M1.(a) $\quad\left[\mathrm{H}_{2} \mathrm{O}\right]$ is very high (compared with $\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$)
OR
Very few $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$ions
OR
Only / very slightly dissociates

## OR

Equilibrium lies far to the left
Not partially dissociates
M1
[ $\mathrm{H}_{2} \mathrm{O}$ ] is (effectively) constant
OR is incorporated into the constant K
Allow changes by only a very small amount
M2
(b) (Dissociation OR breaking bonds) is endothermic
$\therefore$ Equilibrium moves to RHS (at higher T) to absorb heat or to lower T or oppose increase in T

Allow to oppose change only if increase $T$ mentioned
(c) $\left[\mathrm{H}^{+}\right] \quad=\sqrt{ } \mathrm{K}_{\mathrm{w}}\left(\mathrm{or}=\sqrt{ } 5.48 \times 10^{-14}\right)$

Correct pH answer scores 3

If wrong method no marks
Using alternative $K_{w}\left(1.00 \times 10^{-14}\right)$ gives $\mathrm{pH}=7 . \underline{00}$ which scores 1
$=2.34 \times 10^{-7}$
$\mathrm{pH}=6.63$
Final answer must have 2dp
(d) $\left[\mathrm{H}^{+}\right]=K_{w} /\left[\mathrm{OH}^{-}\right]$or $\left(=5.48 \times 10^{-14} / 0.12\right)$

Correct pH answer scores 3

If wrong method no marks
If use alternative $K_{w}\left(1.00 \times 10^{-14}\right)$ again, do not penalise repeat error so $\mathrm{pH}=13.08$ scores 3
$=4.566 \times 10^{-13}$
$\mathrm{pH}=12.34$
If use alternative $K_{w}\left(1.00 \times 10^{-14}\right)$ not as a repeat error, $\mathrm{pH}=$ 13.08 scores 1

If $A E$ 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 (c) allow more than 2dp here but not fewer.

M2.(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.

$$
\begin{aligned}
& {\left[\mathrm{H}^{+}\right]=\frac{1 \times 10^{-14}}{0.0240}=4.166 \times 10^{-13} \text { OR } \mathrm{pOH}=1.62 \quad \mathrm{M} 2} \\
& \quad \begin{array}{l}
\text { If } \times 2 \text { missed or used wrongly can only score M3 for correct } \\
\text { calculation of } \mathrm{pH} \text { from their }\left[\mathrm{H}^{+}\right] .
\end{array}
\end{aligned}
$$

$\mathrm{pH}=12 . \underline{38} \quad \mathrm{M} 3$
Lose M3 if not 2 decimal places: 12.4 scores 2.
12.08 scores 1 (missing $\times 2$ ) ; 12.1 scores 0 .
11.78 scores 1 (dividing by 2) 11.8 scores 0 .
(d) (i) $K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}\right]}{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right]}$

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

$$
\begin{aligned}
& {\left[\mathrm{H}^{+}\right]=\sqrt{ }\left(6.31 \times 10^{-5} \times 0.0120\right) \text { or } \sqrt{ }\left(K_{\mathrm{a}} \times\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right]\right)} \\
& \left(=\sqrt{ }\left(7.572 \times 10^{-7}=8.70 \times 10^{\times 4}\right)\right. \\
& p H=6.12 \text { may score } 2 \text { if correct working shown and they }
\end{aligned}
$$

show the square root but fail to take it.
But if no working shown or wrong $K^{a}=\frac{\left[\mathrm{H}^{+}\right]}{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right]}$ used which also leads to 6.12, then zero scored.

M3 $\quad \mathrm{pH}=3 . \underline{06}$
Must be 2 decimal places ie 3.1 loses M3.
$\left[\mathrm{H}^{+}\right]=10^{-4.00}=1.00 \times 10^{-4}$
Correct answer for mass with or without working scores 5 .
Allow $1 \times 10^{-4}$.

M2 $\left[\mathrm{X}^{-}\right]=\frac{\mathrm{Kax}[\mathrm{HX}]}{\left[\mathrm{H}^{+}\right]}$
Ignore () here.
If [HX] / [X-] upside down, can score M1 plus
M4 for $5.26 \times 10^{-7}$.

M3 $=\frac{6.31 \times 10^{-5} \times 0.0120}{1.00 \times 10^{-4}}$
And M5 for $7.57 \times 10^{-5} \mathrm{~g}$.

M5 $\quad$ 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 $\mathrm{SO}_{2}$.

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.

Allow M2 for correct pH calculation from theirwrong [H•] for this pH calculation only
(ii) M1 $\left[\mathrm{H}^{+}\right]=10^{-279}$ OR $1.6218 \ldots \times 10^{-3}$


Allow HA instead of HX

M3 $\mathrm{K}_{\mathrm{a}}=3.09 \times 10^{-5} \quad 3 \mathrm{sfs} \mathrm{min} \quad$ (allow $3.10 \times 10^{-5}$ if 1.6218 rounded to 1.622) Ignore units

If $[H X]$ used as $\left(0.0850-1.62 \times 10^{-3}\right)$
this gives $K_{\mathrm{a}}=3.15 \times 10^{-5}$
$(0.0016)^{2} / 0.085=3.01 \times 10^{-5}$ scores 2 for $A E$
(c) $\mathbf{M} 1 \quad \mathrm{~mol} \mathrm{OH}^{-}\left(=\left(38.2 \times 10^{-3}\right) \times 0.550\right)$
$=2.10(1) \times 10^{-2}$ or $0.0210(1)$
Mark for answer

M2 $\mathrm{Mol} \mathrm{H}^{+}\left(=\left(25.0 \times 10^{-3}\right) \times 0.620\right)$
$=1.55 \times 10^{-2}$ or 0.0155
Mark for answer

M3 excess $\mathrm{mol} \mathrm{OH}=5.5(1) \times 10^{-3}$
Allow conseq for M1 - M2
If wrong method e.g. no subtraction or use of $\sqrt{ }$ can only score max of M1, M2, M3 and M4.

M4 $\quad\left[\mathrm{OH}^{-}\right]=5.51 \times 10^{-3} \times \frac{10^{3}}{63.2} \quad[=0.08718 \quad(0.0872)]$
OR $\left[\mathrm{OH}^{-}\right]=5.5 \times 10^{-3} \times \frac{10^{3}}{63.2}=0.0870(2)$
Page 7
(M1 - M2) / vol in dm ${ }^{3}$ mark for dividing by volume (take use of 63.2 without $10^{-3}$ as AE so 9.94 scores 5) If no use or wrong use of vol lose M4 \& M6 Can score M5 for showing (10-14/ their XS alkali)

M5 $\quad\left[\mathrm{H}^{+}\right]=\frac{10^{-14}}{0.08718}=1.147 \times 10^{-13}$
OR $\quad \frac{10^{-14}}{0.0870}=1.149 \times 10^{-13}$
OR $\mathrm{pOH}=1.06$
If no use or wrong use of $K_{w}$ or pOH no further marks

M6 $\mathrm{pH}=12.9(4)$ allow 3sf
If vol missed score max 4 for 11.7(4)
If acid- alkali reversed max 4 for $\mathrm{pH}=1.06$
Any excess acid - max 4
1
[12]

M4. (a) (i) $-\log \left[\mathrm{H}^{+}\right]$
penalise missing [] here and not elsewhere
(ii) $\left[\mathrm{H}^{+}\right][\mathrm{OH}]$

Allow ( ) brackets, but must have charges
(iii) Mark independently from a(ii)
$\left[\mathrm{H}^{+}\right]=10^{-1372}=1.905 \times 10^{-14}$
If wrong no further mark
$\mathrm{K}_{w}=1.905 \times 10^{-14} \times 0.154==(2.93-2.94) \times 10^{-15}$
(b) (i) $\mathrm{Ka}=\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$

Must have charges and all brackets, allow ()
Acid/salt shown must be $\mathrm{CH}_{3} \mathrm{COOH}$ not HA and correct formulae needed
(ii) In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp
For values above 10, allow 3sfs - do not insist on 2 dp

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]^{2}}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}
$$

$$
\begin{aligned}
\left(\left[\mathrm{H}^{+}\right]^{2}\right. & \left.=1.75 \times 10^{-5} \times 0.154=2.695 \times 10^{-6}=2.70 \times 10^{-6}\right) \\
& \text { If } \sqrt{ } \text { shown but not done gets } \mathrm{pH}=5.57(\text { scores } 2)
\end{aligned}
$$

$\left[\mathrm{H}^{+}\right]=1.64 \times 10^{-3}$
Allow mark for pH conseq to their $[\mathrm{H}+]$ here only
$\mathrm{pH}=2.78$ or 2.79
(c) (i) In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp

For values above 10, allow 3sfs - do not insist on 2 dp
M1 Initially
$\mathrm{mol} \mathrm{OH}^{-}=\left(10 \times 10^{-3}\right) \times 0.154$ and
mol HA $=\left(20 \times 10^{-3}\right) \times 0.154$
or $\mathrm{mol} \mathrm{OH}^{-}=1.54 \times 10^{-3}$ and $\mathrm{mol} \mathrm{HA}=3.08 \times 10^{-3}$

M2 $\left[\mathrm{H}^{\mathrm{H}}\right]=\mathrm{K}_{\mathrm{a}} \frac{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}^{-}\right]}$
or with numbers
Allow Henderson Hasselbach

$$
p H=p K_{\mathrm{a}}+\log \frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}
$$

$\mathbf{M 3} \mathrm{mol}$ ethanoic acid left $=($ mol ethanoate ions $)=1.54 \times 10^{-3}$
$\mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}^{+}\right]$or $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}$ scores $\mathbf{M 1}, \mathbf{M} 2$ and $\mathbf{M} 3$
1 If either mol acid in mixture or mol salt wrong

- max 2 for M1 and M2

Any mention of $\left[\mathrm{H}^{+}\right]^{2}-\max 2$ for M1 and M3

M4 pH $\left(=-\log 1.75 \times 10^{-5}\right)=4.76$ or 4.757
Not 4.75

If no subtraction (so mol ethanoic acid in buffer = original mol) $\mathrm{pH}=4.46$ scores 2 for M1 and M2
If $[\mathrm{H}+]^{2}$ used, $\mathrm{pH}=3.02$ scores 2 for M1 and M3

## (ii) In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp

For values above 10, allow 3sfs - do not insist on 2 dp
M1 XS mol KOH $\left(=\left(20 \times 10^{-3}\right) \times 0.154\right)=3.08 \times 10^{-3}$
If no subtraction: max 1 for correct use of volume
No subtraction and no use of volume scores zero
If wrong subtraction or wrong moles
Can only score M2 and M3 for process

M2 $[\mathrm{OH}]=3.08 \times 10^{-3} \times \frac{10^{3}}{60}=0.0513(3)$
Mark for dividing their answer to M1 by correct volume (method mark)
If no volume or wrong volume or multiplied by volume, max 2 for M1 and M3 process

M3 $\left[H^{+}\right]=\frac{10^{-14}}{0.05133}\left(=1.948 \times 10^{-13}\right.$ to $\left.1.95 \times 10^{-13}\right)$
or $\mathrm{pOH}=1.29$
Mark for $K_{w}$ divided by their answer to M2
If pOH route, give one mark for $14-\mathrm{pOH}$

M4 pH = 12.7(1)
Allow 3sf but not 12.70

If no subtraction and no use of volume ( $\mathrm{pH}=11.79$ scores zero) If no subtraction, max 1 for correct use of volume, $\left(60 \mathrm{~cm}^{3}\right)$ ( $\mathrm{pH}=13.01$ scores 1 )
If volume not used, $\mathrm{pH}=11.49$ (gets 2 )
If multiplied by vol, $\mathrm{pH}=10.27$ (gets 2)

