

Section A

Question Number	Correct Answer	Mark
1(a)	A	1

Question Number	Correct Answer	Mark
1(b)	C	1

Question Number	Correct Answer	Mark
2	B	1

Question Number	Correct Answer	Mark
3	D	1

Question Number	Correct Answer	Mark
4	D	1

Question Number	Correct Answer	Mark
5	B	1

Question Number	Correct Answer	Mark
6(a)	C	1

Question Number	Correct Answer	Mark
6(b)	B	1

Question Number	Correct Answer	Mark
6(c)	D	1

Question Number	Correct Answer	Mark
7	A	1

Question Number	Correct Answer	Mark
8	C	1

Question Number	Correct Answer	Mark
9	B	1

Question Number	Correct Answer	Mark
10	C	1

Question 11: N/A

Question 12: N/A

Question 13: N/A

Question 14: N/A

Section B

Question Number	Acceptable Answers	Reject	Mark
15(a)	(It has) three (moles of) COOH groups / three (moles of) carboxylic acid groups / three (moles of) protons / three (moles of) H ⁺ / it is tribasic / three acid groups/ three (moles of) replaceable hydrogens/triprotic ALLOW Three acid groups	'carbonyl'/'carboxylate'	1

Question Number	Acceptable Answers	Reject	Mark
15(b)(i)	<p>FIRST, CHECK THE FINAL ANSWER IF answer = +546 (J mol⁻¹ K⁻¹) award 2 marks "546" (J mol⁻¹ K⁻¹) scores (1) as sign omitted) ($\Delta S^{\circ}_{\text{system}}$ =)[200.5 + (3 x 213.6) + (3 x 69.9)] - [199.9 + (3 x 101.7)] (1) = [+1051] - [+ 505] = +546 (J mol⁻¹ K⁻¹) (1)</p> <p>Allow + 0.546 kJ mol⁻¹ K⁻¹ 2nd mark is CQ on entropy values used for example</p> <p>EITHER Omission of factor of x3 for some or all substances in the equation</p> <p>OR The use of one incorrect entropy value(s) from the data book</p> <p>OR One missing value</p> <p>Note If two or more of the above three errors are made together, (0) awarded.</p> <p>IGNORE sf except 1 sf</p>	<p>Incorrect units (no 2nd mark)</p>	2

Question Number	Acceptable Answers	Reject	Mark
15(b)(ii)	<p>First mark Gas formed (from solid) OR Liquid formed (from solid) OR Gas and liquid formed (from solid) (1)</p> <p>Second mark EITHER More moles of product than reactants / more moles formed OR 4 mol (of reactants) to 7 mol (of products) OR 4 'molecules' to 7 'molecules' NOTE: If specific numbers are stated, these must be correct (ie 4→7) OR Increase in disorder / increase in ways of arranging particles (1)</p> <p>IGNORE 'entropy increases'</p> <p>NOTE: Both points may be made in the same sentence</p>	<p>Just 'more product' / 'more particles formed'</p> <p>2 substances going to 3 substances</p>	2

Question Number	Acceptable Answers	Reject	Mark
15(b)(iii)	<p>$(\Delta S^{\circ}_{\text{surroundings}} =) \frac{-\Delta H}{T} \text{ OR } \frac{-70000}{298}$ (1) = -234.8993289 = -235 J mol⁻¹ K⁻¹ (1)</p> <p>OR $(\Delta S^{\circ}_{\text{surroundings}} =) \frac{-\Delta H}{T} \text{ OR } \frac{-70}{298}$ (1) = - 0.235 kJ mol⁻¹ K⁻¹ (1)</p> <p>IGNORE sf except 1 sf NOTE: Correct units are required for the award of the second mark +235 with units scores (1)</p>	<p>Incorrect rounding (e.g. -234 / -234.89) no 2nd mark</p> <p>+235 with no units (0) overall</p>	2

Question Number	Acceptable Answers	Reject	Mark
15(b)(iv)	$(\Delta S^{\circ}_{\text{total}} = \Delta S^{\circ}_{\text{system}} + \Delta S^{\circ}_{\text{surroundings}})$ $= (+546) + (-235)$ $= (+)311 \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$ OR $= (+)0.311 \text{ kJ mol}^{-1} \text{ K}^{-1}$ CQ on (i) and (iii) IGNORE sf except 1 sf	Incorrect units	1

Question Number	Acceptable Answers	Reject	Mark
15(b)(v)	Positive so feasible / spontaneous / will occur / reaction goes / reacts (at 298 K) NOTE: LOOK BACK at answer to (b)(iv) IF answer to (b)(iv) has a positive sign (the + sign can be stated or implied) THEN ALLOW JUST feasible / spontaneous / will occur / reaction goes / reacts (at 298 K) Mark CQ on sign of answer to (iv)		1

(Total 9 marks)

Question Number	Acceptable Answers	Reject	Mark
16(a)(i)	$K_w = [\text{H}^+] \times [\text{OH}^-]$ OR $K_w = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$ State symbols are not required IGNORE any incorrect state symbols	Inclusion of $[\text{H}_2\text{O}]$	1

Question Number	Acceptable Answers	Reject	Mark
16(a)(ii)	<p>FIRST, CHECK THE FINAL ANSWER IF answer pH = 11.875 / 11.88 / 11.9 / 12 award 2 marks</p> <p>IGNORE sf except 1 sf</p> $[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.00750}$ $= 1.3333 \times 10^{-12}$ $= 1.33 \times 10^{-12} \quad \textbf{(1)}$ <p>(mol dm⁻³)</p> <p>ALLOW first mark for just</p> $[\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$ $\text{pH} = -\log_{10} [\text{H}^+] = 11.875$ $= 11.88 / 11.9 \quad \textbf{(1)}$ <p>OR</p> $\text{pOH} = -\log_{10} [\text{OH}^-] = 2.12 \quad \textbf{(1)}$ $\text{pH} = \text{p}K_w - \text{pOH}$ $\text{pH} = 11.88 / 11.9 \quad \textbf{(1)}$ <p>Second mark only awarded CQ if pH between 8 and 14</p>		2

Question Number	Acceptable Answers	Reject	Mark
16(b)	<p>First mark</p> $\text{Moles NaOH} = \frac{0.00750 \times 20.0}{1000}$ $= 1.50 \times 10^{-4} \text{ (mol)}$ <p style="text-align: right;">(1)</p> <p>(Since HCOOH : NaOH ratio is 1:1)</p> <p>Second mark</p> $[\text{HCOOH(aq)}] = \frac{1.50 \times 10^{-4}}{0.0250}$ <p>OR</p> $= 1.50 \times 10^{-4} \times \frac{1000}{25.0}$ <p style="text-align: right;">(1)</p> $(\text{= } 6.00 \times 10^{-3} \text{ mol dm}^{-3})$ <p>ALTERNATIVE APPROACH:</p> <p>Use of an expression such as $0.00750 \times 20.0 = 25 \times y$ (1)</p> $y = \frac{0.00750 \times 20.0}{25}$ <p style="text-align: right;">(1)</p>		2

Question Number	Acceptable Answers	Reject	Mark
16(c)(i)	<p>(Weak) dissociates / ionizes to a small extent</p> <p>OR dissociate / ionizes partially</p> <p>OR dissociates / ionizes incompletely</p> <p>OR does not fully dissociate / ionize</p> <p>OR forms an equilibrium when reacted with water (1)</p> <p>(Acid) proton donor</p> <p>ALLOW 'proton donator'</p> <p>OR produces / releases H^+ ions</p> <p>OR produces / releases H_3O^+ ions (1)</p> <p>Ignore reference to typical acid reactions</p>	'not easily dissociated'	2

Question Number	Acceptable Answers	Reject	Mark
16(c)(ii)	$(K_a =) \frac{[\text{HCOO}^-][\text{H}^+]}{[\text{HCOOH}]}$ <p>State symbols are NOT required IGNORE any incorrect state symbols</p>	$(K_a =) \frac{[\text{H}^+]^2}{[\text{HCOOH}]}$ <p>Inclusion of $[\text{H}_2\text{O}]$</p>	1

Question Number	Acceptable Answers	Reject	Mark
16(c)(iii)	<p>IGNORE sf except 1 sf THROUGHOUT FIRST, CHECK THE FINAL ANSWER IF answer $K_a = 1.59 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$ award the first two 2 marks</p> <p>$[\text{H}^+] (= 10^{-\text{pH}} = 10^{-3.01})$ $= 9.77 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$ (1)</p> <p>$K_a = \frac{[\text{H}^+]^2}{[\text{HCOOH}]}$</p> <p>$K_a = \frac{(9.77 \times 10^{-4})^2}{6.00 \times 10^{-3}}$ $= 1.59 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$ (1)</p> <p>Assumption 1 $[\text{H}^+] = [\text{HCOO}^-]$ OR no H^+ from the (ionization of) water OR H^+ only from the acid (1)</p> <p>Assumption 2 Ionization of the (weak) acid is negligible / very small / insignificant OR $[\text{HCOOH}]_{\text{initial}} - x = [\text{HCOOH}]_{\text{eqm}}$ OR $[\text{HCOOH}]_{\text{eqm}} = [\text{HCOOH}]_{\text{initial}}$ OR $[\text{HCOOH}]_{\text{eqm}} = 6.00 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$ OR $[\text{H}^+] \ll [\text{HA}]$ (1)</p> <p>Assumptions can be in either order</p>	<p>If incorrect units max 1</p> <p>Just 'partial' / 'incomplete' Or 'no dissociation'</p>	4

16(c)(iii) cont'd	<p>OR</p> $[\text{H}^+] (= 10^{-\text{pH}} = 10^{-3.01})$ $= 9.77 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \quad \textbf{(1)}$ $K_a = \frac{[\text{H}^+]^2}{[\text{HCOOH}]}$ $K_a = \frac{(9.77 \times 10^{-4})^2}{(6.00 \times 10^{-3} - 9.77 \times 10^{-4})} \quad \textbf{(1)}$ $= 1.90 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \quad \textbf{(1)}$ <p>Assumption $[\text{H}^+] = [\text{HCOO}^-]$</p> <p>OR no $[\text{H}^+]$ from the (ionization of) water OR H^+ only from the acid $\textbf{(1)}$</p> <p>Ignore references to constant temperature</p>		
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(Total 12 marks)

Question Number	Acceptable Answers	Reject	Mark
17(a)(i)	$(K_c =) \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$ ALLOW C ₂ H ₅ for CH ₃ CH ₂ State symbols are not required IGNORE any incorrect state symbols		1

Question Number	Acceptable Answers		Reject		Mark	
17(a)(ii)					2	
	Component	CH ₃ COOH(l)	CH ₃ CH ₂ OH(l)	CH ₃ COOCH ₂ CH ₃ (l)		H ₂ O(l)
	Equilibrium amount / mol	(0.20)	0.10	0.20		0.35
	BOTH 0.10 AND 0.20 (1) 0.35 (1)					
	0.10 and 0.20 scores first mark					
	Allow 0.1 and 0.2					
	0.35 scores second mark					

Question Number	Acceptable Answers	Reject	Mark
17(a)(iii)	Units cancel OR same number of moles /same number of molecules on each side OR volume / V cancels Ignore statements such as 'concentrations cancel' 'products and reactants cancel' 'same number of products as reactants'	Concentrations are the same	1

Question Number	Acceptable Answers	Reject	Mark
17(a)(iv)	$K_c = \frac{(0.20) / V \times (0.35) / V}{(0.20) / V \times (0.10) / V}$ $= 3.5 / 3.50$ Correct answer with or without working scores 1 Ignore omission of V TE from values in (ii) table	$K_c = 4$	1

Question Number	Acceptable Answers	Reject	Mark
17(b)	<ul style="list-style-type: none"> No effect on (position of) equilibrium (1) Rate (of attainment of equilibrium) is faster / equilibrium reached sooner (1) 		2

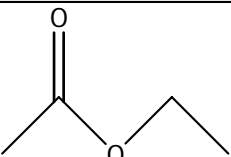
Question Number	Acceptable Answers	Reject	Mark
17(c)(i)	<p>Bonds Broken C—O and O—H (1) Ignore where these bonds are broken in the acid and alcohol molecules.</p> <p>ALLOW C—OH for C—O CO—H for O—H</p> <p>Bonds Made C—O and O—H (1) Ignore where these bonds are made in the ester and water molecules.</p> <p>ALLOW C—OC for C—O H—OH for O—H</p> <p>Marks can be awarded by annotating displayed or structural formulae.</p> <p>Comment: Max 1 if any other bonds mentioned</p>	<p>Two O—H bonds formed in H₂O molecule</p> <p>ONLY C—O bond broken and made scores (0) overall</p>	2

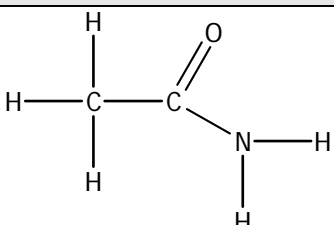
Question Number	Acceptable Answers	Reject	Mark
17(c)(ii)	<p>(C—O and O—H) bond enthalpies differ in: different environments /different molecules /different compounds OR Bond enthalpies/bond energies are average values</p> <p>ALLOW Bonds being broken and made are attached to different atoms</p>	'Heat loss'	1

Question Number	Acceptable Answers	Reject	Mark
17(d)(i)	<p>$\Delta S_{\text{total}} = R \ln K$</p> <p>Allow ΔS_{total} is proportional to <u>ln</u>K</p> <p>ALLOW K_c or K_p instead of K</p>	<p>log instead of ln</p> <p>ΔS_{total} is proportional to K / ΔS_{total} increases as K increases</p>	1

Question Number	Acceptable Answers	Reject	Mark
*17(d)(ii)	<p>First mark:</p> <p>$(\Delta H = 0 \text{ so})$</p> <p>$\Delta S_{\text{surroundings}} = 0$</p> <p>OR</p> <p>$-\frac{\Delta H}{T} = 0$</p> <p style="text-align: right;">(1)</p> <p>IGNORE "$\Delta S_{\text{surroundings}}$ stays the same".</p> <p>Second mark:</p> <p>(so) ΔS_{total} does not change</p> <p>OR</p> <p>(so) $\Delta S_{\text{total}} = \Delta S_{\text{system}}$</p> <p style="text-align: right;">(1)</p> <p>Third mark:</p> <p>(As $\Delta S_{\text{total}} = R \ln K$) K does not alter</p> <p style="text-align: right;">(1)</p> <p>ALLOW "it does not alter" to assume K does not alter.</p> <p>ALLOW use of K_c or K_p instead of K</p> <p>Each point is stand alone</p> <p>IGNORE justifications in terms of Le Chatelier's Principle</p> <p>NOTE:</p> <p>Can award max (1) (i.e. the third scoring point) if the effect on K stated follows on CQ from a change to ΔS_{total}</p>	<p>If only mentions 'no effect on position of equilibrium' rather than the equilibrium constant</p>	3

Question Number	Acceptable Answers	Reject	Mark
17(e)(i)	$\text{CH}_3\text{COCl} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{HCl}$ Allow C_2H_5 for CH_3CH_2 Allow $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$ for $\text{CH}_3\text{COOCH}_2\text{CH}_3$ IGNORE missing or incorrect state symbols	$\text{CH}_3\text{CClO} / \text{CH}_2\text{CH}_3\text{OH}$	1

Question Number	Acceptable Answers	Reject	Mark
17(e)(ii)	 IGNORE Bond angles and length of the lines.		1

Question Number	Acceptable Answers	Reject	Mark
17(e)(iii)	 IGNORE Other products of the reaction if the above structure has been correctly drawn.	NH_2 or CH_3	1

Question Number	Acceptable Answers	Reject	Mark
17(f)(i)	$(\text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{NaOH} \rightarrow)$ $\text{CH}_3\text{COONa} + \text{CH}_3\text{CH}_2\text{OH} / \text{C}_2\text{H}_5\text{OH}$ Allow ionic representations of the sodium salt $\text{CH}_3\text{COO}^-\text{Na}^+$ IGNORE missing or incorrect state symbols	$\text{CH}_2\text{CH}_3\text{OH}$ for ethanol	1

Question Number	Acceptable Answers	Reject	Mark
17(f)(ii)	(Reaction with sodium hydroxide is) not an equilibrium / not reversible / goes to completion OR Reverse argument for acid hydrolysis		1

(Total 19 marks)

Question Number	Acceptable Answers	Reject	Mark
18(a)(i)	<ul style="list-style-type: none"> • In experiments 1 and 2, $[H^+]$ doubles (whilst keeping other concentrations constant) and the rate quadruples / rate increases x 4 (1) • Second order (with respect to H^+) (1) • In experiments 1 and 3, $[Br^-]$ doubles and $[BrO_3^-]$ triples (with $[H^+]$ constant) (1) • Rate increases by 3×2 / rate increases x 6 / rate increases to 5.04×10^{-5} (then to 1.01×10^{-4} stated or implied) (1) • First order with respect to Br^- (1) <p>OR</p> <ul style="list-style-type: none"> • In experiments 2 and 3, $[Br^-]$ doubles and $[BrO_3^-]$ triples and $[H^+]$ halves (1) • Rate increases by $3 \times 0.25 \times 2$ / rate increases x 1.5 (1) • First order with respect to Br^- (1) <p>Penalise OMISSION of Experiment Numbers once only</p> <p>Mark each point independently</p>		5

Question Number	Acceptable Answers	Reject	Mark
18(a)(ii)	<p>Rate = $k [BrO_3^-] [Br^-] [H^+]^2$</p> <p>Mark CQ on (a)(i)</p> <p>Allow "r" or "R" for "rate" in the rate equation.</p> <p>IGNORE</p> <p>If k appears to be in upper case.</p>		1

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

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

Question Number	Acceptable Answers	Reject	Mark
18(c)	<p>REMEMBER TO SCROLL DOWN BELOW THE SPACE LEFT FOR A SKETCH-GRAPH TO SEE WHAT CANDIDATE HAS WRITTEN ON THE DOTTED LINES</p> <ul style="list-style-type: none"> • (Calculate) gradient (of tangent) (1) ALLOW 'slope' for 'gradient' • At $t = 0$ / at the start / at the beginning / when reaction is at its fastest / at the origin (1) <p>Each mark is stand-alone</p> <p>NOTE: Answer may be annotated on a suitable sketch-graph</p> <p>IGNORE any sketch-graph that shows an increase in concentration with time</p> <p>MAX (1) if sketch-graph shows a decrease in the concentration of a reactant / Br_2</p>	<p>Answers relating to half-life score (0) overall</p> <p>If sketch-graph or comments suggest that gradient is measured at other than $t = 0$ or at several values of t then max (1)</p>	2

(Total 12 marks)

Question Number	Correct Answer	Mark
19	C	1

Question Number	Correct Answer	Mark
20	A	1

Section B

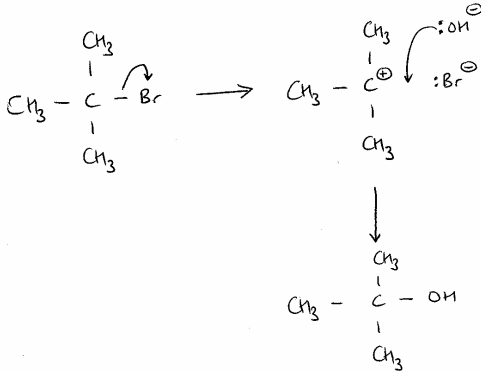
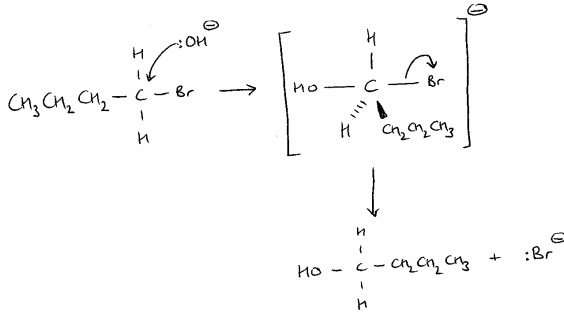
Question Number	Acceptable Answers	Reject	Mark
21 (a)(i)	$5.7 \times 10^{-5} / 5.71 \times 10^{-5} / 5.714 \times 10^{-5} / 0.000057$ <i>IGNORE</i> SF except 1 (ie don't accept 6×10^{-5})		1

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	<p>C_4H_9Br: first order / 1 (1)</p> <p>(going from first to second experiment) rate doubles when concentration / number of moles doubles (and $[OH^-]$ constant)/ rate and concentration increase in proportion (1) <i>ALLOW</i> 'time halves' instead of 'rate doubles'</p> <p>OH^-: zero order / 0 and (going from second to third expt) as increase in concentration does not affect rate (and $[C_4H_9Br]$ constant) (1)</p> <p><i>ALLOW</i> 'doubling in concentration of OH^- instead of 'increase in concentration'</p> <p><i>ALLOW</i> time increases by the same factor as increase in hydroxide concentration (5/3)</p> <p>May refer to experiment number rather than concentrations</p>		3

Question Number	Acceptable Answers	Reject	Mark
(a)(iii)	<p>Rate = $k[C_4H_9Br]$ OR Rate = $k[C_4H_9Br]^1[OH^-]^0$</p> <p><i>ALLOW</i> k in lower or upper case</p> <p>Rate equation must be consistent with orders in (a)(ii) If no order is given for hydroxide in (ii) mark cannot be given</p>		1

Question Number	Acceptable Answers	Reject	Mark
(a)(iv)	$k = \frac{2.9 \times 10^{-5}}{0.017}$ $= 1.7 \times 10^{-3} / 1.71 \times 10^{-3} / 1.706 \times 10^{-3} \text{ s}^{-1}$ <i>ALLOW</i> $k = 1.68 \times 10^{-3}$ (value obtained from experiment 2 or 3) value of k (1) units (1) stand alone mark <i>ALLOW</i> TE from (a)(iii) <i>IGNORE</i> SF except 1 Rate = $k[\text{C}_4\text{H}_9\text{Br}]^2$ gives $k = 0.10036 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ Rate = $k[\text{C}_4\text{H}_9\text{Br}][\text{OH}^-]$ gives $k = 1.42 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <i>ALLOW</i> $k = 1.39 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (value obtained from experiment 2 or 3) Rate = $k[\text{C}_4\text{H}_9\text{Br}][\text{OH}^-]^2$ gives $k = 1184.6 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ Rate = $k[\text{C}_4\text{H}_9\text{Br}]^2[\text{OH}^-]$ gives $k = 83.62 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$		2

Question Number	Acceptable Answers	Reject	Mark
(b)	<p>$[\text{OH}^-]$ is (in chemical equation but) not in rate equation / not in rate determining step (so is in a step other than rate determining step)</p> <p>OR</p> <p>Only $\text{C}_4\text{H}_9\text{Br}$ is in rate equation / rate determining step (so OH^- is in a step other than rate determining step)</p>		1

Question Number	Acceptable Answers	Mark
(c)	<p>First mark Choice of bromoalkane must be consistent with rate equation in (a)(iii). If $[\text{OH}^-]$ is not in rate equation, secondary/tertiary bromoalkane. If $[\text{OH}^-]$ is in rate equation, primary/secondary bromoalkane. (1)</p> <p>Second and third marks Either $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism can score 2 marks regardless of choice of bromoalkane.</p> <div style="text-align: center;">  </div> <p>Lone pairs not required</p> <p>Curly arrow from C-Br bond to Br (making Br^-) (1)</p> <p>Curly arrow from anywhere on $\text{OH}^- / \text{HO}^-$ to C^+ in correct intermediate (making alcohol) (1)</p> <p>OR</p> <div style="text-align: center;">  </div> <p>Both curly arrows from OH^- and from C-Br bond to Br (may both be shown at start) (1)</p> <p>Transition state including minus charge (and product) (1)</p> <p>Do not penalise if C_2H_5 shown instead of C_3H_7. Bonds in transition state can be dotted. Do not penalise the missing H atoms in alkyl groups in mechanism.</p>	3

Question Number	Acceptable Answers	Reject	Mark
(d) QWC	<p>(Primary and tertiary) carbocation intermediates have different stabilities (1) as (inductive effects of) alkyl groups stabilise tertiary carbocation (1)</p> <p>OR</p> <p>Steric hindrance differs for attack on primary and tertiary carbon (in the molecule) / less space available for attack by OH^- on tertiary carbon / more space for attack by OH^- on primary carbon (1) as bulky / three alkyl groups obstruct attack (1)</p>	<p>"Tertiary bromoalkanes react by $\text{SN}1$" without further explanation</p> <p>carbocation intermediates have different reactivity</p> <p>steric hindrance in carbocation</p>	2

Question Number	Acceptable Answers	Reject	Mark
22 (a)(i)	(Acid) hydrolysis	substitution	1

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	$K_2Cr_2O_7$ / $Na_2Cr_2O_7$ / $Cr_2O_7^{2-}$ Potassium dichromate(VI) / sodium dichromate(VI) / dichromate(VI) ions <i>ALLOW</i> manganate(VII) ions, etc	Just "dichromate" chromates Correct formula with wrong name and vice versa Incorrect oxidation number	1

Question Number	Acceptable Answers	Reject	Mark
(a)(iii)	Lithium tetrahydridoaluminate/ lithium aluminium hydride/ $LiAlH_4$ (in dry ether)	Just $[H^-]$	1

Question Number	Acceptable Answers	Reject	Mark
(a)(iv)	Methyl butanoate (1) $CH_3CH_2CH_2COOH + CH_3OH \rightarrow CH_3CH_2CH_2COOCH_3 + H_2O$ (1) <i>ALLOW</i> \rightleftharpoons <i>IGNORE</i> state symbols even if wrong	Methyl butoate	2

Question Number	Acceptable Answers	Reject	Mark
(a)(v)	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C} \begin{array}{l} \text{=O} \\ \text{Cl} \end{array}$ <p>Don't penalise undisplayed methyl groups as here. COCl must be displayed as above.</p>	C ₃ H ₇ for CH ₃ CH ₂ CH ₂	1

Question Number	Acceptable Answers	Reject	Mark
(b)(i)	<p>Nitrogen inert / unreactive / less reactive (than oxygen)</p> <p>OR</p> <p>Oxygen might react with chemicals going through column / sample might oxidise</p>		1

Question Number	Acceptable Answers	Reject	Mark
(b)(ii)	<p>Solubility (in liquid / stationary phase)</p> <p>OR</p> <p>Interaction with liquid / stationary phase</p> <p>OR</p> <p>Interaction between mobile and stationary phase</p> <p>OR</p> <p>Attraction for liquid / stationary phase</p> <p>OR</p> <p>Strength of (named) intermolecular forces</p> <p>OR</p> <p>Adsorption on liquid / stationary phase</p> <p>OR</p> <p>Absorption on liquid / stationary phase</p>	<p>Size of molecule / molar mass</p> <p>Polarity, unless with explanation</p> <p>Boiling point / volatility</p> <p>Viscosity</p> <p>Attraction for carrier gas</p> <p>Just a named intermolecular force</p> <p>Just 'retention time'</p> <p>Density</p>	1

Question Number	Acceptable Answers	Reject	Mark
(c)(i)	$\left[\text{O}-\underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}} \right]$ <p>OR</p> $\left[\underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\underset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O} \right]$ <p>Ester link including C=O (1) Rest of polymer with oxygens at end correct (1)</p> <p>All H atoms must be shown.</p> <p><i>PENALISE</i> lack of displayed C=O once only <i>ACCEPT</i></p> <p>Without brackets around formula but bonds at end should be shown More than two correct units <i>IGNORE</i> n after brackets</p>		2

Question Number	Acceptable Answers	Reject	Mark
(c)(ii)	Hydrolysis OR Splits / breaks ester link OR polymer breaks down to monomers OR equation showing hydrolysis	Just 'breaks polymer down'	1

Question Number	Acceptable Answers	Reject	Mark
23 (a)(i)	$(K_p =) \frac{p_{\text{CH}_3\text{CO}_2\text{H}}}{p_{\text{CH}_3\text{OH}} (x) p_{\text{CO}}}$ Partial pressure symbol can be shown in various ways, eg pp, p_{CO} , (CO)p, etc <i>ALLOW</i> p in upper or lower case, round brackets <i>IGNORE</i> units	[] State symbols given as (l) + in bottom line	1

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	$P_{\text{CH}_3\text{OH}} = 4.9 \text{ (atm) (1)}$ $P_{\text{CO}} = 4.9 \text{ (atm) (1)}$ 1 mark for recognition that pressures are equal <i>IGNORE</i> units		2

Question Number	Acceptable Answers	Reject	Mark
(a)(iii)	$K_p = ((22.2)/(4.9)^2)$ $= 0.925 \text{ (1)}$ $\text{atm}^{-1} \text{ (1)}$ stand alone mark but must match expression used in (a)(iii) OR $9.25 \times 10^4 \text{ Pa}^{-1} / 92.5 \text{ kPa}^{-1} \text{ (2)}$ <i>ALLOW</i> TE from (a)(i) if inverted and/or (a)(ii)	Answers to other than 3 significant figures	2

Question Number	Acceptable Answers	Reject	Mark
(b)(i)	CH_3OH : 3.2 CO : 3.2 (1) for both values $\text{CH}_3\text{CO}_2\text{H}$: 46.8 (1) <i>ALLOW</i> TE for moles of ethanoic acid based on numbers of methanol and carbon monoxide used, as long as moles of methanol and carbon monoxide are equal and moles ethanoic acid + moles methanol = 50		2

Question Number	Acceptable Answers	Reject	Mark
(b)(ii)	$\left(\frac{46.8 \times 32}{53.2} \right) = 28.2 / 28.1504 \text{ (atm)}$ <i>IGNORE</i> sf except 1 Value = 28.16 if mol fraction rounded <i>ALLOW</i> TE from (b)(i)	28.1 $\frac{46.8 \times 32}{50} = 29.95 \text{ (atm)}$	1

Question Number	Acceptable Answers	Reject	Mark
(b)(iii)	exothermic as yield / pp of ethanoic acid / conversion of reactants/ K_p is higher at lower temperature / as equilibrium moves (right) at lower temperature <i>ALLOW</i> if partial pressure of ethanoic acid < 22.2 atm in (b)(ii), endothermic as yield / pp of ethanoic acid / conversion of reactants/ K_p is lower at lower temperature		1

Question Number	Acceptable Answers	Reject	Mark
(c)(i)	No effect and other concentrations change to keep K_p constant / K_p is only affected by temperature/ as equilibrium moves (right) to keep K_p constant / change in pressure does not change K_p	As K_p is a constant	1

Question Number	Acceptable Answers	Reject	Mark
(c)(ii)	Yield increased to restore fraction / quotient / partial pressure ratio back to K_p <i>ALLOW</i> (equilibrium moves) to use up the methanol / answers based on entropy or Le Chatelier Correct prediction in (c)(i) and (c)(ii) with inadequate explanations scores 1 mark in (c)(ii)	Just 'equilibrium moves to the right'	1

Question Number	Acceptable Answers	Reject	Mark
(d)	Mark independently Reaction can occur at lower temperature / has lower activation energy / requires less energy (1) less fuel needed / fewer emissions (from fuels) / fewer raw materials needed / less natural resources used (1) OR Enables use of an alternative process with higher atom economy (1) fewer raw materials needed / less natural resources used (1)	Answer based on car exhaust emissions	2

Question Number	Acceptable Answers	Reject	Mark
24 (a)(i)	<p>Correct answer with or without working scores 2 marks</p> <p>$[H^+] = (1.00 \times 10^{-14} / 0.250) = 4 \times 10^{-14}$ (1)</p> <p>pH = (13.39794 \Rightarrow) 13.4 (1)</p> <p>OR</p> <p>pOH = -log 0.250 = 0.602 (1)</p> <p>pH = (13.39794 \Rightarrow) 13.4 (1)</p> <p>ALLOW TE in second mark if error in $[H^+]$ calculation gives pH more than 7 3 or more sf IGNORE rounding errors e.g. accept 13.39</p>		2

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	<p>$(K_a =) \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ (1)</p> <p>ALLOW H_3O^+ instead of H^+ $\frac{[A^-][H^+]}{[HA]}$ if key to symbols given IGNORE state symbols</p>	$\frac{[H^+]^2}{[CH_3COOH]}$	1

Question Number	Acceptable Answers	Reject	Mark
(a)(iii)	<p>Correct answer with or without working scores 2 marks</p> <p>$1.7 \times 10^{-5} = \frac{[H^+]^2}{0.125}$ (1)</p> <p>$[H^+] = 1.46 \times 10^{-3}$ pH = 2.84/2.8 (1)</p> <p>no TE from an incorrect $[H^+]$</p>		2

Question Number	Acceptable Answers	Reject	Mark
(a)(iv)	<p>pH = 4.8 / 4.77 (1)</p> <p>pH = pK_a / $[H^+] = K_a$ (when acid is half neutralized) (1)</p>	$H^+ = K_a$	2

Question Number	Acceptable Answers	Reject	Mark
(a)(v)	<p>Sigmoid curve starting between pH 2 and 4 (2.8), ending between pH 12 and 14 inclusive (1)</p> <p>with steep rise (may be vertical or gently sloping) of between 3 - 7 units between pH 6 and 12. Sloping section should not extend over more than 5cm³. (1)</p> <p>When 12.5 cm³, NaOH added. (1)</p> <p><i>ALLOW</i> tolerance for grid</p> <p>Reverse curves lose first mark</p>		3

Question Number	Acceptable Answers	Reject	Mark
(a)(vi)	<p>First mark Thymolphthalein more suitable as it changes (from colourless to blue) in steep region of titration (pH 8.3 to 10.6)/ at the equivalence point / at the end point OR thymolphthalein has pH range in steep region of titration (1)</p> <p>Second mark Methyl yellow changes (from red to yellow at pH 2.9 to 4) before equivalence point / before the end point / doesn't change in steep section OR Methyl yellow has pH range before / outside steep region of titration (1)</p> <p><i>ALLOW</i> 'Thymolphthalein more suitable as it changes at the equivalence point but methyl yellow does not.' This scores 2 marks</p> <p>OR</p> <p>First mark $pK_{in} \pm 1$ must lie within vertical region on titration curve (1)</p> <p>Second mark hence thymolphthalein is suitable and methyl yellow is not (1)</p>		2

Question Number	Acceptable Answers	Reject	Mark
(b)	<p>Sodium ethanoate/ CH_3COONa Potassium ethanoate / CH_3COOK</p> <p><i>ALLOW</i> other cations as alternatives to sodium</p>	Use of sodium hydroxide (because it's in food)	1

Question Number	Acceptable Answers	Reject	Mark
25 (a)(i)	$\Delta S^\circ_{\text{system}} = 109.2 + (6 \times 69.9) - 343 \quad (1)$ $= (+)185.6 (\text{J mol}^{-1} \text{K}^{-1}) \quad / \quad (+)186 (\text{J mol}^{-1} \text{K}^{-1}) \quad (1)$ OR $(+)0.186 (\text{kJ mol}^{-1} \text{K}^{-1}) \quad (2)$ IGNORE units even if incorrect correct answer with no working scores 2 Value using 1 for $\text{H}_2\text{O} = -163.9$ scores 1 Use of value for $\text{H}_2\text{O(g)}$ (188.7) gives $898.4 (\text{J mol}^{-1} \text{K}^{-1}) \quad (1)$ correct value with incorrect sign scores 1	185	2

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	Yes as (solid and) liquid forms (from solid) / number of moles increases OR If $\Delta S^\circ_{\text{system}}$ in (i) is negative the sign is not as expected as liquid forms from solid / number of moles increases	Disorder increases, with no ref to liquid or number of moles	1

Question Number	Acceptable Answers	Reject	Mark
(a)(iii)	<p>First mark $\Delta S^{\circ}_{\text{surroundings}} = \frac{-88.1 \times (1000)}{298} \quad (1)$</p> <p>Second mark $= -295.6375$ $= -295.6 \text{ J mol}^{-1} \text{ K}^{-1} \quad (1)$ correct units must be shown but order not important</p> <p>OR</p> <p>$-0.2956 \text{ kJ mol}^{-1} \text{ K}^{-1} \quad (1)$ correct units must be shown but order not important</p> <p>correct answer with or without working and correct units scores (2) ignore sf except 1</p> <p>correct value with positive sign scores 1</p>		2

Question Number	Acceptable Answers	Reject	Mark
(a)(iv)	<p>$(185.6-295.6)$ $= -110 \text{ (J mol}^{-1} \text{ K}^{-1} \text{)}$</p> <p>OR</p> <p>$-0.110 \text{ (kJ mol}^{-1} \text{ K}^{-1} \text{)}$</p> <p>could use 186 or 296 etc</p> <p>TE from (a)(i) and (iii)</p> <p>$(+602.8 \text{ (J mol}^{-1} \text{ K}^{-1} \text{)})$ if value for $6\text{H}_2\text{O(g)}$ was used in (a) (i)</p> <p>$-459.5 \text{ (J mol}^{-1} \text{ K}^{-1} \text{)}$ if value for one H_2O was used in (a) (i)</p>	Answers where values in J are added to kJ	1

Question Number	Acceptable Answers	Reject	Mark
(a)(v)	<p>Decomposition (at 298 K) will not occur as $\Delta S^{\circ}_{\text{total}}$ is negative / Reactions are only spontaneous if total entropy change is positive / decomposition not thermodynamically feasible / (hydrated cobalt chloride) is thermodynamically stable</p> <p>TE if answer to (a)(iv) is positive showing decomposition (at 298 K) may occur</p> <p>OR</p> <p>Positive total entropy change doesn't indicate rate of reaction</p>		1

Question Number	Acceptable Answers	Reject	Mark
(b)(i)	<p>First mark Thermometer (1)</p> <p>Second mark (dependent on first) depends on choosing thermometer</p> <p>as temperature change is small / (%) error in balance smaller than for temperature reading (%) error in pipette smaller than for temperature reading (can be shown by calculation) / as scale with greater degree of precision needed / scale with more graduations needed (1) <i>IGNORE</i> any references to 'accurate thermometer'</p>		2

Question Number	Acceptable Answers	Reject	Mark
(b)(ii)	Use more cobalt chloride / less water (1) To increase temperature rise (1) Mark independently	Just 'use more reactants' Use more cobalt chloride and more water repeat expt add a lid or extra insulation to beaker use distilled water	2

Question Number	Acceptable Answers	Reject	Mark
(c)(i) QWC	Radius (of cation) increases (down group) OR any two values of radius: $\text{Mg}^{2+} = 0.072$, $\text{Ca}^{2+} = 0.100$ / $\text{Sr}^{2+} = 0.113$ (nm) data may be shown beside the table (1) Radius $\text{Co}^{2+} = 0.065$ nm OR Co^{2+} radius smaller than other ions (1) Data on EITHER Co^{2+} OR data showing increase in radius down Group II required for BOTH of first two marks Force of attraction between ions decreases (as radius of ions increases) / charge density of ions decreases / negative ion can come closer to nucleus of positive ion (1) <i>ALLOW</i> "weaker ionic bonds" Predict lattice energy -2550 to -2900 (kJ mol^{-1}) (1) IGNORE sign	Atomic radii unless ionic radii also given Radius of cobalt chloride Polarising power decreases	4

Question Number	Acceptable Answers	Reject	Mark
(c)(ii) QWC	<p>First mark Reference to enthalpy of hydration (may be in equation $\Delta H_{\text{solution}} = -LE + \Delta H_{\text{hydration}}$) (1)</p> <p>Second mark Solubility depends on relative size of lattice energy and enthalpy of hydration (1)</p> <p>Third mark EITHER Solubility more likely if $\Delta H_{\text{solution}}$ is negative</p> <p>OR</p> <p>(If $\Delta H_{\text{solution}}$ is positive,) may / will dissolve if ΔS_{total} is positive</p> <p><i>ACCEPT</i> solvation instead of hydration</p>		3

Question Number	Acceptable Answers	Reject	Mark
(d) QWC	<p>First mark Third ionization energy high(er) for Mg / Mg = 7733 kJ mol^{-1}, (third ionization energy for Co = 3232 kJ mol^{-1}) (1)</p> <p>Second mark (Third ionization energy for Mg is high) because the electron is being removed from an inner shell / full shell / 2p level / 2p orbital (1)</p> <p>OR</p> <p>Not compensated by higher lattice energy for Mg^{3+} (and so $\Delta H_{\text{formation}}$ of MgCl_3 would be highly endothermic) (1)</p>		2