

M1.(a) (i) $[H^+][OH^-]$ **OR** $[H_3O^+][OH^-]$
Ignore (aq)
Must have [] not ()

1

(ii) $\sqrt{3.46 \times 10^{-14}}$ ($= 1.86 \times 10^{-7}$)
If no square root, CE=0

1

pH = 6.73
Must be 2dp

1

(iii) $[H^+] = 10^{-11.36}$ ($= 4.365 \times 10^{-12}$ OR 4.37×10^{-12})
Mark for working

1

$K_w = [4.365 \times 10^{-12}$ **OR** $4.37 \times 10^{-12} \times 0.047] = 2.05 \times 10^{-13}$
Allow $2.05 \times 10^{-13} - 2.1 \times 10^{-13}$
Mark for answer
Ignore units

1

(b) (i) $HCOOH \rightleftharpoons HCOO^- + H^+$
Must have \rightleftharpoons but ignore brackets.

OR $HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$
Allow HCO_2^- or $CHOO^-$ ie minus must be on oxygen, so penalise COOH

1

(ii) $K_a = \frac{[H^+][HCOO^-]}{HCOOH}$ **OR** $\frac{[H_3O^+][HCOO^-]}{HCOOH}$

Must have all brackets but allow ()

Must be HCOOH etc.

Allow ecf in formulae from (b)(i)

1

(iii) M1

$$K_a = \frac{[H^+]^2}{[HCOOH]} \quad \left([H^+]^2 = 1.78 \times 10^{-4} \times 0.056 = 9.97 \times 10^{-6} \right)$$

Allow HA or HX etc.

Allow $[H^+] = \sqrt{K_a \times [HA]}$ for M1

1

M2 $[H^+] = 3.16 \times 10^{-3}$

Mark for answer

1

M3 pH = 2.50 allow more than 2 dp but not fewer

Allow correct pH from their wrong $[H^+]$ here only If square root shown but not taken, pH = 5.00 can score max 2 for M1 and M3

1

(iv) M1 Decrease **Mark M1 independently**

1

M2 Eqm shifts / moves to RHS **OR** more H^+ **OR** K_a increases
OR more dissociation

1

M3 To reduce temperature or oppose increase / change in temperature

Only award M3 following correct M2

1

(c) (i) M1 $[H^+] = \frac{K_a \times [HX]}{[X^-]}$ OR $pH = pK_a - \log \frac{[HX]}{[X^-]}$

If [HX]/[X⁻] upside down, no marks

1

M2 $\frac{1.78 \times 10^{-4} \times 2.35 \times 10^{-2}}{1.84 \times 10^{-2}}$ OR $pH = 3.75 - \log \frac{2.35 \times 10^{-2}}{1.84 \times 10^{-2}}$
 (= 2.27×10^{-4})

1

M3 $pH = 3.64$ allow more than 2 dp but not fewer
pH calc NOT allowed from their wrong [H⁺] here

1

(ii) M1 Mol H⁺ added = 5.00×10^{-4}
Mark on from AE in moles of HCl (eg 5×10^{-3} gives $pH = 3.42$ scores 3)

1

M2 Mol HCOOH = 2.40×10^{-2} and Mol HCOO⁻ = 1.79×10^{-2}
If either wrong no further marks except AE (-1) OR if ECF in mol acid and / or mol salt from (c)(i), can score all 4

1

M3 $[H^+] (= \frac{K_a \times [XH]}{[X^-]}) = \frac{1.78 \times 10^{-4} \times 2.40 \times 10^{-2}}{1.79 \times 10^{-2}}$ (= 2.39×10^{-4})

If [HX]/[X⁻] upside down here after correct expression in (c)(i), no further marks

OR $pH = 3.75 - \log \frac{2.40 \times 10^{-2}}{1.79 \times 10^{-2}}$

If [HX]/[X⁻] upside down here and is repeat error from (c)(i), max 3 (pH = 3.88 after 3.86 in (c)(i))

M4 pH = 3.62 allow more than 2 dp but not fewer
pH calc NOT allowed from their wrong [H⁺] here

1
 [20]

M2.(a) Proton donor or H⁺ donor

Allow donator

1

(b) (i) B B

Both need to be correct to score the mark

1

(ii) A A

Both need to be correct to score the mark

1

(iii) B A

Both need to be correct to score the mark

1

(c) **M1** [H⁺] = 10^{-1.25} OR 0.05623

1

M2 mol HCl = (25 × 10⁻³) × 0.0850 (= 2.125 × 10⁻³)

Mark for Working

1

M3 vol $\left(= \frac{2.125 \times 10^{-3}}{0.05623} \right) = 0.0378 \text{ dm}^3 \text{ or } 37.8 \text{ cm}^3$

allow 0.0375 – 0.038 dm³ or 37.5 – 38 cm³

Units and answer tied

Lose M3 if total given as (25 + 37.8) = 62.8 cm³

Ignore “vol added = 12.8 cm³” after correct answer

1

(d) (i) 4.52

Must be 2dp

1

(ii) $K_a = \frac{[H^+][H^-]}{[HX]}$ ignore = $\frac{[H^+]^2}{[HX]}$ but this may score M1 in (d)(iii)

Must have all brackets but allow () Allow HA etc

NO mark for 10^{-pK_a}

1

(iii) **M1** $K_a = \frac{[H^+]^2}{[HX]}$ or with numbers
Allow $[H^+] = \sqrt{(K_a \times [HA])}$ for M1

1

M2 $[H^+] = (\sqrt{(3.01 \times 10^{-5} \times 0.174)}) = \sqrt{(5.24 \times 10^{-6})}$
 $= 2.29 \times 10^{-3} - 2.3 \times 10^{-3}$

Mark for answer

1

M3 pH = 2.64 (allow more than 2dp but not fewer)

Allow 1 for correct pH from their wrong $[H^+]$

If square root forgotten, pH = 5.28 scores 2 for M1 and M3

1

(e) **M1** mol OH⁻ = $(10.0 \times 10^{-3}) \times 0.125 = 1.25 \times 10^{-3}$

Mark for answer

1

M2 orig mol HX = $(15.0 \times 10^{-3}) \times 0.174 = 2.61 \times 10^{-3}$

Mark for answer

1

M3 mol HX in buffer = orig mol HX – mol OH⁻

Mark for answer

= $2.61 \times 10^{-3} - 1.25 \times 10^{-3} = 1.36 \times 10^{-3}$

Allow conseq on their (M2 – M1)

([HX] = $1.36 \times 10^{-3} / 25 \times 10^{-3} = 0.0544$)

If no subtraction, max 3 for M1, M2 & M4 (pH = 4.20)

If [H⁺] = [X⁻] & √used, max 3 for M1, M2 & M3 (pH = 2.89)

1

M4 mol X⁻ in buffer = mol OH⁻ = 1.25×10^{-3}

([X⁻] = $1.25 \times 10^{-3} / 25 \times 10^{-3} = 0.05$)

May be scored in M5 expression

1

M5 [H⁺] $(= \frac{K_a \times [HX]}{[X^-]})$

If use $K_a = \frac{[H^+]^2}{[HX]}$ no further marks

= $\frac{3.01 \times 10^{-5} \times 1.36 \times 10^{-3}}{1.25 \times 10^{-3}}$ OR $\frac{3.01 \times 10^{-5} \times 0.0544}{0.05}$

(= 3.27×10^{-5})

If either value of HX or X⁻ used wrongly or expression upside down, no further marks

1

M6 pH = 4.48 or 4.49 (allow more than 2dp but not fewer)

*Do **not** allow M6 for correct calculation of pH using their [H⁺] - this only applies in (d)(iii) - apart from earlier AE*

1

[18]

M3. (a) (i) addition of small amounts of acid send eqm to left or extra H⁺ removed by reaction with HCO₃⁻ 1

ratio [H₂CO₃]/[HCO₃⁻] remains constant hence [H⁺] and pH remain const 1

(ii) pH = 7.41 ∴ [H⁺] = 3.89 × 10⁻⁸ mol dm⁻³ 1

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad 1$$

$$= \frac{(3.89 \times 10^{-8})(2.5 \times 10^{-2})}{1.25 \times 10^{-2}} = 7.78 \times 10^{-8} \text{ mol dm}^{-3}$$

allow error carried forward mark. Do not penalise twice. 1

(b) (i) moles H⁺ added = 10 × 10⁻³ × 1.0 = 0.01 1

(ii) moles ethanoic acid after addition = 0.15 + 0.01 = 0.16 1

moles ethanoate ions after addition = 0.10 – 0.01 = 0.09 1

$$(iii) [H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} \quad 1$$

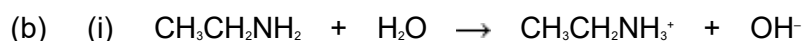
$$= 1.74 \times 10^{-5} \times \frac{0.16/V}{0.09V} \quad 1$$

pH = 4.51 1

[11]

M4.(a) Proton acceptor

1



allow eq with or without \rightleftharpoons

allow $\text{C}_2\text{H}_5\text{NH}_2$ and $\text{C}_2\text{H}_5\text{NH}_3^+$ (plus can be on N or H or 3)

allow RHS as $\text{C}_2\text{H}_5\text{NH}_3\text{OH}$

1

(ii) Mark independently of (b)(i)

Allow

Ethylamine is only partly/slightly dissociated

OR

Ethylamine is only partly/slightly ionized

reaction/equilibrium lies to left or low $[\text{OH}^-]$ **OR** little OH^- formed

OR little ethylamine has reacted

Ignore "not fully dissociated" or "not fully ionized"

Ignore reference to ionisation or dissociation of water

1

(c) **M1** Ethylamine

If wrong no marks in (c)

1

M2 alkyl group is electron releasing/donating

OR alkyl group has (positive) inductive effect

1

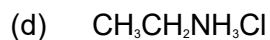
M3 increases electron density on N(H₂)

OR increased availability of lp

OR increases ability of lp (to accept H(+))

Mark M3 is independent of M2

1



Or any amine hydrochloride

allow name (ethylammonium chloride or ethylamine hydrochloride) or other halide for Cl

or a strong **organic acid**

NOT NH_4Cl

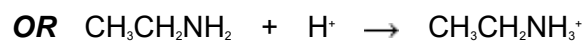
1

(e) Mark independently of (d)

Extra H^+ reacts with ethylamine or OH^-

Or makes reference to *Equilibrium (in (b)(i)) with amine on LHS*

1



Equilibrium shifts to RHS

OR ratio $[\text{CH}_3\text{CH}_2\text{NH}_3^+]/[\text{CH}_3\text{CH}_2\text{NH}_2]$ remains almost constant

1

[9]