

| Question |  | Answer | Marks | Guidance |
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| (b) | (i) |  <br> One straight upward line AND starting at $0,0 \checkmark$ <br> 2nd straight upward line starting at 0,0 and steeper AND <br> Steeper line labelled H OR less steep line labelled $L$ | 2 | ALLOW 1 mark for two upward sloping curves starting at origin <br> AND upper curve labelled H and lower curve labelled L <br> NOTE: ALLOW some leeway for lines starting from origin <br> ALLOW straight line not drawn with ruler, i.e. is a straight line rather than a curve <br> ALLOW similar labelling as long as it is clear which line is which |
| (b) | (ii) | increases $\checkmark$ | 1 |  |
| (c) |  |  | 2 | ALLOW curve touching y axis <br> ALLOW curve touching $x$ axis <br> ALLOW Two half lives are the same <br> IGNORE 'regular' half life (not necessarily the same) |


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| (d) (i) | $\mathrm{H}_{2}+\mathrm{N}_{2} \mathrm{O} \rightarrow \mathrm{N}_{2}+\mathrm{H}_{2} \mathrm{O} \checkmark$ | 1 | ONLY correct answer DO NOT ALLOW multiples |
| (d) | Steps 1 AND Step 2 together give $2 \mathrm{NO}+\mathrm{H}_{2} \checkmark$ | 1 | ALLOW Step 1 AND Step 2 together give species in same ratio as in rate equation <br> ALLOW rate-determining step/slow step for Step 2 <br> ALLOW $\mathrm{H}_{2}$ reacts with $\mathrm{N}_{2} \mathrm{O}_{2}$ which is formed from 2NO <br> NOTE: The response must link Step 1 with Step 2 Steps can be referenced from the species in each step |
|  | Total | 11 |  |


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| 2 | (a) | (i) | 5 OR 5th (order) $\checkmark$ |  | 1 |  |
|  | (a) | (ii) | (stoichiometry in) rate equatio (stoichiometry) in overall eq <br> Collision unlikely with more | n does not match ation $\checkmark$ <br> an 2 ions/species/particles | 2 | ALLOW moles/ions/species/particles/molecules/atoms throughout (i.e. emphasis on particles) <br> IGNORE more reactants in overall equation <br> If number of species is stated, ALLOW 3-5 only (rate equation contains 5 ions) <br> 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) |
|  | (b) |  |  <br> Straight upward line AND starting at $0,0 \checkmark$ |  <br> Curve with increasing gradient, AND starting at $0,0 \checkmark$ | 2 | ALLOW lines starting close to 0,0 <br> ALLOW 2nd order line with 'straight' section early or late as long as an upward curve is seen between. |
|  | (c) | (i) | $\begin{aligned} & \text { 5.4(0) } \checkmark \\ & 614.4(0) \checkmark \end{aligned}$ |  | 2 | IGNORE sign ALLOW 614 OR 610 |


| (c) | (ii) | FIRST, CHECK THE ANSWER ON ANSWER LINE <br> IF answer $=6.7 \times 10^{8}$ OR $670000000 \mathrm{dm}^{12} \mathrm{~mol}^{-4} \mathrm{~s}^{-1}$, award 3 marks <br> IF answer $=6.7 \times 10^{8}$ OR 670000000 with incorrect units, award 2 marks <br> $k$ to $>2$ SF: $666666666.7 \checkmark$ <br> OR <br> $k$ to 2 SF: $6.7 \times 10^{8}$ OR $670000000 \checkmark \checkmark$ <br> units: $\mathrm{dm}^{12} \mathrm{~mol}^{-4} \mathrm{~s}^{-1} \checkmark$ | 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. <br> For $k$, ALLOW 1 mark for the following: <br> $6.6 \times 10^{8}$ recurring <br> $6.6 \times 10^{8}$ <br> 2 SF answer for $k$ BUT one power of 10 out <br> i.e. $6.7 \times 10^{9}$ OR $6.7 \times 10^{7}$ <br> ALLOW units in any order, e.g. $\mathrm{mol}^{-4} \mathrm{dm}^{12} \mathrm{~s}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: |
| (c) | (iii) | $\begin{aligned} & \left(K_{\mathrm{a}}=\right) 10^{-3.75} \text { OR } 1.78 \times 10^{-4}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)^{\checkmark} \\ & {\left[\mathrm{H}^{+}\right]=\sqrt{1.78 \times 10^{-4} \times 0.0200}} \\ & =1.89 \times 10^{-3}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)^{\checkmark} \\ & \\ & \text { initial rate }=6.7 \times 10^{8} \times 0.01 \times 0.015^{2} \times\left(1.89 \times 10^{-3}\right)^{2} \\ & =5.33 \times 10^{-3} \text { to } 5.38 \times 10^{-3}\left(\mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}\right) \\ & \text { OR } 5.3 \times 10^{-3} \text { to } 5.4 \times 10^{-3}\left(\mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}\right) \end{aligned}$ <br> Actual value will depend on amount of acceptable rounding in steps and whether figures kept in calculator even if rounding is written down. <br> ALLOW any value in range given above. | 3 | FULL ANNOTATIONS MUST BE USED <br> For ALL marks, ALLOW 2 SF up to calculator value correctly rounded $1.77827941 \times 10^{-4}$ <br> ALLOW $\sqrt{10^{-3.75} \times 0.0200}$ for first marking point <br> ALLOW $1.88 \times 10^{-3}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$ <br> ALLOW ECF from calculated $\left[\mathrm{H}^{+}(\mathrm{aq})\right]$ and calculated answer for $k$ from 4(c)(ii) <br> e.g. If no square root taken, <br> $\left[\mathrm{H}^{+}\right]=3.56 \times 10^{-6} \mathrm{~mol} \mathrm{dm}^{-3}$ <br> and rate $=1.91 \times 10^{-8}$ OR $1.9 \times 10^{-8}$ by ECF |
|  |  | Total | 13 |  |


| Question |  |  | er | Marks | Guidance |
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| 3 | (a) | (i) | Time for concentration (of reactant) to fall to half original value | 1 | ALLOW time for concentration to fall by half DO NOT ALLOW concentration of product to fall by half ALLOW mass OR amount as alternative to concentration <br> ALLOW time for reactant/substance/atoms to decrease by half |
|  |  | (ii) | At least two half-lives correctly shown on graph AND half-life stated as approx. $54 \mathrm{~s} \checkmark$ <br> 1st order has a constant half-life | 2 | ALLOW half-life in range 50-56 s <br> ALLOW half-life shown on graph <br> Care: Initial concentration is $\sim 5.8$ and NOT 6.0 <br> For constant half-life, <br> ALLOW 'half lives are the same', 'two half-lives are 54 s', etc. <br> ALLOW 2 tangents drawn, one at half conc of first AND evidence that gradient ( $\equiv$ rate) halves |
|  |  | (iii) | No change $\checkmark$ | 1 |  |
|  | (b) | (i) | Tangent <br> On graph, tangent drawn to curve at $t \sim 40 \mathrm{~s} \checkmark$ <br> Calculation of rate from the tangent drawn e.g. rate $=\frac{5.2}{116}=0.045$ OR $4.5 \times 10^{-2} \checkmark$ <br> Units <br> $\mathrm{mol} \mathrm{dm}{ }^{-3} \mathrm{~s}^{-1} \checkmark$ <br> Independent mark | 3 | Annotate tangent on graph <br> Note: This mark can only be awarded from a tangent <br> ALLOW ECF for tangent drawn at different time from 40 s <br> ALLOW $\pm 10 \%$ of gradient of tangent drawn <br> ALLOW 2 SF up to calculator value <br> ALLOW trailing zeroes, e.g. 0.04 for 0.040 <br> IGNORE ‘-‘ sign for rate <br> Note: IF candidate calculates rate via In 2 method (shown in (ii), consult with TL) |


| Question |  | er | Marks | Guidance |
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| (b) | (ii) | $k=\frac{\text { answer to (b)(i) }}{3.45} \checkmark$ <br> units: $s^{-1} \checkmark$ Independent mark | 2 | From 0.045, $k=\frac{0.045}{3.45}=0.013$ <br> ALLOW concentration range 3.4-3.5 <br> ALLOW use of unrounded calculator answer from (b)(i) even if different from answer given on (b)(i) answer line Many will keep this value in calculator for (b)(ii) <br> ALLOW $k=\ln 2 / t_{1 / 2}=0.693 /$ half life from (a)(iii) <br> For $54 \mathrm{~s}, k=0.693 / 54=0.013$ <br> ALLOW 2 SF up to calculator value |
| (c) |  | water is in excess <br> OR <br> concentration of $\mathrm{H}_{2} \mathrm{O}$ is very large/does not change $\checkmark$ | 1 | IGNORE water does not affect the rate |
|  |  | Total | 10 |  |


|  | Question | er | Mark | Guidance |
| :---: | :---: | :---: | :---: | :---: |
| 4 |  | Evidence of at least two half-lives measured on graph OR within text (would need evidence of two half-lives) <br> Any half-life value stated in range 180-220 s OR constant half-life $\checkmark$ <br> 1st order $\checkmark$ <br> Note: This is only correct response for order (ie no ECF). If not stated separately, this mark can be awarded from a rate equation, e.g. rate $=k\left[\mathrm{Br}_{2}\right]^{1}$ OR rate $=k\left[\mathrm{Br}_{2}\right]$ <br> Evidence of tangent on graph drawn to line at $t=0 \mathrm{~s}$ e. | 4 | ANNOTATE ALL Q3 WITH TICKS AND CROSSES, etc <br> MARK ON GRAPH OR IN TEXT <br> LOOK FOR STATEMENT ON GRAPH OR WITHIN TEXT <br> ALLOW almost constant half-life <br> Note: Response may use an alternative approach from half-life for the 1st two marks based on gradients of tangents: <br> 1st mark would be awarded for evidence of two tangents drawn on graph <br> 2nd mark would be awarded for stating that ratio of concentrations = ratio of rates, <br> e.g. gradient of tangent at $0.010 \mathrm{~mol} \mathrm{dm}^{-3}$ has twice the value of gradient of tangent at $0.005 \mathrm{~mol} \mathrm{dm}^{-3}$ <br> MARK TANGENTS ON GRAPH <br> ALLOW some leeway but tangent must coincide with part of curve that is 'straight' (ie between $\left[\mathrm{Br}_{2}\right]=0.010-0.009$ and MUST NOT cross the curve |


| Question | er | Mark | Guidance |
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|  | $\text { rate }=\frac{0.010}{250}=0.000040 \text { OR } 4.0 \times 10^{-5}$ <br> units: $\mathrm{mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1} \checkmark$ | 2 | ALLOW values from 1 SF ( 0.00004 OR $4 \times 10^{-5}$ ) up to calculator value, correctly rounded ALLOW range $\sim \frac{0.010}{160}$ to $\frac{0.010}{300}$ : <br> i.e. ALLOW a calculated gradient in the range $6 \times 10^{-5}-3 \times 10^{-5}$ from a tangent drawn at $t=0$ <br> IF tangent is drawn on graph at a different time or incorrectly (e.g. crossing curve), then mark rate calculation by ECF using the gradient of the tangent drawn by the candidate (ie not the range above). <br> IF no tangent is drawn ALLOW a value in the range above ONLY <br> Credit only attempts at tangents, not just a random straight line <br> IGNORE a '- sign' |
|  | $\begin{aligned} & \text { rate }=k\left[\mathrm{Br}_{2}\right] \text { OR } k=\frac{\text { rate }}{\left[\mathrm{Br}_{2}\right]} \checkmark \\ & k=\text { calculated result from } \frac{\text { calculated value for rate }}{0.010} \\ & \text { units: } \mathrm{s}^{-1} \checkmark \end{aligned}$ | 3 | DO NOT ALLOW rate $=k[\mathrm{Br}]$, ie Br instead of $\mathrm{Br}_{2}$ <br> DO NOT ALLOW just $k\left[\mathrm{Br}_{2}\right]$, <br> ie 'rate $=$ ' OR ' $r=$ ' must be present <br> Calculation of $\boldsymbol{k}$ is from candidate's calculated initial rate <br> From 0.00004, $k=\frac{0.000040}{0.010}=4 \times 10^{-3} \mathrm{~s}$ <br> Note: <br> IF order with respect to $\mathrm{Br}_{2}$ has been shown as 2nd order, then mark this part by ECF, <br> e.g. if $\mathrm{Br}_{2}$ shown to be 2 nd order, rate $=k\left[\mathrm{Br}_{2}\right]^{2}$ <br> $k=$ calculated result from $\frac{\text { calculated value for rate }}{0.010^{2}}$ <br> units: $\mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$ OR $\mathrm{mol}^{-1} \mathrm{dm}^{3} \mathrm{~s}^{-1}$ <br> Note: Units mark must correspond to the candidate's stated rate equation, NOT an incorrectly rearranged $k$ expression |
|  | Total | 9 |  |


| Question | Expected Answers | Marks | Additional Guidance |  |
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| $\mathbf{5}$ | $\mathbf{a}$ | $\mathrm{BrO}_{3}^{-}+5 \mathrm{Br}^{-}+6 \mathrm{H}^{+} \longrightarrow 3 \mathrm{Br}_{2}+3 \mathrm{H}_{2} \mathrm{O} \checkmark$ | 1 | ALLOW multiples |



|  | est |  | Expected answers | Marks | Additional guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 6 | a |  | graph: <br> Rate does not change with concentration AND zero-order with respect to $\mathrm{I}_{2}$ <br> initial rates data: <br> Mark independently <br> When $\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}\right] \times 2$, rate $\times 2\left(2^{1}\right) \checkmark$ 1st order with respect to $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO} \checkmark$ <br> When $[\mathrm{HCl}] \times 2.5$, rate $\times 2.5 \checkmark$ 1st order with respect to $\mathrm{HCl} \checkmark$ |  | ANNOTATIONS MUST BE USED <br> ALLOW (straight) line with zero gradient AND zero-order ALLOW horizontal line AND zero-order IGNORE just 'constant line' OR just 'straight line' also fits 1st order <br> CARE with comparisons in opposite direction ALLOW $\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}\right] \times 0.5$, rate $\times 0.5\left(0.5^{1}\right)$ <br> ALLOW $[\mathrm{HCl}] \times 0.4$, rate $\times 0.4\left(0.4^{1}\right)$ <br> ALLOW $\mathrm{H}^{+}$for HCl <br> CARE: Comparison of Experiments $\mathbf{1}$ and $\mathbf{3}$ may be valid despite BOTH concentrations changing |
|  |  |  | Rate equation and rate constant: $\begin{aligned} & \text { rate }=k\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}(\mathrm{aq})\right][\mathrm{HCl}(\mathrm{aq})] \checkmark \\ & k=\frac{r a t e}{\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}(\mathrm{aq})\right][\mathrm{HCl}(\mathrm{aq})]} \mathrm{OR} \\ & \frac{2.10 \times 10^{-9}}{\left(1.50 \times 10^{-3}\right) \times\left(2.00 \times 10^{-2}\right)} \checkmark \\ & =7(.00) \times 10^{-5} \mathrm{OR} 0.00007(00) \\ & \text { units: } \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1} \checkmark \end{aligned}$ | 9 | ALLOW ECF from incorrect orders <br> In rate equation, square brackets are required $\text { rate }=k\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}(\mathrm{aq})\right][\mathrm{HCl}(\mathrm{aq})]\left[1_{2}(\mathrm{aq})\right]^{0}$ <br> ALLOW H ${ }^{+}$for HCl <br> IGNORE state symbols, even if wrong <br> ALLOW ECF for units 'correct' for incorrect expression used to calculate $k$, e.g. upside down or wrong orders $\frac{\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}(\mathrm{aq})\right]\left[\mathrm{H}^{+}(\mathrm{aq})\right]}{\text { rate }} \times \text { units: mol s dm}{ }^{-3} \checkmark$ |


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| b | b | step 1: $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{ICl}(\mathrm{g})$ $\qquad$ <br> LHS of step 1 $\underset{\text { step 2: } \mathrm{HI}(\mathrm{~g})}{\text { products of step } 1} \underset{\mathrm{ICl}}{\longrightarrow} \mathrm{HCD}(\mathrm{~g})+\mathrm{HI}(\mathrm{~g})$ | 2 | State symbols NOT required <br> 2nd mark can ONLY be awarded provided that <br> - 1st mark has been awarded <br> - step 1 AND step 2 add up to the overall equation. $\begin{array}{ll} \text { e.g. ALLOW } & \longrightarrow \mathrm{H}_{2} \mathrm{ICl}(\mathrm{~g}) \\ \text { step 2: } \mathrm{H}_{2} \mathrm{ICl}(\mathrm{~g})+\mathrm{ICl}(\mathrm{~g}) & \longrightarrow 2 \mathrm{HCl}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \end{array}$ <br> In step 2, ALLOW inclusion of extra species on both sides of the equation only if they cancel, $\text { e.g. } \mathrm{HI}(\mathrm{~g})+\mathrm{HCl}(\mathrm{~g})+\mathrm{ICl}(\mathrm{~g}) \longrightarrow 2 \mathrm{HCl}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g})$ |
|  |  | Total | 11 |  |


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| 7 | (a) |  | FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer $=8.3 \times 10^{4}$ OR 83333 award 2 marks THEN IF units are $\mathbf{d m}^{6} \mathbf{~ m o l}^{-2} \mathbf{s}^{-1}$, award 1 further mark $\begin{aligned} & k=\frac{\text { rate }}{\left[\mathrm{H}_{2}(\mathrm{~g})\right][\mathrm{NO}(\mathrm{~g})]^{2}} \text { OR } \frac{3.6 \times 10^{-2}}{\left(1.2 \times 10^{-2}\right) \times\left(6.0 \times 10^{-3}\right)^{2}} \\ & \checkmark \\ & =8.3 \times 10^{4} \text { OR } 83000 \text { OR } 83333 \end{aligned}$ <br> units: $\mathrm{dm}^{6} \mathrm{~mol}^{-2} \mathrm{~s}^{-1} \checkmark$ | 2 | ALLOW 1 mark for $8.3 \times 10^{x}$ with no working (power of 10 is error) <br> ALLOW 2 SF up to calculator value of $8.33333333 \times 10^{4}$ correctly rounded <br> ALLOW ECF for calculated answer from incorrectly rearranged $k$ expression but not for units (Marked independently see below) <br> ALLOW $\mathrm{dm}^{6}, \mathrm{~mol}^{-2}$ and $\mathrm{s}^{-1}$ in any order, eg $\mathrm{mol}^{-2} \mathrm{dm}^{6} \mathrm{~s}^{-1}$ DO NOT ALLOW other units (Rate equation supplied on paper - not derived from data ) |
|  | (b) | (i) | effect on rate $\times 2 \checkmark$ | 1 | ALLOW 'doubles' OR rate $=7.2 \times 10^{-2}\left(\mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}\right)$ |
|  |  | (ii) | effect on rate $\times 1 / 4 \mathrm{OR} \times 0.25 \checkmark$ | 1 | ALLOW 'a quarter' OR decrease by $1 / 4$ OR decrease by 0.25 OR rate decreases by 4 OR decrease by $75 \%$ OR rate $=0.9 \times 10^{-2}\left(\mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}\right)$ <br> DO NOT ALLOW just $0.5^{2}$ of rate OR rate decreases by $2^{2}$ |
|  |  | (iii) | effect on rate $\times 64 \checkmark$ | 1 | ALLOW rate $=2.3(04)\left(\mathrm{mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}\right)$ <br> DO NOT ALLOW just 'increases by 4 and then by $16 / 4^{2}$ OR increases by $4^{3}$ |


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| (c) | (i) | $\begin{array}{l}\text { (initial) rate increases } \\ \text { AND } \\ \text { more frequent collisions OR more collisions per } \\ \text { second/time } \checkmark\end{array}$ |  | $\begin{array}{l}\text { BOTH points required for mark } \\ \text { ALLOW rate increases AND concentration increases } \\ \text { For concentration increases, ALLOW particles closer together } \\ \text { OR less space between particles }\end{array}$ |
| DO NOT ALLOW just more collisions OR collisions more likely |  |  |  |  |$]$

