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)

(b) (i) $1.50 \times 10^{-3}/25 \times 1000$ (1)

   $= 0.06$ mol dm$^{-3}$ (1)
   1.2 (1)

(ii) Mol OH$^-$ added $= 50 \times 0.150/1000 = 7.5 \times 10^{-3}$ (1)

   Mol H$^+$ used $= 1.5 \times 10^{-3}$ (1)

   Mol 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)

(c) (i) $0.3$ mol dm$^{-3}$ (1)

(ii) $[\text{H}^+]$ at pH = 0.7 is $0.2$ mol dm$^{-3}$ (1)

   $m_1 \times v_1 = m_2 \times v_2 \therefore 0.3 \times 25 = 0.2 \times v$ (1)

   Hence $v = 37.5$ (1)

   Water added $= 37.5 - 25 = 12.5$ (1)

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

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

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

   $K_a = \frac{(1.514 \times 10^{-3})^2}{0.15} = 1.53 \times 10^{-5}$ (1) mol dm$^{-3}$ (1) [2]

(ii) Decreases (1)

   Equilibrium shifts to right (endothermic process) (1)

   $\therefore [\text{H}^+] \uparrow$ as $T \uparrow$ (1)

   pH gets smaller (1)
(b) 

(i) \( \frac{2}{3} n \) (1)  

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

(iii) \( \text{Ka} = \frac{[H^+][X^-]}{[HX]} = \frac{[H^+]}{2} \) (1)  

\[ \text{Ka} = 2.1 \times 10^{-4} \text{ mol dm}^{-3} \] (1)  

(c) Weak acid/strong base : pH at equivalence > 7 (1)  

methy l orange has colour change at pH < 7 (1)  

(d) Buffer can resist change in pH (1)  

on addition of small amounts of H⁺ (or OH⁻) (1)  

\( \text{H}^+ (\text{aq}) + X^- (\text{aq}) \rightleftharpoons \text{HX (aq)} \) (1)  

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)  

(b) 

(i) acid: HBr base: Br⁻  

(ii) acid: H₂SO₄ base: HSO₄⁻  

allow 1 in (b) if both acids / bases are correct (ie give 1 for a correct vertical pair)  

2  

(c) 

(i) \( \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- / 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \) (1)  

(accept other types of arrow)  

1  

(ii) \( K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \) / expression based on H₃O⁺ equation (1)  

\[ [\text{H}_2\text{O}] \text{ is (effectively) constant / concentration of H}_2\text{O} \text{ is large / equilibrium in (i) is to left (1)} \]  

\( (K_c \times [\text{H}_2\text{O}] = K_w = [\text{H}^+][\text{OH}^-] \) (1)  

3  

(iii) \[ [\text{H}^+] = [\text{OH}^-] / [\text{H}^+]^2 = 2.92 \times 10^{-14} \] (1)  

\[ [\text{H}^+] = \sqrt{2.92 \times 10^{-14}} = 1.71 \times 10^{-7} \] (1)  

\[ \text{pH} = -\log_{10}(1.71 \times 10^{-7}) \] (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
4. (a) **Definition of a base**  Proton acceptor (1)

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

**Equation**  
\[ H^+ + OH^- \rightarrow H_2O \] OR \[ H^+ + B \rightarrow BH^- \] (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) 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)
      \[ \therefore \text{molarity} = 0.057 \] (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, \[ HA \equiv H^+ + A^- \], displacement to right
      or \[ HA \] ionises (1)

(ii) The added \[ H^+ \] reacts with \[ A^- \] (1)
      The equilibrium, \[ HA \equiv H^+ + A^- \], displaced to left (1) 4 13

6. (a) \[ CO_3^{2-} + H^+ \rightarrow HCO_3^- \] or \[ \text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{NaCl} \] (1)

\[ \text{HCO}_3^- + H^+ \rightarrow H_2O + \text{CO}_2 \] or \[ \text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{CO}_2 + H_2O \] (1) or \[ \text{H}_2\text{CO}_3 \] 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
(d) \[ \text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2 \]
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 \((1)\)

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

7. (a) A proton donor \(1\)
(b) \[ \text{HCl(g)} + \text{H}_2\text{O(l)} \not\Rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq) \] \((1)\)
Role of water base or proton acceptor \((1)\)
(c) \[ \text{NH}_3(g) + \text{H}_2\text{O(l)} \not\Rightarrow \text{NH}_4^+(aq) + \text{OH}^-(aq) \] \((1)\)
Role of water acid or proton donor \((1)\)
(d) \[ \text{H}_2\text{SO}_4 + \text{HNO}_3 \not\Rightarrow \text{HSO}_4^- + \text{H}_2\text{NO}_3^+ \] \((1)\)
Role of nitric acid base or proton acceptor \((1)\)
\[ \text{H}_2\text{NO}_3^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O} \] \((1)\)
(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 \((1)\)

[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 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 0.01110 – 0.01133
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) $K_a = \frac{[H^+] [A^-]}{[HA]} = 2.00 \times 10^{-4}$
$[H^+] = 2.00 \times 10^{-4} \times 0.1538 / 0.1275 \ (1)$
$= 2.41 \times 10^{-4} \ (1)$
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. (a) only partially ionized / partially dissociated / not fully ionised (1)
not ‘not ionised at all’ 1

(b) (i) $K_a = \frac{[C_6H_5O^-][H_2O^+]}{[C_6H_5OH]} \ (1)$
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)

(iv) lower / smaller number (1)

(c) (i) at end point pH = $pK_a = 9.3$ (1)
colour change detectable over range of 2 pH units $\therefore$ range $= 8.3 \to 10.3$ (1)
(allow $8 \to 10$) 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. (a) (i) \( \text{pH} = -\log_{10} \left[ H^+ \right] \)  
Note; (aq) not required; Not \(-\ln \left[ H^+ \right] \) \( \text{(1)} \)

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

Allow \([A^-]\) and \([HA]\)  
Do NOT allow \([H^+]^2/\left[ HX \right] \) \( \text{(1)} \)

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

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

\[ = 4.37 \times 10^{-3} \text{ (1)} \)

\text{not a conseq mark}

\text{pH} = 2.356 \quad \text{Mark conseq to \([H^+]\) above (1)}

\text{or pH} = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log_{10} \left[ HX \right] = \frac{1}{2} \times 4.37 + \frac{1}{2} \times 0.346 = 2.356 \quad \text{(1)} \)

\text{(2)} \quad \text{(1)} \)

\text{Note pH = 2.4 scores max 3} \quad \text{6}

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

\text{Allow 0.237 – 0.238 and 0.24}

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

\text{Allow 0.62 – 0.63}

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

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

\( \left[ HY \right] = 0.05 \times 0.25 = 0.0125 \) \( \text{(1)} \)

\text{Allow 0.012 – 0.013}

\( K_a = \left[ H^+ \right] \left[ Y^- \right] / \left[ HY \right] \)

\( = (0.2375)^2 / 0.0125 \) \( \text{(1)} \)

\( K_a = 4.51 \) \( \text{(1)} \)

\text{Allow 4.3 – 4.8}

\text{Ignore units}

\text{CE if \([HY]\) is incorrect} \quad \text{6}

[12]

11. (a) \( \text{pK}_a + \log_{10} K_a \)

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

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

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

\text{pH} = \log \left[ H^+ \right] = 2.00 \quad \text{(1)} \)

\text{or pH} = \frac{1}{2} \log_{10} \left[ HX \right]

\( = 1.86 \) \(-0.142\) = 2.00 \( \text{4} \)

6
(c) Ka \[H^+\] [X⁻]/[HX] \(1\)

\[\text{[HX]} = [X^-] \text{ at half neutralisation } \]

Hence Ka= [H⁺] and pKa = pH \(1\)

(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 \(1\)

\[\begin{align*}
\text{12. (a) (i) } K_a &= \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad (1) \\
\text{(ii) (1) } K_a &= \frac{[H^+]^2}{[CH_3COOH]} \quad (1) \\
& \quad 2 \text{ d.p. essential} \\
\text{If forget } \sqrt{\text{can score (1) and (3) for pH = 5.42}} \quad 5 \\
\text{(b) (i) moles acid } &= \frac{25}{1000} \times 0.220 \quad (1) \times 5.50 \times 10^{-3} \\
& = \frac{x}{10^3} \times 0.150 \\
\therefore \ x &= 25 \times \frac{0.220}{0.150} \text{ or } 5.50 \times 10^{-3} \times \frac{1000}{0.150} \\
& = 36.7 \text{ (or 37) cm}^3 \text{ (or 36.6) } (1) \\
\text{NOT 36 NOR 37.0} \\
\text{units must match} \\
\text{(ii) } \text{Indicator: thymol blue } (1) \\
\text{Explanation: weak acid – strong base } (1) \\
\text{equivalent at pH > 7 } (1) \\
\text{or high pH } 5 \]
(c)  

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

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

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

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

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

If expression wrong no marks for 4 / 5 / 6

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

(5) \( [H^+] = 1.74 \times 10^{-5} \times \frac{(0.170)}{(0.05)} \) 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 pH = 4.12 if \( [\text{acid}] \) upside down; answer 5.29 scores 3

for (1) (2) (3)

13.  

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

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

or 18.75 cm\(^3\)

(b)  

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

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

(iii) phenol red / thymol blue / phenolphthalein / thymolphthalein

i.e. indicator with \( 7 < pK_{in} < 11 \)
(c) (i) Only slightly dissociated (1)  
NOT “not fully dissociated / ionised”

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

\[ \text{NOT} \quad \frac{[H^+]^2}{[HA]} \]

(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

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

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

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

(ii) \[ \text{pH} = -\log [H^+] \] (1)  
or in words or below unless contradiction

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

(b) (i) \[ [OH^-] = 0.150 \]  
\[ \therefore [H^+] = 10^{-14}/0.15 = 6.66 \times 10^{-14} \]  
or pOH = 0.82  
\[ \therefore \text{pH} = 13.18 \] (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)\(^b\)  
\[ \therefore \text{excess moles of OH}^- = 4.5 \times 10^{-4} \] (1)\(^c\)  
\[ \therefore [OH^-] = (4.5(0) \times 10^{-4}) \times 1000/75 \] (1)\(^d\)

\[ [H^+] = \frac{10^{-14}}{6.00 \times 10^{-3}} = 1.66 \times 10^{-12} \] or pOH = 2.22  
\[ \therefore \text{pH} = 11.78 \] (1)\(^f\)  
or 11.77
(c) (i) \[ K_a = \frac{[H^+][X^-]}{[HX]} \] (1)

(ii) \[ [H^+] = 1.80 \times 10^{-2} \times 0.150 = 2.70 \times 10^{-3} \] (1)
\[ K_a = \frac{\left(\frac{2.70 \times 10^{-3}}{0.150}\right)^2}{0.1473} = 4.86 \times 10^{-5} \text{ mol dm}^{-3} \] (1)  
or \[ \frac{\left(\frac{2.70 \times 10^{-3}}{0.1473}\right)^2}{0.150} = 4.95 \times 10^{-5} \]

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
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, d, e, f
If uses excess as acid, max 4 for a, b, d, e, f
If uses excess as acid and no volume, max 2 for a, b

(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

15. (a) Hydrogen bonding (1)
between \( H_2O \) and \( NH_3 \) (1)

(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)

(c) A proton donor (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)
Allow a correct strong acid

(e) (i) \[ K_a = \frac{[H^+][A^-]}{[HA]} \] (1)
\[ = \frac{[H^+]}{0.125 \times 4} \] (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)
16. (a) $K_a = \frac{[H^+][A^-]}{[HA]}$  

(All three sets of square brackets needed, penalise missing brackets or missing charge once in the question)
(Do not penalise extra $[H^+]^2/[HA]$)

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

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

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

$pH = 2.22$  

(must be to 2dp)  

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

(c) (i) pH (almost) unchanged

(Must be correct to score explanation)

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

or acid reacts with salt

or more HA formed

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

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

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

$= 2.57 \times 10^{-4}$  

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

(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)

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

$pK_a = 3.84$  

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

[11]
17. (a) (i) \[ \text{pH} = -\log [\text{H}^+] \] (1)

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

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

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

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

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

using \([HX]\) = 0.12 \( \quad \text{6.30} \div 6.32 \)

using \([HX]\) = 0.12 \( \times 2.75 \ldots \quad \text{6.45} \div 6.47 \)

using 2.8 and \([HX]\) = 0.12 \( \quad \text{6.53} \)

using 2.8 and \([HX]\) = 0.12 \( \times 2.8 \quad \text{6.69} \)

upside down \( K_a \)

(b) (i) Expression for \( K_w \): \( K_w = [\text{H}^+] [\text{OH}^-] \) (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 pOH = 1.35 (1)

\( \therefore \) pH = 12.65 (1) \( \text{must be 2dp in final answer} \)

(c) (i) \( \text{H}_2\text{C}_2\text{O}_4 + \text{OH}^- \rightarrow \text{HC}_2\text{O}_4^- + \text{H}_2\text{O} \) (1)

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

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

\[ [\text{H}_2\text{C}_2\text{O}_4] = 9.36 \times 10^{-4} \times 10^3/25 = 0.0374 \] (1)

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

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

[13]

18. (a) (i) B; 1

C; 1

A; 1

(ii) cresolphthalein

*OR*

thymolphthalein; 1
(b) (i) $-\log[H^+]$;  
(ii) $[H^+] = 1.259 \times 10^{-12}$ (or 1.26 or 1.3) \hspace{1cm} OR \hspace{1cm} pOH = 14 - pH;  
\hspace{1cm} OR \hspace{1cm} $[OH^-] = \frac{10^{-14}}{1.258 \times 10^{-12}} = 2.10$;  
\hspace{1cm} OR \hspace{1cm} $[OH^-] = 7.9(4) \times 10^{-3}$;  
\hspace{1cm} (if $[H^+]$ is wrong allow 1 for $[OH] = \sqrt{KW/[H^+]}$ or as numbers)

(c) (i) $K_a = [H^+]^2/[\text{CH}_3\text{CH}_2\text{COOH}]$  
\hspace{1cm} OR \hspace{1cm} $[H^+]^2/[HA]$ \hspace{1cm} OR \hspace{1cm} $[H^+] = [A^-]$ etc;  
\hspace{1cm} $[H^+] = 1.35 \times 10^{-5}$ or expression without numbers;  
\hspace{1cm} $[H^+] = 1.257 \times 10^{-3}$ \hspace{1cm} pH = 2.90;  
\hspace{1cm} (iii) $K_a = [H^+]$  
\hspace{1cm} OR \hspace{1cm} $pK_a = pH$;  
\hspace{1cm} $pH = 4.87$;  
\hspace{1cm} (penalise 1dp once)

19. (a) $-\log[H^+]$  
\hspace{1cm} $4.57 \times 10^{-3}$  
\hspace{1cm} allow $4.6 \times 10^{-3}$ \hspace{1cm} ecf if [] wrong and already penalised \hspace{1cm} ignore units
(b) (i) \( Ka = \frac{[H^+][X^-]}{[HX]} \) allow HA etc

\[ \text{not } \frac{[H^+]^2}{[HX]} \] but mark on

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

(ii) \( \frac{[H^+]^2}{[HX]} = \frac{(4.57 \times 10^{-3})^2}{0.150} \)

If use \( 4.6 \times 10^{-3} \)

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

= \( 1.39 \times 10^{-4} \)

allow 1.39 – 1.41 \( \times 10^{-4} \) mol dm\(^{-3} \)

(iii) \( pK_a = 3.86 \)

Penalise dp of final answer < or > 2 in pH once in paper 1

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

Mark is for answer (M1) 1

(ii) \( \frac{18}{1000} \times 0.350 = 0.0063 \) or 6.3 \( \times 10^{-3} \)

Mark is for answer (M2) 1

(iii) 0.0144 – 2(0.0063) = 1.80 \( \times 10^{-3} \)

\( M3 \) is for (i) – 2(ii)

If x 2 missed, CE i.e. lose \( M3 \) and the next mark gained 1

(iv) 1.80 \( \times 10^{-3} \times \frac{1000}{48} = 0.0375 \) (0.038)

\( M4 \) is for answer 1

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) \( 10^{-14} / 0.0375 = 10^{-14} / 0.038 \)

\( M5 \) for \( K_w/[OH^-] \)

(= \( 2.66 \times 10^{-13} \) (= \( 2.63 \times 10^{-13} \))

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) \( M6 \)

Allow \( M6 \) consequent AE in \( M5 \) if method OK 1

[13]
20. (a) (i) \[\text{[H}^+\text{] [OH}^-\text{]}\] \[= \log [\text{H}^+]\] 

(ii) \[\text{[H}^+\text{]} = [\text{OH}^-]\] 

(iii) \((2.0 \times 10^{-3}) \times 0.5 = 1.0 \times 10^{-3}\) 

(iv) \[\text{[H}^+] = \frac{4.02 \times 10^{-14}}{1.0 \times 10^{-3}} \] \(= 4.02 \times 10^{-11}\) 
\[\text{pH} = 10.40\] 

(b) (i) \[\text{Ka} = \frac{[\text{H}^+] [\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]}\] 
\[= \frac{[\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}\] 
\[[\text{H}^+] = \sqrt{(1.35 \times 10^{-5}) \times 0.125} \] \(= 1.30 \times 10^{-3}\) 
\[\text{pH} = 2.89\] 

(c) (i) \((50.0 \times 10^{-3}) \times 0.125 = 6.25 \times 10^{-3}\) 
(ii) \((6.25 \times 10^{-3}) - (1.0 \times 10^{-3}) = 5.25 \times 10^{-3}\) 
(iii) \text{mol salt formed} = 1.0 \times 10^{-3}\) 
\[\text{[H}^+] = \text{Ka} \times \frac{[\text{CH}_3\text{CH}_2\text{COOH}]}{[\text{CH}_3\text{CH}_2\text{COO}^-]}\] 
\[= (1.35 \times 10^{-5}) \times \frac{(5.25 \times 10^{-3})/V}{(1.0 \times 10^{-3})/V} \] \(= 7.088 \times 10^{-5}\) 
\[\text{pH} = 4.15\] 

21. (a) Concentration of acid: \(m_1v_1 = m_2v_2\) hence \(25 \times m_1 = 18.2 \times 0.150\) 
OR 
\[\text{moles NaOH} = 2.73 \times 10^{-3}\; \text{; \; \; \; m}_1 = 18.2 \times 0.150/25 = 0.109;\] 

(b) (i) \[K_a = [\text{H}^+] [\text{A}^-] / [\text{HA}] \] \text{not} \[K_a = [\text{H}^+]^2 / [\text{HA}]\] 
(ii) \[\text{pK}_a = -\log K_a;\] 
(iii) \[\text{[A}^-\text{]} = [\text{HA}];\] 
\[\text{hence} \; K_a = [\text{H}^+] [\text{A}^-] / [\text{HA}] = [\text{H}^+];\] 
\[\text{and} -\log K_a = -\log[\text{H}^+];\] 

(c) \[\text{ratio [A}^-\text{]} : [\text{HA}] \text{ remains constant};\] 
\[\text{hence as} \; [\text{H}^+] = K_a \; [\text{HA}] / [\text{A}^-]; \] \[\text{[H}^+\text{]} \text{ remains constant};\]
(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

22. (a) proton or H$^+$ donor (1)
(b) (i) partially ionised or dissociated (1)

(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) 

(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$^-$ or methanoate ion (1)

(iii) $K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$ (1)
allow [OH$_3^-$]

(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) OH$^-$ added (1)
or base
H$^+$ reacts with OH$^-$ (1)
or forming water
More 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
23. (a) \[ \text{HCl(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq) \] (1)

(b) \[ \text{pH} = -\log[\text{H}^+] \] (1)
\[ = -0.10 \pm 0.01 \] (1)

(c) \[ \text{pH} = 7 \] (1)
neutral solution or \[ [\text{H}^+] = [\text{OH}^-] \] (1)

(d) (i) moles H\(^+\) = \( \frac{95}{1000} \) = 0.1197 moles (1)
\[ \text{range} \ 0.120 \pm 0.001 \]

(ii) moles \( \text{OH}^- \) = \( 2 \times 1.37 \times \frac{45}{1000} \) = 0.1233 moles (1)
\[ \text{range} \ 0.123 \pm 0.001 \]

(iii) \[ \text{XS OH}^- = 0.1233 - 0.1197 = 3.6 \times 10^{-3} \text{ moles} \] (1)
\[ \text{range} \ 0.001 \text{ to } 0.005 \]

Volume = 95 + 45 = 140 cm\(^3\) (1)
\[ \therefore [\text{OH}^-] = 3.6 \times 10^{-3} \times \frac{1000}{140} = 0.0257 \text{ M} \] (1)
\[ \text{range} \ 0.0071 \text{ to } 0.0357 \]

\[ \text{K}_w = [\text{H}^+] [\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \] (1)

\[ \therefore [\text{H}^+] = \frac{\text{K}_w}{[\text{OH}^-]} = \frac{10^{-14}}{0.0257} = 3.89 \times 10^{-13} \text{ M} \] (1)
\[ \text{range} \ (0.28 \text{ to } 1.35) \times 10^{-12} \]
\[ \therefore \text{pH} = 12.41 \] (1)
\[ \text{must show } 2 \text{ dp} \quad \text{range} \ 11.87 \text{ to } 12.55 \] 8

[13]
24. (a) only partially dissociated in water

(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\(_2\)O (1)
    Equilibrium moves right
    & HA dissociates, restoring [H\(^+\)] and pH (1)

(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)

25. (a) (i) \( pK_a = -\log_{10} K_a \) (1)

(ii) \( 6.31 \times 10^{-5} \) (1)
    mol dm\(^{-3}\) (1)

(iii) \[ [H^+] = [A^-] \text{ or } K_a = [H^+]^2/[HA] \] (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 × 10.5/1000 = 8.4 × 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\(^-\) → HX (1)
    Equilibrium restored HX ⇌ H\(^+\) + X\(^-\) OR 3
26. (a) **Monoprotic acid**

An acid which gives only one proton (I)

Example

HCl etc (I) 2

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

(ii) 1.58 M (allow 1.6) (I) 2

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

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

Excess OH\(^-\) = 4.5 \times 10^{-4} (I)

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

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

\(\text{pH} = -\log_{10} 1.33 \times 10^{-12} = 11.9\) (I)

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) (I)

**Equation for KOH(s)**

KOH(s) \(\rightarrow\) K\(^+\)(aq) + OH\(^-\)(aq) (I) 2

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

(c) strong base, fully dissociated (I) or [OH\(^-\)] = 0.016 M (I)

\[\text{pH} = -\log_{10}[H^+]\] (I)

\[\therefore \text{pH} = 12.2\] (I)

neutral solution, \(\therefore [H^+] = [OH^-]\) (I)

\[\therefore \text{pH} = 7\] (I) 7

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

\[
\frac{0.012 \times 755}{1000} \text{ mol H}^+ = 9.06 \times 10^{-3} \text{ moles (I)}
\]

\[\therefore \text{moles OH}^- \text{ used for neutralisation} = 9.06 \times 10^{-3}\] (I)

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

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

\[\text{in 755 cm}^3 \text{ there are} \frac{3.98 \times 10^{-3} \times 755}{1000} \text{ mol (I)}\]

\[= 3.0 \times 10^3 \text{ mol (I)}\]

(iii) Total moles = \((9.06 + 3.0) \times 10^{-3} = 0.012 \text{ mol (I)}\)

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

\[\therefore m = 56 \times 0.012 = 0.68\text{g (I)}\] 8

[18]
28. (a) \[ \text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^- (1) \]
\[
\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- (1)
\]
for HF, must have reversible arrow
allow (aq) in HCl equation

(b) (i) \[ \text{pH} = -\log_{10}[\text{H}^+] \text{ or equivalent word definition } (1) \]
allow -\log[H_3O^+] or -\log[H^+(aq)]

(ii) \[ [\text{H}^+] = 0.050 \text{ mol dm}^{-3} \]
\[
\text{pH} = 1.3(0) (1)
\]
if correct definition demonstrated in (ii), but word definition in (i)
wrong, allow mark transfer from (ii) to (i)

(c) (i) \[ K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} (1) \]
do not expression allow with [H_2O]; allow [H_3O^+]
allow consequential mark from wrong equation in (b) providing
[H^+] present

(ii) \[ K_a = \frac{[\text{H}^+]^2}{[\text{HF}]} \text{ or } [\text{H}^+] = \sqrt{K_a[\text{HF}]} (1) \]
\[
[\text{H}^+] = \sqrt{5.6 \times 10^{-4} \times 0.050}
\]
= 0.0053 (1)
\[
\text{pH} = 2.3 / 2.28 (1)
\]
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)

29. (a) (i) proton donor (1)

(ii) partially dissociated (into ions) (not weakly dissociated) (1)

(b) (i) \[ K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} (1) \]
allow either [H_3O^+] or [H^+] in expression
must include charges
if [H_2O] included then no mark

(ii) \[ pK_a = -\log(1.7 \times 10^{-5}) = 4.77 / 4.8 / 4.80 (1) \]
(c) (i) indicator: phenolphthalein (1)
   explanation: weak acid-strong base / pH change above 7.0 (1)
   link between pH change and indicator range (1)
   colourless to red / pink / purple (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) NaOH + CH₃COOH → CH₃COONa + H₂O (1)
   if charges shown they must be correct
   accept H⁺ + OH⁻ → H₂O (1)
   (d) excess acid + NaOH / acid + NaOH = NaEt (1)
   in 2:1 ratio of volumes / 2:1 mol / 1:1 acid: salt (1)
   (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)

30. (a) Weak acid An acid which only partially ionises (1)
   Example Ethanoic, carbonic etc (1)
   (b) Expression \( K_a = \frac{[H^+][A^-]}{[HA]} \) (1)
   Units mol dm⁻³ (or mol l⁻¹) (1)
   (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)
   (d) Resists change in pH (1) on addition of small quantities of acid or base (1)
31. (a) (i) Strong = fully dissociated  )
Weak = partially dissociated  ) in aqueous solution both needed (1)

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

Explanation: HX barely dissociates OR [H\(^+\)] very small (1)
so \([HX]_{\text{eqm}} = [HX] \text{ original (1)} \)
and \([H^+] = [X^-] \) in an aqueous solution of weak acid (1)

(b) (i) moles H\(^+\) in 18 cm\(^3\) = 18 \times 0.16 \times 10^{-3} = 2.88 \times 10^{-3} \text{ (1)}
moles OH\(^-\) in \(V_{\text{equiv}} \text{ cm}^3 = 2 \times \frac{V_{\text{equiv}} \times 0.12 \times 10^{-3}}{2} \) (1)
∴ \(V_{\text{equiv}} \) = \(\frac{18 \times 0.16}{0.12 \times 2} = 12.0 \text{ cm}^3 \text{ (1)} \)

<table>
<thead>
<tr>
<th>Volume/cm(^3) Ba(OH)(_2) solution added</th>
<th>Start</th>
<th>Half equivalence</th>
<th>Equivalence</th>
<th>Double equivalence</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td></td>
<td>6.0</td>
<td>12.0</td>
<td>24.0</td>
</tr>
<tr>
<td>pH for titration of S</td>
<td>0.80</td>
<td>1.22</td>
<td>7</td>
<td>12.84</td>
</tr>
<tr>
<td>pH for titration of W</td>
<td>2.74</td>
<td>4.68</td>
<td>8.5</td>
<td>12.84</td>
</tr>
</tbody>
</table>

(ii) Strong acid S

<table>
<thead>
<tr>
<th>Half-equivalence</th>
<th>Strong acid S</th>
<th>Weak acid W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of base</td>
<td>= 6 cm(^3)</td>
<td>[HX] = [X(^-)] \text{ (given)}</td>
</tr>
<tr>
<td>9 cm(^3) of strong acid S \text{ (1)}</td>
<td>\text{pH} = pK(_a) \text{ or } [H(^+)] = K(_a) \text{ (1)}</td>
<td></td>
</tr>
<tr>
<td>in (18 + 6) cm(^3) = 24 cm(^3) \text{ (1)}</td>
<td>= – log (2.07 \times 10^{-5})</td>
<td></td>
</tr>
<tr>
<td>[H^+] = 9 \times 0.16/24 = 0.06 \text{ M (1)} \text{ (1)}</td>
<td>= 4.68 \text{ (1)}</td>
<td></td>
</tr>
<tr>
<td>\text{pH} = 1.22 \text{ (1)}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2 \times equivalence</th>
<th>Strong acid S</th>
<th>Weak acid W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of base</td>
<td>= 24 cm(^3)</td>
<td>Same as for strong acid S</td>
</tr>
<tr>
<td>12 cm(^3) of base B in excess \text{ (1)}</td>
<td>pH = 12.84 \text{ (1)}</td>
<td></td>
</tr>
<tr>
<td>in (18 + 24) cm(^3) = 42 cm(^3) \text{ (1)}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[OH^-] = 12 \times 2 \times 0.12/42 = 0.069 \text{ M (1)}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[H^+] = K(_w)/[OH(^-)] \text{ (1)}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>\text{pH} = 12.84 \text{ (1)}</td>
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Graph: Sensibly scaled volume axis \text{ (1)}
4 points in text correctly plotted \text{ (–1 for each error) (2)}
vertical portion at equivalence on graph for S \text{ (1)}
single high pH curve for both S and W \text{ (1)}
Weak acid \text{ (W)} has marked pH rise at start \text{ (1)}

[13 Max]
(c) (i) **Buffer Properties**

- resists change in pH (1)
- on adding small amounts of acid or base (1)

**W as a Buffer**

- Plenty of $X^-$ present to mop up $H^+$ (1)
- Plenty of $HX$ present to mop up $OH^-$ (1)

OR 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)

OR correct specific example

[30]
32. (a) \( \text{pH} = -\log[H^+] \) 

\[
K_a = \frac{[H^+]^2}{[\text{CH}_3\text{COOH}]} \quad \text{or} \quad [H^+] = [A^-]
\]

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

\[
\text{pH} = 2.79 \quad \text{(penalise 1 dp or more than 2dp once in the qu)}
\]

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

(ii) \( \text{CH}_3\text{COO}^- + H^+ \rightarrow \text{CH}_3\text{COOH} \)

must show an equation full or ionic in which ethanoate ions are converted to ethanoic acid

(c) (i) \[
[H^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}
\]

if rearrangement incorrect, no further marks

\[
= 1.74 \times 10^{-5} \times \frac{0.15}{0.10}
\]

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

\[
\text{pH} = 4.58
\]

(ii) M1 moles \( H^+ \) added = \( 10 \times 10^{-3} \times 1.0 \) = 0.01

M2 moles ethanoic acid after addition = 0.15 + 0.01 = 0.16

M3 moles ethanoate ions after addition = 0.10 - 0.01 = 0.09

M4 \[
[H^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 1.74 \times 10^{-5} \times \frac{0.16}{0.09}
\]

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

M5 pH = 4.51

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)

\[
\text{pH} \quad \text{pK}_a - \log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}
\]

\[
\text{pK}_a = 4.76
\]

\[
\text{pH} = (4.76 - \log \frac{0.15}{0.10}) = 4.58
\]

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

\[
\text{pH} = 4.76 - \log \frac{0.16}{0.09}
\]