M1.(a) [H₂O] is very high (compared with [H⁺] and [OH⁻]) OR Very few H⁺ and OH⁻ ions OR Only / very slightly dissociates OR Equilibrium lies far to the left Not partially dissociates

		M1	1
	[H ₂ O] is (effectively) constant OR is incorporated into the constant K <i>Allow changes by only a very small amount</i>	M2	1
(b)	(Dissociation OR breaking bonds) is endothermic		1
	∴ Equilibrium moves to RHS (at higher T) to absorb heat or to low oppose increase in T Allow to oppose change only if increase T mentioned	<u>ver T or</u>	1
(c)	$[H^{*}] = \sqrt{K_{w}} \text{ (or } = \sqrt{5.48 \times 10^{-14}} \text{)}$ Correct pH answer scores 3 If wrong method no marks Using alternative K_{w} (1.00 × 10 ⁻¹⁴) gives pH = 7.00 wh scores 1	nich	1
	$= 2.34 \times 10^{-7}$		1
	pH = 6.63 Final answer must have 2dp		1

1
1
1 [10]

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M2.(a) (only) slightly or partially dissociated / ionised
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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.

1

(b) $2CH_3CH_2COOH + Na_2CO_3 \longrightarrow 2CH_3CH_2COONa + H_2O + CO_2$

OR

 $2CH_3CH_2COOH + CO_3^{2-} \longrightarrow 2CH_3CH_2COO^- + H_2O + CO_2$

OR

 $\mathsf{CH}_3\mathsf{CH}_2\mathsf{COOH} + \mathsf{Na}_2\mathsf{CO}_3 \longrightarrow \mathsf{CH}_3\mathsf{CH}_2\mathsf{COONa} + \mathsf{NaHCO}_3$

OR

$$CH_{3}CH_{2}COOH + CO_{3}^{2-} \longrightarrow CH_{3}CH_{2}COO^{-} + HCO_{3}^{-}$$

*Must be propanoic acid, allow C*₂*H*₅*COOH.*
Not molecular formulae.
Allow multiples.
Ignore reversible sign.
*Not H*₂*CO*₃.

(c) $[OH^-] = 2 \times 0.0120 = 0.0240$ M1 Correct answer for pH with or without working scores 3.

$$[H^{+}] = \frac{1 \times 10^{-14}}{0.0240} = 4.166 \times 10^{-13} \text{ } \text{OR} \text{ pOH} = 1.62 \text{ M2}$$

If × 2 missed or used wrongly can only score M3 for correct calculation of pH from their [H^+].

pH = 12.<u>38</u> M3 Lose M3 if not 2 decimal places: 12.4 scores 2. 12.08 scores 1 (missing × 2) ; 12.1 scores 0. 11.78 scores 1 (dividing by 2) 11.8 scores 0.

(d) (i)
$$K_a = \frac{[H^+][C_8H_5COO^-]}{[C_8H_5COOH]}$$

Ignore () here but brackets must be present. Must be correct acid and salt. If wrong, mark part (ii) independently.

(ii) M1 $K^{\circ} = \frac{[H^+]^2}{[C_6H_5COOH]}$ 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).

M2 $[H^+] = \sqrt{(6.31 \times 10^{-5} \times 0.0120)}$ or $\sqrt{(K_a \times [C_6H_5COOH])}$ $(= \sqrt{(7.572 \times 10^{-7} = 8.70 \times 10^{\times 4})}$ pH = 6.12 may score 2 if correct working shown and they 1

1

1

1

show the square root but fail to take it.

But if no working shown or wrong $K^* = \frac{[H^+]}{[C_6H_5COOH]}$

1

1

1

1

1

1

1

used which also leads to 6.12, then zero scored.

M3 pH = 3.06Must be 2 decimal places ie 3.1 loses M3.

(iii) M1 $[H^+] = 10^{-4.00} = 1.00 \times 10^{-4}$ Correct answer for mass with or without working scores 5. Allow 1×10^{-4} .

M2
$$[X^{-}] = \frac{Ka \times [HX]}{[H^{+}]}$$

Ignore () here. If $[HX] / [X^-]$ upside down, can score M1 plus M4 for 5.26 × 10⁻⁷.

 $M3 = \frac{6.31 \times 10^{-5} \times 0.0120}{1.00 \times 10^{-4}}$

And M5 for 7.57 × 10^{-₅} g.

M4 = 7.572×10^{-3}

M5 Mass (C_6H_5COONa) = 7.572 × 10⁻³ × 144 =1.09 g or 1.1 g Wrong method, eg using [H⁺]² may only score M1 and M5 for correct multiplication of their M4 by 144

(provided not of obviously wrong substance).

- (e) M1 CO_2 Allow NO_x and SO₂.
 - M2 <u>pH (It) falls / decreases</u> If M1 wrong, no further marks.
 - M3 mark M2 & M3 independently

acidic (gas)

OR reacts with alkali(ne solution) / OH-

 $\textbf{OR}~\textbf{CO}_2 \textbf{+} \textbf{2OH}^{\scriptscriptstyle -} \longrightarrow \textbf{CO}_3^{2\text{-}} \textbf{+} \textbf{H}_2\textbf{O}$

OR $CO_2 + OH^- \longrightarrow HCO_3^-$ Not forms $H_2CO_3 H_2SO_4$ etc OR H^+ ions.

1

1

1

M3.(a) **M1** [H⁺] = 0.0170

M2 pH = 1.77 2 dp Allow M2 for correct pH calculation from theirwrong [H⁺] for this pH calculation only

(b) (i)
$$K_a = \frac{\left[H^+\right]X^-\right]}{\left[HX\right]^2}$$
 Ignore $K_a = \frac{\left[H^+\right]^2}{\left[HX\right]}$

Penalize missing [] here **and not elsewhere** Allow HA instead of HX

1

1

(ii) **M1**
$$[H^*] = 10^{-2.79} \text{ OR } 1.6218... \times 10^{-3}$$



M3 $K_a = 3.09 \times 10^{-5}$ 3sfs min (allow 3.10×10^{-5} if 1.6218 rounded to 1.622) Ignore units If [HX] used as $(0.0850 - 1.62 \times 10^{-3})$ this gives $K_a = 3.15 \times 10^{-5}$ $(0.0016)^2/0.085 = 3.01 \times 10^{-5}$ scores 2 for AE

(c) **M1** mol OH⁻ (=
$$(38.2 \times 10^{-3}) \times 0.550$$
)

M2 Mol H⁺ (=
$$(25.0 \times 10^{-3}) \times 0.620$$
)

1

1

1

M4
$$[OH^{-}] = 5.51 \times 10^{-3} \times \frac{10^{3}}{63.2}$$
 $[= 0.08718 \quad (0.0872)]$
OR $[OH^{-}] = 5.5 \times 10^{-3} \times \frac{10^{3}}{63.2} = 0.0870(2)$

(M1 - M2) / vol in dm³ 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
$$[H^{+}] = \frac{10^{-14}}{0.08718} = 1.147 \times 10^{-13}$$

OR $\frac{10^{-14}}{0.0870} = 1.149 \times 10^{-13}$
OR pOH = 1.06
If no use or wrong use of K_w or pOH no further marks

M6 pH = 12.9(4) allow 3sf If vol missed score max 4 for 11.7(4) If acid– alkali reversed max 4 for pH = 1.06 Any excess acid – max 4

[12]

1

1

M4.	(a)	(i)	- log[H ⁺] penalise missing [] here and not elsewhere	1
	(ii)	[H*]	[OH-] Allow () brackets, but must have charges	1
	(iii)	Ma [H⁺]	rk independently from a(ii) = $10^{-13.72}$ = 1.905×10^{-14}	
			If wrong no further mark	1
		K _w =	$1.905 \times 10^{-14} \times 0.154 = = (2.93 - 2.94) \times 10^{-15}$	1

(b) (i)
$$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

Must have charges and all brackets, allow ()
Acid/salt shown must be CH₃COOH 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
 $K_a = \frac{[H^+]^2}{[CH_3COOH]}$
Allow HA
($[H^+]^2 = 1.75 \times 10^{-5} \times 0.154 = 2.695 \times 10^{-5} = 2.70 \times 10^{-5}$)
If $\sqrt{$ shown but not done gets pH = 5.57 (scores 2)
 $[H^-] = 1.64 \times 10^{-3}$

Allow mark for pH conseq to their [H+] here only

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

mol OH- = (10 \times 10-3) \times 0.154 and

mol HA = $(20 \times 10^{-3}) \times 0.154$

or mol OH⁻ = 1.54×10^{-3} and mol HA = 3.08×10^{-3}

1

1

1

1

$$\mathbf{M2} [\mathrm{H}^{\cdot}] = \mathrm{K}_{*} \frac{[\mathrm{CH}_{3}\mathrm{COOH}]}{[\mathrm{CH}_{3}\mathrm{COOH}^{-}]}$$

or with numbers

Allow Henderson Hasselbach

$$pH = pK_a + log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

M3 mol ethanoic acid left = (mol ethanoate ions) = 1.54×10^{-3}

K_a = [H⁺] or pH = pK_a scores M1, M2 and M3
1 If either mol acid in mixture or mol salt wrong
max 2 for M1 and M2
Any mention of [H⁺]² - max 2 for M1 and M3

M4 pH (= - log 1.75 × 10^{-s}) = 4.76 or 4.757 *Not 4.75*

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

- 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** <u>XS mol KOH</u> (= $(20 \times 10^{-3}) \times 0.154$) = 3.08×10^{-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 [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 1

1

10-14 **M3** [H⁺] = 0.05133 (= 1.948 × 10⁻¹³ to 1.95 × 10⁻¹³) or pOH = 1.29 Mark for K_w divided by their answer to **M2** *If pOH route, give one mark for 14 – pOH* 1 **M4** pH = 12.7(1) Allow 3sf but not 12.70 If no subtraction and no use of volume (pH = 11.79 scores zero) If no subtraction, max 1 for correct use of volume, (60cm³) (pH = 13.01 scores 1)

If volume not used, pH = 11.49 (gets 2) If multiplied by vol, pH = 10.27 (gets 2)

[16]