



AQA Qualifications

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# A-LEVEL CHEMISTRY

CHEM4 Kinetics, Equilibria and Organic Chemistry  
Mark scheme

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2420  
June 2014

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Version: 1.1 Final

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Mark schemes are prepared by the Lead Assessment Writer and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation events which all associates participate in and is the scheme which was used by them in this examination. The standardisation process ensures that the mark scheme covers the students' responses to questions and that every associate understands and applies it in the same correct way. As preparation for standardisation each associate analyses a number of students' scripts: alternative answers not already covered by the mark scheme are discussed and legislated for. If, after the standardisation process, associates encounter unusual answers which have not been raised they are required to refer these to the Lead Assessment Writer.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of students' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

Further copies of this Mark Scheme are available from [aqa.org.uk](http://aqa.org.uk)

Question	Marking Guidance	Mark	Comments
1(a)	Mol of E      1.6(00) Mol of F      0.2(00)	1 1	Ignore extra zeros.
1(b)	$K_c = \frac{[G]^2}{[E][F]^2}$  mol <sup>-1</sup> dm <sup>3</sup>	1 1	Penalise expression containing V. Penalise missing brackets or ( ).  If $K_c$ wrong, allow units consequential to their $K_c$ , but no marks in (c) unless correct $K_c$ used in (c).
1(c)	$K_c = \frac{(0.85/1.5)^2}{(2.50/1.5)(1.20/1.5)^2}$  = 0.3(01)      Allow 0.299–0.304	1 1	Vol missed or used wrongly – no marks. If $K_c$ correct in (b) but squared term missed here, no further marks.  Ignore units.
1(d)	M1    Decrease  M2    More moles on LHS / reactants or fewer / less moles on RHS / products (allow correct ratio 3:2)  M3    (Equilibrium) <u>shifts / moves</u> either to oppose reduction in pressure / or to increase the pressure	1 1 1	If M1 is incorrect CE=0 for the clip. If M1 is blank, mark on and seek to credit the correct information in the explanation. M2 not just a generic statement 'shifts to more moles'. M3 depends on a correct statement for M2  Not 'favours'. Allow 'to oppose change' only if reduction in pressure noted.

1(e)	M1	$T_1$	1	If M1 is incorrect, CE=0 for the clip.
	M2	(Forward*) reaction is <u>exothermic</u> <b>OR</b> <u>Backward</u> reaction is <u>endothermic</u>	1	If M1 is blank, mark on and seek to credit the correct information in the explanation.
	M3	(at $T_2$ or lower temperature) (Equilibrium) <u>shifted / moved</u> to oppose reduction in temp <b>OR</b> at $T_1$ or higher temp, (Equilibrium) <u>shifted / moved</u> to oppose (increase in temp)	1	*Assume answer refers to forward reaction unless otherwise stated.  M3 depends on a correct statement for M2 Allow “to oppose change” only if change in temperature is stated. Not ‘favours’.

Question	Marking Guidance	Mark	Comments
2(a)	(only) slightly or partially dissociated / ionised	1	Ignore 'not fully dissociated'. Allow low tendency to dissociate or to lose / donate a proton. Allow shown equilibrium well to the left. otherwise ignore equations
2(b)	$2\text{CH}_3\text{CH}_2\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_3\text{CH}_2\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$ <b>OR</b> $2\text{CH}_3\text{CH}_2\text{COOH} + \text{CO}_3^{2-} \rightarrow 2\text{CH}_3\text{CH}_2\text{COO}^- + \text{H}_2\text{O} + \text{CO}_2$ <b>OR</b> $\text{CH}_3\text{CH}_2\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{COONa} + \text{NaHCO}_3$ <b>OR</b> $\text{CH}_3\text{CH}_2\text{COOH} + \text{CO}_3^{2-} \rightarrow \text{CH}_3\text{CH}_2\text{COO}^- + \text{HCO}_3^-$	1	Must be propanoic acid, allow $\text{C}_2\text{H}_5\text{COOH}$ not molecular formulae Allow multiples. Ignore reversible sign. Not $\text{H}_2\text{CO}_3$
2(c)	$[\text{OH}^-] = 2 \times 0.0120 = 0.0240$ $[\text{H}^+] = \frac{1 \times 10^{-14}}{0.0240} = 4.166 \times 10^{-13}$ <b>OR</b> $\text{pOH} = 1.62$ $\text{pH} = 12.\underline{38}$	M1 M2 M3	1 1 1 Correct answer for pH with or without working scores 3 If $\times 2$ missed or used wrongly can only score M3 for correct calculation of pH from their $[\text{H}^+]$ Lose M3 if not 2 decimal places: 12.4 scores 2 12.08 scores 1 (missing $\times 2$ ) ; 12.1 scores 0 11.78 scores 1 (dividing by 2) 11.8 scores 0

2(d)(i)	$K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}$		1	<p>Ignore ( ) here but brackets must be present. Must be correct acid and salt. If wrong, mark (d)(ii) independently.</p>
2(d)(ii)	M1	$K_a = \frac{[H^+]^2}{[C_6H_5COOH]} \quad \text{OR with numbers}$	1	<p>Correct answer for pH with or without working scores 3 Allow HX, HA and ignore ( ) here. May score M1 in (d)(i). pH = 6.12 may score 2 if correct working shown and they show the square root but fail to take it. but if no working shown or wrong <math>K_a = \frac{[H^+]}{[C_6H_5COOH]}</math> used which also leads to 6.12, then zero scored. Must be 2 decimal places ie 3.1 loses M3</p>
	M2	$[H^+] = \sqrt{(6.31 \times 10^{-5} \times 0.0120)} \text{ or } \sqrt{(K_a \times [C_6H_5COOH])}$ $(\text{= } \sqrt{(7.572 \times 10^{-7} = 8.70 \times 10^{-4})})$	1	
	M3	pH = 3.06	1	

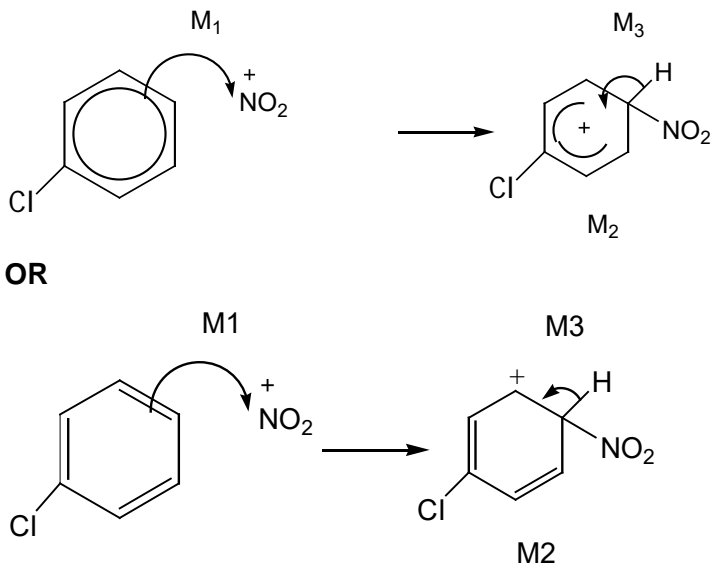
2(d)(iii)	M1	$[H^+] = 10^{-4.00} = 1.00 \times 10^{-4}$	1	Correct answer for mass with or without working scores 5 Allow $1 \times 10^{-4}$ Ignore ( ) here. If $[HX]/[X^-]$ upside down, can score M1 plus M4 for $5.26 \times 10^{-7}$ And M5 for $7.57 \times 10^{-5}$ g  Wrong method, eg using $[H^+]^2$ may only score M1 and M5 for correct multiplication of their M4 by 144 (provided not of obviously wrong substance)
	M2	$[X^-] = \frac{K_a \times [HX]}{[H^+]}$	1	
	M3	$= \frac{6.31 \times 10^{-5} \times 0.0120}{1.00 \times 10^{-4}}$	1	
	M4	$= 7.572 \times 10^{-3}$	1	
	M5	Mass ( $C_6H_5COONa$ ) = $7.572 \times 10^{-3} \times 144 = 1.09$ g or 1.1 g	1	
2(e)	M1	$CO_2$	1	Allow $NO_x$ and $SO_2$ If M1 wrong, no further marks.  Not forms $H_2CO_3$ $H_2SO_3$ $H_2SO_4$ etc OR $H^+$ ions.
	M2	<u>pH (lt) falls/decreases</u>	1	
	M3	mark M2 & M3 independently acidic (gas) <b>OR</b> reacts with alkali(ne solution)/ $OH^-$ <b>OR</b> $CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O$ <b>OR</b> $CO_2 + OH^- \longrightarrow HCO_3^-$	1	

Question	Marking Guidance	Mark	Comments
3(a)(i)	2	1	
3(a)(ii)	0	1	
3(b)(i)	$k = \frac{6.64 \times 10^{-5}}{(4.55 \times 10^{-2}) \times (1.70 \times 10^{-2})^2}$ = 5.05 (range allowed 5.03–5.07)  <u>mol<sup>-2</sup> dm<sup>+6</sup> s<sup>-1</sup></u>	1  1  1	Correct answer for <i>k</i> with or without working scores 2 First mark is for insertion of numbers into a correctly rearranged rate equ , <i>k</i> = etc.  AE (-1) for copying numbers wrongly or swapping two numbers.  Mark units separately, ie only these units but can be in any order.
3(b)(ii)	$8.3 \times 10^{-6}$ (mol dm <sup>-3</sup> s <sup>-1</sup> ) <b>OR</b> if not $8.3 \times 10^{-6}$ , look at their <i>k</i> in 3(b)(i) and if not 5.05 Allow ecf for their (incorrect) $k \times (1.64 \times 10^{-6})$	1	Allow $0.83 \times 10^{-5}$ Ignore units



Question	Marking Guidance	Mark	Comments
4(a)	Hydrogen <u>bond</u> (ing)	1	Allow H bonding. Penalise mention of any other type of bond.
4(b)(i)	Ammonia is a nucleophile Benzene repels nucleophiles	1 1	Allow ammonia has a lone pair. Allow (benzene) attracts/reacts with electrophiles. <b>OR</b> benzene repels electron rich species or lone pairs <b>OR</b> C–Cl bond is short / strong / weakly polar
4(b)(ii)	H <sub>2</sub> /Ni <b>OR</b> H <sub>2</sub> /Pt <b>OR</b> Sn/HCl <b>OR</b> Fe/HCl	1	Ignore dil/conc of HCl Ignore the term 'catalyst'. Allow H <sub>2</sub> SO <sub>4</sub> with Sn and Fe but not conc. Ignore NaOH following correct answer. Not NaBH <sub>4</sub> nor LiAlH <sub>4</sub>

4(b)(iii)	<p><u>conc HNO<sub>3</sub></u></p> <p><u>conc H<sub>2</sub>SO<sub>4</sub></u></p> <p><math>\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-</math></p> <p><b>OR</b> using two equations</p> <p><math>\text{HNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-</math></p> <p><math>\text{H}_2\text{NO}_3^+ \longrightarrow \text{H}_2\text{O} + \text{NO}_2^+</math></p>	<p>1</p> <p>1</p> <p>1</p>	<p>If either or both conc missed can score 1 for both acids</p> <p>Allow 1:1 equation</p> <p><math>\text{HNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^-</math></p>
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4(b)(iv)	<p><u>Electrophilic substitution</u></p>  <p>OR</p>	1	<ul style="list-style-type: none"> <li>Ignore position or absence of Cl in M1 but must be in correct position for M2</li> <li>M1 arrow from within hexagon to N or <u>+ on N</u></li> <li>Allow <math>\text{NO}_2^+</math> in mechanism.</li> </ul> <p>3</p> <ul style="list-style-type: none"> <li>Bond to <math>\text{NO}_2</math> must be to N for structure mark M2</li> <li>Gap in horseshoe must be centered around correct carbon (C1).</li> <li>+ in intermediate not too close to C1 (allow on or “below” a line from C2 to C6).</li> <li>M3 arrow into hexagon unless Kekule.</li> <li>Allow M3 arrow independent of M2 structure.</li> <li>Ignore base removing H in M3</li> <li>+ on H in intermediate loses M2 not M3</li> </ul>
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Question	Marking Guidance	Mark	Comments
5(a)	<p><u>Nucleophilic addition</u></p> <p>M2</p> <p>M1</p> <p>M4 for lp, arrow and H<sup>+</sup></p> <p>M3</p> <p>Allow C<sub>2</sub>H<sub>5</sub><sup>-</sup> for CH<sub>3</sub>CH<sub>2</sub><sup>-</sup></p>	1 4	<ul style="list-style-type: none"> <li>M1 and M4 include lone pair and curly arrow.</li> <li>Allow :CN<sup>-</sup> but arrow must start at lone pair on C</li> <li>M2 not allowed independent of M1, but allow M1 for correct attack on C<sup>+</sup></li> <li>+ rather than δ<sup>+</sup> on C=O loses M2</li> <li>Penalise incorrect partial charges.</li> <li>M3 is for correct structure including minus sign but lone pair is part of M4</li> <li>Penalise extra curly arrows in M4</li> </ul>

5(b)(i)	<p>M1</p> $\begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{CN} \end{array}$ <p>M2</p> $\begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{CN} \end{array} \quad \begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{NC} \end{array}$ <p>Students must <u>show</u> an attempt at mirror images, eg allow</p> $\begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{CN} \end{array} \quad \begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CN} \end{array}$ <p>ie vertical groups same and horizontal swapped as if there was a mirror between them</p> <p>No mirror need be shown</p> <p>Do not penalize wedge bond when wedge comes into contact with both C &amp; N</p>	<p>M1 for correct structure of product of 5(a)</p> <p>1 Allow C<sub>2</sub>H<sub>5</sub>- for CH<sub>3</sub>CH<sub>2</sub>-</p> <p>Penalise wrongly bonded, OH or CN or CH<sub>2</sub>CH<sub>3</sub> once only in clip.</p> <p>1 M2 cannot be gained by simply swapping two or more groups with no attempt to show a mirror image., e.g. do not allow M2 for</p> $\begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{CN} \end{array} \quad \begin{array}{c} \text{CN} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{CH}_2\text{CH}_3 \end{array}$ <p>because these do not <u>show</u> the enantiomers as mirror images.</p> <p>However these two could score M2 if placed as below as if with a "mirror" horizontally between them</p> $\begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CN} \end{array}$ $\begin{array}{c} \text{CN} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{CH}_3 \end{array}$
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5(b)(ii)	M1	(Plane) <u>polarized light</u>	1	M2 only scores following correct M1
	M2	<u>Rotated</u> in <u>opposite</u> directions (equally) (only allow if M1 correct or close)	1	Not just in different directions but allow one rotates light to the left and one to the right. Not molecules rotate.
5(c)	<u>2-hydroxybutane(-1-)nitrile</u>		1	
5(d)	Weak acid / (acid) only slightly / partially dissociated/ionised [CN <sup>-</sup> ] very low		1	Ignore rate of dissociation.
			1	Allow (very) few cyanide ions. Mark independently.
5(e)(i)	$\text{H}_2\text{C}=\text{CH}-\text{CH}_3 + \text{NH}_3 + \frac{3}{2}\text{O}_2 \longrightarrow \text{H}_2\text{C}=\text{CH}-\text{CN} + 3\text{H}_2\text{O}$ <b>OR</b> $\text{H}_2\text{C}=\text{CH}-\text{CH}_3 + \text{NH}_3 + 3\text{O}_2 \longrightarrow \text{H}_2\text{C}=\text{CH}-\text{CN} + 3\text{H}_2\text{O}_2$		1	OR doubled. Allow C <sub>3</sub> H <sub>6</sub> and CH <sub>2</sub> CHCN or C <sub>3</sub> H <sub>3</sub> N on this occasion only.

5(e)(ii)	<p>Must contain, in any order,</p> <p>3 of <math>\begin{array}{c} \text{H} \quad \text{CN} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}</math> or 3 of <math>\begin{array}{c} \text{CN} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}</math> or <math>\left( \begin{array}{c} \text{H} \quad \text{CN} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \right)_3</math></p> <p>and one of <math>\begin{array}{c} \text{H} \quad \text{Cl} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}</math> or <math>\begin{array}{c} \text{Cl} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}</math></p>	1	<p>Ignore n</p> <p>Must show trailing bonds.</p> <p>Do not penalise C—NC bond here on this occasion.</p> <p>allow <math>\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{CN} \end{array}</math> or <math>\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{Cl} \end{array}</math> etc</p> <p>allow <math>-\text{CH}_2\text{CH}(\text{CN})\text{CH}_2\text{CHCl}-</math> etc</p>
5(e)(iii)	Addition (polymerization)	1	<p>Allow self-addition.</p> <p>Do not allow additional.</p>

Question	Marking Guidance	Mark	Comments
6(a)	<u>2,6-diaminohexanoic acid</u>	1	Ignore additional , or – or spaces.
6(b)(i)	$\begin{array}{c} \text{H} \\   \\ \text{H}_3\text{N}^+(\text{CH}_2)_4\text{---C---COOH} \\   \\ \text{NH}_3^+ \end{array} \quad (2\text{Cl}^-)$	1	NB both N must be protonated. Allow $\text{-NH}_3^+$ allow $\text{CO}_2\text{H}$ Allow $\text{-}^+\text{H}_3\text{N}$ Penalise $\text{-C}_4\text{H}_8\text{-}$ here.
6(b)(ii)	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{N}(\text{CH}_2)_4\text{---C---COO}^- \\   \\ \text{NH}_2 \end{array} \quad (\text{Na}^+)$	1	Allow $\text{CO}_2^-$ Allow $\text{-H}_2\text{N}$ Allow $\text{-COONa}$ but penalise $\text{O---Na}$ bond shown.
6(b)(iii)	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{N}(\text{CH}_2)_4\text{---C---COOCH}_3 \\   \\ \text{NH}_2 \end{array}$	1	Allow $\text{CO}_2\text{CH}_3$ Allow $\text{-NH}_3^+$ or $\text{-H}_2\text{N}$



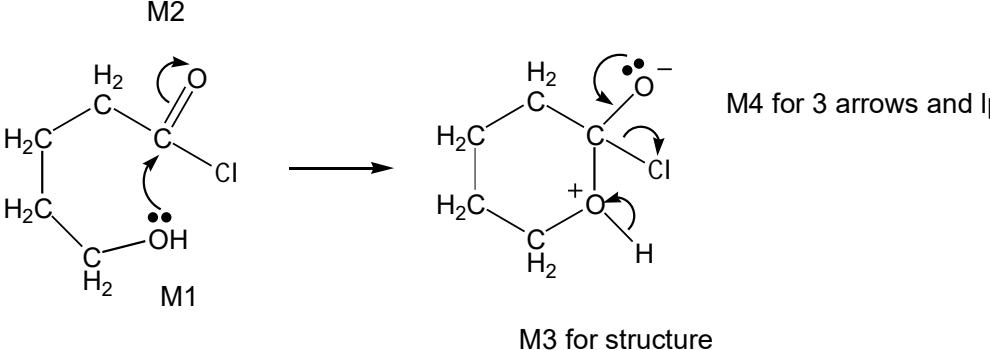
6(c)	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{H}-\text{C}-\text{COOH} \\   \\ \text{NH}_2 \end{array} \right]^+ \bullet \rightarrow \begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}^+ \\   \\ \text{H} \end{array} + \bullet \text{COOH} \quad (1)$	2	<p>1 for <u>displayed formula</u> of fragment ion.</p> <p>1 for molecular ion of alanine AND radical.</p> <p>Allow molecular ion without brackets and fragment ion in brackets with outside +</p> <p>Allow dot anywhere on radical.</p> <p>Allow <math>[\text{C}_3\text{H}_7\text{NO}_2]^+</math> for molecular ion.</p>
6(d)	$\begin{array}{c} \text{H} \qquad \qquad \text{CH}_3 \\   \qquad \qquad   \\ \text{H}_2\text{N}(\text{CH}_2)_4-\text{C}-\text{C}-\text{N}-\text{C}-\text{COOH} \\   \quad \quad \quad    \quad   \quad   \\ \text{NH}_2 \quad \quad \quad \text{O} \quad \text{H} \quad \text{H} \end{array}$ <p><b>OR</b></p> $\begin{array}{c} \text{H} \qquad \qquad (\text{CH}_2)_4\text{NH}_2 \\   \qquad \qquad   \\ \text{CH}_3-\text{C}-\text{C}-\text{N}-\text{C}-\text{COOH} \\   \quad \quad \quad    \quad   \quad   \\ \text{NH}_2 \quad \quad \quad \text{O} \quad \text{H} \quad \text{H} \end{array}$ <p><b>OR</b></p> $\begin{array}{c} \text{H} \qquad \qquad \qquad \qquad \text{H} \\   \qquad \qquad \qquad \qquad   \\ \text{CH}_3-\text{C}-\text{C}-\text{N}-(\text{CH}_2)_4-\text{C}-\text{COOH} \\   \quad \quad \quad \quad \quad   \quad \quad \quad   \\ \text{NH}_2 \quad \quad \quad \quad \quad \text{O} \quad \quad \quad \text{H} \quad \quad \quad \text{NH}_2 \end{array}$	1	<p>Dipeptide, not repeating unit/</p> <p>Allow <math>\text{CO}_2\text{H}</math> Allow <math>-\text{H}_2\text{N}</math></p> <p>Allow <math>-\text{CONH}-</math></p>

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6(e)	M1	In acid lysine has double positive or more positive charge	1	M2 only scores after a correct M1 Ignore greater retention time.
	M2	(Lysine ion) has greater affinity / greater attraction / adheres better / sticks better to polar / stationary phase	1	

Question	Marking Guidance		Mark	Comments
7(a)	M1	Ester 1	1	If Ester 2, can score M3 only.
	M2	peak at $\delta = 4.1$ due to $\begin{array}{c} \text{(H)} \\   \\ \text{(R)-C-O-C-} \\    \quad   \\ \text{O} \quad \text{H} \end{array}$	1	When marking M2 and M3, check any annotation of structures in the stem at the top of the page.
	M3	$(\delta = 4.1$ peak is) quartet as <u>adjacent/next to/attached to CH<sub>3</sub></u>	1	
	M4	Other spectrum quartet at $\delta = 2.1-2.6$ (or value in this range)	1	
7(b)	M1	<u>Quaternary (alkyl) ammonium salt / bromide</u>	1	
	M2	CH <sub>3</sub> Br or bromomethane	1	Penalise contradictory formula and name.
	M3	Excess ( CH <sub>3</sub> Br or bromomethane)	1	Mention of acid eg H <sub>2</sub> SO <sub>4</sub> OR alkali eg NaOH loses both M2 and M3
	M4	Nucleophilic substitution	1	Can only score M3 if reagent correct. Ignore alcohol or ethanol (conditions) or Temp.

7(c)		Bromine (penalise Br but mark on)	Acidified $\text{KMnO}_4$ (Penalise missing acid but mark on)	1	Wrong reagent = no marks. If bromine colour stated it must be red, yellow, orange, brown or any combination, penalise wrong starting colour. Ignore 'clear', 'nothing'. Allow colour fades slowly. Allow 'nvc' for no visible change.
	Benzene	no reaction / colour remains / no (visible) change	no reaction / colour remains / no (visible) change	1	
	cyclohexene	(Bromine) decolourised	(Acidified $\text{KMnO}_4$ ) decolourised	1	

Question	Marking Guidance	Mark	Comments
8(a)(i)	<p>(nucleophilic) <u>addition-elimination</u></p>  <p>M2</p> <p>M1</p> <p>M3 for structure</p> <p>M4 for 3 arrows and lp</p> <p>a 20-50 (ppm) or single value or range entirely within this range</p> <p>b 50-90 (ppm) or single value or range entirely within this range</p>	<p>1</p> <p>4</p> <p>1</p> <p>1</p>	<p>Not electrophilic addition-elimination</p> <p>Ignore esterification</p> <ul style="list-style-type: none"> <li>• If wrong nucleophile used or O–H broken in first step, can only score M2</li> <li>• M2 not allowed independent of M1, but allow M1 for correct attack on C+</li> <li>• + rather than <math>\delta+</math> on C=O loses M2</li> <li>• If Cl lost with C=O breaking lose M2</li> <li>• M3 for correct structure <u>with charges</u> but lone pair on O is part of M4</li> <li>• Only allow M4 after correct / very close M3</li> <li>• Ignore HCl shown as a product</li> </ul> <p>If values not specified as a or b then assume first is a</p>



8(c)	If all the structures are unlabelled, assume that the first drawn ester is L, the second ester is M; the first drawn acid is N, the second P. The cyclic compound should be obvious.	
L ester	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{C}=\text{O} \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array}$ <p><b>OR</b> <math>\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOCH}_3</math></p>	<p>1</p> <p><b>All C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> L to P must have C=C</b></p> <p>Allow CH<sub>3</sub>-</p> <p>Allow -CO<sub>2</sub>CH<sub>3</sub> etc</p> <p>Allow CH<sub>2</sub>C(CH<sub>3</sub>)COOCH<sub>3</sub></p>
M ester	$\begin{array}{ccc} \begin{array}{c} \text{H}_3\text{C} \quad \text{COOCH}_3 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array} & \text{OR} & \begin{array}{c} \text{H}_3\text{C} \quad \text{OOCCH}_3 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array} & \text{OR} & \begin{array}{c} \text{H}_3\text{C} \quad \text{OOCH} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{CH}_3 \end{array} \\ \\ \text{CH}_3\text{CH}=\text{CHCOOCH}_3 & & \text{CH}_3\text{CH}=\text{CHOOCCH}_3 & & \text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{OOCH} \\ \\ \text{OR} & & \text{OR} & & \\ \\ \begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_2\text{OOCH} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array} & & \begin{array}{c} \text{CH}_3\text{CH}_2 \quad \text{OOCH} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array} & & \\ \\ \text{CH}_3\text{CH}=\text{CHCH}_2\text{OOCH} & & \text{CH}_3\text{CH}_2\text{CH}=\text{CHOOCH} & & \end{array}$	<p>1</p> <p>Allow either E-Z isomer.</p> <p>Allow CH<sub>3</sub>- or C<sub>2</sub>H<sub>5</sub>- but not CH<sub>2</sub>CH<sub>3</sub>-</p> <p>Allow CH<sub>3</sub>CHCHCOOCH<sub>3</sub> etc.</p>

<p><b>N</b> acid</p>	$\begin{array}{ccc} \begin{array}{c} \text{H}_3\text{C} \quad \text{COOH} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H}_3\text{C} \quad \text{H} \end{array} & \text{OR} & \begin{array}{c} \text{H} \quad \text{CH}_2\text{COOH} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{CH}_3 \end{array} & \text{OR} & \begin{array}{c} \text{H} \quad \text{COOH} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{CH}_2\text{CH}_3 \end{array} \\ \\ \text{(CH}_3\text{)}_2\text{C}=\text{CHCOOH} & & \text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{COOH} & & \text{H}_2\text{C}=\text{C}(\text{COOH})\text{CH}_2\text{CH}_3 \end{array}$	<p>1</p>	<p>Allow <math>\text{CH}_3-</math> or <math>\text{C}_2\text{H}_5-</math> but not <math>\text{CH}_2\text{CH}_3-</math>  Allow <math>-\text{CO}_2\text{H}</math>  Not cyclic isomers.  Not the optically active isomer</p> $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{C}-\text{CH}_3 \\   \\ \text{H} \\   \\ \text{COOH} \end{array}$ <p>which is P anyway</p> <p>Allow <math>(\text{CH}_3)_2\text{CCHCOOH}</math> etc.</p>
<p><b>P</b> acid</p>	$\begin{array}{c} \text{H}_3\text{C} \quad \text{COOH} \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{CH}=\text{CH}_2 \end{array}$ <p><math>\text{CH}_3\text{CH}(\text{COOH})\text{CH}=\text{CH}_2</math></p>	<p>1</p>	<p>Allow <math>-\text{CO}_2\text{H}</math></p> <p>Allow <math>\text{CH}_3\text{CH}(\text{CO}_2\text{H})\text{CHCH}_2</math> or  <math>\text{CH}_3\text{CH}(\text{CO}_2\text{H})\text{C}_2\text{H}_5</math></p>
<p><b>Q</b></p>	$\begin{array}{ccc} \begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \diagdown \quad / \\ \text{O} \quad \text{C}=\text{O} \\ / \quad \diagdown \\ \text{H}_2\text{C}-\text{CH}_2 \end{array} & \text{OR} & \begin{array}{c} \text{O} \\    \\ \text{C} \\ / \quad \diagdown \\ \text{H}_2\text{C} \quad \text{CH}_3 \\ \diagdown \quad / \\ \text{O} \quad \text{CH}_3 \end{array} & \text{OR} & \begin{array}{c} \text{O} \\    \\ \text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{C} \quad \text{H} \\ \diagdown \quad / \\ \text{H}_3\text{C} \quad \text{O} \quad \text{CH}_3 \end{array} \end{array}$		<p>Not cyclic esters</p>



### General principles applied to marking CHEM4 papers by CMI+ (June 2014)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- Examiners should note that throughout the mark scheme, items that are underlined are required information to gain credit.
- Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.

#### A. The “List principle” and the use of “ignore” in the mark scheme

If a question requires **one** answer and a student gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

NB Certain answers are designated in the mark scheme as those which the examiner should “ignore”. These answers are not counted as part of the list and should be ignored and will not be penalised.

#### B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip. For example, penalise the use of “h” for hydrogen, “CL” for chlorine or “br” for bromine.

#### C. Spelling

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

NB Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the “Quality of Language” (QoL) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

## D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

## E. Reagents

The command word “Identify”, allows the student to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.

For example, **no credit** would be given for

- the cyanide ion or  $\text{CN}^-$  when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or  $\text{OH}^-$  when the reagent should be sodium hydroxide or NaOH;
- the  $\text{Ag}(\text{NH}_3)_2^+$  ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a student provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

## F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

## G. Marking calculations

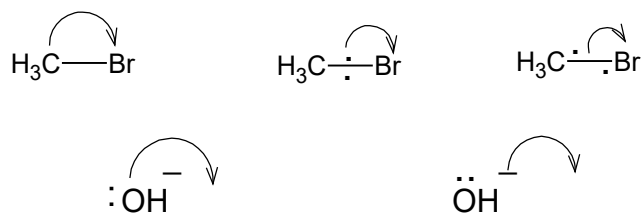
In general

- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

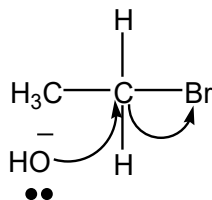
## H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.

**The following representations should not gain credit and will be penalised each time** within a clip.



For example, the following would score zero marks



When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

## I. Organic structures

In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if students show the alcohol functional group as C – HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C – C bonds in alkyl groups, given that CH<sub>3</sub>– is considered to be interchangeable with H<sub>3</sub>C– even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH<sub>2</sub>– C will be allowed, although H<sub>2</sub>N– C would be preferred.
- Poor presentation of vertical C – CH<sub>3</sub> bonds or vertical C – NH<sub>2</sub> bonds should **not** be penalised. For other functional groups, such as – OH and – CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.

By way of illustration, the following would apply.

<b>allowed</b>	<b>allowed</b>	not allowed	not allowed	not allowed
<b>allowed</b>	<b>allowed</b>	<b>allowed</b>	<b>allowed</b>	not allowed

not allowed	not allowed	not allowed	not allowed	not allowed	
not allowed	not allowed	not allowed	not allowed	not allowed	not allowed

- In most cases, the use of “sticks” to represent C – H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C – H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.

- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH<sub>3</sub>COH      for      ethanal

CH<sub>3</sub>CH<sub>2</sub>HO      for      ethanol

OHCH<sub>2</sub>CH<sub>3</sub>      for      ethanol

C<sub>2</sub>H<sub>6</sub>O      for      ethanol

CH<sub>2</sub>CH<sub>2</sub>      for      ethene

CH<sub>2</sub>.CH<sub>2</sub>      for      ethene

CH<sub>2</sub>:CH<sub>2</sub>      for      ethane

NB Exceptions may be made in the context of balancing equations

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

CH<sub>2</sub> = CH<sub>2</sub>      for      ethene, H<sub>2</sub>C=CH<sub>2</sub>

CH<sub>3</sub>CHOHCH<sub>3</sub>      for      propan-2-ol, CH<sub>3</sub>CH(OH)CH<sub>3</sub>

## J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit. Some illustrations are given here.

but-2-ol	should be <b>butan-2-ol</b>
2-hydroxybutane	should be <b>butan-2-ol</b>
butane-2-ol	should be <b>butan-2-ol</b>
2-butanol	should be <b>butan-2-ol</b>
ethan-1,2-diol	should be <b>ethane-1,2-diol</b>
2-methylpropan-2-ol	should be <b>2-methylpropan-2-ol</b>
2-methylbutan-3-ol	should be <b>3-methylbutan-2-ol</b>
3-methylpentan	should be <b>3-methylpentane</b>
3-mythylpentane	should be <b>3-methylpentane</b>
3-methylpentane	should be <b>3-methylpentane</b>
propanitrile	should be <b>propanenitrile</b>
aminethane	should be <b>ethylamine</b> (although aminoethane can gain credit)
2-methyl-3-bromobutane	should be <b>2-bromo-3-methylbutane</b>
3-bromo-2-methylbutane	should be <b>2-bromo-3-methylbutane</b>
3-methyl-2-bromobutane	should be <b>2-bromo-3-methylbutane</b>
2-methylbut-3-ene	should be <b>3-methylbut-1-ene</b>
difluorodichloromethane	should be <b>dichlorodifluoromethane</b>