____

____

____

____

(3)

(f) Deduce the time taken for the reaction at 35 °C

Time ________________ s

(1)

(g) For a different reaction, **Table 2** shows the value of the rate constant at different temperatures.

Table 2

Experiment	**Temperature / K**	**Rate constant / s^{-1}**
1	$T_1 = 303$	$k_1 = 1.55 \times 10^{-5}$
2	$T_2 = 333$	$k_2 = 1.70 \times 10^{-4}$

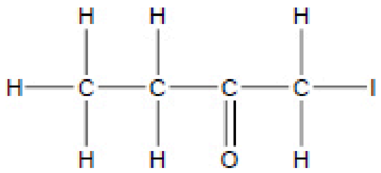
This equation can be used to calculate the activation energy, E_a

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

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

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

(a)



Apply list principle for more than one structure given

M1

1-iodobutan-2-one

Allow 1-iodo-2-butanone

M2

(b) $\frac{\text{Rate}}{[CH_3CH_2COCH_3][H^+]} = k$

Rearranged expression Or with numbers

M1

$k = 4.(04) \times 10^{-5}$ or 0.00004(04)

If upside down = 24752 mol dm^{-3} s

If multiply = 5.20×10^{-4} mol^3 dm^{-9} s$^-$

M2

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

M3

(c) $3.6(25) \times 10^{-5}$ (mol dm^{-3} s^{-1})

Allow 3.59×10^{-5} to 3.63×10^{-5}

1

(d) Brown colour removed

Goes colourless

Allow (orange) brown to colourless

Allow purple to colourless

1

(e) As T increases rate ($1/t$) increases OR time for completion decreases

M1

Exponentially
OR
By a greater/ increasing factor

Or rate increases more and more as temp increases ie description of exponential increase

M2

<u>Many</u> more particles have $E \geq E_a$

NOT just higher collision frequency

NOT just more successful collisions

M3

(f) Time = $\frac{1}{0.03}$ = 33 s

1

(g) $\ln(1.55 \times 10^{-5}/1.70 \times 10^{-4}) = \frac{E_a}{R}\left(\frac{1}{333} - \frac{1}{303}\right)$

Insertion of correct values

M1

$-2.39 = \frac{E_a}{R}(-2.97 \times 10^{-4})$

Evaluate LHS and fraction on RHS

M2

$\frac{2.39 \times 8.31}{2.97 \times 10^{-4}} = E_a$

Re-arrange for E_a

M3

66937

Evaluate

M4

66.9 kJ mol^{-1}

convert to kJ mol^{-1}

M5

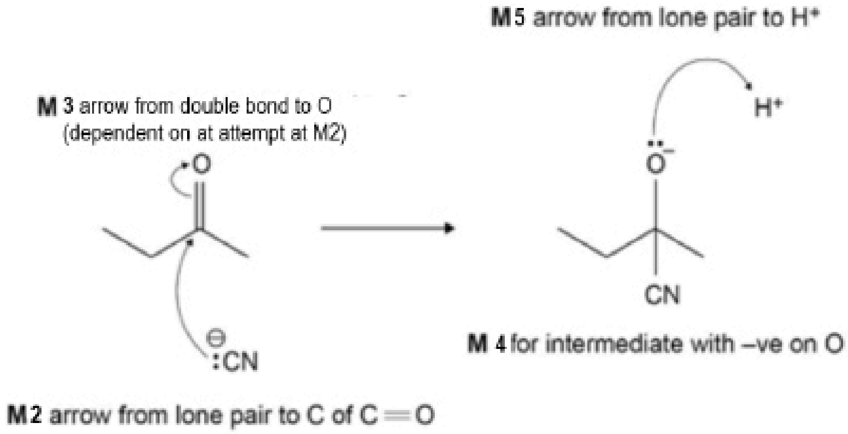
If only k_1 and k_2 reversed this gives a negative answer for E_a Lose M1 and M5

If AE in M2 allow ECF

Allow ECF from M4 to M5 for a correct unit conversion

Allow range 66.3 − 67.1

(h) Nucleophilic Addition



M1M2M3M4M5

ALLOW negative charge anywhere on cyanide

But attacking lone pair must be on C

Do not award M3 without attempt of M2

Allow M2 for attack to a positive carbon following breaking of C=O

Penalise covalent KCN in M2

M3 ignore partial charges unless wrong

Penalise M3 for incorrect connection between CN and C

NB Allow fully displayed or other structural formulae

End of Question

Question - 05

This question is about ethanoic anhydride.

In the gas phase, ethanoic anhydride $(CH_3CO)_2O$ decomposes to form ethenone.

The equation is

$$(CH_3CO)_2O \rightarrow \underset{\text{Ethenone}}{H_2C{=}C{=}O} + CH_3COOH$$

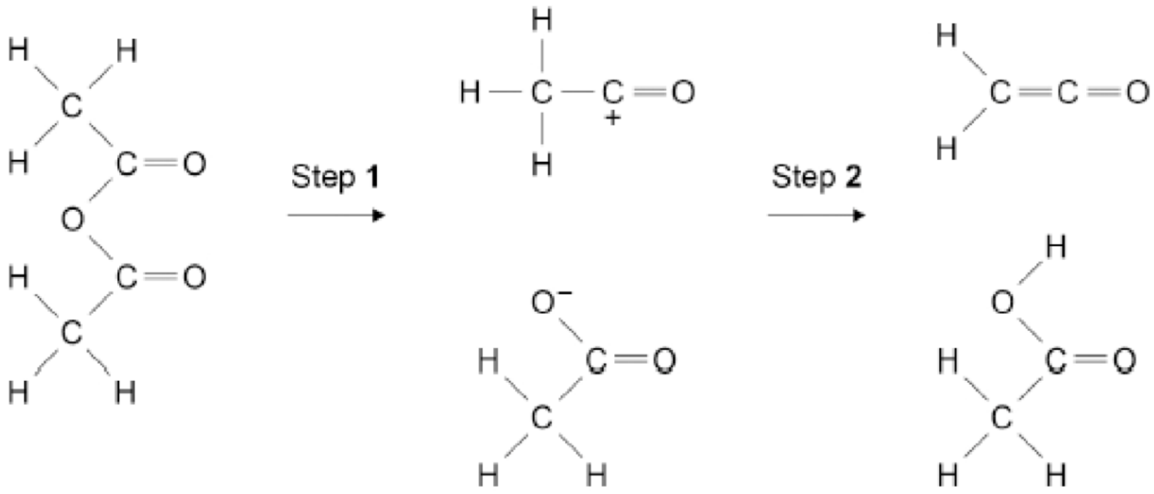
(a) Ethenone is the simplest member of the ketene homologous series. Ketenes all contain one C=C double bond and one C=O double bond.

Deduce the general formula for the ketene homologous series.

____

(1)

(b) The figure below shows an incomplete suggested mechanism for the decomposition of ethanoic anhydride.



Complete the mechanism in the figure above by adding three curly arrows and any relevant lone pairs of electrons.

(3)

(c) For a chemical reaction the relationship between the rate constant, k, and the temperature, T, is shown by the Arrhenius equation.

$$k = Ae^{\frac{-E_a}{RT}}$$

For the decomposition of gaseous ethanoic anhydride

the activation energy, $E_a = 34.5\ \text{kJ mol}^{-1}$
the Arrhenius constant, $A = 1.00 \times 10^{12}\ \text{s}^{-1}$

At temperature T_1 the rate constant, $k = 2.48 \times 10^{8}\ \text{s}^{-1}$

Calculate T_1

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

T_1 ______________________ K

(3)

(d) Sketch the Maxwell–Boltzmann distribution of molecular energies for gaseous ethanoic anhydride at temperature T_1 and at a higher temperature T_2

Include a label for each axis, and mark on the appropriate axis a typical position for the activation energy.

Explain why the rate of reaction is faster at T_2

Explanation

____

____

____

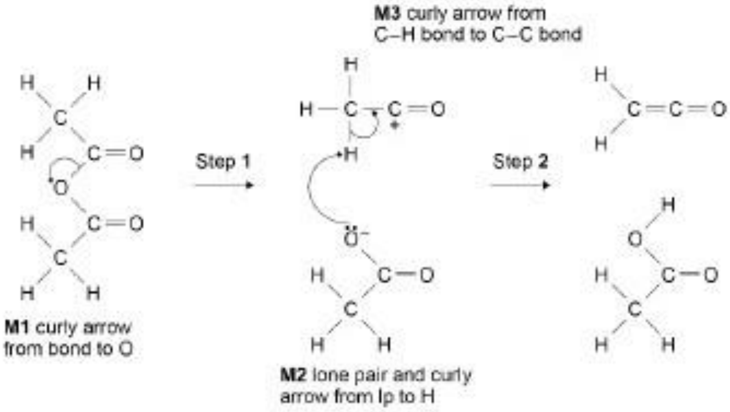
(5)

(a) $C_nH_{2n-2}O$

Allow $C_nH_{2n}CO$ or $(CH_2)_nCO$ or $C_nH_{2(n-1)}O$

1

(b)



Allow other C-O bond breaking for M1

3

(c) M1 $\frac{k}{A} = e^{-Ea/RT}$

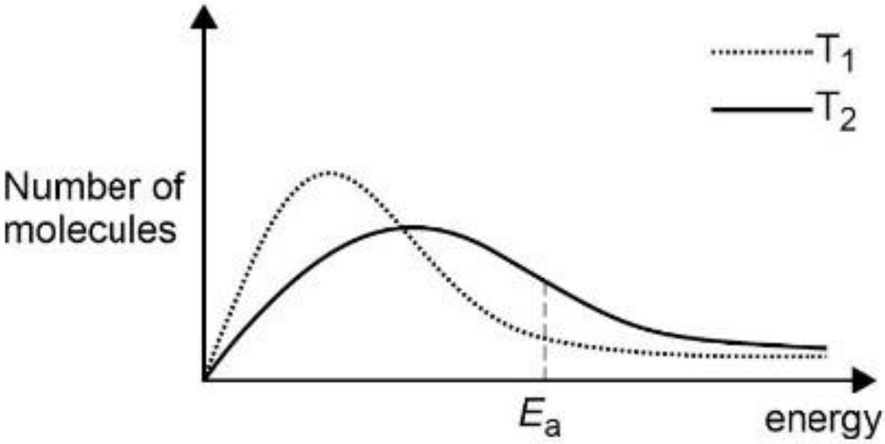
M2 $8.302 = \frac{34500}{8.31 \times T}$

M3 T = 500 K

OR via $\ln k = \ln A - \frac{Ea}{RT}$ or shown with numbers

3

(d)



M5 At T_2 (many) more particles have $E \geq E_a$

M1 x axis labelled correctly (kinetic not required)

AND y axis labelled correctly allow particles

M2 Ea labelled on x axis

M3 Distribution correct shape for T_1

M4 Peak at T_2 lower with max shifted right and only crosses once

5

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

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

The rate equation for this reaction is

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

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

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

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

(3)

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

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

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

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

Deduce the rate-determining step for this reaction.

Give a reason for your answer.

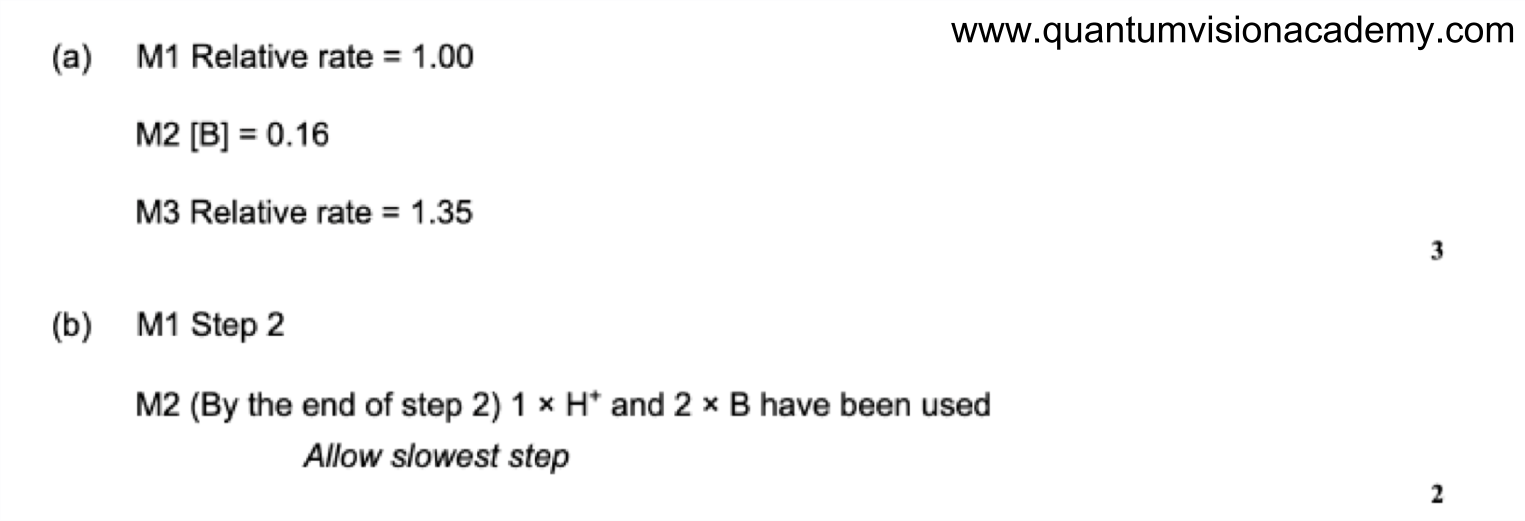
Rate-determining step ____________________

Reason ____________________

____

____

(2)



(a) M1 Relative rate = 1.00

M2 [B] = 0.16

M3 Relative rate = 1.35

3

(b) M1 Step 2

M2 (By the end of step 2) 1 × H^+ and 2 × B have been used

Allow slowest step

2