M1.		(a)	(i)	– log[H⁺] or log 1/[H⁺] penalise missing square brackets here only	
		(ii)	0.81	2dp required, no other answer allowed	1
		(iii)	М1	mol H⁺ = 1.54 × 10⁻³ if wrong no further mark if 1.5 × 10⁻³ allow M1 but not M2 for 2.82	1
			M2	pH = 2.81 allow more than 2dp but not fewer	1
	(b)	M 1	[H⁺]	= 3.31 × 10-₃	1
		M2	K _a =	$\frac{[H^+][X^-]}{[HX]} \text{or } \frac{[H^+]^2}{[HX]}$ or using numbers do not penalise () or one or more missing []	1
		М3	[HX]	$ =\frac{[H^{+}]^{2}}{K_{a}} = \frac{(3.31 \times 10^{-3})^{2}}{4.83 \times 10^{-5}}$ allow conseq on their [H ⁺] ² /(4.83 × 10 ⁻⁵) (AE) if upside down, no further marks after M2	1
		Μ4	[HX]	= 0.227 allow 0.225 – 0.23	1
	(c)	М1	extr	a/added OH \cdot removed by reaction with H \cdot or the acid	1
		M2	corr	ect discussion of equn shift i.e. HX \rightleftharpoons H $^{+}$ + X $^{-}$ moves to right	1
		OR			

ratio $\frac{[HX]}{[X^-]}$ remains almost constant

(d) (i) **M1** mol HY =
$$(50 \times 10^{-3}) \times 0.428 = 0.0214$$

OR [Y] = .0236 ×
$$\frac{1000}{50}$$
 = 0.472
mark for answer

1

M2	[H⁺] = 1.35 × 10⁻⁵ ×	0.0214 0.0236
OR	1.35 × 10⁻₅ = [H⁺] ×	0.0236 0.0214
OR	[H⁺] = 1.35 × 10⁻₅ ×	0.428 0.472
OR		$\frac{0.472}{0.428}$ ot just rearrangement of Ka expression r Y-value wrong, (apart from AE -1) lose

- **M3** $[H^+] = 1.22 \times 10^{-5}$ mark for answer
- M4 pH = 4.91
 allow more than 2dp but not fewer
 allow M4 for correct pH calculation using their [H⁺] (this
 applies in (d)(i) only)

1

1

1

If Henderson Hasselbalch equation used:

M1 mol HY = $(50 \times 10^{-3}) \times 0.428 = 0.0214$

1000 = 0.472[Y] = .0236 × OR mark for answer 1 M2 pKa = 4.87 1 $\log^{\left(\frac{0.0214}{0.0236}\right)} = -0.043$ М3 $\log^{\left(\frac{0.428}{0.472}\right)} = -0.043$ If either HY value or Y- value wrong, (apart from AE-1) lose M3 and M4 1 Μ4 pH = 4.87 - (-0.043) = 4.91allow more than 2dp but not fewer 1 Can score full marks for correct consequential use of their HY and Y⁻ values from d(i)

- M1 Mol HY after adding NaOH = $0.0214 5.0 \times 10^{-4} = 0.0209$ AE in subtraction loses just M1 If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount, lose M1 and M3
- **M2** Mol Y⁻ after adding NaOH = $0.0236 + 5.0 \times 10^{-4} = 0.0241$ AE in addition loses just M2 If wrong mol Y⁻ (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained

1

1

1

M3 $[H^{+}] = 1.35 \times 10^{-5} \times \frac{0.0209}{0.0241}$ (= 1.17 × 10⁻⁵)

if convert to concentrations

if HY/Y- upside down, no further marks

(ii)

M4 pH = 4.93

allow more than 2dp but not fewer NOT allow M4 for correct pH calculation using their [H⁺] (this allowance applies in (d)(i) only)

1

1

	Can score full marks for correct consequential use of their HY and Y [_] values from d(i)	
M1	Mol HY after adding NaOH = $0.0214 - 5.0 \times 10^{-4} = 0.0209$ AE in subtraction loses just M1 If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount lose M1 and M3	1
М2	Mol Y ⁻ after adding NaOH = $0.0236 + 5.0 \times 10^{-4} = 0.0241$ AE in addition loses just M2 If wrong mol Y ⁻ (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained	1
М3	$\log \left(\frac{0.0209}{0.0241}\right) = -0.062$ if HY/Y- upside down, no further marks	1
M4	pH = 4.87 – (– 0.062) = 4.93 allow more than 2dp but not fewer	1

M2. (a) (i) -log[H⁺] or log1/[H⁺] penalise ()

(ii) [H⁺] = 0.56

$$[H_2SO_4] = \frac{1}{2} \times 0.56 = 0.28$$

(b) (i)
$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

OR

$$CH_{3}COOH + OH^{-} \rightarrow CH_{3}COO^{-} + H_{2}O$$

$$Allow CH_{3}CO_{2}H etc$$

1

1

1

(ii) mol acid =
$$(25.0 \times 10^{-3}) \times 0.41 = 1.025 \times 10^{-2}$$
 or 1.03×10^{-2}

1

1

1

OR

[NaOH] = 1.03 × 10⁻²/22.6 × 10⁻³ = 0.456 or 0.46

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

allow molecular formulae or minor slip in formulae

penalise () allow H₃O⁺ not allow HA etc

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 $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers (ii) 1 allow HA etc here This can be scored in part (c)(i) but doesn't score there. $[H^+] = (\sqrt{(1.74 \times 10^{-5} \times 0.410)} = \sqrt{(7.13 \times 10^{-6})} = 2.67 \times 10^{-3}$ 1 mark for 2.67×10^{-3} or 2.7×10^{-3} either gives 2.57pH = 2.57can give three ticks here for (c)(ii) penalise decimal places < 2 > 1 pH mark conseq on their [H⁺] so 5.15 gets 2 marks where square root not taken **M1** mol OH⁻ = $(10.0 \times 10^{-3}) \times 0.10 = 1.0 \times 10^{-3}$ (iii) If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4 1 **M2** orig mol HA = $(25.0 \times 10^{-3}) \times 0.41 = 0.01025$ 1 or 1.025 × 10⁻² or 1.03 × 10⁻² M3 mol <u>HA</u> in buffer = orig mol HA – mol OH-1 = 0.00925 or 0.0093 If A- is wrong, max 3 for M1, M2 and M3 or use of $pH = pKa - \log [HA]/[A]$ **M4** mol A⁻ in buffer = mol OH⁻ = 1.0×10^{-3} Mark is for insertion of correct numbers in correct expression for [H⁺] 1 $\mathbf{M5} \ [\mathrm{H}^{\text{-}}] = \begin{pmatrix} K_a \times [\mathrm{CH}_3 \mathrm{COOH}] \\ [\mathrm{CH}_3 \mathrm{COO}^{\text{-}}] \end{bmatrix} = \end{pmatrix}$ 1 $\frac{(1.74 \times 10^{-6})(0.00925)}{0.0010} \text{ or } \frac{(1.74 \times 10^{-6})(0.00930)}{0.0010}$ $(= 1.61 \times 10^{-4} \text{ or } 1.62 \times 10^{-4})$

M6 pH = 3.79 can give six ticks for 3.79 *if* [HA]/[A⁻] upside down lose M5 & M6 *If wrong method e.g.* [H⁺]*/[HA] max 3 for M1, M2 and M3
Some may calculate concentrations
[HA] = 0.264 and [A⁻] = 0.0286 and rounding this to 0.029
gives pH = 3.80 (which is OK)
NB Unlike (c)(ii), this pH mark is NOT awarded conseq to their
[H⁻] unless following AE
BEWARE: using 0.01025 wrongly instead of 0.00925 gives
pH = 3.75

(this gets 3 for M1, M2 & M4)

1

1

1

1

[18]

M3. (a)	(i)	[H⁺][OH⁻]
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(ii)
$$[H^+] = [OH^-]$$
 1

(iii)
$$(2.0 \times 10^{-3}) \times 0.5 = 1.0 \times 10^{-3}$$

(iv)
$$[H^*] = \frac{4.02 \times 10^{-3}}{1.0 \times 10^{-3}}$$
 (= 4.02 × 10⁻¹¹)

(b) (i) $K_a = [H^+][CH_3CH_2COO^-]$

	[CH ₃ CH ₂ COOH]	1	
	$= [H^+]$ [CH ₃ CH ₂ COOH]	1	
	$[H^+] = \sqrt{(1.35 \times 10^{-5}) \times 0.125} (= 1.30 \times 10^{-3})$	1	
	pH = 2.89	1	
(i)	(50.0 × 10⁻³) × 0.125 = 6.25 × 10⁻³	1	
(ii)	(6.25 × 10 ⁻³) − (1.0 × 10−3) = 5.25 × 10 ⁻³		
(iii)	mol salt formed = 1.0 × 10⁻₃		

$$[H^{+}] = K_a \times \frac{[CH_3CH_2COOH]}{[CH_3CH_2COO-)}$$
1

$$= (1.35 \times 10^{-5}) \times \frac{(5.25 \times 10^{-3})/\vee}{(1.0 \times 10^{-3})/\vee} (= 7.088 \times 10^{-5})$$

[16]	
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1

1

(c)