4.3 ANSWERS TO EXAM QUESTIONS

1. (a) (i) A proton donor **(1)**

(ii) Fully ionised or fully dissociated **(1)**

(iii) $1 \cdot 0 \times 10^{-14}$ **(1)**

$mol^2 \ dm^{-6}$ **(1)**   4

(b) (i) $1 \cdot 50 \times 10^{-3}/25 \times 1000$ **(1)**

$= 0 \cdot 06 \ mol \ dm^{-3}$ **(1)**

$1 \cdot 2$ **(1)**

(ii)

Mol OH^- added	$= 50 \times 0 \cdot 150/1000 = 7 \cdot 5 \times 10^{-3}$	**(1)**
Mol H^+ used	$= 1 \cdot 5 \times 10^{-3}$	**(1)**
Mol OH^- excess	$= 6 \cdot 0 \times 10^{-3}$	**(1)**
$[OH^-] = 6 \cdot 0 \times 10^{-3}/75 \times 1000$	$= 8 \cdot \cdot 0 \times 10^{-2}$	**(1)**
$[H^+] = 10^{-14}/8 \cdot 0 \times 10^{-2}$	$= 1 \cdot 25 \times 10^{-13}$	**(1)**
pH	$= 12 \cdot 9$	**(1)**

8

(c) (i) $0 \cdot 3 \ mol \ dm^{-3}$ **(1)**

(ii) [H+] at pH $= 0 \cdot 7$ is $0 \cdot 2 \ mol \ dm^{-3}$ **(1)**

$m_1 v_1 = m_2 v_2 \ \therefore \ 0 \cdot 3 \times 25 = 0 \cdot 2 \times v$ **(1)**

Hence v $= 37 \cdot 5$ **(1)**

Water added $= 37 \cdot 5 - 25 = 12 \cdot 5$ **(1)**

5

[17]

2. (a) (i) $K_a = \dfrac{[H^+][A^-]}{[HA]}$ **(1)**

$K_a = \dfrac{[H^+]^2}{[HA]}$ **(1)**

$[H+] = 10^{-2.82} = 1.514 \times 10^{-3} \ mol \ dm^{-3}$ **(1)**

$Ka = \dfrac{\left(1.514 \times 10^{-3}\right)^2}{0.15} = 1.53 \times 10^{-5}$ **(1)** $mol \ dm^{-3}$ **(1)** [2]

(ii) Decreases **(1)**

Equilibrium shifts to right (endothermic process) **(1)**

$\therefore \ [H^+] \uparrow$ as T $\uparrow$**(1)**

pH gets smaller   8

(b) (i) $\frac{2}{3}$n **(1)**

    (ii) $\left(\frac{2}{3}n\right) \Big/ \left(\frac{1}{3}n\right)$ **(1)** = 2 **(1)**

    (iii) Ka $= \dfrac{[H^+][X^-]}{[HX]} = \dfrac{[H^+]}{2}$ **(1)**

         $= 2.1 \times 10^{-4}$ 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$_2$SO$_4$ 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$_2$O $\rightleftharpoons$ H$^+$ + OH$^-$ / 2H$_2$O $\rightleftharpoons$ H$_3$O$^+$ + OH$^-$ **(1)**
         (accept other types of arrow)   1

    (ii) $K_c = \dfrac{[H^+][OH^-]}{[H_2O]}$ / expression based on H$_3$O$^+$ equation **(1)**

         [H$_2$O] is (effectively) constant /concentration of H$_2$O is large /
         equilibrium in (i) is to left **(1)**

         ($K_c \times$ [H$_2$O]) $= K_w =$ [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
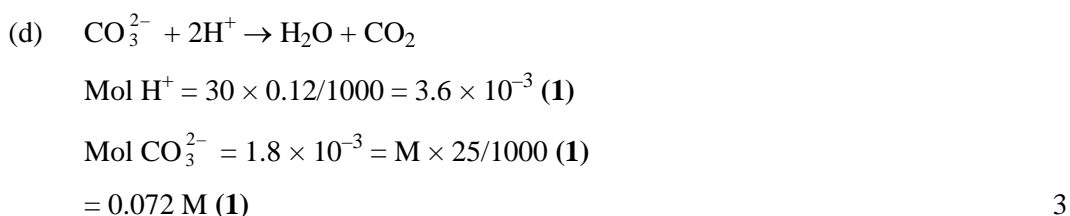
         [14]

4. (a) *Definition of a base*   Proton acceptor **(1)**

       Essential feature   Transfer of protons **(1)**

       Equation $H^+ + OH^- \rightleftharpoons H_2O$

          <u>OR</u> $H^+ + B \rightleftharpoons BH^+$ **(1)**   3

(b) only partially dissociated in solution **(1)**   1

(c) $K_a = \dfrac{[H^+(aq)][CH_3CH_2COO^-(aq)]}{[CH_3CH_2COOH(aq)]}$ **(1)**

     $mol\ dm^{-3}$ **(1)**   2

(d) (i) resists <u>change in pH</u> **(1)**
         on addition of <u>small amounts of strong acid or base</u> **(1)**

    (ii) correct weak acid/co-base
         or correct weak base/co-acid **(1)**

    (iii) any suitable <u>use</u> **(1)**   4

                               [10]

5. (a) (i) $0.12 \times 11.8 = M \times 25$ **(1)**
         $\therefore$ molarity = 0.057 **(1)**

    (ii) $K_a = \dfrac{[H^+][A^-]}{[HA]}$ **(1)**

    (iii) *Volume of NaOH(aq) added* $11.8/2 = 5.9\ cm^3$ **(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) $15\ cm^3$ 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

(d) $CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$

Mol $H^+ = 30 \times 0.12/1000 = 3.6 \times 10^{-3}$ **(1)**

Mol $CO_3^{2-} = 1.8 \times 10^{-3} = M \times 25/1000$ **(1)**

$= 0.072$ M **(1)**   3

(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* $HCl(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$ **(1)**

Role of water   base <u>or</u> proton acceptor **(1)**   2

(c) *Equation* $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ **(1)**

Role of water   acid <u>or</u> proton donor **(1)**   2

(d) *Equation for formation* $H_2SO_4 + HNO_3 \rightleftharpoons HSO_4^- + H_2NO_3^+$ **(1)**

Role of nitric acid   base <u>or</u> proton acceptor **(1)**

$H_2NO_3^+ \rightarrow NO_2^+ + H_2O$ **(1)**   3

(e) (i)   only partially dissociated in aqueous solution **(1)**

(ii) $K_a = \dfrac{[H^+][A^-]}{[HA]}$ **(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) $NaOH + HA \rightarrow NaA + H_2O$ **(1)**

or $HA + OH^- \rightarrow A^- + H_2O$ 1

(b) (i)   Moles $A^- = $ moles NaOH added **(1)**

$= 15 \times 0.34 \times 10^{-3} = 5.10 \times 10^{-3}$ **(1)**

Initial moles 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

4

(ii) 5.10×10^{-3} moles A⁻ in (15 + 25) cm³

Hence [A⁻] = $5.10 \times 10^{-3} \times 1000/40 = 0.1275$ **(1)**

Allow 0.127 – 0.128 and 0.13

6.15×10^{-3} moles HA in 40 cm³

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) $K_a = \dfrac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$ **(1)**

accept [H+]
do not accept with [H₂O] 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 ∴ range = 8.3 → 10.3 **(1)**
(allow 8 – 10)   2

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

[In⁻] ≥ [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) $pH = -\log_{(10)} [H^+]$ Note; (aq) not required; Not $-\ln [H^+]$ **(1)**

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

Allow $[A^-]$ and $[HA]$

Do NOT allow $[H^+]^2/[HX]$

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

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

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

not a conseq mark

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

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

  (1)   **(2)**   **(1)**

Note pH = 2.4 scores max 3   6

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

Allow 0.237 – 0.238 and 0.24

$pH = 0.62$ **(1)**

Allow 0.62 – 0.63

Only allow pH mark if $[H^+]$ is correct

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

$[HY] = 0.05 \times 0.25 = 0.0125$ **(1)**

Allow 0.012 – 0.013

$K_a = [H^+] [Y^-] / [HY]$

$= (0.2375)^2 / 0.0125$ **(1)**

$K_a = 4.51$ **(1)**

Allow 4.3 – 4.8

Ignore units

CE if [HY] is incorrect   6

                                                      [12]

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

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

$K_a = [H^+]^2/0.52$ or $[H^+]=[X^-]$ **(1)**

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

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

or $pH = \frac{1}{2} pK_a - \frac{1}{2} \log [HX]$

$= 1.86 - (-0.142) = 2.00$ 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) $K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ **(1)**

(ii)   (1) $K_a = \dfrac{[H^+]^2}{[CH_3COOH]}$ **(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.<u>71</u> **(1)**
2 d.p. essential
If forget $\sqrt{}$ can score (1) and (3) for pH = 5.42

                                                                                    5

(b)   (i)   moles acid = $\dfrac{25}{1000} \times 0220$ **(1)** $= 5.50 \times 10^{-3}$

$= \dfrac{x}{10^3} \times 0.150$

$\therefore x = 25 \times \dfrac{0.220}{0.150}$ **or** $5.50 \times 10^{-3} \times \dfrac{1000}{0.150}$

$= 36.7$ (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

                                                                                    7

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

If wrong M$_r$: CE m lose marks (1) and (2) then mark on consequentially È max 4

(2)   mol CH_3COOH left = 0.220 - 0.050 = 0.170 **(1)**

(3)   mol CH_3COO^- formed = 0.050 **(1)**

(4) $[H^+] = Ka\ \dfrac{[acid]}{[salt]}$ OR $pH = pKa + \log\left(\dfrac{[A^-]}{[HA]}\right)$ etc **(1)**

If expression wrong no marks for 4 / 5 / 6

can score (1) to (4) in (5)

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

(6)   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 pH = 4.12 if $\dfrac{[acid]}{[salt]}$ upside down; answer 5.29 scores 3

for (1) (2) (3)

6

[16]

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

∴ vol NaOH = $\dfrac{3.75 \times 10^{-3}}{0.20} = 1.875 \times 10^{-2}$ dm^3 **(1)**

or 18.75 cm^3

2

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

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

(iii)   phenol red / thymol blue / phenolphthalein / thymolphthalein
i.e. indicator with 7 < pK$_{in}$ <11

3

(c) (i) Only slightly dissociated **(1)**
NOT "not fully dissociated / ionised"

(ii) $K_a = \dfrac{[H^+][A^-]}{[HA]}$ **(1)**

NOT $\dfrac{[H^+]^2}{[HA]}$

(iii) For weak acid alone:

$Ka = \dfrac{[H^+]^2}{[HA]}$ **(1)**

m $[H^+] = \sqrt{(2.75\times10^{-5})\times0.15}$

$= 2.03 \times 10^{-3}$ **(1)**

$\therefore$ pH = 2.69 **(1)**
pH should be given to 2 decimal places
penalise answer to 1 d.p. once in question

5

(d) moles OH$^-$ added = 1.875×10^{-3} = moles A$^-$ = moles HA left **(1)**
or $[A^-] = [HA]$
$\therefore$ Ka = [H$^+$] **or** pH = pK$_a$ **(1)**
$\therefore$ pH = 4.5$\underline{6}$ **(1)**   3

[13]

14. Penalise pH given to 1 dp <u>first</u> time it would have scored only

(a) (i) $K_w = [H^+] [OH^-]$ **(1)**

(ii) pH = –log [H$^+$] **(1)**
            or in words or below unless contradiction

(iii) *Calculation*: $[H^+] = \sqrt{5.48\times10^{-14}}$ **(1)**
                        $= 2.34 \times 10^{-7}$
            $\therefore$ pH = 6.63 or 6.64 **(1)**

Explanation: pure water $\therefore$ [H$^+$] = [OH$^-$] **(1)**   5

(b) (i) $[OH^-] = 0.150$ $\therefore$ $[H^+] = 10^{-14}/0.15 = 6.66 \times 10^{-14}$
                            or pOH = 0.82

                            $\therefore$ pH = 13.18 **(1)**
                            or pH= 13.17

(ii) moles OH$^-$ = $(35 \times 10^{-3}) \times 0.150 = 5.25 \times 10^{-3}$ **(1)**[a]

moles H$^+$ = $(40 \times 10^{-3}) \times 0.120 = 4.8(0) \times 10^{-3}$ **(1)**[b]

$\therefore$ excess moles of OH$^-$ = 4.5×10^{-4} **(1)**[c]

$\therefore$ $[OH^-] = (4.5(0) \times 10^{-4}) \times 1000/\underline{75}$[d] **(1)**[e]

$[H+] = \dfrac{10^{-14}}{6.00\times10^{-3}} = 1.66 \times 10^{-12}$ or pOH = 2.22

$\therefore$ pH = 11.78 **(1)**[f]
            or 11.77   8

(c) (i) $K_a = \dfrac{\left[H^+\right]\left[X^-\right]}{\left[HX\right]}$ **(1)**

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

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

or $\dfrac{\left(2.70 \times 10^{-3}\right)^2}{0.1473} = 4.95 \times 10^{-5}$

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   answr = 10.65
         If wrong volume max 5 for a, b, c, e, f
         If no substraction 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) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ **(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) $K_a = [H^+][A^-] / [HA]$ **(1)**
         $= [H^+] [0.125 \times 4]$ **(1)** $/ 1.00$
         $[H^+] = 1.70 \times 10^{-5} / 0.125 \times 4 = 3.40 \times 10^{-5}$ **(1)**

         $pH = -\log_{10}[H^+] = 4.47$ **(1)**
             Allow pH conseq to $[H^+]$ if 2 place decimals given

(ii) $H^+ + CH_3COO^- \rightarrow CH_3COOH$ **(1)**   5

                                                                      [14]

16. (a) $K_a = \dfrac{[H^+][A^-]}{[HA]}$ 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) $K_a = \dfrac{[H^+]^2}{[HA]}$ or $[H^+] = [A^-]$ 1

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

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

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 2.6×10^{-4} 1

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

     $= \dfrac{(1.45 \times 10^{-4}] \times 0.25}{2.57 \times 10^{-4}}$ 1

     $= 0.141$ (mol dm^{-3})   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)*

$pH = pK_a - \log\dfrac{[HA]}{[A^-]}$ 1

$pK_a = 3.84$ 1

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

                          [11]

17. (a) (i) pH = –log [H$^+$] **(1)**

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

Calculation: pH = 2.56 ∴ [H$^+$] = 2.75 × 10^{-3} **(1)**

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

or [H$^+$] = [X$^-$] **(1)**   5

depending on approximate made, values of $K_a = 10^{-5}$ ×
using [HX] = 0.12   *6.30 – 6.32*
using [HX] = 0.12 – 2.75...   *6.45 – 6.47*
using 2.8 and [HX] = 0.12   *6.53*
using 2.8 and [HX] = 0.12 – 2.8   *6.69*
upside down K_a

(b) (i) *Expression for K_w*: K_w = [H$^+$] [OH$^-$] **(1)**

Value of K_w: (1.0 ×)10^{-14} (mol^2 dm^{-6}) **(1)**
ignore units

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

or pOH = 1.35 **(1)**

∴ pH = 12.<u>65</u> **(1)**   4
must be 2dp in final answer

(c) (i) $H_2C_2O_4$ + OH$^-$ → $HC_2O_4^-$ + H_2O **(1)**
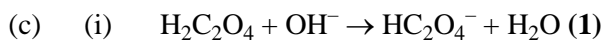
(ii) mol OH$^-$ = (41.6 × 10^{-3}) × 0.0450 **(1)** = 1.87 × 10^{-3}
∴ mol $H_2C_2O_4$ = 9.36 × 10^{-4} **(1)**
[$H_2C_2O_4$] = 9.36 × 10^{-4} × 10^3/25
            = 0.0374 **(1)**   4

if moles of $H_2C_2O_4$ not equal to half moles of OH$^-$, no further marks gained

if mol OH$^-$ = 1.9 × 10^{-3}; hence mol $H_2C_2O_4$ = 9.5 × 10^{-4}; [$H_2C_2O_4$] = 0.038

                                                                           [13]

18. (a) (i) B;   1

           C;   1

           A;   1

(ii) cresolphthalein

OR

thymolphthalein;   1

(b) (i) $-\log[H^+]$; 1

(ii) $[H^+] = 1.259 \times 10^{-12}$ (or 1.26 or 1.3)   *OR*   pOH = 14 − pH; 1

$$[OH^-] = \frac{10^{-14}}{1.258 \times 10^{-12}} \qquad OR \qquad = 2.10;$$ 1

$= 7.9(4) \times 10^{-3}$; 1
(if [H⁺] is wrong allow 1 for [OH] = K_W/[H⁺] or as numbers)

(c) (i) $K_a = [H^+]^2/[CH_3CH_2COOH]$

OR

$[H+]^2/[HA]$

OR

$[H^+] = [A^-]$ etc; 1

$[H^+] = \sqrt{1.35 \times 10^{-5} \times 0.117}$ or expression without numbers; 1

$= 1.257 \times 10^{-3}$

pH $= 2.9\underline{0}$; 1

(iii) $K_a = [H^+]$

OR

$pK_a = pH$; 1

pH = 4.8$\underline{7}$; 1
(penalise 1dp once)

[13]

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

(b) (i) $Ka = \dfrac{[H^+][X^-]}{[HX]}$ allow HA etc

         not $\dfrac{[H^+]^2}{[HX]}$ *but mark on*

         If expression wrong allow conseq units in (ii) but no other marks in (ii)   1

(ii) $\dfrac{[H^+]^2}{[HX]} = \dfrac{(4\cdot57\times10^{-3})^2}{[0\cdot150]}$ 1

        If use 4.6×10^{-3}

        $K_a = 1.4(1) \times 10^{-4}$ *and pKa = 3.85*   1

       $= 1.39 \times 10^{-4}$

        allow $1.39 – 1.41 \times 10^{-4}$

       mol dm^{-3}

(iii) $pK_a = 3.86$ 1

        Penalise dp of final answer < or > 2 in pH once in paper

(c) (i) $\dfrac{30}{1000} \times 0.480 = 0.0144$ or $1.4(4) \times 10^{-2}$ 1

        Mark is for answer (M1)

(ii) $\dfrac{18}{1000} \times 0.350 = 0.0063$ or 6.3×10^{-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) $1.80 \times 10^{-3} \times \dfrac{1000}{48} = 0.0375$ (0.038)   1

        M4 is for answer

        If vol is not 48×10^{-3} (unless AE) lose M4 and next mark gained

        If multiply by 48 - this is AE - i.e. lose only M4

        If multiply by 48×10^{-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) $[H+] = \dfrac{4.02 \times 10^{-14}}{1.0 \times 10^{-3}}$ $(= 4.02 \times 10^{-11})$ 1

              pH = 10.40   1

    (b) (i) $Ka = \dfrac{[H+][CH_3CH_2COO-]}{[CH_3CH_2COOH]}$ 1

             $= \dfrac{[H+]}{[CH_3CH_2COOH]}$ 1

             $[H+] = (1.35 \times 10^{-5}) \times 0.125$ $(= 1.30 \times 10^{-3})$ 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

             $(H+) = Ka \times \dfrac{[CH_3CH_2COOH]}{[CH_3CH_2COO-)}$ 1

             $= (1.35 \times 10^{-5}) \times \dfrac{(5.25 \times 10^{-3})/V}{(1.0 \times 10^{-3})/V} \ (= 7.088 \times 10^{-5})$ 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 mol dm^{-3} HCl   = 0.60
            and pH of 0.150 mol dm^{-3} HCl   = 0.82;   1
            pH change   = 0.22;   1

      (ii) moles 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 = $50 - 30 = 20$ cm^3;   1

                                                                                [12]

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

         (b)   (i)   partially ionised $\underline{or}$ dissociated **(1)**

                     not fully

               (ii) NH$_3$ **(1)**

                     not NH$_4$OH – but allow in equation

                     not H$_2$O – but allow in equation if both weak acid and base stated

                     NH$_3$ + H$_2$O $\rightleftharpoons$ NH$_4^+$ + OH$^-$ **(1)**   3

         (c)   (i)   HCOOH(aq) + H$_2$O(l) $\rightleftharpoons$ HCOO$^-$(aq) + H$_3$O$^+$(aq) **(1)**

                     allow H$_2$O(aq)

               (ii) H$_2$O or water **(1)**
                     HCOO$^-$ $\underline{or}$ methanoate ion **(1)**

               (iii) $K_a = \dfrac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$ **(1)**

                     allow [OH$_3^+$]   4

         (d)   (i)   addition of $\underline{small}$ amounts of $\underline{acid}$ **(1)**
                     addition of $\underline{small}$ amounts of $\underline{base}$ **(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 $\underline{not}$ just an ion (methanoate)

               (iii) $\underline{OH^-}$ added **(1)**

                     or base

                     H$^+$ reacts with $\underline{OH^-}$ **(1)**

                     or forming water

                     More HCOOH $\underline{dissociates}$ 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) $HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$ **(1)**

       allow $H_2O(aq)$ 1

    (b) $pH = -\log[H^+]$ **(1)**
          $= -0.10 \, (\pm 0.01)$ **(1)**   2

    (c) $pH = 7$ **(1)**
          neutral solution <u>or</u> $[H^+] = [OH^-]$ **(1)**   2

    (d)   (i)   moles H+ $= 1.26 \times \dfrac{95}{1000} = 0.1197$ moles **(1)**

                range 0.120 Ë 0.001

        (ii)   moles $OH^- = 2 \times 1.37 \times \dfrac{45}{1000} = 0.1233$ moles **(1)**

                range 0.123 Ë 0.001

        (iii) XS $OH^- = 0.1233 - 0.1197 = 3.6 \times 10^{-3}$ moles **(1)**

                range 0.001 to 0.005

                Volume $= 95 + 45 = 140 \, cm^3$ **(1)**

                $\therefore [OH^-] = 3.6 \times 10^{-3} \times \dfrac{1000}{140} = 0.0257 \, M$ **(1)**

                range 0.0071 to 0.0357

                $K_w = [H^+][OH^-] = 10^{-14} \, mol^2 \, dm^{-6}$ **(1)**

                $\therefore [H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{10^{-14}}{0.0257} = 3.89 \times 10^{-13} \, M$ **(1)**

                range $(0.28$ to $1.35) \times 10^{-12}$

                $\therefore pH = 12.41$ **(1)**

                must show 2 dp   range 11.87 to 12.55   8

                                                                                         [13]

If no × 2 for Ba(OH)₂ then H^+ is in XS	*MAX 4 ex 6*
If no volume used then	*MAX 4 ex 6*
If no × 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) $K_a = \dfrac{[H^+][A^-]}{[HA]}$ 1

       (ii) Equation for [H+] $[H^+] = K_a \times \dfrac{[HA]}{[A^-]}$ **(1)**

                                $[HA]$ and $[A^-]$ **(1)**

                                are altered to same extent

                                maintaining $[H^+]$ and pH **(1)**   3

                                                           [9]

25. (a) (i) $pKa = -\log_{10}Ka$ **(1)**

       (ii) 6.31×10^{-5} **(1)**
          $mol\ dm^{-3}$ **(1)**

       (iii) $[H^+] = [A^-]$ or $Ka = [H^+]^2/[HA]$ **(1)**
          Hence $6.31 \times 10^{-5} = [H^+]^2/0.830$
          $[H^+] = \sqrt{(6.31 \times 10^{-5} \times 0.830)} = 7.24 \times 10^{-3}$ **(1)**
          $pH = -\log_{10}[H^+]$ **(1)**
          $pH = 2.14$ **(1)**
          Marked consequentially to a(ii)   7

     (b) (i) Mol NaOH = mol X^- **(1)**
          $mv/1000 = 0.800 \times 10.5/1000 = 8.4 \times 10^{-3}$ **(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 $K_a = [H^+][X^-]/[HX]$ **(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

                                                               [19]

26. (a) *Monoprotic acid*   An acid which gives only one proton **(1)**

         Example   HCl etc **(1)**   2

     (b) (i) $-\log_{10}[H^+]$ or in words **(1)**

        (ii)   1.58 M   (allow 1.6) **(1)**   2

     (c)   Mol $H^+ = 25 \times 0.15 \times 10^{-3}$ **(1)** $= 3.75 \times 10^{-3}$

           Mol $OH^- = 35 \times 0.12 \times 10^{-3}$ **(1)** $= 4.20 \times 10^{-3}$

           Excess OH^- $= 4.5 \times 10^{-4}$ **(1)**

           $[OH^-] = 4.5 \times 10^{-4} \times 1000/60$ **(1)** $= 7.5 \times 10^{-3}$

           $[H^+] = 10^{-14}/7.5 \times 10^{-3}$ **(1)** $= 1.33 \times 10^{-12}$ **(1)**

           $pH = -\log_{10} 1.33 \times 10^{-12}$

           $= 11.9$ **(1)**

NB Consequential marking if $[OH^-]$ not calculated to maximum of 5   7

                                                                     [11]

27. (a) *Equation for HCl(g)* $HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$ **(1)**

         Equation for KOH(s) $KOH(s) \rightarrow K^+(aq) + OH^-(aq)$ **(1)**   2

     (b) $K_w = [H^+][OH^-]$ 1

     (c)   strong base, fully dissociated **(1)** <u>or</u> $[OH^-] = 0.016$ M **(1)**

           $[H^+] = \dfrac{K_w}{[OH^-]}$ **(1)** $= \dfrac{10^{-14}}{0.016} = 6.25 \times 10^{-13}$ M **(1) (2)**

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

$\therefore$ pH $= 12.2$ **(1)**

neutral solution, $\therefore [H^+] = [OH^-]$ **(1)**

$\therefore$ pH $= 7$ **(1)**   7

     (d) (i)   755 cm^3 of 0.012 M acid contain

           $\dfrac{0.012 \times 755}{1000}$ mol $H^+ = 9.06 \times 10^{-3}$ moles **(1)**

           $\therefore$ moles OH^- used for neutralisation $= 9.06 \times 10^{-3}$ **(1)**

       (ii)   pH $= 11.6 \therefore [H^+] = 10^{-11.6} = 2.5 \times 10^{-12}$ M **(1)**

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

           in 755 cm^3 there are $\dfrac{3.98 \times 10^{-3} \times 755}{1000}$

$= 3.0 \times 10^3$ mol **(1)**

       (iii)   Total moles $= (9.06 + 3.0) \times 10^{-3} = 0.012$ mol **(1)**

         (iv) $M_r = 39 + 16 + 1 = 56$

$\therefore$ m $= 56 \times 0.012 = 0.68$g **(1)**   8

                                                                     [18]

28. (a) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$ **(1)**

        $HCl + H_2O \rightarrow H_3O^+ + Cl^-$ **(1)**   2

        for HF, must have reversible arrow
        allow (aq) in HCl equation

    (b)   (i) $pH = -\log10[H^+]$ **or** equivalent word definition **(1)**   1

               allow $-\log[H_3O^+]$ **or** $-\log[H^+(aq)]$

        (ii) $[H+] = 0.050$ mol dm^{-3}

               $pH = 1.3(0)$ **(1)**   1

               if correct definition demonstrated in (ii), but word definition in (i)
               wrong, allow mark transfer from (ii) to (i)

    (c)   (i) $K_a = \dfrac{[H^+][F^+]}{[HF]}$ **(1)**   1

               do **not** expression allow with $[H_2O]$; allow $[H_3O^+]$

               allow consequential mark from wrong equation in (b) providing
               $[H^+]$ present

        (ii) $K_a = \dfrac{[H^+]^2}{[HF]}$ or $[H^+] = \sqrt{K_a[HF]}$ **(1)**

               $[H^+] = \sqrt{5.6 \times 10^{-4} \times 0.050}$

               $= 0.0053$ **(1)**

               $pH = 2.3 / 2.28$ **(1)**   3

               allow mark for correct pH from wrong $[H^+]$

    (d)   hydrogen fluoride **or** HF **(1)**

        donates a proton (to the nitric acid) **(1)**

        conjugate base 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) $K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ **(1)**   1

               allow either $[H_3O^+]$ or $[H^+]$ in expression
               must include charges
               if $[H_2O]$ included then no mark

        (ii) $pK_a = -\log(1.7 \times 10^{-5}) = 4.77 / 4.8/4.80$ **(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 $\rightarrow$ yellow / orange)

(iii) $NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$ **(1)**

if charges shown they must be correct
accept $H^+ + OH^- \rightarrow H_2O$ 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 δ+ H atom in O–H for δ– 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* $Ka = \dfrac{[H^+][A^-]}{[HA]}$ **(1)**

Units   mol dm^{-3} (or 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
         Kw decreases) **(1)** less H^+ (or[H^+] lower) **(1)**

(ii) Because [H^+] = [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 <u>both</u> needed **(1)**   1

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

Explanation: HX barely dissociates <u>OR</u> [H$^+$] very small **(1)**
            so [HX]$_{eqm}$ = [HX] original **(1)**
            and [H$^+$] = [X$^-$] in an aqueous solution of weak acid **(1)**   3

(b) (i)   moles H$^+$ in 18 cm^3 = 18 × 0.16 × 10^{-3} = 2.88 × 10^{-3} **(1)**
        moles OH$^-$ in V_{eqv} cm^3 = <u>2×</u> **(1)** (V_{eqv} × 0.12 × 10^{-3})

∴ $V_{eqv} = \dfrac{18 \times 0.16}{0.12 \times 2} = 12.0$ cm^3 **(1)**

	Start	Half equivalence	Equivalence	Double equivalence
Volume/cm^3 Ba(OH)$_2$ solution added	0.0	*6.0*	*12.0*	*24.0*
pH for titration of **S**	0.80	*1.22*	7	*12.84*
pH for titration of **W**	2.74	*4.68*	8.5	*12.84*

3

(ii)	**Strong acid S**	**Weak acid W**

Half-equivalence
 	
Volume of base = 6 cm^3
	9 cm^3 of strong acid **S** **(1)**
	in (18 + 6) cm^3 = 24 cm^3 **(1)**
	[H$^+$] = 9 × 0.16/24 = 0.06 M **(1)**
	∴ pH = 1.22 **(1)**
		[HX] = [X$^-$] (given)
		∴ pH = pK$_a$ <u>or</u> [H$^+$] = K_a **(1)**
		    = − log (2.07 × 10^{-5})
		    = 4.68 **(1)**

2 × equivalence
 	
Volume of base = 24 cm^3
	12 cm^3 of base **B** in excess **(1)**
	in (18 + 24) cm^3 = 42 cm^3 **(1)**
	
	[OH$^-$] = 12 × 2 × 0.12/42
	    = 0.069 M **(1)**
	∴ [H$^+$]= K_w/[OH$^-$] **(1)**
	    = 1.46 × 10^{-13} M **(1)**
	∴ pH = 12.84 **(1)**
		Same as for strong acid **S**
		pH = 12.84 **(1)**

[13 Max]

10

(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)**
            <u>single</u> high pH curve for both **S** and **W** **(1)**
            Weak acid (**W**) has marked pH rise at start **(1)**

14
13
12
11
10
9
8
7
pH
6
5
4
3
2
1
0

0   5   10   15   20   25

Volume Ba(OH)$_2$ /cm³

5
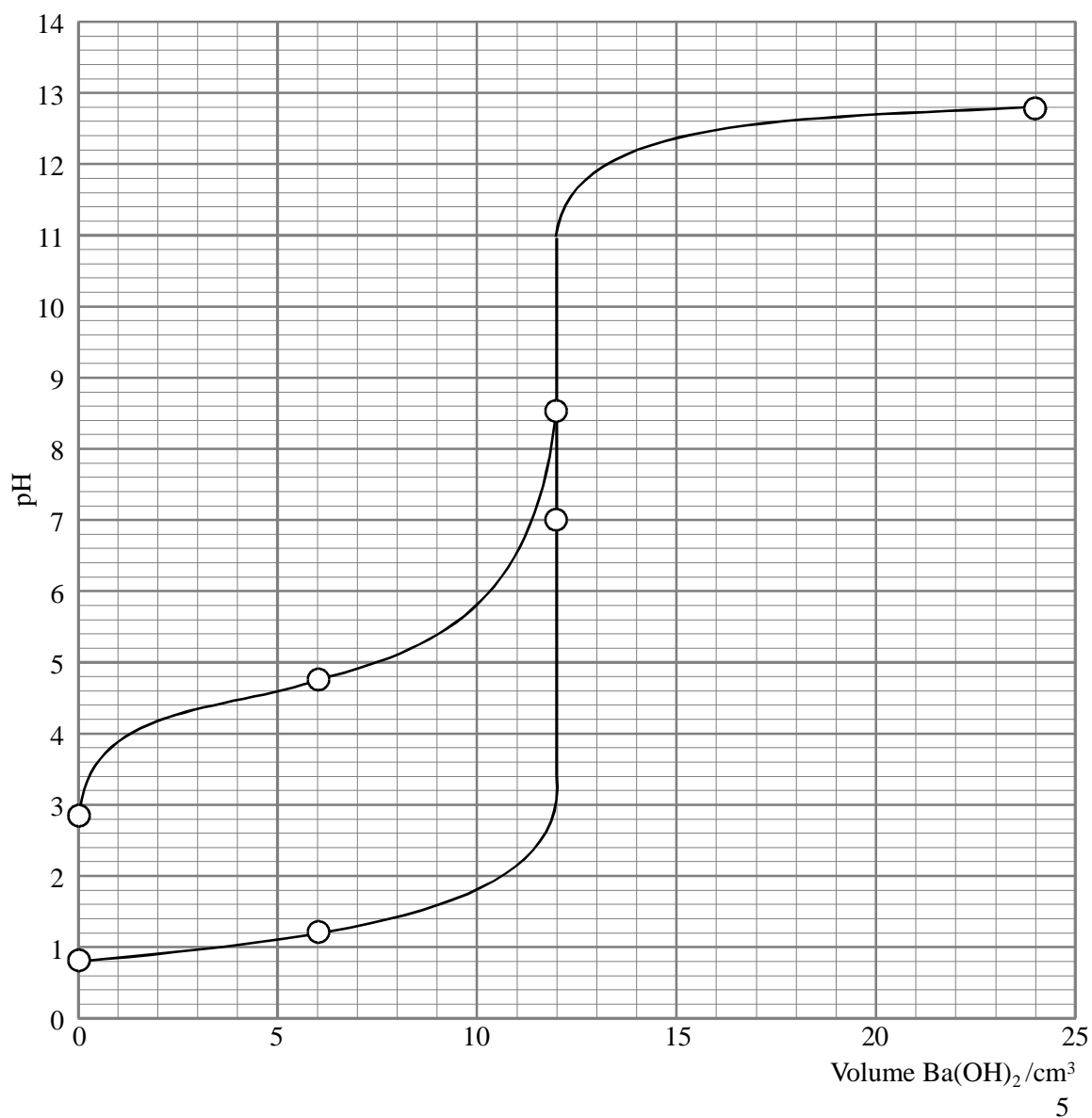
(c)   (i)   *Buffer Properties*   resists change in pH (**1**)
                                        on adding small amounts of <u>acid</u> or <u>base</u> (**1**)

        W *as a Buffer*   Plenty of X⁻ present to mop up H⁺ (**1**)
                                        Plenty of HX present to mop up OH⁻ (**1**)
                                        <u>OR</u> equations showing same
                                        e.g. $H^+ + X^- \rightarrow HX$, $OH^- + HX \rightarrow X^- + H_2O$

        (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**)
                <u>OR</u> correct specific example   6

                                                                            [30]

32. (a) $pH = -\log[H^+]$ 1

$K_a = \dfrac{[H^+]^2}{[CH_3COOH]}$ or $[H^+]=[A^-]$ 1

$[H^+]= \sqrt{1.74 \times 10^{-5} \times 0.15}$ (or 1.62×10^{-3})   1

pH = 2.79   (penalise 1 dp or more than 2dp once in the qu)   1

(b) (i) Solution which resists change in pH /maintains pH   1
despite the addition of (small amounts of) <u>acid/base</u> (or dilution)   1

(ii) $CH_3COO + H^+ \rightarrow CH_3COOH$ 1
must show an equation full or ionic in which ethanoate ions are
converted to ethanoic acid

(c) (i) $[H^+] = \dfrac{K_a[CH_3COOH]}{[CH_3COO^-]}$ if rearrangement incorrect, no further marks   1

$= 1.74 \times 10^{-5} \times \dfrac{0.15}{0.10}$ 1

$(= 2.61 \times 10^{-5})$

pH = 4.58   1

(ii) Ml   moles 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 $[H^+] = \dfrac{K_a[CH_3COOH]}{[CH_3COO^-]} = 1.74 \times 10^{-5} \times \dfrac{0.16/V}{0.09/V}$ 1

$(= 3.09 \times 10^{-5})$

M5   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 Ml 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)

$pH \; pK_a - \log \dfrac{[CH_3COOH]}{[CH_3COO^-]}$ 1

$pK_a = 4.76$ 1

$pH = (4.76 - \log \dfrac{0.15}{0.10}) = 4.58$ 1

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

$pH = 4.76 - \log \dfrac{0.16}{0.09}$ 1