M1. (a) (i) $-\log \left[\mathrm{H}^{+}\right]$
or $\log 1 /\left[\mathrm{H}^{+}\right]$ penalise ()
(ii) $\left[\mathrm{H}^{+}\right]=0.56$
mark for the answer; allow 2dp or more

$$
\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]=1 / 2 \times 0.56=0.28
$$

(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) $K_{a}=\frac{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{}$
allow molecular formulae or minor slip in formulae
penalise ()
allow $\mathrm{H}_{3} \mathrm{O}^{+}$
not allow HA etc
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
$\mathrm{pH}=2.57 \quad$ can give three ticks here for (c)(ii) penalise decimal places < 2 >
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 $\underline{\text { HA }}$ 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 $p H=p K a-\log [H A] /[A-]$
$\mathbf{M 4} \mathrm{mol} \mathrm{A}^{-}$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 $\left[\mathrm{H}^{-}\right]=\left(\frac{\mathrm{Ka}_{\mathrm{a}} \times\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}=\right)$
$\frac{\left(1.74 \times 10^{-5}\right)(0.00925)}{0.0010}$ 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. $\left[H^{+} / /[H A]\right.$ 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 [ H ] unless following AE

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

1
[18]

M2. (a) $\quad-\log \left[\mathrm{H}^{+}\right]$
ecf if [] wrong and already penalised
$4.57 \times 10^{-3}$
allow $4.6 \times 10^{-3}$
ignore units
(b) (i) $K_{a}=\frac{[H][\mathrm{H}]}{[\mathrm{H}}$ allow HA etc
not $\frac{\left[H^{+}\right]^{2}}{[H X]}$ but mark on
If expression wrong allow conseq units in (ii)
but no other marks in (ii)
(ii)

$$
\begin{aligned}
& \frac{\left[\mathrm{H}^{+}\right]^{2}}{[\mathrm{HX}]}=\frac{\left(4.57 \times 10^{-3}\right)^{2}}{[0.150]} \\
& \quad \text { If use } 4.6 \times 10^{-3} \\
& \quad K_{a}=1.4(1) \times 10^{-4} \text { and } p K a=3.85 \\
& =1.39 \times 10^{-4} \\
& \quad \text { allow } 1.39-1.41 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}
\end{aligned}
$$

(iii) $p K_{\mathrm{a}}=3.86$

Penalise $d p$ of final answer <or > 2 in pH once in paper
(c) (i) $\frac{30}{1000} \times 0.480=0.0144$ or $1.4(4) \times 10^{-2}$

Mark is for answer (M1)
(ii) $\frac{18}{1000} \times 0.350=0.0063$ or $6.3 \times 10^{-3}$

Mark is for answer (M2)
(iii) $0.0144-2(0.0063)=1.80 \times 10^{-3}$

M3 is for (i) - 2(ii)
If $x 2$ missed, CE i.e. Iose M3 and the next mark gained
(iv) $\begin{gathered}1.80 \times 10^{-3} \times \frac{1000}{48}=0.0375(0.038) \\ M 4 \text { is for answer }\end{gathered}$

If vol is not $48 \times 10^{-3}$ (unless AE) lose M4 and next mark gained If multiply by 48 - this is AE - i.e. lose only M4
(v) $\quad 10^{-14} / 0.0375 \quad\left(10^{-14} / 0.038\right)$
$M 5$ for $K_{w} /\left[\mathrm{OH}^{-}\right]$

$$
\begin{aligned}
& \left(=2.66 \times 10^{-13}\right) \quad\left(=2.63 \times 10^{-13}\right) \\
& \quad \text { or } \mathrm{pOH} \\
& \text { or } \mathrm{pOH}=1.426 \quad \text { (or pOH = } 1.420) \\
& \quad \text { If no attempt to use } K_{w} \text { or } p O H \text { lose both M5 and M6 }
\end{aligned}
$$

$\mathrm{pH}=12.57 \quad$ (12.58) M6
Allow M6 conseq on AE in M5 if method OK

M3. (a) Concentration of acid: $m_{1} v_{1}=m_{2} v_{2}$ hence $25 \times m_{1}=18.2 \times 0.150$ OR
moles $\mathrm{NaOH}=2.73 \times 10^{-3}$;
$m_{1}=18.2 \times 0.150 / 25=0.109 ;$
(b) (i) $K_{\mathrm{a}}=\left[\mathrm{H}^{+}\right][\mathrm{A}-] /[\mathrm{HA}]$ not $K_{\mathrm{a}}=\left[\mathrm{H}^{+}\right]^{2} /[\mathrm{HA}]$;
(ii) $\mathrm{pK}_{\mathrm{a}}=-\log \mathrm{K}_{\mathrm{a}}$;
(iii) $\left[\mathrm{A}^{-}\right]=[\mathrm{HA}]$;
hence $K_{\mathrm{a}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right] /[\mathrm{HA}]=\left[\mathrm{H}^{+}\right]$
and $-\log \mathrm{K}_{\mathrm{a}}=-\log \left[\mathrm{H}^{+}\right]$;
(c) ratio $[\mathrm{A}]: \quad[\mathrm{HA}]$ remains constant;
hence as $\left[\mathrm{H}^{+}\right]=K_{\mathrm{a}}[\mathrm{HA}] /[\mathrm{A}-] ; \quad\left[\mathrm{H}^{+}\right]$remains constant;
(d) (i) pH of $0.250 \mathrm{~mol} \mathrm{dm}-{ }^{3} \mathrm{HCl} \quad=0.60$ and pH of $0.150 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HCl}=0.82$;
pH change $=0.22$;
(ii) moles $\mathrm{HCl}=30 \times 0.250 \times 10^{-3}=\mathrm{v} \times 0.150 \times 10^{-3}=7.50 \times 10^{-3}$

OR
$v=30 \times 0.250 \times 10^{-3} / 0.150 \times 10^{-3}=50 ;$
water added $=50-30=20 \mathrm{~cm}^{3}$;

M4. (a) (i) $B$;

C;

A;
(ii) cresolphthalein

OR
thymolphthalein;
(b) (i) $-\log \left[\mathrm{H}^{+}\right]$;
(ii) $\left[\mathrm{H}^{+}\right]=1.259 \times 10^{-12}$ (or 1.26 or 1.3 )

OR
$\mathrm{OH}=14-\mathrm{pH} ;$
$\left[\mathrm{OH}^{-}\right]=\frac{10^{-14}}{1.258 \times 10^{-12}}$
OR
= 2.10;
$=7.9(4) \times 10^{-3}$;
(if $\left[\mathrm{H}^{+}\right]$is wrong allow 1 for $[\mathrm{OH}]=K_{w} /\left[\mathrm{H}^{+}\right]$or as numbers)
(c) (i) $\mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}^{+}\right]^{2} /\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}\right]$

OR
$[\mathrm{H}+]^{2} /[\mathrm{HA}]$
OR
$\left[\mathrm{H}^{+}\right]=\left[\mathrm{A}^{-}\right]$etc;
$\left[\mathrm{H}^{+}\right]=\sqrt{ } \mathrm{I} .35 \times 10^{-5} \times 0.117$ or expression without numbers;
$=1.257 \times 10^{-3}$

$$
=1.257 \times 10^{-3}
$$

$$
\mathrm{pH}=2.9 \underline{0}
$$

(iii) $\mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}^{+}\right]$

OR
$\mathrm{pK}_{\mathrm{a}}=\mathrm{pH} ;$
$\mathrm{pH}=4.8 \underline{7}$;
(penalise 1dp once)

