

**M1.(a) M1**  $[H^+] = 0.0170$  1

**M2** pH = 1.77  
2 dp  
**Allow M2 for correct pH calculation from their wrong  $[H^+]$  for this pH calculation only** 1

(b) (i)  $K_a = \frac{[H^+][X^-]}{[HX]^2}$  Ignore  $K_a = \frac{[H^+]^2}{[HX]}$   
**Penalize missing [ ] here and not elsewhere**  
**Allow HA instead of HX** 1

(ii) **M1**  $[H^+] = 10^{-2.79}$  OR  $1.6218... \times 10^{-3}$   
**If  $[H^+]$  wrong, can only score M2** 1

**M2**  $K_a = \frac{[H^+]^2}{[HX]}$  OR  $\frac{[1.62 \times 10^{-3}]^2}{[0.0850]}$   
**Allow HA instead of HX** 1

**M3**  $K_a = 3.09 \times 10^{-5}$  3sfs min (allow  $3.10 \times 10^{-5}$  if 1.6218 rounded to 1.622) Ignore units  
**If  $[HX]$  used as  $(0.0850 - 1.62 \times 10^{-3})$  this gives  $K_a = 3.15 \times 10^{-5}$   $(0.0016)^2 / 0.085 = 3.01 \times 10^{-5}$  scores 2 for AE** 1

(c) **M1** mol  $OH^-$  ( $= (38.2 \times 10^{-3}) \times 0.550$ )  
 $= 2.10(1) \times 10^{-2}$  or 0.0210(1)  
**Mark for answer** 1

**M2** Mol H<sup>+</sup> (= (25.0 × 10<sup>-3</sup>) × 0.620 )

= 1.55 × 10<sup>-2</sup> or 0.0155

*Mark for answer*

1

**M3** excess mol OH<sup>-</sup> = 5.5(1) × 10<sup>-3</sup>

*Allow conseq for M1 – M2*

**If wrong method** e.g. no subtraction or use of √  
**can only score max of M1, M2, M3 and M4.**

1

**M4** [OH<sup>-</sup>] = 5.51 × 10<sup>-3</sup> ×  $\frac{10^3}{63.2}$  [= 0.08718 (0.0872)]

**OR** [OH<sup>-</sup>] = 5.5 × 10<sup>-3</sup> ×  $\frac{10^3}{63.2}$  = 0.0870(2)  
*(M1 – M2) / vol in dm<sup>3</sup> mark for dividing by volume  
(take use of 63.2 without 10<sup>-3</sup> as AE so 9.94 scores 5)  
If no use or wrong use of vol lose M4 & M6  
Can score M5 for showing (10<sup>-14</sup>/ their XS alkali)*

1

**M5** [H<sup>+</sup>] =  $\frac{10^{-14}}{0.08718}$  = 1.147 × 10<sup>-13</sup>

**OR**  $\frac{10^{-14}}{0.0870}$  = 1.149 × 10<sup>-13</sup>

**OR** pOH = 1.06

*If no use or wrong use of K<sub>w</sub> or pOH no further marks*

1

**M6** pH = 12.9(4) allow 3sf

*If vol missed score max 4 for 11.7(4)*

*If acid– alkali reversed max 4 for pH = 1.06*

*Any excess acid – max 4*

1

[12]

- M2.** (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<sub>3</sub>COOH 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 [H+] here only* 1

$$\text{pH} = 2.78 \text{ or } 2.79$$

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*

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

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

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

*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**  $[\text{H}^+] = \frac{10^{-14}}{0.05133}$  ( $= 1.948 \times 10^{-13}$  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, ( $60\text{cm}^3$ )

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

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

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

[16]

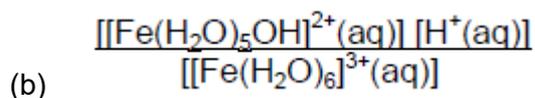
**M3.(a)** Idea that over time / after storage meter does not give accurate readings

*Do not accept 'to get an accurate reading' without further*

qualification.

Allow 'temperature variations affect reading'.

1



Allow without (aq) symbols.

Need at least one set of square brackets around complex ions

1

(c)  $\text{pH} = -\log [\text{H}^+]$

1

$$[\text{H}^+] = 0.0240$$

Do not penalise precision of  $[\text{H}^+]$

Correct answer scores M1 and M2.

1

$$K_a = (0.0240)^2 / 0.1 = 5.75 \times 10^{-3} \text{ or } 5.76 \times 10^{-3}$$

Correct answer without working loses M1 and M2.

Allow  $7.58 \times 10^{-3}$

1

Answer, even if incorrect, given to 3 sig figs

1

(d) Oxygen (in the air) /  $\text{O}_2$

Ignore 'air' or 'the atmosphere' or 'chemicals in soil'.

List principle.

1

(e) 4.0 – 6.9

Do not penalise precision.

[7]

- M4.** (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  $1.5 \times 10^{-3}$  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  $[\text{H}^+]^2 / (4.83 \times 10^{-5})$  (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  $\text{OH}^-$  removed by reaction with  $\text{H}^+$  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  $\frac{[HX]}{[X^-]}$  remains almost constant

(d) (i) **M1** 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<sup>+</sup>] (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**  $[Y] = .0236 \times \frac{1000}{50} = 0.472$   
*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<sup>-</sup> 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<sup>-</sup> 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<sup>-</sup> after adding NaOH =  $0.0236 + 5.0 \times 10^{-4} = 0.0241$   
*AE in addition loses just M2*  
*If wrong mol Y<sup>-</sup> (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<sup>-</sup> 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<sup>+</sup>] (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<sup>-</sup> 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<sup>-</sup> after adding NaOH =  $0.0236 + 5.0 \times 10^{-4} = 0.0241$   
*AE in addition loses just M2*  
*If wrong mol Y<sup>-</sup> (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<sup>-</sup> upside down, no further marks*

1

**M4** pH =  $4.87 - (-0.062) = 4.93$   
*allow more than 2dp but not fewer*

1

[18]