

- M1.** (a) (i) $-\log[\text{H}^+]$
penalise missing [] here and not elsewhere 1
- (ii) $[\text{H}^+][\text{OH}^-]$
Allow () brackets, but must have charges 1
- (iii) Mark independently from a(ii)
 $[\text{H}^+] = 10^{-13.72} = 1.905 \times 10^{-14}$
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) $K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$
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
- $K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$
Allow HA 1
- $([\text{H}^+]^2 = 1.75 \times 10^{-5} \times 0.154 = 2.695 \times 10^{-6} = 2.70 \times 10^{-6})$
If $\sqrt{\quad}$ shown but not done gets pH = 5.57 (scores 2)
- $[\text{H}^+] = 1.64 \times 10^{-3}$
Allow mark for pH conseq to their $[\text{H}^+]$ 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

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

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

$$\text{or mol OH}^- = 1.54 \times 10^{-3} \text{ and mol HA} = 3.08 \times 10^{-3}$$

1

$$\text{M2 } [\text{H}^+] = K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COOH}^-]}$$

or with numbers

Allow Henderson Hasselbach

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\text{M3 mol ethanoic acid left} = (\text{mol ethanoate ions}) = 1.54 \times 10^{-3}$$

$$K_a = [\text{H}^+] \text{ or pH} = \text{p}K_a \text{ scores M1, M2 and M3}$$

1 If either mol acid in mixture or mol salt wrong

- max 2 for M1 and M2

Any mention of $[\text{H}^+]^2$ - max 2 for M1 and M3

1

$$\text{M4 pH} (= -\log 1.75 \times 10^{-5}) = 4.76 \text{ or } 4.757$$

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 $[\text{H}^+]^2$ 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 $(= (20 \times 10^{-3}) \times 0.154) = 3.08 \times 10^{-3}$

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

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

or $\text{pOH} = 1.29$

Mark for K_w divided by their answer to M2

If pOH route, give one mark for $14 - \text{pOH}$

1

M4 $\text{pH} = 12.7(1)$

Allow 3sf but not 12.70

1

If no subtraction and no use of volume ($\text{pH} = 11.79$ scores zero)

If no subtraction, max 1 for correct use of volume, (60cm^3)

($\text{pH} = 13.01$ scores 1)

If volume not used, $\text{pH} = 11.49$ (gets 2)

If multiplied by vol, $\text{pH} = 10.27$ (gets 2)

[16]

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

penalise missing square brackets here only

1

(ii) 0.81

2dp required, no other answer allowed

1

- (iii) **M1** $\text{mol H}^+ = 1.54 \times 10^{-3}$
if wrong no further mark
if 1.5×10^{-3} allow M1 but not M2 for 2.82

1

- M2** $\text{pH} = 2.81$
allow more than 2dp but not fewer

1

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

1

- M2** $K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$ or $\frac{[\text{H}^+]^2}{[\text{HX}]}$ or using numbers
do not penalise () or one or more missing []

1

- M3** $[\text{HX}] = \frac{[\text{H}^+]^2}{K_a} = \frac{(3.31 \times 10^{-3})^2}{4.83 \times 10^{-5}}$
allow conseq on their $[\text{H}^+]/(4.83 \times 10^{-5})$ (AE)
if upside down, no further marks after M2

1

- M4** $[\text{HX}] = 0.227$
allow 0.225 – 0.23

1

- (c) **M1** extra/added OH^- removed by reaction with H^+ or the acid

1

- M2** correct discussion of equin shift i.e. $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$ moves to right

1

OR

- ratio $\frac{[\text{HX}]}{[\text{X}^-]}$ remains almost constant

- (d) (i) **M1** $\text{mol HY} = (50 \times 10^{-3}) \times 0.428 = 0.0214$

OR $[Y] = .0236 \times \frac{1000}{50} = 0.472$
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 $\text{mol HY} = (50 \times 10^{-3}) \times 0.428 = 0.0214$

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

1

M2 $pK_a = 4.87$

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 $\text{pH} = 4.87 - (-0.043) = 4.91$
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 $[\text{H}^+] = 1.35 \times 10^{-5} \times \frac{0.0209}{0.0241} (= 1.17 \times 10^{-5})$

if convert to concentrations

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

1

if HY/Y⁻ upside down, no further marks

M4 $\text{pH} = 4.93$
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) $-\log[\text{H}^+]$
Penalise missing [] here and not elsewhere
 1

(ii) $[\text{H}^+][\text{OH}^-]$
 1

(b) (i) $[\text{H}^+] = 2.34 \times 10^{-7}$
 1

pH = 6.63
Penalise fewer than 3 sig figs but allow more than 2 dp
 1

(ii) $[\text{H}^+] = [\text{OH}^-]$
 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 H₂SO₄ = $(25 \times 10^{-3}) \times 0.15 = 3.75 \times 10^{-3}$
mark for answer 1
- M3** mol H⁺ = $(25 \times 10^{-3}) \times 0.15 \times 2 = 7.5 \times 10^{-3}$
 OR XS mol H₂SO₄ = 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) $k = \text{rate}/[\text{CH}_3\text{CH}_2\text{COOCH}_3][\text{H}^+]$

1

or

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

$$= 1.38 \times 10^{-3} \text{ to } 1.4 \times 10^{-3}$$

1

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

1

(b) $\text{ans} = \text{rate constant} \times (\frac{1}{2} \times 0.150) \times (\frac{1}{2} \times 0.555)$

ignore units

$$= \text{rate constant} \times 0.0208$$

$$2.88 \times 10^{-5} \quad (1.38 \times 10^{-3} \text{ gives } 2.87 \times 10^{-5})$$

$$\text{Allow } 2.87 - 2.91 \times 10^{-5} (1.4 \times 10^{-3} \text{ gives } 2.91 \times 10^{-5})$$

1

(c) $[\text{H}^+] = \text{rate}/k[\text{CH}_3\text{COOCH}_2\text{CH}_3]$

1

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

$$= 0.415 (0.4146)$$

1

$$\text{pH} = 0.38 \text{ mark independently}$$

$$[\text{H}^+] = 0.41 \text{ gives } \text{pH} = 0.39$$

1

[7]

