Calculating pH Changes During Titrations

In practice, the pH changes that occur during a titration process would be *measured* using a calibrated pH meter. However, calculating such values is a good test of your understanding of the theories surrounding the study of acids and bases.

In general, you would be expected to calculate the pH value at:
(a) The start of the reaction
(b) At various points between the start of the reaction and the end-point
(c) At the end-point
(d) At various points after the end-point until a large excess of titrant has been added.

Also, you can expect to be asked to do this for either a strong acid (e.g. $HCl(aq)$) or a weak acid (e.g. $CH_3COOH(aq)$) being titrated against a strong base (e.g. $NaOH(aq)$).

For a Strong Acid against a Strong Base
25.00 cm³ of 0.100 mol dm⁻³ hydrochloric acid is titrated against 0.080 mol dm⁻³ sodium hydroxide solution at 25°C. Calculate the pH of the reaction mixture
(a) at start of the reaction
(b) at the end-point
(c) at each 5.00cm³ addition of sodium hydroxide up to the end-point
(d) at each 5.00cm³ addition of sodium hydroxide after the end-point until a two-fold excess has been added.

(a) $HCl(aq)$ is a strong acid and therefore fully ionized in solution.
Since $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

the molar concentration of H^+ equals the initial concentration of HCl because one mole ionizes to form one mole of H^+ ions.
Hence, $[H^+(aq)] = 0.100$ mol dm⁻³
Hence, starting pH = $-\log_{10}[H^+(aq)] = -\log_{10}(0.100) = $ **1.00**

(b) The reaction equation is:
$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
Since the product, sodium chloride, does not react with water the pH at the end-point will be that of pure water at 25°C.
Hence, the pH at the end-point is **7.00**

(c) The reaction equation is:
$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
Number of moles of HCl titrated = $\dfrac{0.100 \times 25.00}{1000} = 2.50 \times 10^{-3}$

Hence, the number of moles of NaOH needed to reach end-point = 2.50×10^{-3} because the reaction ratio is 1:1.
Hence, the volume of 0.080 mol dm⁻³ NaOH required to reach the end-point
$= \dfrac{2.50 \times 10^{-3}}{0.080} \times 1000 \text{ cm}^3 = 31.25 \text{ cm}^3.$

This means we need to calculate the pH after additions of 5.00, 10.00, 15.00, 20.00, 25.00 and 30.00cm³ of sodium hydroxide solution.

This is *not* six separate calculations. One general formula can be derived and then used six times to quickly find the pH values. This is done as follows:
Suppose V cm³ of 0.08 mol dm⁻³ NaOH has been added.
➔ $0.08 \times V / 1000$ moles NaOH has been added
➔ $0.00008V$ moles NaOH has been added
➔ $0.00008V$ moles HCl has reacted since they react in a 1:1 ratio
➔ $(0.0025 - 0.00008V)$ moles HCl remains in the titration mixture

Also, the total volume of the mixture has become $(25.00 + V)$ cm³

➔ [HCl] in the titration mixture
$= [(0.0025 - 0.00008V) / (25.00 + V)] \times 1000$
$= [(2.5 - 0.08V) / (25.00 + V)]$

➔ Since HCl is fully ionized, $[H^+]$ in the titration mixture
$= [(2.5 - 0.08V)/(25.00 + V)]$

➔ the pH of the titration mixture after adding V cm³ 0.08 mol dm⁻³ NaOH is given by : $-\log_{10}[(2.5 - 0.08V)/(25.00 + V)]$

NB This formula applies only for volumes *LESS* than that required to reach the end-point. Note it also confirms the calculation of the starting pH.

We can now substitute the various values of "V" to obtain the pH values required (try setting up a spreadsheet to do it for you!). This gives:

V / cm³	0.00	5.00	10.00	15.00	20.00	25.00	30.00
pH	1.00	1.15	1.31	1.49	1.70	2.00	2.74

(d) Once past the end-point, the task becomes that of calculating the pH created by the excess NaOH, allowing for its dilution as it is added to the titration mixture.

We need to calculate the pH after additions of 35.00, 40.00, 45.00, 50.00, 55.00, 60.00 and 65.00cm³ of sodium hydroxide solution.

Suppose V cm³ of 0.080 mol dm⁻³ NaOH has been added.
➔ $0.080 \times V / 1000$ moles NaOH has been added
➔ $0.00008V$ moles NaOH has been added
➔ 0.0025 moles NaOH has reacted since 0.0025 moles of HCl was used and they react in a 1:1 ratio
➔ $(0.00008V - 0.0025)$ moles NaOH remains in the titration mixture

Also, the total volume of the mixture has become $(25.00 + V)$ cm³
➔ [NaOH] in the titration mixture
$= [(0.00008V - 0.0025) / (25.00 + V)] \times 1000$
$= [(0.08V - 2.5) / (25.00 + V)]$
➔ Since NaOH is fully ionized, $[OH^-]$ in the titration mixture
$= [(0.08V - 2.5) / (25.00 + V)]$
➔ $[H^+]$ in the titration mixture
$= K_w / [OH^-] = [1.00 \times 10^{-14}] / [(0.08V - 2.5) / (25.00 + V)]$
➔ the pH of the titration mixture after adding V cm³ 0.08 mol dm⁻³ NaOH is given by
$-\log_{10}([1.00 \times 10^{-14}] / [(0.08V - 2.5) / (25.00 + V)])$

NB This formula applies only for volumes *GREATER* than that required to reach the end-point.

We can now substitute the various values of "V" to obtain the pH values required (try that spreadsheet again!). This gives:

V / cm^3	pH
35.00	11.70
40.00	12.03
45.00	12.20
50.00	12.30
55.00	12.38
60.00	12.43
65.00	12.48

When plotted, these and the earlier calculated pH values show very good agreement with those obtained experimentally.

pH Changes for Hydrochloric Acid vs Sodium Hydroxide
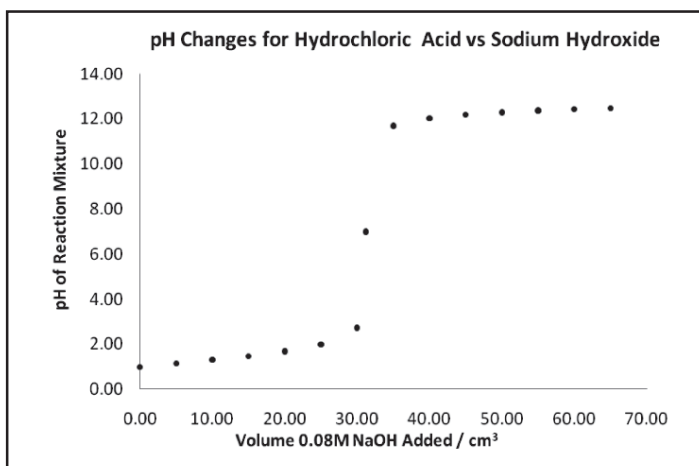
For a Weak Acid against a Strong Base

25.00 cm^3 of 0.0.090 mol dm^{-3} ethanoic is titrated against 0.100 mol dm^{-3} sodium hydroxide solution at 25°C. Calculate the pH of the reaction mixture
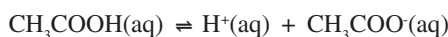*(a) at start of the reaction*
(b) at the end-point
(c) at each 5.00cm^3 addition of sodium hydroxide up to the end-point
(d) at each 5.00cm^3 addition of sodium hydroxide after the end-point until a two-fold excess has been added.

K_a for ethanoic acid is 1.85 x 10^{-5} mol dm^{-3} at 25°C.

(a) CH_3COOH is a weak acid and therefore only partially ionized in solution. Since

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

K_a needs to be used to calculate [H^+], and hence the pH.
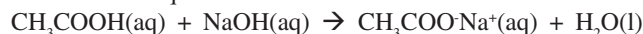
Using the standard approximation $K_a = [H^+]^2 / [CH_3COOH]$

NB This approximation is only valid at the start of the titration because, after that, significant amounts of CH_3COO^- are present as a result of the reaction occurring between CH_3COOH and NaOH.

$[H^+] = \sqrt{K_a \times [CH_3COOH]} = \sqrt{1.85 \times 10^{-5} \times 0.090} = 1.29 \times 10^{-3}$ mol dm^{-3}

Hence, starting pH = $-\log_{10}[H^+(aq)]$ = $-\log_{10}(1.29 \times 10^{-3})$ = **2.89**

(b) The reaction equation is:
$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COO^-Na^+(aq) + H_2O(l)$$
Number of moles of CH_3COOH titrated
$= 0.090 \times 25.00 / 1000 = 2.25 \times 10^{-3}$

Hence, the number of moles of NaOH needed to reach end-point = 2.25×10^{-3} because the reaction ratio is 1:1.

Hence, the volume of 0.100 mol dm^{-3} NaOH required to reach the end-point
$= (2.25 \times 10^{-3} / 0.100) \times 1000$ cm^3 = 22.50 cm^3.

Since the product, sodium ethanoate, reacts with water, the pH at the end-point will **not** be that of pure water at 25°C.
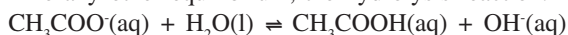
The ethanoate ion is hydrolysed in aqueous solution. It reacts as follows:
$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \mathbf{OH^-(aq)}$$
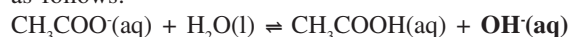
The presence of the excess of OH$^-$ ions at the end-point causes the pH to be *above 7*. It remains now to calculate its actual value.

Note : It is very unlikely that you would be expected to do this part of the calculation in any examination. However, it provides an opportunity to apply some familiar ideas to an unfamiliar situation. Also, it demonstrates why phenolphthalein (active range 8-10) is suitable for this titration but methyl orange, (active range 4-6), is not.

Like any other equilibrium, the hydrolysis reaction:
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
has a K_c expression given by

$$K_c = \frac{[CH_3COOH] \times [OH^-]}{[CH_3COO^-]}$$

In this expression, [OH$^-$] can be replaced by $K_w / [H^+]$.

$$K_c = \frac{[CH_3COOH] \times K_w / [H^+]}{[CH_3COO^-]}$$

Hence, $K_c = \dfrac{[CH_3COOH] \times K_w}{[H^+] \times [CH_3COO^-]} = \dfrac{K_w}{K_a} = \dfrac{1.00 \times 10^{-14}}{1.85 \times 10^{-5}} = 5.41 \times 10^{-10}$ mol dm^{-3}

We can now use this K_c to find the end-point pH.

$$K_c = \frac{[CH_3COOH] \times [OH-]}{[CH_3COO^-]} = \frac{[OH^-]^2}{[CH_3COO^-]}$$

since at the end-point, [CH_3COOH] = [OH-]

Hence, [OH-] = $\sqrt{K_c \times [CH_3COO^-]}$

We know K_c but need to find [CH_3COO^-].

2.25×10^{-3} moles of CH_3COOH were titrated
→ 2.25×10^{-3} moles of CH_3COO^- were formed at the end-point
→ $[CH_3COO^-] = \dfrac{2.25 \times 10^{-3}}{(TOTAL\ volume)} \times 1000$
$= \dfrac{2.25 \times 10^{-3}}{(25.00 + 22.50)} \times 1000$
$= 0.0474$ mol dm^{-3}

Hence, [OH$^-$] = $\sqrt{5.41 \times 10^{-10} \times 0.0474}$ = 5.064×10^{-6} mol dm^{-3}

Hence, [H$^+$] = $\dfrac{K_w}{[OH^-]} = \dfrac{1.00 \times 10^{-14}}{5.064 \times 10^{-6}} = 1.975 \times 10^{-9}$ mol dm^{-3}

Hence, pH at the end-point = $-\log_{10}(1.975 \times 10^{-9})$ = **8.70**

(c) We have already shown that the volume of 0.100 mol dm^{-3} NaOH required to reach the end-point is 22.50 cm^3.

This means we need to calculate the pH after additions of 5.00, 10.00, 15.00 and 20.00 cm^3 of sodium hydroxide solution. Again, one general formula can be derived and then used to quickly find the pH values. This is done as follows:

Suppose V cm^3 of 0.100 mol dm^{-3} NaOH has been added.
➔ $0.100 \times V / 1000$ moles NaOH has been added
➔ $0.00010V$ moles NaOH has been added
➔ $0.00010V$ moles CH_3COOH has reacted since they react in a 1:1 ratio
➔ $(0.00225 - 0.00010V)$ moles CH_3COOH remains in the titration mixture

Also, the total volume of the mixture has become $(25.00 + V)$ cm^3
➔ $[CH_3COOH]$ in the titration mixture
$= [(0.00225 - 0.00010V) / (25.00 + V)] \times 1000$
$= [(2.25 - 0.10V) / (25.00 + V)]$

Also, $0.00010V$ moles NaOH has been added
➔ $0.00010V$ moles CH_3COO^- has been formed
➔ $[CH_3COO^-]$ in the titration mixture
$= [(0.00010V) / (25.00 + V)] \times 1000$
$= [(0.10V) / (25.00 + V)]$

$$K_a = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]}$$

➔ $$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]}$$

$$= \frac{1.85 \times 10^{-5} \times [(2.25 - 0.10V) / \cancel{(25.00 + V)}]}{[(0.10V) / \cancel{(25.00 + V)}]}$$

➔ **pH = -log$_{10}$ [1.85 × 10^{-5} × (2.25 - 0.10V) / 0.10V]**

<u>NB</u> Again, this formula applies only for volumes *LESS* than that required to reach the end-point.

We can now substitute the various values of "V" to obtain the pH values required (again, try setting up a spreadsheet to do it for you!). This gives:

V / cm^3	5.00	10.00	15.00	20.00
pH	4.19	4.64	5.03	5.64

(d) Once past the end-point, the task again becomes that of calculating the pH created by the excess NaOH, allowing for its dilution as it is added to the titration mixture. The formula is analogous to that derived before expect that 0.08 mol dm^{-3} now becomes 0.10 mol dm^{-3}.

i.e. The pH of the titration mixture after adding V cm^3 0.10 mol dm^{-3} NaOH is given by

–log$_{10}$ [1.00 × 10^{-14}] / [(0.10V - 2.25)/ (25.00 + V)]

We need to calculate the pH after additions of 25.00, 30.00, 35.00, 40.00 and 45.00cm^3 of sodium hydroxide solution.

We can now substitute these values of "V" to obtain the pH values required (try that spreadsheet again!). This gives:

V / cm^3	pH
25.00	11.70
30.00	12.12
35.00	12.30
40.00	12.40
45.00	12.47

Again, when plotted, these and the earlier calculated pH values show very good agreement with those obtained experimentally.

pH Changes for Ethanoic Acid vs Sodium Hydroxide
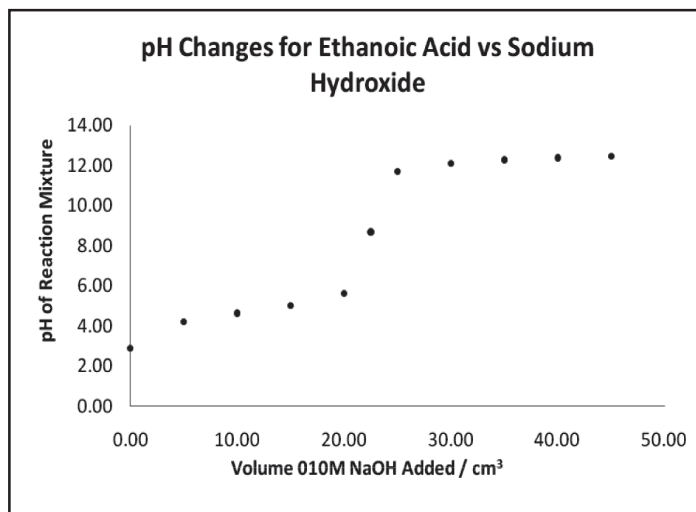
Practice Questions

25.00cm^3 of 0.100 mol dm^{-3} methanoic acid (HCOOH) is titrated against 0.100 mol dm^{-3} sodium hydroxide. If K_a is 2.00×10^{-4} mol dm^{-3}, calculate:
(a) the pH of the acid before titration begins
(b) the pH after addition of 10.00 and 20.00 cm^3 of NaOH
(c) the pH after addition of 30.00 and 40.00 cm^3 of NaOH

Answers
(a) 2.35
(b) 3.52 and 4.30
(c) 11.95 and 12.34