

A-LEVEL CHEMISTRY

CHEM4 Kinetics, Equilibria and Organic Chemistry
Mark scheme

2420
June 2015

Version 1: 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.

Further copies of this Mark Scheme are available from aqa.org.uk

| Question | Marking Guidance | Mark | Comments |
|--------------------------|--|---------------------|--|
| 1(a) Marked with 1(b) | $k = \text{rate} / [\text{A}]^2 \text{ or } \frac{3.3 \times 10^{-5}}{(4.2 \times 10^{-3})^2}$ = 1.87 or 1.9 $\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$ | 1 1 1 | Answer scores 2 1.90 scores first mark only (incorrect rounding) Any order and independent of calculation |
| 1(b) Marked with 1(a) | Expt 2 rate = $1.167 \times 10^{-4} - 1.2 \times 10^{-4} (\text{mol dm}^{-3} \text{ s}^{-1})$ Expt 3 [A] = $9.7 \times 10^{-3} - 9.8(1) \times 10^{-3} (\text{mol dm}^{-3})$ Using alternative value for k Expt 2 rate = $1.4(4) \times 10^{-4} (\text{mol dm}^{-3} \text{ s}^{-1})$ Expt 3 [A] = $8.85 \times 10^{-3} (\text{mol dm}^{-3})$ | 1 1 | If answers in table are not those given here, check their value of k in part 1(a) or use of alternative k . If their k is incorrect in part 1(a) mark 1(b) consequentially e.g. if $k = 7.9 \times 10^{-3}$ due to lack of squaring in 1(a) expt 2 4.9×10^{-7} expt 3 1.5×10^{-1} (expt 2 6.24×10^{-5} x their k) (expt 3 $0.0134 / \sqrt{k}$) |
| 1(c) | Slow step or rds involves only A OR B does not appear in the slow step or the rds OR B only appears after the slow step or the rds | 1 | Not B has no effect on the rate or B is not in the rate equation Allow "it" for B |

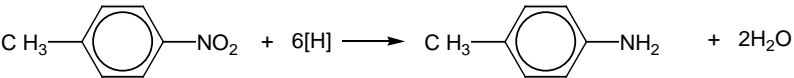
| Question | Marking Guidance | Mark | Comments |
|--------------------------|--|---------------------|--|
| 2(a) Marked with 2(b) | $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$ units = mol ⁻¹ dm ³ | 1 1 | Penalise () in part (a) but can score units; mark on in (b) If K_c expression wrong no marks in (a) but can score M1 & M3 in (b) |
| 2(b) Marked with 2(a) | M1 $[\text{O}_2] = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 K_c} \text{ or } \frac{(0.072/1.4)^2}{(0.055/1.4)^2 \times 27.9} \text{ or } \frac{(0.072)^2}{(0.055)^2 \times 27.9}$ M2 0.061(4) M3 mol O ₂ = 0.0614 × 1.4 = 0.086 (allow 0.085–0.087) | 1 1 1 | Correct answer scores three marks Ignore () in part (b) Penalise contradiction in M1 If K_c expression wrong in (a) can score M1 here for rearrangement of their K_c & M3 for multiplication by 1.4 If K_c or rearrangement wrong here score only M3 for multiplication by 1.4 M3 = correct answer of (M2 × 1.4) |
| 2(c)(i) G | No effect OR none OR no change OR stays the same | 1 | |

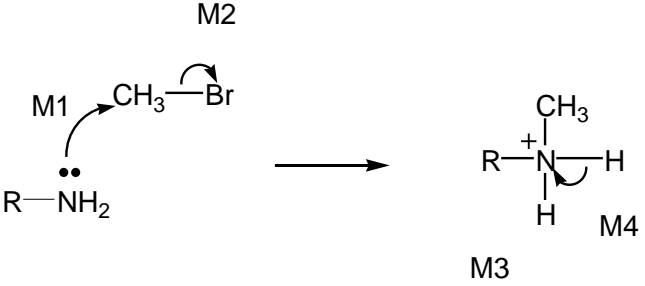
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|----------|----|---|--|---|--|
| 2(c)(ii) | M1 | Effect: Increase or more SO ₃ | Increase or more SO ₃ | 1 | If wrong effect, no further marks, but M2 and M3 are independent of each other |
| | M2 | Fewer mole(cule)s on RHS or 3 moles to 2 moles or (eqm shifts) to side with fewer moles | (V ³ or) residual V decreases in numerator of K _c expression | 1 | |
| | M3 | <u>Equilibrium moves/shifts</u> to reduce the pressure/oppose the increase in pressure | to keep K _c constant, ratio $\frac{(\text{mol SO}_3)^2}{(\text{mol SO}_2)^2(\text{mol O}_2)}$ must increase | 1 | |

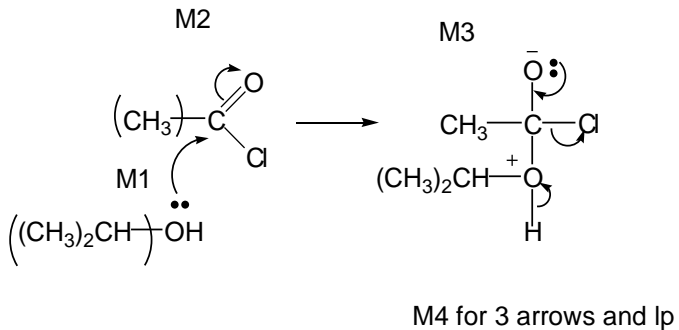
| Question | Marking Guidance | Mark | Comments |
|----------------|-----------------------|------|---|
| 3(a)(i) A | G | 1 | |
| 3(a)(ii) A | F | 1 | |
| 3(a)(iii) A | H | 1 | |
| 3(b)(i) A | cresol purple | 1 | |
| 3(b)(ii) G | yellow to red | 1 | both colours needed and must be in this order |
| 3(b)(iii) G | Yellow or pale yellow | 1 | Not allow any other colour with yellow |

| Question | Marking Guidance | | Mark | Comments |
|----------|--|--|------|---|
| 4(a) | M1 | <p>[H₂O] is <u>very</u> high (compared with [H⁺] and [OH⁻])</p> <p>OR</p> <p><u>Very few</u> H⁺ and OH⁻ ions</p> <p>OR</p> <p><u>Only / very</u> slightly dissociates</p> <p>OR</p> <p>Equilibrium lies <u>far</u> to the left</p> | 1 | Not partially dissociates |
| | M2 | <p>[H₂O] is (effectively) constant</p> <p>OR is incorporated into the constant K</p> | 1 | Allow changes by only a very small amount |
| 4(b) | (Dissociation OR breaking bonds) is endothermic | | 1 | |
| | ∴ Equilibrium moves to RHS (at higher T) <u>to absorb heat or to lower T or oppose increase in T</u> | | 1 | Allow to oppose change only if increase T mentioned |

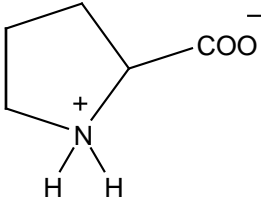
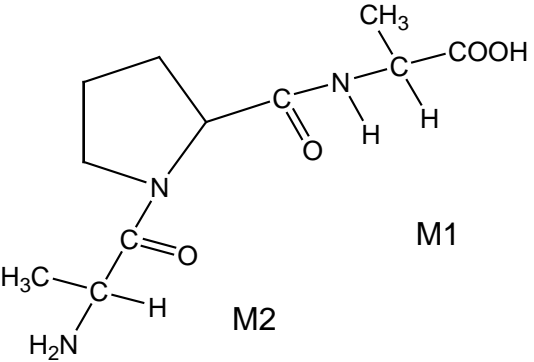
| | | | |
|-----------------------------|--|-----------------|--|
| 4(c) Marked with 4(d) | $[H^+] = \sqrt{K_w}$ (or $= \sqrt{5.48 \times 10^{-14}}$) If wrong method no marks $= 2.34 \times 10^{-7}$ pH = 6.63 | 1 1 1 | Correct pH answer scores 3 Using alternative K_w (1.00×10^{-14}) gives pH = <u>7.00</u> which scores 1 Final answer must have 2dp |
| 4(d) Marked with 4(c) | $[H^+] = K_w / [OH^-]$ or ($= 5.48 \times 10^{-14} / 0.12$) If wrong method no marks $= 4.566 \times 10^{-13}$ pH = 12.34 | 1 1 1 | Correct pH answer scores 3 If use alternative K_w (1.00×10^{-14}) again, do not penalise repeat error so pH = 13.08 scores 3 If use alternative K_w (1.00×10^{-14}) not as a repeat error, pH = 13.08 scores 1 If AE in K_w value made in part (c) is repeated here, do not penalise again. Final answer must have 2dp, but if dp penalised in 4(c) allow more than 2dp here but not fewer. |

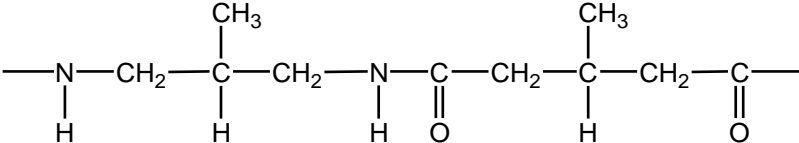
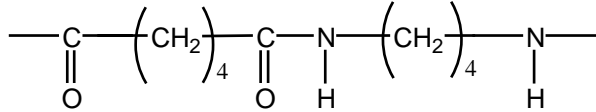
| Question | Marking Guidance | Mark | Comments |
|------------------|--|------|---|
| 5(a) G | Electrophilic substitution | 1 | Both words needed Ignore minor misspellings |
| 5(b)(i) | Sn/HCl OR H ₂ /Ni OR H ₂ /Pt OR Fe/HCl OR Zn/HCl OR SnCl ₂ /HCl | 1 | Ignore conc or dil with HCl, Allow (dil) H ₂ SO ₄ but not conc H ₂ SO ₄ Not allow HNO ₃ or H ⁺ Ignore NaOH after Sn/HCl Ignore catalyst |
| 5(b)(ii) | $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2 + 6[\text{H}] \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{NH}_2 + 2\text{H}_2\text{O}$ OR  | 1 | Allow molecular formulae as structures given C ₇ H ₇ NO ₂ + 6[H] → C ₇ H ₉ N + 2H ₂ O Qu states use [H], so penalised 3H ₂ |
| 5(b)(iii) | <u>making dyes</u> OR <u>making</u> quaternary ammonium salts OR <u>making</u> (cationic) surfactants OR <u>making</u> hair conditioner OR <u>making</u> fabric softener OR <u>making</u> detergents | 1 | |

| | | | | | | | | | | | | | | | | | | | | | |
|-----------|---|----|---|----|--|----|---|-----------|--|----|--|----|---|---|---|---------------------------------|---|--|---|--|--|
| 5(c) | <p style="text-align: center;">M2</p>  <p style="text-align: center;">M3</p> <p>NO Mark for name of mechanism</p> | 4 | Allow SN1 M1 for lone pair on N and arrow to C or mid point of space between N and C M2 for arrow from bond to Br M3 for structure of protonated secondary amine M4 for arrow from bond to N or + on N For M4: ignore RNH ₂ or NH ₃ removing H ⁺ but penalise Br- | | | | | | | | | | | | | | | | | | |
| 5(d) | <table border="0" style="width: 100%;"> <tbody> <tr> <td style="width: 50px;">M1</td> <td><u>lone or electron pair on N</u></td> </tr> <tr> <td>M2</td> <td>in J spread/delocalised into ring (or not delocalised in K)</td> </tr> <tr> <td>M3</td> <td>less available (for protonation or donation in J)</td> </tr> <tr> <td colspan="2" style="text-align: center;">OR</td> </tr> <tr> <td>M2</td> <td>in K there is a positive inductive effect / electron releasing)</td> </tr> <tr> <td>M3</td> <td>more available (for protonation or donation in K)</td> </tr> </tbody> </table> | M1 | <u>lone or electron pair on N</u> | M2 | in J spread/delocalised into ring (or not delocalised in K) | M3 | less available (for protonation or donation in J) | OR | | M2 | in K there is a positive inductive effect / electron releasing) | M3 | more available (for protonation or donation in K) | <table border="0" style="width: 100%;"> <tbody> <tr> <td style="width: 50px;">1</td> <td>If no mention of lone pair CE=0</td> </tr> <tr> <td>1</td> <td>If lone pair mentioned but not on N then lose M1 and mark on</td> </tr> <tr> <td>1</td> <td>Ignore negative inductive effect of benzene Allow interacts with π cloud for M2</td> </tr> </tbody> </table> | 1 | If no mention of lone pair CE=0 | 1 | If lone pair mentioned but not on N then lose M1 and mark on | 1 | Ignore negative inductive effect of benzene Allow interacts with π cloud for M2 | |
| M1 | <u>lone or electron pair on N</u> | | | | | | | | | | | | | | | | | | | | |
| M2 | in J spread/delocalised into ring (or not delocalised in K) | | | | | | | | | | | | | | | | | | | | |
| M3 | less available (for protonation or donation in J) | | | | | | | | | | | | | | | | | | | | |
| OR | | | | | | | | | | | | | | | | | | | | | |
| M2 | in K there is a positive inductive effect / electron releasing) | | | | | | | | | | | | | | | | | | | | |
| M3 | more available (for protonation or donation in K) | | | | | | | | | | | | | | | | | | | | |
| 1 | If no mention of lone pair CE=0 | | | | | | | | | | | | | | | | | | | | |
| 1 | If lone pair mentioned but not on N then lose M1 and mark on | | | | | | | | | | | | | | | | | | | | |
| 1 | Ignore negative inductive effect of benzene Allow interacts with π cloud for M2 | | | | | | | | | | | | | | | | | | | | |

| Question | Marking Guidance | Mark | Comments |
|----------|---|-------------------|---|
| 6(a)(i) | $(\text{CH}_3)_2\text{CHOH} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{CH}_3\text{COOCH}(\text{CH}_3)_2 + \text{CH}_3\text{COOH}$ <p>(1)-methylethyl ethanoate OR Propan-2-yl ethanoate</p> | <p>1</p> <p>1</p> | <p>Allow $\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_3)_2$ and $\text{CH}_3\text{CO}_2\text{H}$ Ignore $(\text{CH}_3)_2\text{-C}$ in equation</p> <p>Ignore extra or missing spaces, commas or hyphens</p> |
| 6(a)(ii) |  <p>M4 for 3 arrows and lp</p> <p>NO Mark for name of mechanism</p> | 4 | <p>M1 for lone pair on O and arrow to C or to mid-point of space between O and C M2 for arrow from C=O bond to O</p> <ul style="list-style-type: none"> M2 not allowed independent of M1, but allow M1 for correct attack on C+ + rather than $\delta+$ on C=O loses M2 If Cl lost with C=O breaking, max1 for M1 <p>M3 for correct structure <u>with charges</u> (penalise wrong alcohol here) but lone pair on O is part of M4</p> <p>Penalise $(\text{CH}_3)_2\text{-C}$ in M3</p> <p>M4 for lone pair on O and three arrows</p> <ul style="list-style-type: none"> only allow M4 after correct/very close M3 M4 can be gained over more than one structure Ignore Cl^- removing H^+ |

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|----------|--|--------------------|--|
| 6(b)(i) | $ \begin{array}{c} \text{CH}_2\text{OOC}\text{C}_{17}\text{H}_{31} \\ \\ \text{CHOOC}\text{C}_{17}\text{H}_{33} \\ \\ \text{CH}_2\text{OOC}\text{C}_{17}\text{H}_{29} \end{array} + 3\text{NaOH} \longrightarrow \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHOH} \\ \\ \text{CH}_2\text{OH} \end{array} + \begin{array}{c} \text{C}_{17}\text{H}_{31}\text{COONa} \\ \text{C}_{17}\text{H}_{33}\text{COONa} \\ \text{C}_{17}\text{H}_{29}\text{COONa} \end{array} $ | LHS 1 RHS 1 | Penalise covalent Na e.g. -O-Na |
| 6(b)(ii) | $\text{C}_{17}\text{H}_{33}\text{COOCH}_3$ | 1 | Allow $\text{C}_{19}\text{H}_{36}\text{O}_2$ |

| Question | Marking Guidance | Mark | Comments |
|----------|---|------------|--|
| 7(a)(i) |  | 1 | Allow CO ₂ ⁻ and NH ₂ ⁺ |
| 7(a)(ii) | <p>NOTE – Two marks for this clip</p>  | 1 1 | <p>M1 for alanine section bonded through N M2 for alanine section bonded through C But penalise error in proline ring</p> <p>Allow MAX 1 for correct tripeptide in polymer structure</p> |
| 7(b)(i) | <u>3-methylpent-2-ene</u> | 1 | Ignore <i>E-Z</i> , commas, spaces or missing hyphens |
| 7(b)(ii) | <u>4-amino-3-methylbutanoic acid</u> | 1 | Ignore commas, spaces or missing hyphens |

| | | | |
|-----------|--|---|--|
| 7(b)(iii) |  | 1 | <p>or any polyamide section containing 8 carbons plus two C=O plus two N-H, such as</p>  <p>Trailing bonds are required</p> |
| 7(b)(iv) | <p>Non polar OR no polar groups/bonds (for attack by water / acids / alkalis / nucleophiles or for hydrolysis)</p> <p>C-C bonds are strong</p> | 1 | |

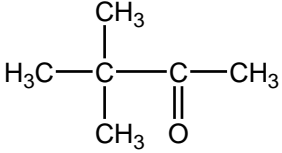
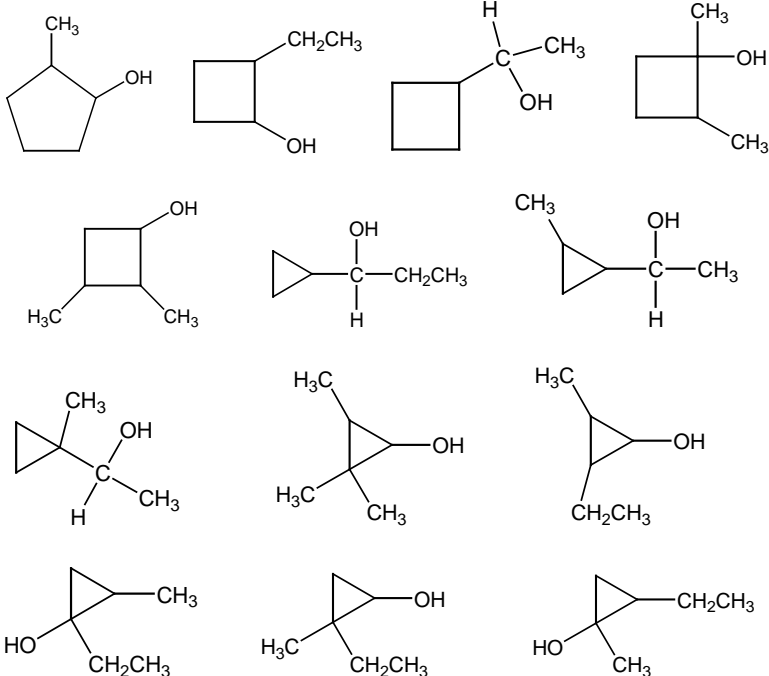
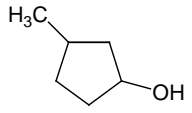
| Question | Marking Guidance | Mark | Comments | | | | | | | | | | | | | | | |
|---------------------|---|------|--|--|----|--|--|----|--|----|--|---|--|----|--|--|-----------------|--|
| 8(a)(i) | $3(-120) - (-208) = -152$ OR $3(120) - 208 = 152 \text{ (kJ mol}^{-1}\text{)}$ | 1 | Must show <u>working</u> and answer and maths must be correct, but ignore sign | | | | | | | | | | | | | | | |
| 8(a)(ii) | Electrons <u>delocalised</u> OR <u>delocalisation</u> (QOL) Or allow reference to <u>resonance</u> (QOL) | 1 | | | | | | | | | | | | | | | | |
| 8(b) G | x, y, w | 1 | Must be in this order | | | | | | | | | | | | | | | |
| 8(c)(i) G | -240 (kJ mol ⁻¹) | 1 | Must have minus sign | | | | | | | | | | | | | | | |
| 8(c)(ii) | between -239 and -121 (kJ mol ⁻¹) | 1 | Must have minus sign | | | | | | | | | | | | | | | |
| 8(c)(iii) | <table border="0"> <tr> <td></td> <td>Must specify which diene:</td> <td></td> </tr> <tr> <td>M1</td> <td>Proximity – for 1,3 C=C bonds are close together</td> <td></td> </tr> <tr> <td>M2</td> <td>Delocalisation – for 1,3 some delocalisation</td> <td>OR</td> </tr> <tr> <td></td> <td>some overlap of electrons, π clouds or p orbitals</td> <td></td> </tr> <tr> <td>M3</td> <td>some extra stability for the 1,3- isomer</td> <td></td> </tr> </table> | | Must specify which diene: | | M1 | Proximity – for 1,3 C=C bonds are close together | | M2 | Delocalisation – for 1,3 some delocalisation | OR | | some overlap of electrons, π clouds or p orbitals | | M3 | some extra stability for the 1,3- isomer | | 1 1 1 | allow converse for 1,4 diene allow converse for 1,4 diene |
| | Must specify which diene: | | | | | | | | | | | | | | | | | |
| M1 | Proximity – for 1,3 C=C bonds are close together | | | | | | | | | | | | | | | | | |
| M2 | Delocalisation – for 1,3 some delocalisation | OR | | | | | | | | | | | | | | | | |
| | some overlap of electrons, π clouds or p orbitals | | | | | | | | | | | | | | | | | |
| M3 | some extra stability for the 1,3- isomer | | | | | | | | | | | | | | | | | |

| Question | Answers | Mark | Comments | |
|----------|---------|---|----------|---|
| 9(a) | M1 | $[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]}$ or = $1.74 \times 10^{-5} \times \frac{0.186}{0.105}$ | 1 | Allow () |
| | M2 | = 3.08×10^{-5} | 1 | If $[HX]/[X^-]$ or $\frac{0.186}{0.105}$ upside down, or any addition or subtraction lose M1 & M2. |
| | M3 | pH = 4.51 (correct answer scores 3) | 1 | Can score M3 for correct pH conseq to their $[H^+]$, so pH = 5.01 scores one Must be to 2 dp |
| 9(b) | M1 | mol HX after addition (= $0.251 + 0.015$) = 0.266 | 1 | For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3 |
| | M2 | mol X^- after subtraction (= $0.140 - 0.015$) = 0.125 | 1 | For X^- if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3 |
| | M3 | $[H^+] = \left(\frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} \right) = \frac{1.74 \times 10^{-5} \times 0.266}{0.125}$ | 1 | If errors above in both addition AND subtraction can only score M3 for insertion of their numbers in rearranged expression. One exception, if addition and subtraction reversed then pH = 4.58 scores 2 |
| | M4 | $[H^+] = 3.703 \times 10^{-5}$ (mol dm ⁻³) | 1 | If $[HX]/[X^-]$ upside down, lose M3 & M4 (or next two marks) but can score M5 for correct pH conseq to their $[H^+]$, so if M1 & M2 correct, pH = 5.09 scores 3. |
| | M5 | pH = 4.43 Correct use of HX and X^- values from 9(a) gives pH = 4.41 and scores 4 | 1 | If wrong method, e.g. $\sqrt{\quad}$ or no use of rearranged K_a expression, may score M1 & M2 but no more. Allow more but not fewer than 2dp here. |

| Questio | Answers | Mar | Comments | |
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| | Alternative using Henderson-Hasselbach Equation | | | |
| 9(a) | M1 | $\text{pH} = \text{pKa} - \log[\text{HX}]/[\text{X}^-] = -\log(1.74 \times 10^{-5}) - \log\left(\frac{0.186}{0.105}\right)$ | 1 | Allow () |
| | M2 | $\text{pKa} = 4.76 - 0.248$ | 1 | If $[\text{HX}]/[\text{X}^-]$ or $\frac{0.186}{0.105}$ upside down, can only score 1 |
| | M3 | $\text{pH} = = 4.51$ | 1 | so $\text{pH} = 5.01$ Must be to 2 dp |
| 9(b) | M1 | $\text{mol acid after addition} = 0.251 + 0.015 = 0.266$ | 1 | For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3 |
| | M2 | $\text{mol salt after addition} = 0.140 - 0.015 = 0.125$ | 1 | For X^- if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3 |
| | M3 | $\text{pH} = (\text{pKa} - \log[\text{HX}]/[\text{X}^-]) = -\log(1.74 \times 10^{-5}) - \log(0.266/0.125)$ | 1 | If errors above in both addition AND subtraction can only score M3 for insertion of their numbers - except |
| | M4 | $\text{pH} = 4.76 - 0.328$ | 1 | if addition and subtraction reversed then $\text{pH} = 4.58$ scores 2 |
| | M5 | $\text{pH} = = 4.43$ | 1 | If $[\text{HX}]/[\text{X}^-]$ upside down, lose M3 & M4 (or next two marks) but can score M5 for correct pH conseq to their working, so if M1 & M2 correct, $\text{pH} = 5.09$ scores 3. Allow more but not fewer than 2dp here. |

| Question | Marking Guidance | | | | | | Mark | Comments |
|----------|------------------------------|--|--------------------------------|----------------------|---|----------------|------|---|
| 10(a) | Reagent | Acidified K ₂ Cr ₂ O ₇ | Acidified KMnO ₄ | I ₂ /NaOH | Named RCOOH with HCl or H ₂ SO ₄ | Named RCOCl | 1 | Allow names including potassium permanganate |
| | P (ketone) | no reaction | no reaction | Yellow ppt | no reaction | no reaction | 1 | Wrong or no reagent CE=0 |
| | S (2° alcohol) | (orange to) green | (purple to) colourless | no reaction | fruity or sweet smell | Misty fumes | 1 | Penalise incorrect formulae or incomplete reagent, such as K ₂ Cr ₂ O ₇ or acidified dichromate, but mark on. Allow no change or nvc but penalise <i>nothing or no observation</i> If 2 reagents added sequentially or 2 different reagents used for P and S then CE=0 |
| 10(b) | Tollens' silver mirror/solid | | Fehling's / Benedicts red ppt | | | | 1 | |
| | | | | | | | 1 | |
| 10(c) | P | | | | | | 1 | If not P then no marks for clip |
| G | 5 OR five | | | | | | 1 | |

| | | | | |
|--------|---|--|-------------------------------|--|
| 10(d) | $C_4H_{12}Si$ Any two from <ul style="list-style-type: none"> • <u>One or single</u> peak OR all (four) carbon atoms are equivalent or one environment • upfield from others or far away from others or far to right • non toxic OR inert • low boiling point or volatile or easy removed from sample | | 1 1 1 | Must be molecular formula Wrong substance CE=0 for clip Ignore and don't credit single peak linked to 12 equivalent H or has a peak at $\delta = 0$ but use list principle for wrong statements |
| 10 (e) | M1 M2 M3 M4 M5 | Figure 2 is R 90-150 (ppm) or value in range is (two peaks for) C=C/alkene Figure 3 is T 50-90 (ppm) or value in range is C—O or alcohol or ether two peaks (so not S which would have only one) | 1 1 1 1 1 | If not R cannot score M2 If not T cannot score M4 or M5 |

| | | | |
|-------|--|---|---|
| 10(f) | <p>U</p> $\text{C}_6\text{H}_{12}\text{O}_6$  | 1 | |
| | <p>Answers include</p> <p>V</p> $\text{C}_6\text{H}_{12}\text{O}_6$  | 1 | <p>Not allow S</p>  <p>because V must be an isomer of S</p> |

| Question | Marking Guidance | | | Mark | Comments |
|----------|------------------|----|---|------|---|
| 11 | Step 1 | M1 | HBr | 1 | In any step, if wrong reagent or extra wrong reagent, can only score mechanism mark, but if AlCl ₃ added in Step 3, lose M7 but can score M8 & M9 If 1-bromobutane structure given for M2 then 1-aminobutane structure for M5, penalise M2 and M5 but mark M8 consequentially If 1-bromobutane structure given for M2 then 2-aminobutane structure for M5, penalise M2, M5 and M8 If 2-bromobutane structure given for M2 then 1-aminobutane structure, penalise M5 and M8 Allow C ₂ H ₅ for CH ₃ CH ₂ Not allow (electrophilic) addition-elimination |
| | | M2 | $\text{CH}_3\text{CH}_2-\underset{\text{Br}}{\text{CH}}\text{CH}_3$ | 1 | |
| | | M3 | electrophilic addition | 1 | |
| | Step 2 | M4 | NH ₃ | 1 | |
| | | M5 | $\text{CH}_3\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}\text{CH}_3$ | 1 | |
| | | M6 | nucleophilic substitution | 1 | |
| | Step 3 | M7 | CH ₃ COCl or (CH ₃ CO) ₂ O | 1 | |
| | | M8 | $\begin{array}{c} \text{CH}_3\text{CH}_2-\text{CHCH}_3 \\ \\ \text{NH} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$ | 1 | |
| | | M9 | (nucleophilic) addition-elimination | 1 | |

General principles applied to marking CHEM4 papers by CMI+ (June 2015)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- **Examiners should note that throughout the mark scheme, items that are underlined are required information to gain credit.**
- **Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.**

A. The “List principle” and the use of “ignore” in the mark scheme

If a question requires **one** answer and a student gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

NB Certain answers are designated in the mark scheme as those which the examiner should “Ignore”. These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip. For example, penalise the use of “h” for hydrogen, “CL” for chlorine or “br” for bromine.

C. Spelling

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

NB Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the “Quality of Language” (QoL) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

E. Reagents

The command word “Identify”, allows the student to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.

For example, **no credit** would be given for

- the cyanide ion or CN^- when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH^- when the reagent should be sodium hydroxide or NaOH;
- the $\text{Ag}(\text{NH}_3)_2^+$ ion when the reagent should be Tollens’ reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a student provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

G. Marking calculations

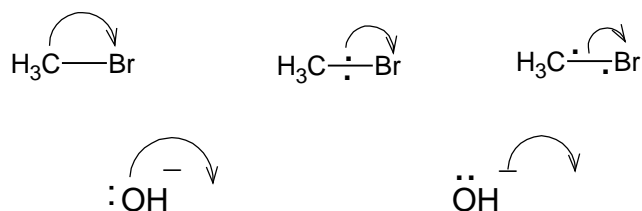
In general

- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

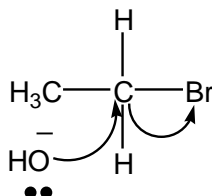
H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.

The following representations should not gain credit **and will be penalised each time** within a clip.



For example, the following would score zero marks



When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

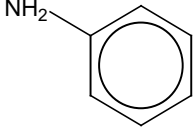
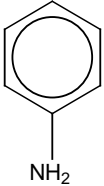
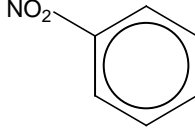
In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

I. Organic structures

In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Structures must not be ambiguous, e.g. 1-bromopropane should be shown as $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ and not as the molecular formula $\text{C}_3\text{H}_7\text{Br}$ which could also represent the isomeric 2-bromopropane.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g. nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if students show the alcohol functional group as $\text{C} - \text{HO}$, they should be penalised **on every occasion**.
- Latitude should be given to the representation of $\text{C} - \text{C}$ bonds in alkyl groups, given that CH_3- is considered to be interchangeable with $\text{H}_3\text{C}-$ even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where $\text{NH}_2 - \text{C}$ will be allowed, although $\text{H}_2\text{N} - \text{C}$ would be preferred.
- Poor presentation of vertical $\text{C} - \text{CH}_3$ bonds or vertical $\text{C} - \text{NH}_2$ bonds should **not** be penalised. For other functional groups, such as $-\text{OH}$ and $-\text{CN}$, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.

By way of illustration, the following would apply.

| | | | | |
|--|--|--|---|---|
| $\begin{array}{c} \\ \text{CH}_3-\text{C}- \\ \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{CH}_3 \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{CH}_3\text{CH}_2 \end{array}$ | $\begin{array}{c} \\ \text{OH}-\text{C}- \\ \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{OH} \end{array}$ |
| allowed | allowed | not allowed | not allowed | not allowed |
| $\begin{array}{c} \\ \text{NH}_2-\text{C}- \\ \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{NH}_2 \end{array}$ |  |  |  |
| allowed | allowed | allowed | allowed | not allowed |

| | | | | | |
|---|---|---|--|--|--|
| $\begin{array}{c} \\ \text{CN}-\text{C}- \\ \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{CN} \end{array}$ | $\begin{array}{c} \\ \text{COOH}-\text{C}- \\ \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{COOH} \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{COOH} \end{array}$ | |
| not allowed | not allowed | not allowed | not allowed | not allowed | |
| $\begin{array}{c} \\ \text{CHO}-\text{C}- \\ \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{CHO} \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{CHO} \end{array}$ | $\begin{array}{c} \\ \text{COCl}-\text{C}- \\ \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{COCl} \end{array}$ | $\begin{array}{c} \\ -\text{C}- \\ \\ \text{COCl} \end{array}$ |
| not allowed | not allowed | not allowed | not allowed | not allowed | not allowed |

- In most cases, the use of “sticks” to represent C – H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C – H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.
- Representation of CH₂ by C–H₂ will be penalised
- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH₃COH for ethanal

CH₃CH₂HO for ethanol

OHCH₂CH₃ for ethanol

C₂H₆O for ethanol

CH₂CH₂ for ethene

CH₂.CH₂ for ethene

CH₂:CH₂ for ethane

NB Exceptions may be made in the context of balancing equations

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

CH₂ = CH₂ for ethene, H₂C=CH₂

CH₃CHOHCH₃ for propan-2-ol, CH₃CH(OH)CH₃

J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit. Some illustrations are given here.

| | |
|-------------------------|--|
| but-2-ol | should be butan-2-ol |
| 2-hydroxybutane | should be butan-2-ol |
| butane-2-ol | should be butan-2-ol |
| 2-butanol | should be butan-2-ol |
| ethan-1,2-diol | should be ethane-1,2-diol |
| 2-methylpropan-2-ol | should be 2-methylpropan-2-ol |
| 2-methylbutan-3-ol | should be 3-methylbutan-2-ol |
| 3-methylpentan | should be 3-methylpentane |
| 3-mythylpentane | should be 3-methylpentane |
| 3-methylpentane | should be 3-methylpentane |
| propanitrile | should be propanenitrile |
| aminethane | should be ethylamine (although aminoethane can gain credit) |
| 2-methyl-3-bromobutane | should be 2-bromo-3-methylbutane |
| 3-bromo-2-methylbutane | should be 2-bromo-3-methylbutane |
| 3-methyl-2-bromobutane | should be 2-bromo-3-methylbutane |
| 2-methylbut-3-ene | should be 3-methylbut-1-ene |
| difluorodichloromethane | should be dichlorodifluoromethane |