M1.(a) $\left[\mathrm{H}^{+}\right]=\frac{\frac{\mathrm{K}_{\mathrm{a}} \times\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\mathrm{CH}_{3} \mathrm{COO}^{-}} \text {or }=1.74 \times 10^{-5} \times \frac{0.186}{0.105}}{0}$

## Allow ()

$=3.08 \times 10^{-5}$
If $[H X] /[X]$ or $\frac{0.186}{0.105}$ upside down, or any addition or subtraction lose M1 \& M2.

M2
$\mathrm{pH}=4.51 \quad$ (correct answer scores 3)
Can score M 3 for correct pH conseq to their $\left[\mathrm{H}^{+}\right]$, so $\mathrm{pH}=$ 5.01 scores one Must be to $2 d p$

Alternative using Henderson-Hasselbach Equation

$$
\begin{gathered}
\left.\mathrm{pH}=\mathrm{pKa}-\log [\mathrm{HX}] / \mathrm{X}^{-}\right]=-\log \left(1.74 \times 10^{-5}\right)-\log \left(\frac{0.186}{0.105}\right) \\
\text { Allow }()
\end{gathered}
$$

$$
\mathrm{pKa}=4.76-0.248
$$

If $[H X] /[X]$ ] or $\frac{0.186}{0.105}$ upside down, can only score 1

$$
\mathrm{pH}==4.51
$$

$$
\text { so } \mathrm{pH}=5.01
$$

$$
\text { Must be to } 2 d p
$$

(b) $\quad \mathrm{mol} \mathrm{HX}$ after addition $(=0.251+0.015)=0.266$

For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3
$\left[\mathrm{H}^{+}\right]=\left(\frac{\mathrm{K}_{\mathrm{a}} \times\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\mathrm{CH}_{3} \mathrm{COO}^{-}}\right)=\frac{1.74 \times 10^{-5} \times 0.266}{0.125}$

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 $\mathrm{pH}=4.58$ scores 2

M3
$\left[\mathrm{H}^{+}\right]=3.703 \times 10^{-} 5\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$
If [HX] / [X] upside down, lose M3 \& M4 (or next two marks) but can score M5 for correct pH conseq to their [ $\mathrm{H}^{+}$], so if M1 \& M2 correct, $\mathrm{pH}=5.09$ scores 3 .
$\mathrm{pH}=4.43$
Correct use of HX and $\mathrm{X}^{-}$values from (d) gives $\mathrm{pH}=4.41$ and scores 4

If wrong method, e.g. $\sqrt{ }$ or no use of rearranged $K_{a}$ expression, may score M1 \& M2 but no more.
Allow more but not fewer than 2dp here.

Alternative using Henderson-Hasselbach Equation
mol acid after addition $=0.251+0.015=0.266$
For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3

$$
\begin{aligned}
& \text { mol salt after addition }=0.140-0.015=0.125 \\
& \text { For } X \text { if no subtraction or error in subtraction (other than AE) } \\
& \text { (or subsequent extra add or sub) MAX } 3 \\
& \mathrm{pH}=\left(\mathrm{pKa}-\log [\mathrm{HX}] /\left[\mathrm{X}^{-}\right]\right)=-\log \left(1.74 \times 10^{-5}\right)-\log (0.266 / 0.125) \\
& \text { If errors above in both addition AND subtraction can only } \\
& \text { score M3 for insertion of their numbers }- \text { except if addition } \\
& \text { and subtraction reversed then } \mathrm{pH}=4.58 \text { scores } 2
\end{aligned}
$$

M2

M3

M4

M5
[8]

M2.(a) $\mathrm{HCO}_{3}^{-}=\mathrm{CO}_{3}{ }^{2-}+\mathrm{H}^{+}$
or
$\mathrm{H}_{2} \mathrm{O}+\mathrm{HCO}_{3}^{-}=\mathrm{CO}_{3}{ }^{2-}+\mathrm{H}_{3} \mathrm{O}^{+}$
Must have equilibrium sign but mark on to (b) Ignore state symbols
(b) Acid: Increase in concentration of $\mathrm{H}^{+}$ions, equilibrium moves to the left. Allow $\mathrm{H}^{+}$ions react with carbonate ions (to form $\mathrm{HCO}_{3}{ }^{-}$)

Alkali: $\mathrm{OH}^{-}$reacts with $\mathrm{H}^{+}$ions, equilibrium moves to the right (to replace the $\mathrm{H}^{+}$ ions)

Concentration of $\mathrm{H}^{+}$remains (almost) constant

M3.(a) Z
Mark independently.

The idea that the solution contains both HA and $\mathrm{A}^{-}$
(b) pH

$$
\begin{aligned}
{[\mathrm{HA}]=\left[\mathrm{A}^{-}\right] } & \\
& \text {Accept solution half neutralised. }
\end{aligned}
$$

$$
\mathrm{pH}=\mathrm{p} K_{\mathrm{a}} \quad \text { Accept }\left[\mathrm{H}^{+}\right]=K_{\mathrm{a}}
$$

M4.(a) (only) slightly or partially dissociated / ionised Ignore 'not fully dissociated'.
Allow low tendency to dissociate or to lose / donate a proton.
Allow shown equilibrium well to the left.
Otherwise ignore equations.
(b) $2 \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{Na}_{2} \mathrm{CO}_{3} \longrightarrow 2 \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$

OR
$2 \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{CO}_{3}{ }^{2-} \longrightarrow 2 \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$
OR

$$
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{Na}_{2} \mathrm{CO}_{3} \longrightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COONa}+\mathrm{NaHCO}_{3}
$$

## OR

$$
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{CO}_{3}^{2-} \longrightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}+\mathrm{HCO}_{3}^{-}
$$

Must be propanoic acid, allow $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$.
Not molecular formulae.
Allow multiples.
Ignore reversible sign.
Not $\mathrm{H}_{2} \mathrm{CO}_{3}$.
(c) $\left[\mathrm{OH}^{-}\right]=2 \times 0.0120=0.0240$

M1
Correct answer for pH with or without working scores 3.

If $\times 2$ missed or used wrongly can only score M3 for correct calculation of pH from their $\left[\mathrm{H}^{+}\right]$.

$$
\begin{aligned}
& \mathrm{pH}=12.38 \mathrm{M} \quad \text { Lose M3 if not } 2 \text { decimal places: } 12.4 \text { scores } 2 . \\
& 12.08 \text { scores } 1 \text { (missing } \times 2 \text { ) ; } 12.1 \text { scores } 0 . \\
& 11.78 \text { scores } 1 \text { (dividing by 2) } 11.8 \text { scores } 0 .
\end{aligned}
$$

(d) (i) $K_{a}=\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right]$

Ignore ( ) here but brackets must be present. Must be correct acid and salt.
If wrong, mark part (ii) independently.
(ii) M1 $K^{a}=\frac{\left[\mathrm{H}^{+}\right]^{2}}{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right]} \quad$ OR with numbers

Correct answer for pH with or without working scores 3.
Allow HX, HA and ignore ( ) here.
May score M1 in part (i).

M3 $\mathrm{pH}=3 . \underline{06}$
Must be 2 decimal places ie 3.1 loses M3.
(iii) M1 $\quad\left[\mathrm{H}^{+}\right]=10^{-4.00}=1.00 \times 10^{-4}$

Correct answer for mass with or without working scores 5 .
Allow $1 \times 10^{-4}$.

$$
\left[\mathrm{X}^{-}\right]=\frac{\mathrm{Ka} \times[\mathrm{HX}]}{\left[\mathrm{H}^{+}\right]}
$$

Ignore () here.
If [HX] / [X-] upside down, can score M1 plus M4 for $5.26 \times 10^{-7}$.
$\mathrm{M} 3=\frac{6.31 \times 10^{-5} \times 0.0120}{1.00 \times 10^{-4}}$
And M5 for $7.57 \times 10^{-5} \mathrm{~g}$.

M5 Mass $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COONa}\right)=7.572 \times 10^{-3} \times 144=1.09 \mathrm{~g}$ or 1.1 g
Wrong method, eg using $\left[\mathrm{H}^{+}\right]^{2}$ may only score M1 and M5 for correct multiplication of their M4 by 144
(provided not of obviously wrong substance).

## (e) $\mathrm{M} 1 \quad \mathrm{CO}_{2}$

Allow $\mathrm{NO}_{\mathrm{x}}$ and $\mathrm{SO}_{2}$.

M2 pH (It) falls / decreases
If M1 wrong, no further marks.

M3 mark M2 \& M3 independently acidic (gas)

OR reacts with alkali(ne solution) / $\mathrm{OH}^{-}$
$\mathrm{OR} \mathrm{CO}+2 \mathrm{OH}^{-} \longrightarrow \mathrm{CO}_{3}{ }^{2-}+\mathrm{H}_{2} \mathrm{O}$
$\mathrm{OR} \mathrm{CO}+\mathrm{OH}^{-} \longrightarrow \mathrm{HCO}_{3}^{-}$
Not forms $\mathrm{H}_{2} \mathrm{CO}_{3} \mathrm{H}_{2} \mathrm{SO}_{3} \mathrm{H}_{2} \mathrm{SO}_{4}$ etc OR $\mathrm{H}^{+}$ions.

M5.(a) This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

All stages are covered and the explanation of each stage is generally correct and virtually complete.

Answer is communicated coherently and shows a logical progression from stage 1 and stage 2 to stage 3 . Steps in stage 3 must be complete, ordered and include a comparison.

All stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages are covered and the explanations are generally correct and virtually complete.

Answer is mainly coherent and shows a progression from stage 1 and stage 2 to stage 3 .

Level 2
3-4 marks
Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies, OR only one stage is covered but the explanation is generally correct and virtually complete.

Answer includes some isolated statements, but these are not presented in a logical order or show confused reasoning.

Level 1
1-2 marks
Insufficient correct Chemistry to warrant a mark.
Level 0
0 marks

## Indicative Chemistry content

Stage 1: difference in structure of the two acids

- The acids are of the form RCOOH
- but in ethanoic acid $\mathrm{R}=\mathrm{CH}_{3}$
- whilst in ethanedioic acid $\mathrm{R}=\mathrm{COOH}$

Stage 2: the inductive effect

- The unionised COOH group contains two very electronegative oxygen atoms
- therefore has a negative inductive (electron withdrawing)effect
- The $\mathrm{CH}_{3}$ group has a positive inductive (electron pushing) effect

Stage 3: how the polarity of OH affects acid strength

- The $\mathrm{O}-\mathrm{H}$ bond in the ethanedioic acid is more polarised / H becomes more $\delta^{+}$
- More dissociation into $\mathrm{H}^{+}$ions
- Ethanedioic acid is stronger than ethanoic acid

$$
\begin{aligned}
& K_{\mathrm{a}}=\left[\mathrm{H}^{+}\right][\mathrm{A}-] /[\mathrm{HA}] \\
& {\left[\mathrm{H}^{+}\right]=K_{\mathrm{a}} \times[\mathrm{HA}] /\left[\mathrm{A}^{-}\right]}
\end{aligned}
$$

$$
\left[\mathrm{H}^{+}\right]=5.89 \times 10^{-2} \times\left(4.00 \times 10^{-2} / \mathrm{V}\right) /\left(6.00 \times 10^{-2} / \mathrm{V}\right)=3.927 \times 10^{-2}
$$

$$
\mathrm{pH}=-\log _{10}\left(3.927 \times 10^{-2}\right)=1.406=1.41
$$

Answer must be given to this precision
(c) $5 \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}+6 \mathrm{H}^{+}+2 \mathrm{MnO}_{4}^{-} \longrightarrow 2 \mathrm{Mn}^{2+}+10 \mathrm{CO}_{2}+8 \mathrm{H}_{2} \mathrm{O}$

$$
\mathrm{OR} 5 \mathrm{C}_{2} \mathrm{O}_{4}^{2-}+16 \mathrm{H}^{+}+2 \mathrm{MnO}_{4}^{-} \longrightarrow 2 \mathrm{Mn}^{2+}+10 \mathrm{CO}_{2}+8 \mathrm{H}_{2} \mathrm{O}
$$

Moles of $\mathrm{KMnO}_{4}=20.2 \times 2.00 \times 10^{-2} / 1000=4.04 \times 10^{-4}$

Moles of $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}=5 / 2 \times 4.04 \times 10^{-4}=1.01 \times 10^{-3}$

Concentration $=$ moles $/$ volume $\left(\right.$ in $\left.\mathrm{dm}^{3}\right)$
$=1.01 \times 10^{-3} \times 1000 / 25=4.04 \times 10^{-2}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$
If 1:1 ratio or incorrect ratio used, M2 and M4 can be scored
[15]

