Do not write outside the box

Section A

Answer **all** questions in this section.

0 1 Iodide ions are oxidised to iodine by hydrogen peroxide in acidic conditions.

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

The rate equation for this reaction can be written as

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

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

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

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

0 1 . 1 Explain why the use of a large excess of H_2O_2 and I^- means that the rate of reaction at a fixed temperature depends only on the concentration of $H^+(aq)$.

[2 marks]

0 1 . 2 Samples of the reaction mixture are removed at timed intervals and titrated with alkali to determine the concentration of $H^+(aq)$.

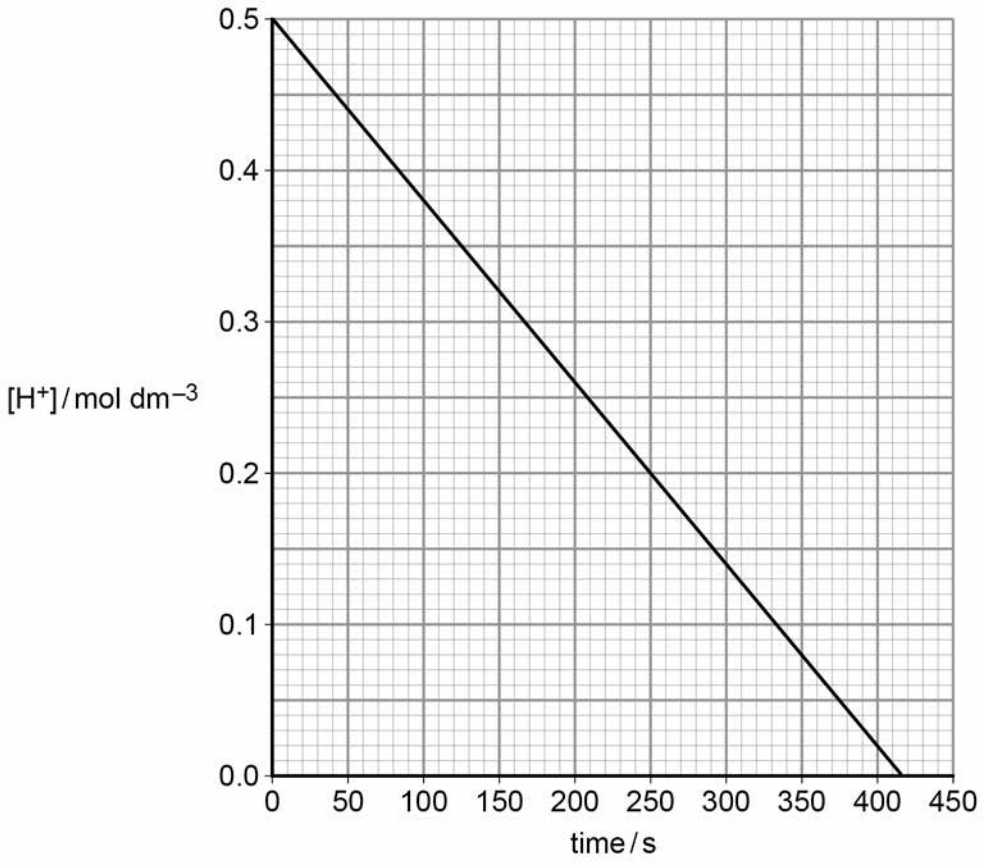
State and explain what must be done to each sample before it is titrated with alkali.

[2 marks]

Do not write outside the box

0 1 . 3 A graph of the results is shown in **Figure 1**.

Figure 1



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

[2 marks]

_____

_____

_____

_____

0 1 . 4 Use the graph in **Figure 1** to calculate the value of k_1
Give the units of k_1

[3 marks]

k_1 _____

Units _____

Turn over ►

Do not write outside the box

0 1 . 5 A second reaction mixture is made at the same temperature. The initial concentrations of $H^+(aq)$ and $I^-(aq)$ in this mixture are both 0.500 mol dm^{-3}
There is a large excess of H_2O_2

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

The results are shown in **Table 1**.

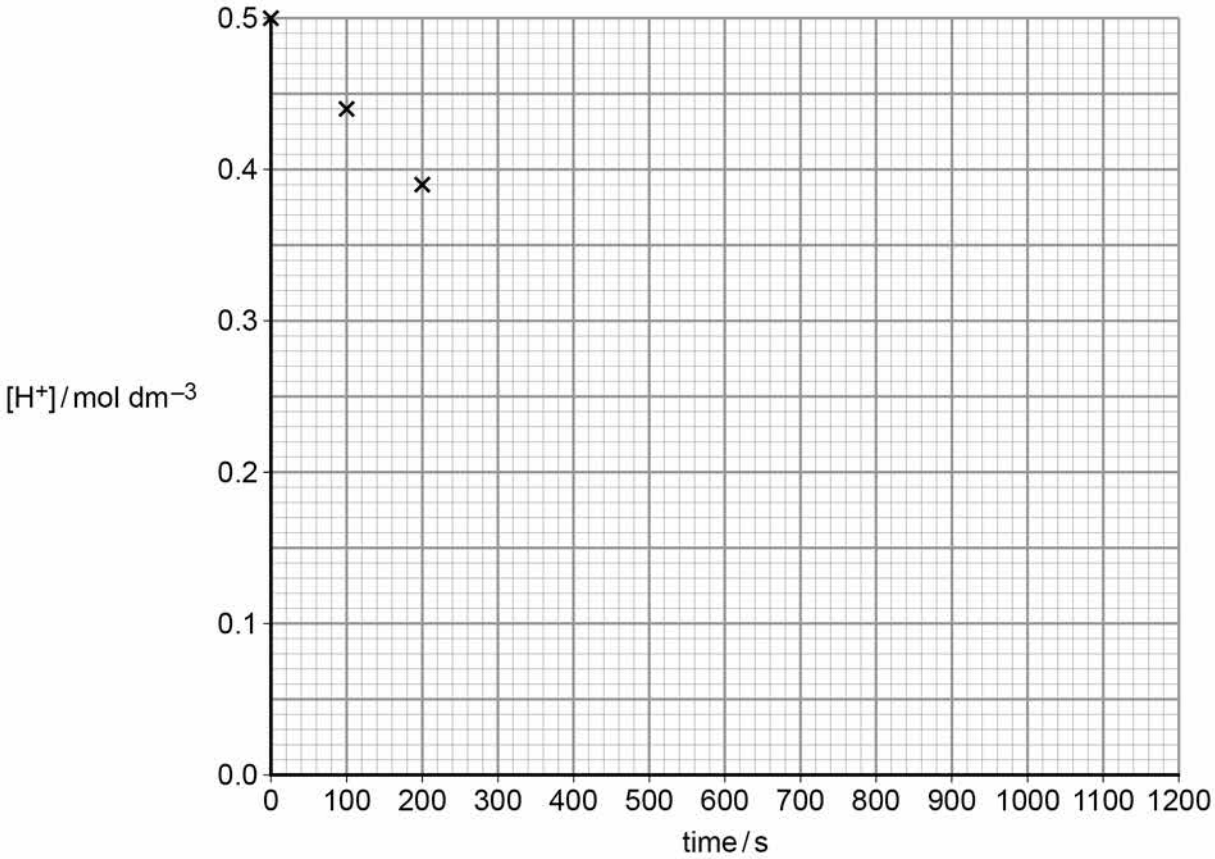
Table 1

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

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

[1 mark]

Figure 2



0 1 . 6 Draw a line of best fit on the grid in **Figure 2**.

[1 mark]

Do not write outside the box

0 1 . 7 Calculate the rate of reaction when $[H^+] = 0.35$ mol dm^{-3}
Show your working using a suitable construction on the graph in **Figure 2**.

[2 marks]

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

Question 1 continues on the next page

Do not write outside the box

0 1 . 8 A general equation for a reaction is shown.

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

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

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

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

[6 marks]

Do not write outside the box

Section A

Answer **all** questions in the spaces provided.

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

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

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

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

.....

(1 mark)

(*Space for working*) .....

.....

.....

.....

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

.....

(1 mark)

(*Space for working*) .....

.....

.....

.....

Do not write outside the box

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

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

The rate equation for this reaction is

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

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

Calculation .....

.....

.....

.....

Units .....

.....

(3 marks)

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

.....

.....

(1 mark)

6

Turn over ▶

Do not write outside the box

Section A

Answer **all** questions in the spaces provided.

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

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

The rate equation for this reaction is known to be

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

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

Calculation .....

.....

.....

.....

.....

Units .....

.....

(3 marks)

(Extra space) .....

.....

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

.....

.....

.....

(1 mark)

Do not write outside the box

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

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

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

.....

.....

.....

(1 mark)

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

.....

.....

.....

(1 mark)

Question 1 continues on the next page

Do not write outside the box

1 (c) The compound $(CH_3)_3CBr$ reacts with aqueous sodium hydroxide as shown in the following equation.

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$$

This reaction was found to be first order with respect to $(CH_3)_3CBr$ but zero order with respect to hydroxide ions.

The following two-step process was suggested.

Step **1** $(CH_3)_3CBr \longrightarrow (CH_3)_3C^+ + Br^-$

Step **2** $(CH_3)_3C^+ + OH^- \longrightarrow (CH_3)_3COH$

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

.....

(1 mark)

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

(1 mark)

8

Do not write outside the box

Section A

Answer **all** questions in the spaces provided.

1 The rate of hydrolysis of an ester **X** ($HCOOCH_2CH_2CH_3$) was studied in alkaline conditions at a given temperature. The rate was found to be first order with respect to the ester and first order with respect to hydroxide ions.

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

.....

(1 mark)

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

.....

(1 mark)

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

Calculation .....

.....

.....

.....

Units .....

.....

(3 marks)

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

.....

.....

(1 mark)

Do not write outside the box

1 (a) (v) In a third experiment at the same temperature, the concentration of **X** was half that used in the experiment in part **1 (a) (iii)** and the concentration of hydroxide ions was three times the original value.
Calculate the initial rate of reaction in this third experiment.

.....

.....
(1 mark)

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

Effect .....

Explanation .....

.....
(2 marks)

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

$$A + 3B \rightarrow AB_3$$

The rate equation for the reaction is

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

A suggested mechanism for the reaction is

Step **1** $A + B \rightarrow AB$

Step **2** $AB + B \rightarrow AB_2$

Step **3** $AB_2 + B \rightarrow AB_3$

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

Explain your answer.

Rate-determining step .....

Explanation .....

.....
(2 marks)

11

Areas outside the box will not be scanned for marking

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

$$CH_3COCH_3 + I_2 \longrightarrow ICH_2COCH_3 + HI$$

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

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

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

.....

(1 mark)

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

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

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

Calculation .....

.....

.....

.....

Units .....

(3 marks)

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

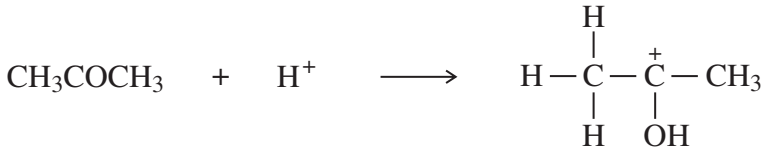
.....

(1 mark)

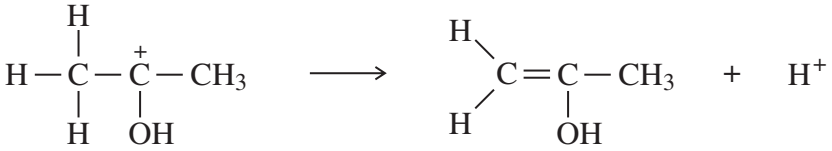
Areas outside the box will not be scanned for marking

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

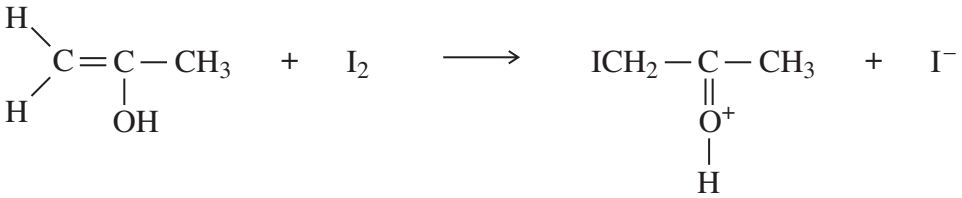
Step **1**



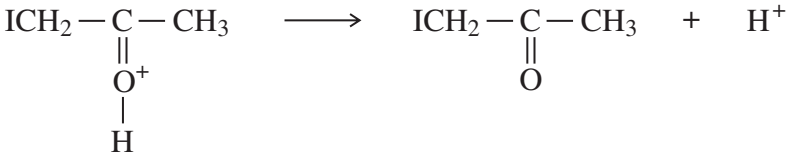
Step **2**



Step **3**



Step **4**



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

Rate-determining step .....

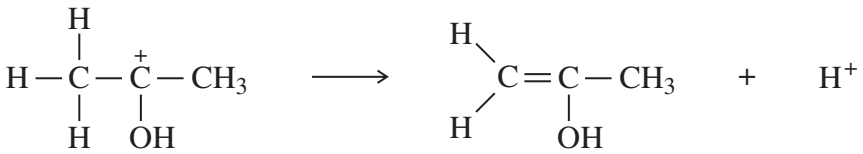
Explanation .....

.....

(2 marks)

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

Step **2**

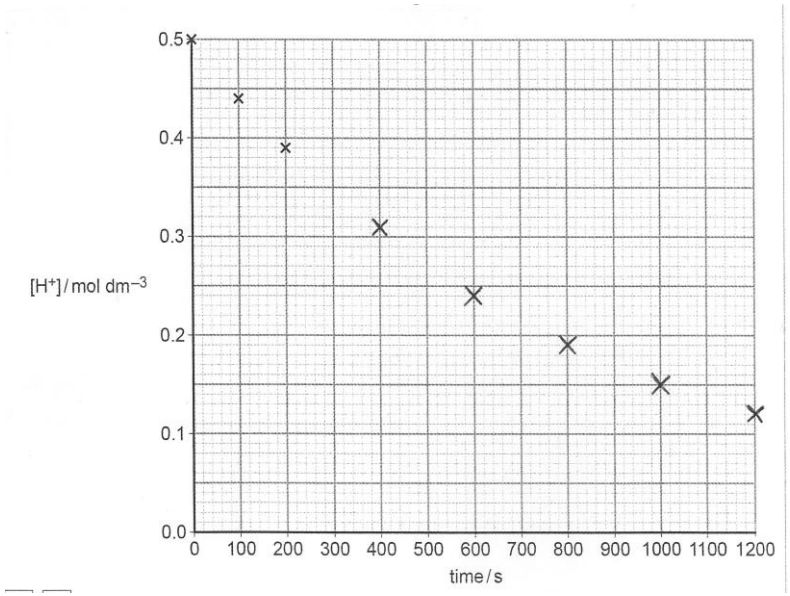


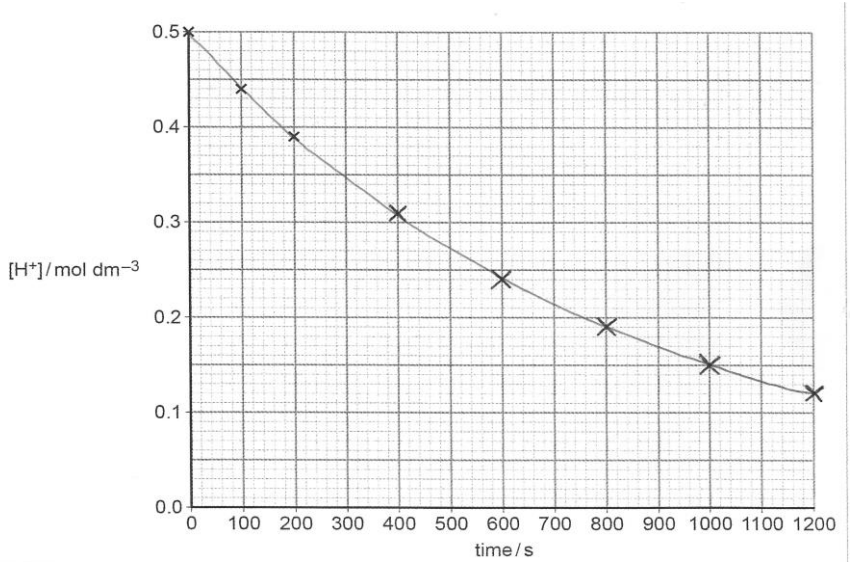
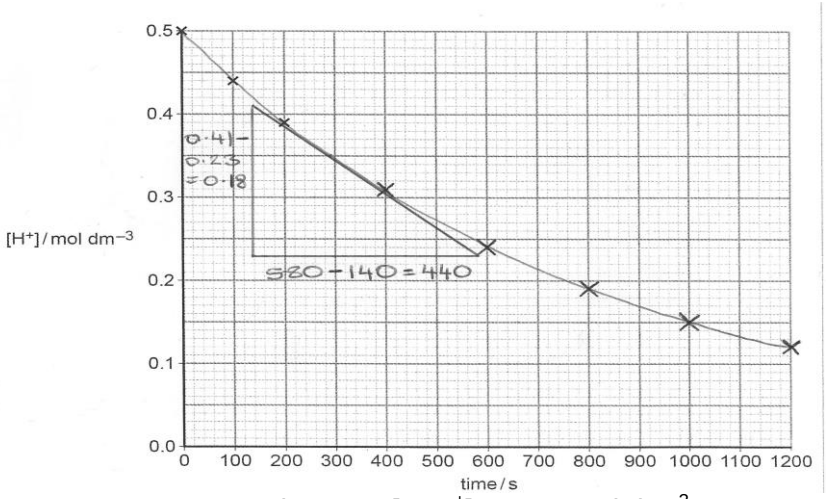
(1 mark)

8

Turn over ▶

Question	Answers	Additional Comments/Guidelines	Mark
01.1	H_2O_2 and/or I^- concentration change is negligible / H_2O_2 and/or I^- concentration (effectively) constant so have a constant/no effect on the rate / so is zero order (w.r.t. H_2O_2 and I^-) / a and b are zero	Only the concentration of H^+ changes. Ignore references to H^+ is limiting reagent / rds / H_2O_2/I^- not in rate equation Do not allow reference to catalyst.	2
01.2	Stop the reaction / quench By dilution / cooling / adding a reagent to react with H_2O_2/I^-	Allow valid suggestions about how to stop the reaction. Do not allow reaction with acid/alkali / neutralisation for M2 Do not penalise other named reagents. Ignore references to measuring volume and adding indicator	2
01.3	M1: constant gradient OR change/decrease in concentration is proportional to time M2: as $[H^+]$ changes/decreases	Allow constant rate / rate = *k* Ignore reference to straight line Not increase in concentration / concentration is inversely proportional / concentration (on its own) is proportional M2 dependent on correct M1 Allow rate v concentration graph would give horizontal straight line owtte Allow so $[H^+]$ has no effect on the rate	2

01.4	evidence of attempt at calculation of gradient via $\Delta y/\Delta x$ k_1 = 0.0012 / 1.2 x 10^{-3} units = <u>mol dm^{-3} s^{-1}</u>	allow construction lines on graph At least 2 sf (0.00118 – 0.00122) Correct answer scores 2/2 No ecf from incorrect or inverted numbers in M1 k_1 = – 0.0012 scores 1/2 Additional processing of data such as including $[H^+]$ loses M2 M3 mark independently	3
01.5	5 points correctly plotted  	Allow ±half a small square for each point	1

01.6		Smooth curve only within one small square of all points (ecf on 01.5) Not a series of straight lines between points	1
01.7	 M1: Tangent to curve drawn at $[H_3O^+]$ = 0.35 mol dm^{-3} e.g. 0.18/440 M2: Rate = 4.09 x 10^{-4} (mol dm^{-3} s^{-1})	M1 for a tangent / triangle / other suitable working Allow ECF for both M1 and M2 following on from straight line drawn in 01.6, but must show suitable construction on graph for M1 Ignore negative signs Allow value in range 3.70 x 10^{-4} - 4.50 x 10^{-4} At least 2sf ecf from any straight line for correctly calculated gradient	2

<table>
<tr>
<td>01.8</td>
<td>This question is marked using levels of response. Refer to the Mark Scheme Instructions for examiners for guidance on how to mark this question
<table>
<tr><td>Level 3

5-6 marks</td><td>All stages are covered and the explanation of each stage is correct and virtually complete.

Answer is coherent and shows progression through all three stages.

A clear explanation of how the order is determined from the results is needed to show coherence.</td></tr>
<tr><td>Level 2

3-4 marks</td><td>All stages are covered (NB ‘covered’ means min 2 from stage 2) but the explanation of each stage may be incomplete or may contain inaccuracies
OR two stages covered and the explanations are generally correct and virtually complete

Answer is coherent and shows some progression through all three stages. Some steps in each stage may be out of order and incomplete</td></tr>
<tr><td>Level 1

1-2 marks</td><td>Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies
OR only one stage is covered but the explanation is generally correct and virtually complete

Answer shows some progression between two stages</td></tr>
<tr><td>Level 0

0 marks</td><td>Insufficient correct Chemistry to warrant a mark</td></tr>
</table>
</td>
<td>

Indicative Chemistry content Method 1

Stage 1 Preparation

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

Stage 2 Procedure

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

Stage 3 Use of Results

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

</td>
<td>6</td>
</tr>
</table>

Total			19

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

Stage 1 Preparation

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

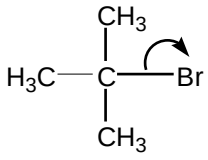
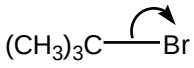
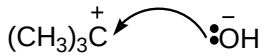
Stage 2 Procedure

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

Stage 3 Use of Results

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

Question	Marking Guidance	Mark	Comments
1(a)(i)	2 or two or second or $[E]^2$	1	
1(a)(ii)	1 or one or first or $[F]^1$ or [F]	1	
1(b)(i)	$k = \dfrac{8.6 \times 10^{-4}}{(3.8 \times 10^{-2})^2 \times (2.6 \times 10^{-2})}$	1	mark is for insertion of numbers into a correctly rearranged rate equ , k = etc. AE (-1) for copying numbers wrongly or swapping two numbers.
	= 22.9 (Allow 22.9 – 24 after correct rounding)	1	
	$\underline{mol^{-2}\,dm^{+6}\,s^{-1}}$	1	Any order.
1(b)(ii)	$6.8(2) \times 10^{-3}$ (mol $dm^{-3}s^{-1}$) ***OR*** if their k is wrong, award the mark consequentially a quick check can be achieved by using $\dfrac{\text{their answer}}{\text{their k}}$ = 2.9768×10^{-4} Allow $2.9 – 3.1 \times 10^{-4}$ for the mark	1	Allow 6.8×10^{-3} to 6.9×10^{-3} Ignore units.

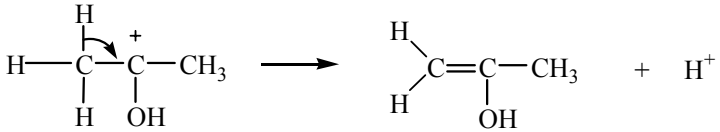
Question	Marking Guidance	Mark	Comments
1(a)(i)	$k = \dfrac{8.4\times10^{-5}}{(4.2\times10^{-2})^2 \times 2.6\times10^{-2}}$ ***OR*** $\dfrac{8.4\times10^{-5}}{(1.76\times10^{-3})\times 2.6\times10^{-2}}$	1	Mark is for insertion of numbers into a correctly rearranged rate equ , k = etc. If upside down, score only units mark from their k
	= 1.8(3)	1	AE (-1) for copying numbers wrongly or swapping two numbers
	$mol^{-2}\,dm^{+6}\,s^{-1}$	1	Any order If *k* calculation wrong, allow units consequential to their *k* = expression
1(a)(ii)	5.67×10^{-4} (mol $dm^{-3}s^{-1}$) ***OR*** their $k \times 3.1 \times 10^{-4}$	1	Allow 5.57×10^{-4} to 5.7×10^{-4}
1(b)(i)	2 or second or $[D]^2$	1	
1(b)(ii)	0 or zero or $[E]^0$	1	
1(c)(i)	Step 1 or equation as shown	1	Penalise Step 2 but mark on
1(c)(ii)	 or  Ignore correct partial charges, penalise full / incorrect partial charges	1	If Step 2 given above, can score the mark here for  allow **:**OH^- (must show lp) If S_N2 mechanism shown then no mark (penalise involvement of $:OH^-$ in step 1) Ignore anything after correct step 1

Question	Marking Guidance		Mark	Comments
1(a)(i)	propyl methanoate		1	must be correct spelling
1(a)(ii)	rate = $k[X][OH^-]$		1	allow $HCOOCH_2CH_2CH_3$ (or close) for X allow ( ) but penalise missing minus
1(a)(iii)	$k = \frac{8.5 \times 10^{-5}}{(0.024)(0.035)}$	In (a)(iii), if wrong orders allow	1	mark is for insertion of numbers in correct expression for k If expression for k is upside down, only score units conseq to their expression
	= 0.10(12) 2sf minimum	1 for conseq answer	1	
	$mol^{-1}\ dm^3\ s^{-1}$	1 for conseq units	1	any order
1(a)(iv)	$2.1(3) \times 10^{-5}$		1	or $2.1(2) \times 10^{-5}$ ignore units allow 2 sf **NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong k** **See * below**

1(a)(v)	1.3×10^{-4} (1.28×10^{-4})	1	allow (1.26×10^{-4}) to (1.3×10^{-4}) ignore units allow 2 sf **NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong k** **See ** below**
	For example, if orders given are 1st in X and second in OH^- [The mark in a(ii) and also first mark in a(iii) have already been lost] So allow mark * in (iv) for rate = their k ×$(0.012)(0.0175)^2$ = their k ×(3.7×10^{-6}) (allow answer to 2sf) ** in (v) for rate = their k × $(0.012)(0.105)^2$ = their k ×(1.32×10^{-4}) (allow answer to 2sf) **The numbers will of course vary for different orders.**		

1(a)(vi)	Lowered fewer particles/collisions have energy >E_a **OR** fewer have sufficient (activation) energy (to react)	1 1	if wrong, no further mark not just fewer successful collisions

1(b)	Step 2 (this step with previous) involves one mol/molecule/particle A and two Bs or 1:2 ratio or same amounts (of reactants) as in rate equation	1 1	if wrong, no further mark

Question	Part	Sub Part		Mark	Comment
3	(a)		2 or two or second	1	
3	(b)		$k = \frac{1.24 \times 10^{-4}}{(4.40)(0.82)}$ $= 3.4\underline{4} \times 10^{-5}$ (min 3sfs) $\underline{mol^{-1}dm^{3}s^{-1}}$	1 1 1	mark is for insertion of numbers into a correctly rearranged rate equ , k = etc if upside down, (or use of I_2 data) score only units mark any order
3	(c)		no change or no effect or stays the same or 1.24×10^{-4}	1	
3	(d)		1 or 2 or 1 and 2 rate equ doesn't involve I_2 or only step which includes 2 species in rate equ	1 1	if wrong no further mark but mark on from no answer
3	(e)			1	any second arrow loses the mark