1. (a) The titration is a 1:1 reaction between a weak acid and a strong base.

(i) As acetic acid is a weak acid, \([H_3O^+]\) must be calculated:

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$COOH</th>
<th>$\rightleftharpoons$</th>
<th>H$_3$O$^+$</th>
<th>CH$_3$COO$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.100</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td></td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>final</td>
<td>0.100 - x</td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant $K_a$ is given by:

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-]}{[CH_3COOH]} = \frac{x^2}{(0.100 - x)}$$

As $pK_a = 4.76 = -\log_{10}K_a$, $K_a = 10^{-4.76}$. As $K_a$ is very small, $0.100 - x \sim 0.100$ and hence:

$$x^2 = 0.1 \times 10^{-4.76} \quad \text{or} \quad x = 0.00132 \, \text{M} = [H_3O^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}(0.00132) = 2.88$$

(ii) Addition of the strong base OH$^-$ (aq) leads to the neutralization reaction:

$$\text{CH}_3\text{COOH(aq) + OH}^-(aq) \rightarrow \text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O(l)}$$

The number of moles of CH$_3$COO$^-$ is equal to the number of moles of OH$^-$ (aq) which have been added. The number of moles of CH$_3$COOH remaining is equal to the initial number of moles of CH$_3$COOH minus the number of moles of OH$^-$ (aq) which have been added.

Initially, there is 50.0 mL of 0.100 M CH$_3$COOH so

$$n(\text{CH}_3\text{COOH})_{\text{initial}} = \text{concentration} \times \text{volume} = 0.100 \, \text{M} \times 0.0500 \, \text{L} = 0.00500 \, \text{mol}$$

25.0 mL of 0.100 M NaOH contains

$$n(\text{OH}^-)_{\text{added}} = \text{concentration} \times \text{volume} = 0.100 \, \text{M} \times 0.0250 \, \text{L} = 0.00250 \, \text{mol}$$

Thus, after addition and the neutralization reaction, there are:

$$n(\text{CH}_3\text{COOH}) = n(\text{CH}_3\text{COOH})_{\text{initial}} - n(\text{OH}^-)_{\text{added}} = (0.00500 - 0.00250) \, \text{mol} = 0.00250 \, \text{mol}$$
\[n(\text{CH}_3\text{COO}^-) = n(\text{OH}^-)_{\text{added}} = 0.00250 \text{ mol}\]

These quantities are now in a solution with total volume \((50.0 + 25.0) \text{ mL} = 75.0 \text{ mL}\), so their concentrations are:

\[c(\text{CH}_3\text{COOH}) = \frac{n}{V} = \frac{0.00250 \text{ mol}}{0.0750 \text{ L}} = 0.0333 \text{ M}\]
\[c(\text{CH}_3\text{COO}^-) = \frac{n}{V} = \frac{0.00250 \text{ mol}}{0.0750 \text{ L}} = 0.0333 \text{ M}\]

Using the Henderson-Hasselbalch equation gives

\[
\text{pH} = \text{pK}_a + \log_{10} \left( \frac{\text{[base]}}{\text{[acid]}} \right)
\]
\[= 4.76 + \log_{10} \left( \frac{0.0333 \text{ M}}{0.0333 \text{ M}} \right) = 4.76
\]

At the \(\frac{1}{2}\) equivalence point, when the number of moles of base added is equal to \(\frac{1}{2}\) the number of moles of acid originally present, the pH is equal to the \(\text{pK}_a\).

(iii) 45.0 mL of 0.100 M NaOH corresponds to

\[n(\text{OH}^-)_{\text{added}} = \text{concentration} \times \text{volume}
\]
\[= 0.100 \text{ M} \times 0.0450 \text{ L} = 0.00450 \text{ mol}\]

Thus, after addition and the neutralization reaction, there are:

\[n(\text{CH}_3\text{COOH}) = n(\text{CH}_3\text{COOH})_{\text{initial}} - n(\text{OH}^-)_{\text{added}}
\]
\[= (0.00500 - 0.00450) \text{ mol} = 0.00050 \text{ mol}\]

\[n(\text{CH}_3\text{COO}^-) = n(\text{OH}^-)_{\text{added}} = 0.00450 \text{ mol}\]

These quantities are now in a solution with total volume \((50.0 + 45.0) \text{ mL} = 95.0 \text{ mL}\), so their concentrations are:

\[c(\text{CH}_3\text{COOH}) = \frac{n}{V} = \frac{0.00050 \text{ mol}}{0.0950 \text{ L}} = 0.00526 \text{ M}\]
\[c(\text{CH}_3\text{COO}^-) = \frac{n}{V} = \frac{0.00450 \text{ mol}}{0.0950 \text{ L}} = 0.0474 \text{ M}\]

Using the Henderson-Hasselbalch equation gives

\[
\text{pH} = 4.76 + \log_{10} \left( \frac{0.0474 \text{ M}}{0.00526 \text{ M}} \right) = 5.71
\]

(iv) The addition of 50.0 mL of 0.100 M NaOH corresponds to the equivalence point as the number of moles of added base is equal to the number of moles of acid initially present. However, the pH is not equal to 7 for this point of the titration of a weak acid with a strong base.
50.0 mL of 0.100 M NaOH corresponds 0.00500 mol so whilst this leads to \(n(\text{CH}_3\text{COOH}) = 0.00\) mol, it also leads to \(n(\text{CH}_3\text{COO}^-) = 0.00500\) mol. A solution of a weak base has \(\text{pH} > 7\).

As the total volume is \((50.0 + 50.0)\) mL = 100.0 mL, the concentration of \(\text{CH}_3\text{COO}^-\) is:

\[
c(\text{CH}_3\text{COO}^-) = \frac{n}{V} = \frac{0.00500 \text{ mol}}{0.1000 \text{ L}} = 0.05000 \text{ M}
\]

The calculation of the pH now follows that in Q1(b) with the concentration of 0.05000 M:

\[
K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.05000 - x} = 9.24
\]

As \(pK_b = 9.24\), \(K_b = 10^{-9.24}\). Again, \(K_b\) is very small, \(0.05000 - x \sim 0.05000\) and hence:

\[
x^2 = 0.05000 \times 10^{-9.24} \text{ or } x = 5.36 \times 10^{-6} \text{ M} = [\text{OH}^-]
\]

Hence, the pOH is given by:

\[
pOH = -\log_{10}[\text{OH}^-] = -\log_{10}[5.36 \times 10^{-6}] = 5.27
\]

Finally, \(\text{pH} + \text{pOH} = 14\) so

\[
\text{pH} = 14.0 - 5.27 = 8.73
\]

(v) Beyond the equivalence point, excess base is being added to a solution of a weak base and the pH is controlled by the excess amount of \(\text{OH}^-\)(aq). The calculation of the pH is then exactly the same as in Q3a (vi) from Problem Sheet 7.

55.0 mL of 0.100 M NaOH corresponds to 0.00550 mol. Of this, 0.00500 mol is used to react with the acid. The total volume is \((0.050 + 0.055)\) L = 0.105 L. Hence

\[
[\text{OH}^- (aq)] = \frac{(0.00550 \text{ mol}) - (0.00500 \text{ mol})}{(0.105L)} = 0.00476 \text{ M}
\]

Hence, \(\text{pOH} = -\log_{10}(0.00476) = 2.32\) and \(\text{pH} = 14.00 - 2.32 = 11.7\).

(vi) 75.0 mL of 0.100 M NaOH corresponds to 0.00750 mol. Of this, 0.00500 mol is used to react with the acid and the total volume is \((0.050 + 0.075)\) L = 0.125 L. Hence

\[
[\text{OH}^- (aq)] = \frac{(0.00750 \text{ mol}) - (0.00500 \text{ mol})}{(0.125L)} = 0.0200 \text{ M}
\]

Hence, \(\text{pOH} = -\log_{10}(0.0200) = 1.70\) and \(\text{pH} = 14.00 - 1.70 = 12.3\)
Using these values, the pH curve for the titration can be constructed and is shown below (in pink).

The figure also includes the data from Q4 in Problem Sheet 7 for a strong acid / strong base titration (in blue).

For a weak acid / strong base titration:

(i) The initial pH is higher. For a strong acid and a weak acid with the same concentration, the pH of the strong acid is lower.

(ii) The pH at the ½ equivalence point is equal to the \( pK_a \) of the weak acid.

(iii) At the equivalence point, the solution contains weak base and so the pH > 7.

(iv) After the equivalence point, the pH is determined only the concentration of excess strong base and is thus the same for the two titrations.

2. The concentration of the acid that has dissociated at equilibrium can be calculated from the pH:

<table>
<thead>
<tr>
<th></th>
<th>HA</th>
<th>( \rightleftharpoons )</th>
<th>( H_3O^+ )</th>
<th>( A^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.6</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>( -x )</td>
<td>( +x )</td>
<td>( +x )</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.6 (-x)</td>
<td>( x )</td>
<td>( x )</td>
<td></td>
</tr>
</tbody>
</table>

At equilibrium, \( [H_3O^+] = [H_3O^+]_{\text{from HA}} + [H_3O^+]_{\text{from water}} \). As \( [H_3O^+]_{\text{from water}} \sim 10^{-7} \), it can be assumed that the pH is due to the \( [H_3O^+]_{\text{from HA}} \). Therefore:

\[
\text{pH} = -\log_{10}[H_3O^+] \sim -\log[H_3O^+]_{\text{from HA}} = -\log x = 4.0
\]
so

\[ x = 10^{-4} \text{ M} \]

The initial concentration of HA is 0.6 so at equilibrium \([HA] = 0.6 - 10^{-4} \sim 0.6 \text{ M}\). The percentage dissociation is:

\[
\frac{[H_3O^+]}{[HA]_{\text{equilibrium}}} = \frac{10^{-4}}{0.6} \times 100\% = \frac{10^{-4}}{0.6} \times 100\% = 0.017\%
\]

3. (a) 0.2 M acetic acid

As acetic acid is a weak acid, \([H_3O^+]\) must be calculated:

<table>
<thead>
<tr>
<th></th>
<th>CH₃COOH</th>
<th>H₃O⁺</th>
<th>CH₃COO⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>final</td>
<td>0.2-x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant \(K_a\) is given by:

\[
K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{x^2}{0.2-x}
\]

As \(pK_a = 4.76 = -\log_{10}K_a\) so \(K_a = 10^{-4.76}\). As \(K_a\) is very small, \(0.2 - x \sim 0.2\) and hence:

\[x^2 = 0.2 \times 10^{-4.76}\quad \text{or} \quad x = 0.0019 \text{ M} = [H_3O^+]\]

Hence, the pH is given by:

\[\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}[0.0019] = 2.7\]

(b) 0.2 M sodium acetate

As CH₃COO⁻ is a weak base, \([OH^-]\) must be calculated in a similar way:

<table>
<thead>
<tr>
<th></th>
<th>CH₃COO⁻</th>
<th>H₂O</th>
<th>OH⁻</th>
<th>CH₃COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.2</td>
<td>large</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>negligible</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>final</td>
<td>0.2-x</td>
<td>large</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant \(K_b\) is given by:

\[
K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = \frac{x^2}{0.2-x}
\]
For an acid and its conjugate base:

\[ pK_a + pK_b = 14.00 \]

so

\[ pK_b = 14.00 - 4.76 = 9.24 \]

As \( pK_a = 4.76 \), \( K_b = 10^{9.24} \). Again, \( K_b \) is very small, \( 0.2 - x \sim 0.2 \) and hence:

\[ x^2 = 0.2 \times 10^{-9.24} \quad \text{or} \quad x = 0.00001 \text{ M} = [OH^-] \]

Hence, the \( pOH \) is given by:

\[ pOH = -\log_{10}[OH^-] = -\log_{10}[0.00001] = 5.0 \]

Finally, \( pH + pOH = 14.0 \) so

\[ pH = 14.0 - 5.0 = 9.0 \]

(c) A buffer that is 0.2 M in acetic acid and 0.2 M in sodium acetate

This solution contains an acid and its conjugate base so the Henderson-Hasselbalch equation can be used:

\[ pH = pK_a + \log_{10} \left( \frac{\text{[base]}}{\text{[acid]}} \right) \]

As \([\text{acetic acid}] = [\text{sodium acetate}], \log_{10} \left( \frac{\text{[base]}}{\text{[acid]}} \right) = \log_{10}(1) = 0 \) and so

\[ pH = pK_a = 4.76 \]

4. The Henderson-Hasselbalch equation can be used for this buffer:

\[ pH = pK_a + \log_{10} \left( \frac{\text{[base]}}{\text{[acid]}} \right) \]

where \([\text{[base]} = [\text{KNO}_2] \text{ and } [\text{[acid]} = [\text{HNO}_2]. \text{ If } K_a \text{ for } HNO_2 = 4.00 \times 10^{-4} \text{ M,} \]

\[ pK_a = -\log_{10}(4.00 \times 10^{-4}) = 3.40 \]

Hence,

\[ \log_{10} \left( \frac{\text{[base]}}{\text{[acid]}} \right) = 3.00 - 3.40 = -0.40 \]

or
\[
\frac{[\text{base}]}{[\text{acid}]} = 10^{-0.40} = 0.40
\]

As the concentrations of the acid and base are the same, the volume of base must be \(0.40 \times\) volume of acid. The volumes must add to give 1L:

0.71 L of HNO\(_2\) and 0.29 L of KNO\(_2\).

5. (a) Na\(_2\)O

\[\text{Na}_2\text{O(s) + H}_2\text{O(l) } \rightarrow 2\text{Na}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) - \text{basic}\]

(b) Cl\(_2\)O\(_7\)

\[\text{Cl}_2\text{O}_7\text{(l) + 3H}_2\text{O(l) } \rightarrow 2\text{ClO}_4^-(\text{aq}) + 2\text{H}_3\text{O}^+(\text{aq}) - \text{acidic}\]