



**General Certificate of Education (A-level)
June 2011**

Chemistry

CHEM4

(Specification 2420)

**Unit 4: Kinetics, Equilibria and Organic
Chemistry**

Final

Mark Scheme

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 events which all examiners participate in and is the scheme which was used by them in this examination. The standardisation process 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 standardisation each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed and legislated for. If, after the standardisation process, examiners encounter unusual answers which have not been raised 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 from: aqa.org.uk

Copyright © 2011 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.

The Assessment and Qualifications Alliance (AQA) is a company limited by guarantee registered in England and Wales (company number 3644723) and a registered charity (registered charity number 1073334).
Registered address: AQA, Devas Street, Manchester M15 6EX.

Question	Marking Guidance	Mark	Comments
1(a)	C A D	1 1 1	
1(b)(i)	Bromocresol green	1	Allow wrong spellings
1(b)(ii)	Purple to yellow	1	Must have both colours: Purple start – yellow finish

Question	Marking Guidance	Mark	Comments
2(a)(i)	$-\log[\text{H}^+]$	1	penalise missing [] here and not elsewhere
2(a)(ii)	$[\text{H}^+][\text{OH}^-]$	1	Allow () brackets, but must have charges
2(a)(iii)	Mark independently from a(ii) $[\text{H}^+] = 10^{-13.72} = 1.905 \times 10^{-14}$	1	If wrong no further mark
	$K_w = 1.905 \times 10^{-14} \times 0.154 = (2.93 - 2.94) \times 10^{-15}$	1	
2(b)(i)	$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$	1	Must have charges and all brackets, allow () Acid/salt shown must be CH_3COOH not HA and correct formulae needed
2(b)(ii)	In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp For values above 10, allow 3sfs - do not insist on 2 dp		
	$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$	1	Allow HA
	$([\text{H}^+]^2 = 1.75 \times 10^{-5} \times 0.154 = 2.695 \times 10^{-6} = 2.70 \times 10^{-6})$		If $\sqrt{\quad}$ shown but not done gets pH = 5.57 (scores 2)
	$[\text{H}^+] = 1.64 \times 10^{-3}$	1	Allow mark for pH conseq to their $[\text{H}^+]$ here only
	$\text{pH} = 2.78 \text{ or } 2.79$	1	

2(c)(i)	In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp For values above 10, allow 3sfs - do not insist on 2 dp		
	M1 Initially mol OH ⁻ = (10 × 10 ⁻³) × 0.154 and mol HA = (20 × 10 ⁻³) × 0.154 or mol OH ⁻ = 1.54 × 10 ⁻³ and mol HA = 3.08 × 10 ⁻³	1	
	M2 [H ⁺] = K _a $\frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$ or with numbers	1	Allow Henderson Hasselbach $\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$
	M3 mol ethanoic acid left = (mol ethanoate ions) = 1.54 × 10 ⁻³ K _a = [H ⁺] or pH = pK _a scores M1, M2 and M3	1	If either mol acid in mixture or mol salt wrong - max 2 for M1 and M2 Any mention of [H ⁺] ² - max 2 for M1 and M3
	M4 pH (= - log 1.75 × 10 ⁻⁵) = 4.76 or 4.757	1	Not 4.75
	If no subtraction (so mol ethanoic acid in buffer = original mol) pH = 4.46 scores 2 for M1 and M2 If [H ⁺] ² used, pH = 3.02 scores 2 for M1 and M3		

2(c)(ii)	In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp For values above 10, allow 3sfs - do not insist on 2 dp		
	M1 <u>XS mol KOH</u> (= $(20 \times 10^{-3}) \times 0.154$) = 3.08×10^{-3}	1	If no subtraction: max 1 for correct use of volume No subtraction and no use of volume scores zero If wrong subtraction or wrong moles Can only score M2 and M3 for process
	M2 $[\text{OH}^-] = 3.08 \times 10^{-3} \times \frac{10^3}{60} = 0.0513(3)$	1	Mark for dividing their answer to M1 by correct volume (method mark) If no volume or wrong volume or multiplied by volume, max 2 for M1 and M3 process
	M3 $[\text{H}^+] = \frac{10^{-14}}{0.05133}$ (= 1.948×10^{-13} to 1.95×10^{-13}) or pOH = 1.29	1	Mark for K_w divided by their answer to M2 If pOH route, give one mark for $14 - \text{pOH}$
	M4 pH = 12.7(1)	1	Allow 3sf but not 12.70
<p>If no subtraction and no use of volume (pH = 11.79 scores zero)</p> <p>If no subtraction, max 1 for correct use of volume, (60cm³) (pH = 13.01 scores 1)</p> <p>If volume not used, pH = 11.49 (gets 2)</p> <p>If multiplied by vol , pH = 10.27 (gets 2)</p>			

Question	Marking Guidance	Mark	Comments
3(a)	Forward and backward reactions proceeding at equal rate Amount (Conc or moles or proportion) of reactants and products remain constant	1 1	Not “reactants and products have equal conc”

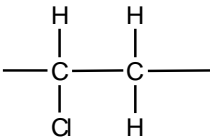
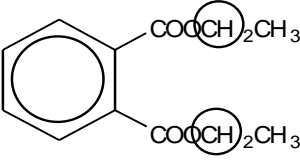
3(b)	M1 $\frac{[R]^2}{[P][Q]^2}$	Allow () but must have all brackets	1	If Kc wrong can only score M3 (process mark) for dividing both R and P by volume)
3(c)	M2 $[Q]^2 = \frac{[R]^2}{K_c[P]}$	Rearrangement of correct Kc expression	1	If wrong Kc used can only score M3 for correct use of vol If wrong rearrangement can only score max 2 for M3 and M5 for correct $\sqrt{\quad}$
	M3 $[Q]^2 = \frac{(5.24/10)^2}{68.0 \times (3.82/10)}$	Process mark for dividing both R and P by volume even in incorrect expression	1	If vol missed can only score max 2 for M2 and M5 for correct $\sqrt{\quad}$ If vol used but then wrong maths can score M2 M3 and M5 for correct $\sqrt{\quad}$ If moles used wrongly, eg (2×5.24) or $(5.24 \times 10/10^3)$ can only score M2 and M5
	M4 $[Q]^2 = 0.0106$	Correct calculation of Q^2	1	
	M5 $[Q] = 0.10(3)$	Correct taking of $\sqrt{\quad}$	1	

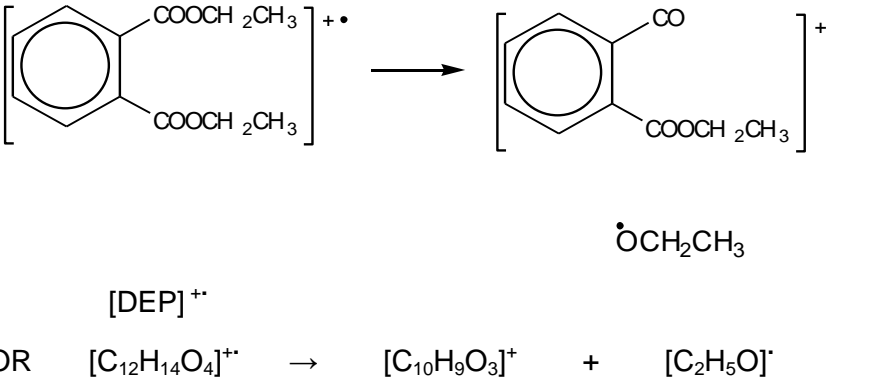
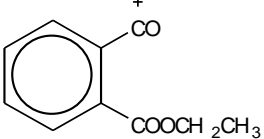
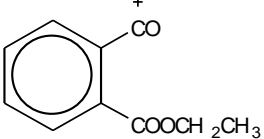
3(c) cont.	Wrong rearrangement and no use of volume	zero	
	Wrong rearrangement	2 max	For Correct use of volume M3 and Correct taking of square root M5
	No use of volume	2 max answer = 0.325 Ignore subsequent multiplying or dividing by 10. 0.0325 or 3.25 still score max 2	For Correct rearrangement M2 and Correct taking of square root M5
	Use of volume but maths error e.g. using (5.24) ² /10 when should be (5.24/10) ²	Scores 3 also giving answer 0.325	for M2, M3 and M5
	Use of volume but Q/10 also used or Q multiplied by 10 at end (i.e.muddling moles with concentration)	2 max Gives answer 1.03	For Correct rearrangement M2 and Correct taking of square root M5
	Wrong use of moles, e.g (5.24 × 2) or (5.24 ×10/10 ³)	2 max	For Correct rearrangement M2 and Correct taking of square root M5
	Wrong Kc used, e.g. missing powers	1 max	For Correct use of volume M3

3(d)	Increase or more or larger	1	Allow moves to left
3(e)	Increase or more or larger	1	Allow moves to left
3(f)	Decrease or less or smaller	1	NOT allow moves left
3(g)	No effect or unchanged or none	1	
3(h)	0.0147 or 0.0148 or 1.47×10^{-2} or 1.48×10^{-2} Allow 0.015 or 1.5×10^{-2} If not 0.0147, look at 3(c) for conseq correct use of their [Q] in new $K_c = 1.39 \times [Q]^2$	1	Not allow just 1/68.0 ignore units

4(b)(i)	<p>(nucleophilic) addition elimination</p> <p>M2</p> <p>M1</p> <p>Not allow N-H₂</p> <p>M3</p> <p>M4 for 3 arrows and lp</p>	1 4	<p>Minus sign on NH₂ loses M1</p> <p>M2 not allowed independent of M1, but allow M1 for correct attack on C+ + rather than δ+ on C=O loses M2</p> <p>If Cl lost with C=O breaking, max 1 for M1</p> <p>M3 for correct structure <u>with charges</u> but lp on O is part of M4</p> <p>only allow M4 after correct/ very close M3</p> <p>For M4, ignore NH₃ removing H⁺ but lose M4 for Cl⁻ removing H⁺ in mechanism, but ignore HCl as a product</p>
4(b)(ii)	<u>N-methylpropanamide</u>	1	Not N-methylpropanamide
4(c)		1	Allow -CONH- or -COHN-
4(d)(i)	<u>2-amino-3-hydroxypropanoic acid</u>	1	

4(d)(ii)	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}-\text{C}-\text{CH}_2\text{COO}^- \\ \\ \text{NH}_2 \end{array} \quad \text{or} \quad \begin{array}{c} \text{COOH} \\ \\ \text{H}-\text{C}-\text{CH}_2\text{COO}^- \\ \\ \text{NH}_2 \end{array} \quad \text{or} \quad \begin{array}{c} \text{COO}^- \\ \\ \text{H}-\text{C}-\text{CH}_2\text{COOH} \\ \\ \text{NH}_2 \end{array}$ <p>Must be salts of aspartic acid</p>	1	allow $-\text{CO}_2^-$ allow NH_2^-
4(d)(iii)	<p>Penalise use of aspartic acid once in d(iii) and d(iv)</p> $\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{COOH} \\ \\ ^+\text{NH}_3 \end{array} \quad (\text{Cl}^-)$	1	allow $-\text{CO}_2\text{H}$ allow $^+\text{NH}_3^-$ don't penalize position of + on NH_3
4(d)(iv)	<p>Penalise use of aspartic acid once in d(iii) and d(iv)</p> $\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{COOH} \\ \\ ^+\text{N}(\text{CH}_3)_3 \end{array} \quad (\text{Br}^-)$	1	allow $-\text{CO}_2^-$ must show C-N bond don't penalize position of + on $\text{N}(\text{CH}_3)_3$

Question	Marking Guidance	Mark	Comments
5(a)	<u>Benzene-1,2-dicarboxylic acid</u>	1	Allow 1,2-benzenedicarboxylic acid
5(b)		1	Must show all bonds including trailing bonds Ignore <i>n</i>
5(c)(i)	2 C ₂ H ₅ OH H ₂ O	1 1	<i>NB Two ethanols</i> <i>but only one water</i>
5(c)(ii)	6 or six	1	
5(c)(iii)		1	Ignore overlap with O to the left or H to the right, but must only include this one carbon. either or allow both (as they are identical)

5(d)	 <p>[DEP]^{+•} OR [C₁₂H₁₄O₄]^{+•} → [C₁₀H₉O₃]⁺ + [C₂H₅O][•]</p>	1 LHS 1 RHS	 <p>Allow + on C or O in </p> <p>Dot must be on O in radical</p>
5(e)(i)	Rate = k[DEP]	1	Must have brackets but can be ()
5(e)(ii)	<p>Any two of</p> <ul style="list-style-type: none"> • experiment repeated/continued <u>over a long period</u> • repeated by independent body/other scientists/avoiding bias • investigate breakdown products • results made public 	2 Max	<p>Not just repetition</p> <p>Ignore animal testing</p>

Question	Marking Guidance	Mark	Comments
6(a)(i)	$k = \frac{6.2 \times 10^{-6}}{(2.9 \times 10^{-2})^2 \times 2.3 \times 10^{-2}}$	1	mark is for insertion of numbers into a correctly rearranged rate equ , k = etc AE (-1) for copying numbers wrongly or swapping two numbers
	= 0.32 (min 2sfs)	1	
	mol ⁻² dm ⁶ s ⁻¹ Units must be conseq to their <i>k</i>	1	Any order If <i>k</i> calculation wrong, allow units conseq to their <i>k</i>
6(a)(ii)	4.95 × 10 ⁻⁵ to 4.97 × 10 ⁻⁵ or 5.0 × 10 ⁻⁵ (min 2 sfs) (ignore units)	1	rate = their <i>k</i> × 1.547 × 10 ⁻⁴
6(b)	Step 2	1	If wrong no further mark
	One H ₂ (and two NO) (appear in rate equation) or species (in step 2) in ratio/proportion as in the rate equation	1	

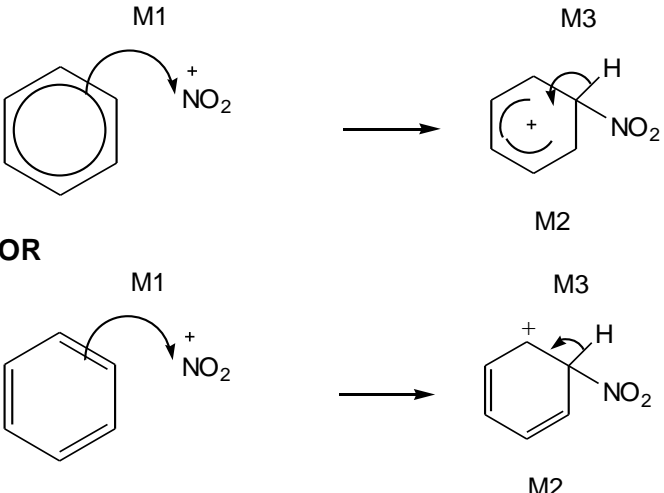
Question	Marking Guidance			Mark	Comments	
7(a)(i)	Single reagent	If wrong single reagent, CE = zero Incomplete single reagent (e.g. carbonate) or wrong formula (e.g. NaCO ₃) loses reagent mark, but mark on For “no reaction” allow “nothing”				
	Different reagents	If different tests on E and F; both reagents and any follow on chemistry must be correct for first (reagent) mark. Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction. Second and third marks are for correct observations. i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.				
		Na ₂ CO ₃ /NaHCO ₃ named carbonate	metal e.g. Mg	named indicator	1	PCl ₅ PCl ₃ SOCl ₂
	E ester	no reaction	no reaction	no effect		1
	F acid	Effervescence or CO ₂	Effervescence or H ₂	acid colour	1	fumes

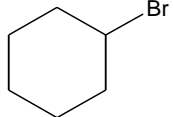
7(a)(ii)	Single reagent	If wrong single reagent, CE = zero Incomplete single reagent (e.g. carbonate) or wrong formula (e.g. NaCO ₃) loses reagent mark, but mark on For “no reaction” allow “nothing”							
	Different reagents	If different tests on E and F; both reagents and any follow on chemistry must be correct for first (reagent) mark. Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction. Second and third marks are for correct observations. i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.							
		AgNO ₃	Na ₂ CO ₃ /NaHCO ₃ named carbonate	water	named indicator	1	Named alcohol	Named amine or ammonia	
	G ketone	no reaction	no reaction	no reaction	no effect		1	no reaction	no reaction
	H Acyl chloride	(white) ppt	Effervescence or CO ₂ or fumes or exothermic	fumes	acid colour		1	Smell or fumes	fumes
Allow iodoform test or Brady's reagent (2,4,dnph) test (both positive for G)									

7(a)(iii)	Single reagent	If wrong single reagent, CE = zero Incomplete single reagent (e.g. carbonate) or wrong formula (e.g. NaCO ₃) loses reagent mark, but mark on For “no reaction” allow “nothing”				
	Different reagents	If different tests on E and F; both reagents and any follow on chemistry must be correct for first (reagent) mark. Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction. Second and third marks are for correct observations. i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.				
		K ₂ Cr ₂ O ₇ / H ⁺	KMnO ₄ / H ⁺	Lucas test (ZnCl ₂ /HCl)	1	Penalise missing H ⁺ but mark on
	J Primary alcohol	goes green	decolourised / goes brown	No cloudiness	1	
	K Tertiary alcohol	no reaction	no reaction	Rapid cloudiness	1	
If uses subsequent tests e.g. Tollens/Fehlings, test must be on product of oxidation						

7(b)(i)	<u>3,3-dimethylbutan-1-ol</u>	1	Allow 3,3-dimethyl-1-butanol
	4	1	
	Triplet or three	1	
7(b)(ii)	<u>2-methylpentan-2-ol</u>	1	Allow 2-methyl-2-pentanol
	5	1	
	Singlet or one or no splitting	1	

Question	Marking Guidance	Mark	Comments
8(a)	M1 Benzene is <u>more stable than cyclohexatriene</u>	1	more stable than cyclohexatriene must be stated or implied If benzene more stable than cyclohexene, then penalise M1 but mark on If benzene less stable: can score M2 only
	M2 Expected ΔH^\ominus hydrogenation of C_6H_6 is $3(-120)$ $= -360 \text{ kJ mol}^{-1}$	1	Allow in words e.g. expected ΔH^\ominus hydrog is three times the ΔH^\ominus hydrog of cyclohexene
	M3 Actual ΔH^\ominus hydrogenation of benzene is 152 kJ mol^{-1} (less exothermic) or 152 kJ mol^{-1} different from expected	1	Ignore energy needed
	M4 Because of delocalisation or electrons spread out or resonance	1	

8(b)	No mark for name of mechanism		
	Conc HNO ₃ Conc H ₂ SO ₄	1 1	If either or both conc missing, allow one; this one mark can be gained in equation
	$2 \text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow 2 \text{HSO}_4^- + \text{NO}_2^+ + \text{H}_3\text{O}^+$ OR $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{HSO}_4^- + \text{NO}_2^+ + \text{H}_2\text{O}$ OR via two equations $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{HSO}_4^- + \text{H}_2\text{NO}_3^+$ $\text{H}_2\text{NO}_3^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}$	1	Allow + anywhere on NO ₂ ⁺
		3	M1 arrow from within hexagon to N or + on N Allow NO ₂ ⁺ in mechanism 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 + on H in intermediate loses M2 not M3

8(c)	If intermediate compound V is wrong or not shown, max 4 for 8(c)			
	M1	 or Cl or chlorocyclohexane or bromocyclohexane	1	Allow M2 and M3 independent of each other
	Reaction 3			
	M2	HBr	1	
	M3	Electrophilic addition	1	Allow M4 and M6 independent of each other If CE e.g. acid conditions, lose M4 and M5
	Reaction 4			
M4	Ammonia if wrong do not gain M5	1		
M5	Excess ammonia or sealed in a tube or under pressure	1		
	M6	Nucleophilic substitution	1	
8(d)	Lone or electron <u>pair on N</u>		1	No marks if reference to “lone pair on N” missing,
	Delocalised or spread into ring in U		1	
	Less available (to accept protons) or less able to donate (to H ⁺)		1	