

### 4.3 ANSWERS TO EXAM QUESTIONS

1. (a) (i) A proton donor (1)  
(ii) Fully ionised or fully dissociated (1)  
(iii)  $1.0 \times 10^{-14}$  (1)  
 $\text{mol}^2 \text{dm}^{-6}$  (1) 4
- (b) (i)  $1.50 \times 10^{-3} / 25 \times 1000$  (1)  
 $= 0.06 \text{ mol dm}^{-3}$  (1)  
1.2 (1)
- (ii) Mol  $\text{OH}^-$  added  $= 50 \times 0.150 / 1000 = 7.5 \times 10^{-3}$  (1)  
Mol  $\text{H}^+$  used  $= 1.5 \times 10^{-3}$  (1)  
Mol  $\text{OH}^-$  excess  $= 6.0 \times 10^{-3}$  (1)  
 $[\text{OH}^-] = 6.0 \times 10^{-3} / 75 \times 1000 = 8.0 \times 10^{-2}$  (1)  
 $[\text{H}^+] = 10^{-14} / 8.0 \times 10^{-2} = 1.25 \times 10^{-13}$  (1)  
pH  $= 12.9$  (1) 8
- (c) (i)  $0.3 \text{ mol dm}^{-3}$  (1)  
(ii)  $[\text{H}^+]$  at pH = 0.7 is  $0.2 \text{ mol dm}^{-3}$  (1)  
 $m_1 v_1 = m_2 v_2 \therefore 0.3 \times 25 = 0.2 \times v$  (1)  
Hence  $v = 37.5$  (1)  
Water added  $= 37.5 - 25 = 12.5$  (1) 5

[17]

2. (a) (i)  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$  (1)  
 $K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$  (1)  
 $[\text{H}^+] = 10^{-2.82} = 1.514 \times 10^{-3} \text{ mol dm}^{-3}$  (1)  
 $K_a = \frac{(1.514 \times 10^{-3})^2}{0.15} = 1.53 \times 10^{-5} \text{ mol dm}^{-3}$  (1) [2]
- (ii) Decreases (1)  
Equilibrium shifts to right (endothermic process) (1)  
 $\therefore [\text{H}^+] \uparrow$  as  $T \uparrow$  (1)  
pH gets smaller 8

- (b) (i)  $\frac{2}{3}n$  (1)
- (ii)  $\left(\frac{2}{3}n\right) \div \left(\frac{1}{3}n\right)$  (1) = 2 (1)
- (iii)  $K_a = \frac{[H^+][X^-]}{[HX]} = \frac{[H^+]}{2}$  (1)  
 $= 2.1 \times 10^{-4} \text{ mol dm}^{-3}$  (1) 5
- (c) Weak acid/strong base  $\therefore$  pH at equivalence  $> 7$  (1)  
 methyl orange has colour change at pH  $< 7$  (1) 2
- (d) Buffer can resist change in pH (1)  
 on addition of small amounts of  $H^+$  (or  $OH^-$ ) (1)  
 $H^+ (aq) + X^- (aq) \rightleftharpoons HX (aq)$  (1) 3

[18]

3. (a) proton donor (1)  
 substance formed when acid has lost proton / substance that becomes an acid by gaining a proton (**not** just proton acceptor) (1) 2
- (b) (i) acid: HBr base:  $Br^-$
- (ii) acid:  $H_2SO_4$  base:  $HSO_4^-$   
 allow 1 in (b) if both acids / bases are correct (ie give 1 for a correct vertical pair) 2
- (c) (i)  $H_2O \rightleftharpoons H^+ + OH^- / 2H_2O \rightleftharpoons H_3O^+ + OH^-$  (1)  
 (accept other types of arrow) 1
- (ii)  $K_c = \frac{[H^+][OH^-]}{[H_2O]}$  / expression based on  $H_3O^+$  equation (1)  
 $[H_2O]$  is (effectively) constant / concentration of  $H_2O$  is large / equilibrium in (i) is to left (1)  
 $(K_c \times [H_2O]) = K_w = [H^+][OH^-]$  (1) 3
- (iii)  $[H^+] = [OH^-] / [H^+]^2 = 2.92 \times 10^{-14}$  (1)  
 $[H^+] = \sqrt{2.92 \times 10^{-14}} = 1.71 \times 10^{-7}$  (1)  
 $pH = -\log_{10}(1.71 \times 10^{-7})$  (1)  
 $= 6.77$  (1) 4
- (iv) endothermic **and** attempt at reason (1)  
 more dissociation / ionization /  $H^+$  ions at higher temperature (1)  
 if (iii) not completed, allow endothermic with sensible reason for 1 mark if answer to (iii) is  $pH > 7$ , allow 1 mark for exothermic with attempt at reason 2

[14]

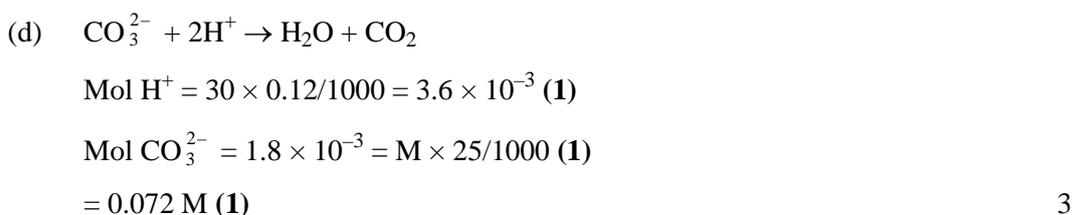
4. (a) *Definition of a base* Proton acceptor (1)  
*Essential feature* Transfer of protons (1)  
*Equation*  $H^+ + OH^- \rightleftharpoons H_2O$   
OR  $H^+ + B \rightleftharpoons BH^+$  (1) 3
- (b) only partially dissociated in solution (1) 1
- (c)  $K_a = \frac{[H^+(aq)][CH_3CH_2COO^-(aq)]}{[CH_3CH_2COOH(aq)]}$  (1)  
 mol dm<sup>-3</sup> (1) 2
- (d) (i) resists change in pH (1)  
 on addition of small amounts of strong acid or base (1)  
 (ii) correct weak acid/co-base  
 or correct weak base/co-acid (1)  
 (iii) any suitable use (1) 4

[10]

5. (a) (i)  $0.12 \times 11.8 = M \times 25$  (1)  
 $\therefore$  molarity = 0.057 (1)
- (ii)  $K_a = \frac{[H^+][A^-]}{[HA]}$  (1)
- (iii) *Volume of NaOH(aq) added*  $11.8/2 = 5.9 \text{ cm}^3$  (1)  
*pH* 4.3 to 4.35 (1)
- (iv) As  $[HA] = [A^-]$  (1)  $K_a = [H^+]$  (1)  
 $pH = -\log_{10} [H^+]$  (1) hence  $K_a = 10^{-4.3}$   
 $= 5.0 \times 10^{-5}$  (1)  
 Note:- Mark  $K_a$  consequentially to pH in a(iii) 9
- (b) (i) The added  $OH^-$  reacts with HA or  $H^+$  (1)  
 The equilibrium,  $HA \rightleftharpoons H^+ + A^-$ , displacement to right  
 or HA ionises (1)  
 (ii) The added  $H^+$  reacts with  $A^-$  (1)  
 The equilibrium,  $HA \rightleftharpoons H^+ + A^-$ , displaced to left (1) 4

[13]

6. (a)  $CO_3^{2-} + H^+ \rightarrow HCO_3^-$  or  $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$  (1)  
 $HCO_3^- + H^+ \rightarrow H_2O + CO_2$  or  $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$  (1) or  $H_2CO_3$  2
- (b)  $15 \text{ cm}^3$  1
- (c) *Indicator* Methyl orange (allow other correct indicators) (1)  
*Explanation* Methyl red changes colour over pH  
 range 3.2 – 4.4 (allow between 3 and 7) (1) 2



(e) *Volume of HCl(aq) added for first end-point* 15 (1)  
*Volume of HCl(aq) added for second end-point* 45 (1) 2

[10]

7. (a) A proton donor 1

(b) *Equation*  $\text{HCl}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$  (1)  
*Role of water* base or proton acceptor (1) 2

(c) *Equation*  $\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$  (1)  
*Role of water* acid or proton donor (1) 2

(d) *Equation for formation*  $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightleftharpoons \text{HSO}_4^- + \text{H}_2\text{NO}_3^+$  (1)  
*Role of nitric acid* base or proton acceptor (1)  
 $\text{H}_2\text{NO}_3^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}$  (1) 3

(e) (i) only partially dissociated in aqueous solution (1)  
 (ii)  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$  (1)  
 (iii) not very big (1)  
 (iv) strong (1)  
 Although HX is not fully dissociated, the relative concentration of undissociated HX is very small (1) 5

[13]

8. (a)  $\text{NaOH} + \text{HA} \rightarrow \text{NaA} + \text{H}_2\text{O}$  (1)  
 or  $\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$  1

(b) (i) Moles  $\text{A}^- = \text{moles NaOH added}$  (1)  
 $= 15 \times 0.34 \times 10^{-3} = 5.10 \times 10^{-3}$  (1)  
 Initial moles  $\text{HA} = 25 \times 0.45 \times 10^{-3} = 0.01125$  (1)  
*Allow 0.0110 – 0.0113*  
 Moles NaOH added = 0.00510  
 Moles HA remaining =  $6.15 \times 10^{-3}$  (1)  
*Allow (5.90 – 6.20)  $\times 10^{-3}$*   
*Mark conseq*

(ii)  $5.10 \times 10^{-3}$  moles  $A^-$  in  $(15 + 25) \text{ cm}^3$   
Hence  $[A^-] = 5.10 \times 10^{-3} \times 1000/40 = 0.1275$  (1)

Allow 0.127 – 0.128 and 0.13

$6.15 \times 10^{-3}$  moles HA in  $40 \text{ cm}^3$

Hence  $[HA] = 6.15 \times 10^{-3} \times 1000/40 = 0.1538$  (1)

Allow 0.147 – 0.155 and 0.15

Allow marks in (ii) conseq to answers in (i)

(iii)  $K_a = [H^+][A^-] / [HA] = 2.00 \times 10^{-4}$   
 $[H^+] = 2.00 \times 10^{-4} \times 0.1538 / 0.1275$  (1)  
 $= 2.41 \times 10^{-4}$  (1)

Allow  $(2.29 - 2.44) \times 10^{-4}$

pH = 3.62 (1)

Allow 3.61 – 3.64 and 3.6

Mark conseq to answers in (ii)

9

[10]

9. (a) only partially ionized / partially dissociated / not fully ionised (1)  
**not** 'not ionised at all'

1

(b) (i)  $K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$  (1)

accept  $[H^+]$

do not accept with  $[H_2O]$  included

must include charges

1

(ii)  $pK_a = -\log K_a$  (1)

allow  $-\log(K_a)$  do not allow  $-\log[K_a]$

1

(iii)  $pK_a = 10$  (ignore units) (1)

1

(iv) lower / smaller number (1)

1

(c) (i) at end point pH =  $pK_a = 9.3$  (1)

colour change detectable over range of 2 pH units  $\therefore$  range =  $8.3 \rightarrow 10.3$  (1)  
(allow 8 – 10)

2

(ii) (colourless to) pink / red (1)

$[In^-] \geq [HIn]$  /  $[In^-]$  increases (1)

**not** just equilibrium shifts to right

2

(iii) equivalence point / end point of titration below pH 7 more acidic / lower than phenolphthalein range / is about pH 4 (1)

**not** just the pH range is wrong

1

[10]

10. (a) (i)  $\text{pH} = -\log_{10} [\text{H}^+]$  Note; (aq) not required; Not  $-\ln [\text{H}^+]$  (1)

(ii)  $K_a = [\text{H}^+][\text{X}^-] / [\text{HX}]$  Note; (aq) not required (1)

Allow  $[\text{A}^-]$  and  $[\text{HA}]$

Do NOT allow  $[\text{H}^+]^2 / [\text{HX}]$

(iii)  $K_a = 4.25 \times 10^{-5} = [\text{H}^+]^2 / [\text{HX}]$  (1)

$$[\text{H}^+] = \sqrt{0.45 \times 4.25 \times 10^{-5}} \quad (1)$$

$$= 4.37 \times 10^{-3} \quad (1)$$

not a conseq mark

$$\text{pH} = \underline{2.36} \quad \text{Mark conseq to } [\text{H}^+] \text{ above} \quad (1)$$

$$\text{or } \text{pH} = \frac{1}{2} \text{p}K_a - \frac{1}{2} \log_{10} [\text{HX}] = \frac{1}{2} \times 4.37 + \frac{1}{2} \times 0.346 = \underline{2.36}$$

(1) (2) (1)

Note pH = 2.4 scores max 3

6

(b) (i)  $[\text{H}^+] = 0.25 \times 0.95 = 0.2375$  (1)

Allow 0.237 – 0.238 and 0.24

$$\text{pH} = 0.62 \quad (1)$$

Allow 0.62 – 0.63

Only allow pH mark if  $[\text{H}^+]$  is correct

(ii)  $[\text{H}^+] = [\text{Y}^-] = 0.2375$  (or a value from b(i)) (1)

$$[\text{HY}] = 0.05 \times 0.25 = 0.0125 \quad (1)$$

Allow 0.012 – 0.013

$$K_a = [\text{H}^+][\text{Y}^-] / [\text{HY}]$$

$$= (0.2375)^2 / 0.0125 \quad (1)$$

$$K_a = 4.51 \quad (1)$$

Allow 4.3 – 4.8

Ignore units

CE if  $[\text{HY}]$  is incorrect

6

[12]

11. (a)  $\text{p}K_a + -\log_{10} K_a$  1

(b)  $K_a = 1.90 \times 10^{-4}$  (1)

$$K_a = [\text{H}^+]^2 / 0.52 \text{ or } [\text{H}^+] = [\text{X}^-] \quad (1)$$

$$[\text{H}^+] = \sqrt{(1.90 \times 10^{-4} \times 0.52)} = 9.94 \times 10^{-3} \quad (1)$$

$$\text{pH} = -\log_{10} [\text{H}^+] = 2.00 \quad (1)$$

or  $\text{pH} = \frac{1}{2} \text{p}K_a - \frac{1}{2} \log [\text{HX}]$   
 $= 1.86 - (-0.142) = 2.00$

4

- (c)  $K_a [H^+] [X^-]/[HX]$  (1)  
 $[HX] = [X^-]$  at half neutralisation (1)  
Hence  $K_a = [H^+]$  and  $pK_a = pH$  (1) 3
- (d) There is no rapid/sharp/steep change in pH during a weak acid - weak base titration (1)  
Indicator need a sharp pH rise to change colour quickly (1) 2

[10]

12. (a) (i)  $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$  (1)
- (ii) (1)  $K_a = \frac{[H^+]^2}{[CH_3COOH]}$  (1)  
(2)  $[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.220} = 1.96 \times 10^{-3}$  (1)  
(3)  $pH = -\log_{10}[H^+]$  (1)  
**can score independently**  
(4)  $pH = 2.71$  (1)  
**2 d.p. essential**  
**If forget  $\sqrt{\quad}$  can score (1) and (3) for  $pH = 5.42$**

5

- (b) (i) moles acid =  $\frac{25}{1000} \times 0.220$  (1) =  $5.50 \times 10^{-3}$   
 $= \frac{x}{10^3} \times 0.150$   
 $\therefore x = 25 \times \frac{0.220}{0.150}$  **or**  $5.50 \times 10^{-3} \times \frac{1000}{0.150}$   
 $= 36.7$  (or 37)  $cm^3$  (or 36.6) (1)  
**NOT 36 NOR 37.0**  
**units must match**

- (ii) *Indicator:* thymol blue (1)  
*Explanation:* weak acid – strong base (1)  
equivalent at  $pH > 7$  (1)  
or high pH 5

(c) (1) mol NaOH added =  $\frac{2.0}{40.0} = 0.050$  (1)

**If wrong  $M_r$ : CE  $\therefore$  lose marks (1) and (2) then mark on consequentially  $\rightarrow$  max 4**

(2) mol  $\text{CH}_3\text{COOH}$  left =  $0.220 - 0.050 = 0.170$  (1)

(3) mol  $\text{CH}_3\text{COO}^-$  formed =  $0.050$  (1)

(4)  $[\text{H}^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$  OR  $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$  etc (1)

**If expression wrong no marks for 4 / 5 / 6  
can score (1) to (4) in (5)**

(5)  $[\text{H}^+] = 1.74 \times 10^{-5} \times \frac{(0.170)}{(0.05)}$  OR  $\text{pH} = 4.76 + \log\left(\frac{0.05}{0.17}\right)$  (1)

(6)  $\text{pH} = 4.23$  (1)

**Correct answer gets ✓✓✓✓✓✓**

**Mark (5) is for use of correct values of (acid moles) and (salt moles)**

**if one wrong allow pH conseq**

**if both wrong, no further marks**

**e.g. if candidate forgets substitution in (2)**

**he loses (2) and (5) but can score (1) (3) (4) (6) = max 4**

**for  $\text{pH} = 4.12$  if  $\frac{[\text{acid}]}{[\text{salt}]}$  upside down; answer 5.29 scores 3**

**for (1) (2) (3)**

6

[16]

13. (a) moles HA =  $\frac{25}{10^3} \times 0.150 = 3.75 \times 10^{-3}$  (1)

$\therefore$  vol NaOH =  $\frac{3.75 \times 10^{-3}}{0.20} = 1.875 \times 10^{-2} \text{ dm}^3$  (1)

**or 18.75 cm<sup>3</sup>**

2

(b) (i)  $\text{pH} = -\log_{10} [\text{H}^+]$  (1)

(ii) Value above 7 but below 11 (1)

(iii) phenol red / thymol blue / phenolphthalein / thymolphthalein  
**i.e. indicator with  $7 < \text{p}K_{\text{in}} < 11$**

3

- (c) (i) Only slightly dissociated (1)  
**NOT “not fully dissociated / ionised”**
- (ii)  $K_a = \frac{[H^+][A^-]}{[HA]}$  (1)  
**NOT**  $\frac{[H^+]^2}{[HA]}$
- (iii) For weak acid alone:  
 $K_a = \frac{[H^+]^2}{[HA]}$  (1)  
 $\therefore [H^+] = \sqrt{(2.75 \times 10^{-5}) \times 0.15}$   
 $= 2.03 \times 10^{-3}$  (1)  
 $\therefore \text{pH} = 2.69$  (1)  
**pH should be given to 2 decimal places**  
**penalise answer to 1 d.p. once in question**

5

- (d) moles  $\text{OH}^-$  added =  $1.875 \times 10^{-3}$  = moles  $\text{A}^-$  = moles HA left (1)  
**or**  $[\text{A}^-] = [\text{HA}]$   
 $\therefore K_a = [\text{H}^+]$  **or**  $\text{pH} = \text{p}K_a$  (1)  
 $\therefore \text{pH} = 4.56$  (1)

3

[13]

**14.** Penalise pH given to 1 dp first time it would have scored only

- (a) (i)  $K_w = [\text{H}^+][\text{OH}^-]$  (1)  
(ii)  $\text{pH} = -\log [\text{H}^+]$  (1)  
*or in words or below unless contradiction*
- (iii) *Calculation:*  $[\text{H}^+] = \sqrt{5.48 \times 10^{-14}}$  (1)  
 $= 2.34 \times 10^{-7}$   
 $\therefore \text{pH} = 6.63$  or  $6.64$  (1)

*Explanation:* pure water  $\therefore [\text{H}^+] = [\text{OH}^-]$  (1)

5

- (b) (i)  $[\text{OH}^-] = 0.150$   $\therefore [\text{H}^+] = 10^{-14}/0.15 = 6.66 \times 10^{-14}$   
or  $\text{pOH} = 0.82$   
 $\therefore \text{pH} = 13.18$  (1)  
or  $\text{pH} = 13.17$
- (ii) moles  $\text{OH}^- = (35 \times 10^{-3}) \times 0.150 = 5.25 \times 10^{-3}$  (1)<sup>a</sup>  
moles  $\text{H}^+ = (40 \times 10^{-3}) \times 0.120 = 4.8(0) \times 10^{-3}$  (1)<sup>b</sup>  
 $\therefore$  excess moles of  $\text{OH}^- = 4.5 \times 10^{-4}$  (1)<sup>c</sup>  
 $\therefore [\text{OH}^-] = (4.5(0) \times 10^{-4}) \times 1000/75$  (1)<sup>d</sup>  
 $[\text{H}^+] = \frac{10^{-14}}{6.00 \times 10^{-3}} = 1.66 \times 10^{-12}$  or  $\text{pOH} = 2.22$   
 $\therefore \text{pH} = 11.78$  (1)<sup>f</sup>  
or 11.77

8

(c) (i)  $K_a = \frac{[H^+][X^-]}{[HX]} \text{ (1)}$

(ii)  $[H^+] = 1.80 \times 10^{-2} \times 0.150 = 2.70 \times 10^{-3} \text{ (1)}$

$$K_a = \frac{[H^+]^2}{[HX]} \text{ (1)} = \frac{(2.70 \times 10^{-3})^2}{0.150} = 4.86 \times 10^{-5} \text{ (1) mol dm}^{-3} \text{ (1)}$$

$$\text{or } \frac{(2.70 \times 10^{-3})^2}{0.1473} = 4.95 \times 10^{-5}$$

### Notes

- (a) If  $K_w$  includes  $H_2O$  allow 6.63 if seen otherwise no marks likely
- (b) (ii) If no vol, max 4 for a, b, c, f answer = 10.65  
 If wrong volume max 5 for a, b, c, e, f  
 If no subtraction max 3 for a, b, d  
 If missing 1000 max 5 for a, b, c, d, f answer = 8.78  
 If uses excess as acid, max 4 for a, b, d, f answer = 2.22  
 If uses excess as acid and no volume, max 2 for a, b answer = 3.35
- (c) If wrong  $K_a$  in (i) max 2 in part (ii) for  $[H^+]$  (1) and conseq units (1)  
*but mark on fully from minor errors*  
*eg no [ ] or charges missing*

[18]

15. (a) Hydrogen bonding (1)  
 between  $H_2O$  and  $NH_3$  (1) 2
- (b) (i)  $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \text{ (1)}$
- (ii) Ammonia is weak base (1)  
*NOT partially ionised*  
 Equilibrium to left or incomplete reaction (1) 3
- (c) A proton donor (1) 1
- (d) *Buffer solution*: A solution which resists change in pH (1)  
 when small amounts of acid or base added or on dilution (1)  
*Reagent*:  $NH_4Cl$  (1) 3  
*Allow a correct strong acid*
- (e) (i)  $K_a = [H^+][A^-] / [HA] \text{ (1)}$   
 $= [H^+][0.125 \times 4] \text{ (1)} / 1.00$   
 $[H^+] = 1.70 \times 10^{-5} / 0.125 \times 4 = 3.40 \times 10^{-5} \text{ (1)}$   
 $pH = -\log_{10} [H^+] = 4.47 \text{ (1)}$   
*Allow pH conseq to  $[H^+]$  if 2 place decimals given*
- (ii)  $H^+ + CH_3COO^- \rightarrow CH_3COOH \text{ (1)}$  5

[14]

16. (a)  $K_a = \frac{[H^+][A^-]}{[HA]}$  1

*(All three sets of square brackets needed, penalise missing brackets or missing charge once in the question)*

*(Don't penalise extra  $[H^+]^2/[HA]$ )*

(b)  $K_a = \frac{[H^+]^2}{[HA]}$  or  $[H^+] = [A^-]$  1

$$[H^+] = \sqrt{(1.45 \times 10^{-4}) \times 0.25}$$

$$= 6.02 \times 10^{-3}$$
 1

$$\text{pH} = 2.22$$
 1

*(must be to 2dp)*

*(allow 4th mark consequential on their  $[H^+]$ )*

1

(c) (i) pH (almost) unchanged 1

*(Must be correct to score explanation)*

$H^+$  removed by  $A^-$  forming HA

or acid reacts with salt

or more HA formed 1

(ii)  $[H^+] = 10^{-3.59} = 2.57 \times 10^{-4}$  or  $2.6 \times 10^{-4}$  1

$$[A^-] = \frac{K_a[HA]}{[H^+]}$$
 1

$$= \frac{(1.45 \times 10^{-4}) \times 0.25}{2.57 \times 10^{-4}}$$
 1

$$= 0.141 \text{ (mol dm}^{-3}\text{)}$$
 1

*(Allow 0.139 to 0.141 and allow 0.14)*

*(If not used 3.59, to find  $[H^+]$  can only score M2 for working)*

*(If 3.59 used but  $[H^+]$  is wrong, can score M2 for correct method and conseq M4)*

*If wrong method and wrong expression, can only score M1)*

(ii) *Alternative scheme for first three marks of part (c)(ii)*

$$\text{pH} = \text{p}K_a - \log \frac{[HA]}{[A^-]}$$
 1

$$\text{p}K_a = 3.84$$
 1

$$3.59 = 3.84 - \log \frac{0.250}{[A^-]}$$
 1

[11]

17. (a) (i)  $\text{pH} = -\log [\text{H}^+] \text{ (1)}$

(ii) Expression for  $K_a$ :  $K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]} \text{ (1)}$

Calculation:  $\text{pH} = 2.56 \therefore [\text{H}^+] = 2.75 \times 10^{-3} \text{ (1)}$

$$K_a = \frac{[\text{H}^+]^2}{[\text{HX}]} = \frac{(2.75 \times 10^{-3})^2}{0.12} = 6.32 \times 10^{-5} \text{ (1) (mol dm}^{-3}\text{)}$$

or  $[\text{H}^+] = [\text{X}^-] \text{ (1)}$

5

depending on approximate made, values of  $K_a = 10^{-5} \times$

using  $[\text{HX}] = 0.12$  6.30 – 6.32

using  $[\text{HX}] = 0.12 - 2.75\dots$  6.45 – 6.47

using 2.8 and  $[\text{HX}] = 0.12$  6.53

using 2.8 and  $[\text{HX}] = 0.12 - 2.8$  6.69

upside down  $K_a$

(b) (i) Expression for  $K_w$ :  $K_w = [\text{H}^+][\text{OH}^-] \text{ (1)}$

Value of  $K_w$ :  $(1.0 \times 10^{-14}) \text{ (mol}^2 \text{ dm}^{-6}\text{) (1)}$

ignore units

(ii)  $[\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.045} = 2.22 \times 10^{-13}$

or  $\text{pOH} = 1.35 \text{ (1)}$

$\therefore \text{pH} = 12.65 \text{ (1)}$

4

must be 2dp in final answer



(ii)  $\text{mol OH}^- = (41.6 \times 10^{-3}) \times 0.0450 \text{ (1)} = 1.87 \times 10^{-3}$

$\therefore \text{mol H}_2\text{C}_2\text{O}_4 = 9.36 \times 10^{-4} \text{ (1)}$

$[\text{H}_2\text{C}_2\text{O}_4] = 9.36 \times 10^{-4} \times 10^3/25$

$= 0.0374 \text{ (1)}$

4

if moles of  $\text{H}_2\text{C}_2\text{O}_4$  not equal to half moles of  $\text{OH}^-$ , no further marks gained

if  $\text{mol OH}^- = 1.9 \times 10^{-3}$ ; hence  $\text{mol H}_2\text{C}_2\text{O}_4 = 9.5 \times 10^{-4}$ ;

$[\text{H}_2\text{C}_2\text{O}_4] = 0.038$

[13]

18. (a) (i) B;

1

C;

1

A;

1

(ii) cresolphthalein

OR

thymolphthalein;

1

- (b) (i)  $-\log[\text{H}^+]$ ; 1
- (ii)  $[\text{H}^+] = 1.259 \times 10^{-12}$  (or 1.26 or 1.3) OR  $\text{pOH} = 14 - \text{pH}$ ; 1
- $[\text{OH}^-] = \frac{10^{-14}}{1.258 \times 10^{-12}}$  OR  $= 2.10$ ; 1
- $= 7.9(4) \times 10^{-3}$ ; 1
- (if  $[\text{H}^+]$  is wrong allow 1 for  $[\text{OH}] = K_w/[\text{H}^+]$  or as numbers)
- (c) (i)  $K_a = [\text{H}^+]^2/[\text{CH}_3\text{CH}_2\text{COOH}]$
- OR
- $[\text{H}^+]^2/[\text{HA}]$
- OR
- $[\text{H}^+] = [\text{A}^-]$  etc; 1
- $[\text{H}^+] = \sqrt{1.35 \times 10^{-5} \times 0.117}$  or expression without numbers; 1
- $= 1.257 \times 10^{-3}$
- $\text{pH} = 2.90$ ; 1
- (iii)  $K_a = [\text{H}^+]$
- OR
- $\text{p}K_a = \text{pH}$ ; 1
- $\text{pH} = 4.87$ ; 1
- (penalise 1dp once)

[13]

19. (a)  $-\log [\text{H}^+]$  1
- $4.57 \times 10^{-3}$  1
- allow  $4.6 \times 10^{-3}$
- ecf if [ ] wrong and already penalised
- ignore units

- (b) (i)  $K_a = \frac{[H^+][X^-]}{[HX]}$  allow HA etc  
 not  $\frac{[H^+]^2}{[HX]}$  but mark on
- If expression wrong allow conseq units in (ii) but no other marks in (ii) 1
- (ii)  $\frac{[H^+]^2}{[HX]} = \frac{(4 \cdot 57 \times 10^{-3})^2}{[0 \cdot 150]}$  1  
 If use  $4.6 \times 10^{-3}$   
 $K_a = 1.4(1) \times 10^{-4}$  and  $pK_a = 3.85$  1  
 $= 1.39 \times 10^{-4}$   
 allow  $1.39 - 1.41 \times 10^{-4}$   
 mol dm<sup>-3</sup>
- (iii)  $pK_a = 3.86$  1  
 Penalise dp of final answer < or > 2 in pH once in paper
- (c) (i)  $\frac{30}{1000} \times 0.480 = 0.0144$  or  $1.4(4) \times 10^{-2}$  1  
 Mark is for answer (M1)
- (ii)  $\frac{18}{1000} \times 0.350 = 0.0063$  or  $6.3 \times 10^{-3}$  1  
 Mark is for answer (M2)
- (iii)  $0.0144 - 2(0.0063) = 1.80 \times 10^{-3}$  1  
 M3 is for (i) - 2(ii)  
 If x 2 missed, CE i.e. lose M3 and the next mark gained
- (iv)  $1.80 \times 10^{-3} \times \frac{1000}{48} = 0.0375$  (0.038) 1  
 M4 is for answer
- If vol is not  $48 \times 10^{-3}$  (unless AE) lose M4 and next mark gained  
 If multiply by 48 - this is AE - i.e. lose only M4  
 If multiply by  $48 \times 10^{-3}$  this is AE - i.e. lose only M4
- (v)  $10^{-14} / 0.0375$  ( $10^{-14} / 0.038$ ) 1  
 M5 for  $K_w/[OH^-]$
- (=  $2.66 \times 10^{-13}$ ) (=  $2.63 \times 10^{-13}$ ) 1  
 or pOH
- or pOH = 1.426 (or pOH = 1.420)  
 If no attempt to use  $K_w$  or pOH lose both M5 and M6
- pH = 12.57 (12.58) M6 1  
 Allow M6 conseq on AE in M5 if method OK

[13]

20. (a) (i)  $[H^+][OH^-]$  1  
 $-\log [H^+]$  1  
(ii)  $[H^+] = [OH^-]$  1  
(iii)  $(2.0 \times 10^{-3}) \times 0.5 = 1.0 \times 10^{-3}$  1  
(iv)  $[H^+] = \frac{4.02 \times 10^{-14}}{1.0 \times 10^{-3}}$  ( $= 4.02 \times 10^{-11}$ ) 1  
pH = 10.40 1
- (b) (i)  $K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$  1  
 $= \frac{[H^+]}{[CH_3CH_2COOH]}$  1  
 $[H^+] = \sqrt{(1.35 \times 10^{-5}) \times 0.125}$  ( $= 1.30 \times 10^{-3}$ ) 1  
pH = 2.89 1
- (c) (i)  $(50.0 \times 10^{-3}) \times 0.125 = 6.25 \times 10^{-3}$  1  
(ii)  $(6.25 \times 10^{-3}) - (1.0 \times 10^{-3}) = 5.25 \times 10^{-3}$  1  
(iii) mol salt formed =  $1.0 \times 10^{-3}$  1  
 $(H^+) = K_a \times \frac{[CH_3CH_2COOH]}{[CH_3CH_2COO^-]}$  1  
 $= (1.35 \times 10^{-5}) \times \frac{(5.25 \times 10^{-3}) / V}{(1.0 \times 10^{-3}) / V}$  ( $= 7.088 \times 10^{-5}$ ) 1  
pH = 4.15 1

[16]

21. (a) Concentration of acid:  $m_1v_1 = m_2v_2$  hence  $25 \times m_1 = 18.2 \times 0.150$   
OR  
moles NaOH =  $2.73 \times 10^{-3}$ ; 1  
 $m_1 = 18.2 \times 0.150 / 25 = 0.109$ ; 1
- (b) (i)  $K_a = [H^+][A^-] / [HA]$  not  $K_a = [H^+]^2 / [HA]$ ; 1  
(ii)  $pK_a = -\log K_a$ ; 1  
(iii)  $[A^-] = [HA]$ ; 1  
hence  $K_a = [H^+][A^-] / [HA] = [H^+]$   
and  $-\log K_a = -\log [H^+]$ ; 1
- (c) ratio  $[A^-] : [HA]$  remains constant; 1  
hence as  $[H^+] = K_a [HA] / [A^-]$ ;  $[H^+]$  remains constant; 1

- (d) (i) pH of  $0.250 \text{ mol dm}^{-3} \text{ HCl}$  = 0.60  
 and pH of  $0.150 \text{ mol dm}^{-3} \text{ HCl}$  = 0.82; 1  
 pH change = 0.22; 1

- (ii) moles  $\text{HCl} = 30 \times 0.250 \times 10^{-3} = v \times 0.150 \times 10^{-3} = 7.50 \times 10^{-3}$   
 OR  
 $v = 30 \times 0.250 \times 10^{-3} / 0.150 \times 10^{-3} = 50$ ; 1  
 water added =  $50 - 30 = 20 \text{ cm}^3$ ; 1

[12]

22. (a) proton or  $\text{H}^+$  donor (1) 1

- (b) (i) partially ionised or dissociated (1)  
*not fully*  
 (ii)  $\text{NH}_3$  (1)  
*not  $\text{NH}_4\text{OH}$  – but allow in equation*  
*not  $\text{H}_2\text{O}$  – but allow in equation if both weak acid and base stated*  
 $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$  (1) 3

- (c) (i)  $\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCOO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$  (1)  
*allow  $\text{H}_2\text{O}(\text{aq})$*   
 (ii)  $\text{H}_2\text{O}$  or water (1)  
 $\text{HCOO}^-$  or methanoate ion (1)  
 (iii)  $K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$  (1)  
*allow  $[\text{OH}_3^+]$*  4

- (d) (i) addition of small amounts of acid (1)  
 addition of small amounts of base (1)  
*allow volumes, allow alkali, penalise missing small once only not weak  
 dilution (1)*  
 (ii) sodium methanoate or sodium hydroxide (1)  
*allow salt of methanoic (or this) acid not just an ion (methanoate)*  
 (iii)  $\text{OH}^-$  added (1)  
*or base*  
 $\text{H}^+$  reacts with  $\text{OH}^-$  (1)  
*or forming water*  
 More  $\text{HCOOH}$  dissociates to restore equilibrium (1)  
*allow equilibrium moves to right*  
*must only describe addition of base;*  
*if both base and acid addition given, MAX 1 ex 3* 7

[15]

23. (a)  $\text{HCl(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$  (1)  
allow  $\text{H}_2\text{O(aq)}$  1
- (b)  $\text{pH} = -\log[\text{H}^+]$  (1)  
 $= -0.10 (\pm 0.01)$  (1) 2
- (c)  $\text{pH} = 7$  (1)  
 neutral solution or  $[\text{H}^+] = [\text{OH}^-]$  (1) 2
- (d) (i) moles  $\text{H}^+ = 1.26 \times \frac{95}{1000} = 0.1197$  moles (1)  
range  $0.120 \pm 0.001$
- (ii) moles  $\text{OH}^- = 2 \times 1.37 \times \frac{45}{1000} = 0.1233$  moles (1)  
range  $0.123 \pm 0.001$
- (iii) XS  $\text{OH}^- = 0.1233 - 0.1197 = 3.6 \times 10^{-3}$  moles (1)  
range  $0.001$  to  $0.005$   
 Volume =  $95 + 45 = 140 \text{ cm}^3$  (1)  
 $\therefore [\text{OH}^-] = 3.6 \times 10^{-3} \times \frac{1000}{140} = 0.0257 \text{ M}$  (1)  
range  $0.0071$  to  $0.0357$   
 $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  (1)  
 $\therefore [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{0.0257} = 3.89 \times 10^{-13} \text{ M}$  (1)  
range  $(0.28$  to  $1.35) \times 10^{-12}$   
 $\therefore \text{pH} = 12.41$  (1)  
must show 2 dp      range  $11.87$  to  $12.55$  8

[13]

*If no  $\times 2$  for  $\text{Ba(OH)}_2$  then  $\text{H}^+$  is in XS      MAX 4 ex 6*  
*If no volume used then      MAX 4 ex 6*  
*If no  $\times 1000$  for molarity then      MAX 4 ex 6*  
*Combinations of TWO of these      MAX 2 ex 6*  
*All THREE      ZERO*

24. (a) only partially dissociated in water 1
- (b) (i) Added  $H^+$  reacts with  $A^-$  (1)  
Equilibrium moves left  
& HA forms, restoring  $[H^+]$  and pH (1)
- (ii) Added  $OH^-$  reacts with  $H^+$  forming  $H_2O$  (1)  
Equilibrium moves right  
& HA dissociates, restoring  $[H^+]$  and pH (1) 4
- (c) (i)  $K_a = \frac{[H^+][A^-]}{[HA]}$  1
- (ii) Equation for  $[H^+]$   $[H^+] = K_a \times \frac{[HA]}{[A^-]}$  (1)  
 $[HA]$  and  $[A^-]$  (1)  
are altered to same extent  
maintaining  $[H^+]$  and pH (1) 3
25. (a) (i)  $pK_a = -\log_{10}K_a$  (1)
- (ii)  $6.31 \times 10^{-5}$  (1)  
 $\text{mol dm}^{-3}$  (1)
- (iii)  $[H^+] = [A^-]$  or  $K_a = \frac{[H^+]^2}{[HA]}$  (1)  
Hence  $6.31 \times 10^{-5} = \frac{[H^+]^2}{0.830}$   
 $[H^+] = \sqrt{6.31 \times 10^{-5} \times 0.830} = 7.24 \times 10^{-3}$  (1)  
 $pH = -\log_{10}[H^+]$  (1)  
 $pH = 2.14$  (1)  
Marked consequentially to a(ii) 7
- (b) (i) Mol NaOH = mol  $X^-$  (1)  
 $\text{mv}/1000 = 0.800 \times 10.5/1000 = 8.4 \times 10^{-3}$  (1)
- (ii) Mol HX remaining = original mol HX – mol NaOH added (1)  
 $(25 \times 0.92/1000) - 8.4 \times 10^{-3} = 0.0146$  (1)
- (iii) Concentration of  $X^-$   $8.4 \times 10^{-3} \times 1000/(25 + 10.5)$   
 $= 0.237$  (1)
- Concentration of HX  $0.0146 \times 1000/35.5$   
 $= 0.411$  (1)
- pH of solution  $K_a = \frac{[H^+][X^-]}{[HX]}$  (1)  
 $[H^+] = 5.25 \times 10^{-5} \times 0.411/0.237$  (1)  
 $pH = 4.04$  (1)  
Marked consequentially to b(iii) 9
- (c) Change in pH Very small fall or slight change (1)
- Explanation  $H^+ + X^- \rightarrow HX$  (1)  
Equilibrium restored  $HX \rightleftharpoons H^+ + X^-$  OR 3

[9]

[19]

26. (a) *Monoprotic acid* An acid which gives only one proton (1)  
*Example* HCl etc (1) 2
- (b) (i)  $-\log_{10}[\text{H}^+]$  or in words (1)  
(ii) 1.58 M (allow 1.6) (1) 2
- (c) Mol  $\text{H}^+ = 25 \times 0.15 \times 10^{-3}$  (1)  $= 3.75 \times 10^{-3}$   
Mol  $\text{OH}^- = 35 \times 0.12 \times 10^{-3}$  (1)  $= 4.20 \times 10^{-3}$   
Excess  $\text{OH}^- = 4.5 \times 10^{-4}$  (1)  
 $[\text{OH}^-] = 4.5 \times 10^{-4} \times 1000/60$  (1)  $= 7.5 \times 10^{-3}$   
 $[\text{H}^+] = 10^{-14}/7.5 \times 10^{-3}$  (1)  $= 1.33 \times 10^{-12}$  (1)  
 $\text{pH} = -\log_{10} 1.33 \times 10^{-12}$   
 $= 11.9$  (1)
- NB Consequential marking if  $[\text{OH}^-]$  not calculated to maximum of 5 7

[11]

27. (a) *Equation for HCl(g)*  $\text{HCl(g)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$  (1)  
*Equation for KOH(s)*  $\text{KOH(s)} \rightarrow \text{K}^+(\text{aq}) + \text{OH}^-(\text{aq})$  (1) 2
- (b)  $K_w = [\text{H}^+][\text{OH}^-]$  1
- (c) strong base, fully dissociated (1) or  $[\text{OH}^-] = 0.016 \text{ M}$  (1)
- $$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} \text{ (1)} = \frac{10^{-14}}{0.016} = 6.25 \times 10^{-13} \text{ M (1) (2)}$$
- $\text{pH} = -\log_{10}[\text{H}^+]$  (1)  
 $\therefore \text{pH} = 12.2$  (1)
- neutral solution,  $\therefore [\text{H}^+] = [\text{OH}^-]$  (1)  
 $\therefore \text{pH} = 7$  (1) 7
- (d) (i) 755  $\text{cm}^3$  of 0.012 M acid contain  

$$\frac{0.012 \times 755}{1000} \text{ mol H}^+ = 9.06 \times 10^{-3} \text{ moles (1)}$$
 $\therefore \text{moles OH}^- \text{ used for neutralisation} = 9.06 \times 10^{-3}$  (1)
- (ii)  $\text{pH} = 11.6 \therefore [\text{H}^+] = 10^{-11.6} = 2.5 \times 10^{-12} \text{ M (1)}$   

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \text{ (1)} \therefore [\text{OH}^-] = 3.98 \times 10^{-3} \text{ M (1) (2)}$$

in 755  $\text{cm}^3$  there are  $\frac{3.98 \times 10^{-3} \times 755}{1000}$   
 $= 3.0 \times 10^{-3} \text{ mol (1)}$

(iii) Total moles  $= (9.06 + 3.0) \times 10^{-3} = 0.012 \text{ mol (1)}$   
(iv)  $M_r = 39 + 16 + 1 = 56$   
 $\therefore m = 56 \times 0.012 = 0.68 \text{ g (1)}$  8

[18]

28. (a)  $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$  (1)  
 $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$  (1) 2  
 for HF, must have reversible arrow  
 allow (aq) in HCl equation
- (b) (i)  $\text{pH} = -\log_{10}[\text{H}^+]$  **or** equivalent word definition (1) 1  
 allow  $-\log[\text{H}_3\text{O}^+]$  **or**  $-\log[\text{H}^+(\text{aq})]$
- (ii)  $[\text{H}^+] = 0.050 \text{ mol dm}^{-3}$   
 $\text{pH} = 1.3(0)$  (1) 1  
 if correct definition demonstrated in (ii), but word definition in (i)  
 wrong, allow mark transfer from (ii) to (i)
- (c) (i)  $K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$  (1) 1  
 do **not** expression allow with  $[\text{H}_2\text{O}]$ ; allow  $[\text{H}_3\text{O}^+]$   
 allow consequential mark from wrong equation in (b) providing  
 $[\text{H}^+]$  present
- (ii)  $K_a = \frac{[\text{H}^+]^2}{[\text{HF}]}$  **or**  $[\text{H}^+] = \sqrt{K_a[\text{HF}]}$  (1)  
 $[\text{H}^+] = \sqrt{5.6 \times 10^{-4} \times 0.050}$   
 $= 0.0053$  (1)  
 $\text{pH} = 2.3 / 2.28$  (1) 3  
 allow mark for correct pH from wrong  $[\text{H}^+]$
- (d) hydrogen fluoride **or** HF (1)  
 donates a proton (to the nitric acid) (1)  
 conjugate base  $\text{F}^-$  (this mark dependent on correct identification of acid) (1) 3
- [11]
29. (a) (i) proton donor (1) 1  
 (ii) partially dissociated (into ions) (**not** weakly dissociated) (1) 1
- (b) (i)  $K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$  (1) 1  
 allow either  $[\text{H}_3\text{O}^+]$  or  $[\text{H}^+]$  in expression  
 must include charges  
 if  $[\text{H}_2\text{O}]$  included then no mark
- (ii)  $\text{p}K_a = -\log(1.7 \times 10^{-5}) = 4.77 / 4.8/4.80$  (1) 1

- (c) (i) indicator: phenolphthalein (1)  
 explanation: weak acid-strong base / pH change above 7.0 (1)  
 link between pH change and indicator range (1) 3
- (ii) colourless to red / pink / purple (1) 1  
 if methyl orange named as indicator - wrong but allow second explanation  
 mark and colour change mark in (ii) (ie pink / red → yellow / orange)
- (iii)  $\text{NaOH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$  (1)  
 if charges shown they must be correct  
 accept  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$  1
- (d) excess acid + NaOH / acid + NaOH = NaEt (1)  
 in 2:1 ratio of volumes / 2:1 mol / 1:1 acid: salt (1) 2
- (e) (i) O–H / C=O bonds are polar (words or on diagram)  
 due to different electronegativities of O and H (or O and C) (1)  
 lone pairs of electrons on O atoms (1)  
 attraction of  $\delta^+$  H atom in O–H for  $\delta^-$  O atom / lone pair in C=O  
 between different molecules (1) Max 3

[14]

30. (a) *Weak acid* An acid which only partially ionises (1)  
*Example* Ethanoic, carbonic etc (1) 2
- (b) *Expression*  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$  (1)  
*Units*  $\text{mol dm}^{-3}$  (or  $\text{mol l}^{-1}$ ) (1) 2
- (c) (i) The dissociation of water is an endothermic process (1)  
 Less dissociation on cooling (or equilibrium moves to water or  
 $K_w$  decreases) (1) less  $\text{H}^+$  (or  $[\text{H}^+]$  lower) (1)
- (ii) Because  $[\text{H}^+] = [\text{OH}^-]$  (1) 4
- (d) Resists change in pH (1) on addition of small quantities of acid or base (1) 2

[10]

31. (a) (i) Strong = fully dissociated ( )  
Weak = partially dissociated ( ) in aqueous solution both needed (1) 1

(ii)  $K_a \approx \frac{[H^+]^2}{[HX]} = \frac{(10^{-2.74})^2}{0.16} = 2.07 \times 10^{-5}$  (1) mol dm<sup>-3</sup> (not M) (1) 2

Explanation: HX barely dissociates OR [H<sup>+</sup>] very small (1)  
so [HX]<sub>eqm</sub> = [HX] original (1)  
and [H<sup>+</sup>] = [X<sup>-</sup>] in an aqueous solution of weak acid (1) 3

- (b) (i) moles H<sup>+</sup> in 18 cm<sup>3</sup> = 18 × 0.16 × 10<sup>-3</sup> = 2.88 × 10<sup>-3</sup> (1)  
moles OH<sup>-</sup> in V<sub>eqv</sub> cm<sup>3</sup> = 2x (1) (V<sub>eqv</sub> × 0.12 × 10<sup>-3</sup>)  
∴ V<sub>eqv</sub> =  $\frac{18 \times 0.16}{0.12 \times 2} = 12.0$  cm<sup>3</sup> (1)

|   | Start | Half equivalence | Equivalence | Double equivalence |
|---|-------|------------------|-------------|--------------------|
| Volume/cm <sup>3</sup> Ba(OH) <sub>2</sub> solution added | 0.0   | <b>6.0</b>       | <b>12.0</b> | <b>24.0</b>        |
| pH for titration of <b>S</b>                              | 0.80  | <b>1.22</b>      | 7           | <b>12.84</b>       |
| pH for titration of <b>W</b>                              | 2.74  | <b>4.68</b>      | 8.5         | <b>12.84</b>       |

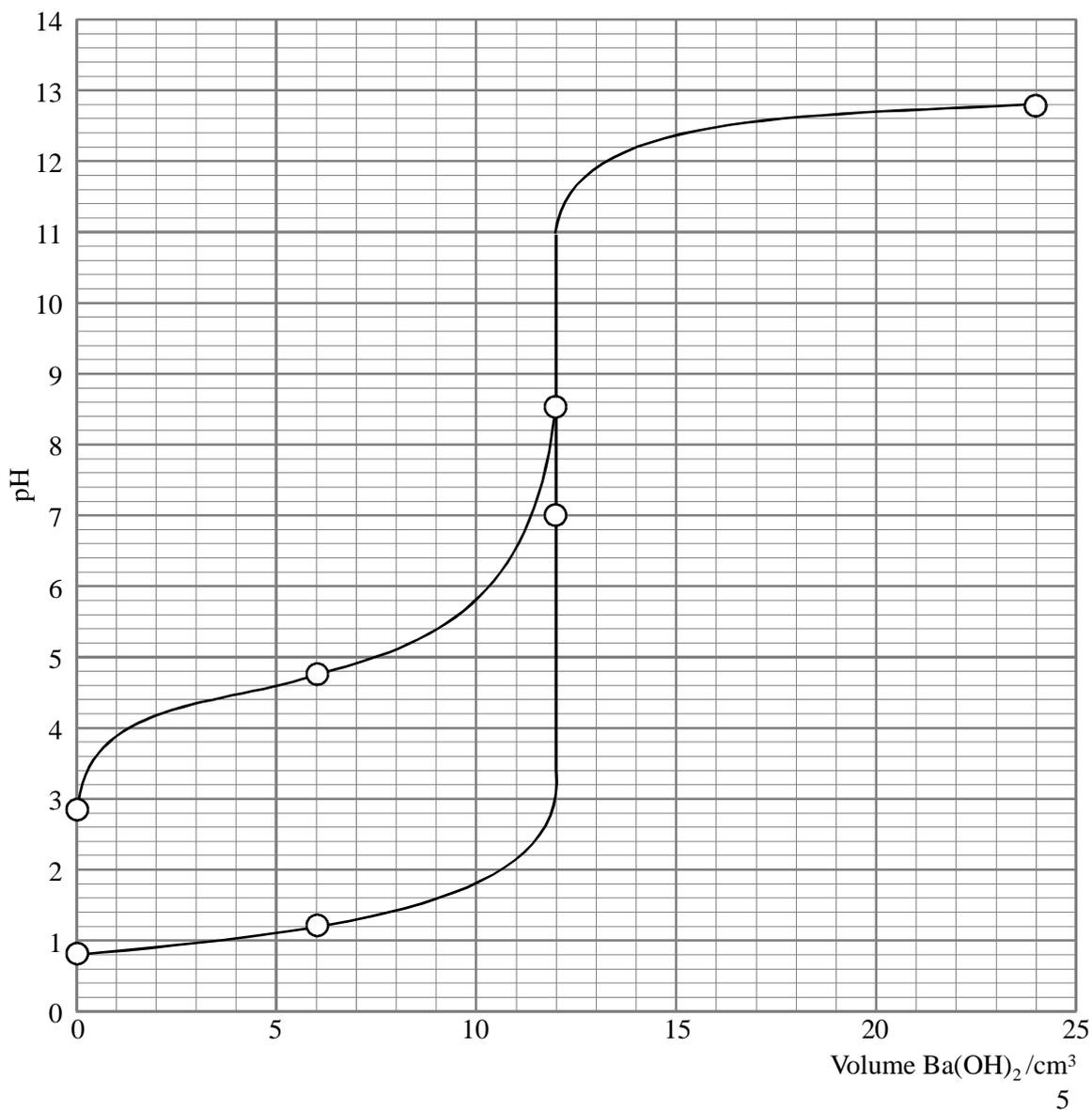
3

| (ii)  | Strong acid S  | Weak acid W  |
|---|--|--|
| <i>Half-equivalence</i><br>Volume of base = 6 cm <sup>3</sup> | 9 cm <sup>3</sup> of strong acid <b>S</b> (1)<br>in (18 + 6) cm <sup>3</sup> = 24 cm <sup>3</sup> (1)<br>[H <sup>+</sup> ] = 9 × 0.16/24 = 0.06 M (1)<br>∴ pH = 1.22 (1)   | [HX] = [X <sup>-</sup> ] (given)<br>∴ pH = pK <sub>a</sub> <u>or</u> [H <sup>+</sup> ] = K <sub>a</sub> (1)<br>= -log (2.07 × 10 <sup>-5</sup> )<br>= 4.68 (1) |
| <i>2 × equivalence</i><br>Volume of base = 24 cm <sup>3</sup> | 12 cm <sup>3</sup> of base <b>B</b> in excess (1)<br>in (18 + 24) cm <sup>3</sup> = 42 cm <sup>3</sup> (1)<br>[OH <sup>-</sup> ] = 12 × 2 × 0.12/42<br>= 0.069 M (1)<br>∴ [H <sup>+</sup> ] = K <sub>w</sub> /[OH <sup>-</sup> ] (1)<br>= 1.46 × 10 <sup>-13</sup> M (1)<br>∴ pH = 12.84 (1) | Same as for strong acid <b>S</b><br>pH = 12.84 (1)   |

[13 Max]

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- (iii) *Graph:* Sensibly scaled volume axis (1)  
4 points in text correctly plotted (-1 for each error) (2)  
vertical portion at equivalence on graph for **S** (1)  
single high pH curve for both **S** and **W** (1)  
Weak acid (**W**) has marked pH rise at start (1)



- (c) (i) *Buffer Properties* resists change in pH (1)  
 on adding small amounts of acid or base (1)
- W as a Buffer* Plenty of X<sup>-</sup> present to mop up H<sup>+</sup> (1)  
 Plenty of HX present to mop up OH<sup>-</sup> (1)  
OR equations showing same  
 e.g. H<sup>+</sup> + X<sup>-</sup> → HX, OH<sup>-</sup> + HX → X<sup>-</sup> + H<sub>2</sub>O

- (ii) *acid buffers* act at low pH, *basic buffers* act at high pH (1)  
 half-neutralised **W** is an *acid buffer* (1)  
*basic buffer*: mix weak base with the salt of its co-acid (1)  
OR correct specific example

6

[30]

32. (a)  $\text{pH} = -\log[\text{H}^+]$  1
- $$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]} \quad \text{or } [\text{H}^+] = [\text{A}^-] \quad 1$$
- $$[\text{H}^+] = \sqrt{1.74 \times 10^{-5} \times 0.15} \quad (\text{or } 1.62 \times 10^{-3}) \quad 1$$
- $$\text{pH} = 2.79 \quad (\text{penalise 1 dp or more than 2dp once in the qu}) \quad 1$$
- (b) (i) Solution which resists change in pH /maintains pH despite the addition of (small amounts of) acid/base (or dilution) 1
- (ii)  $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH}$  1  
must show an equation full or ionic in which ethanoate ions are converted to ethanoic acid
- (c) (i)  $[\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$  if rearrangement incorrect, no further marks 1
- $$= 1.74 \times 10^{-5} \times \frac{0.15}{0.10} \quad 1$$
- $$(\text{=} 2.61 \times 10^{-5})$$
- $$\text{pH} = 4.58 \quad 1$$
- (ii) M1 moles  $\text{H}^+$  added =  $10 \times 10^{-3} \times 1.0 = 0.01$  1
- M2 moles ethanoic acid after addition =  $0.15 + 0.01 = 0.16$  1
- M3 moles ethanoate ions after addition =  $0.10 - 0.01 = 0.09$  1
- M4  $[\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 1.74 \times 10^{-5} \times \frac{0.16/\text{V}}{0.09/\text{V}}$  1
- $$(\text{=} 3.09 \times 10^{-5})$$
- M5  $\text{pH} = 4.51$  1

The essential part of this calculation is addition/subtraction of 0.01 moles to gain marks M2 and M3. If both of these are missing, only mark M1 is available. Thereafter treat each mark independently, except if the expression in M4 is wrong, in which case both M4 and M5 are lost.

[15]

*alternative scheme for part (c)(i)*

$$\text{pH} = \text{p}K_a - \log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \quad 1$$

$$\text{p}K_a = 4.76 \quad 1$$

$$\text{pH} = (4.76 - \log \frac{0.15}{0.10}) = 4.58 \quad 1$$

*alternative for penultimate mark of part (c)(ii)*

$$\text{pH} = 4.76 - \log \frac{0.16}{0.09} \quad 1$$