



Mark Scheme (Results)

January 2018

Pearson Edexcel International Advanced
Level In Chemistry (WCH04) Paper 01 General
Principles of Chemistry I – Rates, Equilibria
and Further Organic Chemistry

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General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.

Section A (multiple choice)

Question Number	Correct Answer	Mark
1	<p>The only correct answer is D</p> <p><i>A is not correct because this is not the half life</i></p> <p><i>B is not correct because this is not the half life</i></p> <p><i>C is not correct because this is a limiting case of the half life</i></p>	(1)

Question Number	Correct Answer	Mark
2	<p>The only correct answer is C</p> <p><i>A is not correct because the temperature change would be too small to affect the rate as much</i></p> <p><i>B is not correct because the reaction is already in strong acid and the production of CO₂ will not affect pH much (if at all)</i></p> <p><i>D is not correct because although the statement is correct it has no bearing on the question</i></p>	(1)

Question Number	Correct Answer	Mark
3(a)	<p>The only correct answer is B</p> <p><i>A is not correct because P is the graph for a first order reaction</i></p> <p><i>C is not correct because R is the graph for no reaction</i></p> <p><i>D is not correct because S is the graph of reactant concentration against time for a first order reaction</i></p>	(1)

Question Number	Correct Answer	Mark
3(b)	<p>The only correct answer is B</p> <p><i>A is not correct because P is the graph of product concentration against time for a first order reaction</i></p> <p><i>C is not correct because this is a graph of rate against time for a zero order reaction</i></p> <p><i>D is not correct because S is the graph of reactant concentration against time for a first order reaction</i></p>	(1)

Question Number	Correct Answer	Mark
4	<p>The only correct answer is A</p> <p><i>B is not correct because this is generally true but not a reliable explanation</i></p> <p><i>C is not correct because this is probably true but not a reliable explanation</i></p> <p><i>D is not correct because this is true but does not explain the change with temperature</i></p>	(1)

Question Number	Correct Answer	Mark
5	<p>The only correct answer is A</p> <p><i>B is not correct because entropy is expected to increase with the increase in the number of gaseous particles</i></p> <p><i>C is not correct because entropy is expected to increase with the increase in the number of gaseous particles</i></p> <p><i>D is not correct because entropy is expected to increase with the increase in the number of gaseous particles</i></p>	(1)

Question Number	Correct Answer	Mark
6	<p>The only correct answer is C</p> <p><i>A is not correct because this is true for enthalpy of formation but not molar entropy</i></p> <p><i>B is not correct because this is incorrect</i></p> <p><i>D is not correct because this is incorrect</i></p>	(1)

Question Number	Correct Answer	Mark
7	<p>The only correct answer is A</p> <p><i>B is not correct because this is K_c for the reverse reaction</i></p> <p><i>C is not correct because the expression includes substances in the solid state</i></p> <p><i>D is not correct because the expression includes substances in the solid state</i></p>	(1)

Question Number	Correct Answer	Mark
8	<p>The only correct answer is A</p> <p><i>B is not correct because yield decreases as pressure increases</i></p> <p><i>C is not correct because yield increases as temperature increases</i></p> <p><i>D is not correct because yield increases as pressure decreases and temperature increases</i></p>	(1)

Question Number	Correct Answer	Mark
9	<p>The only correct answer is C</p> <p><i>A is not correct because K_p expression depends on the chemical equation</i></p> <p><i>B is not correct because relationship is given the wrong way round</i></p> <p><i>D is not correct because a power of 2 should be used, not a factor of 2</i></p>	(1)

Question Number	Correct Answer	Mark
10	<p>The only correct answer is C</p> <p><i>A is not correct because K_p unaffected by pressure</i></p> <p><i>B is not correct because K_p unaffected by pressure</i></p> <p><i>D is not correct because when pressure increases, a gaseous equilibrium shifts towards side with fewer moles</i></p>	(1)

Question Number	Correct Answer	Mark
11	<p>The only correct answer is D</p> <p><i>A is not correct because bases are the wrong way round</i></p> <p><i>B is not correct because ethanoic acid is not the acid and HSO_4^- is the conjugate base of H_2SO_4</i></p> <p><i>C is not correct ethanoic acid is not the acid</i></p>	(1)

Question Number	Correct Answer	Mark
12	<p>The only correct answer is C</p> <p><i>A is not correct because litmus is unsuitable for titrations and is a mid-range indicator</i></p> <p><i>B is not correct because methyl orange is used for strong acid weak base titrations</i></p> <p><i>D is not correct because UI is never used as a titration indicator</i></p>	(1)

Question Number	Correct Answer	Mark
13	<p>The only correct answer is B</p> <p><i>A is not correct because this is from $10^{-4.76}$</i></p> <p><i>C is not correct because this is calculated using the standard approximations and ignoring the $[H^+]$ due to water</i></p> <p><i>D is not correct because this is calculated using the standard approximations and ignoring the $[H^+]$ and omitted to square root $[H^+]$</i></p>	(1)

Question Number	Correct Answer	Mark
14	<p>The only correct answer is B</p> <p><i>A is not correct because the compound has a geometric isomer</i></p> <p><i>C is not correct because the compound does not have an asymmetric carbon</i></p> <p><i>D is not correct because the compound does not have an asymmetric carbon</i></p>	(1)

Question Number	Correct Answer	Mark
15	<p>The only correct answer is C</p> <p><i>A is not correct because aldehydes and ketones form hydrogen bonds with water</i></p> <p><i>B is not correct because aldehydes and ketones form hydrogen bonds with water but not in the liquid state</i></p> <p><i>D is not correct because aldehydes and ketones do not form hydrogen bonds in the liquid state</i></p>	(1)

Question Number	Correct Answer	Mark
16	<p>The only correct answer is D</p> <p><i>A is not correct because ketones do not react with Tollens' reagent</i></p> <p><i>B is not correct because aldehydes and ketones react with 2,4-dinitrophenylhydrazine</i></p> <p><i>C is not correct because ketones do not react with Tollens' reagent</i></p>	(1)

Question Number	Correct Answer	Mark
17	<p>The only correct answer is D</p> <p><i>A is not correct because butanoic acid is not oxidised by acidified dichromate(VI)</i></p> <p><i>B is not correct because butanoic acid reacts with PCl_5 but chlorobutane is not the product</i></p> <p><i>C is not correct because the acid product when butyl methanoate is hydrolysed is methanoic acid</i></p>	(1)

Question Number	Correct Answer	Mark
18	<p>The only correct answer is D</p> <p><i>A is not correct because they are all isomeric</i></p> <p><i>B is not correct because they are all isomeric</i></p> <p><i>C is not correct because they are all isomeric</i></p>	(1)

Question Number	Correct Answer	Mark
19	<p>The only correct answer is A</p> <p><i>B is not correct because the central linkage is wrong</i></p> <p><i>C is not correct because this is derived from butanedioic acid and 1,4-dihydroxybenzene</i></p> <p><i>D is not correct because derived from two different monomers</i></p>	(1)

(TOTAL FOR SECTION A = 20 MARKS)

Section B

Question Number	Acceptable Answers	Reject	Mark
20(a)(i)	$\text{C}_6\text{H}_5\text{COOH}(\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$ OR $\text{C}_6\text{H}_5\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_6\text{H}_5\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ ALLOW → in place of ⇌	H ₂ O(aq)	(1)

Question Number	Acceptable Answers	Reject	Mark
20(a)(ii)	$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}^+]}{[\text{C}_6\text{H}_5\text{COOH}]}$ OR H ₃ O ⁺ for H ⁺ ALLOW K _c = IGNORE State symbols even if incorrect [] _{eq} / [] _{eqm}	Other types of bracket Omission of K _a =	(1)

Question Number	Acceptable Answers	Reject	Mark
20(a)(iii)	<p>Concentration of a saturated solution of benzenecarboxylic acid at 25°C $= 3.44/122.1 = 0.028174 \text{ (mol dm}^{-3}\text{)}$</p> <p>ALLOW</p> <p>$3.44/122 = 0.028197 \text{ (mol dm}^{-3}\text{)}$ (1)</p> <p>$K_a = 10^{-4.2} = 6.3096 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$ (1)</p> <p>$[H^+] = \sqrt{(6.3096 \times 10^{-5} \times 0.028174)}$ (1) $= 1.3333 \times 10^{-3}$</p> <p>$\text{pH} = -\log_{10}(1.3333 \times 10^{-3})$ $= 2.87508 / 2.88 / 2.9$ (1)</p> <p>TE at each stage of the calculation</p> <p>Do not penalise premature <u>correct</u> rounding e.g. 0.0282 and 6.31×10^{-5} gives $\text{pH} = 2.8749 = 2.87$</p> <p>If 3.44 is used for the concentration in $\text{(mol dm}^{-3}\text{)}$ $\text{pH} = 1.83172$ scores (3)</p> <p>No TE on the use of an incorrect expression from (a)(i): max (3) (MP1, MP2, MP4)</p> <p>IGNORE SF except 1 SF</p> <p>Correct answer with no working scores 4</p>		(4)

Question Number	Acceptable Answers	Reject	Mark
20(a)(iv)	<p>IGNORE explanations</p> <p>ALLOW [H₃O⁺] for [H⁺] throughout</p> <p>First mark: C₆H₅COOH / benzenecarboxylic acid ionisation negligible</p> <p>ALLOW Acid for C₆H₅COOH</p> <p>Slight / partial / incomplete / does not dissociate for negligible OR [C₆H₅COOH]_{equilibrium} = [C₆H₅COOH]_{initial} / 0.0028174 (mol dm⁻³) (1)</p> <p>Second mark: ([H⁺] due to) ionisation of water negligible OR [H⁺] only due to ionisation of C₆H₅COOH / (benzenecarboxylic) acid OR [C₆H₅COO⁻] = [H⁺] (1)</p> <p>IGNORE references to temperature and to HA and A⁻ Penalise omission of [] in discussion once only</p>		(2)

Question Number	Acceptable Answers	Reject	Mark
20(b)(i)	<p>Value in the range 7.3–8.5 (1)</p> <p>This solution contains a (dilute) solution of the salt of a weak acid and a strong base / alkali (so has a slightly alkaline pH) OR Reaction is between a weak acid and a strong base / alkali (1)</p>		(2)

Question Number	Acceptable Answers	Reject	Mark
20(b)(ii)	<p>Mol acid = $25.0 \times 0.0020 \times 10^{-3} = 5 \times 10^{-5}$</p> <p>Mol NaOH = $V \times 0.0025 \times 10^{-3}$ (1)</p> <p>Neutralisation so these are equal and $V = 25.0 \times 0.0020 / 0.0025$ $= 20 \text{ cm}^3 / 0.020 \text{ dm}^3$ (1)</p> <p>IGNORE SF</p> <p>Correct answer with no working scores (2)</p>	no / incorrect units	(2)

Question Number	Acceptable Answers	Reject	Mark
20(b)(iii)	<p>pH of $0.0025 \text{ mol dm}^{-3}$ NaOH</p> <p>$\text{pOH} = -\log_{10}[\text{OH}^-] = 2.6$ (1)</p> <p>$\text{pH} = \text{p}K_w - \text{pOH} = 14 - 2.6 = 11.4$ (1)</p> <p>OR</p> <p>$K_w = 1 \times 10^{-14} = [\text{H}^+][\text{OH}^-] = 0.0025[\text{H}^+]$ (1)</p> <p>$[\text{H}^+] = 1 \times 10^{-14} / 0.0025 = 4 \times 10^{-12}$</p> <p>$\text{pH} = -\log_{10}[\text{H}^+] = 11.39794 = 11.4$ (1)</p> <p>11.4 with no working scores (2)</p> <p>OR</p> <p>Calculation based on specified excess volume of sodium hydroxide</p> <p>IGNORE SF except 1 SF</p>	11.39 as final answer	(2)

Question Number	Acceptable Answers	Reject	Mark
20(c)(i)	<p>Standalone marks</p> <p>A buffer resists change in pH</p> <p>OR</p> <p>Maintains a fairly / nearly constant pH (1)</p> <p>on the addition of small amounts of acid / H^+ and of alkali / base / OH^- (1)</p>	"prevents change in pH" Just 'constant'	(2)

Question Number	Acceptable Answers	Reject	Mark
20(c)(ii)	<p>In this part of the graph, the pH changes slowly ALLOW This part of the graph is (fairly) flat / horizontal / (nearly) zero gradient (1)</p> <p>So the addition (or removal) of alkali / acid has relatively little effect on the pH of the solution (1)</p> <p>IGNORE References to half equivalence point</p>	no change in pH	(2)

Question Number	Acceptable Answers	Reject	Mark
20(c)(iii)	<p>If answer based on generalised buffer (HA and A⁻) score MP2 and 1 mark for MP3 and MP4 (max 2)</p> <p>MP1 C₆H₅COOH / benzenecarboxylic acid / benzoic acid and C₆H₅COO⁻ / benzenecarboxylate / benzoate (ion) / C₆H₅COO⁽⁻⁾Na⁽⁺⁾ / sodium benzenecarboxylate (1)</p> <p>MP2 C₆H₅COOH and C₆H₅COO⁻ are present in high concentration / large amount / form a large reservoir and so their values / the concentration ratio do(es) not change significantly (when small amounts of acid or alkali are added)</p> <p>ALLOW Ratio remains constant (1)</p> <p>MP3 When acid is added the C₆H₅COO⁻ is protonated / reacts, removing the H⁺ ion from the solution / forming C₆H₅COOH (1)</p> <p>MP4 When alkali is added the C₆H₅COOH is deprotonated / reacts, removing the OH⁻ ion from the solution / forming C₆H₅COO⁻ / C₆H₅COO⁽⁻⁾Na⁽⁺⁾ OR OH⁻ reacts with H⁺ and C₆H₅COOH dissociates to replace the H⁺ (1)</p> <p>For MP3 and MP4: Just "acid reacts with C₆H₅COO⁻ and alkali reacts with C₆H₅COOH" scores (1) equations only scores (1)</p>		(4)

Question Number	Acceptable Answers	Reject	Mark
20(d)	Enzymes are denatured / damaged at high and low pH ALLOW Enzymes do not work at the incorrect pH / only work at correct/optimum pH OR pH affects enzyme activity OR Cells are damaged by high / low pH		(1)

(Total for Question 20 = 23 marks)

Question Number	Acceptable Answers	Reject	Mark
21(a)(i)	<p>Method 1</p> <p>P = (aqueous) sodium hydroxide (1)</p> <p>Q = Iodine (in potassium iodide solution) (1)</p> <p>Method 2</p> <p>P = (aqueous) sodium chlorate(I) (1)</p> <p>and</p> <p>Q = (aqueous) potassium iodide (1)</p> <p>ALLOW</p> <p>Reagents labelled the other way round</p>		(2)

Question Number	Acceptable Answers	Reject	Mark
21(a)(ii)	<p>MP1</p> <p>H₂SO₄(aq) / sulfuric acid</p> <p>HCl(aq) / hydrochloric acid</p> <p>HNO₃(aq) / nitric acid</p> <p>ALLOW</p> <p>Name or formula of any strong acid (1)</p> <p>IGNORE</p> <p>Conc / dilute</p> <p>omission of state</p> <p>H⁺</p> <p>MP2</p> <p>the acid protonates the propanoate ion / sodium propanoate / carboxylate (to form propanoic / carboxylic acid)</p> <p>ALLOW</p> <p>Reaction 1 forms the sodium propanoate OR the sodium salt of propanoic acid (1)</p>	Just 'salt'	(2)

Question Number	Acceptable Answers	Reject	Mark
21(a)(iii)	Triiodomethane ALLOW 1,1,1-triiodomethane Iodoform Triiodomethane IGNORE CHI ₃	1,1,1-iodomethane 1,2,3-triiodomethane	(1)

Question Number	Acceptable Answers	Reject	Mark
21(a)(iv)	These are stand alone marks Lithium tetrahydridoaluminate((III)) / Lithium aluminium hydride / LiAlH ₄ (1) If the oxidation number is given it must be correct ether / ethoxyethane / diethyl ether and essential condition: dry (1) IGNORE Addition of acid	Just 'ether'	(2)

Question Number	Acceptable Answers	Reject	Mark
21(a)(v)	Propanal / product is <u>distilled</u> directly/immediately (out of the reaction mixture) ALLOW Just 'distil' Fractional distillation IGNORE Heat / boil Refs to minimising amount of oxidising agent	Reflux	(1)

Question Number	Acceptable Answers	Reject	Mark
21(a)(vi)	Phosphorus(V) chloride / phosphorus pentachloride / PCl_5 OR Phosphorus(III) chloride / phosphorus trichloride / PCl_3 OR thionyl chloride / SOCl_2		(1)

Question Number	Acceptable Answers	Reject	Mark
21(a)(vii)	propanamide ALLOW propaneamide propionamide IGNORE $\text{CH}_3\text{CH}_2\text{CONH}_2$	N-propanamide ethylamide	(1)

Question Number	Acceptable Answers	Reject	Mark
21(b)(i)	$(m/e = 43 \text{ is due to}) \text{CH}_3\text{CO}^+$ IGNORE $\text{C}_2\text{H}_3\text{O}^+$ (1) $(m/e = 29 \text{ is due to}) \text{CHO}^+ / \text{C}_2\text{H}_5^+ / \text{CH}_3\text{CH}_2^+$ ALLOW $\text{COH}^+ / \text{HCO}^+$ (1) Penalise omission of '+' charge or use of '-' charge once	C_3H_7^+ $\text{CH}_3\text{CH}_2\text{CH}_2^+$ CH_2COH^+ CH_2CHO^+	(2)

Question Number	Acceptable Answers	Reject	Mark
21(b)(ii)	<p>Propanal will have a (C=O stretching peak / absorption) in the range 1740–1720 (cm^{-1}) OR Propanal will have a (C-H stretching peak / absorption) in the range 2900 to 2820 / 2775 to 2700 (cm^{-1}) (1)</p> <p>Butanone will have a (C=O stretching peak / absorption) in the range 1700–1680 (cm^{-1})</p> <p>ALLOW 1720-1710 (cm^{-1}) ALLOW Butanone will not have a (C-H stretching peak/absorption) in the range 2900 to 2820 / 2775 to 2700 (cm^{-1}) and because butanone does not have an aldehyde C-H (1)</p> <p>If aldehydes and ketones used rather than specific molecules max (1) If propanal and butanone wavenumber are transposed max (1) Penalise once only the use of a specific wavenumber rather than a range</p>		(2)

Question Number	Acceptable Answers	Reject	Mark
21(c)(i)	<p>($K_c =$) $[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3(\text{l})] [\text{H}_2\text{O}(\text{l})]$ $[\text{CH}_3\text{CH}_2\text{COOH}(\text{l})][\text{CH}_3\text{CH}_2\text{OH}(\text{l})]$</p> <p>IGNORE state symbols even if incorrect</p>	Other brackets	(1)

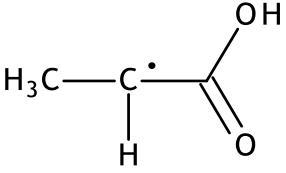
Question Number	Acceptable Answers	Reject	Mark
21(c)(ii)	<p>Catalyst</p> <p>IGNORE Reference to shifting the equilibrium to the right by absorbing water "speeds up the reaction" by itself</p>	Just 'shifts equilibrium to the right'	(1)

Question Number	Acceptable Answers	Reject	Mark
21(c)(iii)	<p>Mark this part independently of the expression given in (c)(i).</p> <p>Data (see table below) (3)</p> <p>NOTE</p> <p>Mr values may be given as 46.1 and 74.1</p> <p>(Let volume of the mixture = V dm³)</p> $K_c = \frac{(0.11/V)(2.11/V)}{(0.14/V)(0.39/V)}$ <p>OR an explanation of why moles can be used rather than concentration (1)</p> <p>= 4.25092 = 4.25 (1)</p> <p>Correct answer with no use of V (4)</p> <p>IGNORE SF except 1 SF</p> <p>if K is inverted, max (4)</p> <p>if [H₂O] omitted, max (3) for</p> <p>M2, M3 and M5 given as 2.015 dm³mol⁻¹</p> <p>OR 2.015 V dm³mol⁻¹</p>	<p>V omitted</p> <p>Units given not consistent with K</p>	(5)

	C ₂ H ₅ COOH	C ₂ H ₅ OH	C ₂ H ₅ COOC ₂ H ₅	H ₂ O	Mark
Initial mass / g	18.5	23	0	36	—
Initial mol	18.5/74 = 0.25	23/46 = 0.50	0	36/18 = 2	(1)
Equil ^m mol	0.25 – 0.11 = 0.14	0.50 – 0.11 = 0.39	0.11	2.11	(2)*

* First mark for calculating 0.11 & second mark for the rest

Question Number	Acceptable Answers	Reject	Mark
21(d)(i)	(Reaction involves / requires) ultraviolet / UV radiation / UV		(1)

Question Number	Acceptable Answers	Reject	Mark
21(d)(ii)	 <p>OR</p> <p>Structural formula</p> <p>OR</p> <p>Combination of displayed and structural formulae</p> <p>OR</p> <p>COOH / CO₂H</p> <p>C—H shown as CH</p>	<p>Omission of unpaired electron</p> <p>unpaired electron on the wrong atom</p> <p>Any charge on the species</p>	(1)

Question Number	Acceptable Answers	Reject	Mark
21(d)(iii)	<p>A racemic mixture is formed (1)</p> <p>AND any two from: The free radical / intermediate flips between different configurations</p> <p>ALLOW the free radical / intermediate is (trigonal) planar (1)</p> <p>Attack (of the molecule / atom / (free) radical) occurs (equally) above & below</p> <p>ALLOW from either side OR from any direction (1)</p> <p>An equimolar mixture of enantiomers is formed OR plane-polarised light rotated equally in opposite directions (1)</p>	<p>Carbocation or molecule for free radical</p> <p>planar about C=O molecule is planar</p> <p>electrophile / nucleophile / Cl⁻</p>	(3)

(Total for Question 21 = 26 marks)

TOTAL FOR SECTION B = 49 MARKS

Section C

Question Number	Acceptable Answers	Reject	Mark
22(a)	<p>MP1 Sampling (by removing a known volume / aliquot of the reaction mixture) (1)</p> <p>MP2 Quenching / stopping (the reaction by cooling or diluting or adding excess acid) (1)</p> <p>MP3 Time of quenching / sampling ALLOW Any mention of timed sampling e.g. 'at (regular) intervals' (1)</p> <p>MP4 Titrate the solution with (a strong) acid (of known concentration to measure [NaOH] / [OH⁻] (and hence deduce [C₄H₉Br]) OR If quenched with acid Titrate the solution with (a strong) alkali (of known concentration to measure [acid] and hence deduce [NaOH] / [OH⁻] reacted and then [C₄H₉Br]) (1)</p> <p>MP5 Plot [C₄H₉Br] against time ALLOW Plot [reactant] against time Plot [NaOH] against time Plot (titre) volume of acid against time (1)</p> <p>MP6 Only award this mark if a graph of concentration or volume against time has been plotted Measure gradient at time = 0 to obtain (initial) rate ALLOW Measure gradient to obtain rate (1)</p>	<p>Quenching with alkali / carbonate / hydrogen-carbonate</p> <p>Titration with acid if quenching with acid</p> <p>Just 'volume'</p>	(6)

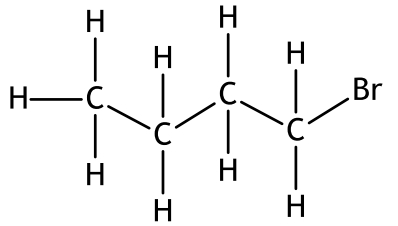
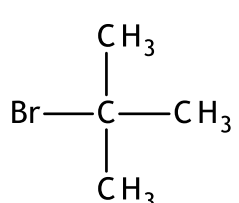
Question Number	Acceptable Answers	Reject	Mark
22(b)	Ethanol will dissolve C ₄ H ₉ Br AND sodium hydroxide / NaOH / OH ⁻ OR Ethanol will dissolve both reactants ALLOW Water will dissolve sodium hydroxide / NaOH / OH ⁻ but not C ₄ H ₉ Br OR Ethanol is a co-solvent / common solvent OR Ethanol enables the reactants to mix IGNORE 'halogenoalkanes are insoluble in water' by itself		(1)

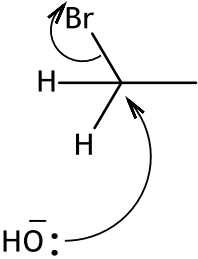
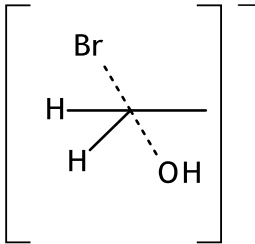
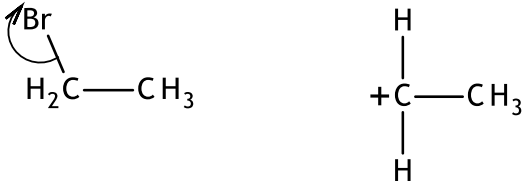
Question Number	Acceptable Answers	Reject	Mark
22(c)(i)	Going from 2 to 1 [C ₄ H ₉ Br] doubles (while [NaOH] remains constant) OR Volume for concentration Rate doubles so order wrt C ₄ H ₉ Br = 1 (1) Going from 3 to 1 [NaOH] / [OH ⁻] doubles (while [C ₄ H ₉ Br] remains constant.) Rate doubles so order wrt [NaOH] / [OH ⁻] = 1 (1) Score max 1 if mixtures not specified Rate = $k[\text{C}_4\text{H}_9\text{Br}][\text{NaOH}]$ OR Rate = $k[\text{C}_4\text{H}_9\text{Br}][\text{OH}^-]$ (1) TE on incorrect orders MP3 cannot be awarded unless the data for both C ₄ H ₉ Br and NaOH have been used in an attempt to deduce the orders of reaction (1 and 1 or 1 and 0)	Use of volume without explanation	(3)

Question Number	Acceptable Answers	Reject	Mark
22(c)(ii)	<p>MP 1 (calculates concentrations) $[C_4H_9Br] = 0.150 \times 100/500$ $(= 0.030 \text{ (mol dm}^{-3}\text{)})$ $[NaOH] = 0.150 \times 250/500$ $(= 0.075 \text{ (mol dm}^{-3}\text{)})$ (1)</p> <p>MP 2 (calculates value of k) $k = \frac{2.50 \times 10^{-4}}{0.030 \times 0.075} = 0.11$</p> <p>ALLOW 1/9 for 0.11</p> <p>TE on incorrect concentrations (1)</p> <p>IGNORE SF except 1 SF</p> <p>MP 3 (units) $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (1)</p> <p>TE on rate = $k[C_4H_9Br]$ gives MP1 $[C_4H_9Br] = 0.150 \times 100/500$ $= 0.030 \text{ (mol dm}^{-3}\text{)}$</p> <p>MP2 $8.33 \times 10^{-3} / 0.00833$</p> <p>MP3 s^{-1}</p>		(3)

Question Number	Acceptable Answers	Reject	Mark
22(c)(iii)	<p>Rate constant would be larger (1)</p> <p>Rate would be faster and because the C–I bond is weaker (than the C–Br bond) (1)</p> <p>IGNORE C–I is longer than C–Br</p>	Just 'rate is faster'	(2)

Question Number	Acceptable Answers	Reject	Mark
22(c)(iv)	<p>The slow / rate-determining step of the mechanism involves C₄H₉Br and NaOH / OH⁻ ALLOW The slow / rate-determining step of the mechanism involves both reactants</p> <p>IGNORE Species for reactants</p> <p>TE on rate = k[C₄H₉Br] for The slow / rate-determining step of the mechanism involves C₄H₉Br only</p> <p>ALLOW Involves one reactant only</p> <p>IGNORE S_N2 / S_N1</p>		(1)

Question Number	Acceptable Answers	Reject	Mark
22(c)(v)	<p>Answers must be consistent with 22(c)(iv) ALLOW CH₃ for methyl groups</p> <div style="text-align: center;">  <p style="text-align: right;">(1)</p> </div> <p>primary halogenoalkanes undergo substitution by an S_N2 mechanism (1)</p> <p>OR (TE on incorrect rate expression and (c)(iv))</p> <div style="text-align: center;">  <p style="text-align: right;">(1)</p> </div> <p>tertiary halogenoalkanes undergo substitution by an S_N1 mechanism (1)</p>		(2)

Question Number	Acceptable Answers	Reject	Mark
22(d)	<p>IGNORE</p> <p>R group / dipoles / stages after the transition state</p> <p>Products even if incorrect</p>  <p>Curly arrow from C—Br bond to Br or just beyond</p> <p>ALLOW</p> <p>This curly arrow drawn on the intermediate (1)</p> <p>Curly arrow from lone pair of O on OH⁻ to C atom (1)</p> <p>COMMENT</p> <p>Award MP2 if arrow closer to lp than to O / charge</p>  <p>Transition state including partial bonds and charge on any part of the intermediate (1)</p> <p>OR (max 1 for S_N1)</p> <p>Curly arrow from C—Br bond to Br or just beyond it and intermediate scores 1</p> 		(3)

(Total for Question 22 = 21 marks)
TOTAL FOR SECTION C = 21 MARKS
TOTAL FOR PAPER = 90 MARKS

