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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.

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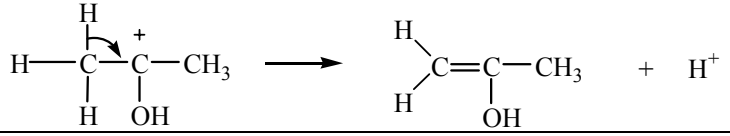
Dr Michael Cresswell Director General

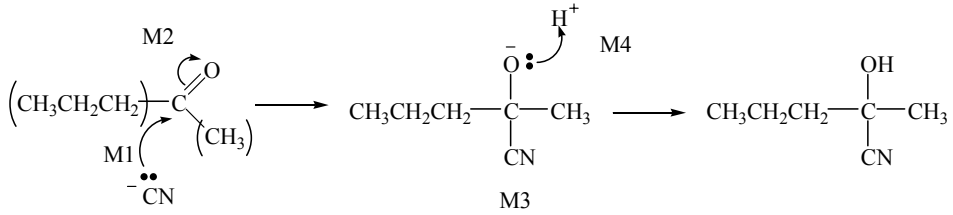
Question	Part	Sub part		Mark	Comments
1	(a)	(i)	acid 0.46 alcohol 1.46 water 5.54	1 1 1	
1	(a)	(ii)	$K_c = \frac{[CH_3CH_2COOCH_2CH_3][H_2O]}{[CH_3CH_2COOH][CH_3CH_2OH]} = \frac{[ester][water]}{[acid][alcohol]}$	1	penalise ( ) allow molecular formulae or minor slip in formulae
1	(a)	(iii)	$\frac{(0.54/V)(5.54/V)}{(0.46/V)(1.46/V)}$ Allow without V 4.45 or 4.5 <u>cancel</u> (as equal no of moles on each side of equation)	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 acid 0.46 √ / alcohol 1.46 √ / water 4.46 X → gives Kc = 3.59 √√ acid 0.46 √ / alcohol 1.46 √ / water 0.54 X → gives Kc = 0.434 √√
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	

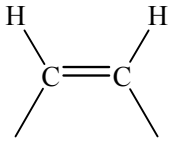
Question	Part	Sub part		Mark	Comments
2	(a)	(i)	$-\log[H^+]$	1	or $\log 1/[H^+]$ penalise ( )
2	(a)	(ii)	$[H^+] = 0.56$ $[H_2SO_4] = ½ \times 0.56 = 0.28$	1 1	mark for the answer; allow 2dp or more
2	(b)	(i)	$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ ***OR*** $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$	1	Allow CH_3CO_2H etc
2	(b)	(ii)	mol acid = $(25.0 \times 10^{-3}) \times 0.41 = 1.025 \times 10^{-2}$ or 1.03×10^{-2} $[NaOH] = 1.025 \times 10^{-2} / 22.6 \times 10^{-3} = 0.45(4)$ ***OR*** $[NaOH] = 1.03 \times 10^{-2} / 22.6 \times 10^{-3} = 0.456$ 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)	$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ allow molecular formulae or minor slip in formulae	1	penalise ( ) allow H_3O^+ not allow HA etc

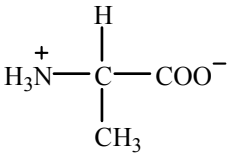
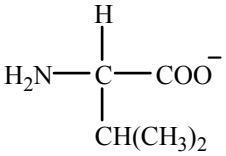
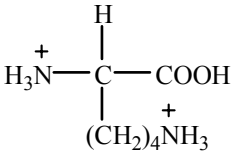
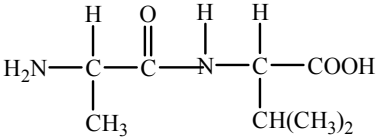
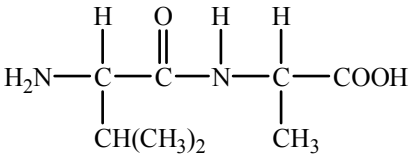
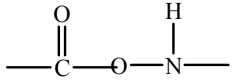
2	(c)	(ii)	$K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers $[H^+] = (\sqrt{(1.74 \times 10^{-5} \times 0.410)} = \sqrt{(7.13 \times 10^{-6})}) = 2.67 \times 10^{-3}$ pH = 2.57 can give three ticks here for (c)(ii) penalise decimal places < 2 >	1 1 1	allow HA etc here This can be scored in part(c)(i) but doesn't score there. mark for 2.67×10^{-3} or 2.7×10^{-3} either gives 2.57 pH mark conseq on their $[H^+]$ so 5.15 gets 2 marks where square root not taken

2	(c)	(iii)	**M1** mol OH^- = $(10.0 \times 10^{-3}) \times 0.10 = 1.0 \times 10^{-3}$ **M2** orig mol HA = $(25.0 \times 10^{-3}) \times 0.41 = 0.01025$ or 1.025×10^{-2} or 1.03×10^{-2} **M3** mol <u>HA</u> in buffer = orig mol HA – mol OH^- = 0.00925 or 0.0093 **M4** mol A^- in buffer = mol OH^- = 1.0×10^{-3} **M5** $[H^+] = (\frac{Ka \times [CH_3COOH]}{[CH_3COO^-]} =)$ $\frac{(1.74 \times 10^{-5})(0.00925)}{0.0010}$ or $\frac{(1.74 \times 10^{-5})(0.00930)}{0.0010}$ $(= 1.61 \times 10^{-4}$ or $1.62 \times 10^{-4})$ **M6** pH = 3.79 can give six ticks for 3.79 NB Unlike Qu 2(c)(ii), this pH mark is NOT awarded conseq to their $[H^+]$ unless following AE	1 1 1 1 1 1	If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4 If A^- is wrong, max 3 for M1, M2 and M3 or use of pH = pKa – log [HA]/ $[A^-]$ Mark is for insertion of correct numbers in correct expression for $[H^+]$ if [HA]/[A^-] upside down lose M5 & M6 If wrong method e.g. $[H^+]^2/[HA]$ max 3 for M1, M2 and M3 Some may calculate concentrations [HA] = 0.264 and $[A^-]$ = 0.0286 and rounding this to 0.029 gives pH = 3.80 (which is OK) BEWARE: using 0.01025 wrongly instead of 0.00925 gives pH = 3.75 (this gets 3 for M1, M2 & M4)

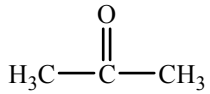
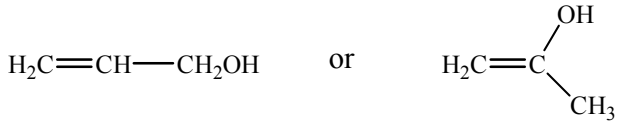
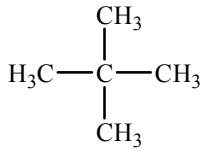
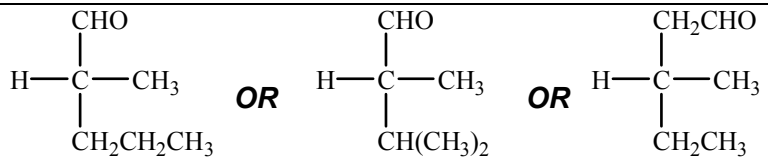
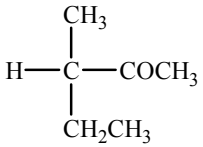
Question	Part	Sub Part		Mark	Comment
3	(a)		2 or two or second	1	
3	(b)		$k = \frac{1.24 \times 10^{-4}}{(4.40)(0.82)}$ $= 3.44 \times 10^{-5}$ (min 3sfs) $mol^{-1}dm^3s^{-1}$	1 1 1	mark is for insertion of numbers into a correctly rearranged rate equ , k = etc if upside down, (or use of I_2 data) score 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

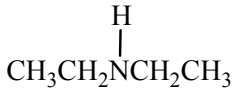
Question	Part	Sub Part		Mark	Comments
4	(a)		nucleophilic addition  M3 for completely correct structure not including lp M4 for lp and arrow 2-hydroxy-2-methylpentan(e)nitrile	1 4 1	Attack by HCN loses M1 and M2 M2 not allowed independent of M1, but allow M1 for correct attack on C+ +C=O loses M2 M2 only allowed if correct carbon attacked allow minus charge on N i.e. $:CN^-$ allow C_3H_7 in M3 allow without – allow 2-hydroxy-2-methylpentanonitrile
4	(b)		Product from **Q** is a racemic mixture/ equal amounts of enantiomers racemic mixture is inactive or inactive explained Product from **R** is inactive (molecule) or has no chiral centre	1 1 1	if no reference to products then no marks; not **Q** is optically active or has a chiral centre etc
4	(c)	(i)	**mark the three sections of Qu 4(c) separately** **R** or $CH_3CH_2COCH_2CH_3$	1	
4	(c)	(ii)	$[CH_3CH_2COCH_2CH_3]^{+\cdot}$ ***OR*** $[C_5H_{10}O]^{+\cdot}$ $\rightarrow$ $[CH_3CH_2CO]^+ + {}^{\cdot}CH_2CH_3$ ***OR*** $\rightarrow$ $[C_3H_5O]^+ + {}^{\cdot}C_2H_5$	1 1	allow molecular formulae allow without brackets if brackets not shown, allow dot anywhere on radical or + anywhere on ion
4	(c)	(iii)	m/z = 43 or 71	1	

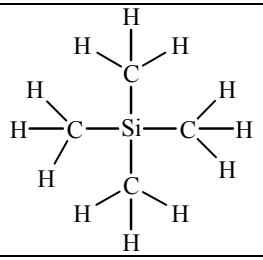
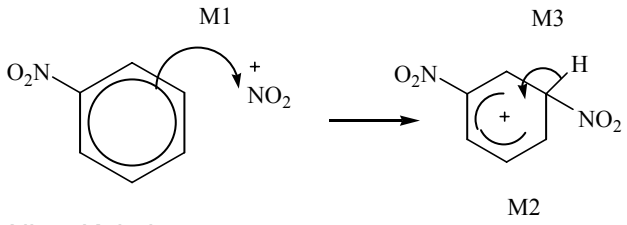
Question	Part	Sub Part		Mark	Question
5	(a)	(i)	propan(e)-1,2,3-triol or 1,2,3- propan(e)triol	1	not propyl ignore hyphen, commas
5	(a)	(ii)	soaps	1	allow anionic surfactant not cationic surfactant not detergents, not shampoos
5	(b)	(i)	(bio)<u>diesel</u>	1	Allow fuel for <u>diesel</u> engines not biofuel, not oils
5	(b)	(ii)		1	ignore anything else attached except any more H atoms.
5	(b)	(iii)	$CH_3(CH_2)_{12}COOCH_3 + 21½\ O_2 \rightarrow 15CO_2 + 15\ H_2O$ ***OR*** $C_{15}H_{30}O_2$ or 43/2	1	**not** allow equation doubled

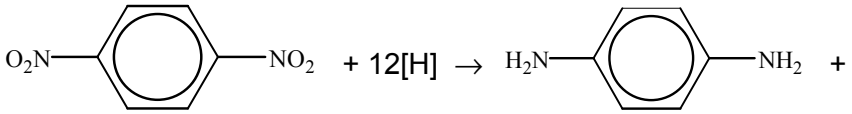
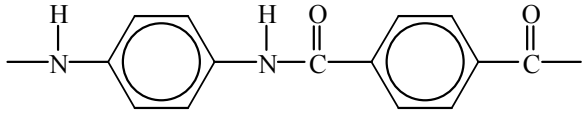
Question	Part	Sub Part		Mark	Comments
6	(a)	(i)		1	allow $-CO_2^-$ allow $^+NH_3-$ don't penalize position of + on NH_3
6	(a)	(ii)		1	allow $-CO_2^-$ allow NH_2- allow C_3H_7
6	(a)	(iii)		1	allow $-CO_2H$ allow $^+NH_3-$ don't penalize position of + on NH_3
6	(b)		 	1 1	allow $-CO_2H$ allow NH_2- allow C_3H_7 allow as zwitterions if error in peptide link e.g.  if twice, penalise both times not polymers if wrong amino acid in both can score Max 1

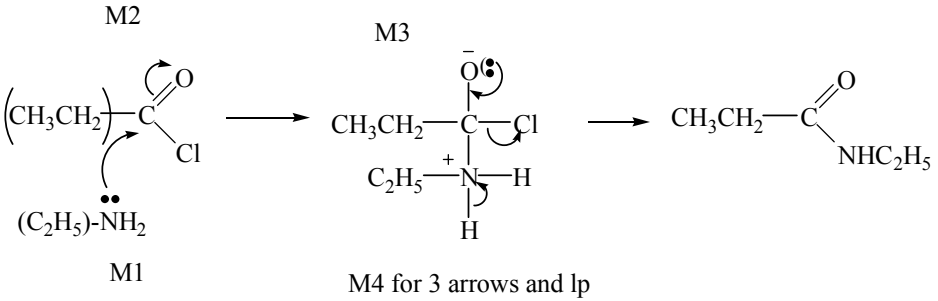
6	(c)		chromatography or electrophoresis	1	ignore qualification to chromatography

Question	Part	Sub Part		Mark	Comments
7	(a)		A 	1	allow CH_3COCH_3
			B 	1	must show C=C Penalise sticks once per pair
7	(b)		C $CH_3CH_2CH_2CH_2CH_3$	1	
			D 	1	NOT cyclopentane which is only C_5H_{10} Penalise sticks once per pair
7	(c)		E $CH_3CH_2COOCH_3$	1	Allow $C_2H_5CO_2CH_3$
			F $CH_3COOCH_2CH_3$	1	Allow $CH_3CO_2CH_2CH_3$ or $CH_3CO_2C_2H_5$ Penalise sticks once per pair
7	(d)		G  allow C_3H_7 allow C_3H_7 allow C_2H_5	1	not C_5H_{11} nor C_4H_9 Penalise sticks once per pair
			H  allow C_2H_5	1	

7	(e)		I 	1	allow C_2H_5
			J 	1	NOT C_3H_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^+ $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$ ***OR*** $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$	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 $^+NO_2$ (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)	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  $4H_2O$ Or $6H_2$	1 1	Not $NaBH_4$ Not $LiAlH_4$ Not Na/C_2H_5OH not conc H_2SO_4 or any HNO_3 allow $C_6H_4(NO_2)_2$ etc , allow NO_2– NH_2– i.e. be lenient on structures, the mark is for balancing equ
8	(c)	(ii)	 1st mark for correct peptide link 2nd mark for the rest correct including trailing bonds	 2	allow –CONH- ignore [ ]n as in polymer
8	(c)	(iii)	**M1** Kevlar is <u>biodegradeable</u> but polyalkenes not **M2** Kevlar has <u>polar</u> bonds / is a (poly) amide / has peptide link **M3** can be hydrolysed/attacked by nucleophiles/acids/bases/enzymes **M4** polyalkenes <u>non polar</u> /has <u>non-polar</u> bonds	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)		(nucleophilic) addition-elimination	1	
			 M4 for 3 arrows and lp	4	minus on NH_2 loses M1 M2 not allowed independent of M1, but allow M1 for correct attack on C+ +C=O loses M2 only allow M4 after correct or very close M3 lose M4 for Cl^- removing H^+ in mechanism, but ignore HCl as a product
			<u>N-ethylpropanamide</u>	1	Not N-ethylpropaneamide
9	(b)		CH_3CN or ethan(e)nitrile or ethanonitrile	1	not ethanitrile but allow correct formula with ethanitrile
			for each step wrong or no reagent loses condition mark	1	contradiction loses mark
			Step 1 Cl_2		
			uv or above 300 ^oC	1	wrong or no reagent loses condition mark
			Step 2 KCN	1	
			aq and alcoholic (both needed)	1	allow uv light / (sun)light / uv radiation
			Step 3 H_2/Ni or $LiAlH_4$ or Na/C_2H_5OH	1	not CN^- but mark on NOT HCN or KCN + acid, and this loses condition mark NOT $NaBH_4$ Sn/HCl (forms aldehyde!) ignore conditions