

Version 1



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

Chemistry

CHEM4

(Specification 2420)

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

Final

Mark Scheme

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CHEM4 Unit 4: Kinetics, Equilibria and Organic Chemistry –June 2011

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

CHEM4 Unit 4: Kinetics, Equilibria and Organic Chemistry –June 2011

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)	1	If wrong no further mark
	$[\text{H}^+] = 10^{-13.72} = 1.905 \times 10^{-14}$ $K_w = 1.905 \times 10^{-14} \times 0.154 = (2.93 - 2.94) \times 10^{-15}$	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		
	$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$ $([\text{H}^+]^2 = 1.75 \times 10^{-5} \times 0.154 = 2.695 \times 10^{-6} = 2.70 \times 10^{-6})$ $[\text{H}^+] = 1.64 \times 10^{-3}$ <p>pH = 2.78 or 2.79</p>	1	Allow HA
		1	If $\sqrt{\quad}$ shown but not done gets pH = 5.57 (scores 2)
		1	Allow mark for pH conseq to their $[\text{H}^+]$ here only

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		

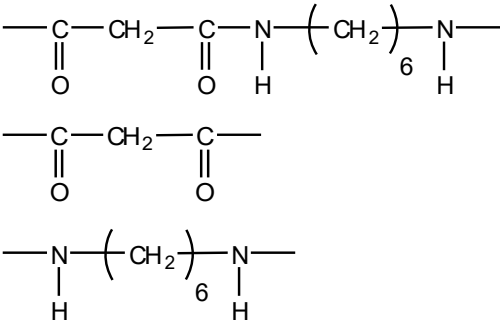
2(c)(ii)	In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp For values above 10, allow 3sfs - do not insist on 2 dp		
	M1 <u>XS mol KOH</u> ($= (20 \times 10^{-3}) \times 0.154$) $= 3.08 \times 10^{-3}$	1	If no subtraction: max 1 for correct use of volume No subtraction and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

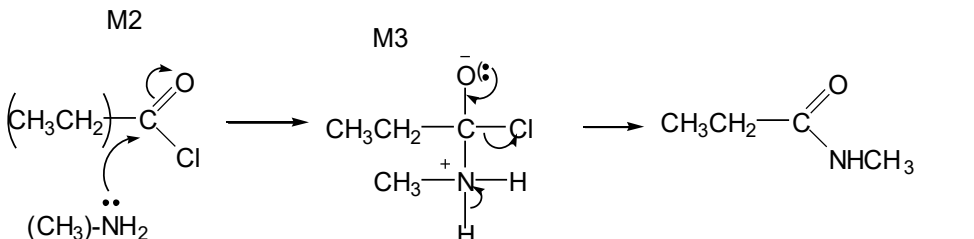
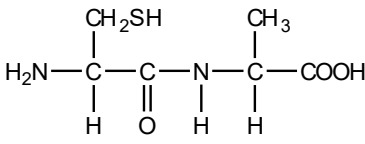
Question	Marking Guidance	Mark	Comments
3(a)	Forward and backward reactions proceeding at equal rate Amount (Conc or moles or proportion) of reactants and products remain constant	1 1	Not "reactants and products have equal conc"

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

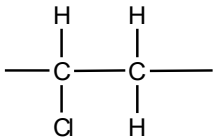
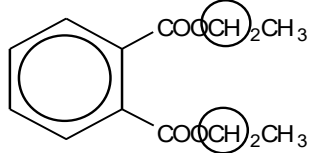
3(d)	Increase or more or larger	1	Allow moves to left
3(e)	Increase or more or larger	1	Allow moves to left
3(f)	Decrease or less or smaller	1	NOT allow moves left
3(g)	No effect or unchanged or none	1	
3(h)	0.0147 or 0.0148 or 1.47×10^{-2} or 1.48×10^{-2} Allow 0.015 or 1.5×10^{-2} If not 0.0147, look 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

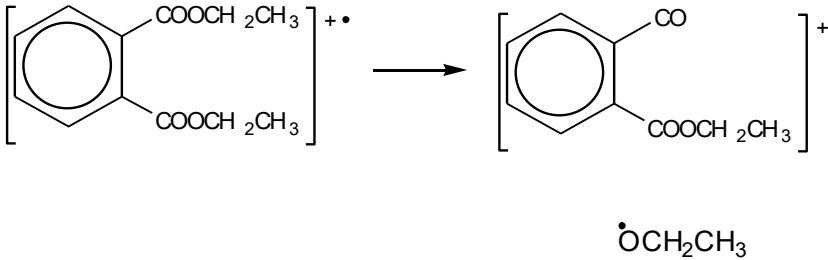
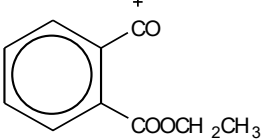
Question	Marking Guidance	Mark	Comments
4(a)(i)		1 1	<p>Allow –CONH- or - COHN -</p> <p>Mark two halves separately</p> <p>lose 1 each for missing trailing bonds at one or both ends or error in peptide link or either or both of H or OH on ends</p> <p>Not allow $-(C_6H_{12})-$</p> <p>Ignore n</p>
4(a)(ii)	<p>M1 in polyamides - H bonding</p> <p>M2 in polyalkenes - van der Waals forces</p> <p>M3 Stronger forces (of attraction) in polyamides Or H bonding is stronger (must be a comparison of correct forces to score M3)</p>	1 1 1	<p>Penalise forces between atoms or van der Waals bonds</p> <p>Do not award if refer to stronger bonds</p>

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

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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 style="text-align: center;">[DEP]^{+•}</p> <p style="text-align: center;">OR [C₁₂H₁₄O₄]^{+•} → [C₁₀H₉O₃]⁺ + [C₂H₅O][•]</p>	<p style="text-align: center;">1 LHS</p> <p style="text-align: center;">1 RHS</p>	<p style="text-align: center;">Allow + on C or O in </p> <p style="text-align: center;">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 k	1	Any order If k calculation wrong, allow units conseq to their k
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 k × 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	

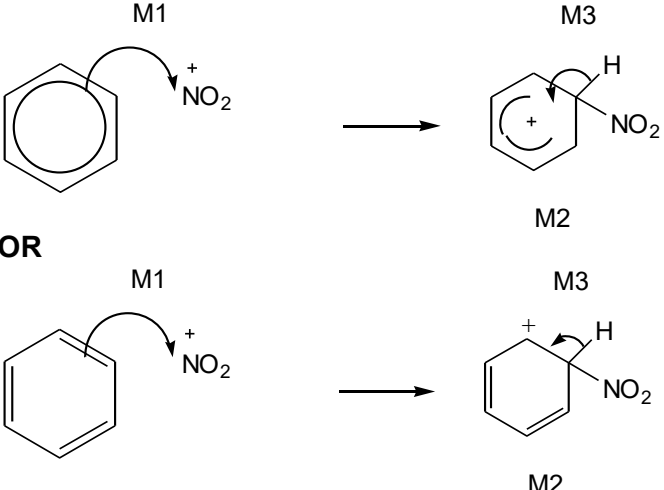
Question	Marking Guidance			Mark	Comments		
7(a)(i)	Single reagent	If wrong single reagent, CE = zero Incomplete single reagent (e.g. carbonate) or wrong formula (e.g. NaCO ₃) loses reagent mark, but mark on For “no reaction” allow “nothing”					
	Different reagents	If different tests on E and F; both 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	No reaction
	F acid	Effervescence or CO ₂	Effervescence or H ₂	acid colour	1	fumes	

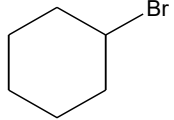
7(a)(ii)	Single reagent	If wrong single reagent, CE = zero Incomplete single reagent (e.g. carbonate) or wrong formula (e.g. NaCO ₃) loses reagent mark, but mark on For “no reaction” allow “nothing”							
	Different reagents	If different tests on E and F; both reagents and any follow on chemistry must 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
	Reaction 3		Allow M2 and M3 independent of each other
	M2	HBr	
	M3	Electrophilic addition	1
	Reaction 4		Allow M4 and M6 independent of each other If CE e.g. acid conditions, lose M4 and M5
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
	Delocalised or spread into ring in U		1
	Less available (to accept protons) or less able to donate (to H ⁺)		1