M1. (a) (i) $-\log \left[\mathrm{H}^{+}\right]$or $\log 1 /\left[\mathrm{H}^{+}\right]$
penalise missing square brackets here only
(ii) 0.81

2dp required, no other answer allowed
(iii) M1 $\mathrm{mol} \mathrm{H}^{+}=1.54 \times 10^{-3}$
if wrong no further mark
if $1.5 \times 10^{-3}$ allow M1 but not M2 for 2.82

M2 $\quad \mathrm{pH}=2.81$
allow more than 2dp but not fewer
(b) $\quad \mathbf{M} 1 \quad\left[\mathrm{H}^{+}\right]=3.31 \times 10^{-3}$

M2 $\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{X}^{-}\right]}{[\mathrm{HX}]}$ or $\frac{\left[\mathrm{H}^{+}\right]^{2}}{[\mathrm{HX}]}$ or using numbers do not penalise () or one or more missing [ ]

M3 $[\mathrm{HX}]=\frac{\left[\mathrm{H}^{+}\right]^{2}}{\mathrm{~K}_{\mathrm{a}}}=\frac{\left(3.31 \times 10^{-3}\right)^{2}}{4.83 \times 10^{-5}}$
allow conseq on their $\left[\mathrm{H}^{+}\right]^{2} /\left(4.83 \times 10^{-5}\right)(A E)$
if upside down, no further marks after M2
1
M4 $[H X]=0.227$
allow $0.225-0.23$
(c) M1 extra/added $\mathrm{OH}^{-}$removed by reaction with $\mathrm{H}^{+}$or the acid

M2 correct discussion of equn shift i.e. $\mathrm{HX} \rightleftharpoons \mathrm{H}^{+}+\mathrm{X}$ - moves to right
(d) (i) M1 mol HY $=\left(50 \times 10^{-3}\right) \times 0.428=0.0214$

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

M2 $\quad\left[\mathrm{H}^{+}\right]=1.35 \times 10^{-5} \times \frac{0.0214}{0.0236}$
OR $\quad 1.35 \times 10^{-5}=\left[\mathrm{H}^{+}\right] \times \frac{0.0236}{0.0214}$
OR $\quad\left[\mathrm{H}^{+}\right]=1.35 \times 10^{-5} \times \frac{0.428}{0.472}$
OR $\quad 1.35 \times 10^{-5}=\left[\mathrm{H}^{+}\right] \times \frac{0.472}{0.428}$
must be numbers not just rearrangement of Ka expression If either HY value or $Y$-value wrong, (apart from AE-1) lose M2 and M3

M3 $\quad\left[\mathrm{H}^{+}\right]=1.22 \times 10^{-5}$
mark for answer

M4 $\quad \mathrm{pH}=4.91$
allow more than 2dp but not fewer allow M4 for correct pH calculation using their [ H ] (this applies in (d)(i) only)

## If Henderson Hasselbalch equation used:

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

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

M2 $\mathrm{pKa}=4.87$

M3 $\quad \log \left(\frac{0.0214}{0.0236}\right)=-0.043$
$\log \left(\frac{0.428}{0.472}\right)=-0.043$
If either HY value or $Y^{-}$value wrong, (apart from AE-1) lose M3 and M4

M4 $\quad \mathrm{pH}=4.87-(-0.043)=4.91$ allow more than 2dp but not fewer
(ii) Can score full marks for correct consequential use of their HY and $\mathrm{Y}^{-}$values from $\mathrm{d}(\mathrm{i})$

M1 Mol HY after adding $\mathrm{NaOH}=0.0214-5.0 \times 10^{-4}=0.0209$ 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 $\mathrm{NaOH}=0.0236+5.0 \times 10^{-4}=0.0241$ 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

M3 $\left[\mathrm{H}^{+}\right]=1.35 \times 10^{-5} \times \frac{0.0209}{0.0241}\left(=1.17 \times 10^{-5}\right)$
if convert to concentrations

$$
\left[\mathrm{H}^{+}\right]=1.35 \times 10^{-5} \times \frac{0.418}{0.482}\left(=1.17 \times 10^{-5}\right)
$$

if $H Y / Y^{-}$upside down, no further marks

M4 $\quad \mathrm{pH}=4.93$
allow more than 2dp but not fewer
NOT allow M4 for correct pH calculation using their [ $\mathrm{H}^{+}$] (this allowance applies in (d)(i) only)

## If Henderson Hasselbalch equation used:

Can score full marks for correct consequential use of their $H Y$ and $Y^{-}$values from $d(i)$

M1 Mol HY after adding $\mathrm{NaOH}=0.0214-5.0 \times 10^{-4}=0.0209$
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 $\mathrm{NaOH}=0.0236+5.0 \times 10^{-4}=0.0241$
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

M3 $\log \left(\frac{0.0209}{0.0241}\right)=-0.062$
if $H Y / Y-$ upside down, no further marks

M4 $\mathrm{pH}=4.87-(-0.062)=4.93$
allow more than $2 d p$ but not fewer

M2. (a) (i) $-\log \left[\mathrm{H}^{+}\right]$
or $\log 1 /\left[\mathrm{H}^{+}\right]$
penalise ()
(ii) $\quad\left[\mathrm{H}^{+}\right]=0.56$
(b) (i) $\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaOH} \rightarrow \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}$

OR
$\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O}$
Allow $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ etc
(ii) $\quad$ mol acid $=\left(25.0 \times 10^{-3}\right) \times 0.41=1.025 \times 10^{-2}$ or $1.03 \times 10^{-2}$
$[\mathrm{NaOH}]=1.025 \times 10^{-2} / 22.6 \times 10^{-3}=0.45(4)$
mark for answer
if not 0.454 look back for error

## OR

$[\mathrm{NaOH}]=1.03 \times 10^{-2} / 22.6 \times 10^{-3}=0.456$ or 0.46
(iii) cresol purple
(iv) NaOH reacts with carbon dioxide (in the air)
(c) (i)
$\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}$
allow molecular formulae or minor slip in formulae penalise ()
allow $\mathrm{H}_{3} \mathrm{O}^{+}$
not allow HA etc
(ii) $\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]^{2}}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}$ or with numbers
allow HA etc here
This can be scored in part (c)(i) but doesn't score there.
$\left[H^{+}\right]=\left(\sqrt{ }\left(1.74 \times 10^{-5} \times 0.410\right)=\sqrt{ }\left(7.13 \times 10^{-6}\right)\right)=2.67 \times 10^{-3}$
mark for $2.67 \times 10^{-3}$ or $2.7 \times 10^{-3}$ either gives 2.57
$\begin{array}{ll}\mathrm{pH}=2.57 & \begin{array}{l}\text { can give three ticks here for (c)(ii) } \\ \text { penalise decimal places }\langle 2>\end{array}\end{array}$
pH mark conseq on their [ $\mathrm{H}^{+}$]
so 5.15 gets 2 marks where square root not taken
(iii) $\quad \mathbf{M} 1 \mathrm{~mol} \mathrm{OH}^{-}=\left(10.0 \times 10^{-3}\right) \times 0.10=1.0 \times 10^{-3}$

If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4

M2 orig mol HA $=\left(25.0 \times 10^{-3}\right) \times 0.41=0.01025$ or $1.025 \times 10^{-2}$ or $1.03 \times 10^{-2}$

M3 mol $\underline{\mathrm{HA}}$ in buffer $=$ orig mol $\mathrm{HA}-\mathrm{mol} \mathrm{OH}^{-}$
$=0.00925$ or 0.0093
If $A^{-}$is wrong, max 3 for M1, M2 and M3 or use of $p H=p K a-\log [H A] /[A-]$

M4 mol A- in buffer $=\mathrm{mol} \mathrm{OH}^{-}=1.0 \times 10^{-3}$
Mark is for insertion of correct numbers in correct expression for [ $\mathrm{H}^{+}$]

M5 $\left[\mathrm{H}^{+}\right]=\left(\frac{\mathrm{K}_{a} \times\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}=\right)$
$\frac{\left(1.74 \times 10^{-5}\right)(0.00925)}{0.0010}$ or $\frac{\left(1.74 \times 10^{-5}\right)(0.00930)}{0.0010}$
$\left(=1.61 \times 10^{-4}\right.$ or $\left.1.62 \times 10^{-4}\right)$

M6 $\mathrm{pH}=3.79$ can give six ticks for 3.79
if [HA]/[A-] upside down lose M5 \& M6
If wrong method e.g. $\left[\mathrm{H}^{+}\right]^{2} /[H A]$ max 3 for M1, M2 and M3
Some may calculate concentrations
$[H A]=0.264$ and $[A-]=0.0286$ and rounding this to 0.029 gives $\mathrm{pH}=3.80$ (which is OK)

NB Unlike (c)(ii), this pH mark is NOT awarded conseq to their [ $\mathrm{H}^{+}$] unless following AE

BEWARE: using 0.01025 wrongly instead of 0.00925 gives pH $=3.75$
(this gets 3 for M1, M2 \& M4)

M3.(a) (i) $\quad\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$
$-\log \left[\mathrm{H}^{+}\right]$
(ii) $\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]$
(iii) $\quad\left(2.0 \times 10^{-3}\right) \times 0.5=1.0 \times 10^{-3}$
(iv) $\left[\mathrm{H}^{+}\right]=\frac{4.02 \times 10^{-14}}{1.0 \times 10^{-3}} \quad\left(=4.02 \times 10^{-11}\right)$
$\mathrm{pH}=10.40$
1

1
(b) (i) $\mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}\right.$

$$
\mathrm{pH}=2.89
$$

(c) (i) $\left(50.0 \times 10^{-3}\right) \times 0.125=6.25 \times 10^{-3}$
(ii) $\left(6.25 \times 10^{-3}\right)-(1.0 \times 10-3)=5.25 \times 10^{-3}$
(iii) mol salt formed $=1.0 \times 10^{-3}$

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

1
$=\left(1.35 \times 10^{-5}\right) \times \frac{\left(5.25 \times 10^{-3}\right) / V}{\left(1.0 \times 10^{-3}\right) / V}\left(=7.088 \times 10^{-5}\right)$
$\mathrm{pH}=4.15$

