Version 1

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.

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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)	$-\log[H^+]$	1	penalise missing [ ] here **and not elsewhere**
2(a)(ii)	$[H^+][OH^-]$	1	Allow ( ) brackets, but must have charges
2(a)(iii)	Mark independently from a(ii) $[H^+] = 10^{-13.72} = 1.905 \times 10^{-14}$ $K_w = 1.905 \times 10^{-14} \times 0.154 = = (2.93 - 2.94) \times 10^{-15}$	 1 1	 If wrong no further mark
2(b)(i)	$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$	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**		
	$K_a = \frac{[H^+]^2}{[CH_3COOH]}$ $([H^+]^2 = 1.75 \times 10^{-5} \times 0.154 = 2.695 \times 10^{-6} = 2.70 \times 10^{-6})$ $[H^+] = 1.64 \times 10^{-3}$ pH = 2.78 or 2.79	1 1 1	Allow HA If √ shown but not done gets pH = 5.57 (scores 2) Allow mark for pH conseq to their $[H^+]$ **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 $[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$ or with numbers	1	Allow Henderson Hasselbach $pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$
	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 XS mol KOH (= $(20\times10^{-3}) \times 0.154$) = 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 $[OH^-] = 3.08 \times 10^{-3} \times \frac{10^3}{60} = 0.0513(3)$	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 $[H^+] = \frac{10^{-14}}{0.05133}$ (= 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 – pOH
	M4 pH = 12.7(1)	1	Allow 3sf but not 12.70
	If no subtraction and no use of volume (pH = 11.79 scores zero) If no subtraction, max 1 for correct use of volume, ($60cm^3$) (pH = 13.01 scores 1) If volume not used, pH = 11.49 (gets 2) If multiplied by vol , pH = 10.27 (gets 2)		

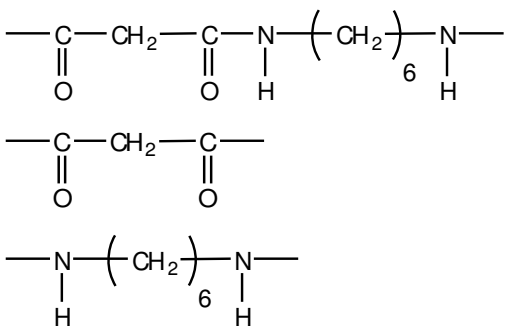
Question	Marking Guidance	Mark	Comments
3(a)	Forward and backward reactions proceeding at equal rate Amount (Conc or moles or proportion) of reactants and products remain constant	1 1	Not “reactants and products have equal conc”

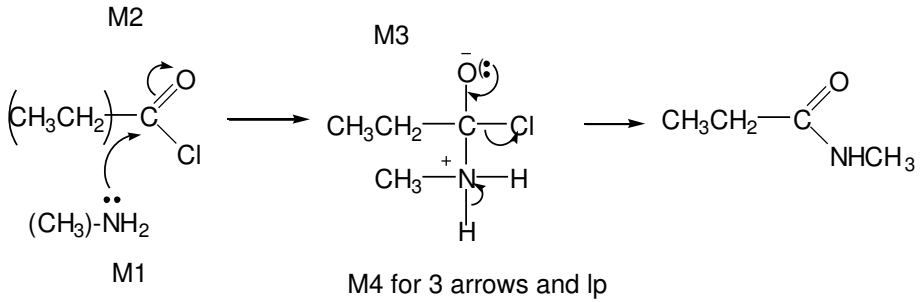
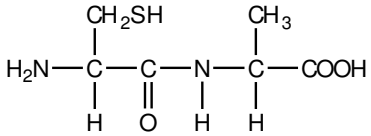
3(b)	**M1** $\frac{[R]^2}{[P][Q]^2}$	Allow ( ) but must have all brackets	1	If Kc wrong can only score **M3** (process mark) for dividing both R and P by volume)

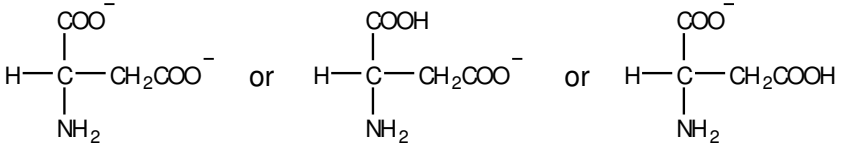
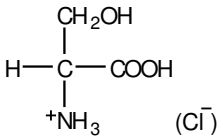
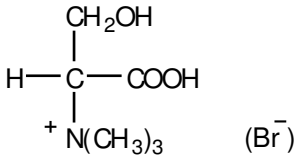
3(c)	**M2** $[Q]^2 = \frac{[R]^2}{K_c[P]}$	Rearrangement of correct Kc expression	1	If wrong Kc used can only score **M3** for correct use of vol If wrong rearrangement can only score max 2 for **M3** and **M5** for correct √
	M3 $[Q]^2 = \frac{(5.24/10)^2}{68.0 \times (3.82/10)}$	Process mark for dividing 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 √ If vol used but then wrong maths can score **M2** **M3** and **M5** for correct √ 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 √	1	

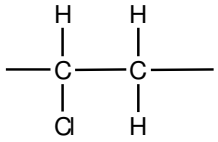
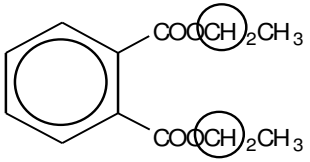
3(c) cont.	Wrong rearrangement and no use of volume	zero	
	Wrong rearrangement	2 max	For Correct use of volume M3 and Correct taking of square root M5
	No use of volume	2 max **answer = 0.325** Ignore subsequent multiplying or dividing by 10. **0.0325 or 3.25** still score max 2	For Correct rearrangement 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 $\times 10/10^3$)	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

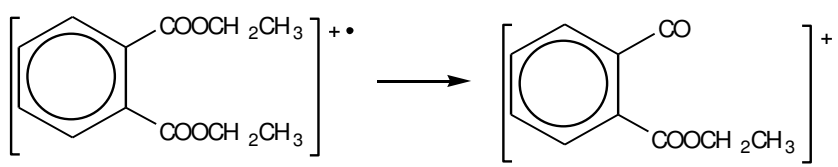
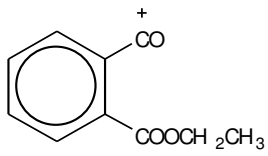
3(d)	Increase or more or larger	1	Allow moves to left
3(e)	Increase or more or larger	1	Allow moves to left
3(f)	Decrease or less or smaller	1	NOT allow moves left
3(g)	No effect or unchanged or none	1	
3(h)	0.0147 or 0.0148 or 1.47×10^{-2} or 1.48×10^{-2} Allow 0.015 or 1.5×10^{-2} If not 0.0147, look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

Question	Marking Guidance	Mark	Comments
4(a)(i)		1 1	Allow –CONH- or - COHN - Mark two halves separately 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 Not allow $-(C_6H_{12})-$ Ignore *n*
4(a)(ii)	**M1** in polyamides - H bonding **M2** in polyalkenes - van der Waals forces **M3** Stronger forces (of attraction) in polyamides Or H bonding is stronger (must be a comparison of correct forces to score M3)	1 1 1	 Penalise forces between atoms or van der Waals bonds Do not award if refer to stronger bonds

4(b)(i)	(nucleophilic) addition elimination  M4 for 3 arrows and lp Not allow N–H_2	1 4	Minus sign on NH_2 loses M1 M2 not allowed independent of M1, but allow M1 for correct attack on C+ + rather than δ+ on C=O loses M2 If Cl lost with C=O breaking, max 1 for M1 M3 for correct structure <u>with charges</u> but lp on O is part of M4 only allow M4 after correct/ very close M3 For M4, ignore NH_3 removing H^+ but lose M4 for Cl^- removing H^+ in mechanism, but ignore HCl as a product
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)	 or or Must be salts of aspartic acid	1	allow $-CO_2^-$ allow NH_2-
4(d)(iii)	Penalise use of aspartic acid once in d(iii) and d(iv) 	1	allow $-CO_2H$ allow $^+NH_3-$ don't penalize position of + on NH_3
4(d)(iv)	Penalise use of aspartic acid once in d(iii) and d(iv) 	1	allow $-CO_2^-$ must show C-N bond don't penalize position of + on $N(CH_3)_3$

Question	Marking Guidance	Mark	Comments
5(a)	Benzene-1,2-dicarboxylic acid	1	Allow 1,2-benzenedicarboxylic acid
5(b)		1	Must show all bonds including trailing bonds Ignore *n*
5(c)(i)	2 C_2H_5OH H_2O	1 1	*NB Two ethanols* *but only one water*
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)	 $\dot{O}CH_2CH_3$ $[DEP]^{+\cdot}$ OR $[C_{12}H_{14}O_4]^{+\cdot} \rightarrow [C_{10}H_9O_3]^{+} + [C_2H_5O]^{\cdot}$	1 LHS 1 RHS	Allow + on C or O in  Dot must be on O in radical
5(e)(i)	Rate = k[DEP]	1	Must have brackets but can be ( )
5(e)(ii)	Any **two** of • 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	Not just repetition Ignore animal testing

Question	Marking Guidance	Mark	Comments
6(a)(i)	$k = \frac{6.2\times10^{-6}}{(2.9\times10^{-2})^2 \times 2.3\times10^{-2}}$	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 $k \times 1.547 \times 10^{-4}$
6(b)	Step 2 One H_2 (and two NO) (appear in rate equation) or species (in step 2) in ratio/proportion as in the rate equation	1 1	If wrong no further mark

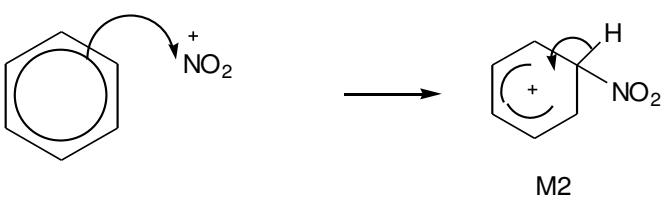
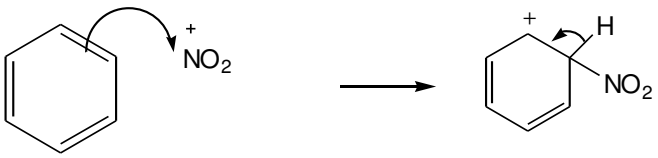
Question	Marking Guidance				Mark	Comments	
7(a)(i)	Single reagent	If wrong single reagent, CE = zero Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on For "no reaction" allow "nothing"					
	Different reagents	If different tests on E and F; **both** 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_2CO_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	

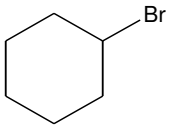
7(a)(ii)	Single reagent	If wrong single reagent, CE = zero Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on **For "no reaction" allow "nothing"**						
	Different reagents	If different tests on E and F; **both** reagents and any follow on chemistry 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_2CO_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)							

<table>
<tr><td rowspan="6">7(a)(iii)</td><td>Single reagent</td><td colspan="6">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”</td></tr>
<tr><td>Different reagents</td><td colspan="6">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.</td></tr>
<tr><td></td><td>$K_2Cr_2O_7$/ H^+</td><td>$KMnO_4$/ H^+</td><td>Lucas test ($ZnCl_2$/HCl)</td><td>1</td><td></td><td>Penalise missing H^+ but mark on</td></tr>
<tr><td>J
Primary alcohol</td><td>goes green</td><td>decolourised / goes brown</td><td>No cloudiness</td><td>1</td><td></td><td></td></tr>
<tr><td>K
Tertiary alcohol</td><td>no reaction</td><td>no reaction</td><td>Rapid cloudiness</td><td>1</td><td></td><td></td></tr>
<tr><td colspan="7">If uses subsequent tests e.g. Tollens/Fehlings, test must be on product of oxidation</td></tr>
</table>

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

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 $\Delta H^{\ominus}$ hydrogenation of C_6H_6 is 3(–120) = –360 kJ mol^{-1}	1	Allow in words e.g. expected $\Delta H^{\ominus}$ hydrog is three times the $\Delta H^{\ominus}$ hydrog of cyclohexene
	M3 Actual $\Delta H^{\ominus}$ 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_2SO_4	1 1	If either or both conc missing, allow one; this one mark can be gained in equation
	$2\ H_2SO_4 + HNO_3 \rightarrow 2\ HSO_4^- + NO_2^+ + H_3O^+$ **OR** $H_2SO_4 + HNO_3 \rightarrow\ HSO_4^- + NO_2^+ + H_2O$ **OR via two equations** $H_2SO_4 + HNO_3 \rightarrow\ HSO_4^- + H_2NO_3^+$ $H_2NO_3^+ \rightarrow\ NO_2^+ + H_2O$	1	Allow + anywhere on NO_2^+
	M1 M3  M2 **OR** M1 M3  M2	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 **M2** HBr **M3** Electrophilic addition	1 1	Allow M2 and M3 independent of each other
	Reaction 4 **M4** Ammonia if wrong do not gain M5 **M5** Excess ammonia or sealed in a tube or under pressure **M6** Nucleophilic substitution	1 1 1	Allow M4 and M6 independent of each other If CE e.g. acid conditions, lose M4 and M5
8(d)	Lone or electron pair on N Delocalised or spread into ring in U Less available (to accept protons) or less able to donate (to H^+)	1 1 1	No marks if reference to "lone pair on N" missing,

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