PEARSON EDEXCEL A-LEVEL CHEMISTRY · 9CH0

CHEMISTRY



MARK SCHEME

TOPIC 9: KINETICS I

SCORE	PERCENTAGE
/189	%

STEMUP

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(i) Give **one** reason why obtaining these further data may be considered useful.

(1)

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(ii) Deduce the rate equation for this reaction, explaining how you arrived at your answer.

(5)

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(iii) Use your answer from (c)(ii), and appropriate data from **Experiment 4**, to calculate the value of the rate constant, *k*. Include units in your answer.

(2)

(Total for question = 15 marks)

Mark Scheme

Q1.

Question Number	Answer	Mark
	The only correct answer is A (area A) ***B*** *is not correct because this is the area representing the number of particles with sufficient energy to react in the absence of a catalyst* ***C*** *is not correct because this area subtraction does not represent the increase in the number of particles with sufficient energy to react* ***D*** *is not correct because this sum of areas represents the total number of particles with sufficient energy to react in the presence of a catalyst*	**(1)**

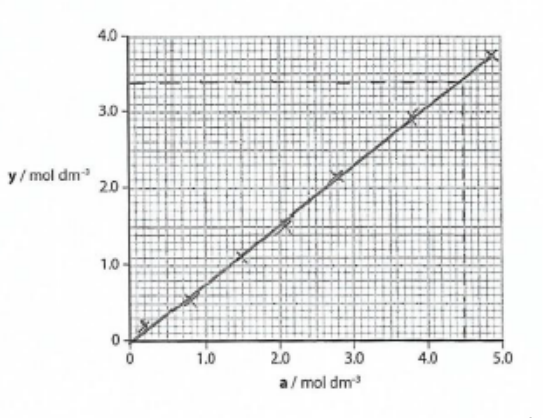
Q2.

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(i)	$(K_c =) \dfrac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$	Ignore missing state symbols or units Do not award round brackets	**(1)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(ii)	$(K_c =) \dfrac{4y^2}{(a-y)^2}$ • Numerator term correct **(1)** • Denominator term correct **(1)**	Allow square brackets Allow $(2y)^2$ Allow $(a^2 - 2ay+y^2)$ or (a-y)(a-y)	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(i)	• both values correct to 2 DP	1.13 2.93	**(1)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(ii)	• All 7 points plotted correctly **(1)** • Appropriate straight line of best fit, drawn through the origin **(1)**	Allow TE for incorrect values from 9(b)(i) Do not allow all points above or below the line of best fit Allow line of best fit to intersect one square either side of the origin	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(iii)	• co-ordinates correctly read off the line on graph **(1)**  • gradient correctly calculated **(1)**	At least 1 line must be shown on the graph to indicate selection of co-ordinates <u>Example of calculation</u> $\frac{3.40 - 0.00}{4.50 - 0.00}$ = gradient of graph Gradient = 0.76 Ignore SF except 1SF Do not allow units for the gradient Allow a value from 0.71 to 0.81 inclusive	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(iv)	• $\frac{\sqrt{K_c}}{2 + \sqrt{K_c}}$ = gradient / $\frac{y}{a}$ **(1)** • re-arrangement of expression and calculation of K_c **(1)**	<u>Example of calculation</u> $\frac{\sqrt{K_c}}{2 + \sqrt{K_c}} = 0.76$ K_c = 40.1 /40 (no units) Allow TE on gradient from part (iii) $K_c = [(2 \times \text{grad})/(1-\text{grad})]^2$ Correct answer with no working scores (2)	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(c)	• hydrogen is flammable / explosive	Allow iodine vapour damages eyes /toxic Allow hydrogen iodide is corrosive / acidic / irritant (if qualified) / lachrymator Ignore references to high pressure Ignore references to safety precautions	**(1)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(d)	• Faster rate of reaction / increased rate **(1)** • K_c unchanged **(1)**	Ignore references to shifting position of equilibrium	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(e)(i)	An explanation that makes reference to the following points: • (K_c is) smaller / decreases / gets less **(1)** • (forward) reaction is exothermic **(1)**	Allow reverse/backwards reaction is endothermic MP2 dependent on MP1	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(e)(ii)	• straight line drawn on the graph with a less steep gradient (and goes through the origin)	Do not allow if lines cross	**(1)**

Q3.

Question Number	Acceptable Answer	Additional Guidance	Mark
(a)	• +5		**1**

Question Number	Acceptable Answer	Additional Guidance	Mark
(b) (i)	• choice of suitable reducing agent	From Data Booklet of the standard electrode potentials, the right hand substance in numbers 16-24	**1**

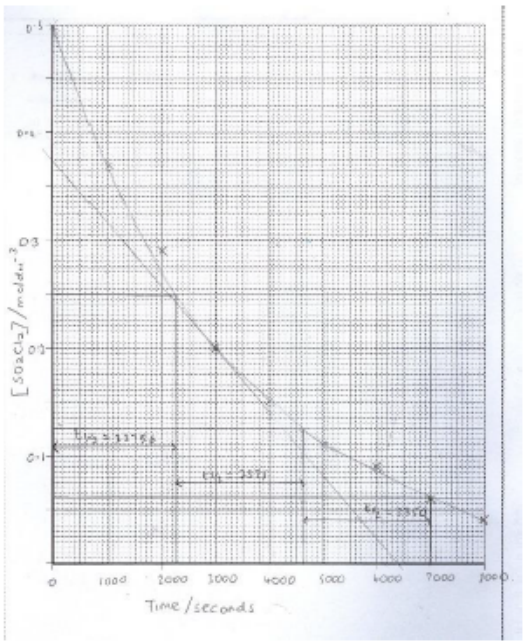
Question Number	Acceptable Answer	Additional Guidance	Mark
(b) (ii)	An answer that makes reference to the following point: • may be kinetically hindered **or** activation energy may be too high	Allow reaction may be too slow	**1**

Question Number	Acceptable Answer	Additional Guidance	Mark
(b) (iii)	An explanation that makes reference to the following points: • (yellow to) green then blue (1) • when the blue colour initially forms, it mixes with the yellow unreacted VO_2^+ (to turn green) (1)	Ignore colours caused by contamination with reducing agent chosen	**2**

Question Number	Acceptable Answer	Additional Guidance	Mark
(b) (iv)	An explanation that makes reference to the following point: • justification of choice (1) • correct equation for reaction (1)	$E^\ominus$ value is between +0.34 V and −0.26 V Allow by comparison of electrode potentials / calculation of E_{cell} / use of anti-clockwise rule $S_2O_3^{2-} + VO^{2+} + 2H^+ \rightarrow V^{3+} + H_2O + \frac{1}{2}S_4O_6^{2-}$ or multiples	**2**

Q4.

Question Number	Acceptable Answer	Additional Guidance	Mark
(a)(i)	• suitable scale and axes labelled including units (1) • all points plotted correctly (1) • line of best fit (1)	Plotted points use at least half the available space in both directions ±½ a square Smooth line, no dot to dot NOTE: Points at t = 2000 and 6000 s should not be on the line of best fit.	**3**

Question Number	Acceptable Answer	Additional Guidance	Mark
(a)(ii)	• 1st order with respect to SO_2Cl_2 as half-life is constant (1) • values of two half-lives shown in graph in range 2000 – 2400 (s) (1) • rate = $k[SO_2Cl_2]$ (1)	<u>Example of graph</u> 	**3**

Question Number	Acceptable Answer	Additional Guidance	Mark
(a)(iii)	• tangent drawn at 0.200 mol dm^{-3} SO_2Cl_2 (1) • value of gradient (1) • k = rate / 0.200 (1) • value of k to 2 or 3 SF and units (1)	Example of calculation e.g. gradient = (-) 0.375/6400 = (-) 5.859×10^{-5} must be consistent with tangent shown on graph $k = 5.859 \times 10^{-5} / 0.200$ $= 2.9 \times 10^{-4}\ s^{-1}$ / $2.93 \times 10^{-4}\ s^{-1}$ Allow TE from incorrect rate equation / allow TE from incorrect gradient Units must be consistent with rate equation	**4**

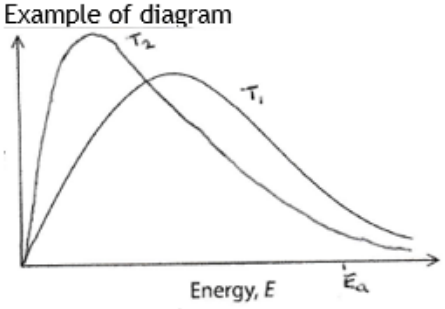
Question Number	Acceptable Answer	Additional Guidance	Mark
(b)	• RDS Step 1 $SO_2Cl_2 \rightarrow SO_2Cl + Cl$ (1) • Step 2 $SO_2Cl + Cl \rightarrow SO_2 + Cl_2$ (1)	The RDS must involve one mol of SO_2Cl_2 The equations taken together must add up to the overall equation $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ e.g. $SO_2Cl_2 \rightarrow SO_2 + 2Cl$ $2Cl \rightarrow Cl_2$ Ignore state symbols	**2**

Q5.

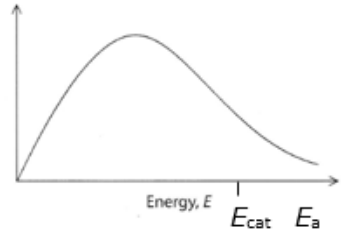
Question Number	Answer	Additional Guidance	Mark
(i)	An explanation that makes reference to the following points: • increases the rate of reaction because it lowers the activation energy (1) • by providing alternative reaction mechanism /pathway (1) • so greater proportion of particles collide with sufficient energy (1)	Responses in terms of heterogeneous catalysis can score a maximum of 2 marks Point 1 Reactants bond onto catalyst surface (adsorption) Point 2 Increases concentration of reactant (at surface) Point 3 Products break away from catalyst surface (desorption) All 3 points scores 2 marks A combination of any 2 points scores 1 Any single point only scores 0 marks	3
(ii)	• one Maxwell-Boltzmann distribution shown drawn with appropriate shape (1) • second distribution shown with maximum lower and to right of that shown by first curve, with larger area below curve beyond E_a (1) (to score 2nd mark there must be a clear indication that the second distribution is at a higher temperature)	Curves should not cross x- axis	2

Q6.

Question Number	Answer	Additional Guidance	Mark
(i)	• fraction / proportion / number of molecules / particles with energy, E	Allow fraction / proportion / number of molecules / particles Allow label written on y axis on diagram	(1)

Question Number	Answer	Additional Guidance	Mark
(ii)	• peak for T_2 to the left of T_1 **(1)** • peak for T_2 higher than T_1 **and** asymptote lower than T_1 line and not touching the x axis **(1)**	Example of diagram  Ignore missing label from added line Do not award M2 if added line curves upwards at the end	(2)

Question Number	Answer	Additional Guidance	Mark
(iii)	An explanation that makes reference to the following points: • (at a lower temperature the) molecules / particles / collisions have lower (kinetic) energy **(1)** • so fewer molecules / particles / collisions have energy greater than (or equal to) the activation energy / E_a **(1)**	Ignore molecules / particles move more slowly Allow fewer molecules / particles have (enough energy to overcome) the activation energy Allow this shown as labelled shading on the diagram Ignore just 'fewer successful collisions'	**(2)**

Question Number	Answer	Additional Guidance	Mark
(iv)	• E_{cat} labelled anywhere between the energy corresponding to the highest point of the peak and to the left of E_a	Example of label  Allow other clear labels for E_{cat}	**(1)**

Q7.

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr><td>*</td><td>This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning.

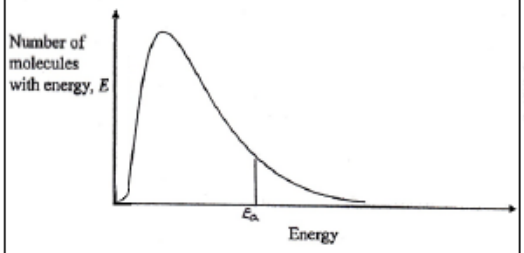
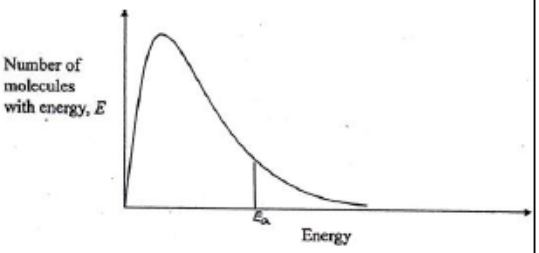
Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.

The following table shows how the marks should be awarded for indicative content.
<table><tr><td>Number of indicative marking points seen in answer</td><td>Number of marks awarded for indicative marking points</td></tr><tr><td>6</td><td>4</td></tr><tr><td>5–4</td><td>3</td></tr><tr><td>3–2</td><td>2</td></tr><tr><td>1</td><td>1</td></tr><tr><td>0</td><td>0</td></tr></table></td><td>Guidance on how the mark scheme should be applied:
The mark for indicative content should be added to the mark for lines of reasoning.
For example, an answer with five indicative marking points, which is partially structured with some linkages and lines of reasoning, scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).
If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).</td><td>6</td></tr>
<tr><td>* Cont.</td><td>The following table shows how the marks should be awarded for structure and lines of reasoning.
<table><tr><td></td><td>Number of marks awarded for structure of answer and sustained line of reasoning</td></tr><tr><td>Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout.</td><td>2</td></tr><tr><td>Answer is partially structured with some linkages and lines of reasoning.</td><td>1</td></tr><tr><td>Answer has no linkages between points and is unstructured.</td><td>0</td></tr></table>Indicative content:
• activation energy (E_A) for the formation of A is lower than that for B (E_B)
• hence at 40 °C more collisions exceed E_A than exceed E_B
• so A is formed more quickly than B at 40 °C

• at 160 °C more collisions exceed E_B (and E_A) than at 40 °C
• therefore both isomers are formed
• but the reactions are reversible and B is the more stable isomer, therefore A will convert to B</td><td></td><td></td></tr>
</table>

Q8.

Question Number	Acceptable Answer	Additional Guidance	Mark
(a)	An answer that makes reference to the following point: • different phase	Allow different physical state	**1**

Question Number	Acceptable Answer	Additional Guidance	Mark
(b)(i)	 • both axes labelled y axis = number/fraction of molecules (with energy, *E*) x axis = (kinetic) energy/*E* (1) • curve starting at or going towards origin, asymmetric, asymptotic to x axis and correct shape (1) • E_a shown (well to right of the peak) (1)	Allow 	**3**

Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	An explanation that makes reference to the following points: • E_a(cat) shown on graph at a lower energy than E_a or stated to be at a lower energy (1) • greater proportion/more of the molecules/collisions have energy greater than the activation energy with a catalyst **OR** shows this with labelled shading on the graph (1) • greater proportion/more of the collisions lead to a reaction (1)		**3**

Q9.

Question Number	Acceptable Answer	Additional Guidance	Mark
(i)	• $SO_2 + ½O_2 \rightarrow SO_3$	Allow multiples Ignore state symbols	**1**

Question Number	Acceptable Answer	Additional Guidance	Mark
***(ii)**	This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning. Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning. The following table shows how the marks should be awarded for indicative content. Number of indicative marking points seen in answer / Number of marks awarded for indicative marking points 6 / 4 5–4 / 3 3–2 / 2 1 / 1 0 / 0 The following table shows how the marks should be awarded for structure and lines of reasoning.	Guidance on how the mark scheme should be applied: The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points which is partially structured	

	<table><tr><td></td><td>Number of marks awarded for structure of answer and sustained line of reasoning</td></tr><tr><td>Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout</td><td>2</td></tr><tr><td>Answer is partially structured with some linkages and lines of reasoning</td><td>1</td></tr><tr><td>Answer has no linkages between points and is unstructured</td><td>0</td></tr></table> **Indicative Content:** • V_2O_5 acts as a heterogeneous catalyst • SO_2 is adsorbed onto surface and reacts with the V_2O_5 • SO_3 forms and is only weakly bonded to surface • the SO_3 desorbs from the surface • oxygen reacts with the VO_2, regenerating the V_2O_5 catalyst • reaction follows different mechanism with lower activation energy	with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning). If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages). Ignore comments related to collision theory	**6**

Q10.

Question Number	Acceptable Answer	Mark
	The only correct answer is **C** ***A*** *is incorrect because gaseous reactants attach only to the surface* ***B*** *is incorrect because this happens after adsorption* ***D*** *is incorrect because this is detachment of the products from the surface*	**(1)**

Q11.

Question Number	Acceptable Answer	Additional guidance	Mark
	An explanation that makes reference to the following: • increase surface (area) / more active sites **(1)** • (honeycomb structure) allows gases to flow through (the exhaust) **(1)**	Do not award **ab**sorption Ignore reference to rate of reaction / remove pollutants Do not award if comments are made that refer to the structure acting like a filter for the particulates or other substances	**(2)**

Q12.

Question Number	Acceptable Answer	Additional Guidance	Mark
	An explanation that makes reference to the following points: • (the initial rate of reaction is slow) because both reacting species are negatively charged / repel each other **or** the reaction has a high activation energy / few particles have energy greater than (or equal to) the activation energy **(1)** • (the rate of reaction increases) because **Mn^{2+} ions** (are formed) **and** they act as a catalyst / are autocatalytic / provide an alternative route with a lower activation energy **(1)** • (the rate decreases) because the concentrations /amounts of the reactants decrease / the reactants are used up **(1)**	Allow because there is no catalyst / no Mn^{2+} ions present at the start Allow a description of how the Mn^{2+} ions are acting as a catalyst e.g. the idea of Mn^{2+} ions reacting **and** being regenerated Do not award 'enzyme' Allow example of one of the reagents used up / becoming a limiting factor Do not award 'the Mn^{2+} ions are used up'	**(3)**

Q13.

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)	0.816 / 8.16 x 10^{-1} (g)		(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)	• calculation of moles of CO_2	Example of calculation: (moles CO_2 = $\frac{225}{24000}$ = 0.009375) Allow 9.375 x 10^{-3} / 9.38 x 10^{-3} / 9.4 x 10^{-3} Ignore SF except 1SF	(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(c)	• moles of MCO_3 **(1)** • method for calculation of molar mass of MCO_3 **(1)** • molar mass final answer to 1, 2 or 3 SF **(1)** • consequential identification of Group 2 metal by name or formula **(1)** NOTE Alternative method can score 3 MAX Calculation of moles of CO_3^{2-} **(1)** (Calculation of mass of CO_3^{2-}) Deduction of mass of M by subtraction **(1)** Calculation of Ar of M to 1, 2 or 3 SF **AND** Identification of group 2 metal **(1)**	Example of calculation: Moles of MCO_3 = moles CO_2 = 0.009375 (mol) Molar mass of MCO_3 = $\frac{0.816}{0.009375}$ (= 87.04 (g mol^{-1})) M2 subsumes mark for M1 = 87.0 / 87 / 90 (g mol^{-1}) NOTE M3 mark subsumes mark for M2 and M1 (87.0 – 60) = 27 **AND** Mg / Magnesium / $MgCO_3$ Allow TE on answers to parts (a) and (b), with Metal consequential on calculated molar mass but M must be a Group 2 element Moles CO_3^{2-} = 0.009375 (Mass of CO_3^{2-} = 0.009375 x 60 = 0.5625 g) Mass of M = 0.2535 g Ar = 0.2535/0.009375 = 27.0 / 27 / 30 (g mol^{-1}) **AND** Mg / Magnesium / $MgCO_3$	(4)

Question Number	Acceptable Answers	Additional Guidance	Mark
(d)(i)	An explanation that makes reference to the following points: • the bung was not replaced quickly enough **(1)** • (So) CO_2 / gas lost (to the surroundings) **(1)**	 Allow bung not fitting tightly resulting in leaks Ignore references to CO_2 dissolving Ignore references to other types of gas leak Allow 'smaller volume of gas collected' / lower reading of gas volume Mark points M1 and M2 independently	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(d)(ii)	An answer that makes reference to the following point: The acid was (already) in excess (and more acid won't affect this)	Allow The carbonate is the limiting reactant / the acid is not the limiting reactant	**(1)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(d)(iii)	An explanation that makes reference to the following points: • rate of reaction is faster **and** powder has greater surface area **(1)** • no effect on (final) volume of gas **and** moles of (metal) carbonate are unchanged **or** because the rate is faster more gas will be lost before the bung is replaced so the (final) volume will be less **(1)**	Mark points M1 and M2 independently Both parts of statement needed Both parts of statement needed Allow mass / amount for moles Allow reactant for metal carbonate	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(e)(i)	• balanced equation with state symbols	<u>Example of equation:</u> $MCO_3(s) \rightarrow MO(s) + CO_2(g)$ Allow a correct equation for the decomposition of any Group 2 carbonate	**(1)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(e)(ii)	• subtractions to obtain masses **(1)** • calculation of moles of CO_2 **(1)** • calculation of molar mass of MCO_3 **(1)**	Example of calculation: (mass of CO_2 = 20.447 – 20.205) = 0.242 **AND** (mass of MCO_3 = 20.447 – 19.996) = 0.451 moles of $CO_2 = \frac{0.242}{44}$ = 0.0055(0) (mol) / 5.5(0) x 10^{-3} (mol) ALLOW TE from M2 to M3 Mr of $MCO_3 = \frac{0.451}{0.0055(0)}$ = 82 (g mol^{-1}) Correct answer with or without working scores 3 Ignore SF except 1 Ignore attempts to identify the metal	**(3)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(f)	An answer that makes reference to the following point: Student 3 used a smaller mass / less (and the uncertainty of the balance was the same) **or** Student 1 used a larger mass / more (and the uncertainty of the balance was the same)	Allow calculations comparing the two percentage errors: e.g. Student 1:- (0.001/0.816) x 100% = 0.12% **and** Student 3:- 0.001/0.451 x 100% = 0.22%	**(1)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(g)	An explanation that makes reference to the following points: • more CO_2 (would appear to be) given off **(1)** • (So) calculated molar mass is smaller **(1)** **OR** • Less MO would appear to have been formed **(1)** • Calculated molar mass would be greater **(1)**	 M2 dependent on M1 M2 dependent on M1	**(2)**

Q14.

Question Number	Answer	Additional Guidance	Mark
(i)	• concentration of NO in experiment 2 (1) • concentration of Cl_2 in experiment 3 (1)	Example of calculation 0.244 0.121 Do not award 0.1205 **Both** values must be to **3SF**	**(2)**

Question Number	Answer	Additional Guidance	Mark
(ii)	**M1** rearrangement of rate equation to find *k* (1) **M2** calculation of *k* (1) **M3** correct units for *k* (1)	Example of calculation $k = \frac{\text{rate}}{[NO]^2[Cl_2]}$ $\frac{1.09 \times 10^{-2}}{(0.122 \times 0.122 \times 0.241)}$ =3.03871 = 3.04 Ignore SF Correct numerical answer for *k* scores both M1 and M2 $dm^6\ mol^{-2}\ s^{-1}$ Allow units in any order M3 stand alone mark	**(3)**

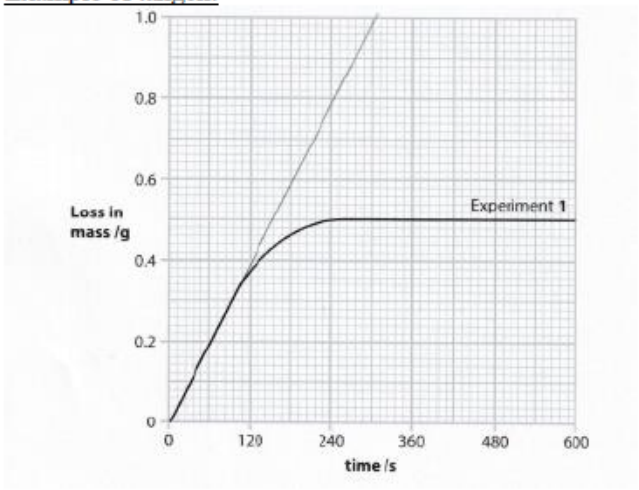
Question Number	Answer	Additional Guidance	Mark
(iii)	An explanation that makes reference to the following points: *k* increases because • the catalyst provides an alternative pathway of lower activation energy (1) • so a greater proportion of molecules / more molecules have energy greater than the activation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

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

Q15.

Question Number	Answer	Additional Guidance	Mark
(i)	• 2nd order		1
(ii)	An explanation that makes reference to the following points: • rate increases because increased concentration of propanone means more propanone molecules in a given volume (1) • so more frequent collisions / greater rate of collisions / more collisions per second (1)		2

Q16.

Question Number	Answer	Additional Guidance	Mark
	• tangent drawn to curve when time = 0 tangent must touch curve (1) for at least first 3 small squares on x axis and extend to at least 120 s (1) • calculation of gradient • units	Example of tangent  gradient = $\frac{1.0}{300}$ = 3.33×10^{-3} Allow 3.13×10^{-3} to 3.53×10^{-3} TE on tangent drawn or measurements from line on graph with no tangent Ignore SF including 1SF $g\ s^{-1}$ or g/s stand alone mark	(3)

Q17.

Question Number	Acceptable Answers	Reject	Mark
(a)(i)	• In experiments 1 and 2, $[H^+]$ doubles (whilst keeping other concentrations constant) **and** the rate quadruples / rate increases x 4 **(1)** • Second order (with respect to H^+) **(1)** • In experiments 1 and 3, $[Br^-]$ doubles **and** $[BrO_3^-]$ triples (with $[H^+]$ constant) **(1)** • Rate increases by 3 x 2 / rate increases x 6 / rate increases to 5.04×10^{-5} (then to 1.01×10^{-4} stated or implied) **(1)** • First order with respect to Br^- **(1)** **OR** • In experiments 2 and 3,$[Br^-]$ doubles **and** $[BrO_3^-]$ triples **and** $[H^+]$ halves **(1)** • Rate increases by 3 x 0.25 x 2 / rate increases x 1.5 **(1)** • First order with respect to Br^- **(1)** **Penalise OMISSION of Experiment Numbers once only** **Mark each point independently**		**5**

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	Rate = $k\,[BrO^-_3]\,[Br^-]\,[H^+]^2$ Mark CQ on (a)(i) Allow "r" or "R" for "rate" in the rate equation. **IGNORE** If *k* appears to be in upper case.		**1**

Question Number	Acceptable Answers	Reject	Mark
(a)(iii)	**IGNORE** sf except 1 sf THROUGHOUT **FIRST, CHECK THE FINAL ANSWER** **IF** answer $k = 1.49 \times 10^{-2}$ **dm^9 mol^{-3} s^{-1}** award **(3)** marks $k = \frac{\text{rate}}{[BrO^-_3]\ [Br^-]\ [H^+]^2}$ $= \frac{1.68 \times 10^{-5}}{0.05 \times 0.25 \times (0.30)^2}$ **(1)** $= 0.014933333$ $= 0.0149$ **(1)** **dm^9 mol^{-3} s^{-1} / mol^{-3} dm^9** s^{-1} **(1)** **IGNORE** sf except 1 sf Mark CQ from (a)(ii) or, if no rate equation in (a)(ii), then any rate equation stated in (a)(iii) **NOTE:** **IF** the rate equation in (a)(ii) is given as Rate $= k\,[BrO^-_3]\,[H^+]^2$ CQ $k = 3.73 \times 10^{-3}$ $dm^6\,mol^{-2}\,s^{-1}$ scores **(3)** **IF** $[H^+]$ is not squared in the correct rate equation: $k = 4.48 \times 10^{-3}$ $dm^9\,mol^{-3}\,s^{-1}$ OR $k = 4.48 \times 10^{-3}$ $dm^6\,mol^{-2}\,s^{-1}$ scores **(2)** **ALLOW** Correct answers derived from the data in the table for Experiment 2 or Experiment 3		**3**

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Question Number	Acceptable Answers	Reject	Mark
(b)	The number(s) (of particles) in the rate equation / rate-determining step do not match those in the equation for the reaction **OR** The chance of (simultaneous) collision of 12 particles is unlikely **OR** The chance of (simultaneous) collision of 4 particles is unlikely **OR** The chance of (simultaneous) collision of 3 reactants is unlikely **ALLOW** 'molecules' / 'substances' for 'particles' ***NOTE*** **ALLOW AS A CQ from (a)(ii)** Br^- ions not in rate equation / Br^- ions not in rate-determining step / Zero order with respect to Br^- / (Only) two reactants in the rate-determining step / (only) two reactants in the rate-equation/ particles are in the equation (for the reaction) that are not in the rate equation		**1**

Question Number	Acceptable Answers	Reject	Mark
(c)	**REMEMBER TO SCROLL DOWN BELOW THE SPACE LEFT FOR A SKETCH-GRAPH TO SEE WHAT CANDIDATE HAS WRITTEN ON THE DOTTED LINES** • (Calculate) gradient (of tangent) **(1)** **ALLOW** 'slope' for 'gradient' • At t = 0 / at the start / at the beginning / when reaction is at its fastest / at the origin **(1)** **Each mark is stand-alone** **NOTE:** Answer may be annotated on a suitable sketch-graph **IGNORE** any sketch-graph that shows an increase in concentration with time **MAX (1)** if sketch-graph shows a **decrease** in the concentration of a reactant / Br_2	Answers relating to half-life score **(0)** overall If sketch-graph or comments suggest that gradient is measured at other than t = 0 or at several values of t then **max (1)**	**2**

Q18.

Question Number	Acceptable Answers	Reject	Mark
(a)(i)	(Sodium thiosulfate) (rapidly) reacts with / reduces the iodine (as it is formed) **(1)** So prevents the starch-iodine colour appearing until a fixed amount of reaction has occurred ALLOW (for second mark) So prevents the starch-iodine colour appearing until all the thiosulfate has reacted OR Moles of iodine reacted / thiosulfate ÷ time is (approximately) proportional to the (initial) rate of reaction **(1)** ALLOW Use of 'thio' for thiosulfate	iodide / I^-	**2**

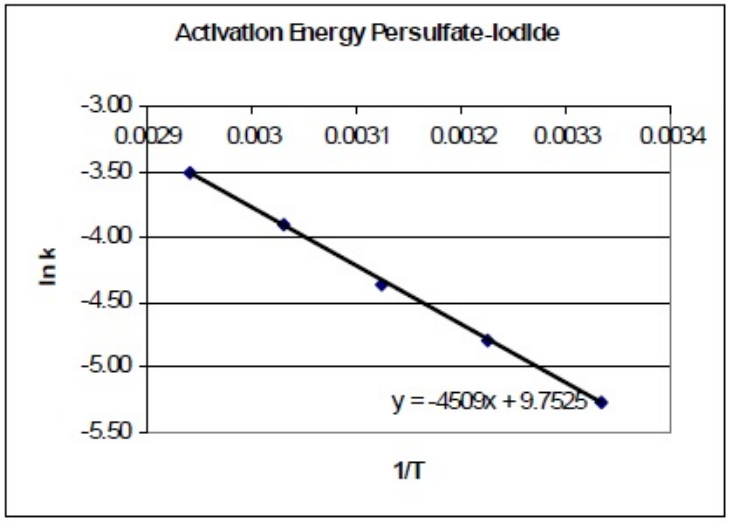
Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	(From 2 to 1) **$[S_2O_8^{2-}]$** doubles ($[I^-]$ unchanged) and rate doubles / time halves so order wrt $S_2O_8^{2-}$ = 1 **(1)** (From 3 to 1) **$[I^-]$** doubles ($[S_2O_8^{2-}]$ unchanged) and rate doubles / time halves so order **wrt I^-** = 1 OR (if first mark awarded) (From 3 to 2) **$[I^-]$** doubles ($[S_2O_8^{2-}]$ halved) and rate unchanged so order **wrt I^-** = 1 **(1)** Penalise omission of concentration/square brackets once only Rate = $k[S_2O_8^{2-}][I^-]$ **(1)** Third mark stand alone if no working & TE on incorrect orders IGNORE case of k	Rate equation =	**3**

Question Number	Acceptable Answers	Reject	Mark
(b)(i)	**First mark** Colorimetry /Use a colorimeter **(1)** **Second mark** Measure transmittance / absorbance (at various times) **(1)** **Third mark** (Use a calibration curve to) convert transmittance / absorbance into concentration. OR transmittance / absorbance proportional to concentration ALLOW Colorimetry may be used because iodine (solution) is coloured (and other reagents are colourless) / to measure intensity of the iodine colour **(1)** ALLOW (for the same three marks) Electrical conductivity Measured at various times / (use a calibration curve to) convert conductivity into concentration. Conductivity reduces as reaction proceeds because 3 mol ions converted to 2 mol ions / fewer ions on right hand side	Sampling methods calorimeter pH meter Just conductivity changes	**3**

Question Number	Acceptable Answers	Reject	Mark
(b)(ii)	$[(NH_4)_2S_2O_8]$ / $[S_2O_8^{2-}]$ / [peroxodisulfate] / [persulfate] remains (approximately) unchanged during the reaction. OR [KI] / $[I^-]$ is the only variable	$(NH_4)_2S_2O_8$ in excess. $[(NH_4)_2S_2O_8]$ etc does not affect the rate Only [KI] / $[I^-]$ affects the rate	**1**

Question Number	Acceptable Answers	Reject	Mark
(b)(iii)	Plot a graph of concentration (of iodine/I_2) (on the y axis) against time **(1)** Measure the initial gradient / gradient at t=0 **(1)** 'Plot a graph and measure the initial gradient / gradient at t=0' alone scores second mark		**2**

Question Number	Acceptable Answers	Reject	Mark
(b)(iv)	TE on 20(a)(ii) on numerical answer and appropriate units $8.75 \times 10^{-5} = k \times 2.0 \times 0.025$ $k = 8.75 \times 10^{-5} / (2.0 \times 0.025)$ $= 1.75 \times 10^{-3}$ **(1)** $dm^3\ mol^{-1}\ s^{-1}$ **(1)** ALLOW units in any order Correct answer including units with no working scores 2	1 SF	**2**

Question Number	Acceptable Answers	Reject	Mark
(c)(i)	 Use the overlay to mark the graph At least 4 points within the circles on the overlay **(1)** Best fit line on points given **(1)**		**2**

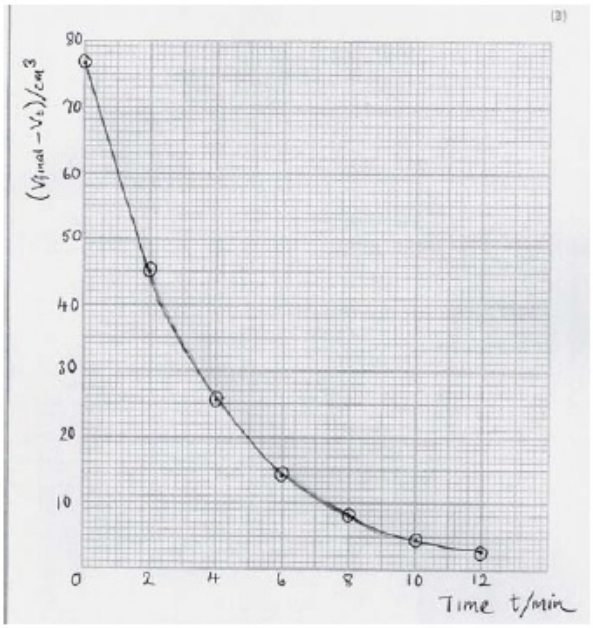
Question Number	Acceptable Answers	Reject	Mark
(c)(ii)	Gradient = −(−3.50 − −5.27) / (0.00333 − 0.00294) = (−)4538 = (−)4500 ALLOW values from (−)4300 to (−)4700 **(1)** gradient value negative **(1)** E_a = −gradient x R = −−4538 x 8.31 = (+)37700 J mol^{-1} (= (+)38 kJ mol^{-1}) **(1)** TE on value of gradient even if it is positive −4300 gives 35.7; −4700 gives 39.1 Correct units **(1)** Correct answer from the gradient calculation with units scores final 2 marks **BUT** correct answer with units but no gradient calculation scores units mark only		**4**

Q19.

Question Number	Acceptable Answers	Reject	Mark
(a)(i)	Mass of bromobutane = 0.6 x 1.276 (=0.7656 (g)) **(1)** Amount of bromobutane = $\frac{0.6 \times 1.276}{137.0}$ = 5.5883×10^{-3} = 5.59×10^{-3} / 0.00559 (mol) OR Amount of bromobutane = $\frac{0.6 \times 1.276}{136.9}$ = 5.5924×10^{-3} = 5.59×10^{-3} / 0.00559 (mol) TE on incorrect mass ALLOW 6×10^{-3} (mol) **(1)** Correct answer with no working scores 2 marks		**2**

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	$5.5883 \times 10^{-3} \times 24\,000$ = 134.12 (134.22 from 136.9)=134 cm^3 **(1)** ALLOW answer from (i) x 24000 IGNORE SF except 1 Any two from: Formation of butan-1-ol / other / side reactions Incomplete reaction Some but-1-ene may remain in solution **(2)** IGNORE Reaches equilibrium / reaction reversible But-1-ene reacts with ethanol/ solvent	Transfer losses Gas escapes Gas reacts with water But-1-ene condenses	**3**

Question Number	Acceptable Answers	Reject	Mark
(b)(i)	So [OH^-] remains (effectively) constant OR [1-bromobutane] is the only variable IGNORE So [OH^-] is not the limiting factor	Ensure that all C_4H_9Br reacts [OH^-] is in excess [OH^-] does not affect the rate Just 'Only [1-bromobutane] affects the rate'	**1**

Question Number	Acceptable Answer	Reject	Mark
(b)(ii)	 Axes correct with sensible scales to use at least half of graph paper on both axes **(1)** Labels ((V_{final} - V_t) and t) fully correct with units **(1)** All 7 points correctly plotted and smooth curve drawn **(1)**	Axes plotted wrong way round 'Volume'	**3**

Question Number	Acceptable Answers	Reject	Mark
(b)(iii)	(V_{final} - V_t) is proportional to the concentration of 1-bromobutane		**1**

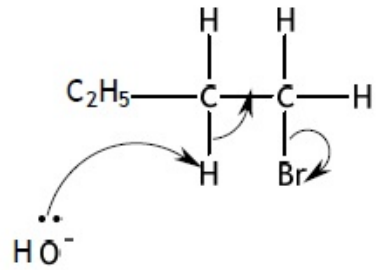
Question Number	Acceptable Answers	Reject	Mark
(b)(iv)	Two values 2.5 ± 0.3 (min) (each scores one mark) **(2)**		**2**

Question Number	Acceptable Answers	Reject	Mark
(b)(v)	Answer must be consistent with values in (iv) Because half lives are constant / similar **(1)** The reaction is first order... **(1)** If values in (iv) are 2.5 and 5, then: Reaction is 2nd order because half lives are increasing scores both marks. Reaction is 1st order because half lives are constant scores 1 mark		**2**

Question Number	Acceptable Answers	Reject	Mark
(c)(i)	Order one **(1)** Any one of: (Exp 1 and 2) $[OH^-]$ halves and rate halves. (Exp 1 and 3) $[OH^-]$ 1/5 and rate 1/5 (Exp 2 and 3) $[OH^-]$ 2/5 and rate 2/5 ALLOW reverse logic **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
(c)(ii)	Rate = $k[C_4H_9Br][OH^-]$ IGNORE case of K/k TE on b(v) and c(i)		**1**

Question Number	Acceptable Answers	Reject	Mark
(c)(iii)	$dm^3\ mol^{-1}\ min^{-1}$ ALLOW $dm^3\ mol^{-1}\ s^{-1}$ any sequence of units TE on (ii)		**1**

Question Number	Acceptable Answers	Reject	Mark
(c)*(iv)	 Arrows from OH-to H and from C-H bond to make additional bond between carbons **(1)** Third arrow from bond between carbon and bromine to bromine **(1)** (Because) both 1–bromobutane and hydroxide ion appear in the RDS ALLOW Attack of OH- on H is slow, therefore this is the RDS (Because) both 1–bromobutane and hydroxide ion appear in the slow step **(1)** IGNORE mention of rate equation	Both are involved in the reaction Mechanism described as S_N2	**3**

Q20.

<table>
<tr><th>Question number</th><th>Acceptable Answer</th><th>Additional Guidance</th><th>Marks</th></tr>
<tr><td>* (iii)</td><td>This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning.

Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.

The following table shows how the marks should be awarded for indicative content.

<table>
<tr><th>Number of indicative marking points seen in answer</th><th>Number of marks awarded for indicative marking points</th></tr>
<tr><td>6</td><td>4</td></tr>
<tr><td>5–4</td><td>3</td></tr>
<tr><td>3–2</td><td>2</td></tr>
<tr><td>1</td><td>1</td></tr>
<tr><td>0</td><td>0</td></tr>
</table>

The following table shows how the marks should be awarded for structure and lines of reasoning.

<table>
<tr><th></th><th>Number of marks awarded for structure of answer and sustained line of reasoning</th></tr>
<tr><td>Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout.</td><td>2</td></tr>
<tr><td>Answer is partially structured with some linkages and lines of reasoning.</td><td>1</td></tr>
<tr><td>Answer has no linkages between points and is unstructured.</td><td>0</td></tr>
</table>

Indicative content

Similarity</td><td>Guidance on how the mark scheme should be applied:
The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).
If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).</td><td></td></tr>
</table>

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	• reaction is between Mg and H^+ / $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$	both acids produce one H^+ / are monobasic / are monoprotic	**6**
	• 100 cm^3 of HCl and 100 cm^3 HCOOH contain the same initial number of moles of the acid	the same volume and concentration of both acids is used	
	• therefore same total volume of gas evolved	a calculation to show the same volume	
	Difference • HCl is fully dissociated/ionised but HCOOH only partially dissociated/ionised	dissociation/ionisation of HCOOH requires energy	
	• $[H^+]$ is greater in HCl / $[H^+]$ is smaller in HCOOH		
	• therefore rate is greater with HCl / lower with HCOOH	therefore larger activation energy with HCOOH	

Q21.

Question Number	Acceptable Answer	Additional guidance	Mark
(a)(i)	correct equation	Example of equation: $2NaN_3 \rightarrow 2Na + 3N_2$ Allow multiples Ignore state symbols even if incorrect	**(1)**

Question Number	Acceptable Answer	Additional guidance	Mark
(a)(ii)	• conversion of volume and temperature to correct units **(1)** • rearrangement of ideal gas equation so $n=pV \div RT$ and calculation of $n(N_2)$ in moles **(1)** • evaluation of $n(NaN_3)$ **(1)** • answer converted into mass to 2/3 SF **(1)** Allow TE at each stage	Example of calculation: 67 dm^3 = 0.067 m^3, 300°C = 573 K $n(N_2) = \frac{140\,000 \times 0.067}{8.31 \times 573}$ = 1.9699…..(mol) $n(NaN_3)$ = (2/3 x 1.9699…..=) 1.313…. (mol) m= (1.313 …. x 65 = 85.3629..=) = 85.4 / 85 (g) Correct answer without working scores (4)	**(4)**

Question Number	Acceptable Answer	Additional guidance	Mark
(b)	An answer that makes reference to the following points: • Nitrogen (is reduced) from +5 to 0 **(1)** • Sodium (is oxidised) from 0 to +1 **(1)** • Balanced equation **(1)**	Look for oxidation numbers annotated on the equation Do not award potassium oxidised Penalise omission of "+" sign, once only Example of balanced equation: **10**Na +**2**$KNO_3 \rightarrow K_2O$+ **5**Na_2O + N_2 Allow multiples	**(3)**

Question Number	Acceptable Answer	Additional guidance	Mark
(c)	An answer that makes reference to the following points: • Neutralisation reaction / acid base reaction **(1)** • Sodium and/or potassium oxides are caustic / corrosive **(1)** • Salts (silicates) formed are inert / unreactive **(1)**	Allow salt formation Allow "metal oxides" Ignore "harmful" / "alkaline" Allow "not harmful"/ "not caustic" Ignore "neutral"	**(3)**

Question Number	Acceptable Answer	Mark
(d)	The only correct answer is **A** ***B*** *is incorrect because the peak would shift to the left and be higher* ***C*** *is incorrect because the peak would shift to the left not to the right* ***D*** *is incorrect because the peak would be shift to the left not to the right*	**(1)**

Q22.

Question Number	Correct Answer	Reject	Mark
(a)	**1st mark:** Take **samples** (of reaction mixture) at various times OR Using of different mixtures (e.g. in separate conical flasks) **(1)** THEN: **EITHER** Quench (with ice) / remove the catalyst **(1)** **Titrate** with **acid of known concentration/standard** (using a suitable indicator) **(1)** **OR** Quench with acid **(1)** **Titrate** with **alkali of known concentration** (using a suitable indicator) **(1)** If no quenching, M3 can only be awarded if titrate with acid of known concentration	$NaHCO_3$ $NaHCO_3$	**3**

Question Number	Correct Answer	Reject	Mark
(b)(i)	(As) rate is (directly) proportional to concentration / as [A] doubles so does rate / rate ∞ concentration / rate ∞ [A] ALLOW Just 'straight line through origin/(0,0)' IGNORE References just to a 'constant gradient' References to **just** 'it is a straight line' References to positive correlation		**1**

Question Number	Correct Answer	Reject	Mark
(b)(ii)	**1st mark:** Rate higher than expected / rate unusually high / higher rate (for the anomalous points on the graph) **(1)** **2nd mark:** Reaction is exothermic / (heat) energy is released during the reaction **(1)** **3rd mark:** **EITHER** (So) there are more particles/collisions with energy > E_a ALLOW Higher **proportion of** successful collisions / just more successful collisions **IGNORE** **Just** 'more collisions' / 'more frequent collisions' **OR** At higher concentrations of **A**, the effect of the reaction being exothermic is greater **(1)**		**3**

Question Number	Correct Answer	Reject	Mark
(c)(i)	Increases reliability / improves validity (of the data obtained) / confirms the initial results / to check for anomalous results IGNORE References to average / precision / accuracy **OR** To determine order w.r.t. B and X / to see the effect of B and X (on the rate) / enables order of other reagents to be determined / to determine order w.r.t. B / find overall order / determine rate equation / to calculate *k*		**1**

Question Number	Correct Answer	Reject	Mark
(c)(ii)	0 order w.r.t. B **(1)** 1st order w.r.t. X **(1)** Rate = k [A][X] OR Rate = k [A][X][B]^0 ALLOW TE for CQ correct rate equation on incorrect order(s) **(1)** **Correct** reasoning **using data from table** to deduce the **CORRECT** order w.r.t. B NOTE that there must be reference to **TWO** relevant concentrations changing Eg (Expt 1 & 3) [A] triples, so does rate **AND** [B] doubles so order w.r.t. B is 0 (Expt 2 & 3) [A] x 1.5, rate x 1.5 **AND** [B] doubles so order w.r.t. B is 0 This mark can only be awarded if the reasoning shows that order w.r.t B is zero. **(1)** Not enough **just** to say 'as [B] doubles, rate unchanged' **Correct** reasoning **using data from table** to		**5**

	deduce the **CORRECT** order w.r.t. X NOTE that there must be reference to **TWO** relevant concentrations changing E.g. (Expt 1 & 4) [A] x 4 (and [B] x 2) **AND** [X] ÷ 2 rate doubles so order w.r.t. X is 1 (Expt 2 & 4) [A] x 2 (and [B] x 2) **AND** [X] ÷ 2 rate stays the same so order w.r.t. X is 1 (Expt 3 & 4) [A] x 4/3 (and [B] stays the same) **AND** [X] ÷ 2 rate decreases by 2/3, so order w.r.t. X is 1 This mark can only be awarded if the reasoning shows that order w.r.t X is one. Not enough **just** to say 'as [X] doubles, rate doubles' **(1)** IGNORE Any justification not concluded from data in the table Working to confirm order w.r.t. A = 1 (already given in question) NOTE Correct rate equation **alone** scores M1, M2 and M3		

Question Number	Correct Answer	Reject	Mark
(c)(iii)	k = rate / [A][X] = 4.2 x 10^{-3} ÷ (0.08 x 0.25) = 0.21 **(1)** $dm^3\ mol^{-1}\ s^{-1}$ / $mol^{-1}\ dm^3\ s^{-1}$ ALLOW units in any order **(1)** Comment Unit mark is independent of the value **Allow use of data from experiments 1, 2 & 3** Allow TE from an incorrect rate equation given in answer to Q14(c)(ii) or a 'new' rate equation given at the start of answer to Q14(c)(iii), if of the form rate = k ...		**2**