M1.(a) (i) $[H^+][OH^-]$ ***OR*** $[H_3O^+][OH^-]$

Ignore (aq)

Must have [ ] not ( )

1

(ii) $\sqrt{3.46 \times 10^{-14}}$ (= 1.86×10^{-7})

If no square root, CE=0

1

pH = 6.73

Must be 2dp

1

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

Mark for working

1

$Kw = [4.365 \times 10^{-12}$ ***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) $$K_a = \frac{[H^+][HCOO^-]}{HCOOH} \quad \textit{OR} \quad \frac{[H_3O^+][HCOO^-]}{HCOOH}$$

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 $[H^+] = \sqrt{(Ka \times [HA])}$ *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 <u>shifts / moves</u> 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 $[H^+] = \frac{Ka \times [HX]}{[X^-]}$ ***OR*** $pH = pK_a - \log\frac{[HX]}{[X^-]}$

If [HX]/[X⁻] upside down, no marks

1

M2 $\frac{1.78\times10^{-4} \times 2.35 \times 10^{-2}}{1.84\times10^{-2}}$ ***OR*** $pH = 3.75 - \log\frac{2.35\times10^{-2}}{1.84\times10^{-2}}$

(= 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

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

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

OR $pH = 3.75 - \log\frac{2.40\times10^{-2}}{1.79\times10^{-2}}$

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

1

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 = $(25 \times 10^{-3}) \times 0.0850$ (= 2.125×10^{-3})

Mark for Working

1

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

allow 0.0375 – 0.038 dm^3 or 37.5 – 38 cm^3

Units and answer tied

Lose M3 if total given as (25 + 37.8) = 62.8 cm^3

Ignore “vol added = 12.8 cm^3 ” 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^{-pKa}*

1

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

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

1

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

$= 2.29 \times 10^{-3}$ - 2.3×10^{-3}

Mark for <u>answer</u>

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 $[H^+]$ $\left(= \frac{Ka \times [HX]}{[X^-]}\right)$

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 HCO_3^-

1

ratio $[H_2CO_3]/[HCO_3^-]$ remains constant hence $[H^+]$ and pH remain const

1

(ii) pH = 7.41 ∴ $[H^+] = 3.89 \times 10^{-8}$ mol dm^{-3}

1

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

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 = $10 \times 10^{-3} \times 1.0 = 0.01$

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

1

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

1

pH = 4.51

1

[11]

M4.(a) <u>Proton acceptor</u>

1

(b) (i) $CH_3CH_2NH_2$ + H_2O $\longrightarrow$ $CH_3CH_2NH_3^+$ + OH^-

allow eq with or without $\rightleftharpoons$

allow $C_2H_5NH_2$ and $C_2H_5NH_3^+$ (plus can be on N or H or 3)

allow RHS as $C_2H_5NH_3OH$

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 $[OH^-]$ ***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 <u>on N(H_2)</u>

OR increased availability of <u>lp</u>

OR increases ability of <u>lp</u> (to accept H(+))

Mark M3 is independent of M2

1

(d) $CH_3CH_2NH_3Cl$

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

OR $CH_3CH_2NH_2 + H^+ \longrightarrow CH_3CH_2NH_3^+$

OR $H^+ + OH^- \longrightarrow H_2O$

Equilibrium shifts to RHS

OR ratio $[CH_3CH_2NH_3^+]/[CH_3CH_2NH_2]$ remains almost constant

1

[9]