

Titration of weak acid with strong base

Remember:

- Before adding the base: It is a weak acid HA (K_a)
- After adding the base: It is a buffer: $\text{pH} = \text{p}K_a + \log [\text{base}]/[\text{acid}]$
- At half the volume of the equivalence point: $[\text{base}] = [\text{acid}]$ or $[\text{A}^-] = [\text{HA}]$
 - $\text{pH} = \text{p}K_a$
 - So, $[\text{H}^+] = K_a$
 - Buffer is most effective
- At the equivalence point: It is a weak base ($K_b = 10^{-14}/K_a$)
 - pH is governed by the concentration of the buffer base (A^-)
 - pH at the equivalence point is greater than 7 ($\text{pH} > 7$).
- After the equivalence point: It is a strong base.
- $[\] = \text{moles} / \text{Volume (L)}$

Note: For the titration of weak base with a strong acid. The pH at the equivalence point is lower than 7 ($\text{pH} < 7$)

Indicator: $\text{pH} = \text{p}K_a \pm 1$

The $\text{p}K_a$ of the weak acid to be used in the buffer should be as close as possible to the desired pH.

$\text{pH} = \text{p}K_a + \log [\text{base}]/[\text{acid}]$. For most effective buffer: $[\text{base}]/[\text{acid}] = 1$

Case Study

50 ml (0,05 l) of 0.1M acetic acid solution ($\text{HC}_2\text{H}_3\text{O}_2$, $K_a = 1.8 \times 10^{-5}$) with 0.1 M NaOH.

1) First calculate the volume of the base needed for the equivalence point:

$$\begin{aligned} M \text{ acid} \times V \text{ acid} &= M \text{ base} \times V \text{ base} \\ 0.1 \times 50 &= 0.1 \times V \text{ base} \\ V \text{ base} &= 50 \text{ ml} \end{aligned}$$

So, we need 50 ml of NaOH to completely neutralize the 50 mL of acetic acid.

2) At a volume half the volume of the equivalence point, $\text{pH} = \text{p}K_a$

$$\text{So, at 25 ml, } \text{pH} = \text{p}K_a = -\log K_a = -\log 1.8 \times 10^{-5}$$

3) Calculate the moles of the acid;

$$\begin{aligned} \text{Moles of } \text{HC}_2\text{H}_3\text{O}_2 &= \text{moles of } \text{H}^+ = \text{Volume} \times \text{Molarity} \\ &= 0.05 \times 0.1 = 0.005 \text{ moles} \end{aligned}$$

A) No base is added:

It is a weak acid

| | | | | |
|-------------|-----------------------------------|---|------------------------------------|----------------|
| | $\text{HC}_2\text{H}_3\text{O}_2$ | = | $\text{C}_2\text{H}_3\text{O}_2^-$ | + H^+ |
| Initial | 0.1 | | | |
| Change | - X | | X | X |
| Equilibrium | 0.1 - X | | X | X |

$$K_a = x^2 / 0.1$$

$$X = 1.3 \times 10^{-3} \text{ M}$$

$$\text{pH} = \mathbf{2.87}$$

B) Add 10 mL of 0.1 M NaOH:

Calculate the moles of NaOH = Molarity x Volume (L)
 $= 0.1 \times 0.01 = 0.001 \text{ mole}$

Mole of $\text{HC}_2\text{H}_3\text{O}_2 = 0.005 \text{ mole}$

Total volume is: $50 + 10 = 60 \text{ ml} = 0.060 \text{ Liter}$

| | | | | | | | |
|-----------------|-----------------------------------|---|---------------|---|------------------------------------|---|----------------------|
| | $\text{HC}_2\text{H}_3\text{O}_2$ | + | OH^- | = | $\text{C}_2\text{H}_3\text{O}_2^-$ | + | H_2O |
| Before reaction | 0.005 mole | | 0.001 | | | | |
| After reaction | $0.005 - 0.001$ | | 0 | | 0.001 | | |
| | = 0.004 mole | | | | 0.001 | | |
| [] : | $0.004 / 0.06$ | | | | $0.001 / 0.06$ | | |

Buffer: $\text{pH} = \text{pK}_a + \log [\text{base}]/[\text{acid}] = -\log 1.8 \times 10^{-5} + \log (0.001/0.06) \times (0.06/0.004)$

$$\text{pH} = \mathbf{4.14}$$

C) Add 25 mL of NaOH

Half the volume of the equivalence point: $\text{pH} = \text{pK}_a$
So, $[\text{H}^+] = K_a$

D) Add 40 mL of NaOH

$$\text{pH} = 5.35$$

$$K_b = 10^{-14}/K_a$$

$$K_b = 10^{-14}/1.8 \times 10^{-5}$$

$$K_b = 5.6 \times 10^{-10}$$

$$K_b = x^2 / 0.05$$

$$X = 5.3 \times 10^{-6} = [\text{OH}^-]$$

$$\text{pH} = 14 - \text{pOH} = \mathbf{8.72}$$

F) Add 60 mL of 0.1 M NaOH

Calculate the moles of NaOH = Molarity x Volume (L)
 $= 0.1 \times 0.06 = 0.006$ mole

Mole of $\text{HC}_2\text{H}_3\text{O}_2 = 0.005$ mole

Total volume is: $50 + 60 = 110$ ml = 0.11 Liter



Before reaction 0.005 mole 0.006

After reaction 0.005 - 0.005
 $= 0$ mole 0.006 - 0.005
 $= 0.001$

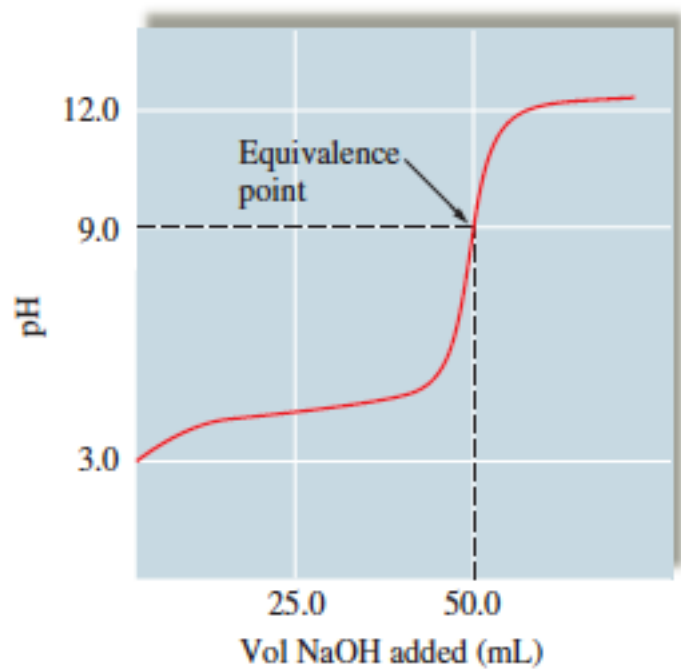
[.] : 0.001/0.11 = 9.1×10^{-3} M

$$[\text{OH}^-] = 9.1 \times 10^{-3} \text{ M}$$

$$\text{pH} = 14 - \text{pOH} = \mathbf{11.96}$$

G) Add 75 mL of 0.1 M NaOH

$$\text{pH} = 14 - \text{pOH} = \mathbf{12.3}$$



Titration of strong acid with strong base.

Titration of 50 mL (0.05 L) of 0.200 M HNO_3 with 0.100 M solution of NaOH.

[] = Molarity = Moles / Volume (L)

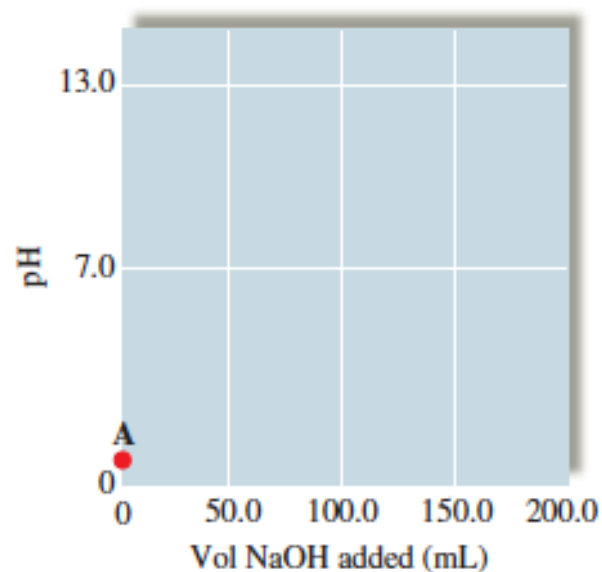
Moles = Molarity x Volume (L)

Moles of HNO_3 = moles of H^+ = Volume x Molarity = $0.05 \times 0.2 = 0.01$ moles

A) No NaOH was added

1) $[\text{HNO}_3] = [\text{H}^+] = 0.2 \text{ M}$,

$$\text{pH} = -\log [\text{H}^+] = -\log 0.2 = \mathbf{0.699}$$



B) Add 10 mL (0.01L) of 0.1 M NaOH

Moles of NaOH = Volume (l) x Molarity = 0.01 x 0.1 = 0.001 moles of OH⁻

Total volume: 0.05 + 0.01 = 0.06 Liter = V_t

Moles of HNO₃ = 0.01 moles of H⁺



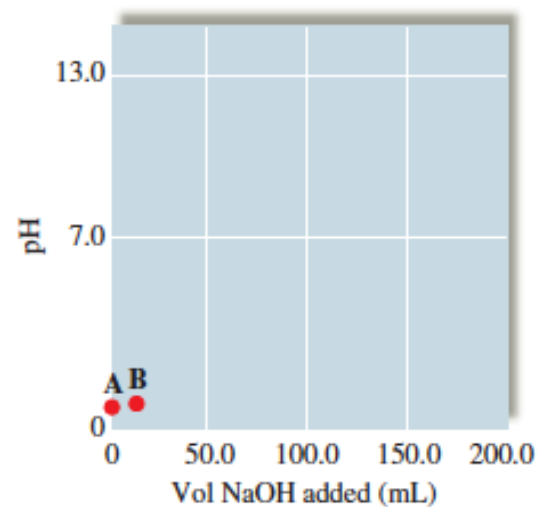
Before addition 0.01 0.001

After addition 0.01-0.001 0

0.009 moles

[H⁺] = moles/V_t 0.009/0.06 = 0.15 M

pH = -log [H⁺] = -log 0.15 = **0.82**



C) Add 20 mL (0.02 L) of 0.1 M NaOH

Moles of NaOH = Volume (l) x Molarity = 0.02 x 0.1 = 0.002 moles of OH⁻

Total volume: 0.05 + 0.02 = 0.07 Liter = V_t

Moles of HNO₃ = 0.01 moles H⁺

| | H ⁺ | + | OH ⁻ | =. | H ₂ O |
|--|-------------------------------|---|-----------------|----|------------------|
| Before addition | 0.01 | | 0.002 | | |
| After addition | 0.01-0.002 | | 0 | | |
| | 0.008 moles | | | | |
| [H⁺] = moles/V_t | 0.008/0.07 = 0.11 M | | | | |
| | pH = -log 0.11 = 0.942 | | | | |

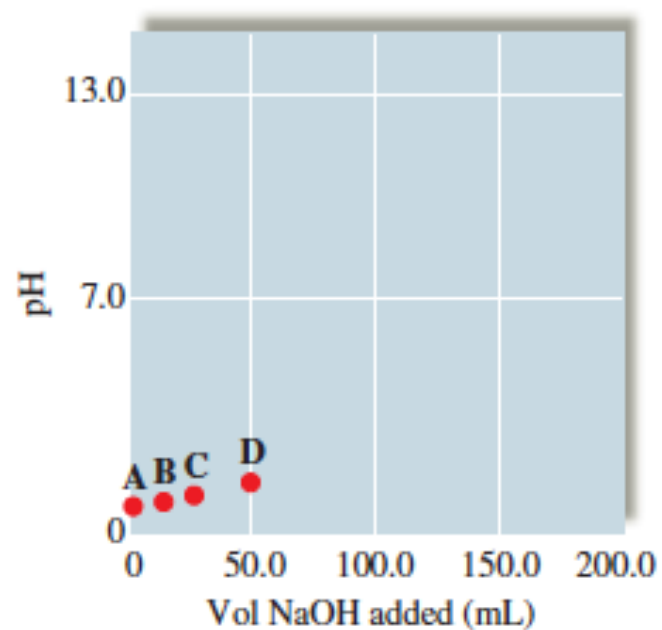
D) Add 50 mL (0.05 L) of 0.1 M NaOH

Moles of NaOH = Volume (l) x Molarity = 0.05 x 0.1 = 0.005 moles of OH⁻

Total volume: 0.05 + 0.05 = 0.1 Liter = V_t

Moles of HNO₃ = 0.01 moles of H⁺

| | H ⁺ | + OH ⁻ | =. | H ₂ O |
|--|-----------------------------|-------------------|----|------------------|
| Before addition | 0.01 | 0.005 | | |
| After addition | 0.01-0.005 | 0 | | |
| | 0.005 moles | | | |
| [H⁺] = moles/V_t | 0.005/0.1 = 0.05 M | | | |
| | pH = -log 0.05 = 1.3 | | | |

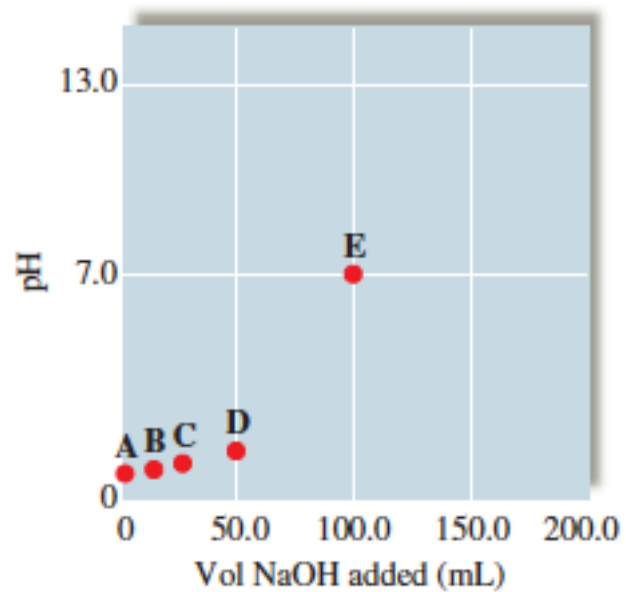


E) Add 100 mL (0.1 L) of 0.1 M NaOH

Moles of NaOH = Volume (l) x Molarity = 0.1 x 0.1 = 0.01 moles of OH⁻

Moles of HNO₃ = 0.01 moles of H⁺

Equivalence point: pH = 7



F) Add 150 mL (0.15 L) of 0.1M NaOH

Moles of NaOH = Volume (l) x Molarity = 0.15 x 0.1 = 0.015 moles of OH⁻

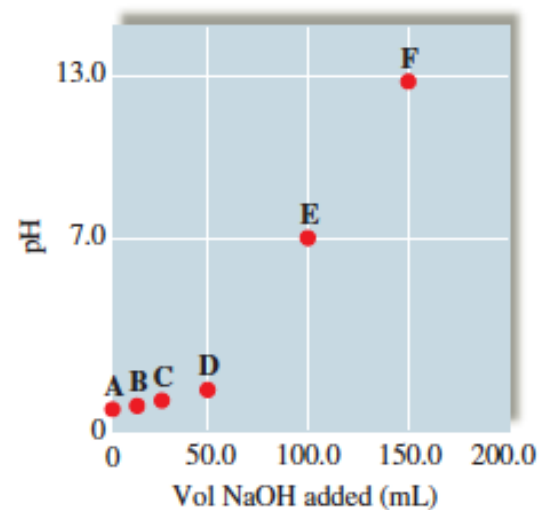
Total volume: 0.05 + 0.15 mL = 0.2 Liter = V_t

Moles of HNO₃ = 0.01 moles H⁺

| | H ⁺ | + | OH ⁻ | =. | H ₂ O |
|---|----------------|---|-----------------------|----|------------------|
| Before addition | 0.01 | | 0.015 | | |
| After addition | 0.01-0.01 | | 0.015-0.01 | | |
| | 0 | | 0.005 mole | | |
| [OH⁻] = moles/V_t | | | 0.005 / 0.2 = 0.025 M | | |

$$\text{pOH} = -\log [\text{OH}^-] = -\log 0.025$$

$$\text{pH} = 14 - \text{pOH} = \mathbf{12.4}$$



G) Add 200 mL (0.2 L) of 0.1M NaOH

Moles of NaOH = Volume (l) x Molarity = 0.2 x 0.1 = 0.02 moles of OH⁻

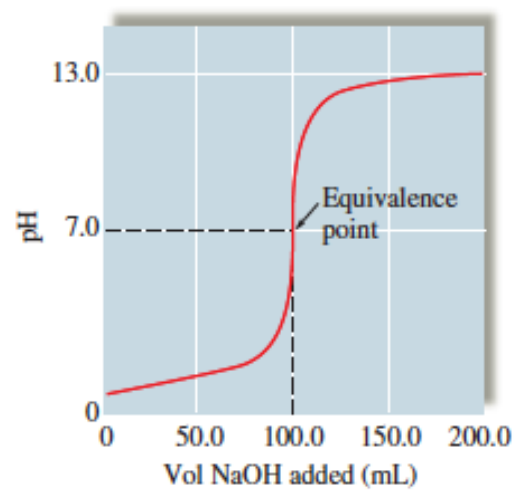
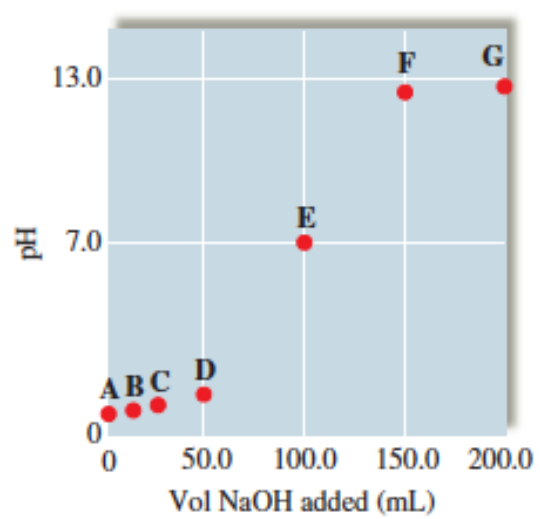
Total volume: 0.05 + 0.2 = 0.25 Liter = V_t

Moles of HNO₃ = 0.01 moles H⁺

| | H⁺ | + OH⁻ | =. | H₂O |
|---|----------------------|-------------------------|-----------|-----------------------|
| Before reaction | 0.01 | 0.02 | | |
| After reaction | 0.01-0.01 | 0.02-0.01 | | |
| | 0 | 0.01mole | | |
| [OH⁻] = moles/V_t | | 0.01/0.25 = 0.04 M | | |

$$\text{pOH} = -\log [\text{OH}^-] = -\log 0.04$$

$$\text{pH} = 14 - \text{pOH} = \mathbf{12.60}$$



Titration of strong base with strong acid

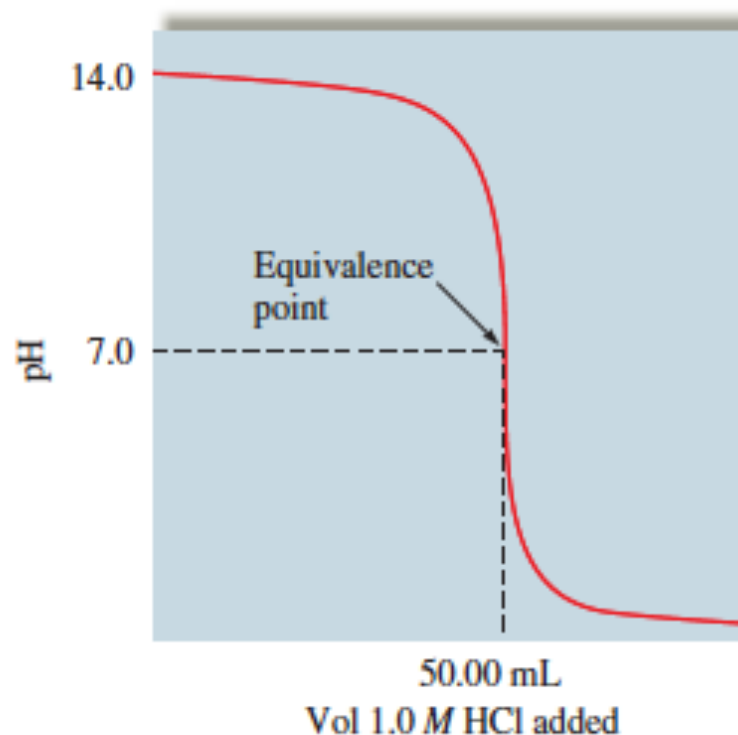


FIGURE 15.2

The pH curve for the titration of 100.0 mL of 0.50 M NaOH with 1.0 M HCl. The equivalence point occurs at 50.00 mL of HCl added, since at this point 5.0 mmol H^+ has been added to react with the original 5.0 mmol OH^- .