| Question |  |  | Answer | Marks | Guidance |
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| 1 | (a) |  | Proton/ $\mathrm{H}^{+}$donor <br> AND <br> Partially dissociates/ionises $\checkmark$ | 1 |  |
|  | (b) |  | FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 13.7(0), award 2 marks $\begin{aligned} & {\left[\mathrm{H}^{+}\right]=\frac{1.00 \times 10^{-14}}{0.5(00)} \text { OR } 2(.00) \times 10^{-14}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)} \\ & \mathrm{pH}=-\log 2(.00) \times 10^{-14}=13.7(0) \end{aligned}$ | 2 | For pOH method:, <br> ALLOW $\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]=0.3(0) \checkmark$ <br> (calculator 0.301029995) <br> ALLOW pH $=14-0.3=13.7 \checkmark$ <br> ALLOW 13.7 up to calculator value of 13.69897 correctly rounded. <br> ALLOW ECF from incorrect $\left[\mathrm{H}^{+}(\mathrm{aq})\right]$ provided that $\mathrm{pH}>7$ |
|  | (c) | (i) | $\left(K_{\mathrm{a}}=\right) \frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}\right]}{\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right]}$ | 1 | IGNORE $\frac{\left[\mathrm{H}^{+}\right]^{2}}{\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right]}$ OR $\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$ <br> ALLOW $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$for $\left[\mathrm{H}^{+}\right]$ <br> IGNORE state symbols |


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| (c) | (ii) | FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 2.9(0), award 3 marks <br> $\left[\mathrm{C}{ }_{2} \mathrm{H}_{5} \mathrm{COOH}\right]=0.12(0) \mathrm{mol} \mathrm{dm}^{-3} \checkmark$ $\left[\mathrm{H}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{a}} \times\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right]}=\sqrt{1.35 \times 10^{-5} \times 0.12(0)}$ <br> OR $1.27 \times 10^{-3}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)^{\checkmark}$ $\mathrm{pH}=-\log 1.27 \times 10^{-3}=2.9(0)$ <br> NOTE: The final two marks are ONLY available from attempted use of $K_{\mathrm{a}}$ AND $\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right]$ | 3 | ALLOW HA for $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$ and $\mathrm{A}^{-}$for $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}$ <br> ALLOW ECF from incorrectly calculated $\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right]$ <br> ALLOW $1.27 \times 10^{-3}$ to calculator value of $1.272792206 \times$ $10^{-3}$ correctly rounded <br> ALLOW 2.9(0) $\times 10^{-3}$ to calculator value of 2.895242493 correctly rounded <br> ALLOW use of quadratic equation which gives same answer of 2.90 from $0.120 \mathrm{~mol} \mathrm{dm}^{-3}$ <br> COMMON ERRORS (MUST be to AT LEAST 2 DP unless $2^{\text {nd }}$ decimal place is 0 ) |


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| (d) | (i) | $2 \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}+\mathrm{Na}_{2} \mathrm{CO}_{3} \rightarrow 2 \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COONa}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \checkmark$ | 1 | IGNORE state symbols and use of equilibrium sign FOR $\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$ ALLOW $\mathrm{H}_{2} \mathrm{CO}_{3}$ <br> ALLOW $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-} \mathrm{Na}^{+} \mathrm{OR} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}+\mathrm{Na}^{+}$ BUT BOTH + and - charges must be shown ALLOW $\mathrm{NaC}_{2} \mathrm{H}_{5} \mathrm{COO}$ |
| (d) | (ii) | $\mathrm{H}^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O} \checkmark$ | 1 | ALLOW $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}+\mathrm{OH}^{-} \rightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O}$ IGNORE state symbols |
| (e) | (i) | $\mathrm{pH}=-\log 1.35 \times 10^{-5}=4.87$ | 1 | ONLY correct answer DO NOT ALLOW 4.9 <br> (Question asks for 2 DP) |
| (e) | (ii) | Added ammonia <br> $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$ removes added $\mathrm{NH}_{3} /$ alkali/base <br> $\mathrm{OR} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}+\mathrm{NH}_{3} / \mathrm{OH}^{-} \rightarrow$ <br> OR $\mathrm{NH}_{3} /$ alkali reacts with/accepts $\mathrm{H}^{+}$ <br> OR H ${ }^{+}+\mathrm{NH}_{3} \rightarrow$ <br> $\mathrm{ORH}^{+}+\mathrm{OH}^{-} \rightarrow \checkmark$ <br> Equlibrium $\rightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}$OR Equilibrium $\rightarrow$ right $\checkmark$ | 2 | ALLOW use of HA/weak acid/acid for $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$; <br> ALLOW use of $\mathrm{NH}_{4} \mathrm{OH}$ for $\mathrm{NH}_{3}$ <br> ALLOW A- for $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}$ <br> ASSUME that equilibrium applies to that supplied in the question, i.e. IGNORE any other equilibria |


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| (e) ${ }^{\text {(iii) }}$ | CHECK WORKING CAREFULLY AS CORRECT NUMERICAL ANSWER IS POSSIBLE FROM WRONG VALUES <br> ALLOW HA and $\mathrm{A}^{-}$throughout <br> Amount of Mg <br> (1 mark) $n(\mathrm{Mg})=\frac{6.075}{24.3}=0.25(0) \mathrm{mol}$ <br> Moles/concentrations(2 marks) $\begin{aligned} & n\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right)=1.00-(2 \times 0.25) \\ &\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}\right)=1.00+(2 \times 0.25)=1.50(\mathrm{~mol}) \\ &(\mathrm{mol}) \end{aligned}$ <br> $\left[\mathrm{H}^{+}\right]$and $\mathrm{pH} \quad$ ( 1 mark) $\begin{aligned} {\left[\mathrm{H}^{+}\right] } & =1.35 \times 10^{-5} \times \frac{0.50}{1.50} \text { OR } 4.5 \times 10^{-6}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right) \\ \mathrm{pH} & =-\log 4.5 \times 10^{-6}=5.35 \quad 2 \mathrm{dp} \text { required } \checkmark \end{aligned}$ <br> NOTE: IF there is no prior working, <br> ALLOW 4 MARKS for $\left[\mathrm{H}^{+}\right]=1.35 \times 10^{-5} \times \frac{0.50}{1.50}$ AND $\mathrm{pH}=5.35$ <br> IF the ONLY response is $\mathrm{pH}=5.35$, award 1 mark ONLY | 4 | FULL ANNOTATIONS MUST BE USED <br> For $\boldsymbol{n}(\mathrm{Mg}), 1$ mark <br> ALLOW ECF for ALL marks below from incorrect $n(\mathrm{Mg})$ <br> ECF ONLY available from concentrations that have <br> - subtracted 0.50 OR 0.25 from 1 for $\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right]$ <br> - added 0.50 OR 0.25 to 1 for $\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}\right]$ <br> $i$. <br> For moles/concentration 1 mark ( 1 mark lost) <br> 1. $n\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right)=0.75$ AND $n\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}\right)=1.25$ <br> 2. $n\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right)=0.50$ AND $n\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}\right)=1.25$ <br> 3. $n\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right)=0.75$ AND $n\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}\right)=1.50$ <br> ALLOW ECF ONLY for the following giving 1 additional mark and a total of 3 marks <br> 1. $\left[\mathrm{H}^{+}\right]=1.35 \times 10^{-5} \times \frac{0.75}{1.25} \mathrm{pH}=-\log 8.1 \times 10^{-6}=5.09$ <br> 2. $\left[\mathrm{H}^{+}\right]=1.35 \times 10^{-5} \times \frac{0.50}{1.25} \mathrm{pH}=-\log 5.4 \times 10^{-6}=5.27$ <br> 3. $\left[\mathrm{H}^{+}\right]=1.35 \times 10^{-5} \times \frac{0.75}{1.50} \mathrm{pH}=-\log 6.75 \times 10^{-6}=5.17$ |
|  | Award a maximum of 1 mark (for $\boldsymbol{n}(\mathbf{M g})=0.25 \mathrm{~mol}$ ) for: <br> pH value from $K_{\mathrm{a}}$ square root approach (weak acid pH ) <br> pH value from $K_{\mathrm{w}} / 10^{-14}$ approach (strong base pH ) <br> ALLOW alternative approach based on Henderson-Hasselbalch equation for final 1 mark $\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{1.5}{0.5} \mathrm{OR} \mathrm{p} K_{\mathrm{a}}-\log \frac{0.5}{1.5} \quad \mathrm{pH}=4.87+0.48=5.35 \checkmark \quad \text { ALLOW }{ }_{-\log } K_{\mathrm{a}} \text { for } \mathrm{p} K_{\mathrm{a}}$ |  |  |
|  | Total | 16 |  |


| Question |  |  | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | (a) |  | $\underset{\text { Acid 1 }}{\mathrm{CH}_{3} \mathrm{COOH}}+\underset{\text { Base 2 }}{\mathrm{H}_{2} \mathrm{O}} \rightleftharpoons \underset{\text { Acid 2 }}{\mathrm{H}_{3} \mathrm{O}^{+}}+\underset{\text { Base } 1 \checkmark}{\mathrm{CH}_{3} \mathrm{COO}^{-} \checkmark}$ | 2 | IGNORE state symbols (even if incorrect) <br> ALLOW 1 AND 2 labels the other way around. <br> ALLOW 'just acid' and 'base' labels if linked by lines so that it is clear what the acid-base pairs are ALLOW A and B for 'acid' and 'base' <br> IF proton transfer is wrong way around ALLOW 2nd mark for idea of acid-base pairs, i.e. $\underset{\text { Base 2 }}{\mathrm{CH}_{3} \mathrm{COOH}}+\underset{\text { Acid 1 }}{\mathrm{H}_{2} \mathrm{O}} \rightleftharpoons \underset{\text { Acid } 2}{\mathrm{CH}_{3} \mathrm{COOH}_{2}^{+}+\mathrm{OH}^{-} \times} \text {Base } 1 \checkmark$ <br> NOTE For the 2nd marking point (acid-base pairs), this is the ONLY acceptable ECF i.e., NO ECF from impossible chemistry |
|  | (b) | (i) | Water dissociates/ionises OR $\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}^{+}+\mathrm{OH}^{-}$ <br> OR $2 \mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \checkmark$ | 1 | ALLOW $K_{\mathrm{w}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$ <br> OR $\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=10^{-14}\left(\mathrm{~mol}^{2} \mathrm{dm}^{-6}\right)$ <br> IGNORE breaking for dissociation <br> IGNORE water contains $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$ <br> IGNORE $\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}^{+}+\mathrm{OH}^{-} \quad$ i.e. no equilibrium sign <br> IGNORE $2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-}$i.e. no equilibrium sign |


| (b) | (ii) | FIRST, CHECK THE ANSWER ON ANSWER LINE <br> IF answer $=1.15 \times 10^{-11}$, award 2 marks $\begin{aligned} & {\left[\mathrm{H}^{+}\right]=10^{-3.06}=8.71 \times 10^{-4}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right) \checkmark} \\ & {\left[\mathrm{OH}^{-}\right]=\frac{1.00 \times 10^{-14}}{8.71 \times 10^{-4}}=1.15 \times 10^{-11}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)^{\vee}} \end{aligned}$ <br> ALLOW answer to two or more significant figures 2SF: $1.1 \times 10^{-11}$; 4 SF: $1.148 \times 10^{-11}$; <br> calculator $1.148153621 \times 10^{-11}$ | 2 | IF there is an alternative answer, check to see if there is any ECF credit possible using working below. <br> ALLOW 2 SF: $8.7 \times 10^{-4}$ up to calculator value of $8.7096359 \times 10^{-4}$ correctly rounded <br> ALLOW alternative approach using pOH : $\begin{aligned} & \mathrm{pOH}=14-3.06=10.94 \checkmark \\ & {\left[\mathrm{OH}^{-}\right]=10^{-10.94}=1.15 \times 10^{-11}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right) \checkmark} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: |
| (c) | (i) | $2 \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{CaCO}_{3} \rightarrow\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2} \mathrm{Ca}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \checkmark$ | 1 | IGNORE state symbols <br> ALLOW $\rightleftharpoons$ provided that reactants on LHS <br> For $\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$, ALLOW $\mathrm{H}_{2} \mathrm{CO}_{3}$ <br> ALLOW $\mathrm{Ca}\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2}$ <br> ALLOW $\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)_{2} \mathrm{Ca}^{2+}$ <br> BUT DO NOT ALLOW if either charge is missing or incorrect |


| (c) | (ii) | solution contains $\mathrm{CH}_{3} \mathrm{COOH}$ AND $\mathrm{CH}_{3} \mathrm{COO}^{-} \checkmark$ |
| :--- | :--- | :--- | :--- | :--- | :--- |$\quad$| ALLOW names: ethanoic acid for $\mathrm{CH}_{3} \mathrm{COOH}^{\text {ethanoate for } \mathrm{CH}_{3} \mathrm{COO}^{-}}$ |
| :--- |


| (c) | (iii) | Quality of written communication, QWC |  | FULL ANNOTATIONS MUST BE USED |
| :---: | :---: | :---: | :---: | :---: |
|  |  | 2 marks are available for explaining how the equilibrium system allows the buffer solution to control the pH on addition of $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$(see below) |  | Note: If there is no equilibrium equation then the two subsequent equilibrium marks are not available: max 2 |
|  |  | $\mathrm{CH}_{3} \mathrm{COOH} \rightleftharpoons \mathrm{H}^{+}+\mathrm{CH}_{3} \mathrm{COO}^{-} \checkmark$ |  | DO NOT ALLOW HA $\rightleftharpoons \mathrm{H}^{+}+\mathrm{A}^{-}$ DO NOT ALLOW more than one equilibrium equation. |
|  |  |  |  | ALLOW response in terms of $\mathrm{H}^{+}, \mathrm{A}^{-}$and HA |
|  |  | $\mathrm{OR} \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-} \rightarrow$ OR added alkali reacts with $\mathrm{H}^{+}$ $\mathrm{OR} \mathrm{H}+\mathrm{OH}^{-} \rightarrow \checkmark$ |  | IF more than one equilibrium shown, it must be clear which one is being referred to by labeling the equilibria. |
|  |  | Equilibrium $\rightarrow$ right OR Equilibrium $\rightarrow \mathrm{CH}_{3} \mathrm{COO}^{-} \checkmark$ (QWC) |  | ALLOW weak acid reacts with added alkali DO NOT ALLOW acid reacts with added alkali |
|  |  | $\mathrm{CH}_{3} \mathrm{COO}^{-}$reacts with added acid $\checkmark$ |  |  |
|  |  | Equilibrium $\rightarrow$ left OR Equilibrium $\rightarrow \mathrm{CH}_{3} \mathrm{COOH} \checkmark$ (QWC) | 5 | ALLOW conjugate base reacts with added acid DO NOT ALLOW salt/base reacts with added acid |





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| (b) | $2 \mathrm{Al}+6 \mathrm{CH}_{3} \mathrm{COOH} \longrightarrow 2\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{3} \mathrm{Al}+3 \mathrm{H}_{2} \checkmark$ $2 \mathrm{Al}+6 \mathrm{H}^{+} \longrightarrow 2 \mathrm{Al}^{3+}+3 \mathrm{H}_{2} \checkmark$ | 2 | IGNORE state symbols <br> ALLOW correct multiples, e.g.: <br> $\mathrm{Al}+3 \mathrm{CH}_{3} \mathrm{COOH} \longrightarrow\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{3} \mathrm{Al}+1.5 \mathrm{H}_{2}$ <br> ALLOW any unambiguous formula for $\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{3} \mathrm{Al}$, <br> i.e. $\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{3} \mathrm{Al}, \mathrm{Al}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{3},\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)_{3} \mathrm{Al}^{3+}$, etc. <br> Note: IF charges are shown, they must be correct with <br> both - and 3+ shown <br> ALLOW multiples, e.g.: <br> $\mathrm{Al}+3 \mathrm{H}^{+} \longrightarrow \mathrm{Al}{ }^{3+}+1.5 \mathrm{H}_{2}$ |
| (c) | FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 13.6(0), award 2 marks $\qquad$ <br> $\left[\mathrm{H}^{+}\right]=\frac{K_{w}}{\left[\mathrm{OH}^{-}\right]}$OR $\frac{1.0 \times 10^{-14}}{\left[\mathrm{OH}^{-}\right]}$OR $\frac{1.0 \times 10^{-14}}{0.4(0)}$ <br> OR $2.5 \times 10^{-14}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)^{\checkmark}$ <br> Correctly calculates $\mathrm{pH}=-\log 2.5 \times 10^{-14}=13.6(0) \checkmark$ | 2 | ALLOW alternative approach using pOH : $\begin{aligned} & \mathrm{pOH}=0.4(0) \checkmark \\ & \mathrm{pH}=14-0.40=13.6(0) \checkmark \end{aligned}$ <br> ALLOW ECF from $\left[\mathrm{H}^{+}\right]$derived using $K_{w}$ and $\left[\mathrm{OH}^{-}\right]$ BUT DO NOT ALLOW an acid pH. <br> ALLOW one or more decimal places |


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| (d) | (i) | A buffer solution minimises pH changes on addition of small amounts of acid $/ \mathrm{H}^{+}$or alkali/ $\mathrm{OH}^{-} /$base $\qquad$ $\mathrm{HCOOH} \rightleftharpoons \mathrm{H}^{+}+\mathrm{HCOO}^{-} \checkmark$ <br> Equilibrium sign essential | 7 | ANNOTATE WITH TICKS AND CROSSES, etc <br> ALLOW resists pH changes <br> ALLOW buffer solutions maintains a nearly/virtually constant pH <br> DO NOT ALLOW a response that implies that the pH is actually constant, e.g. does not change pH ; maintains pH <br> DO NOT ALLOW $\mathrm{COOH}^{-}$OR CHOOH OR COOH <br> DO NOT ALLOW HA $\rightleftharpoons \mathrm{H}^{+}+\mathrm{A}^{-}$ |
|  |  | For effect of acid and alkali, ALLOW wrong carboxylic acid (e.g. $\mathrm{CH}_{3} \mathrm{COOH}$ ) OR HA; ALLOW CHOOH for acid (effectively ECF) ALLOW $\mathrm{COOH}^{-}$for base <br> ALLOW responses based on $\mathrm{COOH} \rightleftharpoons \mathrm{H}^{+}+\mathrm{COO}^{-}$ DO NOT ALLOW other incorrect formula, e.g. $\mathrm{CH}_{3} \mathrm{OOH}$ |  | ality of written communication, QWC <br> arks are for explaining how the equilibrium system allows buffer solution to control the pH on addition of $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$ |
|  |  | Added alkali <br> HCOOH reacts with added alkali/base/ $\mathrm{OH}^{-}$ <br> OR added alkali/ $\mathrm{OH}^{-}$reacts with $\mathrm{H}^{+} \checkmark$ <br> QWC: Equilibrium shifts forming $\mathrm{HCOO}^{-} \mathrm{OR} \mathrm{H}^{+}$ OR (HCOOH) Equilibrium $\rightarrow$ right $\checkmark$ <br> Added acid <br> $\mathrm{HCOO}^{-}$reacts with added acid $/ \mathrm{H}^{+} \checkmark$ <br> QWC: Equilibrium shifts forming HCOOH OR ( HCOOH ) Equilibrium $\rightarrow$ left $\checkmark$ |  | ALLOW HA OR weak acid reacts with added alkali <br> DO NOT ALLOW this mark if there is no equilibrium system shown, e.g. $\mathrm{HCOOH} \rightleftharpoons \mathrm{H}^{+}+\mathrm{HCOO}^{-}$is absent <br> ALLOW A- OR conjugate base reacts with added acid IGNORE salt reacts with added acid <br> DO NOT ALLOW this mark if there is no equilibrium system shown, e.g. $\mathrm{HCOOH} \rightleftharpoons \mathrm{H}^{+}+\mathrm{HCOO}^{-}$is absent |



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| 4 | (a) | (i) | $\left(K_{\mathrm{a}}=\right) \frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}\right]}$ | 1 | ALLOW CH $3_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COOH} \mathrm{OR} \mathrm{C}_{3} \mathrm{H}_{7} \mathrm{COOH}$ in expression <br> DO NOT ALLOW use of HA and $\mathrm{A}^{-}$in this part. <br> DO NOT ALLOW: $\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}\right]}=\frac{\left[\mathrm{H}^{+}\right]^{2}}{\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}\right]}: \mathrm{CON}$ |
|  |  | (ii) | $\mathrm{p} K_{\mathrm{a}}=-\log K_{\mathrm{a}}=4.82 \checkmark$ | 1 | ALLOW 4.82 up to calculator value of 4.821023053 DO NOT ALLOW 4.8 |
|  |  | (iii) | FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer $=2.71$ award $\mathbf{3}$ marks $\begin{aligned} & {\left[\mathrm{H}^{+}\right]=\sqrt{\left[\mathrm{K}_{\mathrm{a}}\right]\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}\right]} \text { OR } \sqrt{1.51 \times 10^{-5} \times 0.250}} \\ & \checkmark \\ & {\left[\mathrm{H}^{+}\right]=1.94 \times 10^{-3}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)^{\checkmark}} \\ & \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=2.71 \checkmark \end{aligned}$ | 3 | IF alternative answer to more or fewer decimal places, check calculator value and working for 1st and 2nd marks <br> ALLOW use of HA and $A^{-}$in this part <br> Calculator: $1.942935923 \times 10^{-3}$ <br> ALLOW use of calculated $K_{\mathrm{a}}$ value, either calculator value or rounded on script. <br> pH must be to 2 decimal places <br> ALLOW ECF from incorrectly calculated $\left[\mathrm{H}^{+}\right]$and pH ONLY when values for both $K_{\mathrm{a}}$ AND [ $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COOH}$ ] have been used, i.e. $1.5 \times 10^{-5}$ AND 0.250 . e.g.: $\left[\begin{array}{llrl} \mathrm{pH}=5.42 & 2 \text { marks } & -\log \left(1.51 \times 10^{-5} \times 0.250\right) & \text { No } \sqrt{ } \\ \mathrm{pH}=2.11 & 2 \text { marks } & -\log \left(\sqrt{\frac{1.51 \times 10^{-5}}{0.250}}\right) & \\ \mathrm{pH}=4.22 & 1 \text { mark } & -\log \left(\frac{1.51 \times 10^{-5}}{0.250}\right) & \text { No } \sqrt{ } \end{array}\right.$ <br> DO NOT ALLOW just $-\log \left(1.51 \times 10^{-5}\right)=4.82$ NO MARKS |



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| (c) | (ii) | ```Moles (2 marks) amount \(\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}=0.0100(\mathrm{~mol})\) amount \(\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}=0.0025(\mathrm{~mol})\) Concentration (1 mark) \(\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}\right]=0.100 \mathrm{~mol} \mathrm{dm}^{-3}\) AND \(\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}\right]=0.025 \mathrm{~mol} \mathrm{dm}^{-3} \checkmark\) [ \(\mathrm{H}^{+}\)] and pH (2 marks) \(\left[\mathrm{H}^{+}\right]=1.51 \times 10^{-5} \times \frac{0.100}{0.025}=6.04 \times 10^{-5}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)\) \(\mathrm{pH}=-\log 6.04 \times 10^{-5}=4.22 \checkmark\) pH to 2 DP``` | 2 1 1 2 | ANNOTATIONS MUST BE USED <br> ALLOW HA and $\mathrm{A}^{-}$throughout <br> Mark by ECF throughout <br> ONLY award final 2 marks via a correct pH calculation via $K_{\mathrm{a}} \times \frac{\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}\right]}{\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}\right]}$ using data derived from that in the question (i.e. not just made up values) |
|  |  | ALLOW alternative approach based on Henderson-Hasselbalch equation for final 2 marks$\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{0.025}{0.100} \text { OR } \mathrm{p} K_{\mathrm{a}}-\log \frac{0.100}{0.025} \checkmark \quad \mathrm{pH}=4.82-0.60=4.22 \checkmark \quad \text { ALLOW }-\log K_{\mathrm{a}} \text { for } \mathrm{p} K_{\mathrm{a}}$ |  |  |
|  |  | TAKE CARE with awarding marks for $\mathrm{pH}=4.22$ <br> There is a mark for the concentration stage. <br> If this has been omitted, the ratio for the last 2 marks will be 0.0100 and 0.0025 . 4 marks max. <br> Common errors $\mathrm{pH}=5.42$ <br> As above for 4.22 but with acid/base ratio inverted. <br> Award 4 OR 3 marks <br> Award zero marks for: <br> 4.12 from no working or random values <br> pH value from $K_{\mathrm{a}}$ square root approach (weak acid pH ) <br> pH value from $K_{\mathrm{w}} / 10^{-14}$ approach (strong base pH ) |  | Common errors $\mathrm{pH}=4.12$ <br> use of initial concentrations: 0.250 and 0.050 given in question. <br> Award last 3 marks for: <br> 0.250/2 AND 0.050/2 $=0.125$ AND $0.025 \checkmark$ $\begin{aligned} & 1.51 \times 10^{-5} \times \frac{0.125}{0.025}=7.55 \times 10^{-5}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)^{\checkmark} \\ & \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=4.12 \end{aligned}$ <br> Award last 2 marks for: $\mathrm{pH}=5.52$ $\begin{aligned} & 1.51 \times 10^{-5} \times \frac{0.250}{0.050}=7.55 \times 10^{-5}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right) \\ & \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=4.12 \end{aligned}$ <br> As above for 4.12 but with acid/base ratio inverted. Award 2 OR 1 marks as outlined for 4.12 above |


| Quest | Answer | Marks | Guidance |
| :---: | :---: | :---: | :---: |
| (d) | $\begin{aligned} & \mathrm{HCOOH}+\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH} \underset{ }{\rightleftharpoons} \mathrm{HCOO}+\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}_{2}^{+} \\ & \\ & \text {acid 1 base 2 base 1 acid } 2 \checkmark \\ & \\ & \text { CARE: } \\ & \begin{array}{l} \text { Both + and - charges are required for the products in } \\ \text { the equilibrium } \\ \text { DO NOT AWARD the 2nd mark from an equilibrium } \\ \text { expression that omits either charge } \end{array} \\ & \hline \end{aligned}$ | 2 | State symbols NOT required <br> ALLOW 1 and 2 labels the other way around. <br> ALLOW 'just acid' and 'base' labels throughout if linked by lines so that it is clear what the acid-base pairs are <br> For 1st mark, DO NOT ALLOW $\mathrm{COOH}^{-}$ <br> (i.e. H at end rather than start) <br> but within 2nd mark ALLOW $\mathrm{COOH}^{-}$by ECF <br> IF proton transfer is wrong way around then ALLOW 2nd mark for idea of acid-base pairs, i.e. $\begin{array}{ccc} \mathrm{HCOOH}+\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH} \underset{\sim}{\rightleftharpoons} \\ \text { base 2 } & \text { acid 1 } & \\ & & \text { acid 2 } \end{array}$ <br> For $\mathrm{H}_{2} \mathrm{COOH}^{+}$shown with wrong proton transfer, DO NOT ALLOW an ECF mark for acid-base pairs |
|  | Total | 16 |  |

