SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

17 The reaction between hydrogen peroxide and iodide ions in acid conditions is known as the Harcourt–Esson reaction after the scientists who first studied its kinetics.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

(a) A student carried out experiments to determine the rate equation for this reaction at 293 K.

(i) The rate of this reaction may be obtained by adding a fixed volume of sodium thiosulfate solution and a few drops of starch solution to the reaction mixture.

Explain how this method gives the rate of reaction.

(3)

(ii) The student's results are shown.

Run	$[H_2O_2(aq)]$ / mol dm^{-3}	$[I^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.0210	0.0198	0.00105	0.00181
2	0.0105	0.0400	0.00105	0.00181
3	0.0105	0.0797	0.00099	0.00364
4	0.0210	0.0801	0.00201	0.00730

Deduce the rate equation for this reaction.

(3)

(iii) Calculate the rate constant for this reaction at 293 K, using the results from Run 1. Include units with your answer.

(3)

(b) The student carried out a second series of experiments with this reaction at 313 K. The rate of reaction was found to be 4.45 times faster at 313 K than at 293 K.

Calculate the activation energy, E_a, for this reaction, using the Arrhenius equation. Give your answer to an appropriate number of significant figures and include units.

$$\ln k = -\frac{E_a}{RT} + \text{constant}$$

(4)

(Total for Question 17 = 13 marks)

20 Cracking reactions are used to obtain more useful compounds from the alkanes found in crude oil. An equation for the cracking of butane is shown.

$$C_4H_{10}(g) \rightarrow C_2H_6(g) + C_2H_4(g)$$

Thermodynamic data for the compounds in this reaction are given in the table.

	$C_4H_{10}(g)$	$C_2H_6(g)$	$C_2H_4(g)$
Standard molar entropy $S^{\ominus}$ / J K^{-1} mol^{-1}	310.1	229.5	219.5
Standard molar enthalpy change of formation $\Delta_f H^{\ominus}$ / kJ mol^{-1}	–126.5	–84.7	+52.2

(a) (i) Calculate the entropy change in the system, $\Delta S^{\ominus}_{system}$, for the cracking of butane.
Include a sign and units with your answer.

(2)

(ii) Calculate the enthalpy change of reaction, $\Delta_r H^{\ominus}$, for the cracking of butane.
Include a sign and units with your answer.

(2)

(iii) Calculate the entropy change in the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, at 298 K for the cracking of butane, using your answer to (a)(ii).
Include a sign and units with your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{\text{total}}$, at 298 K for the cracking of butane, using your answers to (a)(i) and (a)(iii).
Include a sign and units with your answer.

(1)

(v) Calculate the temperature at which the cracking reaction becomes feasible.

(2)

(b) 5 mol of butane is cracked at 750 K. At equilibrium, 4.45 mol of ethene is formed and the total pressure is 1.20 atm.

$$C_4H_{10}(g) \rightleftharpoons C_2H_6(g) + C_2H_4(g)$$

(i) Give the expression for the equilibrium constant, K_p, for this reaction.

(1)

(ii) Calculate the value of K_p, including units if required.

(5)

(Total for Question 20 = 15 marks)

TOTAL FOR SECTION B = 51 MARKS

Section B

Question number	Answer	Additional guidance	Mark
17(a)(i)	An answer that makes reference to the following • sodium thiosulfate reacts with the iodine formed (1) • when (all) the sodium thiosulfate is used up has reacted the iodine reacts with the starch giving a blue-black colour (1) • the reciprocal of the time taken for the blue-black colour to appear is a measure of the rate (1)	Accept equation $S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ Allow a blue-black colour forms at the end of the reaction Allow iodine reacts with the starch giving a blue-black colour Allow blue or black for blue-black Ignore reference to the colour of the solution before the starch-iodine complex forms Do not award iodide reacts with starch Allow 1/t = rate of reaction / 1/t $\propto$ rate of reaction Allow [reactant]/t $\propto$ rate of reaction Do not award thiosulfate as a reactant Allow (for M3) repeat experiment varying concentration of a reactant; plot concentration against time (for blue-black colour to appear) and measure **initial** gradient Ignore references to colorimeter	**(3)**

Question number	Answer	Additional guidance	Mark
17(a)(ii)	An answer that makes reference to the following • correct form of the rate equation (1)	Rate = $k[H_2O_2(aq)]^a[I^-(aq)]^b[H^+(aq)]^c$ or Rate = $k[H_2O_2(aq)]^a[I^-(aq)]^b$ Allow any values of a, b and c for M1 provided at least one value >0. Zero order species do not need to be shown Allow K for *k*	**(3)**
	• values of three powers (including $[H^+]$ not shown) (2)	Rate = $k[H_2O_2(aq)][I^-(aq)][H^+(aq)]^0$ Accept Rate = $k[H_2O_2(aq)][I^-(aq)]$ For M2 deduct a mark for each incorrect power (reactant not shown order = 0) **Overall** mark for some of these responses including M1: Rate = $k[H_2O_2(aq)][I^-(aq)][H^+(aq)]$ scores (2) Rate = $k[H_2O_2(aq)]$ scores (2) Rate = $k[I^-(aq)]$ scores (2) Rate = $k[H_2O_2(aq)]^2[I^-(aq)]$ scores (2) Rate = $k[H_2O_2(aq)][H^+(aq)]$ scores (1) Rate = $k[I^-(aq)][H^+(aq)]$ scores (1) Ignore state symbols even if incorrect Correct answer with no intermediate stages scores (3) Use of round brackets deduct 1 mark	

Question number	Answer	Additional guidance	Mark
17(a)(iii)	- rearrangement of rate equation (1) - calculation of value from Run 1 data (1) - units of *k* (1)	Example of calculation TE on (a)(ii) for equations in correct form. Units must match the equation used k = rate /([H_2O_2(aq)][I^-(aq)]) ignore state symbols $k = \frac{0.00181}{0.0210 \times 0.0198} = 4.3531$ Allow use of data from any run $dm^3\ mol^{-1}\ s^{-1}$ Allow units in any order Allow mol^- for mol^{-1} here and throughout paper Ignore SF except 1 SF $k[I^-(aq)][H^+]$ gives 87.06 $dm^3\ mol^{-1}\ s^{-1}$ scores (3) if TE on (a)(ii) Correct answer with units but no working scores (3)	**(3)**

Question number	Answer	Additional guidance	Mark
17(b)	- substitution of values for both temperatures into the Arrhenius equation (1) - subtraction and rearrangement of the two equations (1) - solving equation to give value for E_a (1) - answer to 2/3 SF **and** correct units (1)	Example of calculation $\ln k_{293} = \text{constant} - \frac{E_a}{293\,xR}$ and $\ln k_{313} = \text{constant} - \frac{E_a}{313\,xR}$ $\ln\left(\frac{k_{313}}{k_{293}}\right) = \ln 4.45 = \frac{E_a}{R}\left(\frac{1}{293} - \frac{1}{313}\right)$ $E_a = (+)56887$ (+)57000 / (+)56900 J mol^{-1} Or (+)57 / (+)56.9 kJ mol^{-1} Correct answer with some working scores (4) Some attempt at a calculation using the Arrhenius equation, giving a positive value to 2 or 3 SF and correct units scores M4	**(4)**

(Total for Question 17 = 13 marks)

Question number	Answer	Additional guidance	Mark
20(a)(i)	- substitution of values into $\Delta S^{o}_{system} = S_{products} - S_{reactants}$ (1) - calculation of value from correct equation **and** sign and units (1)	In parts (i), (ii), (iii) and (iv) penalise omission of or incorrect units once only Allow units in any order Allow (e.g.) J/K/mol Do not award J/K mol Positive signs are not required Ignore SF except 1 SF throughout (a). Example of calculation $\Delta S^{o}_{system} = 229.5 + 219.5 - 310.1$ $= (+)138.9 \text{ J K}^{-1} \text{ mol}^{-1}$ TE for transcription errors on values only Correct answer with no working scores (2)	**(2)**

Question number	Answer	Additional guidance	Mark
20(a)(ii)	- substitution of values into $\Delta_r H^{o} = \Delta_f H^{\ominus}(\text{products}) - \Delta_f H^{\ominus}(\text{reactants})$ (1) - calculation of value from correct equation **and** sign and units (1)	Example of calculation $\Delta_r H^{o} = (-84.7 + 52.2) - (-126.5)$ $= (+)94.0 \text{ kJ mol}^{-1}$ Correct answer with no working scores (2) TE for transcription errors on values $-94.0 \text{ kJ mol}^{-1}$ scores (1) $-159.0 \text{ kJ mol}^{-1}$ scores (1) $(+)263.4 \text{ kJ mol}^{-1}$ scores (1) $-10.4 \text{ kJ mol}^{-1}$ scores (1)	**(2)**

Question number	Answer	Additional guidance	Mark
20(a)(iii)	- equation for $\Delta S^\circ_{\text{surroundings}}$ **and** substitution of values (1) - calculation of value from correct equation **and** sign and units (1)	Example of calculation $\Delta S^\circ_{\text{surroundings}} = -\Delta H / T$ $= -94000 \div 298$ Accept $= -94 \div 298$ $= -315.44\ \text{J K}^{-1}\ \text{mol}^{-1}$ / $-0.31544\ \text{kJ K}^{-1}\ \text{mol}^{-1}$ TE on $\Delta_r H^\circ$ from (a)(ii) Do not award use of incorrect equation Correct answer with no working scores (2)	**(2)**

Question number	Answer	Additional guidance	Mark
20(a)(iv)	- equation for $\Delta S^\circ_{\text{total}}$ **and** substitution of values **and** calculated value with sign and units	Example of calculation $\Delta S^\circ_{\text{total}} = \Delta S^\circ_{\text{system}} + \Delta S^\circ_{\text{surroundings}}$ $= +138.9 + -315.44$ $= -176.54\ \text{J K}^{-1}\ \text{mol}^{-1}$ Accept $= +0.1389 + -0.31544$ $= -0.17654\ \text{kJ K}^{-1}\ \text{mol}^{-1}$ TE on valuesfrom (a)(i) and (a)(iii) Do not award use of incorrect equation Do not award value obtained using mixed units Correct answer with no working scores (1)	**(1)**

Question number	**Answer**	**Additional guidance**	**Mark**
20(a)(v)	- equation for feasibility (1) substitution of values **and** evaluation of T (1)	Example of calculation $(\Delta S^{o}_{\text{system}} + (-\Delta H/T) = \Delta S^{o}_{\text{total}} = 0)$ $\Delta S^{o}_{\text{system}} = \Delta H/T$ or $-\Delta S^{o}_{\text{system}} = -\Delta H/T$ $T = 94000 \div 138.9$ $= 676.746$ (K) (from unrounded values) Accept 403.746(°C) TE on valuesfrom (a)(i) and (a)(ii) Do not award use of incorrect equation (e.g. omission of negative sign in $\Delta S^{o}_{\text{surroundings}}$ expression) Do not award value obtained using mixed units Correct answer with no working scores (2)	**(2)**

Question number	**Answer**	**Additional guidance**	**Mark**
20(b)(i)	- equilibrium constant expression	Example of expression $K_p = \dfrac{p(C_2H_6) \text{ x } p(C_2H_4)}{p(C_4H_{10})}$ Accept p_x where x = formula or pp(X) Ignore state symbols even if incorrect Do not award square brackets	**(1)**

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr>
<td>20(b)(ii)</td>
<td>

moles of reactants and products (1)
mole fractions (1)
partial pressures (1)
substitution of values into K_p equation and evaluation (1)
units (1)

</td>
<td>
Example of calculation
<table>
<tr><th></th><th>C_4H_{10}</th><th>C_2H_6</th><th>C_2H_4</th></tr>
<tr><td>mol at equil^m</td><td>5 – 4.45
= 0.55</td><td>4.45</td><td>4.45</td></tr>
<tr><td>mole fraction</td><td>$\frac{0.55}{9.45}$
= 0.05820</td><td>$\frac{4.45}{9.45}$
= 0.47090</td><td>$\frac{4.45}{9.45}$
= 0.47090</td></tr>
<tr><td>partial pressures</td><td>1.20 x 0.05820
= 0.06984</td><td>1.20 x 0.47090
= 0.56508</td><td>1.20 x 0.47090
= 0.56508</td></tr>
</table>
$K_p = \frac{0.56508^2}{0.069841} = 4.5721$ (4.5720 with unrounded numbers)
= (4.5721) atm
Ignore SF except 1 SF
TE on expression in (b)(i) that contains at least two species
TE at each stage
Correct answer with units but no working scores (5)

Omission of partial pressure gives K_p = 3.8100 atm scores (4)
Omission of mole fraction gives K_p = 43.21 atm scores (4)
</td>
<td>(5)</td>
</tr>
</table>

(Total for Question 20 = 15 marks)

TOTAL FOR SECTION B = 51 MARKS

(c) Some energy data are shown.

Compound	Theoretical lattice energy / kJ mol^{-1}	Experimental lattice energy / kJ mol^{-1}
$CaCl_2$	–2223	–2258
CaI_2	–1905	–2074

Explain why the difference between the theoretical and the experimental values for lattice energy is very much greater for calcium iodide than for calcium chloride.

(4)

20 Nitrous oxide, N_2O, decomposes at high temperature to form nitrogen and oxygen.

$$N_2O(g) \rightleftharpoons N_2(g) + ½O_2(g)$$

(a) (i) Some standard molecular entropy data are shown.

Substance	Standard molecular entropy $S^\ominus$ / $J\,K^{-1}\,mol^{-1}$
nitrogen, N_2	192
oxygen, O_2	205
nitrous oxide, N_2O	220

Calculate the standard entropy change of the system for the decomposition shown.
Include a sign and units in your answer.

(2)

(ii) The standard enthalpy change of the forward reaction is −82 kJ mol^{-1}.

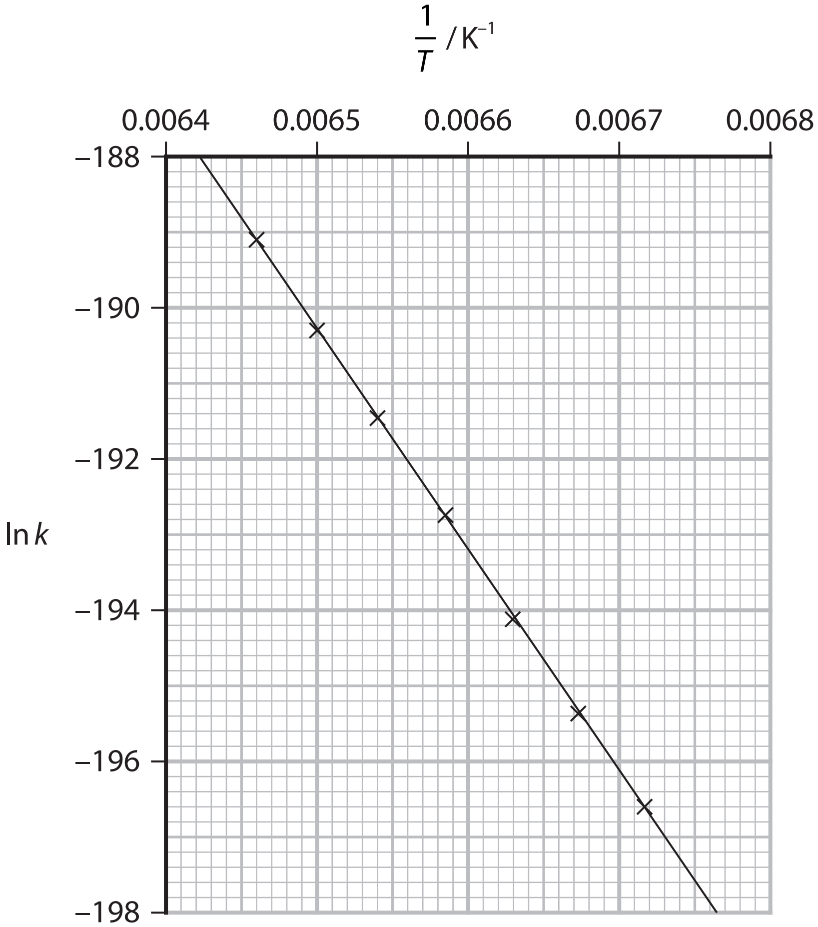
Calculate the entropy change of the surroundings at 2048 K.
Include a sign and units in your answer.

(2)

(iii) Calculate the total entropy change of the reaction at 2048 K.
Include a sign and units in your answer.

(1)

(b) Rate experiments on the decomposition of nitrous oxide produced the following graph.



Calculate the activation energy for the reaction in kJ mol^{-1}.
Include the value of the gradient.

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \text{constant}$$

$R = 8.31$ J K^{-1} mol^{-1}

(2)

(c) Explain whether or not this reaction occurs at 2048 K by considering the values calculated in (a) and (b).

(2)

....

....

....

....

(Total for Question 20 = 9 marks)

Question Number	Answer	Additional Guidance	Mark
17(c)	An explanation that makes reference to the following points: • calcium chloride is almost completely ionic **(1)** • calcium iodide has partially covalent character **(1)** • iodide (ion) is larger (than chloride (ion)) **(1)** • (so) more (easily) polarised **(1)**	Allow reverse arguments Accept $CaCl_2$ is 100% ionic Allow LE is calculated assuming a pure ionic structure Allow shows more covalent character Allow $CaCl_2$ has less covalent character than CaI_2 Ignore polar Do not award M2 for CaI_2 is covalent Do not award M2 for Intermolecular forces Accept iodide has a lower charge density Allow iodine ion Ignore iodine is larger Do not award molecules, Cl_2 or I_2 loses M3 Accept more (easily) distorted Allow (more) polarisable Do not award CaI_2 is more polarised If no comparison for M3 and M4 allow 1 mark, e.g., "iodide is large and is polarised" Penalise iodine/chlorine or incorrect ions once only.	**(4)**

Question Number	Answer	Additional Guidance	Mark
20(a)(i)	• expression or suitable working **(1)** • correct answer **(1)**	Example of a calculation: $(192 + 0.5 \times 205) - (220)$ (+)74.5 (J K^{-1} mol^{-1}) Correct answer scores 2 –74.5 scores 0 TE on small errors in M1 e.g., miss out 0.5, as long as the answer is positive Penalise incorrect units once only for ai-aiii Allow J K^{-} mol^{-} Allow J/K mol but not J/K/mol	**(2)**

Question Number	Answer	Additional Guidance	Mark
20(a)(ii)	• balanced equation or suitable working **(1)** • correct answer **(1)**	Example of a calculation: ΔS surroundings = $-\Delta H/T$ $= - (-82000) \div (2048)$ $= 82000 \div 2048$ (+) 40.039 (J K^{-1} mol^{-1}) Correct answer scores 2 Ignore SF – 40 scores 1 mark 0.04 scores 1 mark with correct units or without units, 2 marks with kJ K^{-1} mol^{-1}	**(2)**

Question Number	Answer	Additional Guidance	Mark
20(a)(iii)	- total entropy change	Example of a calculation: $74.5 + 40.0 = (+)114.5$ (J K^{-1} mol^{-1}) TE on ai and aii, but both must be in the correct units Ignore SF except 1SF	**(1)**

Question Number	Answer	Additional Guidance	Mark
20(b)	- gradient **(1)** - activation energy **(1)**	Example of a calculation: $\frac{(-197)-(-190)}{(0.00673)-(0.00649)} = \frac{-7}{0.00024}$ gradient = –29 167 (K) (allow any negative value between 28 300-30 000) (– 8.31 × – 29 167) ÷1000 = (+)242.4 (kJ mol^{-1}) (allow values between 235.1 to 249.3 for 2 marks) Ignore SF except 1 SF Allow TE from M1 Answers in J mol^{-1} score both marks if in the allowed range (235100-249300)	**(2)**

Question Number	Answer		Additional Guidance	Mark
20(c)	An explanation that makes reference to the following points: • (thermodynamically) feasible because ΔS_{total} is positive • activation energy high so the reaction is very slow (at low temperatures)	 **(1)** **(1)**	 Ignore thermodynamically stable/unstable Allow high temperature will provide E_a so reaction will proceed Allow reaction may not happen as E_a is (very) high Allow high E_a so kinetically stable Allow high E_a so kinetically non-feasible TE on 20(a)(iii) but not on 20(b)	**(2)**

(Total for Question 20 = 9 marks)

3 This question is about an experiment to investigate the kinetics of the reaction between iodine and propanone with an acid catalyst.

The equation for the reaction is shown.

$$I_2(aq) + CH_3COCH_3(aq) + H^+(aq) \rightarrow CH_3COCH_2I(aq) + 2H^+(aq) + I^-(aq)$$

To obtain the order of reaction with respect to iodine, the concentration of iodine in the reaction mixture was determined at various times.

Procedure

Step **1** Mix 25 cm^3 of 1.0 mol dm^{-3} sulfuric acid with 25 cm^3 of 1.0 mol dm^{-3} propanone in a beaker.

Step **2** Start a clock as 50 cm^3 of 0.020 mol dm^{-3} iodine solution is added to the beaker. Mix the reactants thoroughly.

Step **3** Tip a spatula measure of sodium hydrogencarbonate into a conical flask. After 3 minutes, pipette a 10.0 cm^3 sample of the reaction mixture into the conical flask and mix thoroughly.

Step **4** Titrate the iodine in the sample with 0.010 mol dm^{-3} sodium thiosulfate solution using a suitable indicator. Record the titre.

Step **5** Repeat Steps **3** and **4** every 3 minutes to obtain four more titres.

(a) State why the sulfuric acid and propanone concentrations are both much larger than the iodine concentration.

(1)

....

....

(b) State why sodium hydrogencarbonate is used in Step **3**.

(1)

....

....

(c) Name the indicator that would be used for the titration in Step **4**, stating the colour **change** that would be seen at the end-point of the reaction.

(2)

....

....

(d) Titration results from the experiment are shown.

Time / minutes	3	6	9	12	15
Titre / cm^3	16.05	15.30	14.50	13.70	12.95

(i) Plot a graph of titre against time.

(3)

(ii) State why the volume of thiosulfate may be used for plotting the graph rather than the concentration of iodine.

(1)

....

....

....

(iii) State the order of reaction with respect to iodine.
Justify your answer by referring to your graph.

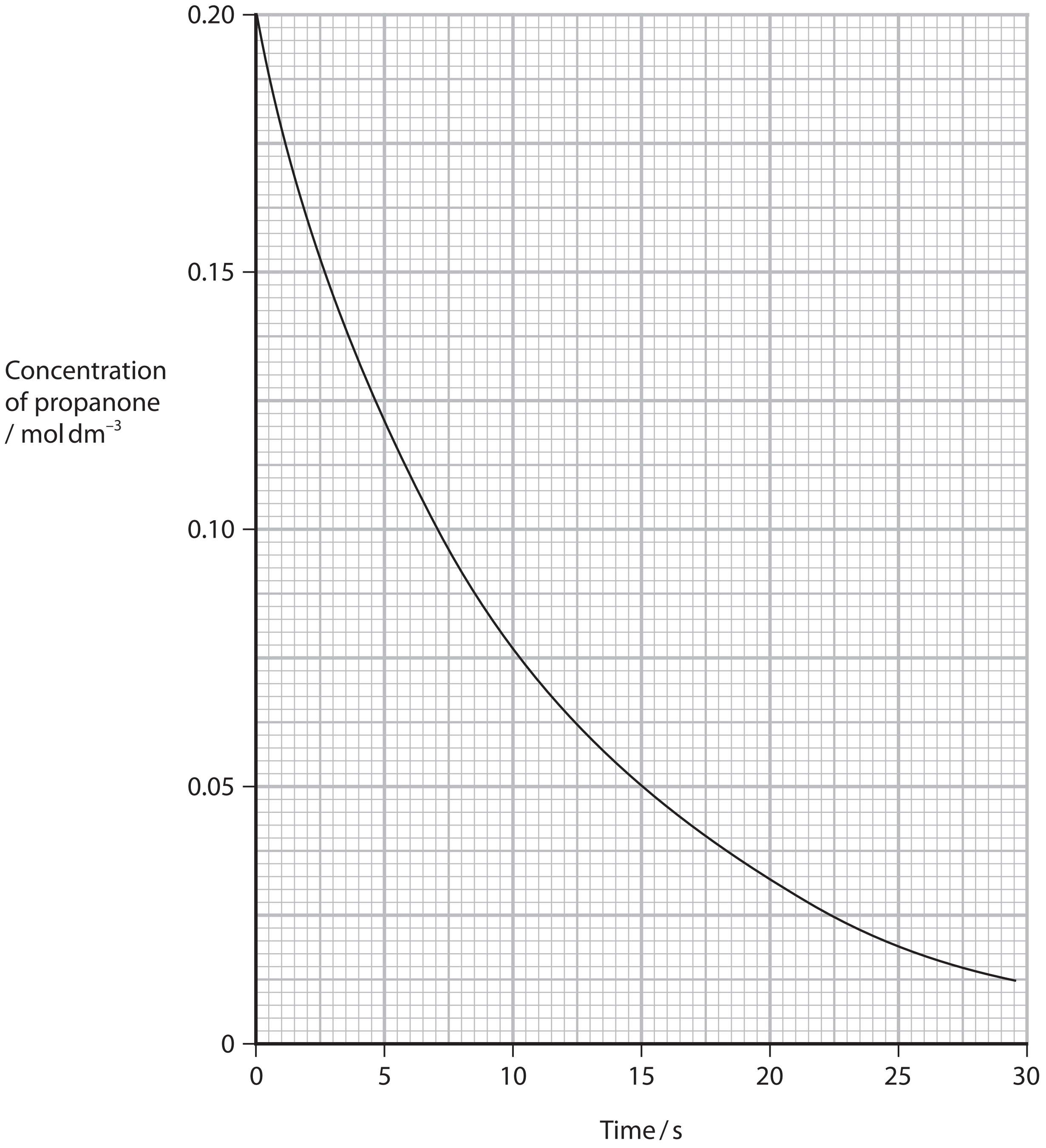
(1)

....

....

(e) Further experiments were carried out to determine the reaction orders with respect to propanone and sulfuric acid.

(i) A graph of the concentration of propanone against time is shown.



The reaction is first order with respect to propanone.

Determine two half-lives for this reaction.
You **must** show your working on the graph.

(2)

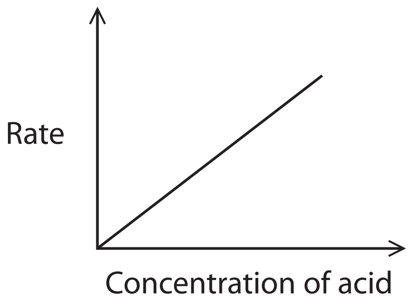
First half-life

....

Second half-life

....

(ii) A graph of the reaction rate against the concentration of sulfuric acid is shown.



Deduce the rate equation for the overall reaction of iodine and propanone with an acid catalyst.
Use your answer from (d)(iii) and information from (e)(i) and the graph in (e)(ii).

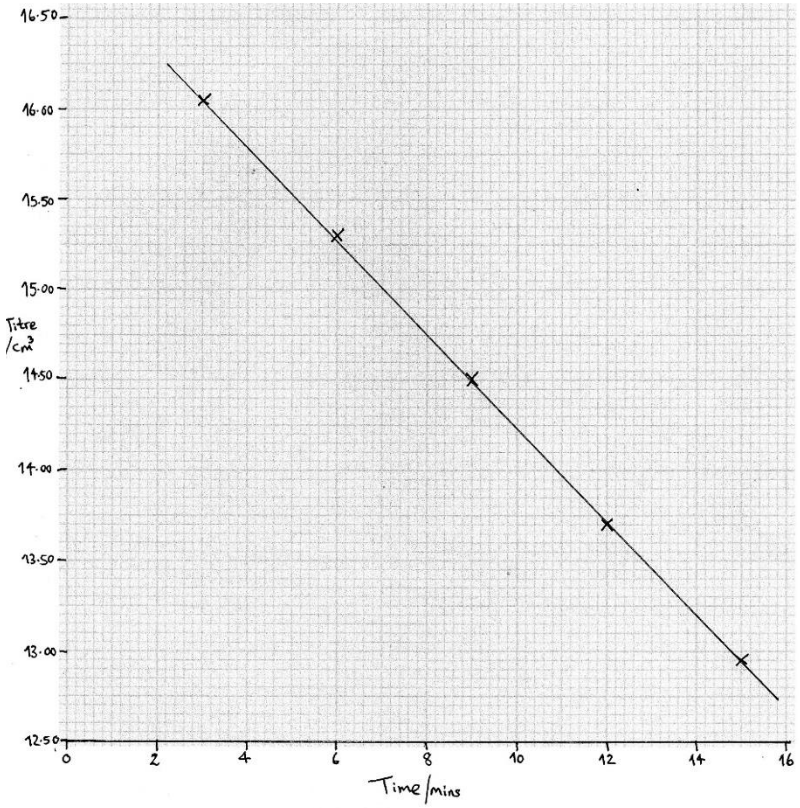
(1)

(Total for Question 3 = 12 marks)

Question Number	Answer	Additional Guidance	Mark
3(a)	An answer that makes reference to the following point: • only the iodine concentration affects the rate OR so the concentrations of sulfuric acid and propanone do not affect the rate	Allow so only the iodine concentration changes (significantly) Allow $[H^+]$ and $[CH_3COCH_3]$ do not change (significantly) / (effectively) zero order (wrt $[H^+]$ and $[CH_3COCH_3]$) Ignore just concentrations of H_2SO_4 and CH_3COCH_3 are in excess Ignore comments on limiting reagents	**(1)**

Question Number	Answer	Additional Guidance	Mark
3(b)	An answer that makes reference to the following point: • to stop / quench the reaction	Allow neutralise/remove the (sulfuric) acid/H^+ (catalyst) Ignore slow the reaction Do not award to remove OH^-	**(1)**

Question Number	Answer	Additional Guidance	Mark
3(c)	An answer that makes reference to the following points: • (indicator) starch (solution) **(1)** • (colour change) blue-black/(dark)blue/black to colourless **(1)**	**M2 is dependent on M1** Ignore colour before addition of starch	**(2)**

Question Number	Answer		Additional Guidance	Mark
3(d)(i)			Example of graph:  	**(3)**
	- axes labelled correctly with units and suitable scale	**(1)**	Points plotted must cover at least 50% of the graph in both directions	
	- all points plotted correctly	**(1)**	Allow ±1 small square	
	- best fit **straight** line	**(1)**	Ignore extrapolation	

Question Number	Answer	Additional Guidance	Mark
3(d)(ii)	An answer that makes reference to the following point: • the volume of (sodium) thiosulfate / titre is (directly) proportional to the concentration of iodine	Allow they are (directly) proportional Ignore any comments on correlation	**(1)**

Question Number	Answer	Additional Guidance	Mark
3(d)(iii)	An answer that makes reference to the following point: • zero (order) / 0 **and** straight line (with a negative gradient) graph	Accept rate is proportional to 1/time Accept changes to iodine concentration have no affect on rate Accept zero order **and** gradient is constant Ignore reference to sign of gradient NOTE: the order wrt iodine must be used in (e)(ii) COMMENT: allow linear for straight line	**(1)**

Question Number	Answer	Additional Guidance	Mark
3(e)(i)	An answer that makes reference to the following points: • working shown on graph for two half lives **(1)** • two half-lives of 7 and 8 (seconds) **(1)**	Allow a range of 6 – 9 (seconds) Ignore references to constant half life Do not award minutes / min	**(2)**

Question Number	Answer	Additional Guidance	Mark
3(e)(ii)	An answer that makes reference to the following point: • rate = k$[CH_3COCH_3][H^+]$	Allow r for rate Allow H_2SO_4 / acid for H^+ Allow names for formulae Accept inclusion of ‘1’ for powers Allow TE from diii Ignore inclusion of $[I_2]^0$ NOTE: The order wrt to iodine must be consistent with the answer in 3(d)(iii) Ignore state symbols even if incorrect	**(1)**

(Total for Question 3 = 12 marks)