AQA Qualifications

A-LEVEL

Chemistry

CHEM4 Kinetic, Equilibria and Organic Chemistry

Mark scheme

2420
June 2016

Version: 1.0 Final

Mark schemes are prepared by the Lead Assessment Writer 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 associates participate in and is the scheme which was used by them in this examination. The standardisation process ensures that the mark scheme covers the students' responses to questions and that every associate understands and applies it in the same correct way. As preparation for standardisation each associate analyses a number of students' scripts: alternative answers not already covered by the mark scheme are discussed and legislated for. If, after the standardisation process, associates encounter unusual answers which have not been raised they are required to refer these to the Lead Assessment Writer.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of students' 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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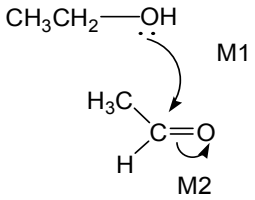
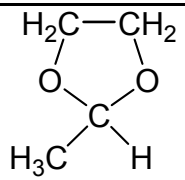
Question	Answers	Mark	Additional Comments/Guidance	ID detail
1a	$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ OR $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$	1	Must show ⇌ allow CH_3CO_2H, $CH_3CO_2^-$ Ignore state symbols	
1b	$CH_3COOH + \underline{HNO_3} \rightarrow CH_3COOH_2^+ + NO_3^-$	1	Ignore ⇌ Allow CH_3CO_2H, $CH_3CO_2H_2^+$, $CH_3C^+(OH)_2$	

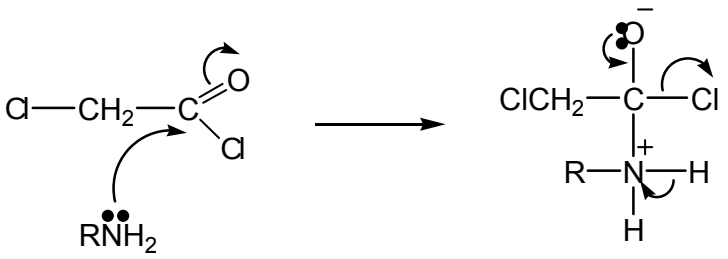
1c(i) marked with 1c(ii)	(new $[HNO_3] = [H^+] = \frac{100}{150} \times 0.0125$) M1 $[H^+] = 8.3(3) \times 10^{-3}$ (mol dm^{-3}) M2 pH = –log M1 OR 2.08	 1 1	OR new $[HNO_3] = \frac{\text{mol } HNO_3}{\text{total vol}} = \frac{1.25 \times 10^{-3}}{150 \times 10^{-3}}$ Must be 2 dp Allow correct pH conseq to their $[H^+]$ concentration	
1c(ii) marked with 1c(i)	M1 mol NaOH (= $50 \times 10^{-3} \times 0.0108$) = 5.40×10^{-4} M2 Subtraction of M1 from moles of HNO_3 (1.25×10^{-3} or conseq from 1c(i)) Excess mol $H^+ = 7.10 \times 10^{-4}$ M3 $[H^+] = \frac{M2}{150 \times 10^{-3}}$ OR $\frac{7.10 \times 10^{-4}}{150 \times 10^{-3}} = 4.73 \times 10^{-3}$ M4 pH = –log M3 OR 2.32	1 1 1 1	 M2 allow ecf for subtraction of mol **If no subtraction, no further marks** M3 **if no use of volume, no further marks (**pH=3.15) If incorrect volume used, can score M4 M4 Allow 2.33 Must be 2 dp	

1d(i)	M1 $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ M2 $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers or with HA M3 $[H^+] = [\sqrt{(1.74 \times 10^{-5} \times 0.0125)}] = 4.66 \times 10^{-4}$ M4 pH = 3.33	1 1 1 1	penalise ( ) once here Not [H+][A-] / [HA] if K_a expression wrong – Allow correct pH conseq to their $[H^+]$ concentration M4 only mark for answer Must be 2 dp Allow correct pH conseq to their $[H^+]$ concentration (pH = 3.83 can score M1, M2 and M4)	
G 1d(ii)	<u>sodium ethanoate</u>	1	Ignore formula allow sodium acetate	
1d(iii)	M1 $[H^+] = 1.45 \times 10^{-5}$ M2 $\frac{[salt]}{[acid]}$ (OR $\frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{Ka}{[H^+]} = \frac{1.74 \times 10^{-5}}{1.45 \times 10^{-5}}$) M3 1.2(0)	1 1 1	Accept 1.445×10^{-5} or 1.4×10^{-5} If M1 incorrect CE=0 Inclusion of 0.0125 in calculation can only score M1 ignore units 1.4×10^{-5} gives 1.24	
1e	M1 (Electronegative) chlorine withdraws electrons M2 Stabilises/reduces charge on COO- **OR** weakens <u>O-H</u> bond **OR** makes <u>O-H</u> more polar	1 1	Allow Cl has negative inductive effect Ignore chloroethanoic acid dissociates more readily Mark independently	

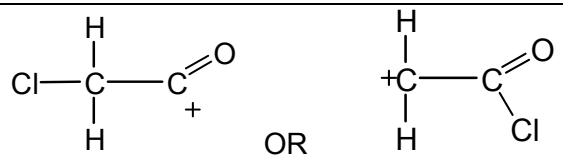
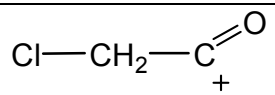
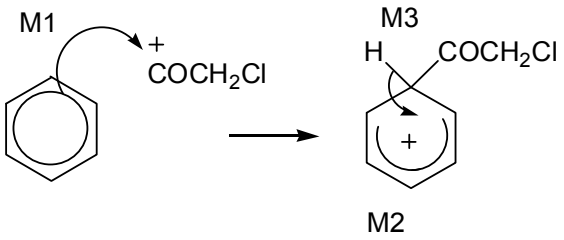
1f	M1	Strong acids (almost) completely dissociated/ionised **OR** not an equilibrium **OR** equilibrium lies <u>far</u> to the right	1 1	Cannot have $\underline{K_a}$ value for a reaction not in equilibrium scores both marks	
	M2	$\underline{K_a}$ value for strong acids tends to infinity/is very large **OR** can't divide by zero in $\underline{K_a}$			
Total			**20**		

Question	Answers	Mark	Additional Comments/Guidance	ID details
G 2a(i)	<u>Nucleophilic addition</u>	1	any extra loses the mark allow minor spelling errors e.g. nucleophyllic	
2a(ii)		1 1	M1 for arrow from lone pair on oxygen in ethanol to C of C=O (or to space half way between O and C) M2 for arrow from C=O bond to oxygen in ethanal Do not allow M2 as first step without nucleophilic attack, but can allow M1 for attack on C+ produced + rather than δ+ on C=O loses M2 Ignore any further steps Mark independently	
2b(i)	<u>Equal</u> mixture of enantiomers/optical isomers OWTTE	1		
2b(ii)	(non-superimposable) mirror images	1	Ignore rotates light in opposite directions Ignore stereoisomers	

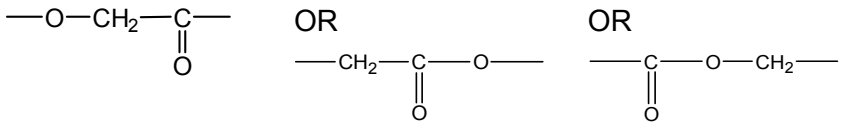
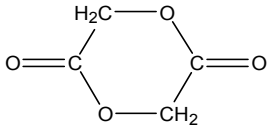
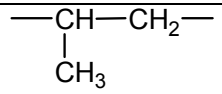
2c(i)	Ethan**al** 0.33 Ethan**ol** 4.16	1 1	 Allow 4.2 for ethanol	
2c(ii)	$K_c = \frac{[acetal][H_2O]}{[CH_3CHO][CH_3CH_2OH]^2}$ or with names $\frac{(0.37/0.31)(0.65/0.31)}{(0.58/0.31)(3.76/0.31)^2}$ **OR** $\frac{(0.37)(0.65)}{(0.58)(3.76)^2} \times 0.31$ 9.1×10^{-3} $mol^{-1}dm^3$	M1 M2 M3 M4	Ignore slips in acetal structure or formula $C_6H_{14}O_2$ If K_c wrong, allow M4 only for units conseq to their K_c If volume omitted (gives 2.93×10^{-2}) may only score M1 and M4 If volume used = 310 cm^3 allow M2 then award M3 for 9.08 – 9.23 only and M4 for $mol^{-1}cm^3$ only Treat error in converting 310 cm^3 to dm^3 as AE Allow range 9.08×10^{-3} – 9.23×10^{-3} Not $moles^{-1}dm^3$	
2d		1		
Total		**12**		

Question	Answers	Mark	Additional Comments/Guidance	
3a(i)	(2-)chloroethan (-1-) oyl chloride	1	2 not required but penalise 1- or other numbers at start. Ignore 1 in ethanoyl Ignore hyphens, commas, spaces	
3a(ii)		4	M1 for arrow from lp on N to C (or to space half way between N and C) If full amine drawn, ignore slips except in $-NH_2$ M2 for arrow from C=O bond to O Not score M2 as an independent first step, but can allow M1 for attack on C+ produced If Cl lost at this stage, Max 1 for M1 M3 for structure of ion including 2 charges M4 for 3 arrows and lp on O - may be scored in two steps Ignore use of RNH_2 to remove H+ in M4, but penalise use of Cl^-	
3b **G**	nucleophilic substitution	1	allow minor spelling errors e.g. nucleophyllic	
3c **A**	9	1		

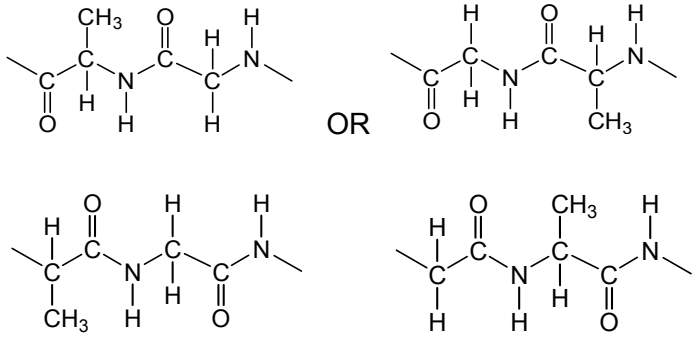
3d	M_r = 234(.0) % H = 9.4(0)	1 1	9.4 scores 2 marks M2 = $\frac{22}{M1}$ × 100 If M_r = 234 not shown, can score M1 if their answer × 234 = their no of H	
3e	tertiary amine OR 3° amine OR III° amine	1	Ignore N- substituted	
3f(i)	If ***a*** given: CE=0, can only score if answer given is **b** M1 lp on N^{b} or on **b** M2 alkyl groups donate electron density or positive inductive effect or electron donating groups attached M3 (lp on N^{b}) more available or protonated amine stabilised or better lp donor/H^+ acceptor Ignore reference to nucleophiles	 1 1 1	NOTE – there is NO mark for **b** alone Alternatives: M1 lp on N^{a} or on **a** M2 lp or electrons (on N^{a}) delocalised into ring /towards O in C=O M3 (lp on N^{a}) less available (to bond to H^+/accept proton)	
3f(ii)	Salt is ionic (more) soluble (in blood/body fluids/water)	1 1	Independent marks	
Total		**15**		

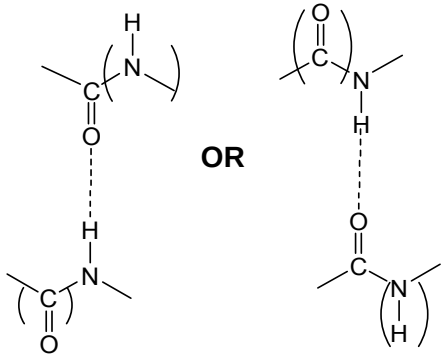
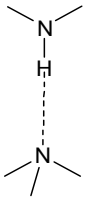
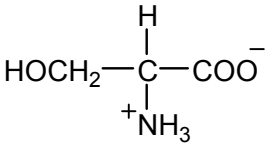
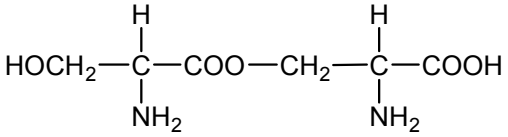
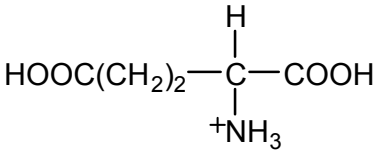
Question	Answers	Mark	Additional Comments/Guidance	
4a(i)	112(.0)	1	Not 112.5 ignore working	
4a(ii)	 OR	1	<u>Must be displayed and show + on relevant carbon</u> Penalise extra dots or $[\ ]^+$ penalise ^{37}Cl	
4a(iii)	$[ClCH_2COCl]^{+\cdot} \rightarrow [^{35}ClCH_2]^{\cdot} + [CO^{37}Cl]^+$	 1 1	Allow without brackets M1 for molecular ion M2 for both fragments with mass numbers Allow dot or + anywhere on formula	
4b(i)		1	Allow $[ClCH_2CO]^+$	
4b(ii)		1 1 1	M1 Arrow from inside hexagon to C or + on C on correct electrophile M2 Structure of intermediate • horseshoe centred on C1; • + in intermediate not too close to C1 (allow on or "below" a line from C2 to C6) M3 Arrow from bond to H into ring • Allow M3 arrow independent of M2 structure • + on H in intermediate loses M2 not M3 • Ignore Cl^- removing H^+ (different from Qu3a(ii))	

4c	reagent	water	(Aqueous) silver nitrate	NaOH followed by acidified silver nitrate	(Water +) named indicator	1	Named alcohol	Na_2CO_3 or $NaHCO_3$	ammonia	
	P	no reaction	no reaction (or slow formation of ppt)	no reaction (or slow formation of ppt)	No colour change	1	NVC	NVC	no reaction	Do NOT award No observation
	Q	Steamy /misty/ white fumes	white precipitate (immediately formed)	white precipitate (immediately formed)	Indicator turns to correct acid colour	1	Fruity or sweet smell or misty fumes	Fizzing or effervescence (not just gas produced)	white smoke	

4d(i)		1	One unit only must have trailing bonds ignore n and brackets allow —O—CH_2—CO—	
4d(ii)		1	Allow CO for C=O	
4e(i)		1	One unit only must have trailing bonds ignore n and brackets	

4e(ii)	PGA sutures react/dissolve/break down/are biodegradable/ are hydrolysed / attacked by water or nucleophiles /no need to remove (Ester links have) <u>polar bonds</u>	1 1	OR Polypropene not biodegradeable/ not hydrolysed / not attacked by water/nucleophiles polypropene contains <u>non-polar bonds</u> ignore intermolecular forces	
Total		**16**		

Question	Answers	Mark	Additional Comments/Guidance	ID details
5a(i)		2	Only one molecule of each used M1 for 2 amide links M2 CH_2 and $CH(CH_3)$ Allow 1 mark after one error Dipeptide max 1 Treat both trailing bonds missing as one error Ignore *n*	

5a(ii)	 **OR**	1	No need to show lp The covalent bond and the hydrogen bond either side of the H must be linear. Allow 	
5b(i)	2-amino-4-methylpentan(-1-)oic acid	1	Ignore hyphens, commas, spaces	
5b(ii)		1	Allow $-NH_3^+$	
5b(iii)		1		
5b(iv)		1	Allow $-NH_3^+$	
Total				**7**

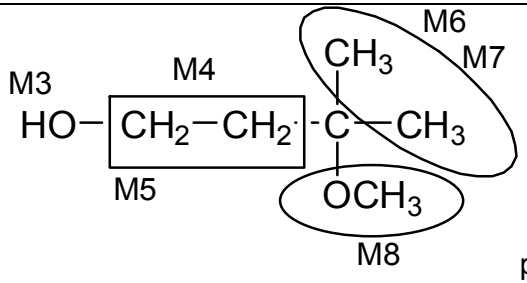
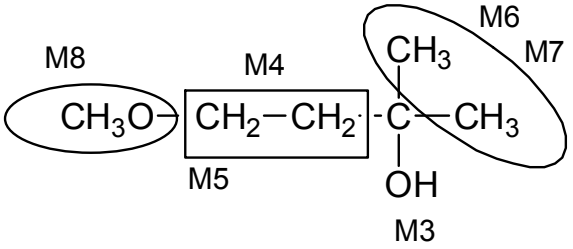
Question	Answers	Mark	Additional Comments/Guidance	ID details
G 6a	Order wrt **D** = 1 OR first OR [D] OR [D]^1 Order wrt **E** = 2 OR second OR [E]^2	1 1	Ignore working	
6b	(At time zero/start) the concentrations are known	1		
6c	M1 (Calculate) gradient (of tangent/curve/graph) M2 at t=0 or at start of graph/curve	1 1	Allow description of gradient calculation: Change in conc / time M2 scored only if M1 gained Ignore the word initial	
Total		**5**		

Question	Answers	Mark	Additional Comments/Guidance	ID details
7a	Iodine is not involved in (or before) the rate determining / slow(est) / limiting step (in the mechanism)	1	Ignore, iodine does not appear in the rate equation or iodine concentration does not affect the rate	
7b	$k = \left(\frac{8.64\times10^{-7}}{(5.82\times10^{-2})\times(4.76\times10^{-1})}\right) = 3.1(2)\times10^{-5}$ $\underline{mol^{-1}\ dm^{+3}\ s^{-1}}$	1 1	Mark for answer Mark units separately, i.e. only these units but can be in any order	
7c	rate = k $[H^+]$ (large excess of propanone) so $\underline{[CH_3COCH_3]\ is}$ (effectively) $\underline{constant}$	1 1	If wrong or missing CE = 0	
Total		**5**		

Question	Answers	Mark	Additional Comments/Guidance	ID details
8a	M1 NaOH	1	Only score M2 if M1 gained, but mark on from hydroxide. Mention of acid loses M1 & M2	
	M2 Aqueous/(warm)	1	ignore alcoholic / conc / dil.	
	M3 (Fractional) distillation or described	1	Not just evaporation; not reflux Allow chromatography	
8b	M1 S is $CH_3CH(CN)CH_2CH_3$	1	Allow without brackets	
	Step 3			
	M2 KCN (mark on from CN^-)	1	Not HCN, not KCN with acid	
	M3 Alcoholic (/aqueous)	1	Allow ethanolic can only score M3 if M2 gained	
	Step 4			
	M4 H_2 / $LiAlH_4$ / Na	1	can only score M5 if M4 gained	
	M5 Ni or Pt or Pd / Ethoxyethane or ether / ethanol	1	NOT $NaBH_4$ OR Sn/HCl penalise other extras as list ignore pressure or temperature	
	$LiAlH_4$ with acid loses both M4 and M5 Ignore 'followed by acid'			
Total		**8**		

Question	Answers	Mark	Additional Comments/Guidance	ID details
9a	Method 1 M1 % O = 27.1 $\frac{61.0}{12.0}$ $\frac{11.9}{1.0}$ $\frac{27.1}{16.0}$ = 5.08 = 11.9 = 1.69 M2 3 7 1 M3 C_3H_7O = 59 which is half of M_r so MF = 2EF **OR** Method 2 M1 61% of 118 = 72.0 and 11.9 % of 118 = 14.0 M2 72 + 14 = 86 so oxygen = 32 out of 118 OR 27.1% of 118 = 32.0 M3 $\frac{72.0}{12.0}$ $\frac{14.0}{1.0}$ $\frac{32.0}{16.0}$ = 6 = 14 = 2	3	Method 3 Alternative using given molecular formula M1 C = $\frac{12\times6}{118}$ × 100 = 61.0% M2 H = $\frac{14\times1}{118}$ × 100 = 11.9% M3 O = $\frac{16\times2}{118}$ × 100 = 27.1%	

Question	Additional Comments/Guidance	
9b	For this question, marks can be awarded either for a description of how the structure is derived or from the given structure itself. The maximum mark to be awarded is nine from the ten marks listed. Marks fall into three sections: • Infrared evidence : two marks are available for use of the infrared evidence, (M1 and M10) • Chemical evidence: one mark is available for use of the chemical evidence (M2) • N.m.r. evidence: six marks are available for use of the n.m.r. evidence (M3 – M8 inclusive) plus one mark (M9) for a completely correct structure. **Suggested procedure for marking** First look at the infrared spectrum: marks M1 and M10 may be scored there or in the written answer. Then look for use of the acidified potassium dichromate(VI) evidence, (M2). Then look at the final structure: this may lead to the award of marks M3 to M9 as shown on the structures below. Beware contradictions, e.g. using the chemical evidence they may state that **R** is a primary or secondary alcohol but then draw a tertiary alcohol. This will lose M2 but may score M3. The written 'evidence' frequently simply contains extracts from the Table **B** on the Data Sheet and, if only this is given, is unlikely to score many marks.	

Q9b	Described	Or drawn
M1	infrared peak/absorbance at 3400 (cm^{-1}) = <u>O-H</u> <u>alcohol</u> (reference to ir spectrum needed)	Note: please check the spectrum If peak at 3000 (cm^{-1}) is identified as acid then cannot score M1 (contradiction)
M10	**Either** No peak between 1680-1750 (cm^{-1}) so no C=O or not aldehyde/acid **OR** peak at 1000-1300 (cm^{-1}) so C–O present	Apply list principle to IR analysis for M10
M2	(Acidified potassium dichromate(VI) turns green) so primary alcohol or secondary alcohol or not tertiary alcohol	Ignore aldehyde here Lose M2 if just tertiary alcohol in structure
M3	δ = 3.1 singlet or integration =1 is O-H	Award M3 if structure has 1 O-H group only (can be primary, secondary or tertiary). Lose M3 if more than one OH group shown
M4	two triplets at 1.4 & 3.8 = $-CH_2-CH_2-$	Allow $-CH_2-CH_2-CH_2-$
M5	δ = 3.8 means CH_2 attached to O (in ether NOT ester) δ = 1.4 means CH_2 attached to C (but not to C=O)	Allow $O-CH_2-CH_2-CH_2-C$
M6	δ = 1.1 (singlet) integration 6 = 2 × equivalent CH_3 on same C	$-C(CH_3)_2-$
M7	δ = 1.1 singlet so no H attached to $-C(CH_3)_2-$	$R-C(CH_3)_2-R$
M8	δ = 3.2 singlet integration 3 = $-OCH_3$	$-OCH_3$
M9	For completely correct	If no structure given then Max 8
R is  plus M9	This close alternative  would not score M9, but could score up to 8 marks	