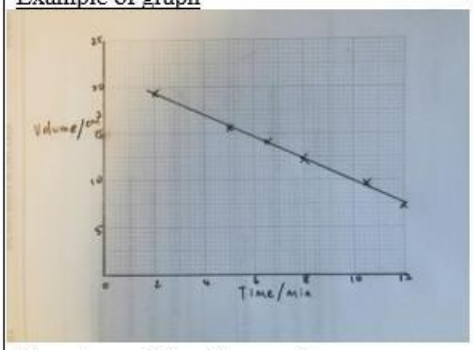
Mark Scheme

Q1.

Question Number	Answer	Additional Guidance	Mark
(i)	y axis labelled with volume and cm^3 **and** x axis • labelled with time and min **and** suitable scale **(1)** all points plotted • correctly and line of best fit **(1)**	Example of graph  Do not award time in seconds Suitable scale so that points cover at least half the available space along the x axis and at least 2 large squares on y axis (as shown) ± ½ a small square Allow M2 as TE if axes wrong way around Ignore extrapolations	**(2)**

Question Number	Answer	Additional Guidance	Mark
(ii)	An explanation that makes reference to the following points: • $[I_2]$ is proportional to the volume (of sodium thiosulfate) **(1)** • gradient does not change / is constant / the graph shows a straight line / is linear (as $[I_2]$ decreases) **(1)** • which means the rate doesn't change / increase or decrease (as $[I_2]$ increases or decreases) **(1)**	Ignore references to half-life Allow description of proportional Allow decreases at a constant rate Ignore volume (of sodium thiosulfate) / $[I_2]$ is proportional to time Allow $[I_2]$ does not affect the rate (of reaction) / rate is independent of $[I_2]$	**(3)**

Q2.

Question Number	Answer	Additional Guidance	Mark
(i)	An answer that makes reference to the following points: • Step **1** is the rate determining step **(1)** • as it involves (1 mol of) both propanone and hydrogen ions (which matches the rate equation) **(1)**	Stand alone Allow RDS / slow step Conditional on M1 Allow it does not involve I_2 (which is zero order) Allow it involves both species in the rate equation Allow I_2 is not involved in the RDS so RDS must be before Step 2	**(2)**

Question Number	Answer	Additional Guidance	Mark
(ii)	An explanation that makes reference to the following points: (The statement is not valid because) • one hydrogen ion is regenerated / reformed (so is acting as a catalyst) **(1)** • the other hydrogen ion is lost from the propanone (when replaced by iodine) / is a (by-)product of the reaction / is used to form HI **(1)**	Ignore reference to specific steps. Do not award M1 if candidate states that it is valid Ignore it is an autocatalyst	**(2)**

Q3.

Question Number	Answer	Additional Guidance	Mark
(a)	• rate equation	Rate = $k[CH_3CHO]^2$ Allow K for *k* Allow r or R for Rate Allow displayed, semi-structural or skeletal formula for ethanal Do not allow rounded brackets Do not allow missing rate Do not allow "rate equation = "	(1)

Question Number	Answer	Additional Guidance	Mark
(b)	• rate constant units	$dm^3\ mol^{-1}\ s^{-1}$ Allow units in any order Do not penalise use of mol^- / s^- No TE on incorrect equation in (a)	(1)

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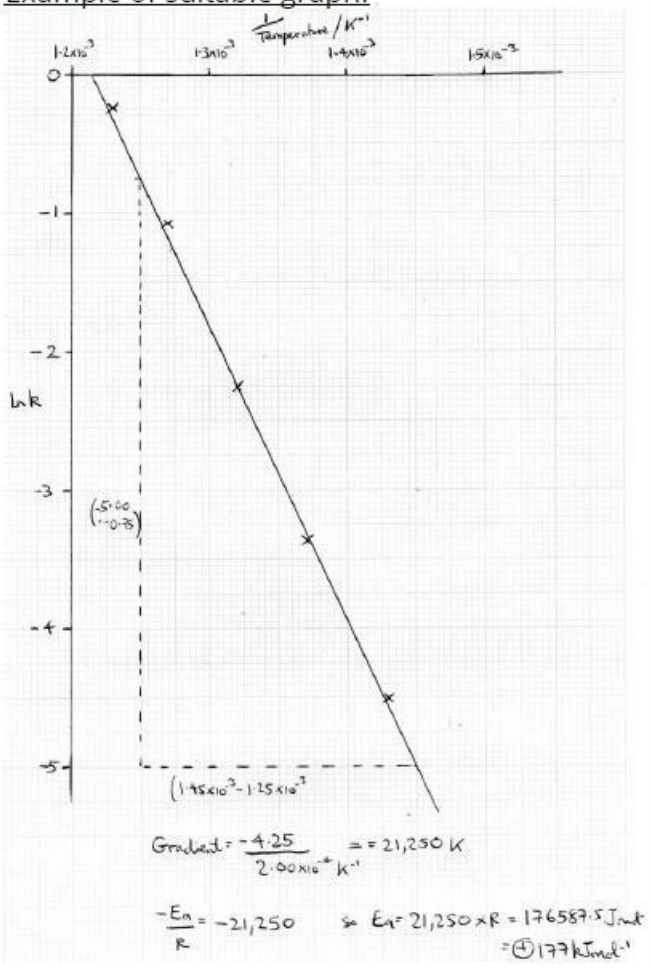
Q4.

Question Number	Answer	Additional Guidance	Mark
(c)	• calculation of average rate between 0 – 420 s to 1/2 SF **(1)** • calculation of average rate between 420 – 1260 s to 1/2 SF **(1)**	Example of calculation Rate = ((0.72- 0.36) ÷ (420 - 0) = 8.5714 x 10^{-4}) = 9 x 10^{-4} / 8.6 x 10^{-4} (mol dm^{-3} s^{-1}) Rate = ((0.36 - 0.18) ÷ (1260 – 420) = 2.1429 x 10^{-4}) = 2 x 10^{-4} / 2.1 x 10^{-4} (mol dm^{-3} s^{-1}) Penalise lack of 1/2 SF once only Ignore units even if incorrect Ignore negative sign in front of rate	**(2)**

Question Number	Answer	Additional Guidance	Mark
(d)	An explanation that makes reference to • not zero order because the rate is not constant **(1)** • not first order because the time taken for the concentration to halve is not equal/ half lives are not constant or not first order because the rate change is not (directly) proportional to the concentration change **(1)**	Allow the rates calculated in (c) are not the same Allow different times are taken for the concentration to halve Allow the concentration is halved but the rate decreases by a quarter If no other mark awarded allow (1) for reference to justification of second order due to concentration decreasing by ½ but rate decreasing by ¼ or due to rate change proportional to concentration squared/ exponential change	**(2)**

Q5.

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

Question Number	Answer	Additional Guidance	Mark
	• calculation of 1/*T* value **(1)**	1.27×10^{-3}	
	• calculation of ln *k* value **(1)**	−1.07 Penalise values not to 3 SF once only in M1 and M2	
	• axes: correct way round and in the correct direction, labelled with units, suitable scale **(1)**	Accept use of 1×10^{3} or 1×10^{-3} on x axis Do not award 1/t for 1/T Plotted points must cover at least ½ the graph paper on each axis	
	• all points plotted correctly, with best-fit straight line **(1)**	Allow ±1 square	
	• calculation of gradient **(1)**	Gradient = (−) 21250 Allow ±900	
	• sign **and** units of gradient **(1)**	− and K	
	• use of gradient to calculate activation energy **(1)**	E_a = − (−21250 x 8.31) / 1000 = (+) 177 (kJ mol^{-1}) Allow ±7 Allow 177000 **J mol^{-1}** ±7000 Ignore SF except 1 SF Do not penalise mol^{-} TE on numerical value of gradient Final answer must be positive	

Q6.

Question Number	Answer	Additional Guidance	Mark
	Correct answer to 2 SF	<u>Example of calculation:</u> (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)**

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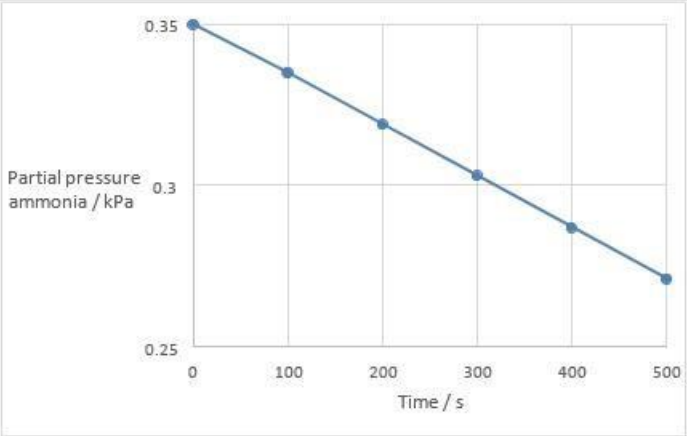
Q7.

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 x 10^{-4} / 0.000158 Allow any value in the range 1.50 to 1.65 x 10^{-4} 1.58 x 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)**

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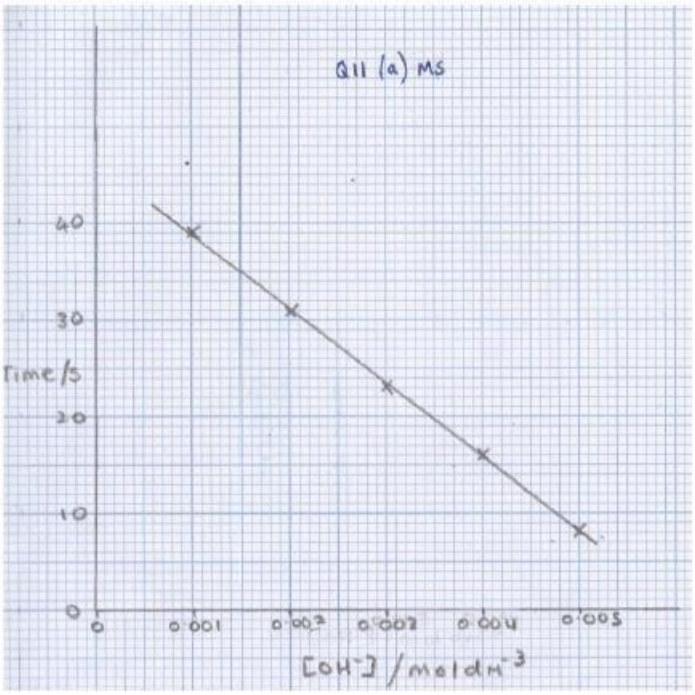
Q8.

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)

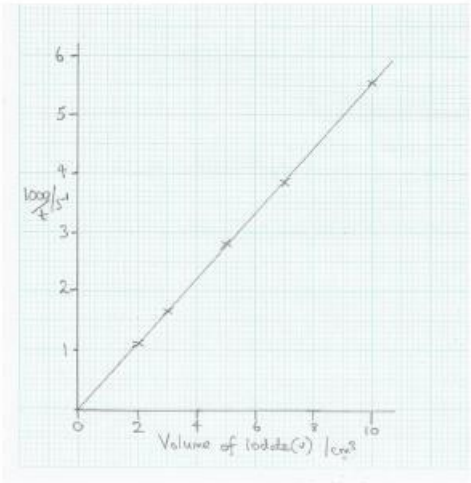
Question Number	Answer	Additional Guidance	Mark
(b)	An answer that makes reference to the following points • zero order with respect to hydroxide ions (1) • The graph is a straight line so the rate of reaction is independent of the concentration of the hydroxide ions (1)	M2 dependent on M1	(2)

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)

Q9.

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)**

Q10.

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)**

Q11.

Question Number	Acceptable Answer	Additional Guidance	Mark
	An explanation that makes reference to the following points:		(3)
	• (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)**	Allow because there is no catalyst / no Mn^{2+} ions present at the start	
	• (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)**	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'	
	• (the rate decreases) because the concentrations /amounts of the reactants decrease / the reactants are used up **(1)**	Allow example of one of the reagents used up / becoming a limiting factor Do not award 'the Mn^{2+} ions are used up'	

Q12.

Question Number	Acceptable Answer	Additional Guidance	Mark
(i)	• value of rate constant to 2 or 3 SF **(1)** • units of rate constant **(1)**	Example of calculation: (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)

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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)

Q13.

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 $k = \frac{\text{rate}}{[NO]^2[Cl_2]}$ 1.09×10^{-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)

Q14.

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

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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] 8.20×10^{-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)

Q15.

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)

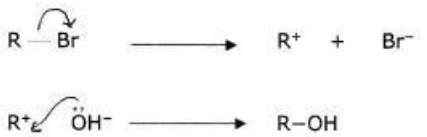
Q16.

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)**

Q17.

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)**

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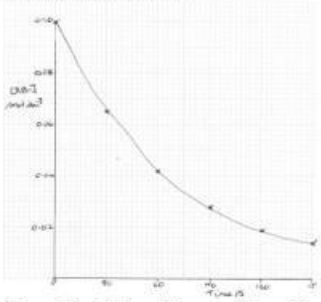
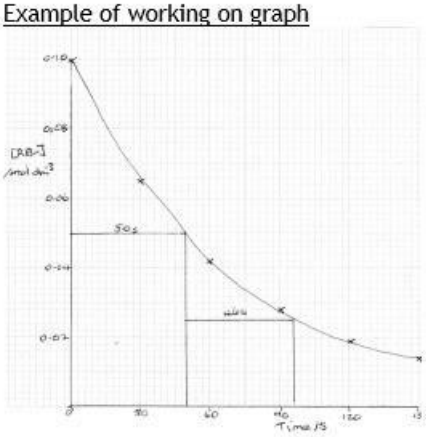
Q18.

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	