M1. (a) (i) $-\log[H^+]$

*penalise missing [ ] here **and not elsewhere***

1

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

Allow ( ) brackets, but must have charges

1

(iii) Mark independently from a(ii)

$[H^+] = 10^{-13.72} = 1.905 \times 10^{-14}$

If wrong no further mark

1

$K_w = 1.905 \times 10^{-14} \times 0.154 = = (2.93 – 2.94) \times 10^{-15}$

1

(b) (i) $Ka = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Must have charges and all brackets, allow ( )

Acid/salt shown must be CH_3COOH not HA

and correct formulae needed

1

(ii) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**
For values above 10, allow 3sfs - do not insist on 2 dp

$K_a = \dfrac{[H^+]^2}{[CH_3COOH]}$

Allow HA

1

($[H^+]^2 = 1.75 \times 10^{-5} \times 0.154 = 2.695 \times 10^{-6} = 2.70 \times 10^{-6}$)

If √ shown but not done gets pH = 5.57 (scores 2)

$[H^+] = 1.64 \times 10^{-3}$

*Allow mark for pH conseq to their [H+] **here only***

1

pH = 2.78 or 2.79

1

(c) (i) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**

For values above 10, allow 3sfs - do not insist on 2 dp

M1 Initially

mol OH^- = $(10 \times 10^{-3}) \times 0.154$ **and**

mol HA = $(20 \times 10^{-3}) \times 0.154$

or mol OH^- = 1.54×10^{-3} **and** mol HA = 3.08×10^{-3}

1

M2 $[H^+] = K_a \dfrac{[CH_3COOH]}{[CH_3COOH^-]}$

or with numbers

Allow Henderson Hasselbach

$pH = pK_a + log \dfrac{[CH_3COO^-]}{[CH_3COOH]}$

M3 mol ethanoic acid left = (mol ethanoate ions) = 1.54×10^{-3}

$K_a = [H^+]$ **or** $pH = pK_a$ scores **M1**, **M2** and **M3**

1 If either mol acid in mixture or mol salt wrong
- max 2 for M1 and M2
Any mention of $[H^+]^2$ *- max 2 for M1 and M3*

1

M4 pH (= - log 1.75×10^{-5}) = 4.76 or 4.757

Not 4.75

1

If no subtraction (so mol ethanoic acid in buffer = original mol)
pH = 4.46 scores 2 for **M1** and **M2**
If $[H+]^2$ used, pH = 3.02 scores 2 for **M1** and **M3**

(ii) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**
For values above 10, allow 3sfs - do not insist on 2 dp

M1 XS mol KOH (= $(20 \times 10^{-3}) \times 0.154$) = 3.08×10^{-3}

If no subtraction: max 1 for correct use of volume

No subtraction and no use of volume scores zero

If wrong subtraction or wrong moles

*Can only score **M2** and **M3** for process*

1

M2 $[OH^-] = 3.08 \times 10^{-3} \times \frac{10^3}{60} = 0.0513(3)$

*Mark for dividing their answer to **M1** by correct volume (method mark)*

*If no volume or wrong volume or multiplied by volume, max 2 for **M1** and **M3** process*

1

M3 $[H^+] = \frac{10^{-14}}{0.05133}$ (= 1.948×10^{-13} to 1.95×10^{-13})

or pOH = 1.29

*Mark for K_w divided by their answer to **M2***

If pOH route, give one mark for 14 – pOH

1

M4 pH = 12.7(1)

Allow 3sf but not 12.70

1

If no subtraction and no use of volume (pH = 11.79 scores zero)
If no subtraction, max 1 for correct use of volume, ($60cm^3$)
(pH = 13.01 scores 1)
If volume not used, pH = 11.49 (gets 2)
If multiplied by vol, pH = 10.27 (gets 2)

[16]

M2. (a) (i) $-\log[H^+]$ or $\log 1/[H^+]$

penalise missing square brackets here only

1

(ii) 0.81

2dp required, no other answer allowed

1

(iii) **M1** mol $H^+ = 1.54 \times 10^{-3}$

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) **M1** $[H^+] = 3.31 \times 10^{-3}$

1

M2 $K_a = \frac{[H^+][X^-]}{[HX]}$ or $\frac{[H^+]^2}{[HX]}$ or using numbers

do not penalise ( ) or one or more missing [ ]

1

M3 $[HX] = \frac{[H^+]^2}{K_a} = \frac{(3.31 \times 10^{-3})^2}{4.83 \times 10^{-5}}$

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/added OH^- removed by reaction with H^+ or the acid

1

M2 correct 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 $[H^+] = 1.35 \times 10^{-5} \times \frac{0.0214}{0.0236}$

OR $1.35 \times 10^{-5} = [H^+] \times \frac{0.0236}{0.0214}$

OR $[H^+] = 1.35 \times 10^{-5} \times \frac{0.428}{0.472}$

OR $1.35 \times 10^{-5} = [H^+] \times \frac{0.472}{0.428}$

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

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

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

mark for answer

1

M2 p*K*a = 4.87

1

M3 $\log\left(\frac{0.0214}{0.0236}\right) = -0.043$

$\log\left(\frac{0.428}{0.472}\right) = -0.043$

If either HY value or Y^- value wrong, (apart from AE-1) lose M3 and M4

1

M4 pH = 4.87 – (– 0.043) = 4.91

allow more than 2dp but not fewer

1

(ii) 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

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

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

if convert to concentrations

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

1

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 $[H^+]$ (this allowance applies in (d)(i) only)

1

If Henderson Hasselbalch equation used:

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

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

M3 $\log\left(\frac{0.0209}{0.0241}\right) = -0.062$

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

[18]

M3.(a) (i) $-\log[H^+]$

*Penalise missing [ ] here **and not elsewhere***

1

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

1

(b) (i) $[H^+] = 2.34 \times 10^{-7}$

1

pH = 6.63

Penalise fewer than 3 sig figs but allow more than 2 dp

1

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

1

(iii) **M1** $[H^+] = K_w/[OH^-]$

if upside down or CE, allow M3 only for correct use of their $[H^+]$

1

M2 $(= 5.48 \times 10^{-14}/0.140) = 3.91 \times 10^{-13}$

1

M3 pH = 12.4(1)

not 12.40 (AE from 12.407)

1

Penalise fewer than 3 sig figs but allow more than 3 sfs
For values above 10, allow 3sfs - do not insist on 2 dp.
For values below 1, allow 2dp – do not insist on 3 sig figs
Not allow pH = 14 – pOH but can award M3 only for pH = 13.1(46)
Can award all three marks if $pK_w = 13.26$ is used

(c) **M1** mol NaOH = mol OH^- = $(30 \times 10^{-3}) \times 0.20 = 6.0 \times 10^{-3}$

mark for answer

1

M2 mol H_2SO_4 = $(25 \times 10^{-3}) \times 0.15 = 3.75 \times 10^{-3}$

mark for answer

1

M3 mol H^+ = $(25 \times 10^{-3}) \times 0.15 \times 2 = 7.5 \times 10^{-3}$
OR XS mol H_2SO_4 = 0.75×10^{-3}

if factor of 2 missed or used wrongly, CE - lose M3 and next mark gained. In this case they must then use K_w to score any more.
see examples below

1

M4 XS mol H^+ = 1.5×10^{-3}

1

M5 $[H^+] = (1.5 \times 10^{-3}) \times (1000/55) = 0.0273$

if no use or wrong use of volume, lose M5 and M6 except if 1000 missed
AE –1 (pH = 4.56)

1

M6 pH = 1.56

Penalise fewer than 3 sig figs but allow more than 3 sfs
For values above 10, allow 3sfs - do not insist on 2 dp.
For values below 1, allow 2dp – do not insist on 3 sig figs

1

[14]

M4. (a) k = rate/$[CH_3CH_2COOCH_3][H^+]$

1

or

$$= \frac{1.15 \times 10^{-4}}{(0.150)(0.555)}$$

= 1.38×10^{-3} to 1.4×10^{-3}

1

$mol^{-1}\ dm^3\ s^{-1}$

1

(b) ans = rate constant × (½ × 0.150) × (½ × 0.555)

ignore units

= rate constant × 0.0208

2.88×10^{-5} (1.38×10^{-3} gives 2.87×10^{-5})

Allow 2.87 – 2.91 × 10^{-5} (1.4×10^{-3} gives 2.91×10^{-5})

1

(c) $[H^+]$ = rate/ $k[CH_3COOCH_2CH_3]$

1

$$= \frac{4.56 \times 10^{-5}}{(8.94 \times 10^{-4})(0.123)}$$

= 0.415 (0.4146)

1

pH = 0.38 mark independently

$[H^+]$ = 0.41 gives pH = 0.39

1

[7]