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

Not partially dissociates	
M1	1
[H₂O] 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 lower T or oppose increase in T Allow to oppose change only if increase T mentioned	1
(c) $[H^+] = \sqrt{K_w} \text{ (or } = \sqrt{5.48 \times 10^{-14}} \text{)}$ <i>Correct pH answer scores 3</i> If wrong method no marks <i>Using alternative K_w (1.00 × 10^{-14}) gives pH = 7.00 which</i> <i>scores 1</i>	1
$= 2.34 \times 10^{-7}$	1
pH = 6.63 Final answer must have 2dp	1

(d) [H⁺]	= K_w / [OH ⁻] or (= 5.48 × 10 ⁻¹⁴ / 0.12) Correct pH answer scores 3	1
	If wrong method no marks If use alternative K_w (1.00 × 10 ⁻¹⁴) again, do not penalise repeat error so pH = 13.08 scores 3	
	$= 4.566 \times 10^{-13}$	1
рН	 = 12.34 If use alternative K_w (1.00 × 10⁻¹⁴) not as a repeat error, pH = 13.08 scores 1 If AE 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. 	1 [10]

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.

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

 $CH_{3}CH_{2}COOH + Na_{2}CO_{3} \longrightarrow CH_{3}CH_{2}COONa + NaHCO_{3}$

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)
$$K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}$$

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

(ii) M1 $K^{a} = \frac{[H^{+}]^{2}}{[C_{6}H_{5}COOH]}$ 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 $[H^+] = \sqrt{(6.31 \times 10^{-5} \times 0.0120)} \text{ or } \sqrt{(K_a \times [C_6H_5COOH])}$ $(= \sqrt{(7.572 \times 10^{-7} = 8.70 \times 10^{\times 4})}$ pH = 6.12 may score 2 if correct working shown and they 1

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show the square root but fail to take it.

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

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 $(C_6H_5COONa) = 7.572 \times 10^{-3} \times 144 = 1.09 g$ 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).

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- (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.

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M3.(a) **M1** [H⁺] = 0.0170

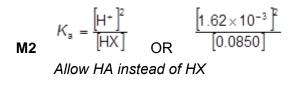
M2 pH = 1.77 2 dp Allow M2 for correct pH calculation from theirwrong [H+] for this pH calculation only

(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

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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

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

1

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

Page 7

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(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

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(a)	(i) - log[H ⁺] penalise missing [] here and not elsewhere	1
(ii)	[H⁺][OH-] Allow () brackets, but must have charges	1
(iii)	Mark independently from a(ii) $[H^{*}] = 10^{-13.72} = 1.905 \times 10^{-14}$ <i>If wrong no further mark</i> $K_{w} = 1.905 \times 10^{-14} \times 0.154 = = (2.93 - 2.94) \times 10^{-15}$	1
	(ii)	penalise missing [] here and not elsewhere (ii) $[H^+][OH^-]$ Allow () brackets, but must have charges (iii) Mark independently from a(ii) $[H^+] = 10^{-13.72} = 1.905 \times 10^{-14}$ If wrong no further mark

(b) (i)
$$K_{a} = \frac{[H^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]}$$

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
 $K_{a} = \frac{[H^{+}]^{2}}{[CH_{3}COOH]}$
Allow HA
([H⁻]² = 1.75 × 10⁻³ × 0.154 = 2.695 × 10⁻⁶ = 2.70 × 10⁻⁶)
If $\sqrt{$ shown but not done gets pH = 5.57 (scores 2)
[H⁻] = 1.64 × 10⁻³
Allow mark for pH conseq to their [H+] here only

pH = 2.78 or 2.79

In pH values penalise fewer than 3 sig figs each time but (C) (i) 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⁻ =
$$1.54 \times 10^{-3}$$
 and mol HA = 3.08×10^{-3}

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M2 [H[·]] =
$$K_a \frac{[CH_3COOH]}{[CH_3COOH^-]}$$

or with numbers

Allow Henderson Hasselbach

$$pH = pK_{a} + log \frac{[CH_{3}COO^{-}]}{[CH_{3}COOH]}$$

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

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 $\mathbf{M3} [H^{+}] = \frac{10^{-14}}{0.05133} (= 1.948 \times 10^{-13} \text{ to } 1.95 \times 10^{-13})$ or pOH = 1.29 Mark for K_{*} divided by their answer to **M2** If pOH route, give one mark for 14 – pOH $\mathbf{M4} \text{ pH} = 12.7(1)$ 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]

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