



General Certificate of Education

Chemistry 2421

**CHEM4 Kinetics, Equilibria and Organic
Chemistry**

Mark Scheme

2010 examination - January series

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

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' 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 to download from the AQA Website: www.aqa.org.uk

Copyright © 2010 AQA and its licensors. All rights reserved.

COPYRIGHT

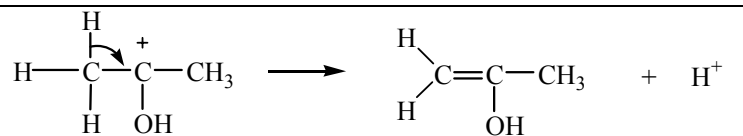
AQA retains the copyright on all its publications. However, registered centres for AQA are permitted to copy material from this booklet for their own internal use, with the following important exception: AQA cannot give permission to centres to photocopy any material that is acknowledged to a third party even for internal use within the centre.

Set and published by the Assessment and Qualifications Alliance.

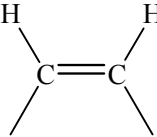
Question	Part	Sub part		Mark	Comments																				
1	(a)	(i)	acid 0.46 alcohol 1.46 water 5.54	1 1 1																					
1	(a)	(ii)	$K_c = \frac{[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]} = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]}$	1	penalise () allow molecular formulae or minor slip in formulae																				
1	(a)	(iii)	$\frac{(0.54/V)(5.54/V)}{(0.46/V)(1.46/V)}$ 4.45 or 4.5 <u>cancel</u> (as equal no of moles on each side of equation) Allow without V	1 1 1	Conseq on values in (a)(i) If values used wrongly or wrong values inserted or wrong Kc no marks for calc Part 1(a)(iii) for info 0.46 × 1.46 = 0.6716 Possible wrong answers <table border="1" data-bbox="1473 901 1989 1013"><tr><td>acid</td><td>0.46</td><td>√</td><td rowspan="3">gives Kc = 3.59 √√</td></tr><tr><td>alcohol</td><td>1.46</td><td>√</td></tr><tr><td>water</td><td>4.46</td><td>X</td></tr></table> <table border="1" data-bbox="1473 1045 1989 1157"><tr><td>acid</td><td>0.46</td><td>√</td><td rowspan="3">gives Kc = 0.434 √√</td></tr><tr><td>alcohol</td><td>1.46</td><td>√</td></tr><tr><td>water</td><td>0.54</td><td>X</td></tr></table>	acid	0.46	√	gives Kc = 3.59 √√	alcohol	1.46	√	water	4.46	X	acid	0.46	√	gives Kc = 0.434 √√	alcohol	1.46	√	water	0.54	X
acid	0.46	√	gives Kc = 3.59 √√																						
alcohol	1.46	√																							
water	4.46	X																							
acid	0.46	√	gives Kc = 0.434 √√																						
alcohol	1.46	√																							
water	0.54	X																							
1	(b)	(i)	decrease or be reduced or fewer	1																					
1	(b)	(ii)	decrease or be reduced or less time or faster or quicker	1																					
1	(b)	(iii)	decrease or be reduced	1																					

Question	Part	Sub part		Mark	Comments
2	(a)	(i)	$-\log[\text{H}^+]$	1	or $\log 1/[\text{H}^+]$ penalise ()
2	(a)	(ii)	$[\text{H}^+] = 0.56$ $[\text{H}_2\text{SO}_4] = \frac{1}{2} \times 0.56 = 0.28$	1 1	mark for the answer; allow 2dp or more
2	(b)	(i)	$\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$ OR $\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$	1	Allow $\text{CH}_3\text{CO}_2\text{H}$ etc
2	(b)	(ii)	$\text{mol acid} = (25.0 \times 10^{-3}) \times 0.41 = 1.025 \times 10^{-2}$ or 1.03×10^{-2} $[\text{NaOH}] = 1.025 \times 10^{-2} / 22.6 \times 10^{-3} = 0.45(4)$ OR $[\text{NaOH}] = 1.03 \times 10^{-2} / 22.6 \times 10^{-3} = 0.456$ or 0.46	1 1	mark for answer if not 0.454 look back for error
2	(b)	(iii)	cresol purple	1	
2	(b)	(iv)	NaOH reacts with <u>carbon dioxide</u> (in the air)	1	
2	(c)	(i)	$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$	1	allow molecular formulae or minor slip in formulae penalise () allow H_3O^+ not allow HA etc

2	(c)	(ii)	$K_a = \frac{[H^+]^2}{[CH_3COOH]}$ <p style="text-align: center;">or with numbers</p> $[H^+] = (\sqrt{(1.74 \times 10^{-5} \times 0.410)} = \sqrt{(7.13 \times 10^{-6})}) = 2.67 \times 10^{-3}$ <p>pH = 2.57</p> <p style="text-align: center;">can give three ticks here for (c)(ii) penalise decimal places < 2 ></p>	1	<p>allow HA etc here This can be scored in part(c)(i) but doesn't score there.</p>
2	(c)	(iii)	<p>M1 mol OH⁻ = (10.0 × 10⁻³) × 0.10 = 1.0 × 10⁻³</p> <p>M2 orig mol HA = (25.0 × 10⁻³) × 0.41 = 0.01025 or 1.025 × 10⁻² or 1.03 × 10⁻²</p> <p>M3 mol HA in buffer = orig mol HA – mol OH⁻ = 0.00925 or 0.0093</p> <p>M4 mol A⁻ in buffer = mol OH⁻ = 1.0 × 10⁻³</p> <p>M5 $[H^+] = \left(\frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} \right) =$ $\frac{(1.74 \times 10^{-5})(0.00925)}{0.0010}$ or $\frac{(1.74 \times 10^{-5})(0.00930)}{0.0010}$ (= 1.61 × 10⁻⁴ or 1.62 × 10⁻⁴)</p> <p>M6 pH = 3.79</p> <p style="text-align: center;">can give six ticks for 3.79</p> <p>NB Unlike Qu 2(c)(ii), this pH mark is NOT awarded conseq to their [H⁺] unless following AE</p>	1 1 1 1 1 1	<p>If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4</p> <p>If A⁻ is wrong, max 3 for M1, M2 and M3 or use of pH = pKa – log [HA]/ [A⁻]</p> <p>Mark is for insertion of correct numbers in correct expression for [H⁺]</p> <p>if [HA]/[A⁻] upside down lose M5 & M6</p> <p>If wrong method e.g. [H⁺]²/[HA] max 3 for M1, M2 and M3</p> <p>Some may calculate concentrations [HA] = 0.264 and [A⁻] = 0.0286 and rounding this to 0.029 gives pH = 3.80 (which is OK)</p> <p>BEWARE: using 0.01025 wrongly instead of 0.00925 gives pH = 3.75 (this gets 3 for M1, M2 & M4)</p>

Question	Part	Sub Part		Mark	Comment
3	(a)		2 or two or second	1	
3	(b)		$k = \frac{1.24 \times 10^{-4}}{(4.40)(0.82)}$ $= 3.44 \times 10^{-5} \quad (\text{min 3sfs})$ $\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	1 1 1	mark is for insertion of numbers into a correctly rearranged rate equ , k = etc if upside down, (or use of I ₂ data) score only units mark any order
3	(c)		no change or no effect or stays the same or 1.24×10^{-4}	1	
3	(d)		1 or 2 or 1 and 2 rate equ doesn't involve I ₂ or only step which includes 2 species in rate equ	1 1	if wrong no further mark but mark on from no answer
3	(e)			1	any second arrow loses the mark

Question	Part	Sub Part		Mark	Comments
4	(a)		<p><u>nucleophilic addition</u></p> <p>M3 for completely correct structure not including lp</p> <p>M4 for lp and arrow</p> <p>2-hydroxy-2-methylpentan(e)nitrile</p>	1 4 1	<p>Attack by HCN loses M1 and M2 M2 not allowed independent of M1, but allow M1 for correct attack on C+ +C=O loses M2 M2 only allowed if correct carbon attacked allow minus charge on N i.e. :CN⁻ allow C₃H₇ in M3</p> <p>allow without – allow 2-hydroxy-2-methylpentanonitrile</p>
4	(b)		<p><u>Product</u> from Q is a racemic mixture/ <u>equal amounts</u> of enantiomers</p> <p>racemic mixture is inactive or inactive explained</p> <p><u>Product</u> from R is inactive (molecule) or has no chiral centre</p>	1 1 1	<p>if no reference to products then no marks; not Q is optically active or has a chiral centre etc</p>
4	(c)	(i)	<p>mark the three sections of Qu 4(c) separately</p> <p>R or CH₃CH₂COCH₂CH₃</p>	1	
4	(c)	(ii)	<p>[CH₃CH₂COCH₂CH₃]⁺ OR [C₅H₁₀O]⁺</p> <p>→ [CH₃CH₂CO]⁺ + ·CH₂CH₃ OR → [C₃H₅O]⁺ + ·C₂H₅</p>	1 1	<p>allow molecular formulae allow without brackets if brackets not shown, allow dot anywhere on radical or + anywhere on ion</p>
4	(c)	(iii)	m/z = 43 or 71	1	

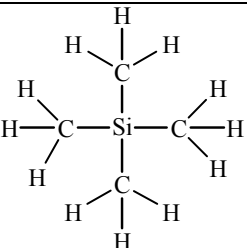
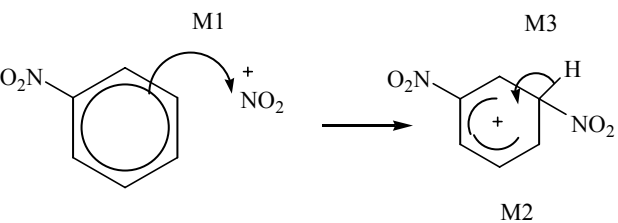
Question	Part	Sub Part		Mark	Question
5	(a)	(i)	propan(e)-1,2,3-triol or 1,2,3- propan(e)triol	1	not propyl ignore hyphen, commas
5	(a)	(ii)	soaps	1	allow anionic surfactant not cationic surfactant not detergents, not shampoos
5	(b)	(i)	(bio) <u>diesel</u>	1	Allow fuel for <u>diesel</u> engines not biofuel, not oils
5	(b)	(ii)		1	ignore anything else attached except any more H atoms.
5	(b)	(iii)	$\text{CH}_3(\text{CH}_2)_{12}\text{COOCH}_3 + 21\frac{1}{2} \text{O}_2 \rightarrow 15\text{CO}_2 + 15 \text{H}_2\text{O}$ OR $\text{C}_{15}\text{H}_{30}\text{O}_2$ or 43/2	1	not allow equation doubled

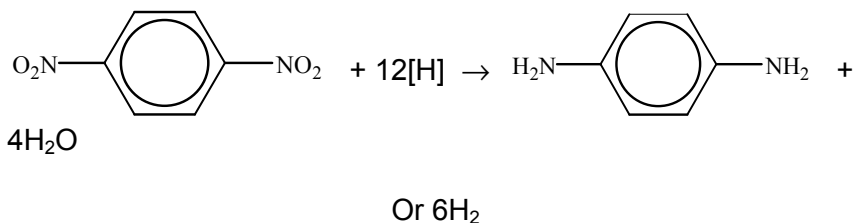
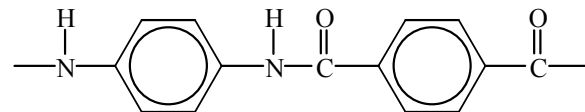
Question	Part	Sub Part		Mark	Comments
6	(a)	(i)	$\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{COO}^- \\ \\ \text{CH}_3 \end{array}$	1	allow $-\text{CO}_2^-$ allow $^+\text{NH}_3-$ don't penalize position of + on NH_3
6	(a)	(ii)	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N} - \text{C} - \text{COO}^- \\ \\ \text{CH}(\text{CH}_3)_2 \end{array}$	1	allow $-\text{CO}_2^-$ allow NH_2- allow C_3H_7
6	(a)	(iii)	$\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{COOH} \\ \\ (\text{CH}_2)_4\text{NH}_3^+ \end{array}$	1	allow $-\text{CO}_2\text{H}$ allow $^+\text{NH}_3-$ don't penalize position of + on NH_3
6	(b)		$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}_2\text{N} - \text{C} - \text{C} - \text{N} - \text{C} - \text{COOH} \\ \quad \quad \quad \\ \text{CH}_3 \quad \quad \quad \text{CH}(\text{CH}_3)_2 \end{array}$ $\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}_2\text{N} - \text{C} - \text{C} - \text{N} - \text{C} - \text{COOH} \\ \quad \quad \quad \\ \text{CH}(\text{CH}_3)_2 \quad \quad \quad \text{CH}_3 \end{array}$	1 1	allow $-\text{CO}_2\text{H}$ allow NH_2- allow C_3H_7 allow as zwitterions if error in peptide link e.g. $\begin{array}{c} \text{O} \quad \quad \text{H} \\ \quad \quad \\ -\text{C} - \text{O} - \text{N}- \end{array}$ if twice, penalise both times not polymers if wrong amino acid in both can score Max 1

6	(c)	chromatography or electrophoresis	1	ignore qualification to chromatography
---	-----	-----------------------------------	---	--

Question	Part	Sub Part		Mark	Comments	
7	(a)		A	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$	1	allow CH_3COCH_3
			B	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{OH} \quad \text{or} \quad \begin{array}{c} \text{OH} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{CH}_3 \end{array}$	1	must show C=C Penalise sticks once per pair
7	(b)		C	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	1	NOT cyclopentane which is only C_5H_{10} Penalise sticks once per pair
			D	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	1	
7	(c)		E	$\text{CH}_3\text{CH}_2\text{COOCH}_3$	1	Allow $\text{C}_2\text{H}_5\text{CO}_2\text{CH}_3$
			F	$\text{CH}_3\text{COOCH}_2\text{CH}_3$	1	Allow $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ Penalise sticks once per pair
7	(d)		G	$\begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_2\text{CH}_2\text{CH}_3 \end{array} \quad \text{OR} \quad \begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{CH}_3 \\ \\ \text{CH}(\text{CH}_3)_2 \end{array} \quad \text{OR} \quad \begin{array}{c} \text{CH}_2\text{CHO} \\ \\ \text{H}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_2\text{CH}_3 \end{array}$	1	not C_5H_{11} nor C_4H_9 Penalise sticks once per pair
			H	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}-\text{COCH}_3 \\ \\ \text{CH}_2\text{CH}_3 \end{array}$ allow C_2H_5	1	

7	(e)	I $\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CH}_2\text{NCH}_2\text{CH}_3 \end{array}$	1	allow C ₂ H ₅
		J $\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{NCH}(\text{CH}_3)_2 \end{array}$	1	NOT C ₃ H ₇ Penalise sticks once per pair

Question	Part	Sub Part		Mark	Comments
(8)	(a)	(i)	W 3 X 4 Y 2	1 1 1	
(8)	(a)	(ii)		1	displayed formula shows ALL bonds
(8)	(b)	(i)	NO_2^+ $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+$ OR $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$	1 1	allow + anywhere can score in equation or use two equations via H_2NO_3^+
(8)	(b)	(ii)	electrophilic substitution  Allow Kekule structures + must be on N of $^+\text{NO}_2$ (which must be correct) both NO_2 must be correctly positioned and bonded to gain M2	1 3	Not Friedel Crafts M1 arrow from circle or within it to N or to + on N horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1 M3 arrow into hexagon unless Kekule allow M3 arrow independent of M2 structure ignore base removing H in M3

8	(c)	(i)	<p>H_2/Ni or H_2/Pt or Sn/HCl or Fe/HCl (conc or dil or neither) allow dil H_2SO_4 ignore mention of NaOH</p> <p>  </p>	1	Not NaBH_4 Not LiAlH_4 Not $\text{Na}/\text{C}_2\text{H}_5\text{OH}$ not conc H_2SO_4 or any HNO_3
8	(c)	(ii)	<p>  </p> <p>1st mark for correct peptide link 2nd mark for the rest correct including trailing bonds</p>	2	allow $-\text{CONH}-$ ignore $[]_n$ as in polymer
8	(c)	(iii)	<p>M1 Kevlar is <u>biodegradeable</u> but polyalkenes not</p> <p>M2 Kevlar has <u>polar</u> bonds / is a (poly) amide / has peptide link</p> <p>M3 can be hydrolysed/attacked by nucleophiles/acids/bases/enzymes</p> <p>M4 polyalkenes <u>non polar</u> /has <u>non-polar</u> bonds</p>	1 1 1 1	allow Kevlar is <u>more</u> biodegradeable comment on structure of Kevlar comment on structure of polyalkenes but not just strong bonds

Question	Part	Sub Part		Mark	Comments
9	(a)		<p>(nucleophilic) addition-elimination</p> <p>M2</p> <p>M3</p> <p>M1</p> <p>M4 for 3 arrows and lp</p> <p><u>N-ethylpropanamide</u></p>	1 4 1	<p>minus on NH₂ loses M1</p> <p>M2 not allowed independent of M1, but</p> <p>allow M1 for correct attack on C+ +C=O loses M2</p> <p>only allow M4 after correct or very close M3</p> <p>lose M4 for Cl⁻ removing H⁺ in mechanism, but ignore HCl as a product</p> <p>Not N-ethylpropaneamide</p>
9	(b)		<p>CH₃CN or ethan(e)nitrile or ethanonitrile</p> <p>for each step wrong or no reagent loses condition mark</p> <p>Step 1 Cl₂ uv or above 300 °C</p> <p>Step 2 KCN</p> <p>aq and alcoholic (both needed)</p> <p>Step 3 H₂/Ni or LiAlH₄ or Na/C₂H₅OH</p>	1 1 1 1 1	<p>not ethanitrile</p> <p>but allow correct formula with ethanitrile</p> <p>contradiction loses mark</p> <p>wrong or no reagent loses condition mark</p> <p>allow uv light / (sun)light / uv radiation</p> <p>not CN⁻ but mark on</p> <p>NOT HCN or KCN + acid, and this loses condition mark</p> <p>NOT NaBH₄ Sn/HCl (forms aldehyde!)</p> <p>ignore conditions</p>