

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  $4.37 \times 10^{-12}$ )  
*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<sup>-</sup>] upside down, no marks*

1

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

1

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

1

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

1

M2 Mol HCOOH =  $2.40 \times 10^{-2}$  and Mol HCOO<sup>-</sup> =  $1.79 \times 10^{-2}$   
*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  $[H^+] (= \frac{K_a \times [XH]}{[X^-]}) = \frac{1.78 \times 10^{-4} \times 2.40 \times 10^{-2}}{1.79 \times 10^{-2}}$  (=  $2.39 \times 10^{-4}$ )

*If [HX]/[X<sup>-</sup>] 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<sup>-</sup>] 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<sup>+</sup>] here*

1  
 [20]

**M2.(a)** Proton donor or H<sup>+</sup> 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<sup>+</sup>] = 10<sup>-1.25</sup> OR 0.05623

1

**M2** mol HCl = (25 × 10<sup>-3</sup>) × 0.0850 (= 2.125 × 10<sup>-3</sup>)  
*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 dm<sup>3</sup> or 37.5 – 38 cm<sup>3</sup>

*Units and answer tied*

*Lose M3 if total given as (25 + 37.8) = 62.8 cm<sup>3</sup>*

*Ignore “vol added = 12.8 cm<sup>3</sup>” 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<sup>-</sup> =  $(10.0 \times 10^{-3}) \times 0.125 = 1.25 \times 10^{-3}$

*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<sup>-</sup>

*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  $[H^+] = [X^-]$  &  $\sqrt{\quad}$  used, max 3 for M1, M2 & M3 (pH = 2.89)*

1

**M4** mol X<sup>-</sup> in buffer = mol OH<sup>-</sup> =  $1.25 \times 10^{-3}$

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

*May be scored in M5 expression*

1

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

*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  $\frac{3.01 \times 10^{-5} \times 0.0544}{0.05}$

(=  $3.27 \times 10^{-5}$ )

*If either value of HX or X<sup>-</sup> 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

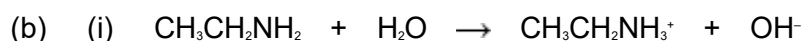
[18]

- 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)  $pH = 7.41 \therefore [H^+] = 3.89 \times 10^{-8} \text{ mol dm}^{-3}$  1
- $$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$
- $$= \frac{(3.89 \times 10^{-8})(2.5 \times 10^{-2})}{1.25 \times 10^{-2}} = 7.78 \times 10^{-8} \text{ mol dm}^{-3}$$
- 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
- $$= 1.74 \times 10^{-5} \times \frac{0.16/V}{0.09/V}$$
- 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  $\text{OH}^-$  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(H<sub>2</sub>)

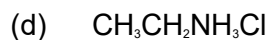
**OR** increased availability of lp

**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**  $\text{NH}_4\text{Cl}$

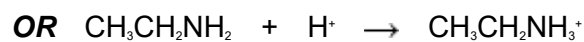
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(e) Mark independently of (d)

Extra  $\text{H}^+$  reacts with ethylamine or  $\text{OH}^-$

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]