Pearson

Mark Scheme (Results)

October 2019

Pearson Edexcel International Advanced Level In Chemistry (WCH04)
Paper 01 General Principles of Chemistry IRates, Equilibria and Further Organic Chemistry

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## General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.


## Using the Mark Scheme

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge. Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

The mark scheme gives examiners:

- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.
/ means that the responses are alternatives and either answer should receive full credit.
( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
Phrases/words in bold indicate that the meaning of the phrase or the actual word is essential to the answer.
ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

## Quality of Written Communication

Questions which involve the writing of continuous prose will expect candidates to:

- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.
Full marks will be awarded if the candidate has demonstrated the above abilities. Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.


## Section A (multiple choice)

| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :---: |
| $\mathbf{1 ( a )}$ | The only correct answer is C (Graph 3) | (1) |
|  | A is not correct because this is a graph of concentration of reactant against time for <br> a first order reaction <br> B is not correct because this is a graph of rate against concentration for a zero <br> order reaction. | D is not correct because this is a graph of rate against temperature |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :--- |
| $\mathbf{1 ( b )}$ | The only correct answer is C (Graph 3) <br> A is not correct because the concentration of product must increase with time. This <br> shows $Y$ decreasing with time | (1) |
|  | B is not correct because the concentration of product must increase with time. This <br> is a graph of rate against concentration for a zero order reaction and shows $Y$ <br> constant. | D is not correct because the concentration of product must increase linearly with <br> time. This is a graph of rate against temperature and shows $Y$ increasing <br> exponentially |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :---: |
| $\mathbf{1 ( c )}$ | The only correct answer is D (Graph 4) <br> A is not correct because rate increases exponentially with temperature. This is a <br> graph of concentration of reactant against time for a first order reaction so Y <br> decreases <br> B is not correct because rate increases exponentially with temperature. This is a <br> graph of rate against concentration for a zero order reaction so Y does not change. <br> C is not correct because rate increases exponentially with temperature; it is not <br> directly proportional to temperature | (1) |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :---: |
| $\mathbf{2}$ | The only correct answer is B (+120) <br> C is not correct because this is the same as the activation energy of the forward <br> reaction <br> $\boldsymbol{D}$ is not correct because this is the sum of the activation energy and the enthalpy <br> change for the forward reaction | (1) |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :--- |
| $\mathbf{3}$ | The only correct answer is D (positive entropy change of the system, $\Delta S$ <br> system) <br> $\boldsymbol{A}$ is not correct because activation energy determines rate not thermodynamic <br> feasibility <br> $\boldsymbol{B}$ is not correct because a positive enthalpy change favours the reverse reaction <br> $\boldsymbol{C}$ is not correct because $\Delta S^{s}$ surroundings is negative for an endothermic reaction | (1) |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :---: |
| $\mathbf{4}$ | The only correct answer is D (more ways of distributing energy quanta) <br> A is not correct because boiling temperature only affects molar entropy when there <br> is change of state. | (1) |
| B is not correct because standard molar enthalpy change of formation does not |  |  |
| affect molar entropy |  |  |
| C is not correct because molar entropy increases as the number of ways of |  |  |
| distributing energy quanta increases |  |  |$\quad$|  |
| :--- |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :---: |
| $\mathbf{5}$ | The only correct answer is A (perfect crystals at absolute <br> zero (0 K)) <br> $\boldsymbol{B}$ is not correct because the molar entropy of gases is never zero <br> $\boldsymbol{C}$ is not correct because this refers to standard enthalpies of formation for elements <br> $\boldsymbol{D}$ is not correct because this is not true | $\mathbf{( 1 )}$ |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :--- |
| $\mathbf{6 ( a )}$ | The only correct answer is D (unchanged and decreases) <br> A is not correct because activation energy does not change with temperature and <br> the equilibrium constant of an exothermic reaction decreases with increasing <br> temperature | (1) <br> B is not correct because activation energy does not change with temperature <br> C is not correct because the equilibrium constant of an exothermic reaction <br> decreases with increasing temperature |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :--- |
| $\mathbf{6 ( b )}$ | The only correct answer is A (increases and increases) <br> B is not correct because equilibrium yield would increase because 2 mol of reactant <br> gives 1 mol of product | (1) |
|  | Cis not correct because rate increases when pressure increases for a gas phase <br> reaction | D is not correct because equilibrium yield would increase because 2 mol of reactant <br> gives 1 mol of product and rate increases when pressure increases for a gas phase <br> reaction |


| Question Number | Correct Answer | Mark |
| :---: | :---: | :---: |
| 6(c) | The only correct answer is $\mathrm{A}\left(K_{\mathrm{p}}=\left(\frac{p\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}\right)}{p\left(\mathrm{C}_{2} \mathrm{H}_{4}\right) \times p\left(\mathrm{H}_{2} \mathrm{O}\right)}\right)\right)$ <br> B is not correct because this is $K_{p}$ for the reverse reaction <br> $\mathbf{C}$ is not correct because water is in the gas phase so it is included in the $K_{p}$ expression <br> D is not correct because the expression has been inverted and because water is in the gas phase so it is included in the $K_{p}$ expression | (1) |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :---: |
| $\mathbf{7}$ | The only correct answer is C (produce an excess of hydrogen ions in solution) | (1) |
|  | $\boldsymbol{A}$ is not correct because this a traditional description of an acid |  |
|  | $\boldsymbol{B}$ is not correct because this is just one of a number of typical reactions of acids |  |
|  | $\boldsymbol{D}$ is not correct because this is the Lewis definition of acids |  |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :---: |
| $\mathbf{8}$ | The only correct answer is D (remains neutral and decreases) | (1) |
|  | A is not correct because water remains neutral and the pH decreases |  |
| B is not correct because water remains neutral |  |  |
| C is not correct because the pH of water decreases |  |  |


| Question Number | Correct Answer | Mark |
| :---: | :---: | :---: |
| 9 | The only correct answer is B <br> A is not correct because ammonia is a Brønsted-Lowry base <br> C is not correct because both species are Brønsted-Lowry bases. <br> D is not correct because the deprotonated urea is a Brønsted-Lowry base | (1) |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :--- |
| $\mathbf{1 0}$ | The only correct answer is C (optical isomerism only) | (1) |
|  | $\boldsymbol{A}$ is not correct because limonene does not have geometric isomers |  |
|  | $\boldsymbol{D}$ is not correct because limonene does not have geometric isomers |  |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :--- |
| $\mathbf{1 1}$ | The only correct answer is B (permanent dipole-dipole forces in the liquid <br> state and hydrogen bonds in aqueous solution) | (1) |
|  | C is not correct because ethanal does not form hydrogen bonds in the liquid state <br> and permanent dipole-dipole forces cannot account for the solubility of ethanal in <br> water <br> $\mathbf{D}$ is not correct because permanent dipole-dipole forces cannot account for the <br> solubility of ethanal in water |  |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :--- |
| $\mathbf{1 2}$ | The only correct answer is B (warming with iodine and sodium hydroxide <br> followed by acidifying with sulfuric acid) <br> A is not correct because acidified potassium dichromate(VI) does not react with <br> butanone | (1) |
| $\boldsymbol{C}$ is not correct because this would not reduce the number of carbon atoms |  |  |
| $\boldsymbol{D}$ is not correct because this sequence will give 2-hydroxy-2-methylbutanoic acid |  |  |$\quad$.


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :--- |
| $\mathbf{1 3 ( a )}$ | The only correct answer is C (separate samples of the compound with ethanol <br> and with ethanoic acid) | (1) |
| A is not correct because this reagent does not discriminate between alcohol and |  |  |
| B is not correct because this reagent will only show that an acid is present |  |  |
| $\boldsymbol{D}$ is not correct because 2,4-dinitrophenylhydrazine does not react with the carbonyl |  |  |
| group in carboxylic acids |  |  |$\quad$.


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :---: |
| $\mathbf{1 3 ( b )}$ | The only correct answer is A (two singlets, two triplets and one quintet) <br> B is not correct because this ignores the fact that the protons on C3 are coupled to <br> those on C2 and C4 <br> C is not correct because this pattern includes the OH group on C4 in the coupling <br> D is not correct because this pattern requires a proton on the carboxylic acid <br> carbon which couples with the C2 protons | (1) |


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :---: |
| $\mathbf{1 4}$ | The only correct answer is A (alkyl groups of alcohols replace alkyl groups of <br> esters) <br> B is not correct because the alkyl groups of esters are replaced by alkyl groups of <br> alcohols. <br> C is not correct because the 'trans' does not refer to geometric isomerism | (1) |
|  | $\boldsymbol{D}$ is not correct because transesterification involves esters reacting with alcohols |  |$\quad$


| Question <br> Number | Correct Answer | Mark |
| :--- | :--- | :---: |
| $\mathbf{1 5}$ | The only correct answer is B (high pressures) | (1) |
|  | $\boldsymbol{A}$ is not correct because liquid polymers are not used in HPLC |  |
| C is not correct because lasers are not used in HPLC |  |  |
|  | $\boldsymbol{D}$ is not correct because long columns are not a particular characteristic of HPLC |  |$\quad$.

## Section B

| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 16(a)(i) | ( $\Delta S^{\circ}{ }_{\text {system }}$ ) is positive <br> and <br> because a solid reactant forms gas products <br> OR <br> because gases have higher entropies than solids <br> ALLOW <br> ( $\Delta S^{\circ}{ }_{\text {system }}$ ) is positive <br> and <br> because 1 mol goes to 3 mol <br> OR <br> because more moles of products (than reactants) <br> ALLOW <br> molecules for moles <br> IGNORE references to disorder | Explanations with no comparison e.g. because 3 mol of gas are formed <br> incorrect numbers of moles <br> Just 'more products' | (1) |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 16(a)(ii) | In this question and throughout the paper allow $\mathrm{mol}^{-}$for $\mathrm{mol}^{-1}$ and $\mathrm{J} / \mathrm{K} / \mathrm{mol}^{\prime}$ format / $\mathrm{J} \mathrm{mol}^{-1} \mathrm{~K}^{-1}$ <br> In parts (ii), (iii) and (iv) penalise omission of sign or omitted / incorrect units for 1 mark only and at the first occasion $$ <br> Penalise incorrect values once only $\begin{equation*} \Delta S_{\text {system }}^{\circ}=219.7+2 \times 188.7-151.1 \tag{1} \end{equation*}$ <br> EITHER $=+446(.0) \mathrm{J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ <br> OR $\begin{equation*} =+0.446(0) \mathrm{kJ} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \tag{1} \end{equation*}$ <br> Ignore SF except 1 SF <br> Correct answer with no working scores (3) <br> TE at each stage but no TE if wrong reactants / products used |  | (3) |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 16(a)(iii) | $\begin{align*} & \Delta S_{\text {surroundings }}^{\circ}=-\Delta H / T  \tag{1}\\ & \quad=-(-36000 /(160+273) \tag{1} \end{align*}$ <br> EITHER $=+83.1409 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ <br> OR $\begin{equation*} =+0.0831409 \mathrm{~kJ} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \tag{1} \end{equation*}$ <br> Ignore SF except 1 SF <br> Correct answer with no working scores <br> Omission of 273 (+225.0) scores <br> Sign incorrect ( $-83.14 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ ) scores (2) |  | (3) |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 16(a)(iv) | $\begin{align*} \Delta S_{\text {total }} & =\Delta S_{\text {system }}^{\circ}+\Delta S_{\text {surroundings }}^{\circ} \\ & =446.0+83.1409 \\ & =529.1409 \tag{1} \end{align*}$ <br> EITHER $=+530 / 529 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ <br> OR $\begin{equation*} =+0.53 / 0.529 \mathrm{~kJ} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \tag{1} \end{equation*}$ <br> Correct answer with sign and to 2 or 3 SF with no working scores (2) <br> TE on (a)(ii) and (a)(iii) and M1 | Answers not given to 2 or 3 SF | (2) |


| Question <br> Number | Acceptable Answers | Reject | Mark |
| :--- | :--- | :--- | :---: |
| $\mathbf{1 6 ( b ) ( i )}$ | $\Delta S_{\text {total }}=R \ln K$ |  | (2) |
|  | ALLOW $\Delta S=R \ln K$ only if $\Delta S=555$ is used (1) |  |  |
| In $K=\Delta S_{\text {total }} / R=555 / 8.31=66.787$ |  |  |  |
| $K=1.0121 \times 10^{29}$ |  |  |  |
| OR $K=9.80104 \times 10^{28}$ if $R=8.314$ used (1) |  |  |  |
| Correct answer with no working scores (2) |  |  |  |
| IGNORE units and $K_{c}$ expressions |  |  |  |
| Ignore SF |  |  |  |
| No TE on incorrect expressions |  |  |  |$\quad K=1.02 \times 10^{29}$|  |
| :--- |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| *16(b)(ii) | Route 1 <br> $\Delta S_{\text {system }}$ is (approximately) constant (with temperature) <br> (As $\Delta S_{\text {surroundings }}$ becomes less positive as $T$ increases) <br> $\Delta S_{\text {total }}$ becomes less positive / decreases /gets smaller (with increasing temperature) <br> and <br> so $K$ decreases <br> Route 2 <br> $\Delta S_{\text {system }}$ becomes more positive / increases with temperature and because the products are gases <br> (1) <br> (As $\Delta S_{\text {surroundings }}$ becomes less positive as $T$ increases) <br> cannot tell whether $\Delta S_{\text {total }}$ increases or decreases (with increasing temperature) so cannot tell whether $K$ increases or decreases <br> IGNORE <br> Just 'entropies of substances increase with temperature' <br> Explanations in terms of Le Chatelier's Principle | Just ' $\Delta S^{\prime}$ 'throughout | (2) |

(Total for Question 16 = 13 marks)

| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 17(a)(i) | M1 <br> Plot a graph of $\left[\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{Br}\right]$ (on the y axis) against time (on the x axis) <br> ALLOW <br> Plot a graph of concentration (of reactant) against time <br> OR <br> Diagram of graph with axes labelled <br> M2 <br> Draw a tangent at time $t=0 /$ initial concentration (of 2bromobutane) <br> ALLOW <br> Diagram from M1 with tangent clearly labelled (1) <br> M3 <br> Measure the gradient of the tangent <br> OR <br> Measure the gradient of the graph at time $t=0 /$ the initial concentration of 2-bromobutane <br> ALLOW <br> Measure the initial gradient (of the graph) | [ NaOH$]$ | (3) |
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| Question <br> Number | Acceptable Answers | Reject | Mark |
| :--- | :--- | :--- | :---: |
| 17(a)(ii) | So that the concentration of sodium hydroxide <br> would remain (approximately) constant <br> OR <br> Only the concentration of 2-bromobutane would <br> change <br> OR <br> So that the rate of reaction would only vary with the <br> (change in) concentration of 2-bromobutane <br> OR <br> So that the rate of reaction would not be affected by <br> (the change in concentration of) sodium hydroxide <br> IGNORE <br> References to limiting factors | So that all the 2- <br> bromobutane reacts | (1) |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 17(b)(i) | Standalone marks <br> E1 to $E 2\left[\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{Br}\right] \times 1.5$ and (initial) rate $\times 1.5([\mathrm{NaOH}]$ constant) so $1^{\text {st }}$ order (wrt [ $\left.\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{Br}\right]$ ) (1) <br> E1 to $E 3\left[\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{Br}\right] \times 2$ and $[\mathrm{NaOH}] \times 2$ and (initial) rate $\times$ <br> 4 so $1^{\text {st }}$ order wrt [ NaOH ] <br> (so confirms overall second order) |  | (2) |


| Question <br> Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 17(b)(ii) | $\begin{aligned} k & =\text { rate } /\left(\left[\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{Br}\right] \times[\mathrm{NaOH}]\right) \\ & =1.5 \times 10^{-5} /(0.020 \times 1.0) \\ & =7.5 \times 10^{-4} / 0.00075 \end{aligned}$ <br> ALLOW <br> Use of data from any of the experiments (E2 = $\begin{equation*} \left.7.667 \times 10^{-4} ; \mathrm{E} 3=7.375 \times 10^{-4}\right) \tag{1} \end{equation*}$ <br> Correct answer with no working scores (1) $\mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$ <br> ALLOW <br> Units in any order <br> No TE for either mark on incorrect rate equation |  | (2) |


| Question <br> Number | Acceptable Answers | Reject | Mark |
| :--- | :--- | :--- | :---: |
| $\mathbf{1 7 ( c ) ( \mathbf { i } )}$ | $\left[\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{Br}\right]$ and $[\mathrm{NaOH}] /\left[\mathrm{OH}^{-}\right]$are both involved in the <br> rate-determining step <br> ALLOW <br> both reactants /two reactants / two species / two <br> substances <br> in the slow step <br> in the RDS <br> IGNORE <br> References to the rate equation | Two molecules |  |$\quad$ (1) $\quad$ (


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 17(c)(ii) | Allow skeletal, displayed or semi displayed structures, use of $\mathrm{CH}_{3}$ and $\mathrm{C}_{2} \mathrm{H}_{5}$, omission of one H from $\mathrm{CH}_{3}$ and $\mathrm{C}_{2} \mathrm{H}_{5}$ in a displayed formula <br> IGNORE <br> Incorrect R groups / stages after the transition state <br> Products even if incorrect <br> Use of 1-bromobutane <br> M1 <br> Curly arrow from $\mathrm{C}-\mathrm{Br}$ bond to Br or just beyond and dipole <br> ALLOW <br> This curly arrow drawn on the transition state <br> M2 <br> Curly arrow from lone pair of O on $\mathrm{OH}^{-}$to C atom (1) <br> COMMENT <br> Award MP2 if arrow closer to lone pair than to oxygen / charge <br> M3 <br> Transition state including partial bonds and charge on any part of the transition state <br> IGNORE <br> Dipoles on the transition state <br> $\mathrm{S}_{\mathrm{N}} 1$ may score M1 and M2 | Ione pair shown on H $\mathrm{O}-\mathrm{H}-\mathrm{-}-\mathrm{C}$ in intermediate | (3) |


| Question <br> Number | Acceptable Answers | Reject | Mark |
| :--- | :--- | :--- | :---: |
| 17(d)(i) | (A chiral molecule) has a non-superimposable mirror <br> image <br> ALLOW <br> (A chiral molecule has) <br> an asymmetric carbon atom <br> OR <br> a carbon atom bonded to 4 different atoms / groups <br> OR <br> a carbon atom bonded to 4 different functional groups | Just 'molecule with <br> four different <br> groups' | (1) |
| ALLOW for 'bonded to' |  |  |  |
| Attached to / surrounded by |  |  |  |
| IGNORE |  |  |  |
| References to the rotation of the plane of plane |  |  |  |
| polarised light / optical activity |  |  |  |$\quad$|  |
| :--- |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| *17(d)(ii) | M1 <br> $\mathrm{S}_{\mathrm{N}} 1$ gives a racemic mixture <br> and <br> $\mathrm{S}_{\mathrm{N}} 2$ gives a single enantiomer / optical isomer <br> ALLOW <br> $\mathrm{S}_{\mathrm{N}} 1$ gives a mixture with no optical activity / both enantiomers <br> and <br> $\mathrm{S}_{\mathrm{N}} 2$ gives an optically active mixture / single isomer <br> (1) <br> M2 <br> In $\mathrm{S}_{\mathrm{N}} 1$ the intermediate (carbocation) is planar (about the carbon atom carrying the positive charge) <br> (1) <br> M3 <br> So the nucleophile / $\mathrm{OH}^{-}$attacks (equally) from either side / top and bottom (of the carbocation / intermediate) <br> M4 <br> In $\mathrm{S}_{\mathrm{N}} 2$ the nucleophile attacks one side of the molecule only / on the opposite side to the Br (1) <br> If $\mathrm{S}_{\mathrm{N}} 1$ and $\mathrm{S}_{\mathrm{N}} 2$ are reversed do not award M1 but max 3 available | molecule / carbonyl is planar <br> Alkali (for nucleophile $/ \mathrm{OH}^{-}$) <br> attacks the carbocation | (4) |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 18(a)(i) | IGNORE use / omission of heat / reflux <br> Reaction 1 <br> (dry) Phosphorus(V) chloride / phosphorus <br> pentachloride / $\mathrm{PCl}_{5}$ <br> OR <br> Phosphorus(III) chloride / phosphorus trichloride / $\mathrm{PCl}_{3}$ <br> ALLOW <br> Thionyl chloride $\mathrm{SOCl}_{2}$ <br> Reaction 2 <br> Methanol / CH3OH <br> Reaction 3 <br> Methanol / $\mathrm{CH}_{3} \mathrm{OH}$ and (concentrated) sulfuric acid / $\mathrm{H}_{2} \mathrm{SO}_{4}$ (heat) <br> ALLOW <br> Any strong acid by name or formula <br> Identified dilute strong acids <br> IGNORE H ${ }^{+}$ <br> If the same incorrect / unspecified alcohol is used in <br> Reactions $\mathbf{2}$ and $\mathbf{3}$ award (1) for otherwise correct answers <br> Reaction 4 <br> Lithium tetrahydridoaluminate((III)) / <br> lithium aluminium hydride / $\mathrm{LiAlH}_{4}$ <br> ALLOW <br> Lithal <br> In dry ether /diethyl ether / ethoxyethane | Additional reagents <br> Addition of acid | (5) |


| Question <br> Number | Acceptable Answers | Reject | Mark |
| :--- | :--- | :--- | :---: |
| 18(a)(ii) | Distilling the product directly out of the reaction <br> mixture <br> ALLOW <br> Just distil / distillation <br> IGNORE <br> Controlling temperature <br> Using excess butan-1-ol <br> Using limited amount of oxidising agent | Reflux <br> Fractional distillation <br> Steam distillation | (1) |


| Question <br> Number | Acceptable Answers | Reject | Mark |
| :---: | :--- | :--- | :---: |
| 18(a)(iii) | Advantage: (Overall) reaction goes to completion <br> ALLOW <br> Reaction fast(er) / does not require heat / occurs at <br> room temperature / does not require a catalyst <br> (1) | References to cost | (2) |
|  | IGNORE (For M1) <br> Reference to purity / yield / ease of reaction / vigorous <br> reaction / reaction not reversible / not equilibrium | Disadvantage: (Toxic / corrosive) hydrogen chloride / <br> HCl is formed <br> (1) | reaction not <br> reversible / <br> equilibrium |
| Two-step process / by-products formed |  |  |  |$\quad$|  |
| :--- |


| Question <br> Number | Acceptable Answers | Reject | Mark |
| :--- | :--- | :--- | :---: |
| 18(a)(iv) | Butanal is more easily reduced than butanoic acid <br> Butan-1-ol / butanol / alcohol is (always) formed <br> OR <br> difficult to stop the reduction at the aldehyde | (1) |  |
| IGNORE <br> References to the strength of the reducing agent <br> References to speed of reaction |  |  |  |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 18(b) | Any two from |  | (2) |
|  | But |  |  |
|  | $\mathrm{O}-\mathrm{H}$ at 3300-2500 $\left(\mathrm{cm}^{-1}\right)$ | 3750-3200 ( $\mathrm{cm}^{-1}$ ) |  |
|  | OR |  |  |
|  | Butanoic acid (will have stretching vibrations for) |  |  |
|  | $\mathrm{C}=\mathrm{O}$ at 1725-1700 ( $\mathrm{cm}^{-1}$ ) (1) |  |  |
|  | OR |  |  |
|  | Methyl butanoate (will have stretching vibrations for) |  |  |
|  | $\mathrm{C}=\mathrm{O}$ at 1750-1735 ( $\mathrm{cm}^{-1}$ ) |  |  |
|  | IGNORE |  |  |
|  | Reference to the fingerprint region |  |  |
|  | C-O at 1200-1180 / 1250-1230 / |  |  |
|  | $1200-1150\left(\mathrm{~cm}^{-1}\right)$ |  |  |
|  | If no other mark is awarded two correct wavenumber ranges with no bonds specified scores (1) |  |  |
|  | If no other mark is awarded two correct wavenumbers within the ranges with correct bonds specified scores (1) |  |  |


| Question <br> Number | Acceptable Answers | Reject | Mark |
| :--- | :--- | :--- | :---: |
| 18(c) | 10 parts per billion by volume <br> $=10 \mathrm{dm}^{3}$ butanoic acid (vapour) <br> per $1 \times 10^{9} \mathrm{dm}^{3}$ of air <br> $=1 \times 10^{-8} \mathrm{dm}^{3}$ butanoic acid per $\mathrm{dm}^{3}$ of air (1) <br> IGNORE <br> $1 \times 10^{-8}$ without units / explanation |  | (2) |
| $=1 \times 10^{-8} \div 24.0$ |  |  |  |
| $=4.16667 \times 10^{-10}\left(\right.$ mol $\left.\mathrm{dm}^{-3}\right)$ |  |  |  |
| Correct answer with no working scores (2) |  |  |  |
| IGNORE SF |  |  |  |



| Question <br> Number | Acceptable Answers | Reject | Mark |
| :--- | :--- | :--- | :---: |
| $\mathbf{2 0 ( a ) ( i )}$ | $\mathrm{HCOOH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HCOO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$ <br> OR <br> $\mathrm{HCOOH} \rightleftharpoons \mathrm{HCOO}^{-}+\mathrm{H}^{+}$ <br> ALLOW <br> $\mathrm{HCOOH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HCOO}^{-}+\mathrm{H}^{+}$ <br> $\rightarrow$ for $\rightleftharpoons$ <br> Ignore state symbols even if incorrect | Incorrect formulae <br> (penalise once only in <br> (i), (ii) and (iii) | (1) |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 20(a)(ii) | $K_{a}=\frac{\left[\mathrm{HCOO}^{-}\right]\left[\mathrm{H}^{+}\right]}{[\mathrm{HCOOH}]} \text { OR H} \mathrm{H}_{3} \mathrm{O}^{+} \text {for } \mathrm{H}^{+}$ <br> ALLOW $K_{\mathrm{c}}=\frac{\left[\mathrm{HCOO}^{-}\right]\left[\mathrm{H}^{+}\right]}{[\mathrm{HCOOH}]} \text { OR } \mathrm{H}_{3} \mathrm{O}^{+} \text {for } \mathrm{H}^{+}$ <br> IGNORE <br> State symbols even if incorrect <br> [ ]eq/ [ ]eqm $K_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]^{2}}{[\mathrm{HCOOH}]}$ | Other types of bracket Omission of $K_{a}=$ | (1) |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 20(a)(iii) | No TE on an incorrect expression in (a)(ii) |  | (4) |
|  | $[\mathrm{HCOOH}]=30 / 46=0.65217 \mathrm{~mol} \mathrm{dm}^{-3}$ |  |  |
|  | COMMENT |  |  |
|  | In M1 penalise multiple errors in calculation of the concentration once only |  |  |
|  | $K_{\mathrm{a}}=1.70 \times 10^{-4} \approx\left[\mathrm{H}^{+}\right]^{2} / 0.65217$ |  |  |
|  | $\begin{align*} {\left[\mathrm{H}^{+}\right] } & =\sqrt{ }\left(1.70 \times 10^{-4} \times 0.65217\right. \\ & =1.0529 \times 10^{-2} / 0.010529 \tag{1} \end{align*}$ |  |  |
|  | $\mathrm{pH}=-\log 0.010529=1.9776 / 1.98 / 2.0$ (1) | $\mathrm{pH}=2 / 1.9 / 1.97$ |  |
|  | TE at each stage of the calculation |  |  |
|  | Do not penalise premature correct rounding |  |  |
|  | If 30 is used for the concentration (in $\mathrm{mol} \mathrm{dm}^{-3}$ ) $\mathrm{pH}=$ 1.1462 / 1.15 / 1.1 scores (3) | $\mathrm{pH}=1.2$ |  |
|  | If square root not taken $\mathrm{pH}=3.9552$ scores (3) |  |  |
|  | IGNORE SF except 1 SF |  |  |
|  | Allow other calculation methods |  |  |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 20(a)(iv) | IGNORE explanations |  | (2) |
|  | ALLOW |  |  |
|  | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$for $\left[\mathrm{H}^{+}\right]$throughout |  |  |
|  | Use of HA and $\mathrm{A}^{-}$ |  |  |
|  | First mark: |  |  |
|  | $\mathrm{HCOOH} /$ methanoic acid ionisation / dissociation negligible |  |  |
|  | ALLOW |  |  |
|  | Acid for HCOOH |  |  |
|  | Slight / partial / incomplete / does not dissociate for negligible dissociation | Just 'dissociates less' |  |
|  | $\begin{aligned} & \text { OR } \\ & {[\mathrm{HCOOH}] \text { equilibrium }=[\mathrm{HCOOH}]_{\text {initial }} / 0.65217(\mathrm{~mol}} \end{aligned}$ |  |  |
|  | $\begin{equation*} \left.\mathrm{dm}^{-3}\right) \tag{1} \end{equation*}$ |  |  |
|  | Second mark: |  |  |
|  | ( $\left[\mathrm{H}^{+}\right]$due to) ionisation of water negligible |  |  |
|  | OR |  |  |
|  | [ $\mathrm{H}^{+}$] only due to (ionisation of) $\mathrm{HCOOH} /$ methanoic acid |  |  |
|  | OR |  |  |
|  | $\begin{equation*} \left[\mathrm{HCOO}^{-}\right]=\left[\mathrm{H}^{+}\right] \tag{1} \end{equation*}$ |  |  |
|  | IGNORE references to temperature |  |  |
|  | Penalise omission of [] or use of incorrect acid in discussion once only |  |  |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 20(b)(i) | Standalone marks <br> A buffer resists change in pH <br> OR <br> Maintains a fairly / nearly constant pH <br> ALLOW <br> Negligible change in pH <br> OR <br> resists significant change in pH <br> on the addition of small amounts of acid $/ \mathrm{H}^{+}$and of alkali / base / $\mathrm{OH}^{-}$ | prevents change in pH <br> Just constant pH | (2) |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| *20(b)(ii) | General answer in terms of HA and $\mathrm{A}^{-}$scores max 3 (M2, M3 and M4) <br> ALLOW use of names for formulae <br> M1 <br> HCOOH and $\mathrm{HCOO}^{-} / \mathrm{HCOONa}$ are present in high concentration / large amount / large excess / form a (large) reservoir <br> M2 <br> When acid is added the $\mathrm{HCOO}^{-} / \mathrm{HCOONa}$ is protonated / reacts, removing the $\mathrm{H}^{+}$ion from the solution / forming HCOOH <br> OR $\begin{equation*} \mathrm{HCOO}^{-}+\mathrm{H}^{+} \rightarrow \mathrm{HCOOH} \tag{1} \end{equation*}$ <br> M3 <br> When alkali is added the HCOOH <br> reacts, removing the $\mathrm{OH}^{-}$ion (from the solution) <br> OR <br> reacts forming $\mathrm{HCOO}^{-}$or $\mathrm{HCOO}^{(-)} \mathrm{Na}^{(+)}$or water <br> OR <br> $\mathrm{OH}^{-}$reacts with $\mathrm{H}^{+}$and HCOOH dissociates to replace the $\mathrm{H}^{+}$ <br> OR <br> $\mathrm{HCOOH}+\mathrm{OH}^{-} \rightarrow \mathrm{HCOO}^{-}+\mathrm{H}_{2} \mathrm{O}$ <br> M4 <br> So $[\mathrm{HCOOH}]$ and $[\mathrm{HCOO}]$ do not change (significantly) <br> OR <br> the ratio $[\mathrm{HCOOH}]$ : $\left[\mathrm{HCOO}^{-}\right]$does not change (significantly) <br> ALLOW <br> Use of HCOOH and $\mathrm{HCOO}^{-}$for $[\mathrm{HCOOH}]$ and [ $\mathrm{HCOO}^{-}$] <br> (1) <br> For M2 and M3: <br> Just "acid reacts with $\mathrm{HCOO}^{-}$and alkali reacts with HCOOH" scores (1) |  | (4) |


| Question Number | Acceptable Answers | Reject | Mark |
| :---: | :---: | :---: | :---: |
| 20(c)(i) | Route 1 |  | (3) |
|  | $K_{\mathrm{a}}=\left[\underline{\left.\mathrm{H}^{+}\right] \times\left[\mathrm{HCOO}^{-}\right]}\right.$ |  |  |
|  | $\text { [ } \mathrm{HCOOH}]$ <br> $\left[\mathrm{H}^{+}\right]=K_{a} \times[\mathrm{HCOOH}]$ |  |  |
|  |  |  |  |
|  | $\begin{array}{r} {\left[\mathrm{H}^{+}\right]=K_{\mathrm{a}} \times\left[\mathrm{HCOOH}^{\mathrm{COO}]}\right.}  \tag{1}\\ {\left[\mathrm{HCOO}^{-}\right]} \end{array}$ |  |  |
|  | $=1.70 \times 10^{-4} \times 1.25 / 1.50$ |  |  |
|  | $=1.41667 \times 10^{-4}$ |  |  |
|  | $\mathrm{pH}=3.8487=3.85 / 3.8$ | $\mathrm{pH}=3.84 / 3.9$ |  |
|  | Route 2 |  |  |
|  | $\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \left[\mathrm{HCOO}^{-}\right]$ |  |  |
|  |  |  |  |
|  | $=-\log \left(1.70 \times 10^{-4}\right)+\log (1.50 / 1.25)$ |  |  |
|  | $=3.8487=3.85$ | $\mathrm{pH}=3.84 / 3.9$ |  |
|  | Correct answer with no working scores (3) |  |  |
|  | Inversion of concentrations pH = 3.69 scores (2) |  |  |
|  | Penalise inversion once only in (i) and (ii) |  |  |
|  | IGNORE SF except 1 SF |  |  |


(Total for Question $20=20$ marks)
TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

