



IGC HK EXAM - WJEC

WJEC & Eduqas - Chemistry

Mock 1 Practice Paper

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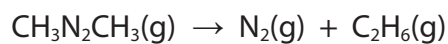
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16 Azomethane, $\text{CH}_3\text{N}_2\text{CH}_3$, decomposes to form nitrogen and ethane.

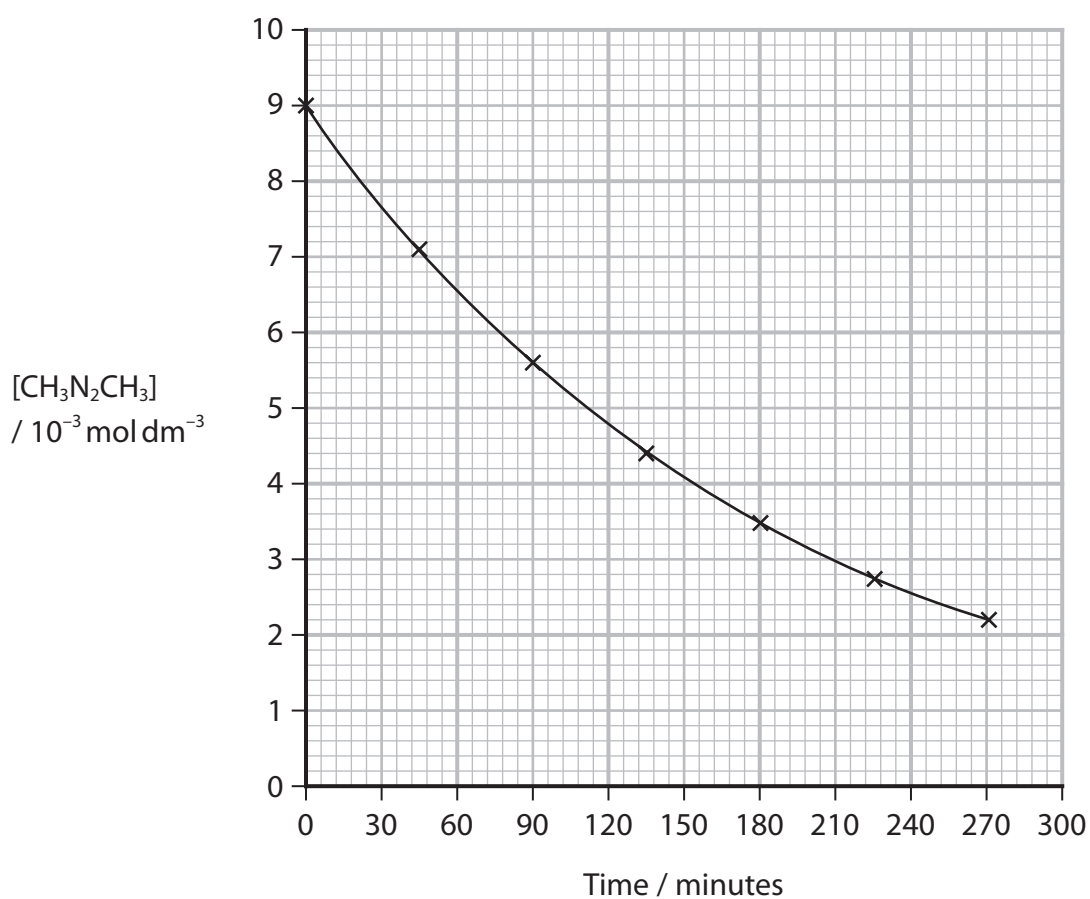


(a) Write the rate equation for this first order reaction.

(1)

(b) The concentration of azomethane, $[\text{CH}_3\text{N}_2\text{CH}_3]$, was measured at various times during its decomposition at 573 K.

A graph of the data obtained is shown.



- (i) Determine values for the half-life, $t_{1/2}$, of the decomposition of azomethane from the graph, stating whether or not these data confirm that the reaction is first order.

You must show your working on the graph.

(2)

- (ii) Calculate the rate constant, k , in s^{-1} , for the decomposition of azomethane at 573 K, using your answer to (b)(i) and the expression shown.

$$t_{1/2} = \frac{\ln 2}{k}$$

(2)

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(c) The rate constant for the decomposition of azomethane is $1.1 \times 10^{-6} \text{ s}^{-1}$ at 523 K and $3.5 \times 10^{-3} \text{ s}^{-1}$ at 623 K.

(i) Explain why the rate constant for this reaction is higher at 623 K than at 523 K.

(2)

(ii) The rate constant changes with temperature according to the expression shown.

$$\log_{10} \left(\frac{k_1}{k_2} \right) = -\frac{E_a}{2.3R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Calculate the activation energy, E_a , for the decomposition of azomethane using this expression and the values for k at 523 K and 623 K.

Include units and give your answer to **two** significant figures.

$[R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}]$

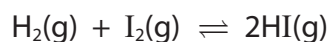
(3)



SECTION C

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

18 This question is about the homogeneous system



(a) Write the expression for the equilibrium constant, K_c , of this system.

(1)

(b) Chemist **A** carried out an experiment to determine K_c .

0.00500 mol of H_2 and 0.0100 mol of I_2 were heated in a sealed container of volume 1.00 dm^3 .

At equilibrium, the mixture was found to contain 0.00968 mol of HI.

Calculate K_c , using these data and your expression from (a).

Include units, if any.

Give your answer to an appropriate number of significant figures.

(4)



(c) Chemist **B** determined the value of K_c at five different temperatures.

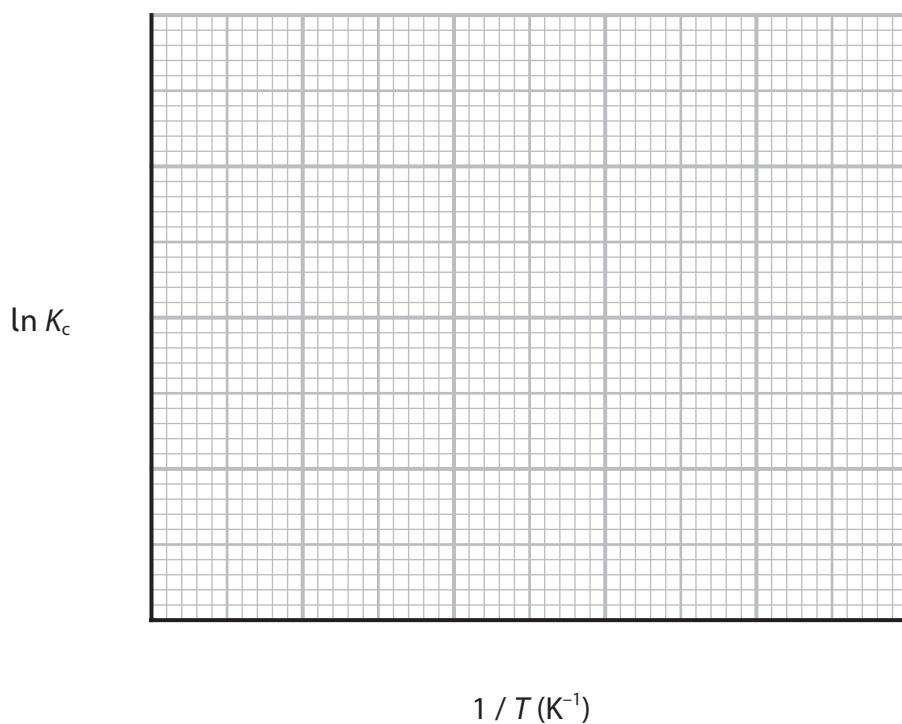
Temperature, T/K	$1/T (K^{-1})$	K_c	$\ln K_c$
523		122	4.80
577	0.00173	99.2	
620	0.00161	86.5	4.46
669	0.00149	75.6	4.33
721	0.00139	66.8	4.20

(i) Complete the table of data.

(2)

(ii) Plot a graph of $\ln K_c$ against $1/T$.
Include a line of best fit.

(3)



(iii) Determine the gradient of your graph.
You **must** show your working on the graph.

(1)

- (iv) The gradient of the graph from (c)(iii) is related to the enthalpy change of the reaction, ΔH .

$$\text{gradient} = -\frac{\Delta H}{R}$$

Calculate ΔH , in J mol^{-1} , using your value for the gradient.

(2)

- (v) The free energy change for the reaction, ΔG , is related to entropy and can be calculated from K_c .

$$\Delta G = -RT \ln K_c$$

Calculate ΔG at **620 K**, using this equation and data from the table.
Include units.

(2)

- (vi) The equation relating ΔG , ΔH and ΔS_{system} is shown.

$$\Delta G = \Delta H - T\Delta S_{\text{system}}$$

Calculate ΔS_{system} at 620 K, using your answers to (c)(iv) and (c)(v).

(2)

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- (d) Explain, in terms of the total entropy change, ΔS_{total} , why this reaction is feasible at any temperature.

Assume that both ΔH and ΔS_{system} are independent of temperature.

(3)

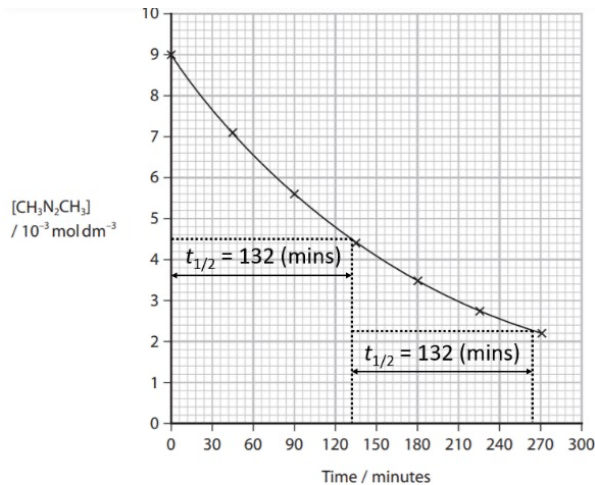
(Total for Question 18 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS

TOTAL FOR PAPER = 90 MARKS



Question Number	Answer	Additional Guidance	Mark
16(a)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> (rate =) $k[\text{CH}_3\text{N}_2\text{CH}_3]$ 	<p>Accept rate = $k[\text{azomethane}]$ Ignore state symbols even if incorrect Do not award non-square brackets</p>	1

Question Number	Answer	Additional Guidance	Mark
16(b)(i)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> determination of one half-life (with some working shown on graph) second half-life (with some working shown on graph) and constant (half-life shows reaction is first order) 	<p>Example of working on graph:</p>  <p>(1) Allow half-life value between 126 and 138 Ignore units even if incorrect</p> <p>(1) Allow half-life value between 126 and 138 Ignore units even if incorrect</p> <p>(1) Allow similar for constant</p>	2

Question Number	Answer	Additional Guidance	Mark
16(b)(ii)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> $t_{1/2}$ expression rearranged for k calculation of k in s^{-1} 	<p>Example of calculation:</p> $k = \frac{\ln 2}{t_{1/2}}$ <p>(1)</p> $k = \frac{0.69315}{(132 \times 60)} = 8.7519 \times 10^{-5} / 0.000087519 \text{ (s}^{-1}\text{)}$ <p>(1)</p> <p>TE on (b)(i) Ignore SF except 1SF Do not award $0.0052511 \text{ (s}^{-1} / \text{min}^{-1}\text{)}$</p> <p>Correct answer with some working scores (2)</p>	2

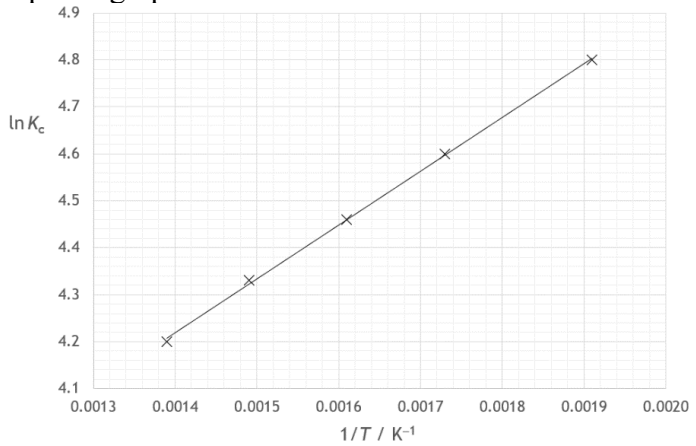
Question Number	Answer	Additional Guidance	Mark
16(c)(i)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> at a higher temperature more particles/collisions have $(E \geq) E_a$ (therefore the) rate (of reaction) is higher 	<p>Accept reverse arguments in M1 and M2</p> <p>Ignore reference to successful collisions Ignore just particles/collision have more energy Ignore reference to collision frequency</p> <p>M2 is standalone mark Allow (therefore the) half-life decreases</p>	2

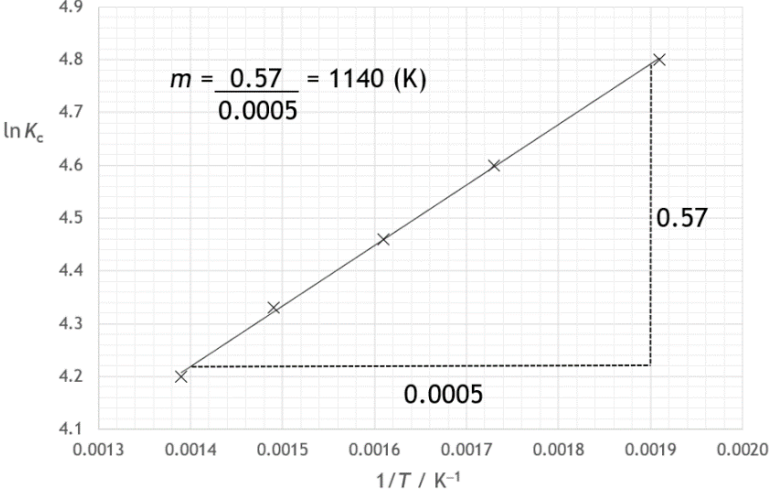
Question Number	Answer	Additional Guidance	Mark
16(c)(ii)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> substitution of k and T values into expression calculation of E_a units of J mol^{-1} or kJ mol^{-1} and calculated answer to 2SF 	<p>Example of calculation:</p> $\log \left[\frac{1.1 \times 10^{-6}}{3.5 \times 10^{-3}} \right] = - \frac{E_a}{2.3 R} \left[\frac{1}{523} - \frac{1}{623} \right]$ <p>or</p> $\log \left[\frac{3.5 \times 10^{-3}}{1.1 \times 10^{-6}} \right] = - \frac{E_a}{2.3 R} \left[\frac{1}{623} - \frac{1}{523} \right]$ <p>(1) $E_a = 218\,130 \text{ (J mol}^{-1}\text{)} / 218.13 \text{ (kJ mol}^{-1}\text{)}$ Ignore sign Ignore units Ignore SF except 1SF TE on transposition of k and T values</p> <p>(1) $E_a = (+)220\,000 \text{ J mol}^{-1} / (+)220 \text{ kJ mol}^{-1}$</p> <p>Correct answer with some working scores (3)</p>	3

Question Number	Answer	Additional Guidance	Mark
18(a)	An answer that makes reference to the following point: <ul style="list-style-type: none"> • correct expression 	Example of correct expression: $(K_c =) \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$ Allow omission of state symbols Ignore any reference to units, even if incorrect Do not award non-square brackets	1

Question Number	Answer	Additional Guidance	Mark
18(b)	An answer that makes reference to the following points: <ul style="list-style-type: none"> • moles H₂ and I₂ reacting (1) • equilibrium moles H₂ and equilibrium moles I₂ (1) • calculation of K_c (1) • calculated answer to 3SF or 2SF and no units (1) 	Correct answer with some working scores (4) Example of calculation: $\frac{9.68 \times 10^{-3}}{2} = 4.84 \times 10^{-3} \text{ (mol)}$ $n(\text{H}_2) = 5.00 \times 10^{-3} - 4.84 \times 10^{-3} = 1.6 \times 10^{-4} \text{ (mol)}$ $n(\text{I}_2) = 1.00 \times 10^{-2} - 4.84 \times 10^{-3} = 5.16 \times 10^{-3} \text{ (mol)}$ TE on moles reacting provided +ve moles (Because volume is 1 dm ³ , mol = concentration) $(K_c =) \frac{(9.68 \times 10^{-3})^2}{(1.6 \times 10^{-4} \times 5.16 \times 10^{-3})} = 113.496$ TE on equilibrium moles TE on K _c expression from (a) for inverted expression or use of [HI] for [HI] ² only Do not award -ve K _c value (K _c =) 113 / 110 and no units Allow 114 and no units if 9.7 × 10 ⁻³ moles reacting TE on M3 TE on units from any K _c expression in (a)	4

Question Number	Answer	Additional Guidance	Mark
18(c)(i)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> $1/T$ value to 3SF (1) $\ln K_c$ value to 3SF (1) 	<p>Penalise SF once only</p> <p>0.00191 Accept 1.91×10^{-3} Calculator value is 0.001912045889</p> <p>4.60 Calculator value is 4.5971138014</p>	2

Question Number	Answer	Additional Guidance	Mark
18(c)(ii)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> linear scales (1) five points correctly plotted (1) straight line of best fit covering all points (1) 	<p>Example of graph:</p>  <p>points plotted must cover at least half of grid in each direction (1)</p> <p>Allow accuracy to \pm half a small square (1)</p> <p>Ignore extrapolations of line of best fit (1)</p>	3

Question Number	Answer	Additional Guidance	Mark
18(c)(iii)	<p>An answer that makes reference to the following point:</p> <ul style="list-style-type: none"> calculation of gradient (with some working) 	<p>Example of working on graph:</p>  <p>gradient = (+)1140 (K) Allow any value between 1060 and 1220</p> <p>Allow use of data from the table provided points used lie on line of best fit</p> <p>Ignore units even if incorrect Ignore SF except 1 SF</p>	1

Question Number	Answer	Additional Guidance	Mark
18(c)(iv)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> • rearrangement of expression for ΔH (1) • calculation of ΔH (1) 	<p>Example of calculation:</p> <p>$\Delta H = -\text{gradient} \times R$</p> <p>$\Delta H = -1140 \times 8.31 = -9473.4 \text{ (J mol}^{-1}\text{)}$ Accept $-9.4734 \text{ kJ mol}^{-1}$ Accept use of 8.314 for R</p> <p>TE on value of gradient from (c)(iii)</p> <p>Ignore SF except 1SF</p> <p>Do not award incorrect units</p>	2

Question Number	Answer	Additional Guidance	Mark
18(c)(v)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> • calculation of ΔG • units of ΔG 	<p>Example of calculation:</p> <p>(1) $\Delta G = -RT \ln K_c$ $= -8.31 \times 620 \times 4.46$ $= -22979 \text{ (J mol}^{-1}\text{)}/-22.979 \text{ (kJ mol}^{-1}\text{)}$ Accept $-22980/-22.980$ from use of $\ln(86.5)$ for 4.46</p> <p>Accept use of 8.314 for R</p> <p>Ignore SF except 1SF</p> <p>Do not award omission of $-ve$ sign</p> <p>(1) M2 dependent on use of $R \times T$ in M1 J mol^{-1} (from 8.31×620) OR kJ mol^{-1} (from $8.31/1000 \times 620$)</p> <p>Calculation of ΔG at any other temperature with correct units scores (1)</p>	2

Question Number	Answer	Additional Guidance	Mark
18(c)(vi)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> • rearrangement of expression for ΔS_{system} (1) • calculation of ΔS_{system} (1) 	<p>Example of calculation:</p> $\Delta S_{\text{system}} = \frac{(\Delta H - \Delta G)}{T}$ $\Delta S_{\text{system}} = \frac{(-9473.4 - (-22979))}{620}$ <p>= (+)21.783 (J mol⁻¹ K⁻¹, units can be in any order) Accept 0.021783 (kJ mol⁻¹ K⁻¹, units can be in any order)</p> <p>TE on ΔH from (c)(iv) and ΔG from (c)(v)</p> <p>Ignore SF except 1SF</p> <p>Do not award incorrect units</p> <p>Correct answer scores (2)</p>	2

Question Number	Answer	Additional Guidance	Mark
18(d)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> • $\Delta S_{\text{surroundings}}$ is (always) positive and (as) ΔH is negative • ΔS_{system} is positive • (so) ΔS_{total} is (always) positive 	<p>(1) Allow (as) reaction is exothermic</p> <p>Allow $\Delta S_{\text{surroundings}}$ is (always) negative and (as) ΔH is positive / reaction is endothermic as TE on (c)(iv)</p> <p>(1) Allow $T\Delta S$ is positive</p> <p>Allow $\Delta S_{\text{system}} / T\Delta S$ is negative as TE on (c)(vi)</p> <p>(1) M3 dependent on positive $\Delta S_{\text{surroundings}}$ and positive ΔS_{system} Accept (so) $\Delta S_{\text{total}} > 0$</p>	3

Total for Question 18 = 20 marks

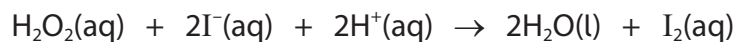
Total for Section C = 20 marks

Total for Paper = 90 marks

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.



- (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)

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(ii) The student's results are shown.

Run	$[\text{H}_2\text{O}_2(\text{aq})] / \text{mol dm}^{-3}$	$[\text{I}^-(\text{aq})] / \text{mol dm}^{-3}$	$[\text{H}^+(\text{aq})] / \text{mol dm}^{-3}$	Rate / $\text{mol dm}^{-3} \text{s}^{-1}$
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.

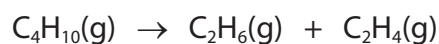
Calculate the activation energy, E_a , for this reaction, using the Arrhenius equation. Give your answer to an appropriate number of significant figures and include units.

$$\ln k = -\frac{E_a}{RT} + \text{constant} \quad (4)$$

(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.



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

	$\text{C}_4\text{H}_{10}(\text{g})$	$\text{C}_2\text{H}_6(\text{g})$	$\text{C}_2\text{H}_4(\text{g})$
Standard molar entropy $S^\ominus / \text{JK}^{-1} \text{mol}^{-1}$	310.1	229.5	219.5
Standard molar enthalpy change of formation $\Delta_f H^\ominus / \text{kJ mol}^{-1}$	-126.5	-84.7	+52.2

- (a) (i) Calculate the entropy change in the system, $\Delta S_{\text{system}}^\ominus$, 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, $\Delta S_{\text{surroundings}}^{\ominus}$, 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, $\Delta S_{\text{total}}^{\ominus}$, 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)

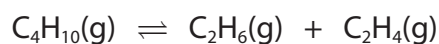
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- (b) 5 mol of butane is cracked at 750 K. At equilibrium, 4.45 mol of ethene is formed and the total pressure is 1.20 atm.



- (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)	<p>An answer that makes reference to the following</p> <ul style="list-style-type: none"> 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) 	<p>Accept equation $\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$</p> <p>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</p> <p>Allow $1/t = \text{rate of reaction} / 1/t \propto \text{rate of reaction}$ Allow $[\text{reactant}]/t \propto \text{rate of reaction}$ Do not award thiosulfate as a reactant</p> <p>Allow (for M3) repeat experiment varying concentration of a reactant; plot concentration against time (for blue-black colour to appear) and measure initial gradient</p> <p>Ignore references to colorimeter</p>	(3)

Question number	Answer	Additional guidance	Mark
17(a)(ii)	<p>An answer that makes reference to the following</p> <ul style="list-style-type: none"> correct form of the rate equation (1) values of three powers (including $[H^+]$ not shown) (2) 	<p>Rate = $k[H_2O_2(aq)]^a[I^-(aq)]^b[H^+(aq)]^c$ or Rate = $k[H_2O_2(aq)]^a[I^-(aq)]^b$</p> <p>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</p> <p>Rate = $k[H_2O_2(aq)][I^-(aq)][H^+(aq)]^0$ Accept Rate = $k[H_2O_2(aq)][I^-(aq)]$</p> <p>For M2 deduct a mark for each incorrect power (reactant not shown order = 0)</p> <p>Overall mark for some of these responses including M1:</p> <p>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)</p> <p>Ignore state symbols even if incorrect Correct answer with no intermediate stages scores (3) Use of round brackets deduct 1 mark</p>	(3)

Question number	Answer	Additional guidance	Mark
17(a)(iii)	<ul style="list-style-type: none"> rearrangement of rate equation (1) calculation of value from Run 1 data (1) units of k (1) 	<p>Example of calculation</p> <p>TE on (a)(ii) for equations in correct form. Units must match the equation used</p> <p>$k = \text{rate} / ([\text{H}_2\text{O}_2(\text{aq})][\text{I}^-(\text{aq})])$ ignore state symbols</p> <p>$k = \frac{0.00181}{0.0210 \times 0.0198} = 4.3531$ Allow use of data from any run</p> <p>$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ Allow units in any order Allow mol^- for mol^{-1} here and throughout paper Ignore SF except 1 SF</p> <p>$k[\text{I}^-(\text{aq})][\text{H}^+]$ gives $87.06 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ scores (3) if TE on (a)(ii)</p> <p>Correct answer with units but no working scores (3)</p>	(3)

Question number	Answer	Additional guidance	Mark
17(b)	<ul style="list-style-type: none"> 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) 	<p>Example of calculation</p> $\ln k_{293} = \text{constant} - \frac{E_a}{293 \times R}$ $\text{and } \ln k_{313} = \text{constant} - \frac{E_a}{313 \times R}$ $\ln\left(\frac{k_{313}}{k_{293}}\right) = \ln 4.45 = \frac{E_a}{R}\left(\frac{1}{293} - \frac{1}{313}\right)$ $E_a = (+)56887$ $(+)57000 / (+)56900 \text{ J mol}^{-1}$ <p>Or</p> $(+)57 / (+)56.9 \text{ kJ mol}^{-1}$ <p>Correct answer with some working scores (4)</p> <p>Some attempt at a calculation using the Arrhenius equation, giving a positive value to 2 or 3 SF and correct units scores M4</p>	(4)

(Total for Question 17 = 13 marks)

Question number	Answer	Additional guidance	Mark
20(a)(i)	<ul style="list-style-type: none"> substitution of values into $\Delta S^\circ_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$ (1) calculation of value from correct equation and sign and units (1) 	<p>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).</p> <p>Example of calculation $\Delta S^\circ_{\text{system}} = 229.5 + 219.5 - 310.1$</p> <p style="text-align: center;">$= (+)138.9 \text{ J K}^{-1} \text{ mol}^{-1}$</p> <p>TE for transcription errors on values only Correct answer with no working scores (2)</p>	(2)

Question number	Answer	Additional guidance	Mark
20(a)(ii)	<ul style="list-style-type: none"> substitution of values into $\Delta_r H^\circ = \Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{reactants})$ (1) calculation of value from correct equation and sign and units (1) 	<p>Example of calculation $\Delta_r H^\circ = (-84.7 + 52.2) - (-126.5)$</p> <p style="text-align: center;">$= (+)94.0 \text{ kJ mol}^{-1}$</p> <p>Correct answer with no working scores (2) TE for transcription errors on values</p> <p>-94.0 kJ mol⁻¹ scores (1) -159.0 kJ mol⁻¹ scores (1) (+)263.4 kJ mol⁻¹ scores (1) -10.4 kJ mol⁻¹ scores (1)</p>	(2)

Question number	Answer	Additional guidance	Mark
20(a)(iii)	<ul style="list-style-type: none"> equation for $\Delta S^\circ_{\text{surroundings}}$ and substitution of values (1) calculation of value from correct equation and sign and units (1) 	<p>Example of calculation</p> $\Delta S^\circ_{\text{surroundings}} = -\Delta H / T$ $= -94000 \div 298$ <p>Accept $= -94 \div 298$</p> $= -315.44 \text{ J K}^{-1} \text{ mol}^{-1} / -0.31544 \text{ kJ K}^{-1} \text{ mol}^{-1}$ <p>TE on $\Delta_r H^\circ$ from (a)(ii) Do not award use of incorrect equation Correct answer with no working scores (2)</p>	(2)

Question number	Answer	Additional guidance	Mark
20(a)(iv)	<ul style="list-style-type: none"> equation for $\Delta S^\circ_{\text{total}}$ and substitution of values and calculated value with sign and units 	<p>Example of calculation</p> $\Delta S^\circ_{\text{total}} = \Delta S^\circ_{\text{system}} + \Delta S^\circ_{\text{surroundings}}$ $= +138.9 + -315.44$ $= -176.54 \text{ J K}^{-1} \text{ mol}^{-1}$ <p>Accept $= +0.1389 + -0.31544$</p> $= -0.17654 \text{ kJ K}^{-1} \text{ mol}^{-1}$ <p>TE on values from (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)</p>	(1)

Question number	Answer	Additional guidance	Mark
20(a)(v)	<ul style="list-style-type: none"> equation for feasibility substitution of values and evaluation of T	Example of calculation $(\Delta S^\circ_{\text{system}} + (-\Delta H/T) = \Delta S^\circ_{\text{total}} = 0)$ $\Delta S^\circ_{\text{system}} = \Delta H/T$ or $-\Delta S^\circ_{\text{system}} = -\Delta H/T$ $T = 94000 \div 138.9$ $= 676.746 \text{ (K)}$ (from unrounded values) Accept 403.746(°C) TE on values from (a)(i) and (a)(ii) Do not award use of incorrect equation (e.g. omission of negative sign in $\Delta S^\circ_{\text{surroundings}}$ 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)	<ul style="list-style-type: none"> equilibrium constant expression 	Example of expression $K_p = \frac{p(\text{C}_2\text{H}_6) \times p(\text{C}_2\text{H}_4)}{p(\text{C}_4\text{H}_{10})}$ Accept p_x where x = formula or pp(X) Ignore state symbols even if incorrect Do not award square brackets	(1)

Question number	Answer	Additional guidance	Mark																
20(b)(ii)	<ul style="list-style-type: none"> moles of reactants and products mole fractions partial pressures substitution of values into K_p equation and evaluation units 	<p>Example of calculation</p> <table border="1"> <thead> <tr> <th></th><th>C₄H₁₀</th><th>C₂H₆</th><th>C₂H₄</th></tr> </thead> <tbody> <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> </tbody> </table> <p> $K_p = \frac{0.56508^2}{0.069841} = 4.5721$ (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) </p>		C ₄ H ₁₀	C ₂ H ₆	C ₂ H ₄	mol at equil ^m	5 – 4.45 = 0.55	4.45	4.45	mole fraction	$\frac{0.55}{9.45}$ = 0.05820	$\frac{4.45}{9.45}$ = 0.47090	$\frac{4.45}{9.45}$ = 0.47090	partial pressures	1.20 x 0.05820 = 0.06984	1.20 x 0.47090 = 0.56508	1.20 x 0.47090 = 0.56508	(5)
	C ₄ H ₁₀	C ₂ H ₆	C ₂ H ₄																
mol at equil ^m	5 – 4.45 = 0.55	4.45	4.45																
mole fraction	$\frac{0.55}{9.45}$ = 0.05820	$\frac{4.45}{9.45}$ = 0.47090	$\frac{4.45}{9.45}$ = 0.47090																
partial pressures	1.20 x 0.05820 = 0.06984	1.20 x 0.47090 = 0.56508	1.20 x 0.47090 = 0.56508																

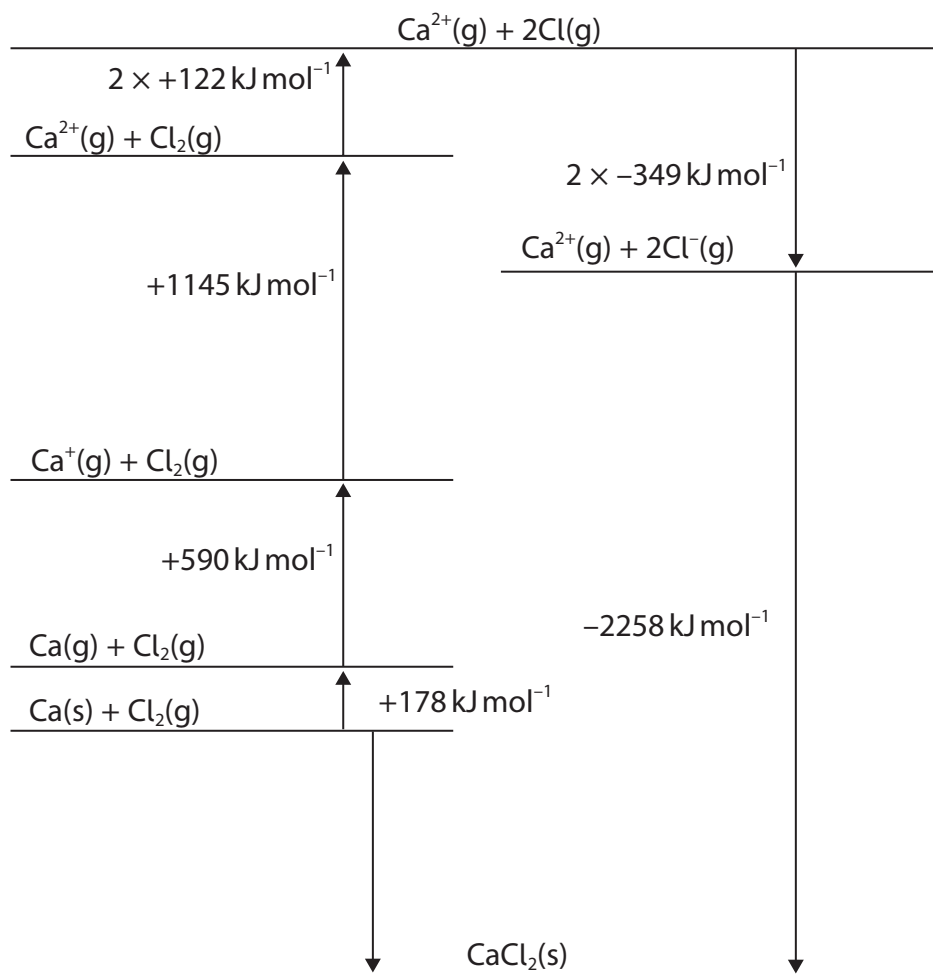
(Total for Question 20 = 15 marks)

TOTAL FOR SECTION B = 51 MARKS

SECTION B

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

17 A Born–Haber cycle for calcium chloride is shown.



(a) State the value of the $\Delta_{\text{at}}H$ for calcium.

(1)

(b) Calculate the enthalpy change of formation for calcium chloride.

(2)



(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)

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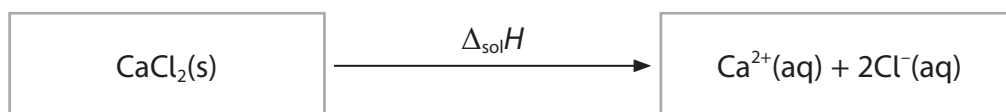
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(d) Calcium chloride is soluble in water.

(i) Complete the energy cycle including labelled arrows.

(2)



(ii) Calculate the enthalpy change of solution, $\Delta_{\text{sol}}H$, for calcium chloride using the data given and the completed energy cycle in (d)(i).

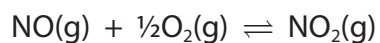
(2)

Data	Energy change / kJ mol^{-1}
LE ($\text{CaCl}_2(\text{s})$)	-2258
$\Delta_{\text{hyd}}H (\text{Ca}^{2+}(\text{g}))$	-1579
$\Delta_{\text{hyd}}H (\text{Cl}^{-}(\text{g}))$	-378

(Total for Question 17 = 11 marks)



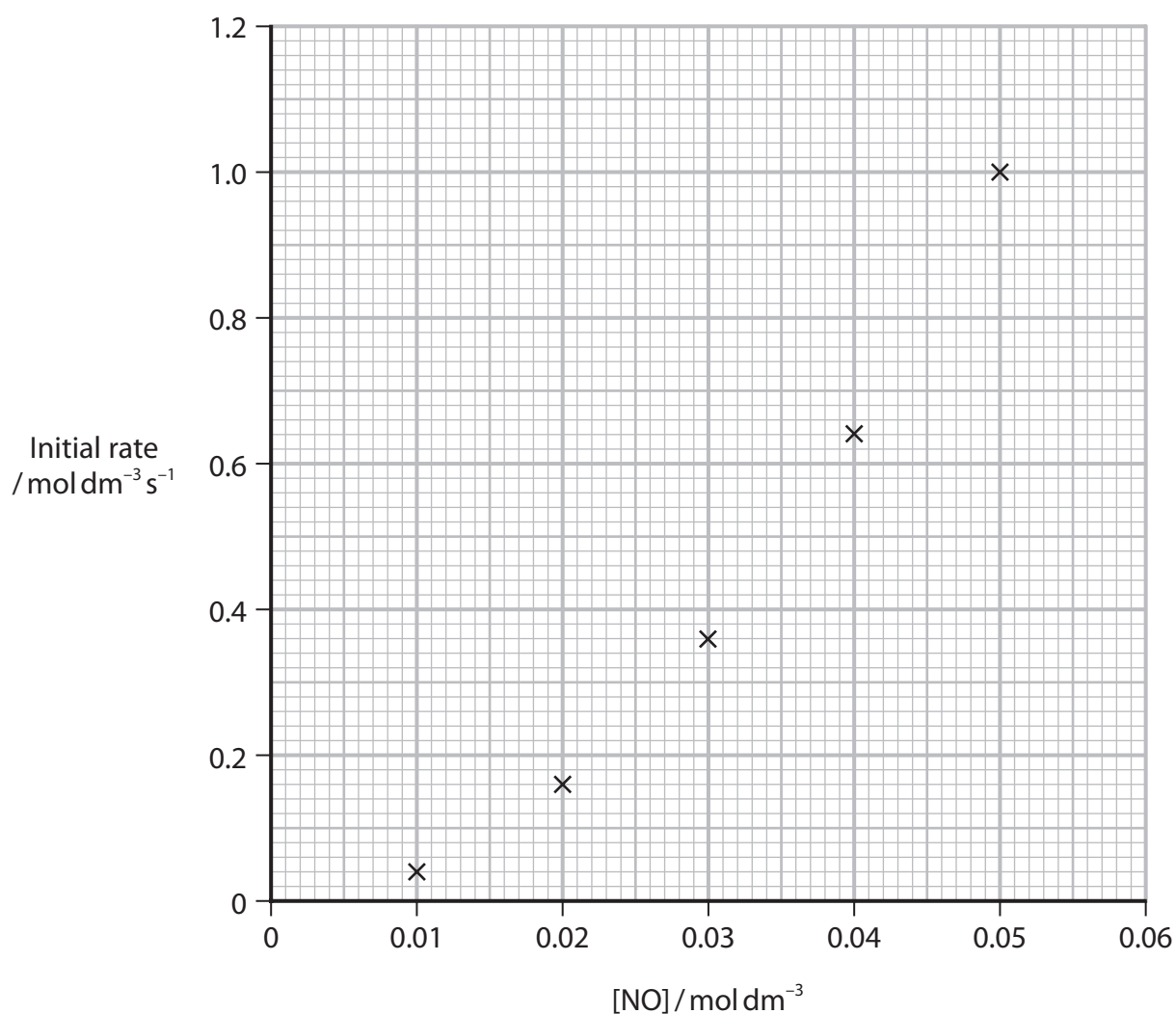
18 This question is about the reaction between nitrogen monoxide and oxygen.



(a) The results of a series of kinetics experiments are shown.

Experiment	Initial [NO] / mol dm ⁻³	Initial [O ₂] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.010	0.050	0.040
2	0.020	0.050	0.160
3	0.030	0.050	0.360
4	0.040	0.050	0.641
5	0.050	0.050	1.001
6	0.020	0.025	0.080

The data for experiments 1–5 were plotted on a graph.



(i) Draw a best-fit line on the graph.

(1)

- (ii) State how the graph shows that the reaction is **not** first order with respect to nitrogen monoxide.

(1)

- (iii) Deduce the orders of reaction with respect to NO and O₂, using the data from experiments 1–6.

(2)

Order with respect to NO =

Order with respect to O₂ =

- (iv) Write the rate equation for the reaction, using your answer to (a)(iii).

(1)

- (v) Calculate the rate constant for this reaction using the data from experiment 1 and your rate equation. Include units in your answer.

(2)

- (b) The equilibrium constant, K_p , for the reaction at 298 K is $1.55 \times 10^6 \text{ atm}^{-1/2}$.

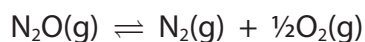
State what this value of the equilibrium constant indicates about the position of the equilibrium. Justify your answer.

(2)

(Total for Question 18 = 9 marks)



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



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

Substance	Standard molecular entropy S^\ominus $/\text{JK}^{-1}\text{mol}^{-1}$
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.

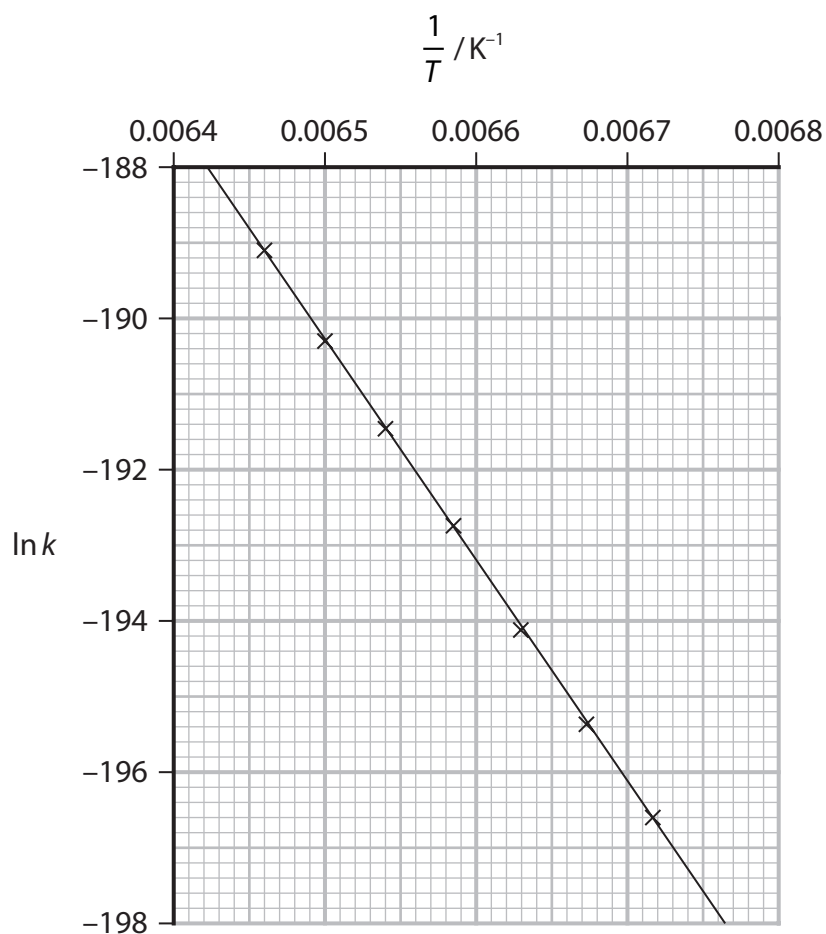
(2)

(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.

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

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

(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)



Section B

Question Number	Answer	Additional Guidance	Mark
17(a)	<ul style="list-style-type: none"> (+)178 (kJ mol⁻¹) 	Do not award -178 (kJ mol ⁻¹) Ignore units even if incorrect	(1)

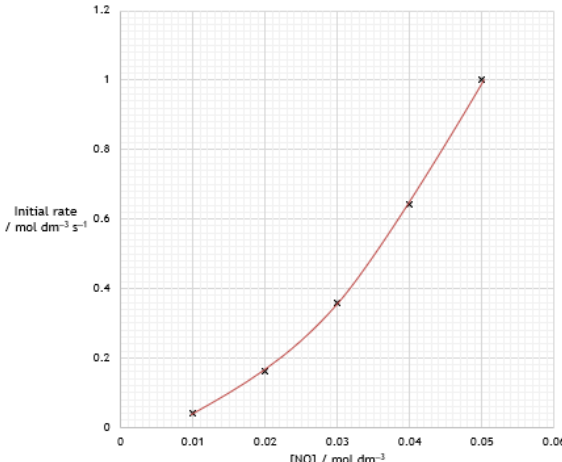
Question Number	Answer	Additional Guidance	Mark
17(b)	<ul style="list-style-type: none"> equation or workings (1) answer to 3SF with negative sign (1) 	Example of calculation: $\Delta_f H = \Sigma(\text{all other terms})$ $\Delta_f H = 178 + 590 + 1145 + (2 \times 122) + (2 \times -349) + (-2258)$ -799 (kJ mol ⁻¹) Correct answer scores (2) TE on incorrectly transferred values e.g. -394 Penalise omission of $\times 2$ once only (-572 scores 1 mark) TE on one incorrect sign No TE on incorrect expression Penalise M2 for incorrect units +799 scores 1 mark	(2)

Question Number	Answer	Additional Guidance	Mark
17(c)	<p>An explanation that makes reference to the following points:</p> <ul style="list-style-type: none"> calcium chloride is almost completely ionic calcium iodide has partially covalent character iodide (ion) is larger (than chloride (ion)) (so) more (easily) polarised 	<p>Allow reverse arguments</p> <p>(1) Accept CaCl_2 is 100% ionic Allow LE is calculated assuming a pure ionic structure</p> <p>(1) 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</p> <p>(1) 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</p> <p>(1) Accept more (easily) distorted Allow (more) polarisable Do not award CaI_2 is more polarised</p> <p>If no comparison for M3 and M4 allow 1 mark, e.g., “iodide is large and is polarised”</p> <p>Penalise iodine/chlorine or incorrect ions once only.</p>	(4)

Question Number	Answer	Additional Guidance	Mark
17(d)(i)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> two labelled arrows in the correct direction (1) formulae including state symbols (1) 	<p>An example of a completed cycle:</p> <p>Accept two arrows on right-hand side Allow $\Delta_{latt}H/ \Delta H_{latt}$ Allow $\Delta_{hyd}H$ alone on right-hand arrow Allow ΔH_{hyd} Allow numerical values rather than the symbols Allow missing 2 for the $\Delta_{hyd}H Cl^-$ Allow left arrow going down if labelled as lattice dissociation energy or $-LE$</p>	(2)

Question Number	Answer	Additional Guidance	Mark
17(d)(ii)	<ul style="list-style-type: none"> calculation (1) enthalpy change of solution (1) 	<p>Example of a calculation:</p> $-(-2258) - 1579 - (2 \times 378)$ $= -77 \text{ (kJ mol}^{-1}\text{)}$ <p>No TE on an incorrect cycle, but (+)77 scores 1 mark Allow TE on transcription errors from M1, and award M2 Allow $\times 2$ omitted, answer = (+)301 (kJ mol⁻¹) scores (1)</p>	(2)

(Total for Question 17 = 11 marks)

Question Number	Answer	Additional Guidance	Mark
18(a)(i)	<ul style="list-style-type: none"> smooth line of best-fit through all the points 	<p>An example of a graph:</p>  <p>Ignore extrapolation at either end of the best-fit line Allow non-smooth lines, within 1 square of each point Do not award use of a ruler</p>	(1) Expert

Question Number	Answer	Additional Guidance	Mark
18(a)(ii)	<ul style="list-style-type: none"> graph is not a straight line (through the origin) 	<p>Accept reverse argument Accept 1st order would be a straight line Accept the relationship is not linear / directly proportional Allow 2nd order with justification e.g., as it's a curve or rate quadruples when concentration doubles Ignore half lives Allow rate not doubling when concentration is doubled Ignore gradient not constant. Ignore exponential No TE 18(a)(i)</p>	(1)

Question Number	Answer	Additional Guidance	Mark
18(a)(iii)	An answer that makes reference to the following points: <ul style="list-style-type: none"> order of reaction for NO order of reaction for O₂ 	(1) 2 / 2 nd / second (1) 1 / 1 st / first	(2)

Question Number	Answer	Additional Guidance	Mark
18(a)(iv)	<ul style="list-style-type: none"> rate = k[NO]²[O₂] 	Allow TE on incorrect orders in a(iii) Allow r on LHS Do not award round brackets Must be a rate equation to gain the mark Correct answer scores 1	(1)

Question Number	Answer	Additional Guidance	Mark
18(a)(v)	<ul style="list-style-type: none"> substitution or rearrangement answer and units 	(1) (1) Example of a calculation: $0.040 = k (0.010)^2(0.05)$ $k = \frac{0.040}{(0.010)^2(0.05)}$ $= 8000 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ Allow units in any order Allow s ⁻ Allow dm ⁶ /mol ² s but not dm ⁶ /mol ² /s Allow TE on a(iv) for both marks, units must match order for M2 Correct answer with units scores 2, even if expression in Q18(a)(iv) is incorrect	(2)

Question Number	Answer	Additional Guidance	Mark
18(b)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> the equilibrium constant is (very) large the equilibrium position is (far) to the right / (heavily) favours the products 	<p>(1) Allow $K_p \gg 1$ Allow synonyms e.g., huge, massive, etc. Allow high Ignore quite large Ignore $K_p > 1$, positive Ignore numerator is larger than the denominator Ignore references to partial pressures</p> <p>(1) Allow goes to completion Do not award “shifts to the right” Ignore favours the forward reaction Do not award M2 for comments on rate</p> <p>For two marks there must be a comment on extent/magnitude</p>	(2)

(Total for Question 18 = 9 marks)

Question Number	Answer	Additional Guidance	Mark
20(a)(i)	<ul style="list-style-type: none"> expression or suitable working (1) correct answer (1) 	<p>Example of a calculation:</p> $(192 + 0.5 \times 205) - (220)$ $(+74.5 \text{ (J K}^{-1} \text{ mol}^{-1})$ <p>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</p>	(2)

Question Number	Answer	Additional Guidance	Mark
20(a)(ii)	<ul style="list-style-type: none"> balanced equation or suitable working (1) correct answer (1) 	<p>Example of a calculation:</p> $\Delta S_{\text{surroundings}} = -\Delta H/T$ $= - (-82000) \div (2048)$ $= 82000 \div 2048$ $(+40.039 \text{ (J K}^{-1} \text{ mol}^{-1})$ <p>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}</p>	(2)

Question Number	Answer	Additional Guidance	Mark
20(a)(iii)	<ul style="list-style-type: none"> total entropy change 	<p>Example of a calculation:</p> $74.5 + 40.0 = (+)114.5 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$ <p>TE on ai and aii, but both must be in the correct units Ignore SF except 1SF</p>	(1)

Question Number	Answer	Additional Guidance	Mark
20(b)	<ul style="list-style-type: none"> gradient activation energy 	<p>Example of a calculation:</p> $\frac{(-197) - (-190)}{(0.00673) - (0.00649)} = \frac{-7}{0.00024}$ <p>gradient = $-29\,167 \text{ (K)}$ (allow any negative value between 28 300-30 000)</p> <p>$(-8.31 \times -29\,167) \div 1000 = (+)242.4 \text{ (kJ mol}^{-1}\text{)}$ (allow values between 235.1 to 249.3 for 2 marks)</p> <p>Ignore SF except 1 SF Allow TE from M1 Answers in J mol^{-1} score both marks if in the allowed range (235100-249300)</p>	<p>(1)</p> <p>(1)</p> <p>(2)</p>

Question Number	Answer	Additional Guidance	Mark
20(c)	<p>An explanation that makes reference to the following points:</p> <ul style="list-style-type: none"> (thermodynamically) feasible because ΔS_{total} is positive (1) activation energy high so the reaction is very slow (at low temperatures) (1) 	<p>Ignore thermodynamically stable/unstable</p> <p>Allow high temperature will provide E_a so reaction will proceed</p> <p>Allow reaction may not happen as E_a is (very) high</p> <p>Allow high E_a so kinetically stable</p> <p>Allow high E_a so kinetically non-feasible</p> <p>TE on 20(a)(iii) but not on 20(b)</p>	(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.



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 cm³ of 1.0 mol dm⁻³ sulfuric acid with 25 cm³ of 1.0 mol dm⁻³ propanone in a beaker.

Step 2 Start a clock as 50 cm³ 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 cm³ 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)

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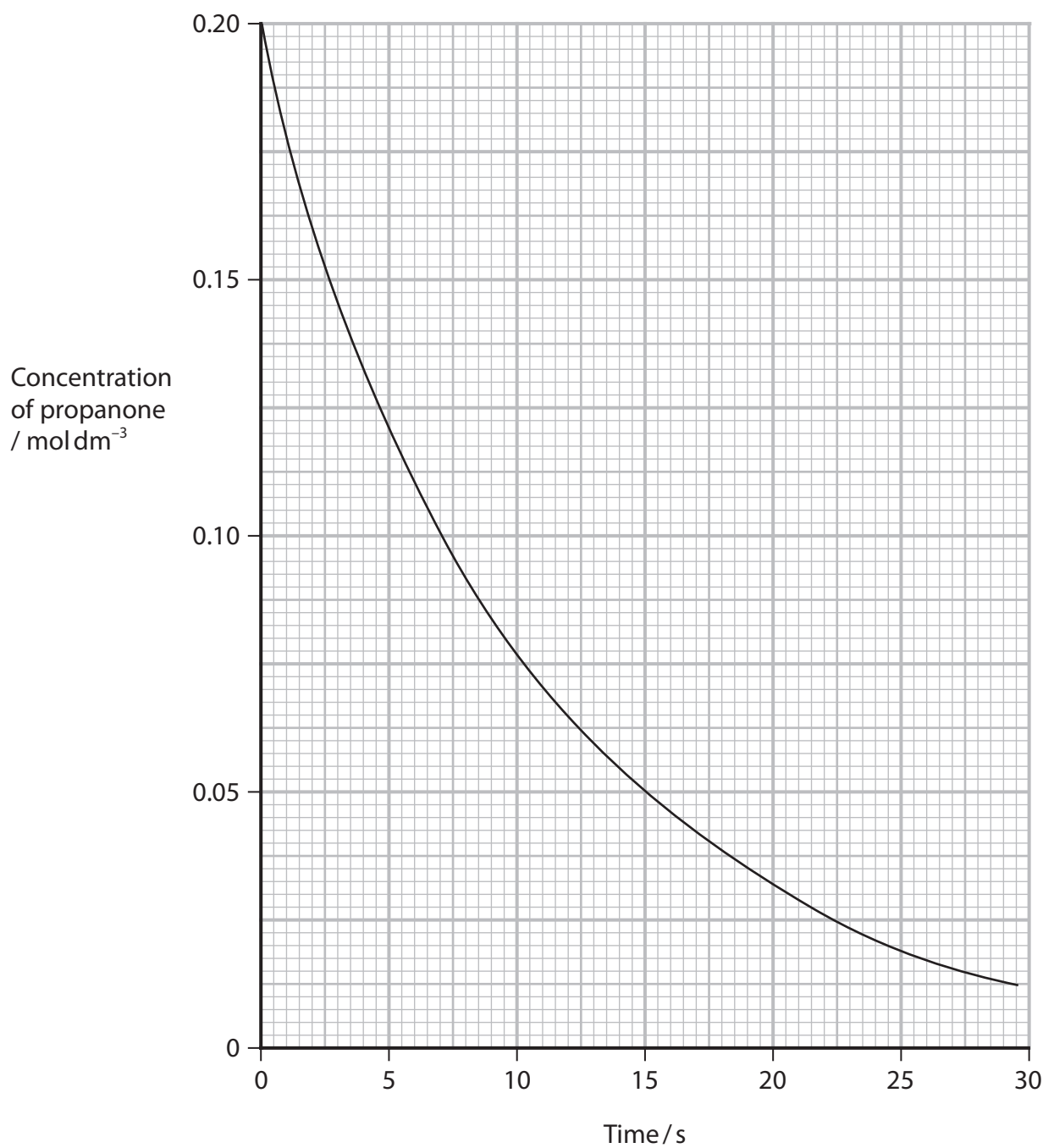
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(e) Further experiments were carried out to determine the reaction orders with respect to propanone and sulfuric acid.

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



The reaction is first order with respect to propanone.

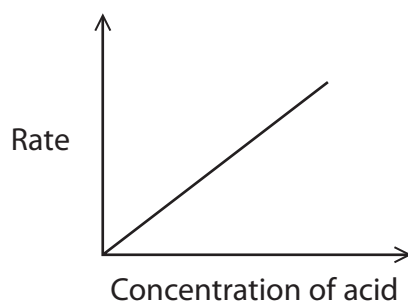
Determine two half-lives for this reaction.
You **must** show your working on the graph.

(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)	<p>An answer that makes reference to the following point:</p> <ul style="list-style-type: none"> only the iodine concentration affects the rate <p>OR</p> <p>so the concentrations of sulfuric acid and propanone do not affect the rate</p>	<p>Allow so only the iodine concentration changes (significantly)</p> <p>Allow $[H^+]$ and $[CH_3COCH_3]$ do not change (significantly) / (effectively) zero order (wrt $[H^+]$ and $[CH_3COCH_3]$)</p> <p>Ignore just concentrations of H_2SO_4 and CH_3COCH_3 are in excess</p> <p>Ignore comments on limiting reagents</p>	(1)

Question Number	Answer	Additional Guidance	Mark
3(b)	<p>An answer that makes reference to the following point:</p> <ul style="list-style-type: none"> to stop / quench the reaction 	<p>Allow neutralise/remove the (sulfuric) acid/H^+ (catalyst)</p> <p>Ignore slow the reaction</p> <p>Do not award to remove OH^-</p>	(1)

Question Number	Answer	Additional Guidance	Mark
3(c)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> (indicator) starch (solution) (1) (colour change) blue-black/(dark)blue/black to colourless (1) 	<p>M2 is dependent on M1</p> <p>Ignore colour before addition of starch</p>	(2)

Question Number	Answer	Additional Guidance	Mark
3(d)(i)	<ul style="list-style-type: none"> axes labelled correctly with units and suitable scale all points plotted correctly best fit straight line 	<p>Example of graph:</p> <p>(1) Points plotted must cover at least 50% of the graph in both directions</p> <p>(1) Allow ± 1 small square</p> <p>(1) Ignore extrapolation</p>	(3)

Question Number	Answer	Additional Guidance	Mark
3(d)(ii)	<p>An answer that makes reference to the following point:</p> <ul style="list-style-type: none"> the volume of (sodium) thiosulfate / titre is (directly) proportional to the concentration of iodine 	<p>Allow they are (directly) proportional</p> <p>Ignore any comments on correlation</p>	(1)

Question Number	Answer	Additional Guidance	Mark
3(d)(iii)	<p>An answer that makes reference to the following point:</p> <ul style="list-style-type: none"> zero (order) / 0 and straight line (with a negative gradient) graph 	<p>Accept rate is proportional to 1/time</p> <p>Accept changes to iodine concentration have no affect on rate</p> <p>Accept zero order and gradient is constant</p> <p>Ignore reference to sign of gradient</p> <p>NOTE: the order wrt iodine must be used in (e)(ii)</p> <p>COMMENT: allow linear for straight line</p>	(1)

Question Number	Answer	Additional Guidance	Mark
3(e)(i)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> working shown on graph for two half lives two half-lives of 7 and 8 (seconds) 	<p>(1)</p> <p>(1)</p> <p>Allow a range of 6 – 9 (seconds)</p> <p>Ignore references to constant half life</p> <p>Do not award minutes / min</p>	(2)

Question Number	Answer	Additional Guidance	Mark
3(e)(ii)	<p>An answer that makes reference to the following point:</p> <ul style="list-style-type: none"> rate = $k[\text{CH}_3\text{COCH}_3][\text{H}^+]$ 	<p>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 $[\text{I}_2]^0$ NOTE: The order wrt to iodine must be consistent with the answer in 3(d)(iii)</p> <p>Ignore state symbols even if incorrect</p>	(1)

(Total for Question 3 = 12 marks)

- 15** A reaction vessel contained nitrogen monoxide and oxygen in a 2:1 molar ratio. The mixture was allowed to come to equilibrium forming nitrogen dioxide. The equation for the reaction is shown.



The volume of the vessel was 15 dm^3 and the reaction was carried out at a constant temperature and at a pressure of $200\,000 \text{ Pa}$.

At equilibrium there was a total of 0.69625 mol of gas in the reaction vessel and the mass of oxygen was 7.000 g .

- (a) (i) Calculate the number of moles of each substance at equilibrium.

(3)

- (ii) Calculate the value of K_c under these conditions. Include units in your answer.

(4)



- (b) Calculate the temperature, in K , of the reaction mixture at equilibrium under these conditions.

Use the equation $pV = nRT$ and the data at the start of the question.

(3)

- (c) Under a different set of conditions, the reaction was carried out to find the initial rate of reaction.

Experiment number	Initial $[\text{NO}] / \text{mol dm}^{-3}$	Initial $[\text{O}_2] / \text{mol dm}^{-3}$	Initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	6.50×10^{-2}	1.25×10^{-2}	6.87×10^{-4}

The rate equation for this reaction is

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

- (i) Give the reason why colorimetry can be used to monitor the rate of the reaction.

(1)

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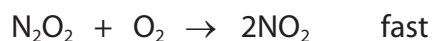
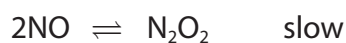
- (ii) Use the data from Experiment 1 to find the value of the rate constant, k .
Include units in your answer.

(2)

- (iii) State why the reaction is unlikely to proceed in a single step.

(1)

- (iv) A student proposed the mechanism shown for this reaction.



Justify whether or not this mechanism is consistent with the overall equation
for the reaction **and** with the rate equation.

(2)

(Total for Question 15 = 16 marks)



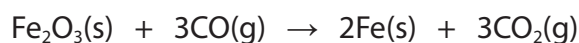
16 Iron, lead and zinc can be extracted using a blast furnace but aluminium cannot.

In a blast furnace, iron is extracted from iron(III) oxide, Fe_2O_3 , at high temperature.

Some standard enthalpy changes of formation, $\Delta_f H^\ominus$, and standard molar entropies, S^\ominus , are shown.

Substance	Al(s)	$\text{Al}_2\text{O}_3(\text{s})$	$\text{CO}(\text{g})$	$\text{CO}_2(\text{g})$	Fe(s)	$\text{Fe}_2\text{O}_3(\text{s})$
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	0	-1676	-111	-394	0	-824
$S^\ominus / \text{JK}^{-1} \text{mol}^{-1}$	28.3	50.9	197.6	213.6	27.3	87.4

(a) The main reaction occurring in the blast furnace to form iron is shown.



This reaction is feasible at all temperatures.

(i) Calculate the standard entropy change of the system for this reaction.

(3)

(ii) Calculate the standard enthalpy change for this reaction.

(3)



(iii) Explain how your answers to (a)(i) and (a)(ii) show that this reaction is feasible at all temperatures.

(3)

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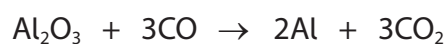
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(b) The main reduction reaction of aluminium oxide in a blast furnace is shown.



(i) Calculate the temperature at which this reaction becomes feasible.

(4)

(ii) Suggest why aluminium is not extracted from its oxide using a blast furnace.

(1)

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(Total for Question 16 = 14 marks)

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Question Number	Answer	Additional Guidance	Mark
15(a)(i)	<ul style="list-style-type: none"> calculation of moles of oxygen at equilibrium calculation of moles of NO at equilibrium calculation of moles of NO₂ at equilibrium 	<p><u>Example of calculation</u></p> <p>= $7.000 \div 32 = 0.21875 / 0.219$ (mol) Allow 7/32</p> <p>= moles of oxygen x 2 = $0.4375 / 0.438$ (mol) Allow 7/16</p> <p>= total moles – moles of O₂ – moles of NO = $0.69625 - 0.21875 - 0.4375 = 0.0400$ (mol)</p> <p>COMMENT: (a)(ii) may help with confusion about which number of moles goes with which molecule. If you cannot work out which goes with which award 1 mark for all 3, but as soon as 1 can be identified ignore other values which cannot Allow TE throughout Ignore SF</p>	(3)

Question Number	Answer	Additional Guidance	Mark
15(a)(ii)	<ul style="list-style-type: none"> divides the moles of the three substances by 15 to find the concentrations gives the formula for K_c substitution of concentrations in the expression given in M2 calculation of final value including units 	<p><u>Example of calculation</u></p> <p>$[\text{NO}_2] = 0.0400 \div 15 = 0.0026667 / 2.6667 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$ $[\text{NO}] = 0.4375 \div 15 = 0.029167 / 2.9167 \times 10^{-2} \text{ (mol dm}^{-3}\text{)}$ $[\text{O}_2] = 0.21875 \div 15 = 0.014583 / 1.4583 \times 10^{-2} \text{ (mol dm}^{-3}\text{)}$ Allow TE on incorrect values in (a)(i)</p> <p>$= [\text{NO}_2]^2 \div [\text{NO}]^2 [\text{O}_2]$ Allow an expression showing moles \div V for each substance Do not award round brackets Do not award K_p expressions</p> <p>$K_c = 0.0026667^2 \div (0.029167^2 \times 0.014583)$ $K_c = 7.1113 \times 10^{-6} \div (8.5071 \times 10^{-4} \times 1.4583 \times 10^{-2})$ Award M2 for the correct expression if no formula has been given Allow TE on incorrect formula in M2 Allow TE on incorrect values calculated in M1 Allow TE on moles in (a)(i) used without converting to concentration</p> <p>$= 0.57320 / 5.7320 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} / \text{mol}^{-1} \text{ dm}^3$ Allow TE on incorrect formula in M2</p> <p>0.038213 $\text{dm}^3 \text{ mol}^{-1}$ (not $\div 15$) scores (3) 68.57 add Correct answer with some working scores (4) Ignore SF except 1 SF in final answer</p>	(4)

Question Number	Answer	Additional Guidance	Mark
15(b)	<ul style="list-style-type: none"> rearrangement of $pV = nRT$ conversion of volume in dm^3 to m^3 and moles of gas = 0.69625 calculation of final value 	<p><u>Example of calculation</u></p> <p>(1) $T = pV \div nR$ Allow with values substituted in</p> <p>(1) $15 \text{ dm}^3 = 0.015 / 1.5 \times 10^{-2} \text{ m}^3 / 15 \times 10^{-3} \text{ m}^3$</p> <p>(1) $= (200,000 \times 0.015) \div (0.69625 \times 8.31)$ $= 518.51 / 519 \text{ (K)}$ Allow use of 8.314 rather than 8.31</p> <p>Allow conversion of pressure to kPa and use of dm^3 giving $= (200 \times 15) \div (0.69625 \times 8.31)$ $= 518.51 / 519 \text{ (K)}$ Allow 245.5(1) °C / 246 °C</p> <p>518510 / 519000 (no conversion) scores (2)</p> <p>If given in °C units must be given Allow TE on incorrect moles of gas and volume Do not award 518(K) or 519°C Correct answer with some working scores (3) Ignore SF except 1 SF</p>	(3)

Question Number	Answer	Additional Guidance	Mark
15(c)(i)	<p>An answer that makes reference to the following point:</p> <ul style="list-style-type: none"> the reactants / NO and O₂ are colourless but the product / NO₂ is reddish brown / coloured 	<p>Allow just NO / O₂ is colourless and NO₂ is brown Allow just nitrogen dioxide / product is reddish brown / coloured / dark colour Allow any combination of yellow, red, orange and brown for the colour of NO₂ Allow measure the time for the brown gas to form</p> <p>Ignore just 'there will be a colour change' / mixture will darken Ignore NO₂ is a different colour form NO and O₂ Do not award NO is coloured so there is a colour change Do not award NO is yellow / red / orange / brown</p>	(1)

Question Number	Answer	Additional Guidance	Mark
15(c)(ii)	<ul style="list-style-type: none"> rearrangement of rate equation expression and inserting values calculation of <i>k</i> and units 	<p><u>Example of calculation</u></p> $= 6.87 \times 10^{-4} \div ((6.50 \times 10^{-2})^2 \times 1.25 \times 10^{-2})$ $= 13.008 / 13.0 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ <p>Correct answer with no working scores (2) Correct numerical answer with incorrect units scores (1) Allow units in any order Allow dm⁶/mol²s</p> <p>0.84554 / 0.846 dm³ mol⁻¹ s⁻¹ (not squaring 6.50 × 10⁻²) scores (1) for final value and units for M2 Ignore SF except 1SF</p>	(2)

Question Number	Answer	Additional Guidance	Mark
15(c)(iii)	<p>An answer that makes reference to the following point</p> <ul style="list-style-type: none"> a three particle collision is unlikely 	<p>Accept it is unlikely that more than two molecules will collide /</p> <p>Allow hard / difficult / impossible instead of unlikely</p> <p>Allow there are three molecules involved in the reaction</p> <p>Ignore it is a third order reaction</p> <p>Do not award just three moles colliding / just three reactants colliding</p>	(1)

Question Number	Answer	Additional Guidance	Mark
15(c)(iv)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> adding the two steps together gives the overall equation the steps do not match the rate equation because the slow step should be the second step 	<p>(1) Allow the two steps match the overall equation as the reactants and products are the same</p> <p>Allow N_2O_2 is formed then reacts / cancels out / is an intermediate</p> <p>Ignore just the overall equation is $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$</p> <p>(1) Allow it does not match because there is no oxygen in the slow step / rate determining step / rds</p> <p>Allow because in this mechanism oxygen is zero order / is not first order</p> <p>Allow because with these steps the rate equation would be $\text{rate} = k[\text{NO}]^2$</p>	(2)

(Total for Question 15 = 16 marks)

Question Number	Answer	Additional Guidance	Mark
16(a)(i)	<ul style="list-style-type: none"> calculation of the standard entropy of the reactants calculation of the standard entropy of the products calculation of the entropy change (products – reactants) 	<p><u>Example of calculation</u> COMMENT If enthalpy and entropy calculations are swapped allow max (2) scoring enthalpy calculation in enthalpy answer space and vice versa</p> <p>Penalise units once only</p> <p>(1) $= 87.4 + (3 \times 197.6) = (680.2) \text{ (J K}^{-1} \text{ mol}^{-1})$</p> <p>(1) $= (2 \times 27.3) + (3 \times 213.6) = (695.4) \text{ (J K}^{-1} \text{ mol}^{-1})$</p> <p>(1) $= (695.4 - 680.2) = (+)15.2 \text{ (J K}^{-1} \text{ mol}^{-1})$</p> <p>Ignore SF in final answer except 1 SF Correct answer with no working scores (3) Allow TE</p>	(3)

Question Number	Answer	Additional Guidance	Mark
16(a)(ii)	<ul style="list-style-type: none"> calculation of the standard enthalpy of formation of the reactants (1) calculation of the standard enthalpy of formation of the products (1) calculation of the enthalpy change (products – reactants) (1) 	<p><u>Example of calculation</u> COMMENT If enthalpy and entropy calculations are swapped allow max (2) scoring enthalpy calculation in enthalpy answer space and vice versa</p> <p>$= -824 + (3 \times -111) = (-1157 \text{ (kJ mol}^{-1}\text{)})$</p> <p>$= 3 \times -394 = (-1182) \text{ (kJ mol}^{-1}\text{)}$</p> <p>$= (-1182) - (-1157) = -25 \text{ (kJ mol}^{-1}\text{)}$</p> <p>-2339 (kJ mol⁻¹) scores M1 and M2 +25 (kJ mol⁻¹) scores M1 and M2 Ignore calculates the enthalpy change and then goes on to calculate $\Delta S_{\text{surroundings}}$ BUT allow the equations in (a)(iii) Ignore SF except 1 SF Correct answer with no working scores (3)</p>	(3)

Question Number	Answer	Additional Guidance	Mark
16(a)(iii)	<p>An answer that makes reference to the following points:</p> <p>Either (using entropy arguments)</p> <ul style="list-style-type: none"> • $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ and $\Delta S_{\text{surroundings}} = -\Delta H \div T$ • (ΔH is negative so) $\Delta S_{\text{surroundings}}$ or $-\Delta H \div T$ is (always) positive and ΔS_{system} is positive • ΔS_{total} is positive (at all temperatures) and so the reaction is feasible (at all temperatures) 	<p>Candidates may use their values instead of symbols Penalise omission of Δ once only</p> <p>$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H}{T}$ scores M1 Allow either equation described in words</p> <p>COMMENT These may be scored in (a)(ii) COMMENT If they have a +ve ΔH in (a)(ii), they must have -ve $\Delta S_{\text{surroundings}}$ (and ΔS_{system} is +ve) to score M2, but then cannot score M3</p> <p>Allow spontaneous</p>	(3)

	<p>OR (using Gibbs free energy arguments)</p> <ul style="list-style-type: none"> • $\Delta G = \Delta H - T\Delta S$ (1) • (ΔS is positive so) $T\Delta S$ or ΔS is (always) positive and ΔH is negative (1) • ΔG is (always) negative and so the reaction is (always) feasible (1) 	<p>Allow spontaneous Allow TE on values in (a)(i) and (a)(ii) Allow > 0 for positive and < 0 for negative throughout</p>	
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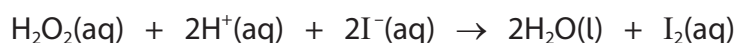
Question Number	Answer	Additional Guidance	Mark
16(b)(i)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> • calculation of ΔS_{system} • calculation of ΔH • conversion of ΔS_{system} or ΔH so units match • rearrange $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ when $\Delta S_{\text{total}} = 0$ and calculation of T 	<p>(1) $= ((2 \times 28.3) + (3 \times 213.6)) - (50.9 + (3 \times 197.6))$ $= 697.4 - 643.7$ $= 53.7 \text{ (J K}^{-1} \text{ mol)}$</p> <p>(1) $= (3 \times -394) - (-1676 + (3 \times -111))$ $= -1182 + 2009$ $= 827 \text{ (kJ mol}^{-1}\text{)}$</p> <p>(1) $\Delta S = 0.0537 \text{ (kJ K}^{-1} \text{ mol)}$ or $\Delta H = 827000 \text{ (J mol}^{-1}\text{)}$</p> <p>(1) $T = \Delta H \div \Delta S_{\text{system}}$ $= \frac{827000}{53.7} = 15400 / 1.5400 \times 10^4 \text{ (K)}$</p> <p>Correct answer scores (4) 15.4 (no M3) scores (3) Ignore incorrect units throughout except in final answer Allow TE throughout except for M4 for a negative temperature</p>	(4)

Question Number	Answer	Additional Guidance	Mark
16(b)(ii)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> because this temperature cannot be achieved in a Blast Furnace 	<p>COMMENT</p> <p>Unfortunately we cannot see (b)(i). Award only answers which suggest that the temperature is too high for the blast furnace to reach</p> <p>Allow the temperature in the Blast Furnace is too low Allow the temperature required is too high Ignore temperature required is very high Ignore the energy needed is too high Ignore activation energy is too high Ignore cost</p>	(1)

(Total for Question 16 = 14 marks)

- 5 A group of students carried out a series of experiments to investigate the kinetics of the reaction between hydrogen peroxide and iodide ions in acidic conditions.

The equation for the reaction is shown.



Procedure

- Step 1** Measure 10 cm^3 of aqueous sodium thiosulfate solution into a conical flask. Add 5 cm^3 of aqueous starch solution and 25 cm^3 of distilled water.
- Step 2** Measure 5 cm^3 of aqueous potassium iodide solution and 5 cm^3 of dilute sulfuric acid and add these to the mixture in the conical flask from Step 1.
- Step 3** Measure 5 cm^3 of aqueous hydrogen peroxide solution into a test tube.
- Step 4** Add the hydrogen peroxide solution to the conical flask, mix thoroughly and start the timer.
- Step 5** Record the time when the solution turns blue-black.
- Step 6** Repeat the experiment varying the volumes of aqueous potassium iodide solution and distilled water, keeping the total volume of the mixture constant.

- (a) Explain the purpose of adding the sodium thiosulfate solution in Step 1.

(2)

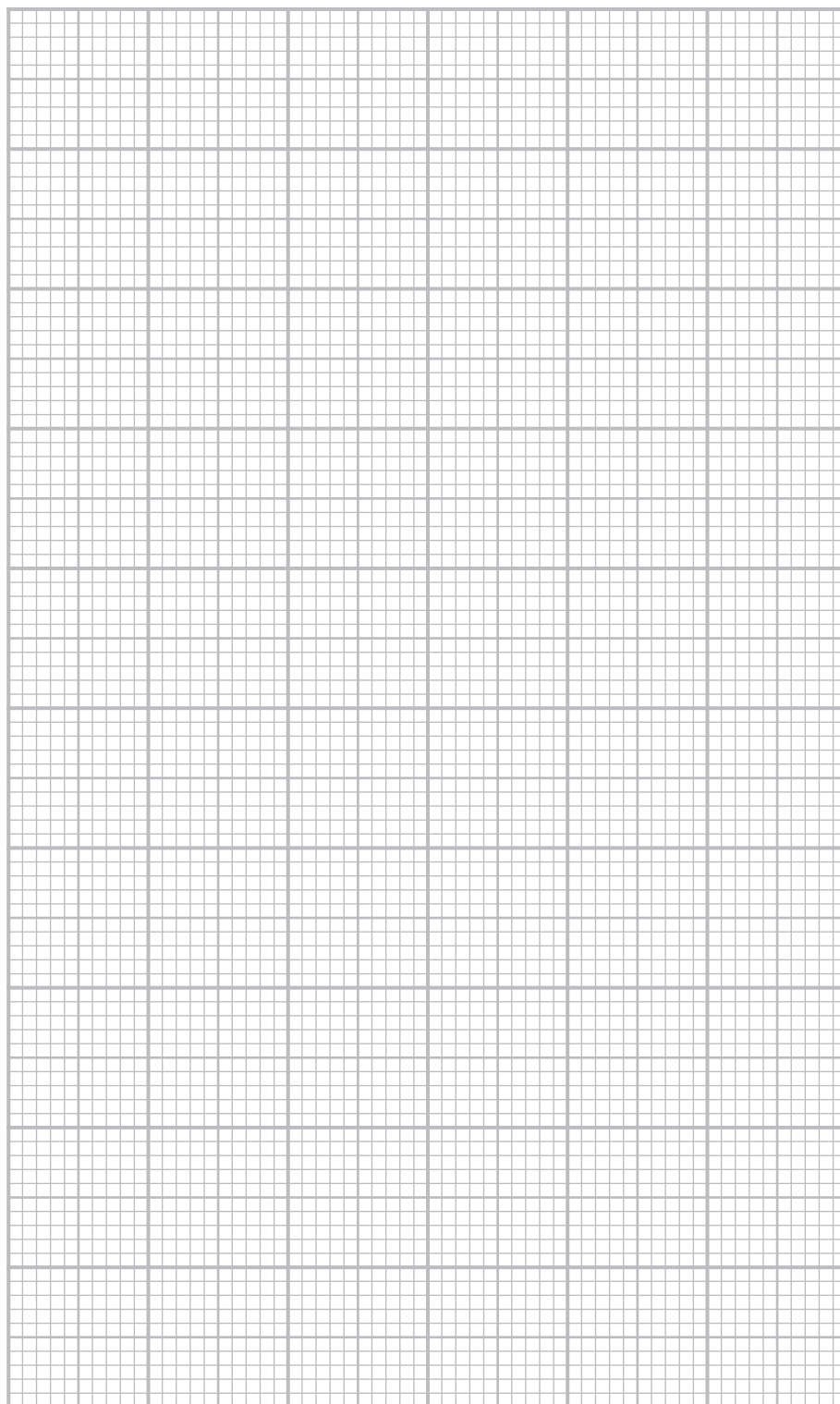
- (b) A set of results is shown.

Run	Volume of solutions / cm^3						Time (t) / s	$1/t$ / s^{-1}
	$\text{Na}_2\text{S}_2\text{O}_3$	Starch	H_2O	KI	H_2SO_4	H_2O_2		
1	10	5	25	5	5	5	270	0.0037
2	10	5	20	10	5	5	138	0.0072
3	10	5	15	15	5	5	93	0.011
4	10	5	10	20	5	5	71	0.014
5	10	5	5	25	5	5	55	0.018



(i) Plot a graph of $1/t$ against the volume of potassium iodide.

(3)



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- (ii) Deduce the order of the reaction with respect to iodide ions, using your graph. Justify your answer.

(2)

- (c) Give a reason why the concentration of the potassium iodide solution is significantly lower than that of the hydrogen peroxide solution and the sulfuric acid.

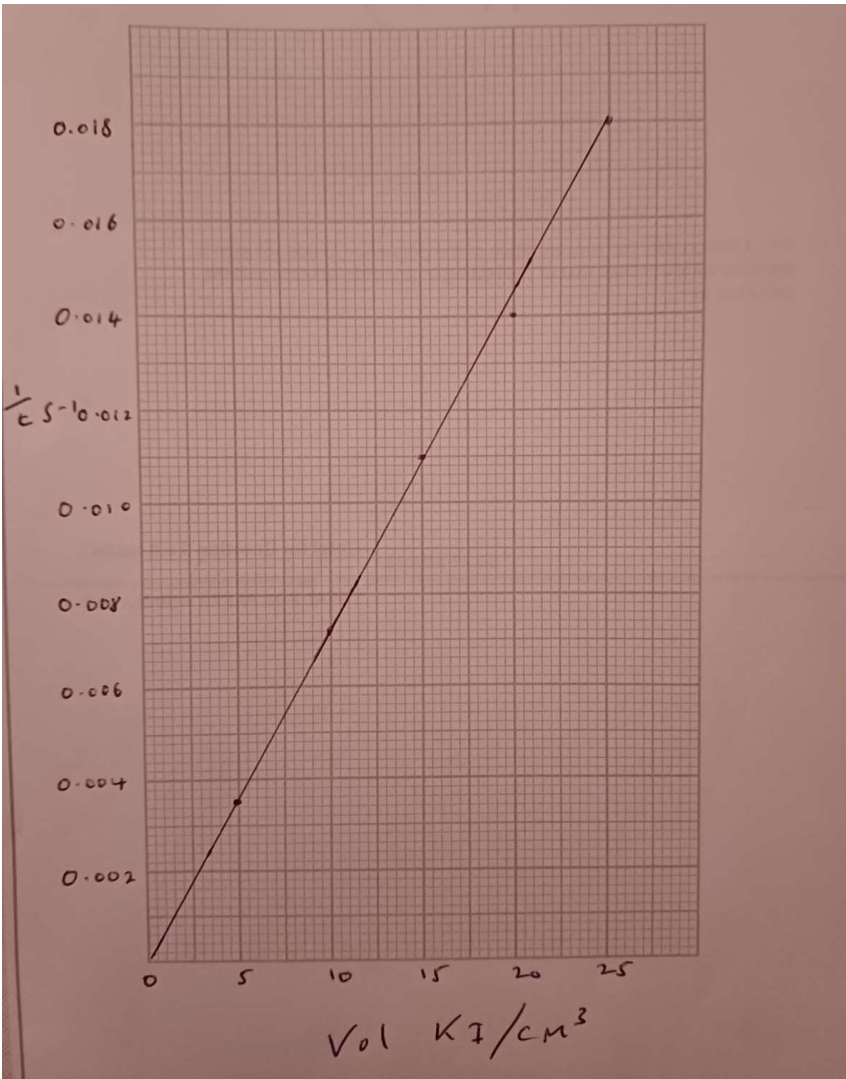
(1)

(Total for Question 5 = 8 marks)

TOTAL FOR PAPER = 50 MARKS



Question Number	Answer	Additional Guidance	Mark
5(a)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> to react with the iodine formed so a colour change occurs when a certain amount of reaction has taken place <p>Standalone marks</p>	<p>(1) Allow to remove the iodine Allow to reduce the iodine (to iodide ions) Allow balanced equation</p> <p>(1) Allow to delay the colour change / solution turning blue-black Allow so the solution does not immediately change colour</p> <p>Allow when all the sodium thiosulfate is used up the iodine reacts with the starch/ there is a colour change (2)</p> <p>Do not award to slow down the reaction to delay the colour change</p>	(2)

Question Number	Answer	Additional Guidance	Mark												
5(b)(i)	<div><ul style="list-style-type: none">• suitable axes and labels with units (1) Axes wrong way round lose M1• points plotted correctly within half a square (1)• points joined with a straight line through the origin/would hit the origin if the line was extended Be lenient here as many have a scale that has no origin and so it will need estimating. Allow +/- two squares (1)<p>Points here for convenience</p><ul style="list-style-type: none">• <table><thead><tr><th>Volume</th><th>$1/t \text{ s}^{-1}$</th></tr></thead><tbody><tr><td>5</td><td>0.0037</td></tr><tr><td>10</td><td>0.0072</td></tr><tr><td>15</td><td>0.011</td></tr><tr><td>20</td><td>0.014</td></tr><tr><td>25</td><td>0.018</td></tr></tbody></table></div>	Volume	$1/t \text{ s}^{-1}$	5	0.0037	10	0.0072	15	0.011	20	0.014	25	0.018	<p>The points plotted must cover at least half the grid in both directions</p> 	(3)
Volume	$1/t \text{ s}^{-1}$														
5	0.0037														
10	0.0072														
15	0.011														
20	0.014														
25	0.018														

Question Number	Answer	Additional Guidance	Mark
5(b)(ii)	<p>An answer that makes reference to the following points:</p> <ul style="list-style-type: none"> first order with respect to iodide ions (1) because graph is a straight line through the origin (1) 	<p>Allow the graph (of rate and concentration) is a straight line/ linear</p> <p>Allow rate is proportional to concentration/volume</p> <p>Allow 1/t is proportional to concentration /volume</p> <p>Allow the relationship between two points</p> <p>Allow constant gradient</p>	(2)

Question Number	Answer	Additional Guidance	Mark
5(c)	<p>An answer that makes reference to the following point:</p> <ul style="list-style-type: none"> (the concentrations of hydrogen peroxide and sulfuric acid are effectively constant) so the rate is only dependent on the iodide ions/KI 	<p>Allow they (hydrogen peroxide and sulfuric acid) do not affect the rate</p> <p>Ignore iodide ions are the only variable/only the concentration of iodide ions is changing</p>	(1)

(Total for Question 5 = 8 marks)

(Total for Paper = 50 marks)