



General Certificate of Education

Chemistry 2421

**CHEM4 Kinetics, Equilibria and Organic
Chemistry**

Mark Scheme

2010 examination - January series

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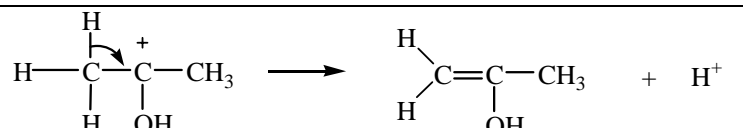
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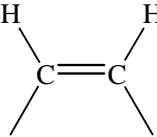
Question	Part	Sub part		Mark	Comments																				
1	(a)	(i)	acid 0.46 alcohol 1.46 water 5.54	1 1 1																					
1	(a)	(ii)	$K_c = \frac{[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]} = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]}$	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
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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> <p>1 mark for 2.67×10^{-3} or 2.7×10^{-3} either gives 2.57</p> <p>1 pH mark conseq on their $[H^+]$</p> <p>so 5.15 gets 2 marks where square root not taken</p>
2	(c)	(iii)	<p>M1 mol $OH^- = (10.0 \times 10^{-3}) \times 0.10 = 1.0 \times 10^{-3}$</p> <p>M2 orig mol HA = $(25.0 \times 10^{-3}) \times 0.41 = 0.01025$ 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 $OH^- = 1.0 \times 10^{-3}$</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 $pH = pK_a - \log [HA]/[A^-]$</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>1 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	

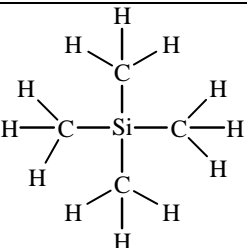
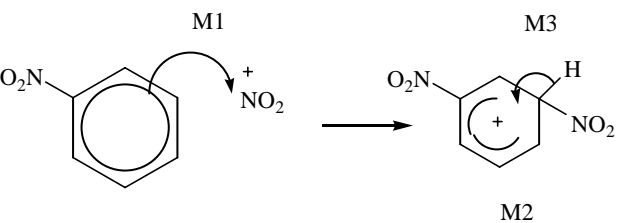
Question	Part	Sub Part		Mark	Question
5	(a)	(i)	propan(e)-1,2,3-triol or 1,2,3- propan(e)triol	1	not propyl ignore hyphen, commas
5	(a)	(ii)	soaps	1	allow anionic surfactant not cationic surfactant not detergents, not shampoos
5	(b)	(i)	(bio) <u>diesel</u>	1	Allow fuel for <u>diesel</u> engines not biofuel, 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

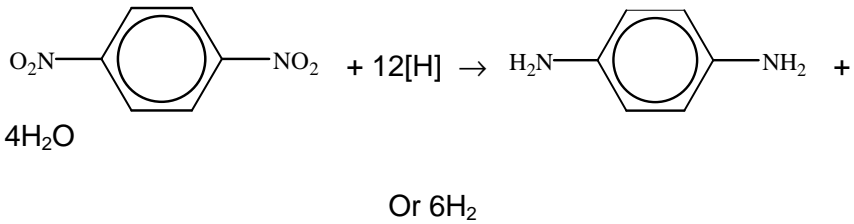
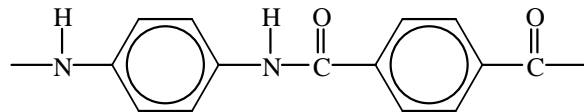
Question	Part	Sub Part		Mark	Comments
6	(a)	(i)	$\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{COO}^- \\ \\ \text{CH}_3 \end{array}$	1	allow $-\text{CO}_2^-$ allow $^+\text{NH}_3-$ don't penalize position of + on NH_3
6	(a)	(ii)	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N} - \text{C} - \text{COO}^- \\ \\ \text{CH}(\text{CH}_3)_2 \end{array}$	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
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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	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}-\text{COCH}_3 \\ \\ \text{CH}_2\text{CH}_3 \end{array}$	1	allow C_3H_7 allow C_3H_7 allow C_2H_5 allow C_2H_5

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>H₂/Ni or H₂/Pt or Sn/HCl or Fe/HCl (conc or dil or neither) allow dil H₂SO₄ ignore mention of NaOH</p>  <p>Or 6H₂</p>	1	<p>Not NaBH₄ Not LiAlH₄ Not Na/C₂H₅OH not conc H₂SO₄ or any HNO₃</p>
8	(c)	(ii)	 <p>1st mark for correct peptide link 2nd mark for the rest correct including trailing bonds</p>	2	<p>allow -CONH- ignore []_n as in polymer</p>
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	<p>allow Kevlar is <u>more</u> biodegradeable</p> <p>comment on structure of Kevlar</p> <p>comment on structure of polyalkenes but not just strong bonds</p>

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>