Chemistry AS 91392
Titration Calculations
In order to graph a titration curve there are a number of points that need to be calculated in their specific order:

1. The pH before any base is added
2. The volume of the base at equivalence point
3. The volume of base when pH = pKa
4. The pH at equivalence point
5. The pH after all of the base has been added

**Question:**

20.0 mL of 0.0896 mol L⁻¹ ethanoic acid is titrated with 0.100 mol L⁻¹ sodium hydroxide up to a total of 30mL pKₐ (CH₃COOH) = 4.76
Find the pH of:

\[ \text{CH}_3\text{COOH} \text{ (aq)} \rightarrow \text{CH}_3\text{COO}^- \text{ (aq)} + \text{H}_3\text{O}^+ \text{ (aq)} \]

\[ \text{CH}_3\text{COOH} \text{ (aq)} + \text{H}_2\text{O} \text{ (l)} \rightleftharpoons \text{CH}_3\text{COO}^- \text{ (aq)} + \text{H}_3\text{O}^+ \text{ (aq)} \]

\[ K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 10^{-pK_a} \]

\[ = 10^{-4.76} \]

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

Assume

1. \[ [\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+] \]
2. \[ [\text{CH}_3\text{COOH}] = 0.0896 \text{ mol L}^{-1} \]
Step One: Start pH

Equilibrium expression of acid dissociation in water

\[
K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{1.74 \times 10^{-5}}{0.0896 \text{ mol L}^{-1}}
\]

Rearrange:

\[
\sqrt{1.74 \times 10^{-5} \times 0.0896 \text{ mol L}^{-1}} = [\text{H}_3\text{O}^+]
\]

\[
1.25 \times 10^{-3} \text{ mol L}^{-1} = [\text{H}_3\text{O}^+]
\]

Could also use \(10^{-\text{P}k_a}\) in formula

\[
\text{pH} = -\log (1.25 \times 10^{-3} \text{ mol L}^{-1}) = 2.90
\]
Step Two: Calculate the volume of NaOH at the endpoint.

Titration reaction is:

\[
\text{CH}_3\text{COOH}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{CH}_3\text{COONa}_{(aq)} + \text{H}_2\text{O}_{(l)}
\]

\[
n(\text{CH}_3\text{COOH}) = cV
\]

\[
= 0.0896 \text{ mol L}^{-1} \times 0.0200 \text{L}
\]

\[
= 1.79 \times 10^{-3} \text{ mol}
\]

\[
n(\text{NaOH}) = n(\text{CH}_3\text{COOH})
\]

\[
= 1.79 \times 10^{-3} \text{ mol}
\]

\[
V(\text{NaOH}) = \frac{n}{c}
\]

\[
= \frac{1.79 \times 10^{-3} \text{ mol}}{0.100 \text{ molL}^{-1}}
\]

\[
V(\text{NaOH}) = 17.9 \text{mL}
\]

Volume of acid at start

From equation 1 mol acid = 1 mole base
Step Three: Mid-point of Buffer

Calculate the volume of NaOH when pH = pKa

The volume of NaOH at equivalence point is 17.9mL

17.9mL /2 = 8.96mL (x)
pKa = 4.76 (y)

The pH = pKa when 8.96 mL of NaOH has been added

The buffer zone will be 1 pH point above and below pH 4.76

Once the curve is drawn this can be sketched as a circle around the area from 3.76 – 5.76 on the line.
Step Four: pH of equivalence

Calculate the pH at equivalence point. At the Equivalence point we will have:

- 1.79 x 10^{-3} \text{ mol} \text{ of } \text{CH}_3\text{COONa} \text{ in 37.9 mL of solution}

\[ C(\text{CH}_3\text{COONa}) = \frac{1.79 \times 10^{-3} \text{ mol}}{0.0379 \text{ L}} = 0.0472 \text{ mol L}^{-1} \]

We need to calculate the pH of a solution of \text{CH}_3\text{COONa} with this concentration: 0.0472 \text{ mol L}^{-1}

Use same mol of conjugate base as base calculated from step 2. as they are produced 1 mol = 1 mol
Step Four: pH of equivalence

\[
\text{CH}_3\text{COO}^-_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{CH}_3\text{COOH}_{(aq)} + \text{OH}^-_{(aq)}
\]

\[
K_b = \frac{1 \times 10^{-14}}{K_a}
\]

\[
K_b = \frac{1 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.75 \times 10^{-10}
\]

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

Assume

1. \([\text{CH}_3\text{COOH}] = [\text{OH}^-]

2. \([\text{CH}_3\text{COO}^-] = 0.0472 \text{ mol L}^{-1}

Concentration calculated from previous step \(c = \frac{n}{v}\)
Step Four: pH of equivalence

\[
K_b = \frac{[\text{OH}^-]^2}{c(\text{conj base})}
\]

\[
5.75 \times 10^{-10} = \frac{[\text{OH}^-]^2}{0.0472 \text{ molL}^{-1}}
\]

\[
\sqrt{5.75 \times 10^{-10} \times 0.0472} = [\text{OH}^-]
\]

\[
5.21 \times 10^{-6} \text{ molL}^{-1} = [\text{OH}^-]
\]

\[
[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}
\]

\[
[\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{5.21 \times 10^{-6} \text{ molL}^{-1}}
\]

\[
[\text{H}_3\text{O}^+] = 1.92 \times 10^{-9} \text{ molL}^{-1}
\]

\[
\text{pH} = -\log (1.92 \times 10^{-9} \text{ molL}^{-1})
\]

\[
\text{pH} = 8.72
\]
Although the CH₃COONa formed hydrolyses slightly in water, the [OH⁻] from this reaction is very small compared to the [OH] from the NaOH so we assume all [OH⁻] comes from NaOH.

Calculate the pH after 30mL of NaOH has been added.

Since the equivalence point is at 17.9mL of NaOH, this results in an excess of 12.1mL of NaOH.

Total volume of solution = 20mL + 30mL = 50mL

\[ C(\text{NaOH}) = \frac{12.1 \text{mL}}{50 \text{mL}} \times 0.100 \text{molL}^{-1} \]

\[ = 0.0242 \text{ molL}^{-1} \]

(30mL - 17.9mL = 12.1mL)
Step Five: Final pH

NaOH is a strong base

Assume \([\text{OH}^-] = c(\text{NaOH})\)

\([\text{OH}^-] = 0.0242 \text{ molL}^{-1}\)

\([\text{H}_3\text{O}^+] = \frac{K_w}{0.0242 \text{ molL}^{-1}}\)

\([\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{0.0242 \text{ molL}^{-1}}\)

\([\text{H}_3\text{O}^+] = 4.13 \times 10^{-13} \text{ molL}^{-1}\)

\(\text{pH} = \log(4.13 \times 10^{-13} \text{ molL}^{-1})\)

\(\text{pH} = 12.4\)
Now we have the key data points:

- The pH before any Base added = 2.90
- The volume of NaOH at equivalence point: 17.9 mL
- The volume of NaOH when pH = pKa: 8.96 mL
- The pH at equivalence point: 8.72
- The pH after 30mL of NaOH is added: 12.4
Plot these points on a graph

<table>
<thead>
<tr>
<th>Volume (mL)</th>
<th>pH</th>
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<tbody>
<tr>
<td>0.00</td>
<td>2.90</td>
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<tr>
<td>8.96</td>
<td>4.76</td>
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<tr>
<td>17.9</td>
<td>8.72</td>
</tr>
<tr>
<td>30.0</td>
<td>12.4</td>
</tr>
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</table>

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