M1.		(a)	(i)	<ul> <li>log[H<sup>+</sup>] or log 1/[H<sup>+</sup>]</li> <li>penalise missing square brackets here only</li> </ul>	1
		(ii)	0.81	2dp required, no other answer allowed	1
		(iii)	M1	mol H <sup>+</sup> = $1.54 \times 10^{-3}$ if wrong no further mark if $1.5 \times 10^{-3}$ allow M1 but not M2 for 2.82	1
			M2	pH = 2.81 allow more than 2dp but not fewer	1
	(b)	<b>M</b> 1	[H⁺]	= 3.31 × 10-₃	1
		М2	K <sub>a</sub> =	$\frac{[H^+][X^-]}{[HX]} \text{ or } \frac{[H^+]^2}{[HX]}$ 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 $[H^+]^2/(4.83 \times 10^{-5})$ (AE) if upside down, no further marks after M2	1
		M4	[HX]	= 0.227 allow 0.225 - 0.23	1
	(c)	M1	extra	a/added OH- removed by reaction with H $^{\cdot}$ or the acid	1
		M2	corre	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 × 10⁵ = [H⁺] ×	0.0236 0.0214
OR	[H⁺] = 1.35 × 10-⁵ ×	0.428 0.472
OR	1.35 × 10⁵ = [H⁺] ×	0.472 0.428
	must be numbers no If either HY value or M2 and M3	ot just rearrangement of Ka expression ∙Y-value wrong, (apart from AE -1) lose

1

**M3**  $[H^+] = 1.22 \times 10^{-5}$ mark for answer

- 1
- 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

## 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<sup>-</sup> 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

1

1

**M2** Mol Y<sup>-</sup> after adding NaOH =  $0.0236 + 5.0 \times 10^{-4} = 0.0241$ AE in addition loses just M2 If wrong mol Y<sup>-</sup> (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained

M3 [H<sup>+</sup>] = 1.35 × 10<sup>-₅</sup> × 0.0209 0.0241 (= 1.17 × 10<sup>-₅</sup>)

if convert to concentrations

(ii)

if HY/Y- upside down, no further marks

**M4** pH = 4.93

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

1

1

	Can score full marks for correct consequential use of their HY and Y <sup>-</sup> 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
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
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	

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

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

(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  $1.03 \times 10^{-2}$ 

1

1

## OR

[NaOH] = 1.03 × 10<sup>-2</sup>/22.6 × 10<sup>-3</sup> = 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

1

 $K_{a} = \frac{[H^{+}]^{2}}{[CH_{3}COOH]}$  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  $2.67 \times 10^{-3}$  or  $2.7 \times 10^{-3}$  either gives 2.57pH = 2.57can give three ticks here for (c)(ii) penalise decimal places < 2 > 1 pH mark conseq on their [H<sup>+</sup>] so 5.15 gets 2 marks where square root not taken **M1** mol OH<sup>-</sup> =  $(10.0 \times 10^{-3}) \times 0.10 = 1.0 \times 10^{-3}$ (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<sup>-2</sup> or 1.03 × 10<sup>-2</sup> 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<sup>-</sup> in buffer = mol OH<sup>-</sup> =  $1.0 \times 10^{-3}$ Mark is for insertion of correct numbers in correct expression for [H⁺] 1  $\mathbf{M5} \ [\mathrm{H}^{\text{-}}] = \left( \frac{K_a \times [\mathrm{CH}_3 \mathrm{COOH}]}{[\mathrm{CH}_3 \mathrm{COO}^{\text{-}}]} = \right)$ 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 × 10<sup>-4</sup> or 1.62 × 10<sup>-4</sup>)

M6 pH = 3.79 can give six ticks for 3.79 *if* [HA]/[A<sup>-</sup>] upside down lose M5 & M6 *If wrong method* e.g. [H<sup>+</sup>]<sup>2</sup>/[HA] max 3 for M1, M2 and M3
Some may calculate concentrations
[HA] = 0.264 and [A<sup>-</sup>] = 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<sup>-</sup>] 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

[18]

<b>M3.</b> (a) (i) [H	l⁺][OH⁻]
-----------------------	----------

– log [H⁺]		
		1

(ii) 
$$[H^+] = [OH^-]$$
 1

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

(iv) 
$$[H^*] = \frac{4.02 \times 10^{-14}}{1.0 \times 10^{-3}}$$
 (= 4.02 × 10<sup>-11</sup>)

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

	[CH <sub>3</sub> CH <sub>2</sub> COOH]	1	
	$= [H^*]$ [CH <sub>3</sub> CH <sub>2</sub> 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 <sup>-3</sup> ) × 0.125 = 6.25 × 10 <sup>-3</sup>		
(ii)	(6.25 × 10 <sup>-3</sup> ) − (1.0 × 10−3) = 5.25 × 10 <sup>-3</sup>		
(iii)	mol salt formed = 1.0 × 10⁻₃	1	

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

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

(c)

1