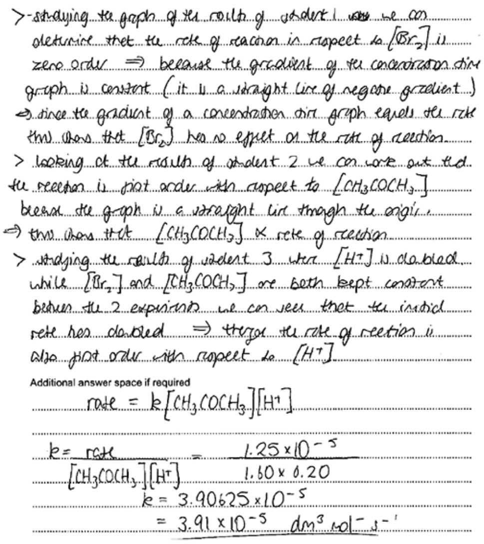
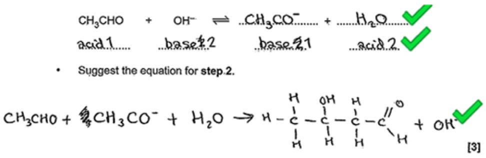
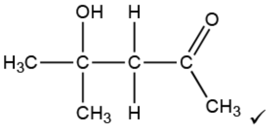
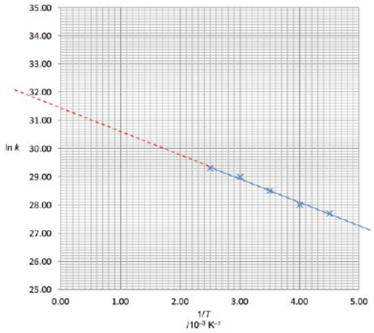
Mark scheme – How Fast

Question			Answer/Indicative content	Marks	Guidance
1		i	To keep [CH_3OH] (effectively) constant **OR** Zero order with respect to CH_3OH **OR** To ensure equilibrium is far to the right ✓	1 (AO 3.3)	**ALLOW** Change in [CH_3OH] is negligible **ALLOW** rate is independent of [CH_3OH] **IGNORE** Methanol doesn't run out/is not limiting reagent. **<u>Examiner's Comments</u>** Most candidates used incorrect ideas about reaction going to completion or the methanol not being limiting.
		ii	One half-life *t*½ between 102 and 110 (mins) Two half-lives calculated **OR** evidence on the graph of two half-lives **AND** constant half-life/values (means first order) ✓	2 (AO 3.1) (AO 3.1)	**ALLOW** any two combinations of positions, e.g. 5 and 2.5 **AND** 4 and 2 **AND** 3 and 1.5 **<u>Examiner's Comments</u>** Very few candidates were given full marks. Higher-attaining students calculated one half life in range but very few could come up with a second half life as the graph did not allow another successive half life to be obtained. Higher-attaining candidates chose alternative half lives from the data given. **Misconception** Candidates are advised that half lives can be calculated from any numerical values on the graph. Further guidance on rates of reaction can be found at: https:/www.ocr.org.uk/Images/371956-experiments-on-rates-of-reaction.doc
		iii	**Using gradients** Evidence of tangent at *t* = 0 and intercept between 100 -140 (min) ✓ Correctly calculated gradient in the range of 2.9 × 10^{-5} to 4.0 × 10^{-5} (mol dm^{-3} min^{-1}) ✓ **OR** **Using half-life**	2 (AO 3.1×1) (AO 3.2×1)	**ALLOW ECF** from value of t½ in **(ii)** **<u>Examiner's Comments</u>**

			For $t_{½}$ = 106 min, $k = \frac{\ln 2}{t_{½}}$ = 0.00654 (min^{-1}) ✓ rate = 0.00654 × 5 × 10^{-3} = 3.27×10^{-5} (mol dm^{-3} min^{-1}) ✓		This question required the candidate to draw a line of best fit and then draw a tangent at t=0. Many candidates did not draw a line of best fit, and many did not get a tangent in the acceptable range. Very few candidates processed the gradient by using the correct subtraction on the y axis (scale was from 1 to 5) or by using the 10^{-3} on the axis label.
			Total	**5**	
2			***Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.*** **Level 3 (5–6 marks)** Most evidence used to determine the correct orders **AND** rate equation **AND** rate constant. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.* **Level 2 (3–4 marks)** Some evidence used to determine two orders correctly **AND** rate equation **AND** rate constant consistent with orders. **OR** Little evidence used to determine all three orders correctly **AND** rate equation **AND** rate constant. *There is a line of reasoning presented with some structure. The information presented is in the most part relevant and supported by some evidence.* **Level 1 (1–2 marks)** Little evidence used to determine two orders correctly **OR** One order correct, with attempt to determine the rate equation **AND** rate constant. *There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.* **0 marks** *No response or no response worthy of credit.*	6 (AO 3.1 ×4) (AO 3.2 ×2)	**Indicative scientific points may include:** **Orders** **Student 1** • zero order wrt Br_2 **Student 2** • 1st order wrt CH_3COCH_3 **Student 3** • 1st order wrt H^+ **Explanation** **Student 1** • constant gradient **OR** linear negative gradient **OR** constant rate **OR** rate independent of concentration **OR** decreasing half-life **Student 2** • straight line through 0,0 • **OR** rate directly proportional to [CH_3COCH_3] **OR** [CH_3COCH_3] × 2, rate × 2 **Student 3** • [H^+] × 2, rate × 2 **Rate equation, rate constant and units** **Student 1** • rate = k [CH_3COCH_3] [H^+] **ALLOW** rate = k $[Br_2]^0$ $[CH_3COCH_3]^1$ $[H^+]^1$ • $k = \frac{\text{rate}}{[CH_3COCH_3][H^+]}$ **OR** $\frac{1.25 \times 10^{-5}}{1.6 \times 0.2}$ • $k = 3.9\ldots \times 10^{-5}$ • units: dm^3 mol^{-1} s^{-1} (Any order, e.g. mol^{-1} dm^3 s^{-1})

					Examiner's Comments The second Level of Response question in the paper was also answered very well. Almost all candidates determined the order with respect to H^+ to be first order and gave suitable explanations. A very high proportion of candidates determined the order with respect to CH_3COCH_3 to be first order and related this to the direct proportionality shown on the graph. The zero order with respect to Br_2 proved a little more problematic with many candidates just giving an order with no attempted explanation. Having determined orders, nearly all candidates were able to give a corresponding rate equation and could calculate a value for the rate constant, albeit with frequent omission of units and forgetting that the initial rates given were in terms of 10^{-5}. An example of a complete answer achieving L3 (6 marks) is given. **Exemplar 8**  > studying the graph of the results of student 1 we can determine that the rate of reaction in respect to $[Br_2]$ is zero order ⇒ because the gradient of the concentration time graph is constant (it is a straight line of negative gradient) ⇒ since the gradient of a concentration time graph equals the rate this shows that $[Br_2]$ has no effect on the rate of reaction. > looking at the results of student 2 we can work out that the reaction is first order with respect to $[CH_3COCH_3]$ because the graph is a straight line through the origin. ⇒ this shows that $[CH_3COCH_3] \propto$ rate of reaction > studying the results of student 3 when $[H^+]$ is doubled while $[Br_2]$ and $[CH_3COCH_3]$ are both kept constant between the 2 experiments we can see that the initial rate has doubled ⇒ therefore the rate of reaction is also first order with respect to $[H^+]$ Additional answer space if required $rate = k[CH_3COCH_3][H^+]$ $k = \frac{rate}{[CH_3COCH_3][H^+]} = \frac{1.25 \times 10^{-5}}{1.60 \times 0.20}$ $k = 3.90625 \times 10^{-5}$ $= 3.91 \times 10^{-5}$ $dm^3 mol^- s^{-1}$ This candidate gave each order clearly followed by a concise explanation of each choice. The rate equation (based on the orders given) is clearly stated, the calculation clearly shows working and correct units are given.
			Total	**6**	

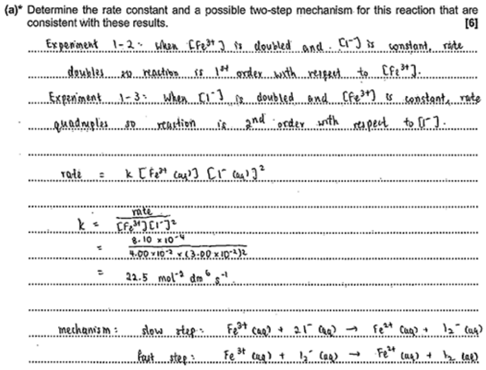
3		i	3-hydroxybutanal ✓	1	**ALLOW** 3-hydroxybutan-1-al **IGNORE** lack of hyphens or addition of commas **ALLOW** 4-oxobutan-2-ol **OR** 1-oxobutan-3-ol **DO NOT ALLOW** • 3-hydroxybutal • 3-hydroxylbutanal **<u>Examiner's Comments</u>** Most candidates made good attempts at the name, the difficulty being that hydroxyl group needed to be shown as a hydroxy- prefix, rather than the suffix -ol. Common errors included 2-hydroxybutanal (counting the carbon chain from the wrong end) and 2- or 3-hydroxybutanoic acid (reading the aldehyde group as a carboxylic acid).
		ii	Addition ✓	1	**IGNORE** nucleophilic **OR** electrophilic **OR** radical **DO NOT ALLOW** addition–elimination, condensation, polymerisation **<u>Examiner's Comments</u>** This part was answered well with most choosing nucleophilic addition. Credit was given just for 'addition'.
		iii	**ALLOW** any formula provided that number and type of atoms and charge are correct, e.g. For CH_3CHO, **ALLOW** CH_3COH, C_2H_4O, etc. **Step 1**: • Correct equation ✓ One correct acid–base pair ✓ • i.e. A1 and B1 **OR** A2 and B2 $CH_3CHO + OH^- \rightleftharpoons {}^-CH_2CHO + H_2O$ **OR** $CH_3CHO + OH^- \rightleftharpoons CH_3CO^- + H_2O$ ✓ **A1 B2 B1 A2** **OR A2 B1 B2 A1** **Step 2**: $CH_3CHO + {}^-CH_2CHO + H_2O \rightarrow CH_3CHOHCH_2CHO + OH^-$ ✓ For $^-CH_2CHO$: **ALLOW** CH_2CHO^-; CH_3CO^-; $C_2H_3O^-$	3	Throughout, **IGNORE** 'connectivity in any formula or structures shown. Examples in Answer column and in 6a(iv) guidance below **Step 1: ALLOW** H^+ transfer from OH^-, i.e. $CH_3CHO + OH^- \rightleftharpoons CH_3CH_2O^+ + O^{2-}$ ✓ **B2 A1 A2 B1** **OR B1 A2 A1 B2** **Step 2:** $CH_3CHO + CH_3CH_2O^+ + O^{2-} \rightarrow CH_3CHOHCH_2CHO + OH^-$ ✓ For $CH_3CH_2O^+$: **ALLOW** CH_3CHOH^+, $C_2H_5O^+$ **<u>Examiner's Comments</u>**

			For $CH_3CHOHCH_2CHO$, **ALLOW** $C_4H_8O_2$		This novel question linked together acid–base equilibria with a multi-step process. Many candidates completed an equation to generate acid–base pairs, which were then usually assigned correctly. The final equation was challenging but the highest ability candidates were able to combine together all the information with their earlier responses to arrive at the correct equation. See Exemplar 15. **Exemplar 15**  CH_3CHO + OH^- ⇌ CH_3CO^- + H_2O ✓ acid 1 base 2 base 1 acid 2 ✓ • Suggest the equation for **step 2.** $CH_3CHO + CH_3CO^- + H_2O \rightarrow$ + OH^- ✓ [3]
		iv	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous For connectivity, **ALLOW** $\overset{\vert}{\text{OH}}$ $\overset{\vert}{\text{CH}_3}$ CH_3– C_3H– OH— *(Connectivity not being assessed)* **<u>Examiner's Comments</u>** This part was one of the most challenging on the paper. Candidates needed to link the earlier information for combining two ethanal molecules to derive the product for combining two propanone molecules. Despite the challenge, the highest ability candidates were able to come up with the correct structure.
			Total	**6**	
4	a	i	 **Gradient** Correct gradient calculated from best-fit straight line drawn within the range ±800 → ±1040 ✓	**3**	**ALLOW** lines which do not intercept y-axis

			E_a calculation E_a = (−) gradient × 8.314 ✓ *e.g. from ±820, E_a = (+)6817.48* (J mol^{-1}) **E_a to 3 SF AND** use of 10^{-V3} for gradient ✓ *e.g. from ±820, E_a = (+)6820* (J mol^{-1})		**ALLOW** mark for gradient if correct working shown within E_a calculation without gradient being calculated separately **ALLOW** ±0.8(00) → ±1.04(0) *(omission of 10^{-3})* **ALLOW** ECF for calculated gradient × 8.314 If value of gradient not shown separately, **ALLOW** E_a in range: 6650 → 8650 **OR** 6.65 → 8.65 (*omission of 10^{-3}*) **This mark subsumes gradient mark** **NOTE: Omission of 10^{-3} can get 1st 2 marks** **<u>Examiner's Comments</u>** Higher ability candidates realised that the gradient was equivalent to $-E_a/R$ and determined a gradient within the range ± 800 to ± 1040, depending upon the line drawn. Credit was given to gradients of ± 0.800 to ± 1.040 resulting from calculations which omitted 10−3 on the x-axis. The negative gradient was multiplied by *R* to determine E_a with a value rounded to 3 significant figures. Common errors were omission of 10^{-3} in the calculation which led to E_a values between 6.65 and 8.65 J mol^{-1}, or not rounding to 3 significant figures.
		ii	Intercept shown on graph *could be by extrapolation of line, or label on y axis* **AND** ln A linked to intercept value *e.g. ln A = 31.4* ✓ Calculation of *A* = $e^{intercept}$ ✓ *e.g.* $A = e^{31.4} = 4.33 \times 10^{13}$	2	***ALLOW** y = 31.4* **ALLOW** substitution of correct values of ln k and 1/T into ln k = $-E_a/R$ x 1/T + ln A to give a value of ln A which approximately matches the intercept if given *ln A = ln k + (E_a/R x 1/T)* Calculation of A = $e^{\ln A}$ **OR** $e^{\ln k + (Ea/R \times 1/T)}$ **ALLOW** ECF from incorrect ln *A* $e^{31.2}$ = 3.55 × 1013 $e^{31.3}$ = 3.92 × 1013 $e^{31.35}$ = 4.12 × 1013 $e^{31.45}$ = 4.56 × 1013 $e^{31.5}$ = 4.79 × 1013 $e^{31.6}$ = 5.29 × 1013 $e^{31.7}$ = 5.85 × 1013 $e^{31.8}$ = 6.46 × 1013 $e^{31.9}$ = 7.14 × 1013

					$e^{32.0}$ = 7.9(0) × 1013 $e^{32.1}$ = 8.73 × 1013 IF 2 DP answer given, check rounding from calculator value, not 3 DP values given Eg *$e^{31.7}$ = 5.8497 × 10^{13} and = 5.8 × 10^{13}(2SF)* **Examiner's Comments** Higher ability candidates realised that the y-intercept of ln *k* was equivalent to ln *A* and *A* was equivalent to $e^{(\ln A)}$ and were able to process this readily in their calculators. Common errors were to mis-read the intercept. For example, 31.5 was frequently seen as 31.05. Other candidates assumed the y-intercept was log *A* and tried to determine *A* by $10^{(\log A)}$.
	b		*Please refer to the marking instructions on page 5 of this mark scheme for guidance on how to mark this question.* **Level 3 (5–6 marks)** A comprehensive conclusion which uses quantitative results for determination of the reaction orders. **AND** Determines *k* from correct rate equation. **AND** Proposes the two-step mechanism which adds up to overall equation *with no intermediate electrons*. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated. The working for the scientific content is clearly linked to the experimental evidence.* **Level 2 (3–4 marks)** Reaches a sound, but not comprehensive, conclusion based on the quantitative results. **AND** Correctly identifies the orders and rate equation. **AND** Calculates the rate constant **OR** Proposes the two-step mechanism with reactants of first step matching rate equation or matches orders *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence. The working for the scientific content is clearly linked to the experimental evidence.* **Level 1 (1−2 marks)**	**2**	**Indicative scientific points may include:** **Orders and rate equation** • Fe^{3+} 1st order **AND** I^- 2nd order **OR** *rate* = $k[Fe^{3+}][I^-]^2$ • Supported by experimental results **Calculation of *k*, including units** • *k* correctly calculated AND correct units, e.g. $k = \frac{8.10 \times 10^{-4}}{(4.00 \times 10^{-2}) \times (3.00 \times 10^{-2})^2} = 22.5$ • $dm^6\ mol^{-2}\ s^{-1}$ **OR** $mol^{-2}\ dm^6\ s^{-1}$ **Two-step mechanism** • Two steps add up to give overall equation • Slow step/ rate-determining step matches stoichiometry of rate equation. • Each step balances by species and charge **e.g.** $Fe^{3+}(aq) + 2I^-(aq) \rightarrow [FeI2]^+$ SLOW $Fe^{3+}(aq) + [FeI2]^+ \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ FAST $Fe^{3+}(aq) + 2I^-(aq) \rightarrow Fe^{2+}(aq) + I_2^-(aq)$ SLOW $Fe^{3+}(aq) + I_2^-(aq) \rightarrow Fe^{2+}(aq) + I_2(aq)$ FAST $Fe^{3+}(aq) + 2I^-(aq) \rightarrow Fe^+ + I_2$ SLOW $Fe^{3+}(aq) + Fe^+ \rightarrow 2Fe^{2+}(aq)$ FAST There may be other feasible possibilities **Examiner's Comments** Most candidates were able to use the information in the table to determine the order of reaction with respect to

			Attempts to reach a simple conclusion for orders **AND** Attempts a relevant rate equation. *There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant* *The working for the scientific content is clearly linked to the experimental evidence.* **0 marks** No response or no response worthy of credit.		Fe^{3+} ions and I^- ions, which were 1 and 2 respectively. Most candidates were then able to use this knowledge and further information from the table to determine the rate constant, including units (22.5 $dm^6\ mol^{-1}\ s^{-1}$). Many candidates appreciated that the mechanism involved a stoichiometric ratio of 1 : 2 with respect to Fe^{3+} ions and I^- ions, but only the more able were able to suggest a suitable possible two step mechanism. Common errors in proposing a mechanism included equations such as $Fe^{3+}(aq) + 2I^-(aq) \rightarrow Fe^{2+}(aq) + {}^1/_2I_2(aq) + I-(aq)$ which gives a net ratio of 1 : 1 for the reactants. or $Fe^{3+}(aq) + 2I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(aq) + e^-$ which although introducing a correct ratio of reactants also introduces a ‘floating’ electron which in all reality would have attached itself to one of the product species. In questions such as 17a where the quality of extended responses is assessed candidates need to be aware of the need for explanation of their answers. For instance, just giving a correct order of a species in the rate equation is not as strong an answer as one which explains how altering, say doubling, the concentration of a reactant effects the overall rate of reaction, leading to determination of the order. **Exemplar 1**

					 (a)* Determine the rate constant and a possible two-step mechanism for this reaction that are consistent with these results. [6] Experiment 1-2: When $[Fe^{3+}]$ is doubled and $[I^-]$ is constant, rate doubles so reaction is 1st order with respect to $[Fe^{3+}]$. Experiment 1-3: When $[I^-]$ is doubled and $[Fe^{3+}]$ is constant, rate quadruples so reaction is 2nd order with respect to $[I^-]$. rate = $k\,[Fe^{3+}(aq)]\,[I^-(aq)]^2$ $k = \frac{rate}{[Fe^{3+}][I^-]^2}$ $= \frac{8.10 \times 10^{-4}}{4.00 \times 10^{-2} \times (3.00 \times 10^{-2})^2}$ $= 22.5\ mol^{-2}\ dm^6\ s^{-1}$ mechanism: slow step: $Fe^{3+}(aq) + 2I^-(aq) \rightarrow Fe^{2+}(aq) + I_2^-(aq)$ fast step: $Fe^{3+}(aq) + I_2^-(aq) \rightarrow Fe^{2+}(aq) + I_2(aq)$ This exemplifies how a concise response can gain full marks on a Level of Response question. The candidate has clearly identified which data they have referred to in the table, and explained the conclusions that can be drawn. The rate equation is then clearly shown, along with subsequent working to determine the value of the rate constant. Finally, the suggested mechanism is given, along with an indication of which is the slow step. The line breaks clearly identify each stage in the response, and it fully satisfies the level 3 criteria in the mark scheme.
			Total	**11**	
5	a		Measure mass (loss) ✓	1	**ALLOW** weight for mass **ALLOW** take samples and titrate (remaining H_2O_2) **Examiner's Comments** The idea of measuring mass loss (over time) was frequently given as a correct response. The idea of titrating samples to determine the concentration of hydrogen peroxide during the course of the reaction was occasionally seen and given credit.
	b		*Please refer to the marking instructions on page 5 of mark scheme for guidance on marking this question.* **Level 3 (5–6 marks)** A comprehensive conclusion using quantitative data from the graph to correctly determine initial rate **AND** half lives / gradient with 1st order conclusion for H_2O_2 **AND** determination of *k.* *There is a well-developed line of reasoning which is clear and logically structured.* *Clear working for initial rate, half* life / gradient *and order and k.* *Units mostly correct throughout.*	6	**Indicative scientific points may include:** **Initial rate** • Tangent shown on graph as line at t = 0 s • Gradient determined in range: 1.5 − 2.0 × 10^{-3} e.g. $\frac{2.3}{1300}$ = 1.77 × 10^{-3} • *initial rate* as gradient value with units: mol dm^{-3} s^{-1}, *For other methods contact TL* **Evidence for 1st order 2 methods**

			Level 2 (3–4 marks) Attempts to describe all three scientific points but explanations may be incomplete. **OR** Explains two scientific points thoroughly with few omissions. *There is a line of reasoning with some structure and supported by some evidence. The scientific points are supported by evidence from the graph.* **Level 1 (1–2 marks)** Reaches a simple conclusion using at least one piece of quantitative data from the graph. Attempts to calculate initial rate **OR** half life. *There is an attempt at a logical structure with a reasoned conclusion from the evidence.* **0 marks** *No response worthy of credit.*		• 1st order clearly linked to half-life **OR** 2 gradients: **1. Half life** • Half life shown on graph • Half life range 800-1000 s • Two 'constant' half lives ±50 s **2. Two gradients → two rates** • 2 tangents shown on graph at *c* and *c*/2 • Gradient at *c*/2 is half gradient at *c* e.g. c = 2.3 mol dm^{-3}, gradient = 1.6 × 10^{-3} **AND** c = 1.15 mol dm^{-3}, gradient = 0.8 × 10^{-3} • For chosen method, conclusion: H_2O_2 is 1st order **Determination of *k*** **2 methods** • *k* clearly linked to rate **OR** half-life: $k = \frac{rate}{[H_2O_2]}$ e.g. $k = \frac{1.6 \times 10^{-3}}{2.3}$ $= 7 \times 10$ s^{-1} **OR** $k = \frac{\ln 2}{t_{1/2}}$ e.g. $k = \frac{0.693}{950}$ $= 7.3 \times 10^{-4}$ s **Examiner's Comments** This was the first of the two extended response questions in which the candidates had to determine three values based initially upon the graph. Some of the workings on the graph were a little hard to follow. Many candidates scored highly on this question, showing a good understanding of the chemistry involved. Weaker candidates sometimes struggled to express the link between the different values being calculated and were awarded a lower level mark.
	c		$n(H_2O_2) = 2.30 \times \frac{25.0}{1000}$ **OR** = 0.0575 (mol) ✓ vol $O_2 = \frac{0.0575}{2} \times 24000 = 690$ **cm^3** ✓ Collect in 1000 cm^3/1 dm^3 measuring cylinder ✓	3	**ALLOW** 0.69(0) **dm^3** 2nd mark subsumes 1st mark **ALLOW** 1000 cm^3/1 dm^3 syringe

					Needs a **name** of actual apparatus, not just 'container' 'measuring cylinder' without volume is insufficient **DO NOT ALLOW** burette For other possible apparatus, contact Team Leader **ALLOW** volumes from 700−1000 cm^3 but should be realistic apparatus, e.g. 700, 750, 800, 850, 900, 950. **Examiner's Comments** The majority of candidates were able to score the two marks for determining the volume of oxygen to be 690 cm^3 (or 0.690 dm^3). Only a very small proportion of candidates were able to suggest a suitably sized piece of apparatus.
			Total	**10**	
6		i	*(rate =)* $k\,[H_2O_2]\,[I^-]$ ✓ $k = \frac{rate}{[H_2O_2]\,[I^-]} = \frac{2.00 \times 10^{-6}}{0.0100 \times 0.0100} = 0.02(00)$ ✓ units: $dm^3\ mol^{-1}\ s^{-1}$ ✓	**3**	**Square brackets required** **IGNORE** any state symbols **IGNORE** $[H^+]^0$ **ALLOW ECF** from incorrect rate equation **BUT** units must fit with rate equation used **ALLOW** $mol^{-1}\ dm^3\ s^{-1}$ **OR** in any order **NOTE** K_c expression with calculation and units **0 marks** **Examiner's Comments** This rates calculation was generally well answered. Surprisingly, some candidates did not write the rate equation, despite being part of the question. A common mistake was omission of $\times 10^{-6}$. Most candidates find determination of orders from initial rates data a straightforward task. Despite this, many obtained an incorrect rate equation, the most common being *rate* = $k[I^-]$. The mark scheme allowed error carried forward from an incorrect rate equation for both the calculated value of k and its units.
		ii	Plot graph using ln k **AND** $1/T$ ✓ (Measure) gradient ✓ *Independent mark*	**3**	**Unless otherwise stated, assume, that ln *k* is on y axis and 1/*T* is on x axis** **IGNORE** intercept **ALLOW** gradient $= (-)\frac{E_a}{R}$ …………………………………………………… **NOTE: ALLOW 'Inverse graph' (special case)**

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<td>$E_a = (–)R \times$ gradient OR (–)8.314 × gradient ✓

<i>• Independent mark, even if variables for graph are incorrect</i>
<i>• Subsumes ‘gradient‘ mark</i></td>
<td></td>
<td>Plot graph of $1/T$ against ln k ✓

(Measure) gradient ✓
<i>Independent mark</i>

$E_a = (–)\frac{R}{\text{gradient}}$ OR $(–)\frac{8.314}{\text{gradient}}$

OR gradient $= (–)\frac{R}{E_a}$ ✓

<i>Subsumes ‘gradient’ mark</i>

Examiner’s Comment:
Most candidates used the logarithmic form of the Arrhenius equation from the Data Sheet and recognised that a graph of ln k against $1/T$ would produce a gradient of $−E_a/R$. Errors were sometimes made with the graph itself with many opting for ln k against T or k against T. A significant number of candidates seemed muddled by the term ‘against’ in describing their graph. A safer option is to state the axes for each variable.</td>
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<td>Total</td>
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<td>7</td>
<td>a</td>
<td></td>
<td>Iodine (solution) has a yellow/orange/brown colour
AND
Concentration of I_2 decreases/I_2 is used up ✓</td>
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<td>ALLOW products are colourless</td>
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<table>
<tr><th>Time/s</th><th>[I_2(aq)]/mol dm^{-3}</th></tr>
<tr><td>0</td><td>0.0100 ✓</td></tr>
<tr><td>500</td><td>0.00225 ✓</td></tr>
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<td>2</td>
<td>ALLOW 0.01 and 0.010

ALLOW 0.0023</td>
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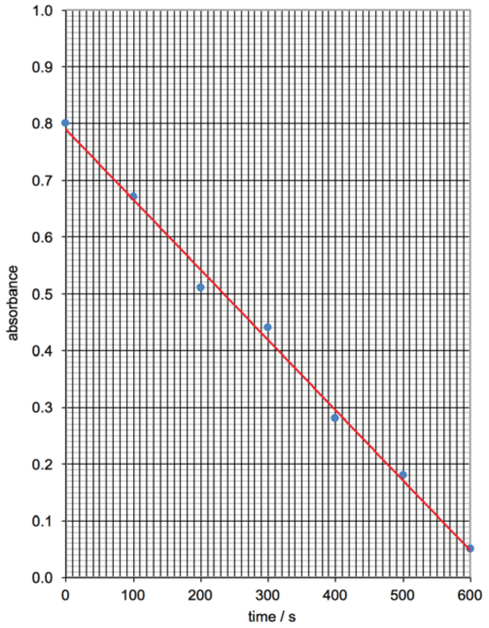
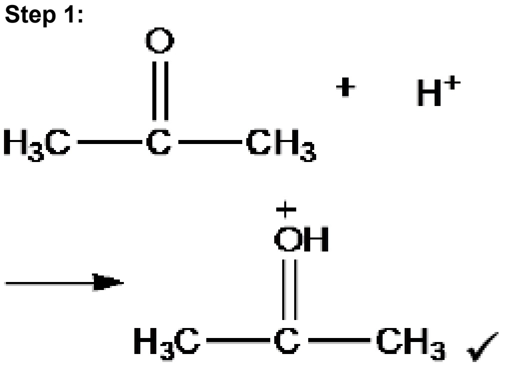
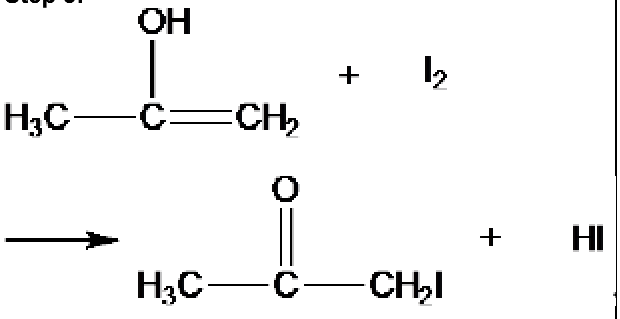
	c	i	 Axes labelled with units **AND** linear scales **AND** at least half of the graph paper used ✓ Points correctly plotted ✓ Best fit straight line ✓	3	Each point **must** be within one small square on graph paper of value in table
		ii	Order = 0 ✓ Straight line graph shows rate is constant throughout **OR** rate does not depend on $[I_2]$ ✓	2	
	d		**Step 1:**  **Step 3:** 	2	**ALLOW** correct molecular, structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non−ambiguous
			Total	**10**	

8			*Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.* **Level 3 (5−6 marks)** A comprehensive conclusion which outlines control of concentrations for each experiment with all volumes shown **AND** uses quantitative results for determination of orders and rate equation **AND** calculates a value for the rate constant with units. *There is a well-developed conclusion showing a line of reasoning which is clear and logically structured. The working for control of variables, determination of orders/rate equation and rate constant are clearly linked to the experimental evidence.* **Level 2 (3−4 marks)** Reaches a sound, but not comprehensive, conclusion based on the quantitative results **AND** outlines control of all concentrations, diluting each solution at a time **OR** correctly identifies the orders supported by results and calculates a value for the rate constant. *The conclusion has a line of reasoning with some structure. The working for control of variables **OR** orders/rate equation **AND** rate constant are linked to the experimental evidence.* **Level 1 (1−2 marks)** Attempts to controls concentrations by diluting each solution in turn **AND** reaches a simple conclusion for orders to obtain a rate equation with few errors. *The working for orders, and rate equation are linked to the experimental data, but the evidence may not be clearly shown.* **0 marks** − No response or no response worthy of credit.	6	**Indicative scientific points may include:** **<u>Control of variables</u>** *Initial concentrations throughout* • mix 10 cm^3 of Br^-, BrO_3^- and H^+ • dilute each solution in turn with water • only one solution changed at a time • total volume kept the same **NOTE:** Volumes of each mixture could be shown and illustrates all points above, e.g. *Expt 1*: 10 / 10 / 10 *Expt 2*: 2.5 + 7.5 H_2O / 10 / 10 *Expt 3*: 10 / 5 + 5 H_2O /10 *Expt 4*: 10 / 5 + 5 H_2O / 5 + 5 H_2O …………………………………………………. **<u>Orders/rate equation</u>** • Br^- 1st order BrO_3^- 1st order H^+ 2nd order **OR** *rate* = $k[Br^-]\,[BrO_3^-]\,[H^+]^2$ • Supported by reasoning from the experimental results **<u>Calculation of *k* including units</u>** • Value of *k* correctly calculated**:** k = 12 • Units: dm^9 mol^{-3} s^{-1} **OR** mol^{-3} dm^9 s^{-1}
			Total	**6**	
9	a		***initial rates data (3 marks)*** **NOTE**: Each comparison **MUST** relate to the **actual** change in concentration / rate in the experiments	3	***FULL ANNOTATIONS MUST BE USED*** ………………………………………. **THROUGHOUT**, • Square brackets **NOT REQUIRED** around H_2O_2, H^+ and I^-

			EXPTS **H_2O_2:** $[H_2O_2]$ × 2 rate × 2 (1 & 2) **AND** 1st order ✓ **H^+:** $[H^+]$ × 2 rate does not change (2 & 3) **AND** Zero order ✓ **I^-:** $[I^-]$ × 2 **AND** $[H_2O_2]$ × 2 rate × 4 (2 & 4) **OR** $[I^-]$ × 2 **AND** $[H_2O_2]$ × 4 rate × 8 (1 & 4) **OR** $[I^-]$ × 2 **AND** $[H_2O_2]$ × 2 rate × 4 (3 & 4) **AND** 1st order ✓		• **ALLOW** ‘doubles’ for × 2; quadruples for × 4 **ALLOW** direct comparison of concentrations and rate, e.g. $[H_2O_2]$ changes by $\frac{0.0020}{0.0010} = 2$, rate changes by $\frac{1.14 \times 10^{-5}}{5.70 \times 10^{-6}} = 2$ **AND 1**st order (Expts 1 & 2) **DO NOT ALLOW** I_2 for I^- **IGNORE** $[H^+]$ for Expts 3 & 4
			Calculation of rate constant (3 marks), **EITHER** $k = \frac{5.70 \times 10^{-6}}{0.0010 \times 0.20}$ **OR** 2.85×10^{-2} **OR** 0.0285 **OR** 0.029 ✓ $k = 2.9 \times 10^{-2}$ ✓ (2 SF in standard form) *Subsumes previous mark if no working shown* $dm^3\ mol^{-1}\ s^{-1}$ ✓	3	**IGNORE working** **DO NOT ALLOW** 0.03 **ALLOW ECF** from error in powers of 10 **ONLY** e.g. 2.9×10^{-3} by use of 0.010 instead of 0.0010 **DO NOT ALLOW 2.90** × 10^{-2} **(3 SF)** **OR 29** × 10^{-3} (Not standard form) **ALLOW** mol^{-1}, dm^3 and s^{-1} in any order, e.g. $mol^{-1}\ dm^3\ s^{-1}$ **Examiner's Comments** This question assessed different aspects of reaction rates, based around the reaction of hydrogen peroxide with hydrogen and iodide ions. This part required candidates to show that the experimental results provided evidence for a provided rate equation. Most candidates were able to link concentration changes within the experiments with rate for H_2O_2 and H^+. For I^-, there were two concentration changes but weaker candidates often ignored the H_2O_2 change. The best answers were well-structured and succinct. Many longer, less focussed responses were seen which often omitted important detail. The rate constant was usually calculated correctly but many candidates did not show their calculated answer in standard form or to two significant figures. Candidates are advised to look carefully at the requirements of the question. Answer: $k = 2.9 \times 10^{-2}$ $dm^3\ mol^{-1}\ s^{-1}$.
	b		H^+ ions are consumed / used up **OR** H^+ ions are in the (overall) equation ✓	1	**ALLOW** H^+ is **not** regenerated / reformed **ALLOW** H^+ is a reactant but not a product **ALLOW** ‘it’ for H^+

					IGNORE H^+ is not in the rate equation / does not affect rate **IGNORE** does not take part in rate-determining step **Examiner's Comments** This question assessed different aspects of reaction rates, based around the reaction of hydrogen peroxide with hydrogen and iodide ions. This part was answered well, with most candidates recognising that H^+ was used up in the overall equation. Some candidates were distracted by the absence of H^+ in the rate equation.
	c	i	The slowest / slow step ✓	1	**ALLOW** step that takes the longest time **Examiner's Comments** This question assessed different aspects of reaction rates, based around the reaction of hydrogen peroxide with hydrogen and iodide ions. Almost all candidates were aware that the rate-determining step is the slowest step in a multi-step mechanism.
		ii	**NO ECF from incorrect rate equation Principles** • H_2O_2 and I^- **must be** the reactants in **1st step** • 2nd mark **only to be awarded** if 1st mark scored • Step 4 is independent **Reactants of Step 1 as H_2O_2 + I^-** **1 mark** **Step 1**: $H_2O_2 + I^-$ ✓ **Products of Step 1 AND all of Step 2** **1 mark** **Step 1** $\rightarrow IO^- + H_2O$ **AND Step 2**: $H^+ + IO^- \rightarrow HIO$ ✓ **Step 4 (Independent mark)** **1 mark** $H^+ + OH^- \rightarrow H_2O$ ✓	3	**IGNORE state symbols** Elements can be in any order in formulae **Alternatives for 2nd mark** **Step 1**: $\rightarrow HIO + OH^-$ **AND Step 2**: $H^+ + OH^- \rightarrow H_2O$ ✓ **Step 1**: $\rightarrow H_2O_2I^-$ **AND Step 2**: $H^+ + H_2O_2I^- \rightarrow HIO + H_2O$ ✓ Other possibilities, contact TL

<table>
<tr><td></td><td></td><td></td><td></td><td></td><td>ALLOW $2H^+ + 2OH^- \rightarrow 2H_2O$
$H_3O^+ + OH^- \rightarrow 2H_2O$

Examiner's Comments

This question assessed different aspects of reaction rates, based around the reaction of hydrogen peroxide with hydrogen and iodide ions.

This part was attempted very well, the majority identifying that the reactants of the rate-determining step (Step 1) are obtained from the rate equation. Various possible equations were allowed for the remaining steps. Some otherwise correct equations could not be credited as charges had been omitted. Candidates are advised to check that charges, as well as species, balance on each side of any equation.</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>11</td><td></td></tr>
<tr><td>10</td><td>a</td><td></td><td>NOTE: First 3 marks are ONLY available from an expression using $[NO]^2$
Units are marked independently
……………………………………………………
Using values ON THE CURVE in CORRECT expression 1 mark
Use of any two correct values for rate and [NO] from graph e.g. for 5.0×10^{-4} and 4.2×10^{-4},
$k = \dfrac{6.0 \times 10^{-4}}{(2.0 \times 10^{-2}) \times (6.0 \times 10^{-4})^2}$

OR
$4.2 \times 10^{-4} = k\,(2.0 \times 10^{-2}) \times (5.0 \times 10^{-4})^2$ ✓
……………………………………………………
Calculation of <i>k</i> 2 marks

FOR 1 MARK

<i>k</i> calculated correctly from values obtained from graph
BUT NOT in standard form AND / OR more than 2 SF
e.g. $k = \dfrac{6.0 \times 10^{-4}}{(2.0 \times 10^{-2}) \times (6.0 \times 10^{-4})^2} = 83333.33$ ✓

OR FOR 2 MARKS

<i>k</i> calculated correctly from values obtained from graph
AND in standard form AND TO 2 SF
e.g. <i>k</i> = 83333.33 gives 8.3×10^4 ✓
……………………………………………………</td><td>4</td><td>Note: rate and [NO] are any correct pair of readings from the graph,
The [NO] below are the most commonly seen.
For these [NO] values, these are the ONLY rates allowed
<table>
<tr><th>[NO]</th><th>rate</th><th><i>k</i></th><th><i>k</i></th></tr>
<tr><td>1.0×10^{-4}</td><td>0.1×10^{-4} to
0.2×10^{-4}</td><td>50000
100000</td><td>5.0×10^4
1.0×10^5</td></tr>
<tr><td>2.0×10^{-4}</td><td>0.6×10^{-4} to
0.7×10^{-4}</td><td>75000
87500</td><td>7.5×10^4
8.8×10^4</td></tr>
<tr><td>3.0×10^{-4}</td><td>1.5×10^{-4}</td><td>83333</td><td>8.3×10^4</td></tr>
<tr><td>4.0×10^{-4}</td><td>2.7×10^{-4}</td><td>84375</td><td>8.4×10^4</td></tr>
<tr><td>5.0×10^{-4}</td><td>4.2×10^{-4}</td><td>84000</td><td>8.4×10^4</td></tr>
<tr><td>6.0×10^{-4}</td><td>6.0×10^{-4}</td><td>83333</td><td>8.3×10^4</td></tr>
<tr><td>7.0×10^{-4}</td><td>8.2×10^{-4}</td><td>83673</td><td>8.4×10^4</td></tr>
</table>

IF OTHER values are given, mark using the same principle. If any doubt, contact TL.

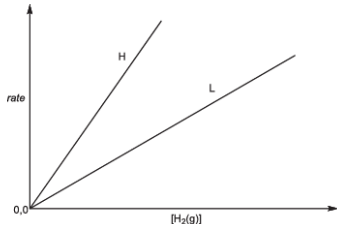
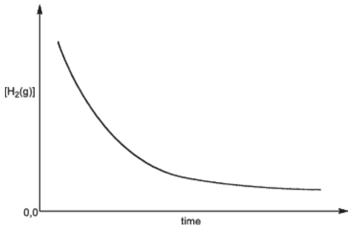
NOTE: IGNORE any numbers used from tangents
……………………………………………………
SPECIAL CASES that ALLOW ECF for calculation of <i>k</i> from ONLY ONE of the following <i>(2 marks)</i>
1. Powers of 10 incorrect or absent in initial <i>k</i> expression
2. $[H_2]^2[NO]$ used instead of $[H_2][NO]^2$.
3. Any value within ±0.2 of actual values from graph

……………………………………………………

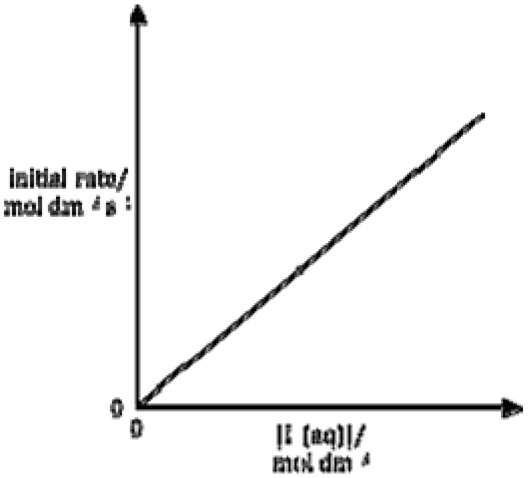
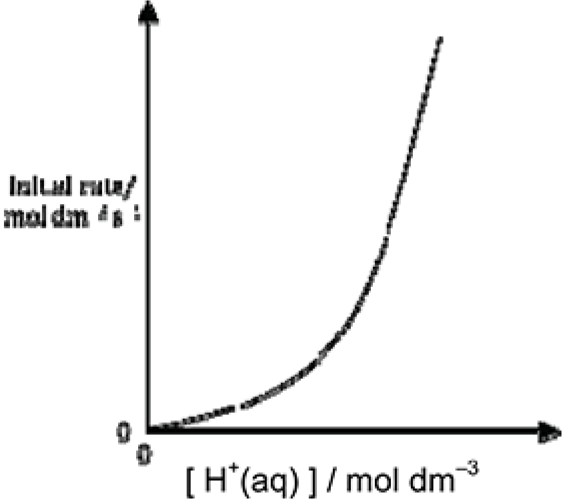
ALLOW units in any order, e.g. $mol^{-2}\ dm^6\ s^{-1}$

Examiner's Comments

This part required candidates to calculate a rate constant from a rate–concentration graph and a rate equation. Most candidates were able to obtain correct values from the rate–concentration graph, with a tolerance of ±0.1 allowed, and to calculate a value for the rate constant; three or four marks were common.</td></tr>
</table>

			UNITS FOR 1 MARK: dm^6 mol^{-2} s^{-1} ✓		In the calculation, almost all candidates were able to rearrange the rate equation and to calculate a value for the rate constant, although this was not always expressed to two significant figures and to standard form. A significant number of candidates omitted one or both the powers of 10 for rate and concentration in their calculation. Answers: The value of k allowed depended on the values of rate and concentration that had been used from the supplied graph and the required value of *k* was usually either 8.3 × 10^4 or 8.3 × 10^4 dm^6 mol^{-2} s^{-1}. This part was almost universally correct. The commonest error was two upwardly sloping curves, starting from the origin, and this response was awarded one mark.
	b	i	 One straight upward line **AND** starting at 0,0 ✓ 2nd straight upward line starting at 0,0 and steeper		**ALLOW** 1 mark for two upward sloping curves starting at origin **AND** upper curve labelled H and lower curve labelled L **NOTE: ALLOW** some leeway for lines starting from origin **ALLOW** straight line not drawn with ruler, i.e. is a straight line rather than a curve
		i	**AND** Steeper line labelled H **OR** less steep line labelled L ✓	2	**ALLOW** similar labelling as long as it is clear which line is which
		ii	increases ✓	1	**Examiner's Comments** Almost all candidates were aware that a rate constant increases in value with increasing temperature.
	c		**MARK INDEPENDENTLY** …………………………………………………………  Downward curve ✓		**ALLOW** curve touching y axis **ALLOW** curve touching x axis **ALLOW** Two half lives are the same

			Half life is constant ✓	2	**IGNORE** 'regular' half life (not necessarily the same) **Examiner's Comments** This part was answered extremely well, with the expected downward slope and a comment about a constant half-life. Comparatively few incorrectly shaped lines were seen.
	d	i	$H_2 + N_2O \rightarrow N_2 + H_2O$ ✓	1	**ONLY** correct answer **DO NOT ALLOW** multiples **Examiner's Comments** Most candidates were aware that the equations for the three steps must add to give the overall equation and the majority of candidates obtained the correct equation.
		ii	Steps 1 **AND** Step 2 together give $2NO + H_2$ ✓	1	**ALLOW** Step 1 **AND** Step 2 together give species in same ratio as in rate equation **ALLOW** rate-determining step / slow step for Step 2 **ALLOW** H_2 reacts with N_2O_2 which is formed from 2NO **NOTE:** The response must link Step 1 with Step 2 Steps can be referenced from the species in each step **Examiner's Comments** Candidates found this part far more difficult. Most were clearly expecting to answer in terms of the species in the slow step being present in the rate equation and many responded in this way. This strategy will only work if the slow step is also the first step. Only the best candidates were able to interpret the data, explaining that N_2O_2 in the slow step had been formed from 2NO in the preceding fast step.
			Total	**11**	
11	a	i	5 **OR** 5th (order) ✓	1	**Examiner's Comments** This part was almost universally correct.
		ii	(stoichiometry in) rate equation does not match (stoichiometry) in **overall** equation ✓ Collision unlikely with more than 2 ions / species / particles ✓	2	**ALLOW** moles / ions / species / particles / molecules / atoms throughout *(i.e. emphasis on particles)* **IGNORE** more reactants in overall equation **If number of species is stated, ALLOW 3–5 only** *(rate equation contains 5 ions)* **DO NOT ALLOW** negative ions would repel

					(there is a mixture of positive and negative ions) **IGNORE** more than two **reactants** collide *(not related to rate equation)* **Examiner's Comments** Able candidates were often able to suggest one of the two acceptable reasons in the mark scheme: different coefficients in the rate and overall equation or the unlikelihood of more than 2 species colliding. Although the reacting species were all ions, the examiners did allow various terms provided that they were indicative of particles. Reactants was not allowed as the reactants in the two equations were the same and collisions are specific to particles.
	b		 Straight upward line **AND** starting at 0,0 ✓  Curve with increasing gradient, **AND** starting at 0,0 ✓	2	**ALLOW** lines starting close to 0,0 **ALLOW** 2nd order line with 'straight' section early or late as long as an upward curve is seen between. **Examiner's Comments** It was common to see correct lines for both graphs. Incorrect sketches often showed curves reminiscent of a half life relationship of an inverse 2nd order curve.
	c	i	5.4(0) ✓ 614.4(0) ✓	2	**IGNORE** sign **ALLOW** 614 **OR** 610 **Examiner's Comments** Able candidate usually obtained both marks but average and weaker candidates often experienced problems, particularly with the rate for Experiment 3. The

					commonest mistakes stemmed from not using the squared terms in the rate equation, resulting in rates of 1.80 for Experiment 2 and 9.60 for Experiment 3. Other incorrect answers for Experiment 3, such as 21.6 were the result of multiplying the rate in Experiment 1 by various multiples of 4. Answers: Experiment 2, 5.40 mol dm^{-3} s^{-1}; Experiment 3, 614.40 mol dm^{-3} s^{-1}
		ii	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 6.7×10^8 **OR** 670000000 dm^{12} mol^{-4} s^{-1}, award **3 marks** **IF** answer = 6.7×10^8 **OR** 670000000 with incorrect units, award **2 marks** *k* to <2 SF: 666666666.7 ✓ **OR** *k* to 2 SF: 6.7×10^8 **OR** 670000000 ✓✓ units: dm^{12} mol^{-4} s^{-1} ✓	3	**ALLOW ECF** from incorrect initial rates if 1st experimental results have **not** been used. **(Look to 4(c)(i) to check)** *i.e.* **IF** other rows have been used, then calculate the rate constant from data chosen. For *k*, **ALLOW** 1 mark for the following: 6.6×10^8 recurring 6.6×10^8 2 SF answer for *k* **BUT** one power of 10 out i.e. 6.7×10^9 **OR** 6.7×10^7 **ALLOW** units in any order, e.g. mol^{-4} dm^{12} s^{-1} **Examiner's Comments** Almost all candidates used the information from Experiment 1 to calculate a value for the rate constant. Most were able to obtain 6.6 recurring with most middle and able candidates correctly rounding their answer to the required two significant figures. Weaker responses showed incorrect powers of 10, rounding to two decimal places (in this case three significant figures) and incorrect rounding to 6.6. Rounding and significant figures are a basic GCSE mathematical skill. Candidates are well advised to check any significant figure or decimal place requirements in calculations before moving on the next question. Candidates coped well with the unfamiliar units for the rate constant of a fifth order reaction. The examiners accepted units in any order but the more correct positive before negative order of indices was usually seen. Answer: 6.7 10^8 dm^{12} mol^{-4} s^{-1}
		iii	(K_a =) $10^{-3.75}$ **OR** 1.78×10^{-4} (mol dm^{-3}) ✓ $[H^+]$ **=** $\sqrt{1.78 \times 10^{-4} \times 0.0200}$ = 1.89×10^{-3} (mol dm^{-3}) ✓ initial rate = 6.7×10^8 x 0.01 x 0.015^2 x $(1.89 \times 10^{-3})^2$ = 5.33×10^{-3} to 5.38×10^{-3} (mol dm^{-3} s^{-1}) **OR** 5.3×10^{-3} to 5.4×10^{-3} (mol dm^{-3} s^{-1}) ✓	3	***FULL ANNOTATIONS MUST BE USED*** …………………………………… **For ALL marks, ALLOW 2 SF** up to calculator value correctly rounded $1.77827941 \times 10^{-4}$ **ALLOW** $\sqrt{10^{-3.75} \times 0.0200}$ for first marking point **ALLOW** 1.88×10^{-3} (mol dm^{-3}) **ALLOW ECF** from calculated $[H^+(aq)]$ and calculated answer for *k* from **4(c)(ii)** e.g. If no square root taken,

			Actual value will depend on amount of acceptable rounding in steps and whether figures kept in calculator even if rounding is written down. **ALLOW** any value in range given above.		$[H^+] = 3.56 \times 10^{-6}$ mol dm^{-3} and *rate* = 1.91×10^{-8} **OR** 1.9×10^{-8} by **ECF** **Examiner's Comments** This question linked two areas of the specification, pH calculations of weak acids with reaction rates. Overall candidates coped admirably with the challenge and most calculated the $[H^+]$ successfully. Weaker candidates often made no further progress but many candidates then moved forwards to correctly calculate the initial rate. The examiners used the candidate answer from 4(c)(ii) for ECF purposes. Because of the range of possible intermediate roundings in this calculation, a generous range of values was allowed for the initial rate. Answer: $5.33\ 10^{-3}$ to $5.38\ 10^{-3}$ dm^{12} mol^{-4} s^{-1}
			Total	**13**	
12		i	N_2O_4 = +4 **AND** NO_3^- = +5 **AND** NH_4^+ = −3 ✓	1	**ALL** 3 oxidation numbers required **DO NOT ALLOW** missing '+' or '−' **OR** oxidation numbers shown as charges e.g. N^{5+}
		ii	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **If answer = 7.9(0) (g) award 2 marks** $n(KMnO_4) = \frac{0.200 \times 250}{1000}$ = 0.0500 (mol) ✓ mass of $KMnO_4$ = 0.0500 × 158.0 = 7.9(0) (g) ✓	2	
		iii	dm^6 mol^{-2} s^{-1} ✓	1	
		iv	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **If answer = 1.54×10^{23} award 2 marks** $n(\text{tartaric acid}) = \frac{38.25}{150}$ = 0.255 (mol) ✓ number of molecules = $0.255 \times 6.02 \times 10^{23}$ = 1.54×10^{23} ✓ (***3 SF** required from least significant data*)	2	**ALLOW ECF** from *n*(tartaric acid) Common error: use of 148 *(missing 2H Structure)* → 1.56×10^{23}
			Total	**6**	
13	a		Measure reduction of colour of bromine	1	
	b		Measure volume of CO_2 (produced)	1	
	c		Concentration of HCOOH would be constant	1	
	d		* *Please refer to the marking instruction point 10 for guidance on how to mark this question.*	6	**Indicative scientific points may include:Initial rate**

			Level 3 (5–6 marks) A comprehensive conclusion which uses quantitative data from the graph to correctly identify and calculate initial rate **AND** half lives and reasoned order of Br_2 **AND** determination of *k* with units. *There is a well-developed conclusion showing a line of reasoning which is clear and logically structured. The working for initial rate, half life and order are clearly shown. Determination of k is clear and correct.* **Level 2 (3–4 marks)** Reaches a sound, but not comprehensive, conclusion based on quantitative data from the graph. Correctly identifies and calculates initial rate **AND** half lives and reasoned order of Br_2. *The conclusion has a line of reasoning presented with some structure. The initial rate and order is relevant and supported by correct evidence from the graph. There may be errors in the calculations which prevent the correct determination of k.* **Level 1 (1–2 marks)** Reaches a simple conclusion using at least one piece of quantitative data from the graph. Attempts calculation of initial rate **OR** half lives and reasoned order of Br_2. *The information selected from the graph is basic and communicated in an unstructured way. The calculations may not be clear and the evidence used from the graph may not be clearly shown.* **0 marks** No response or no response worthy of credit.		• Evidence of tangent on graph drawn to line at t = 0 s **AND** gradient determined in range $4 \pm 1 \times 10^{-5}$ • *initial rate* expressed as gradient value with units of mol dm^{-3} s^{-1}, e.g. *initial rate* = 4×10^{-5} mol dm^{-3} s^{-1} **Half lives and reasoned order of Br_2** • Half life measured on graph **OR** within text **OR** stated in range 180−200 s • Constant half life **OR** two stated half lives within ±20 s **AND** conclusion that Br_2 is 1st order **Determination of *k* with units** • Rate constant *k* clearly linked to initial rate **OR** half-life: $k = \frac{rate}{[Br_2]}$ **OR** $k = \frac{\ln 2}{t_{1/2}}$ • *k* determined correctly from measured initial rate or measured half life with units of s^{-1}, e.g. $k = 4 \times 10^{-3}$ s^{-1} from initial rate of 4×10^{-5} mol dm^{-3} s^{-1} **OR** $t_{1/2}$ of 175 s
			Total	**9**	
1 4	a		*Please refer to the marking instruction point 10 for guidance on how to mark this question.* **Level 3 (5–6 marks)** A comprehensive conclusion which uses quantitative results for determination of the reaction orders **AND** determination of *k* with units **AND** proposes the two-step mechanisms. *There is a well-developed conclusion showing a line of reasoning which is clear and logically structured. The working for orders, rate equation, rate constant and two-step mechanism are clearly linked to the experimental evidence.* **Level 2 (3–4 marks)** Reaches a sound, but not comprehensive, conclusion	6	**Indicative scientific points may include:** **Orders and rate equation** • NO_2 and O_3 both 1st order **OR** *rate* = $k[O_3]\ [NO_2]$ • Supported by experimental results **Calculation of *k*, including units** • *k* correctly calculated **AND** correct units, i.e. $k = 1.28 \times 10^{-2}$ • $dm^3 mol^{-1} s^{-1}$ **OR** $mol^{-1} dm^3\ s^{-1}$ **Two-step mechanism**

<table>
<tr>
<td></td>
<td></td>
<td></td>
<td>based on the quantitative results.
Correctly identifies the orders and rate equation AND calculates the rate constant with units OR proposes the two-step mechanism.

<i>The conclusion has a line of reasoning presented with some structure. The working for orders, rate equation AND rate constant OR the two-step mechanism are linked to the experimental evidence.</i>

Level 1 (1–2 marks)
Reaches a simple conclusion for orders AND rate equation.

<i>The working for orders, and rate equation are linked to the experimental data, but the evidence may not be clearly shown.</i>

0 marks
No response or no response worthy of credit.</td>
<td></td>
<td>

Two steps add up to give overall equation
Slow step / rate-determining step matches stoichiometry of rate equation.

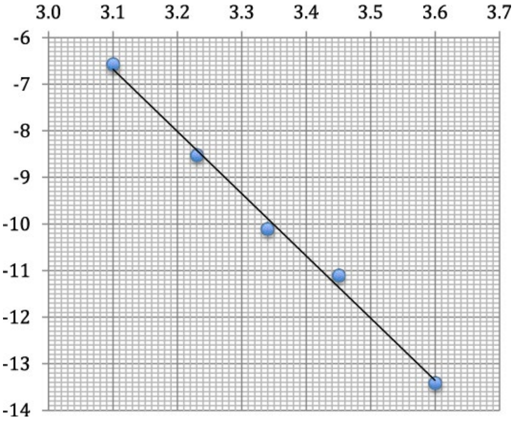
e.g. $O_3 + NO_2 \rightarrow O_2 + NO_3$ rate-determining step
$NO_3 + NO_2 \rightarrow N_2O_5$

OR
$O_3 + NO_2 \rightarrow 2O_2 + NO$ rate-determining step
$NO + O_2 + NO_2 \rightarrow N_2O_5$</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td></td>
<td>
<table>
<tr><th>Temperature, T / K</th><th>Rate constant, k / s^{-1}</th><th>1 / T / K^{-1}</th><th>ln k</th></tr>
<tr><td>278</td><td></td><td></td><td></td></tr>
<tr><td>290</td><td></td><td>3.45×10^{-3}</td><td></td></tr>
<tr><td>298</td><td></td><td></td><td></td></tr>
<tr><td>308</td><td></td><td></td><td>−8.52</td></tr>
<tr><td>323</td><td></td><td></td><td></td></tr>
</table>

two missing values: 3.45×10^{-3} AND −8.52

all points plotted correctly
AND
best straight line drawn through points

gradient = $\pm 1.36 \times 10^4$
<i>acceptable range: $1.30-1.40 \times 10^4$</i>

multiplication by 8.314
AND
division by 10^3 to give E_a = (+)113 (kJ mol^{-1})</td>
<td>4</td>
<td>
ALLOW mark for gradient if correct working shown within E_a calculation without gradient being calculated separately.

ALLOW ECF from value of gradient
BUT
DO NOT ALLOW '−' sign for E_a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>i</td>
<td>FIRST CHECK THE ANSWER ON THE ANSWER LINE
IF answer = 0.163 $dm^3\ mol^{-1}\ s^{-1}$ OR 0.1632 $dm^3\ mol^{-1}\ s^{-1}$ award 4 marks
IF answer = 0.163 OR 0.1632 with incorrect units award 3 marks

Order w.r.t. ICl = 1 and order w.r.t H_2 = 1 (1)</td>
<td>4</td>
<td>If there is an alternative answer, check to see if there is any ECF credit possible using working below

both orders = 1 mark

correct rate equation or rearranged form = 1 mark</td>
</tr>
</table>

			rate = $k[ICl][H_2]$ (1) $k = \frac{2.04 \times 10^{-2}}{0.250 \times 0.500}$ = 0.163 **OR** 0.1632 (1) $dm^3\ mol^{-1}\ s^{-1}$ (1)		candidates may use experimental data from experiments 2 or 3 to calculate the rate constant **do not allow** 0.16
		ii	rate = $k[ICl][H_2]$ (from **(i)**) = $0.163 \times 3 \times 10^{-3} \times 2 \times 10^{-3} = 9.78 \times 10^{-7}$ ($mol\ dm^{-3}\ s^{-1}$) (1)	1	**allow ecf** from **(i)** Note use of 0.1632 from **(i)** gives $9.79(2) \times 10^{-7}$
			Total	**5**	