M1. (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;

$$
\begin{aligned}
{\left[\mathrm{H}^{+}\right] } & =\sqrt{ } \mathrm{I} .35 \times 10^{-5} \times 0.117 \text { or expression without numbers; } \\
& =1.257 \times 10^{-3} \\
\mathrm{pH} & =2.9 \underline{0} ;
\end{aligned}
$$

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

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

M2. (a) Concentration of acid: $\quad m_{1} v_{1}=m_{2} v_{2}$ 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 $K_{\mathrm{a}}=\left[\mathrm{H}^{+}\right][\mathrm{A}] /[\mathrm{HA}]=\left[\mathrm{H}^{+}\right]$
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 $\mathrm{HCl}=30 \times 0.250 \times 10^{-3}=v \times 0.150 \times 10^{-3}=7.50 \times 10^{-3}$

OR
$v=30 \times 0.250 \times 10^{-3} / 0.150 \times 10^{-3}=50 ;$
water added $=50-30=20 \mathrm{~cm}^{3}$;
1
[12]

M3. (a) $K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
(All three sets of square brackets needed, penalise missing brackets or missing charge once in the question) (Don't penalise extra $\left[H^{+}\right]^{2}[H A]$ )
(b) $\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]^{2}}{[\mathrm{HA}]}$ or $\left[\mathrm{H}^{+}\right]=[\mathrm{A}]$

$$
\begin{aligned}
{\left[\mathrm{H}^{+}\right]=} & \sqrt{\left(1.45 \times 10^{-4}\right) \times 0.25} \\
= & 6.02 \times 10^{-3} \mathrm{pH}=2.22 \\
& \quad \text { (must be to } 2 \mathrm{dp}) \\
& \text { (allow 4th mark consequential on their } \left.\left[\mathrm{H}^{+}\right]\right)
\end{aligned}
$$

(c) (i) pH (almost) unchanged
(Must be correct to score explanation)
$\mathrm{H}^{+}$removed by $\mathrm{A}^{-}$forming HA or acid reacts with salt or more HA formed
(ii) $\left[\mathrm{H}^{+}\right] \quad=10^{-3.59}=2.57 \times 10^{-4}$ or $2.6 \times 10^{-4}$
$[\mathrm{A}]=\frac{\frac{\mathrm{K}_{\mathrm{a}}[\mathrm{HA}]}{\left[\mathrm{H}^{+}\right]}}{}$
$=\frac{\left(1.45 \times 10^{-4}\right] \times 0.25}{2.57 \times 10^{-4}}$
$=0.141\left(\mathrm{~mol} \mathrm{dm}^{3}\right)$
(Allow 0.139 to 0.141 and allow 0.14 )
(If not used 3.59, to find [ $\mathrm{H}^{+}$] can only score M2 for working) (If 3.59 used but $\left[\mathrm{H}^{+}\right]$is wrong, can score M2 for correct method and conseq M4)
If wrong method and wrong expression, can only score M1)
(ii) Alternative scheme for first three marks of part (c)(ii)
$\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}-\log \frac{[\mathrm{HA}]}{\left[\mathrm{A}^{-}\right]}$
$\mathrm{pK}_{\mathrm{a}}=3.84$

$$
3.59=3.84-\log \frac{0.250}{\left[\mathrm{~A}^{-}\right]}
$$

## M4. (a) $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]^{2}}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]} \text { or }\left[\mathrm{H}^{+}\right]=\left[\mathrm{A}^{-}\right]
$$

$\left[\mathrm{H}^{+}\right]=\sqrt{ } 1.74 \times 10^{-5} \times 0.15\left(\right.$ or $\left.1.62 \times 10^{-3}\right)$
$\mathrm{pH}=2.79$ (penalise 1 dp or more than 2dp once in the qu )
(b) (i) Solution which resists change in $\mathrm{pH} /$ maintains pH despite the addition of (small amounts of) $\underline{\text { acid/base (or dilution) }}$
(ii) $\mathrm{CH}_{3} \mathrm{COO}+\mathrm{H}^{+} \rightarrow \mathrm{CH}_{3} \mathrm{COOH}$
must show an equation full or ionic in which ethanoate ions are converted to ethanoic acid
(c) (i) $\left[\mathrm{H}^{+}\right]=\frac{\mathrm{K}_{a}\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}$if rearrangement incorrect, no further marks
$=1.74 \times 10^{-5} \times \frac{0.15}{0.10}$
$\left(=2.61 \times 10^{-5}\right)$
$\mathrm{pH}=4.58$
(ii) $\quad \mathrm{Ml} \quad$ moles $\mathrm{H}^{+}$added $=10 \times 10^{-3} \times 1.0=0.01$

M2 moles ethanoic acid after addition $=0.15+0.01=0.16$

M3 moles ethanoate ions after addition $=0.10-0.01=0.09$

$$
\left[\mathrm{H}^{+}\right]=\frac{\mathrm{K}_{\mathrm{a}}\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}=1.74 \times 10^{-5} \times \frac{0.16 \mathrm{~N}}{0.09 \mathrm{~N}}
$$

$$
\left(=3.09 \times 10^{-5}\right)
$$

M5 pH $=4.51$
The essential part of this calculation is addition/subtraction of 0.01 moles to gain marks M2 and M3. If both of these are missing, only mark M1 is available. Thereafter treat each mark independently, except if the expression in M4 is wrong, in which case both M4 and M5 are lost.
alternative scheme for part (c)(i)
$\mathrm{pH} \mathrm{pK}_{\mathrm{a}}-\log \frac{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}$
$\mathrm{pK}_{\mathrm{a}}=4.76$
$\mathrm{pH}=\left(4.76-\log \frac{0.15}{0.10}\right)=4.58$
alternative for penultimate mark of part (c)(ii)
$p H=4.76-\log \frac{0.16}{0.09}$

