PEARSON EDEXCEL A-LEVEL CHEMISTRY · 9CH0

CHEMISTRY



MARK SCHEME

TOPIC 16: KINETICS II

SCORE	PERCENTAGE
/277	%

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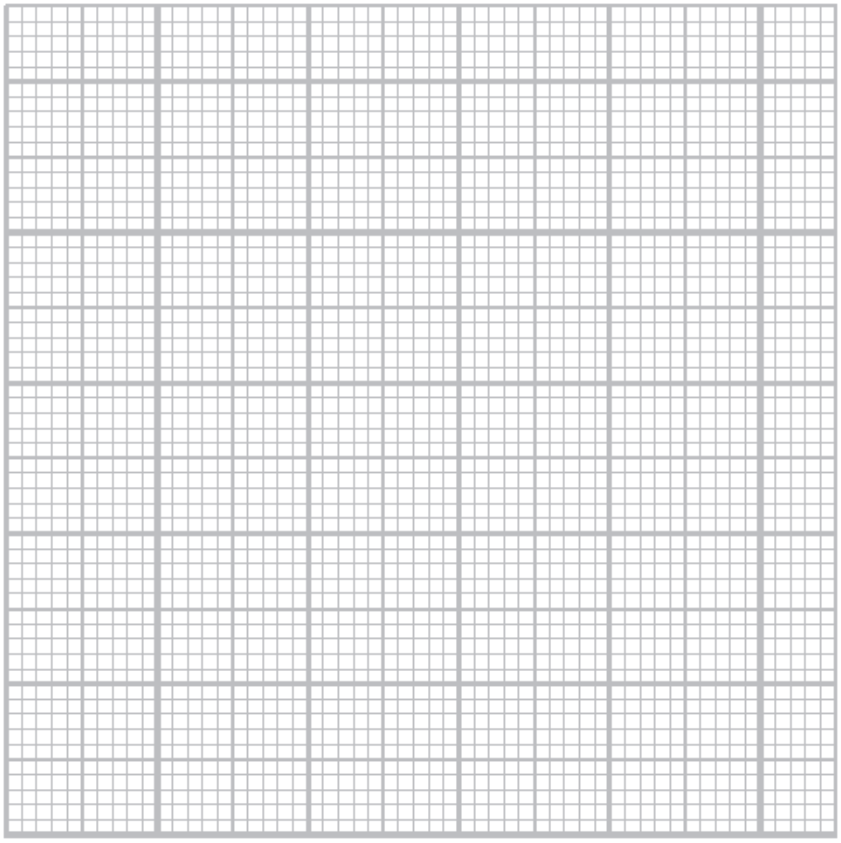
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Results

Time / s	[RBr] / mol dm^{-3}
0	0.100
30	0.065
60	0.042
90	0.028
120	0.019
150	0.014

Plot a graph of [RBr] against time.

(3)



(Total for question = 3 marks)

Mark Scheme

Q1.

Question Number	Correct Answer	Mark
	B	**1**

Q2.

Question Number	Correct Answer	Mark
	D	**1**

Q3.

Question Number	Answer	Additional Guidance	Mark
(i)	<table><tr><th>Temperature / K</th><th>Rate / mol dm^{-3} s^{-1}</th><th>1/Temperature</th><th>ln rate</th></tr><tr><td>700</td><td>0.0108</td><td>1.43×10^{-3}</td><td>**–4.53**</td></tr><tr><td>850</td><td>4.90</td><td>**1.18×10^{-3}**</td><td>1.59</td></tr></table>	values must be to at least 3SF Allow –4.5282 1.1765×10^{-3}	(1)

Question Number	Answer	Additional Guidance	Mark
(ii)	• recognition that (difference in ln rate) / (difference in $1/T$) = $-E_a / R$ (1) • calculation of $-E_a / R$ (1) • calculation of E_a with correct units (1)	<u>Example of calculation</u> $-6.12 / 2.5 \times 10^{-4}$ Can be subsumed within M2 = – 24480 (K) 24480 x 8.31 = (+) 203428.8 J mol^{-1} = (+) 203000 J mol^{-1} = (+) 203 kJ mol^{-1} Ignore SF final answer between 200 -204 kJ mol^{-1} with **no** working scores (3)	(3)

Q4.

Question Number	Correct Answer	Reject	Mark
(a)	B		**1**

Question Number	Correct Answer	Reject	Mark
(b)	D		**1**

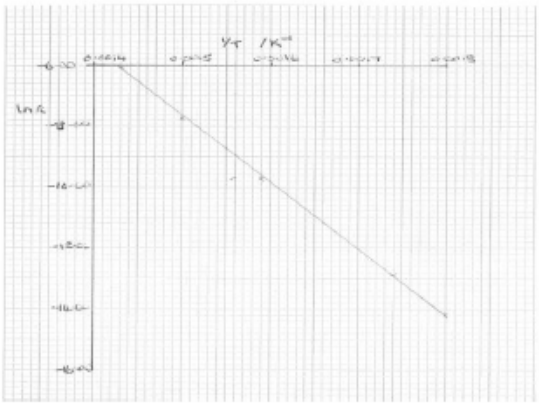
Question Number	Correct Answer	Reject	Mark
(c)	D		**1**

Question Number	Correct Answer	Reject	Mark
(d)	C		**1**

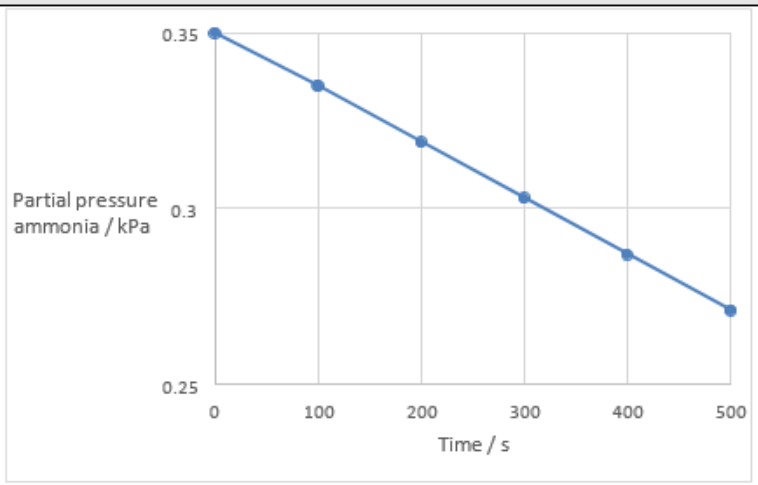
Q5.

Question Number	Answer	Additional Guidance	Mark
	Correct answer to 2 SF	Example of calculation: (Four half-lives to decrease 600 g to 37.5 g so 4 x 14 mins) = 56 (mins) Penalise wrong units, e.g. "m"	**(1)**

Q6.

Question Number	Acceptable Answer	Additional Guidance	Mark
			
	• axes labelled and correct unit (1)		
	• points correct, ± half square <u>and</u> best fit straight line (1)		
	• calculates gradient (1)	gradient = -21 892 (K) Allow -21 000 to -22 800 (K)	
	• calculates E_a = -gradient x R (1)	E_a= - - 21 892 x 8.31 = (+)181 923 J mol^{-1} **or** =(+)181.923 kJ mol^{-1}	
	• E_a given to 2/3 SF <u>and</u> correct units for E_a to match answer given (1)	E_a = (+)180 000 / (+)182 000 J mol^{-1} **or** (+)180/ (+)182 kJ mol^{-1}	
		TE on value of gradient but do not allow the mark if E_a is negative	**5**

Q7.

Question Number	Acceptable Answers	Additional Guidance	Mark
(i)		 Example of graph	(2)
	• axes with time on x axis **and** labelled, including units **and** suitable scale **(1)**	Allow y axis labelled with partial pressure / pressure and unit Do not allow partial pressure axis starting at 0 Both axes must cover at least half the graph paper	
	• **all** points plotted correctly **and** best fit line **(1)**	Allow ± ½ square M2 can be awarded if axes the wrong way around in M1	

Question Number	Acceptable Answers	Additional Guidance	Mark
(ii)	• rate = k / rate = k x $p(NH_3)^0$ **(1)**	Allow r for rate Allow −rate = k / rate = $k[NH_3]^0$ Ignore $[H_2]^0$ or $[N_2]^0$	(2)
	• (zero / 0 order) because the rate is independent of the partial pressure of ammonia / rate is constant **or** because the graph is a straight line / linear **(1)**	Conditional on M1 Allow because the gradient is constant	

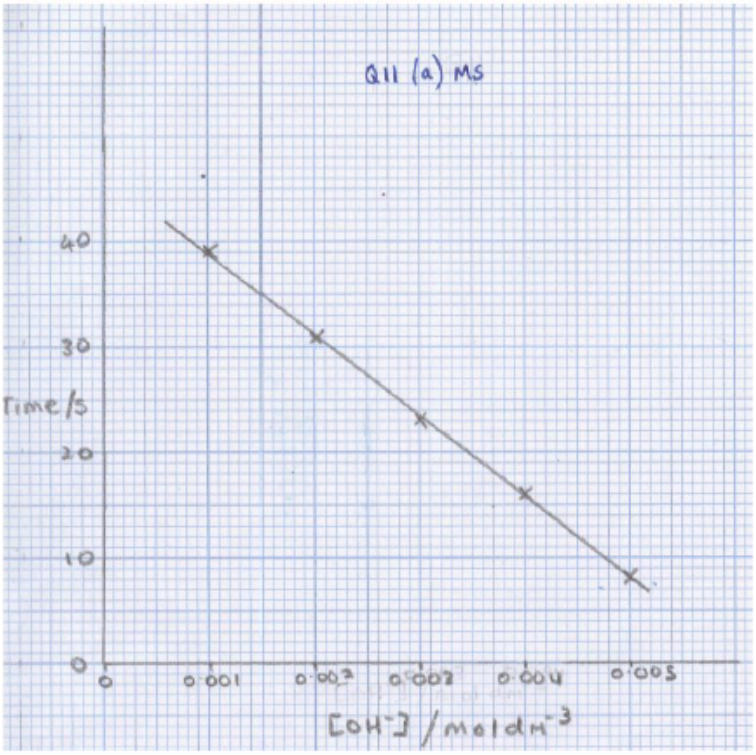
Question Number	Acceptable Answers	Additional Guidance	Mark
(iii)	• calculation of gradient of graph / rate / rate constant **(1)** • corresponding units for rate constant **(1)**	Example of calculation $\frac{(0.271 - 0.350}{500} = (-)\frac{0.079)}{500}$ $k = 1.58 \times 10^{-4}$ / 0.000158 Allow any value in the range 1.50 to 1.65 x 10^{-4} 1.58×10^{-4} / 0.000158 kPa s^{-1} Allow 158 x 10^{-6} kPa s^{-1} / 0.158 Pa s^{-1} / 1.58 x 10^{-1} Pa s^{-1} Do not award units of mol dm^{-3} s^{-1} Ignore SF except 1 SF Ignore negative value for *k* Correct answer with corresponding units and no working scores (2)	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(iv)	A description that makes reference to the following points: • adsorption of ammonia / reactant onto surface of tungsten / catalyst **(1)** • breaking bonds in ammonia / reactant **or** breaking N-H bonds **(1)** • desorption of nitrogen and hydrogen / products / gases from surface of tungsten / catalyst **(1)**	Ignore reference to heterogeneous / homogeneous / active sites Allow gas for ammonia Allow adsorb / adsorp for adsorption Ignore "stick" Do not award absorption Allow bonds weaken instead of break Ignore mention of atoms / radicals Allow products released / detached from catalyst surface Allow de-adsorbed / desorped for desorption Do not award desorption of ammonia	**(3)**

Q8.

Question Number	Correct Answer	Reject	Mark
	Correct feature **ANY <u>one</u> of:** First step does involve carbocation formation / carbocation is correct / two electrons taken by Br atom in C–Br bond / C–Br bond breaks (heterolytically) (Second step does involve) attack of hydroxide ion First order wrt the halogenoalkane / 1st order wrt 2-bromomethylpropane (S_N1) is a two-step process Curly arrow**<u>s</u>** are correct **(1)** **Incorrect features** **ANY <u>two</u> of:** • Should be S_N1 (not S_N2) • First step is slow • Second step is fast • (It is not) S_N2 • $C^{\delta+} - Br^{\delta-}$ not shown / dipole on C–Br bond not shown **(2)**		**3**

Q9.

Question Number	Answer	Additional Guidance	Mark
(a)	• **M1** axes labelled with units on axes, suitable uniform scale with points covering at least half the available space in both directions **(1)** • **M2** all points plotted correctly with straight line of best fit **(1)**	Example of graph  Allow variables on either axis	**(2)**

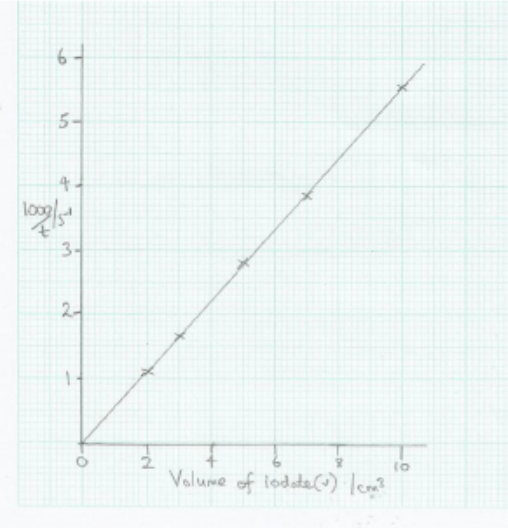
Question Number	Answer	Additional Guidance	Mark
(b)	An answer that makes reference to the following points • zero order with respect to hydroxide ions **(1)** • The graph is a straight line so the rate of reaction is independent of the concentration of the hydroxide ions **(1)**	M2 dependent on M1	**(2)**

Question Number	Answer	Additional Guidance	Mark
(c)	An answer that makes reference to the following points • S_N1 **(1)** • as there is only one reactant in the rate determining step / as the hydroxide ions do not affect the rate **(1)**	Mark consequentially on order Allow TE from (b) e.g. if first order in (b) allow S_N2	**(2)**

Question Number	Answer	Additional Guidance	Mark
(d)	• the chloroalkane is tertiary	Allow TE from first order in (b) and/or S_N2 in (c) e.g. if S_N2 in (c) allow primary NOTE if first order wrt hydroxide ions in (b) but S_N1 given in (c) can score 1 mark in (d) for tertiary	(1)

Q10.

Question Number	Acceptable Answer	Additional Guidance	Mark
(i)	A statement that makes reference to the following: • So that the volume of iodate(V) ions is proportional to the concentration.	Allow the volume of iodate(V) ions can be used instead of the concentration in plotting the graph. Ignore reference to "fair tests".	(1)

Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	• calculation of all three 1000/t values **(1)** • axes: correct way round, labelled and including units **(1)** • suitable scale **(1)** • all points plotted correctly, with best-fit straight line through the origin **(1)**	(5.56) 3.85, 2.80, 1.65, (1.11) Do not award 2.8 or ≥3SF Do not award use of T for t Plotted points must cover at least ½ the graph paper on each axis Allow ±½ square Ignore plotting of experiment 6 Exemplar graph 	**(4)**

Question Number	Acceptable Answer	Additional Guidance	Mark
(iii)	An answer that makes reference to the following: • first order (with respect to iodate(V) ions) **(1)** • because straight line goes through the origin / rate is (directly) proportional to concentration **(1)**	Mark independently Allow "volume" for "concentration" Do not award references of proportionality to time Ignore references to half life	**(2)**

Q11.

Question Number	Acceptable Answer	Additional Guidance	Mark
(i)	An answer that makes reference to the following points: • second order (1) • as the concentration of HI triples, the initial rate increases by a factor of 9 / 3^2 (1)		**2**

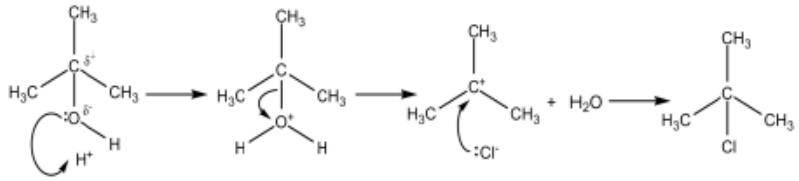
Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	Both marks TE on order in d(i) • rate equation (1) • calculate rate (1)	rate = $k[HI]^2$ rate = $7.040 \times 10^{-9} \times (0.5/0.1)^2$ = 1.76×10^{-7} (mol dm^{-3} s^{-1}) **or** k = rate/$[HI]^2$ = $7.040 \times 10^{-9}/(0.1)^2$ = 7.040×10^{-7} and rate = $7.040 \times 10^{-7} \times 0.5^2$ = 1.76×10^{-7} (mol dm^{-3} s^{-1})	**2**

Q12.

Question Number	Acceptable Answer	Additional Guidance	Mark
(a)	An explanation that makes reference to the following point: • production of CO_2 (1) • $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$ (1)	Allow $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ Ignore state symbols	**2**

Question Number	Acceptable Answer	Additional Guidance	Mark
(b)	An answer that makes reference to the following points: • drying agent (1) • mixture becomes transparent / clear (from cloudy) (1)	Allow to remove water Allow drying agent stops clumping together	**2**

Question Number	Acceptable Answer	Additional Guidance	Mark
(c)	An explanation that makes reference to the following points: • they will reduce the yield (1) • as some of the 2-chloro-2-methylpropane will react with the water (and reform the alcohol) (1)	Allow 'as some of the 2-chloro-2-methylpropane might dissolve in the water'	**2**

Question Number	Acceptable Answer	Additional Guidance	Mark
(d)	 • breaking of CO bond in protonated alcohol (1) • structure of intermediate (1) • correct charge on carbon in intermediate (1) • attack of chloride ion with lone pair (1)	Arrow must originate from bond and finish on oxygen Arrow must originate from lone pair on Cl^-	**4**

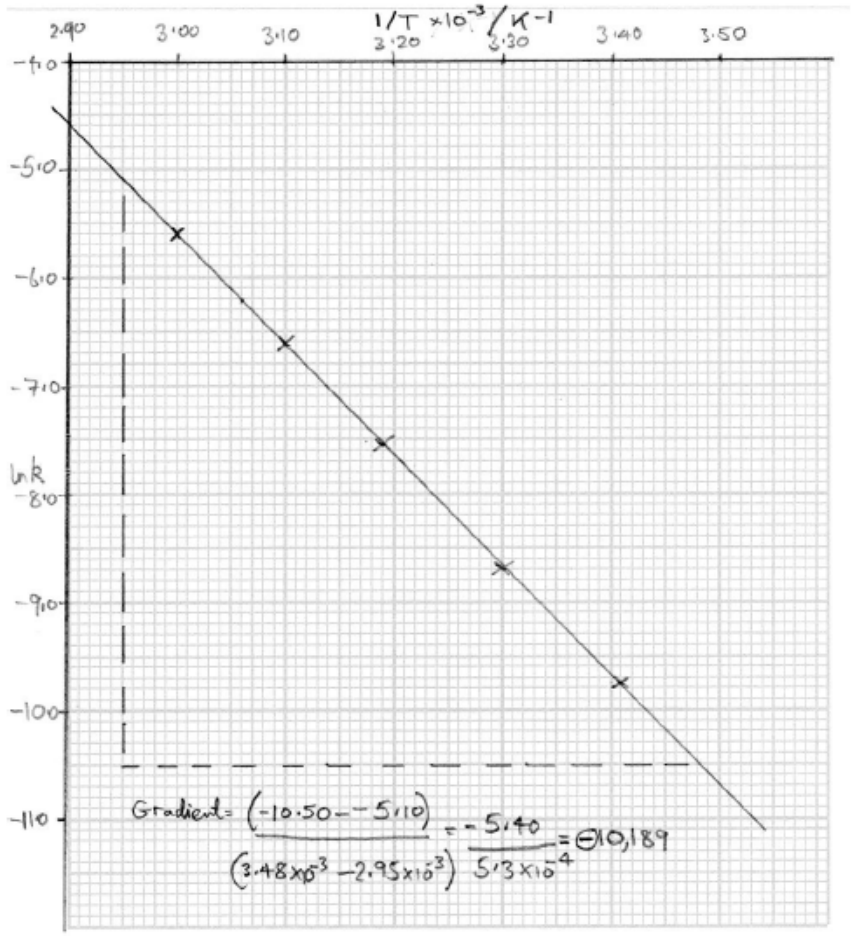
Q13.

Question Number	Acceptable Answer	Additional Guidance	Mark
	An answer that makes reference to the following points: • two half-lives measured and both about 2 min (1) • half-lives are constant so first order (1)		**2**

Q14.

Question number	Answer	Additional guidance	Mark
(a)(i)	• evaluation of number of moles of propanone (1) $= 0.025 \times 2.0 = 0.050$ mol • which is greater than the amount of iodine, which is $0.050 \times 0.020 = 0.0010$ mol (1)		2
(a)(ii)	• measuring cylinder/burette		1
(a)(iii)	• pipette		1
(b)	An explanation that makes reference to the following points: • the order with respect to iodine is zero (1) • because the graph is a straight line, showing that the change in iodine concentration is constant (1)		2
(c)	An answer that makes reference to the following points: • 1st order with respect to H^+ and propanone (1) • H^+ and propanone involved in reaction before rate determining step (therefore 1st order) (1) • iodine involved after rate determining step / slow step (therefore zero order) (1)		3

Q15.

Question Number	Answer	Additional Guidance	Mark
	Example of suitable graph 		(7)

	• calculation of all three 1/T values x 10^{-3} **(1)**	(3.41), 3.30, 3.19, 3.10, (3.00)	
	• calculation of all three ln k values **(1)**	(−9.75), −8.70, −7.55, −6.60, (−5.58) Allow omission of end zero Penalise more than 3SF once only	
	• axes: correct way round, labelled, suitable scale **(1)**	Plotted points must cover at least ½ the graph paper on each axis Do not award 1/t	
	• all points plotted correctly, with best-fit straight line **(1)**	Allow ±½ square	
	• calculation of gradient with sign **(1)**	Gradient = − 10200 Allow ±500 Allow this mark if the value is seen in the E_a calculation	
	• units of gradient **(1)**	K	
	• use of gradient to calculate activation energy **(1)**	E_a = 10200 x 8.31 / 1000 = (+) 84.8 (kJ mol^{-1}) Final answer must be positive and in the range (+) 80.6 – 88.9 (kJ mol^{-1}) Allow value given in J mol^{-1} but then these units are essential Ignore SF for gradient and activation energy values	

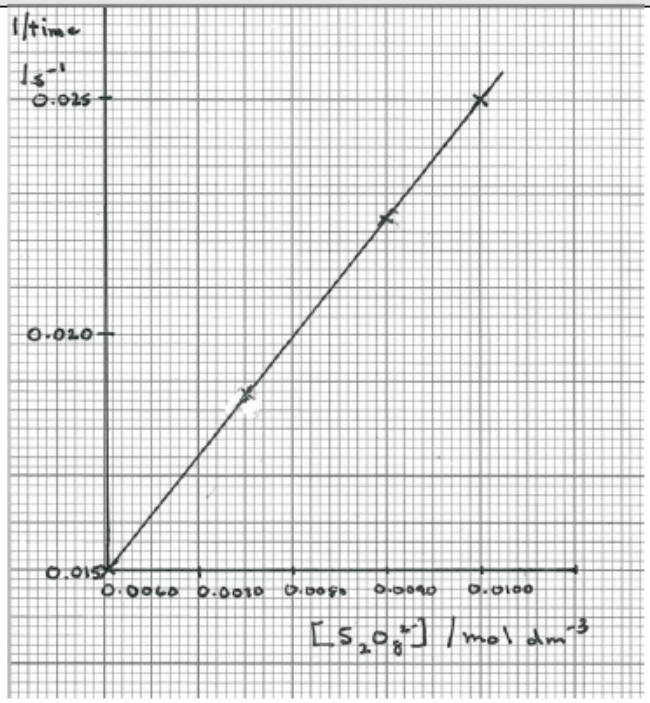
Q16.

Question Number	Correct Answer	Reject	Mark
(a)	$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$ ALLOW multiples Ignore state symbols even if incorrect		**1**

Question Number	Correct Answer	Reject	Mark
(b)(i)	Blue/black /blue-black OR Colourless to blue-black/ blue/black	Purple	**1**

Question Number	Correct Answer	Reject	Mark
(b)(ii)	The mixture would change colour/ go blue/black /blue-black **immediately/straight away** ALLOW ...too quick(ly)/too early ...quicker ...no time delay		**1**

Question Number	Correct Answer	Reject	Mark
(b)(iii)	(As quickly as iodide reacts to form iodine it is) reduced/turned back to iodide by the thiosulfate ions ALLOW Persulfate reacts with thiosulfate first. OR Iodine reacts with thiosulfate.		**1**

Question Number	Correct Answer	Reject	Mark
(c)(i)	 **First mark** Correct graph of rate v concentration, with axes correct **and** values increasing on both axes labelled with quantity **and** units Note Units may be given in brackets with no slash. s/time meaning s divided by time is fine. **(1)**		**2**
	Second mark Sensible scales to use at least half the graph paper but allow graphs starting at the origin and points cover two by two big squares. Linear scales All points reasonably correct with straight line drawn **(1)** Second mark depends on correct graph of rate v concentration, but not other detail of first mark		

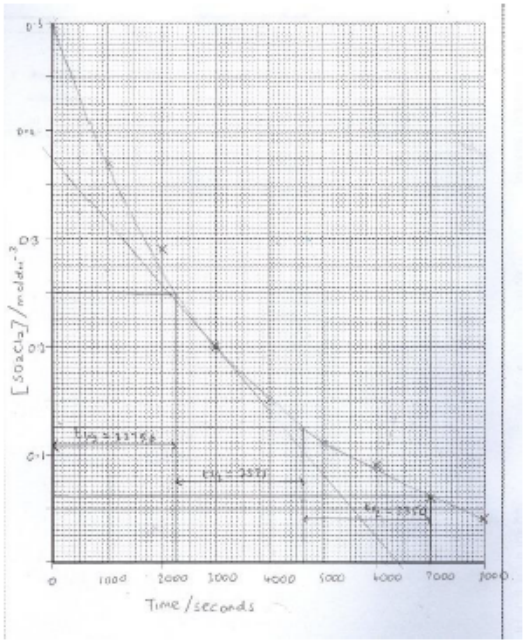
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Question Number	Correct Answer	Reject	Mark
(c)(ii)	First order This mark is independent of the graph drawn **(1)** Because the graph is a straight line (through the origin)/ rate is proportional to $[S_2O_8^{2-}]$ OR As concentration increases by (factor of) 2 rate increases by 2 (or any other numbers, including 'x') OR Rate increases linearly (with concentration) OR Gradient of line is constant **(1)** Second mark depends on first order	Just 'as concentration increases rate increases'	**2**

Question Number	Correct Answer	Reject	Mark
(c)(iii)	Rate = $k[S_2O_8^{2-}][I^-]$ **(1)** TE from (c)(ii) Units - $dm^3\ mol^{-1}\ s^{-1}$ ALLOW Internal TE from rate equation **(1)** Units in any order	Incorrect formulae	**2**

Q17.

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**

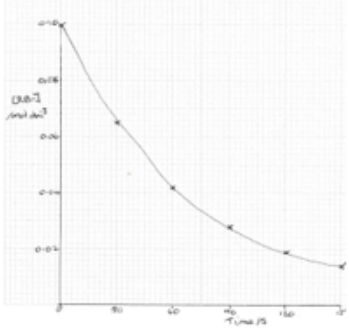
Q18.

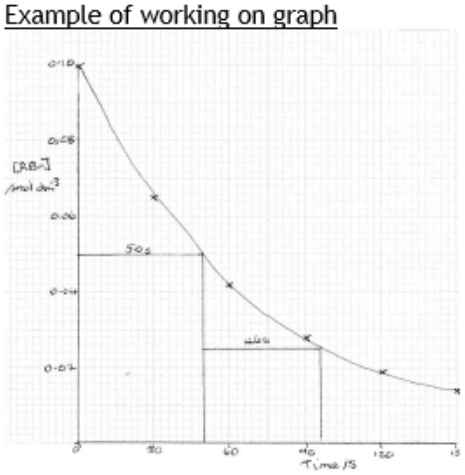
Question Number	Answer	Additional Guidance	Mark
		Example of calculation	(5)
	• substitution of numbers into expression **(1)**	$\ln \frac{4.87 \times 10^{-3}}{1.50 \times 10^{-3}} = \frac{-E_a}{8.31}\left(\frac{1}{338} - \frac{1}{328}\right)$	
	• evaluation of k_2/k_1 or $\ln k_2/k_1$ **and** $1/T_1 - 1/T_2$ **(1)**	$k_2/k_1 = 3.2467$ or $\ln k_2/k_1 = 1.1776$ Allow 487/150 for $\ln k_2/k_1$ **and** $1/T_1 - 1/T_2 = (-)9.0201 \times 10^{-5}$ Allow (−)5/55432 for $(-)9.0201 \times 10^{-5}$	
	• rearrangement of expression **(1)**	e.g. $E_a = \frac{1.1776 \times 8.31}{9.0201 \times 10^{-5}}$ or $\frac{E_a}{R} = \frac{1.1776}{9.0201 \times 10^{-5}}$ / = 13056	
	• evaluation of expression **(1)**	$E_a = 108\,493$ TE on $\ln (k_2/k_1)$ and $1/T_1 - 1/T_2$	
	• answer given to 2/3 SF **and** corresponding units **(1)**	= (+)108 000 / 110 000 J mol^{-1} or (+)108 / 110 kJ mol^{-1} Do not award negative value Expression may be rearranged before any evaluation Correct answer to 2/3 SF and units with no working scores (5)	

Q19.

Question number	Answer	Additional guidance	Mark
	• axes: correct way round, labelled, suitable scale (1)	plotted points must cover at least half the graph paper on each axis allow ±½ a square	4
	• all points plotted correctly, with best fit straight line (1)		
	• calculation of gradient of straight line (1)	gradient = (-) 5970 allow ± 200	
	• use of gradient = $-E_a$ /R to calculate E_a (in kJ mol^{-1}) (1)	activation energy = 5970 x 8.31 / 1000 = 49.6 (kJ mol^{-1}) final answer must be positive.	

Q20.

Question Number	Answer	Additional Guidance	Mark
(i)		Example of graph 	(3)
	• both axes labelled, including units **(1)**	Allow T / t for time with units Allow just 'concentration' with units Do not award RBr without square brackets	
	• suitable scales and points taking up at least half the graph paper in both directions **(1)**	Allow ± half square	
	• points plotted correctly **and** smooth curve through the points **(1)**	Do not award point-to-point straight lines	

Question Number	Answer	Additional Guidance	Mark
(ii)		Example of working on graph 	(2)
	• first half-life 50 s **and** second half-life 50 s **(1)**	Allow ± 6 s for both half-lives Do not award M1 if no working is shown on the graph	
	• reaction is first order because the half-lives are (almost) the same **(1)**	Allow rate ∝ [RBr] / rate = k[RBr] for first order Conditional on 2 half-lives within 12 s **or** the second half-life is (about) twice the first half-life	

Q21.

Question Number	Answer	Additional Guidance	Mark
(i)	Reaction Orders: • **X** First/1 **(1)** • **Y** Second/2 **(1)** • **Z** Zero/0 **(1)**	Allow "none"/"no order"	**(3)**

Question Number	Answer	Additional Guidance	Mark
(ii)	Marking point 1 • Rate = $k[X][Y]^2[Z]^0$ **(1)** Marking point 2 • rearrangement of rate expression **(1)** Marking point 3 • calculation of value for k to 2/3 SF **(1)** Marking point 4 • units $dm^6\ mol^{-2}\ s^{-1}$ **(1)**	Reactants can be in any order Z does not have to be included in the rate equation TE from (b)(i) which will apply for all four marking points Example of calculation: $k = rate / [X][Y]^2$ $k = \frac{2.17 \times 10^{-6}}{0.00100 \times 0.00300^2}$ $= 241.11$ $= 241/240$ Any 'run' can be used No TE on incorrect rearrangement Allow units in any order Correct answer without working and with correct units to 2/3 SF scores marking points 2, 3 and 4	**(4)**

Q22.

Question Number	Correct Answer	Reject	Mark
(a)	A		1

Question Number	Correct Answer	Reject	Mark
(b)	B		1

Question Number	Correct Answer	Reject	Mark
(c)	D		1

(d)	C		1

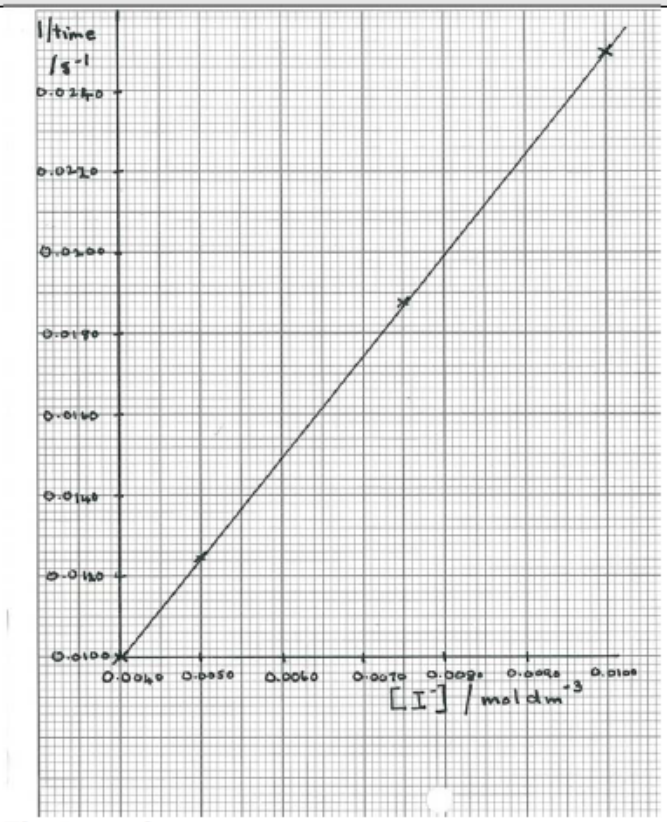
Q23.

Question Number	Correct Answer	Reject	Mark
(a)	$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$ ALLOW multiples Ignore state symbols even if incorrect **COMMENT** 2 in front of sulfate is often missed.		1

Question Number	Correct Answer	Reject	Mark
(b)(i)	Blue/black /blue-black OR Colourless to blue-black/ blue/black	purple	1

Question Number	Correct Answer	Reject	Mark
(b)(ii)	The mixture would change colour/ go blue/black /blue-black **immediately/straight away** ALLOW ...too quick(ly)/too early ...quicker ...no time delay		1

Question Number	Correct Answer	Reject	Mark
(b)(iii)	(As quickly as iodide reacts to form iodine it is) reduced/turned back to iodide by the thiosulfate ions ALLOW Persulfate reacts with thiosulfate first. OR Iodine reacts with thiosulfate.		1

Question Number	Correct Answer	Reject	Mark
(c)(i)	 **First mark** Correct graph of rate v concentration, with axes correct **and** values increasing on both axes labelled with quantity **and** units Note Units may be given in brackets with no slash. s/t meaning s divided by time is fine. **(1)**		2
	Second mark Sensible scales to use at least half the graph paper but allow graphs starting at the origin and points cover two by two big squares. Linear scales All points reasonably correct with straight line drawn **(1)** Second mark depends on correct graph of rate v concentration, but not other detail of first mark		

Question Number	Correct Answer	Reject	Mark
(c)(ii)	First order This mark is independent of the graph drawn **(1)** Because the graph is a straight line (through the origin)/ rate is proportional to $[I^-]$ OR As concentration increases by (factor of) 2 rate increases by 2 (or any other numbers, including 'x') OR Rate increases linearly (with concentration) OR Gradient of line is constant **(1)** Second mark depends on first order	Just 'as concentration increases rate increases'	2

Question Number	Correct Answer	Reject	Mark
(c)(iii)	Rate = $k[S_2O_8^{2-}][I^-]$ **(1)** Units - $dm^3\ mol^{-1}\ s^{-1}$ **(1)** TE from (c)(ii) ALLOW Units in any order Internal TE from rate equation	Incorrect formulae	2

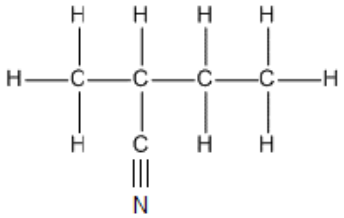
Q24.

Question Number	Acceptable Answer	Additional Guidance	Mark
(i)	• calculation of gradient of straight line **(1)** • numerical value of E_a **(1)** • sign and units **(1)**	Example of calculation Gradient = −19500 Allow ±500 $-E_a$ = −19500 x 8.31 / 1000 = 162 ± 5 **+ and** kJ mol^{-1} Accept +162000 **Jmol^{-1}** Final answer with or without working scores (3) Allow TE for incorrect gradient as long as the final value is not negative Ignore SF except 1SF	**(3)**

Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to the following: • (Reason) anomalous point	Allow description of Allow 'outlier'	**(1)**

Q25.

Question Number	Acceptable Answer	Additional Guidance	Mark
(a)(i)	NH_3	Do not allow just the name ammonia	**1**

Question Number	Acceptable Answer	Additional Guidance	Mark
(a)(ii)		Do not award skeletal/structural formulae or a combination of these	**1**

Question Number	Answer	Additional Guidance	Mark
(b)	**A** (the C-Cl bond has a higher bond enthalpy than the C-Br bond)		**1**

Question Number	Acceptable Answer	Additional Guidance	Mark
(c)(i)	An answer that makes reference to the following points: • hydroxide ions are nucleophiles as they donate a (lone) pair of electrons (to form a covalent bond) (1) • substitution because OH replaces the halogen atom (in the molecule) (1)		**2**

Question Number	Answer	Additional Guidance	Mark
(c)(ii)	**D** (2-bromo-2-methylpropane, 2-bromobutane, 1-bromobutane)		**1**

Question Number	Acceptable Answer	Additional Guidance	Mark
(c)(iii)	An answer that makes reference to the following points: • rate = k[$(CH_3)_3CBr$] / rate = k[$(CH_3)_3CBr$]^1 (1) • only the reactants/$(CH_3)_3CBr$ in the slow/rate determining step appear in the rate equation (1)		**2**

Q26.

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)**

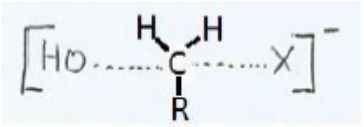
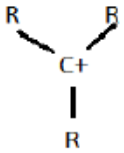
Q27.

<table>
<tr><th>Question Number</th><th>Acceptable Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr>
<td></td>
<td>This question assesses the 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</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, a response with four 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 were no linkages between the points, then the same indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and zero marks for linkages).</td>
<td>(6)</td>
</tr>
</table>

		Number of marks awarded for structure of answer and sustained lines of reasoning	In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning. If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded do not deduct mark(s). More than one indicative marking point may be made within the same comment or explanation	
	Answer shows a coherent logical structure with linkages and fully sustained lines of reasoning demonstrated throughout	2		
	Answer is partially structured with some linkages and lines of reasoning	1		
	Answer has no linkages between points and is unstructured	0		
	Indicative content • (similarity)(both) are nucleophilic substitution **(1)** • Hydrolysis mechanism for RCH_2X/primary is S_N2 via a transition state **and** R_3CX/tertiary is S_N1 via a carbocation/intermediate **(1)**		Words needed at least once provided S_N1 and S_N2 are given	

	• RCH_2X and OH^- in the RDS **(1)** • R_3CX only in the RDS **(1)** • (RCH_2X forms a transition state with OH^-) diagram, including dotted lines and charge **(1)** • (R_3CX forms a carbocation / intermediate) diagram, including charge **(1)**	Allow "both/two species in the RDS" Allow correct rate equations for IP3 and IP4  Allow "-" either on the "OH" or the "X" Ignore point of attachment of OH Ignore dipoles within structure  Ignore shape Ignore references to comparative rates of reaction between 1° and 3° even if incorrect Ignore references to optical activity.	

Q28.

Question Number	Acceptable Answer	Additional Guidance	Mark
(i)	• value of rate constant to 2 or 3 SF **(1)** • units of rate constant **(1)**	<u>Example of calculation:</u> (Rate=$k[H_2O_2][I^-]$ so k= rate ÷ ($[H_2O_2][I^-]$) =$1.24\times10^{-3}\div(1.50\times10^{-3}\times2.10\times10^{-3})$ =393.65...) = 390/394 $dm^3\ mol^{-1}\ s^{-1}$ Accept units in any order No TE on incorrect rate equation	**(2)**

Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	An explanation that makes reference to • starch is an indicator (to react with the iodine) **(1)** • the time taken for the formation of the blue-black complex (can be used to calculate the reaction rate) **(1)**	 Do not award references to iodide/I^- Allow Reacts with iodine/produces a blue-black colour when the reaction is complete. Allow Changes colour when all the thiosulfate is used up. Allow indication of 'time taken'	**(2)**

Q29.

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)

Q30.

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

Q31.

Question Number	Answer	Additional Guidance	Mark
(i)	• order with respect to Hb = 1		(1)

Question Number	Answer	Additional Guidance	Mark
(ii)	• order with respect to CO = 1 (1) • justification (1)	standalone mark Either using experiments 1 and 3 the concentration of Hb goes up by a factor of 1.56 and the concentration of CO doubles and the rate goes up by a factor of 3.12 Or using experiments 2 and 3 the concentration of Hb goes down by a factor of 0.78 but the rate increases by a factor of 1.56 so doubling the concentration of CO means doubling the rate M2 dependent on M1	(2)

Question Number	Answer	Additional Guidance	Mark
(iii)	• rate equation	Example of rate equation rate = k[Hb][CO] allow e.g R / r for rate and K for k Allow expressed in terms of k Allow TE from 6(d)(i) and 6(d)(ii) Note – must be consistent with 6(d)(i) and 6(d)(ii)	(1)

Question Number	Answer	Additional Guidance	Mark
(iv)	• rearrangement of rate equation to find k (1) • calculation of k (1) • correct units of k (1)	Example of calculation k = rate / [Hb][CO] $8.20 \times 10^{-7} / (2.09 \times 10^{-6} \times 1.40 \times 10^{-6})$ = 280246 = 280000 Ignore SF except 1 SF $dm^3\ mol^{-1}\ s^{-1}$ Allow units in any order Allow use of data from experiments 2 or 3 Correct answer including units with no working scores 3 marks Allow TE on rate equation from (d)(iii) No TE for mistake with rate equation **within** (d)(iv) e.g. rearrangement error	(3)

Q32.

Question Number	Acceptable Answer	Additional Guidance	Mark
	A statement that makes reference to the following: • The chance of five or more ions colliding in the rate determining step is negligible	Allow 'at the same time' for the RDS	(1)

Q33.

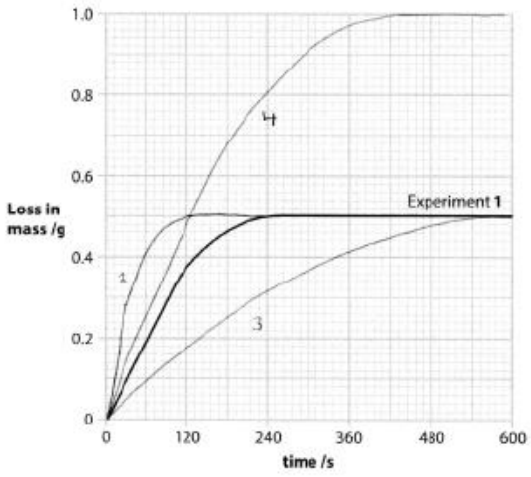
Question Number	Answer	Additional Guidance	Mark
(a)	C		1
(b)(i)	• Comparison of runs 1 and 2 to determine order wrt A = 1 (1) • Comparison of runs 1 and 3 to determine order wrt B = 2 (1)	Allow comparisons of other relevant pairs of runs	2
(b)(ii)	(When comparing runs 2 and 4) • [A] constant so no effect but [B] x 4 so increases rate by 16 / to 0.0768 (1) • [C] x 3 and rate increases by 0.23 ÷ 0.0768 (= 2.99 i.e. 3), so first order with respect to C (1)	Allow comparisons of other relevant pairs of runs, e.g. runs 3 and 4	2
(b)(iii)	• rate = k[A][B]^2[C]		1
(b)(iv)	• rearrangement of rate expression (1) • evaluation of value for k to 2.s.f (1) • units dm^9 mol^{-3} s^{-1} (1)	Example of calculation k = rate / [A][B]^2[C] = 7.324…. = 7.3 dm^9 mol^{-3} s^{-1} Allow ecf from b (iii) Allow units in any order Correct answer with no working and units to 2.s.f scores 3 marks	3

Q34.

Question Number	Answer	Mark
(i)	**The only correct answer is D** (Fourth) ***A*** *is not correct because this is the individual reaction order with respect to bromate(V) ions and with respect to bromide ions but is not the overall reaction order* ***B*** *is not correct because this is the reaction order with respect to hydrogen ions but is not the overall reaction order* ***C*** *is not correct because this is the number of species in the rate equation but is not the overall reaction order*	**(1)**

Question Number	Answer	Additional Guidance	Mark
(ii)	• rearrange rate equation so $[Br^-]$ = **(1)** • calculation of value to 2/3 SF **(1)**	Example of calculation: $[Br^-] = \frac{\text{rate}}{k\,[BrO_3^-][H^+]^2}$ $= 0.255/0.26$ (mol dm^{-3}) Correct answer without working to 2/3 SF scores 2 marks If units given then must be correct No TE on incorrect rearrangement	**(2)**

Q35.

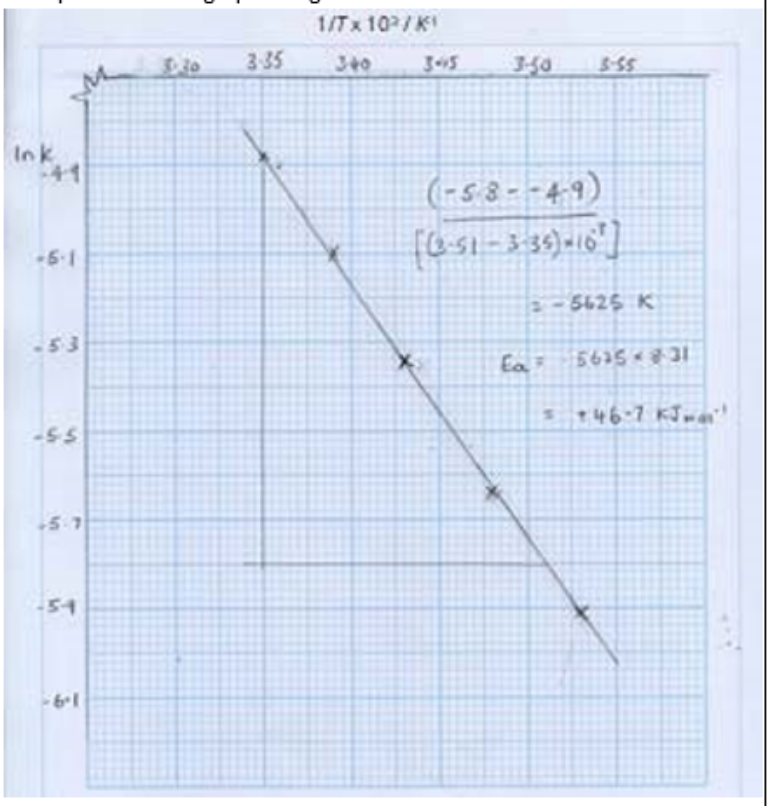
Question Number	Answer	Additional Guidance	Mark
	• curve for Experiment **2** steeper than Experiment **1** and Experiment **4** **and** finishing at the same mass loss as Experiment **1** (1) (1) (1) • curve for Experiment **3** shallower than Experiment **1** **and** finishing at the same mass loss • curve for Experiment **4** steeper than Experiment **1** **and** finishing at mass loss 1.0 g	Examples of curves  Allow curve for Experiment **4** steeper than Experiments **1** and **2** and finishing at mass loss 1.0 g	**(3)**

Q36.

Question Number	Answer	Additional Guidance	Mark
(i)	• calculation of missing $1/T$ value **and** calculation of missing ln k value	Example of calculation 3.43×10^{-3} -5.64 Ignore SF	(1)

Question Number	Answer	Additional Guidance	Mark
(ii)	• **M1** axes correct way round and labelled with units on x-axis (1) • **M2** suitable scale, must be uniform (1) • **M3** all points plotted correctly, with straight line of best fit (1) • **M4** calculation of gradient, including minus sign (1) • **M5** units of gradient (1) • **M6** calculation of activation energy with units (1) **Comment** If ln$k$ plotted with most negative value at the top or -lnk. then all marks can still be scored, but gradient should still be negative	Example of calculation and graph award $1/T \times 10^3$ / K^{-1} **or** $1/T$ / 10^{-3} K^{-1} or $1/T$ / K^{-1} (10^{-3}) Do not award $1/T \times 10^{-3}$ / K^{-1} Do not award **M1** if units given for ln k on y-axis Do not award small "t" for "T" Points must cover at least half the graph paper in each direction -5775 (± 400) Award gradient value between -5375 to -6175 **K** (+)48.0 / (+)48 kJ mol^{-1} ; allow TE for gradient outside range Award E_a values (+)44.7 to (+)51.3 kJ mol^{-1} Award E_a if correct in J mol^{-1} Do not award M6 if given in just "kJ" or "J" Ignore SF Do not award M6 if final answer is a negative E_a value See next page for graph **Comment** If $1/T$ (y-axis) plotted against ln k (x-axis) Can only award **M2, M3** and TE for **M4** If either or both variables incorrect, then only **M2** can be scored	(6)

Example of suitable graph and gradient



Q37.

Question Number	Correct Answer	Mark
(a)	A	**1**

Question Number	Correct Answer	Mark
(b)	C	**1**

Q38.

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**

Q39.

Question Number	Correct Answer	Reject	Mark
(a)	C		**1**
(b)	A		**1**

Q40.

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**

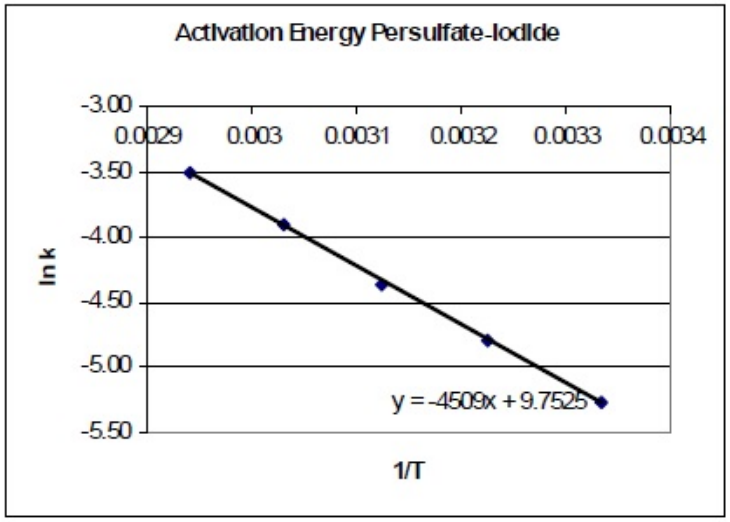
Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	(From 2 to 1) **$[S_2O_8^{2-}]$** doubles ($[I^-]$ unchanged) and rate doubles / time halves so order wrt $S_2O_8^{2-}$ = 1 **(1)** (From 3 to 1) **$[I^-]$** doubles ($[S_2O_8^{2-}]$ unchanged) and rate doubles / time halves so order **wrt I^-** = 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**

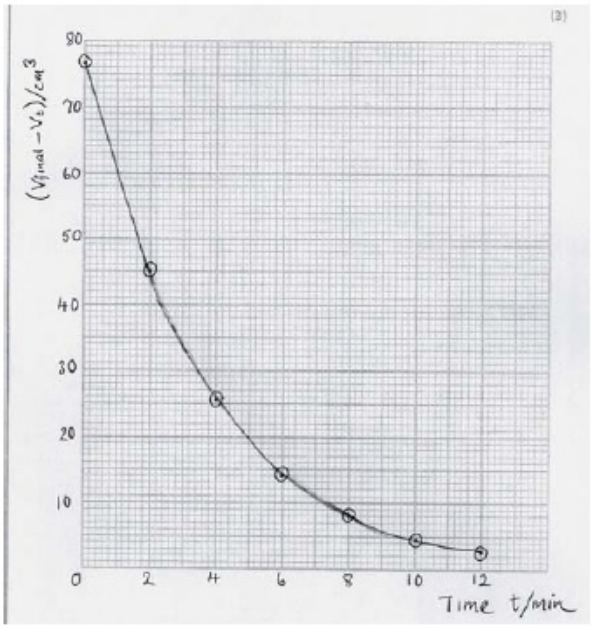
Question Number	Acceptable Answers	Reject	Mark
(c)(ii)	Gradient = −(−3.50 − −5.27) / (0.00333 − 0.00294) = (−)4538 = (−)4500 ALLOW values from (−)4300 to (−)4700 **(1)** gradient value negative **(1)** E_a = −gradient x R = −−4538 x 8.31 = (+)37700 J mol^{-1} (= (+)38 kJ mol^{-1}) **(1)** TE on value 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**

Q41.

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**

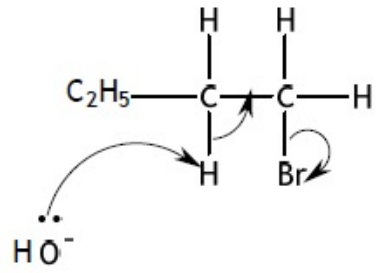
Question Number	Acceptable Answers	Reject	Mark
(b)(iv)	Two values 2.5 ± 0.3 (min) (each scores one mark) **(2)**		**2**

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**

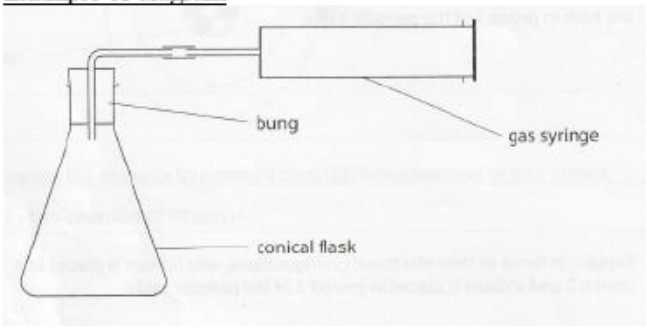
Question Number	Acceptable Answers	Reject	Mark
(c)*(iv)	 Arrows from OH-to H and from C-H bond to make additional bond between carbons **(1)** Third arrow from bond between carbon and bromine to bromine **(1)** (Because) both 1–bromobutane and hydroxide ion appear in the RDS ALLOW Attack of OH- on H 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**

Q42.

Question Number	Answer	Additional Guidance	Mark
(i)	• zero (order0 / 0 (order)	Allow x = 0 / rate is proportional to $[OH^-]^0$ / rate = k[R-Br]$[OH^-]^0$	**(1)**

Question Number	Answer	Additional Guidance	Mark
(ii)	• curly arrow from R-Br bond to, or just beyond, Br **(1)** • R^+ **and** Br^- **(1)** • lone pair on O of OH^- **and** curly arrow from lone pair to R^+ **(1)**	Example of mechanism  Ignore dipole on RBr	**(3)**

Q43.

Question Number	Answer	Additional Guidance	Mark
	An answer that makes reference to the following points: • a diagram showing (calcium carbonate in a conical) flask attached to a gas syringe / a delivery tube passing into a container of water with an upturned measuring cylinder (1) • add the hydrochloric acid and (immediately) stopper the flask (1) • record the volume of gas (1) • collected at regular time intervals (1)	Example of diagram  Ignore missing labels Ignore heat / water bath Do not award inclusion of a condenser Do not award test tube or beaker for collecting gas Allow carbonate added to acid and stopper the flask Allow acid in a tube / beaker in the flask and tip the flask for them to mix Allow specified time intervals Allow collected in a specified time	(4)

Q44.

Question Number	Answer	Additional Guidance	Mark
	An explanation that makes reference to the following points: • a racemic mixture / racemate is formed **or** equal amounts / an equimolar mixture of both optical isomers forms **(1)** • intermediate / carbocation is (trigonal) planar around the reaction site / C^+ / central carbon **(1)** • (equal probability of) attack (by nucleophile / hydroxide ions) from either side / above and below / both sides / opposite sides (of the plane) **(1)**	Allow enantiomers / D-L isomers / (+) and (-) isomers Allow the two isomers rotate the plane of plane-polarised light in opposite directions and cancel out Ignore just 'mixture is not optically active' / 'mixture does not rotate the plane of plane-polarised light' Allow the intermediate / carbocation is planar (around the reaction site) Do not award 'the molecule is planar'	**(3)**

Q45.

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**

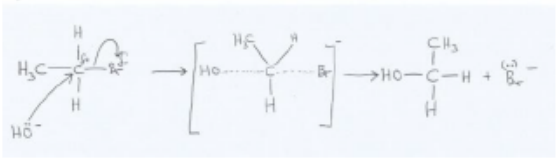
Question Number	Correct Answer	Reject	Mark
(c)(i)	Increases reliability / improves validity (of the data obtained) / confirms the initial results / to check for anomalous results IGNORE References to average / precision / accuracy **OR** To determine order w.r.t. B and X / to see the effect of B and 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		

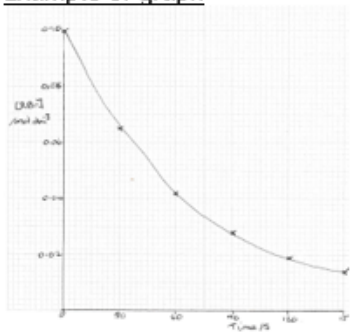
Question Number	Correct Answer	Reject	Mark
(c)(iii)	k = rate / [A][X] = 4.2 x 10^{-3} ÷ (0.08 x 0.25) = 0.21 **(1)** $dm^3\ mol^{-1}\ s^{-1}$ / $mol^{-1}\ dm^3\ s^{-1}$ ALLOW units in any order **(1)** Comment Unit mark is independent of the value **Allow use of data from experiments 1, 2 & 3** Allow 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**

Q46.

Question Number	Answer	Additional Guidance	Mark
(i)	• dipole on C—Br bond **and** curly arrow from C-Br bond to Br or just beyond **(1)** • curly arrow from **lone pair** on oxygen of hydroxide ion to carbon bonded to Br **(1)** • formula of transition state with correct charge, partial bonding **(1)** • correct final products **(1)**	 Dipole and curly arrow may be shown on transition state Allow curly arrow to C^+ of carbocation Do not award if carbocation formed as intermediate Square brackets are not essential Allow charge on Br or OH of transition state Allow longer bonds for partial bonding Ignore geometry of transition state Allow NaBr product if mechanism starts with NaOH Only penalise horizontal bond from the H of OH to C in the product e.g. $OH-CH_2CH_3$ Use of incorrect halogenoalkane loses this mark One mark max deducted for omission of charge on ions, including transition state S_N1 mechanism can score M1, M2 and M4 but not M3. M2 can be awarded for curly arrow from the lone pair on the oxygen of the hydroxide ion to the C+ of the carbocation intermediate	(4)

Question Number	Answer	Additional Guidance	Mark
(ii)	Reagents: nitric acid / HNO_3 **and** silver nitrate (solution) /$AgNO_3$ **(1)**	Use of hydrochloric acid/HCl OR sulfuric acid/H_2SO_4 scores **(0)** Do not award acidified silver nitrate If name and formula given then both must be correct	**(2)**
	(Result) cream/off-white precipitate **(1)**	Allow (very) **pale** yellow Do not award just white or just yellow Ignore subsequent additions of ammonia even if incorrect Result mark dependent on reagents mark or 'near miss' such as omitting to add nitric acid, using ethanolic silver nitrate, incorrect formulae	

Q47.

Question Number	Answer	Additional Guidance	Mark
		Example of graph 	**(3)**
	• both axes labelled, including units **(1)**	Allow T / t for time with units Allow just 'concentration' with units Do not award RBr without square brackets	
	• suitable scales and points taking up at least half the graph paper in both directions **(1)**	Allow ± half square	
	• points plotted correctly **and** smooth curve through the points **(1)**	Do not award point-to-point straight lines	