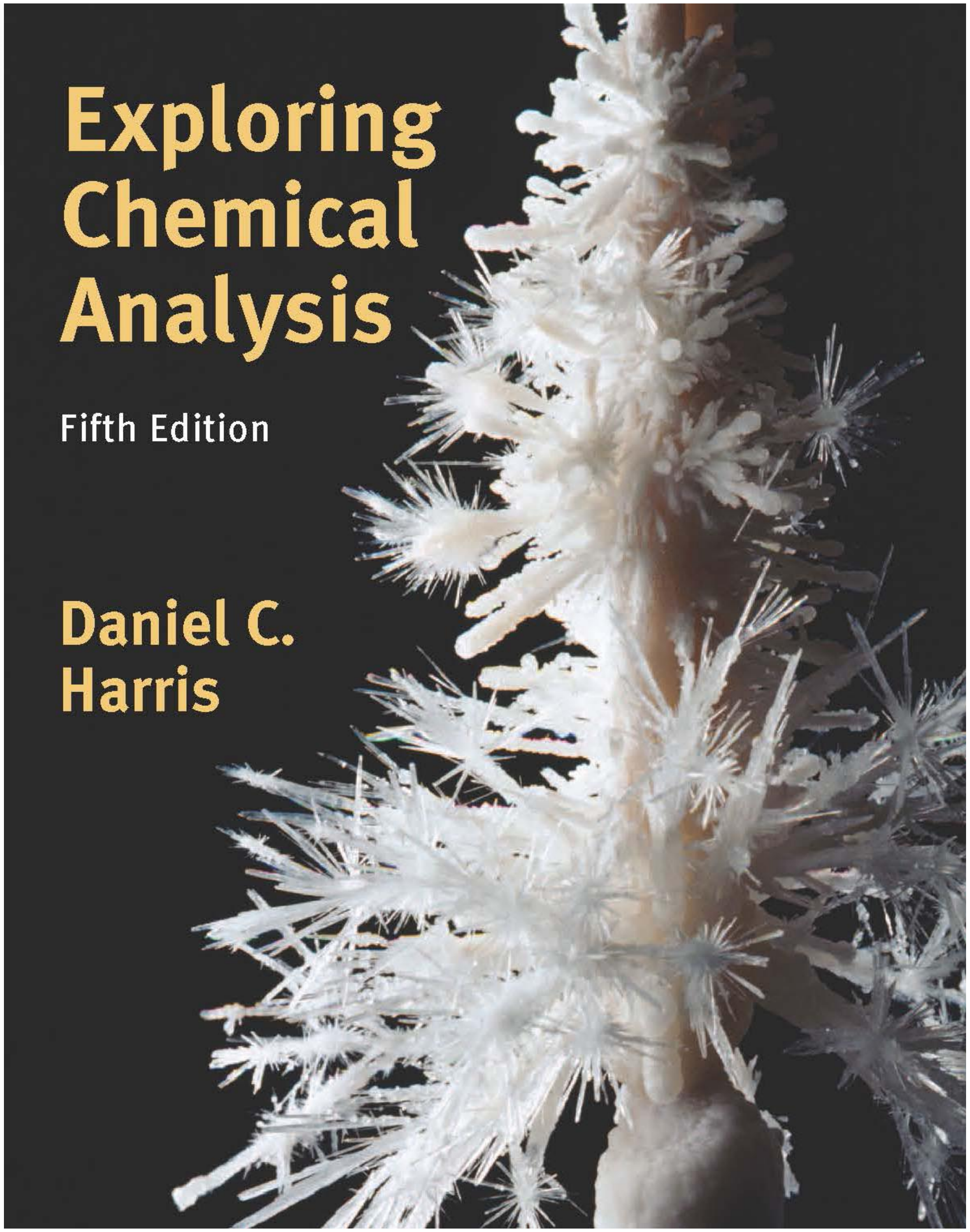
Chapter 10

Acid–Base titrations



Exploring Chemical Analysis

Fifth Edition

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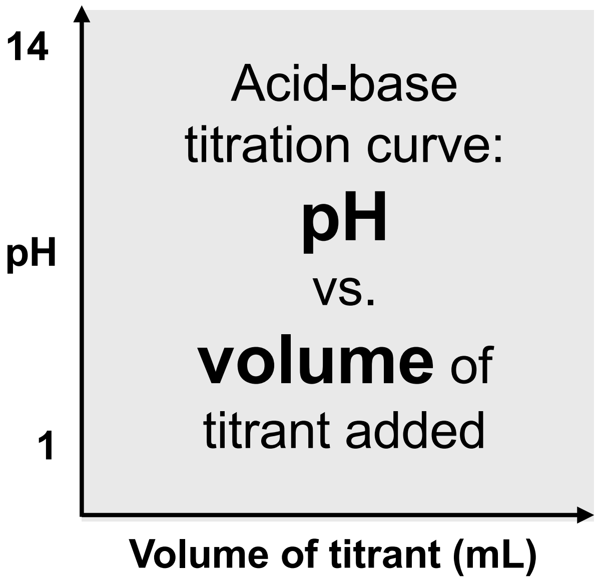
Acid–Base Titrations

- In an **acid-base titration**, the concentration of an acid (or a base) is determined by neutralizing the acid (or base) with a solution of base (or acid) of known concentration.
- The **equivalence point** of the reaction occurs when the number of moles of added titrant (OH^- or H_3O^+) are exactly sufficient for stoichiometric reaction with analyte.
- The **endpoint** occurs when the indicator (HIn) changes color.
- The indicator should be selected so that its color change occurs at a pH close to that of the equivalence point — apply the $\mathrm{pH}_{\text{equivalnce point}} = \mathrm{p}K_{\mathrm{a(Indicator)}} \pm 1$ rule.
- The endpoint and the equivalence point for a neutralization titration can be best matched by plotting a **titration curve**, a graph of pH versus volume of titrant.



Acid-base titration curve: **pH** vs. **volume** of titrant added

10-1 Titration of Strong Base with Strong Acid

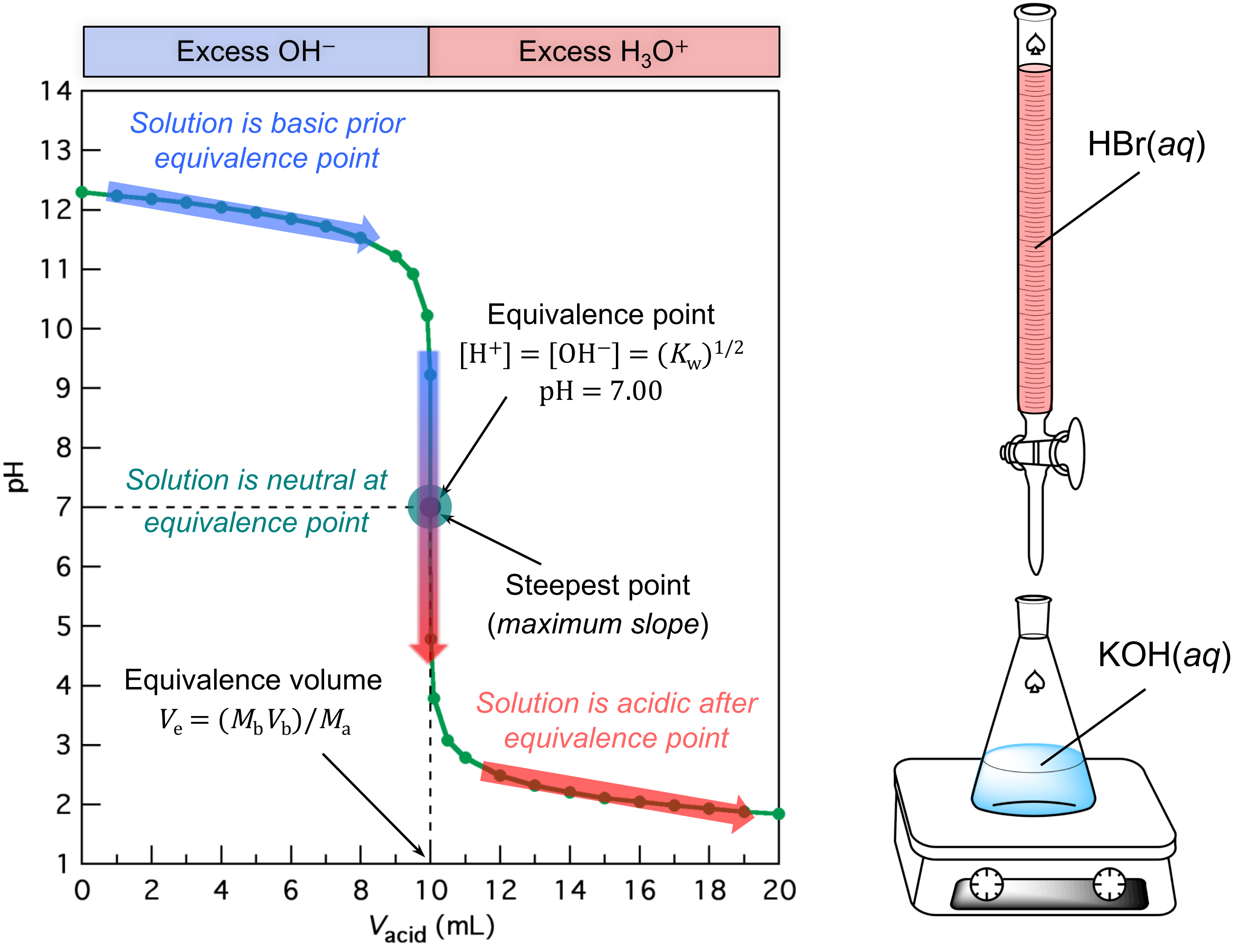
FIGURE 10-1 **Titration of 50.00 mL of 0.02000 M KOH with 0.1000 M HBr**

Titration reaction: $OH^-(aq) + H_3O^+(aq) \longrightarrow 2H_2O(l)$

The initial pH is high, and decreases gradually when the acid is added.

The pH drops very rapidly at the equivalence point, which occurs at **pH = 7.00**.

The pH decreases gradually when excess acid has been added.



10-1 Titration of Strong Base with Strong Acid

Calculating the pH During This Titration

- The **titration reaction** between strong base and strong acid is merely

$$\underset{\text{from KOH}(aq)}{OH^-(aq)} + \underset{\text{from HBr}(aq)}{H_3O^+(aq)} \xrightarrow{100\%} 2H_2O(l) \qquad K_c = \frac{1}{K_w} = \frac{1}{10^{-14}} = 10^{14}$$

- Because the equilibrium constant for this reaction is 10^{14}, its fair to say that it “goes to completion”.

- Prior to the equivalence point, *any amount of* H^+ *added will consume a stoichiometric amount of* OH^-.

- A useful starting point is to calculate the volume of HBr (V_e) needed to reach the equivalence point:

$$\underbrace{(V_e\text{ mL})(0.1000\text{ M})}_{\substack{\text{mmol of HBr}\\ \text{at equivalence point}}} = \underbrace{(50.00\text{ mL})(0.02000\text{ M})}_{\substack{\text{mmol of KOH}\\ \text{being titrated}}} \;\Rightarrow\; V_e = 10.00\text{ mL}$$

- Besides calculating V_e, there are **four** kinds of pH calculations during strong base–strong acid titrations.

10-1 Titration of Strong Base with Strong Acid

Region 1: Before Acid Is Added

1. **Before acid is added**, we have simply a strong base problem:

$$\underset{F}{KOH(aq)} \xrightarrow{100\%} \underset{F}{K^+(aq)} + \underset{F}{OH^-(aq)}$$

$$[OH^-] = [OH^-]_{initial} = F_{OH^-}$$

$$pH = -\log(K_w/F_{OH^-})$$

Before we add any HBr acid from the buret, the flask of base contains 0.02000 M KOH, so:

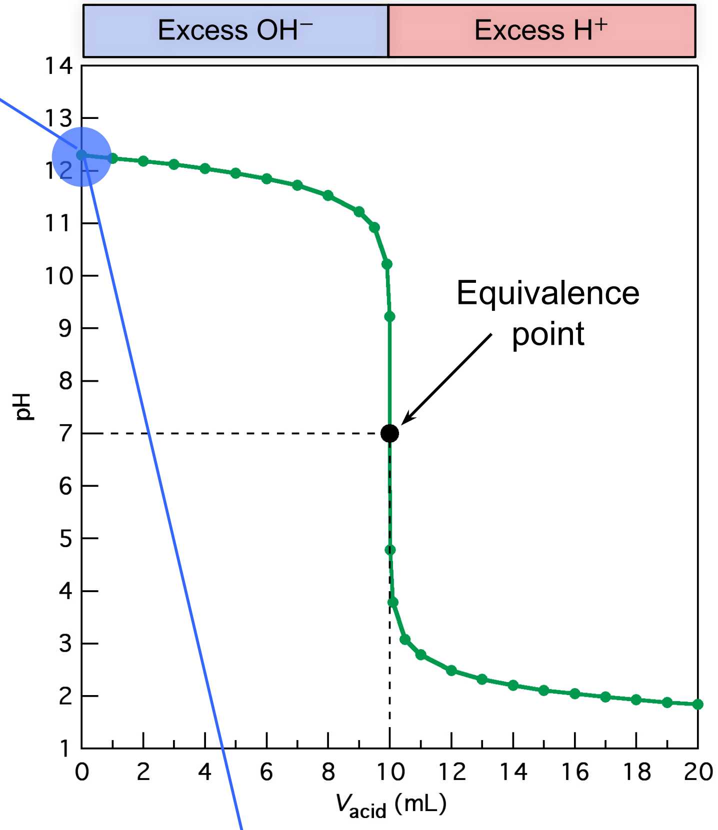
$$[OH^-] = F_{OH^-} = 0.02000\ M$$

$$pH = -\log\,(1.00 \times 10^{-14}/0.02000) = 12.30$$

or $pOH = -\log\,[OH^-] = -\log(0.02000) = 1.70$

$$pH = pK_w - pOH = 14.00 - 1.70 = 12.30$$

Titration of 50.00 mL of 0.02000 M KOH with 0.1000 M HBr



50 + 0 = 50 mL

$[OH^-]_{init}$

(basic)

pH = 12.30

10-1 Titration of Strong Base with Strong Acid

Region 2: Before the Equivalence Point

2. Before the equivalence point, the pH is determined by excess OH^- in the solution:

$$\text{initial mol } OH^- = M_{\text{base}} \times V_{\text{base}}$$

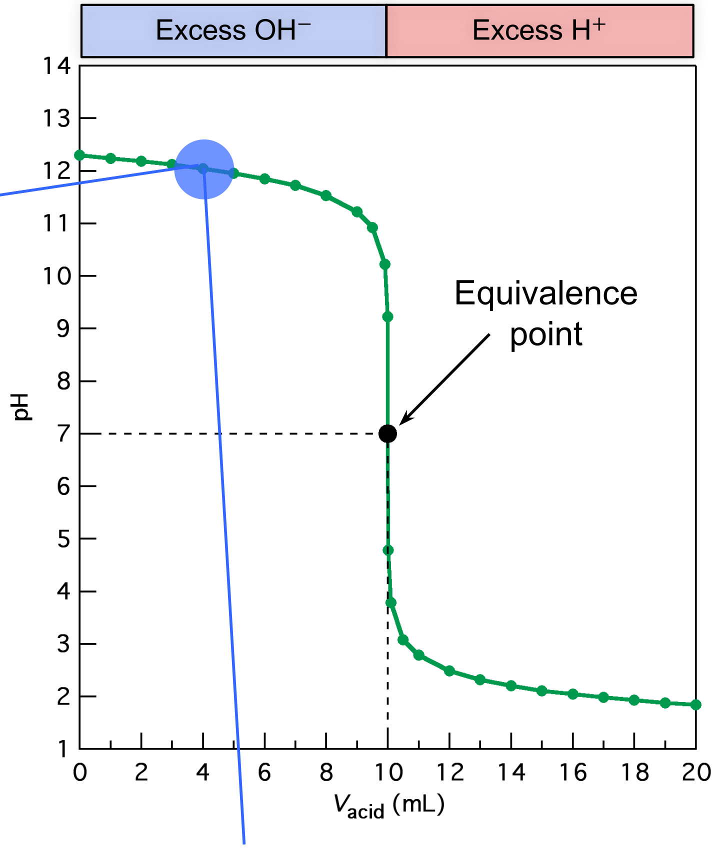
$$\text{mol } H^+ \text{ added} = M_{\text{acid}} \times V_{\text{acid}}$$

$$\text{mol } OH^-_{\text{remaining}} = \text{mol } OH^-_{\text{init}} - \text{mol } H^+_{\text{added}}$$

$$[OH^-] = (\text{mol } OH^-_{\text{remaining}})/(V_{\text{base}} + V_{\text{acid}})$$

$$\text{pH} = -\log(K_w/[OH^-])$$

Titration of 50.00 mL of 0.02000 M KOH with 0.1000 M HBr



For example, after adding 4.00 mL of HBr:

Titration rxn	$OH^-(aq)$	+	$H^+(aq)$	$\xrightarrow{100\%}$	$H_2O(l)$
	0.02000 M × 50.00 mL		0.1000 M × 4.00 mL		
Initial moles	1.000 mmol		0.400 mmol		
Final moles	0.600 mmol		—		

$$[OH^-] = (0.600 \text{ mmol})/(54.00 \text{ mL}) = 0.0111 \text{ M}$$

50 + 4 = 54 mL
$[OH^-] >> [H^+]$
(basic)

pH = 12.04

$$\text{pOH} = -\log[0.0111] = 1.96$$

$$\text{pH} = 14.00 - 1.96 = 12.04$$

10-1 Titration of Strong Base with Strong Acid

Region 3: At the Equivalence Point

3. At the equivalence point, added H^+ is just sufficient to react with all the OH^- to make H_2O. The pH (or $[H^+]$) is determined by dissociation of water:

$$H_2O(l) \overset{K_w}{\rightleftharpoons} H^+(aq) + OH^-(aq)$$

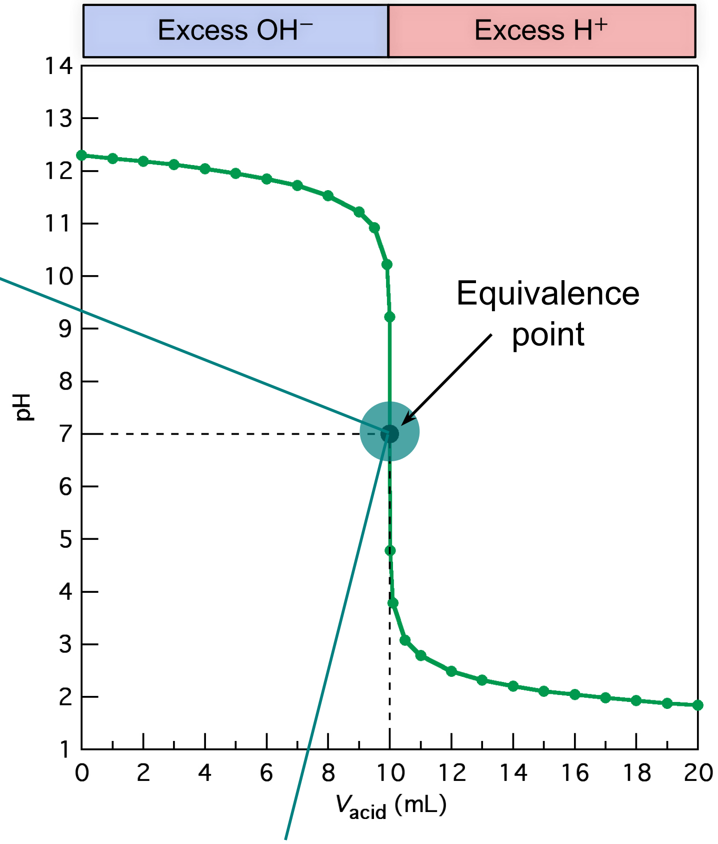
$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \quad @\ 25^\circ C$$

$$[H^+] = (K_w)^{1/2} = 1.0 \times 10^{-7}\ M;\ \ pH = 7.00$$

After 10.00 mL (V_e) of HBr have been added, the titration is complete:

$$\underbrace{(50.00\ mL)(0.02000\ M)}_{\text{1.000 mmol of OH}^-\text{ being titrated}} = \underbrace{(10.00\ mL)(0.1000\ M)}_{\text{1.000 mmol of H}^+\text{ at the equivalence point}}$$

Titration of 50.00 mL of 0.02000 M KOH with 0.1000 M HBr



50 + 10 = 60 mL
$[H^+] = [OH^-]$
(neutral)

$KBr(aq)$

- ➢ The pH at the equivalent point of any strong acid titrated with a strong base, or any strong base titrated with a strong acid is 7.00 at 25°C, so no pH calculations is required.

pH = 7.00

10-1 Titration of Strong Base with Strong Acid

Region 4: After the Equivalence Point

2. **After the equivalence point**, the pH is determined by excess H^+ in the solution:

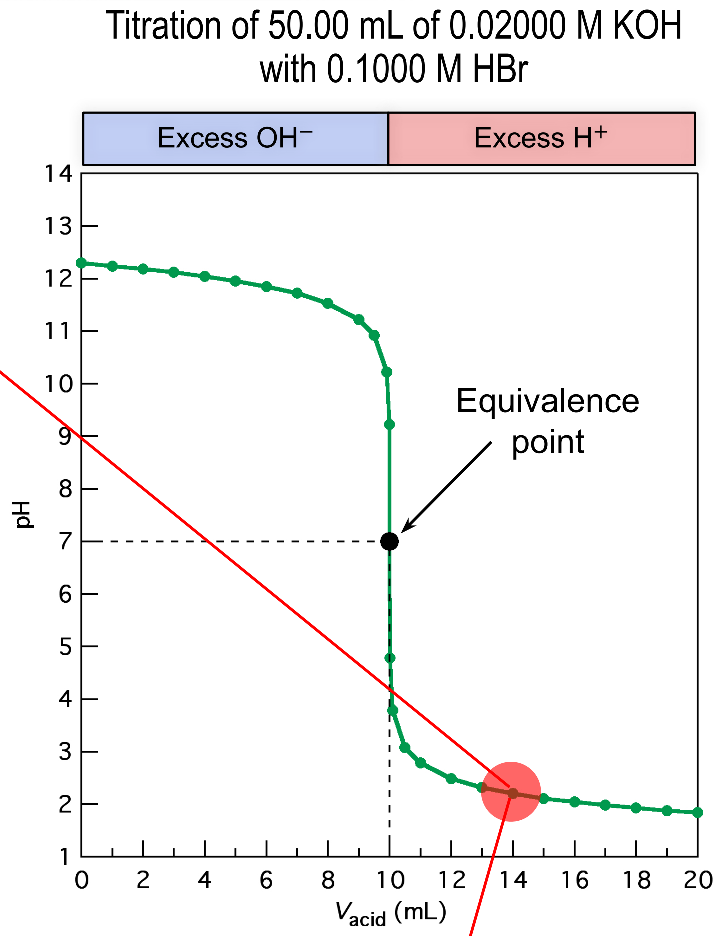
$$\text{initial mol } OH^- = M_{\text{base}} \times V_{\text{base}}$$

$$\text{mol } H^+ \text{ added} = M_{\text{acid}} \times V_{\text{acid}}$$

$$\text{mol } H^+_{\text{excess}} = \text{mol } H^+_{\text{added}} - \text{mol } OH^-_{\text{init}}$$

$$[H^+] = (\text{mol } H^+_{\text{excess}})/(V_{\text{base}} + V_{\text{acid}})$$

$$pH = -\log [H^+]$$



For example, after adding 14.00 mL of HBr:

Titration rxn	$OH^-(aq)$	+	$H^+(aq)$	$\xrightarrow{100\%}$ $H_2O(l)$
	0.02000 M × 50.00 mL		0.1000 M × 14.00 mL	
Initial moles	1.000 mmol		1.400 mmol	
Final moles	—		0.400 mmol	

50 + 14 = 64 mL

$[OH^-] << [H^+]$

(acidic)

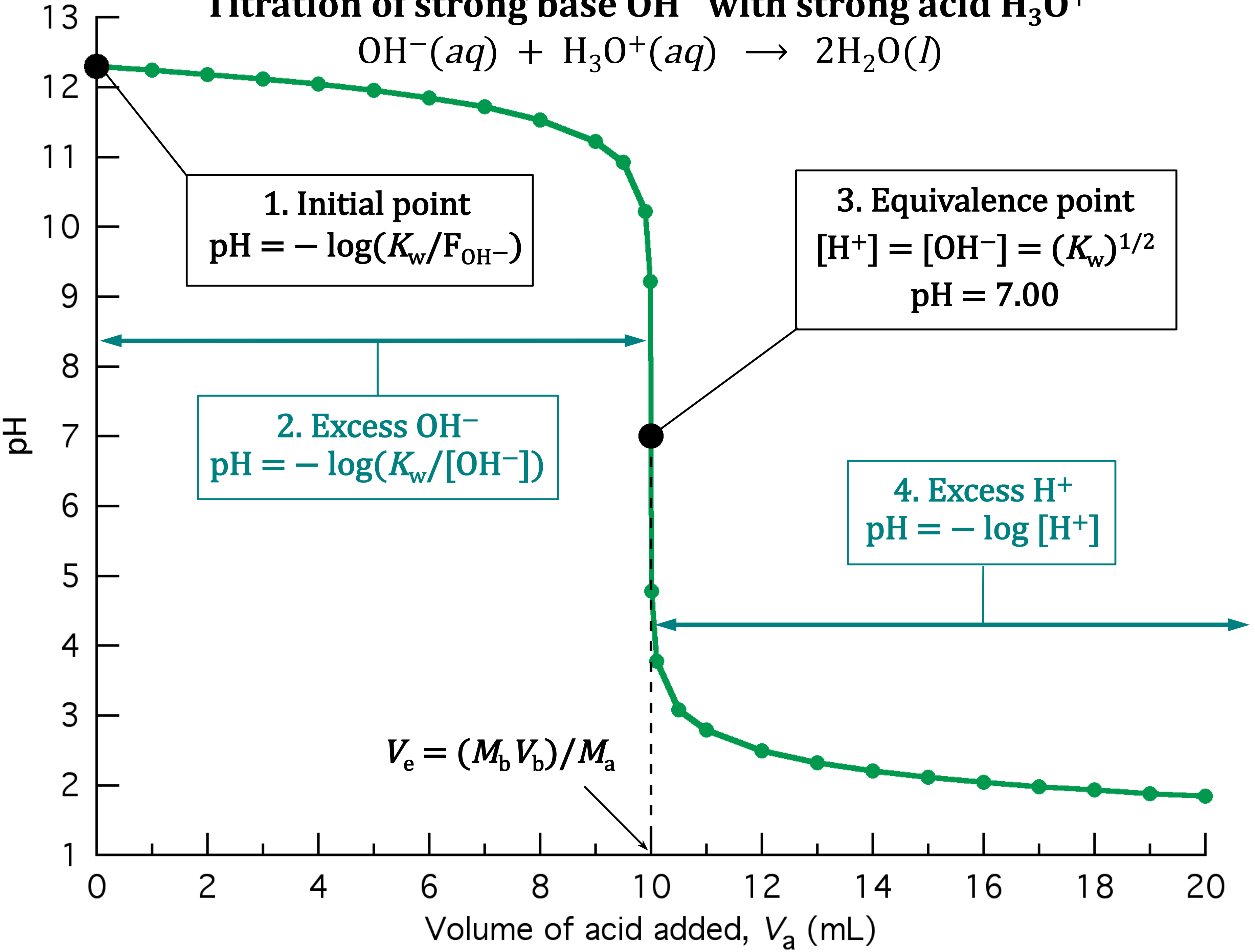
pH = 2.20

$[H^+] = (0.400 \text{ mmol})/(64.00 \text{ mL}) = 0.00625 \text{ M}$

$pH = -\log [0.00625] = 2.20$

Titration of strong base OH^- with strong acid H_3O^+

$$OH^-(aq) + H_3O^+(aq) \longrightarrow 2H_2O(l)$$



1. Initial point
$\mathrm{pH} = -\log(K_w/F_{OH^-})$

2. Excess OH^-
$\mathrm{pH} = -\log(K_w/[OH^-])$

3. Equivalence point
$[H^+] = [OH^-] = (K_w)^{1/2}$
$\mathrm{pH} = 7.00$

4. Excess H^+
$\mathrm{pH} = -\log\,[H^+]$

$V_e = (M_b V_b)/M_a$

10-1 Titration of Strong Acid with Strong Base

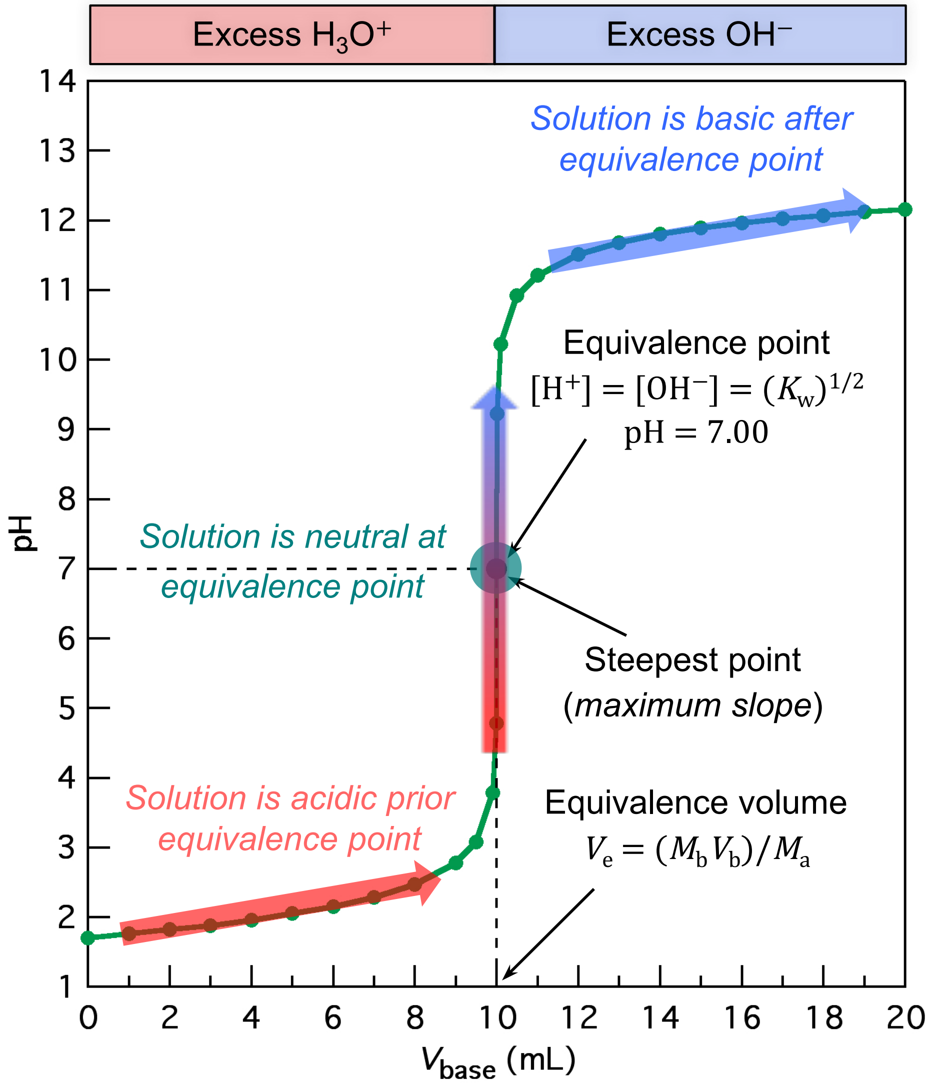
Titration of 50.00 mL of 0.02000 M HNO_3 with 0.1000 M NaOH

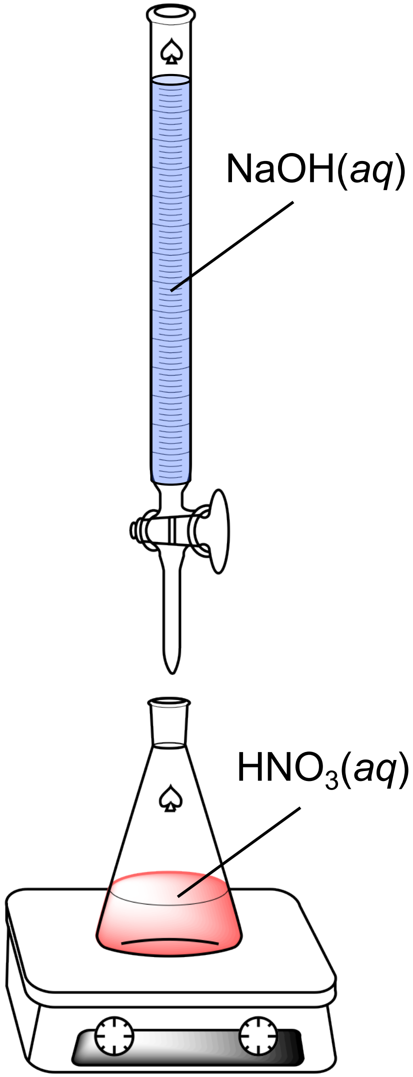
Titration reaction: $H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$

The pH increases gradually when excess base has been added.

The pH rises very rapidly at the equivalence point, which occurs at **pH = 7.00**.

The initial pH is low, and increases gradually when the base is added.





10-1 Titration of Strong Acid with Strong Base

Calculating the pH During This Titration

- The **titration reaction** between strong acid and strong base is merely

$$\underset{\text{from HBr}(aq)}{H_3O^+(aq)} + \underset{\text{from KOH}(aq)}{OH^-(aq)} \xrightarrow{100\%} 2H_2O(l) \qquad K_c = \frac{1}{K_w} = \frac{1}{10^{-14}} = 10^{14}$$

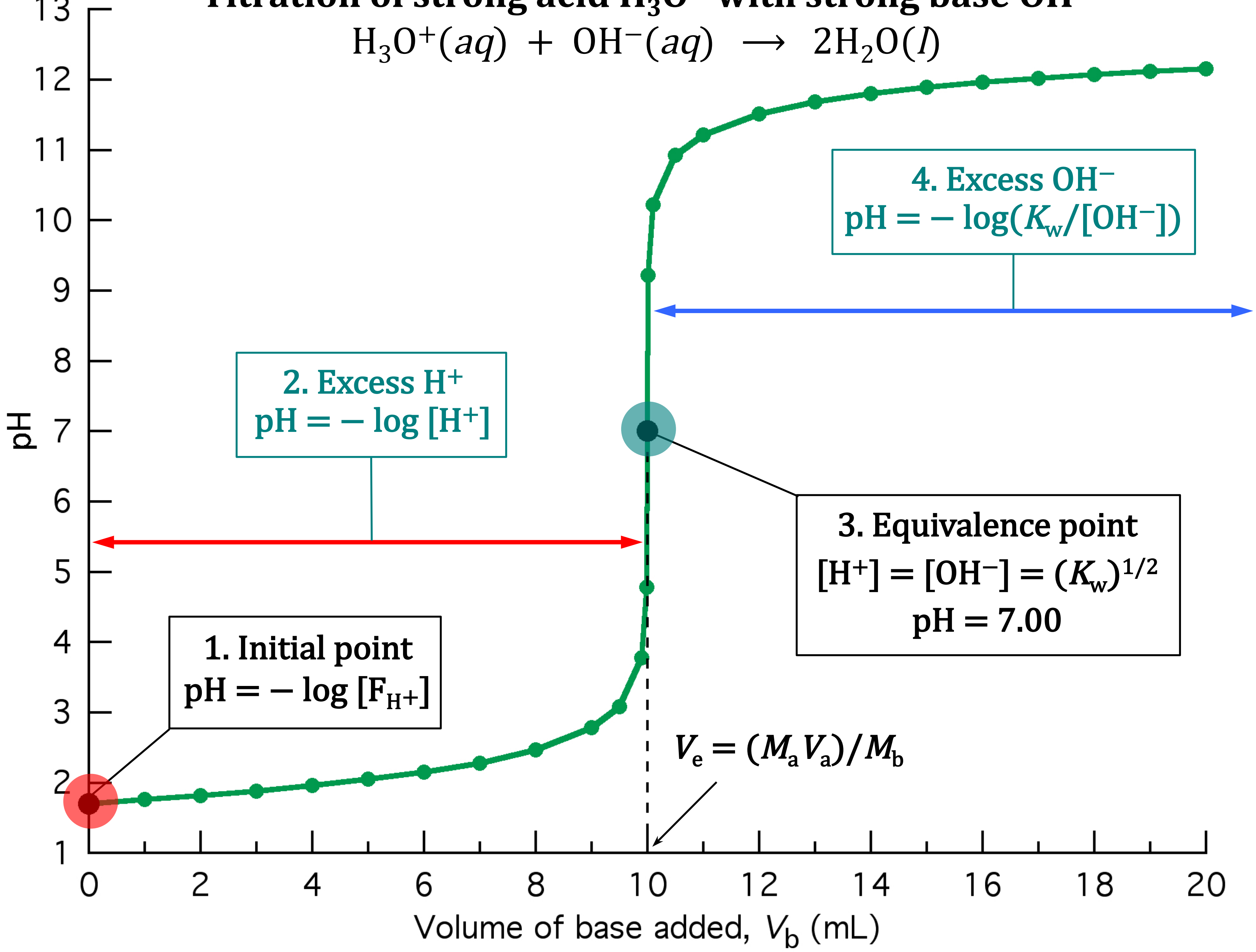
- Because the equilibrium constant for this reaction is 10^{14}, its fair to say that it "goes to completion".
- Prior to the equivalence point, *any amount of OH^- added will consume a stoichiometric amount of H_3O^+*.
- A useful starting point is to calculate the volume of KOH (V_e) needed to reach the equivalence point:

$$\underbrace{(V_e\ \text{mL})(0.1000\ \text{M})}_{\substack{\text{mmol of KOH} \\ \text{at equivalence point}}} = \underbrace{(50.00\ \text{mL})(0.02000\ \text{M})}_{\substack{\text{mmol of HBr} \\ \text{being titrated}}} \implies V_e = 10.00\ \text{mL}$$

- Besides calculating V_e, there are **four** kinds of pH calculations during strong base–strong acid titrations.

Titration of strong acid H_3O^+ with strong base OH^-

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$



1. Initial point
$\text{pH} = -\log[F_{H^+}]$

2. Excess H^+
$\text{pH} = -\log[H^+]$

3. Equivalence point
$[H^+] = [OH^-] = (K_w)^{1/2}$
$\text{pH} = 7.00$

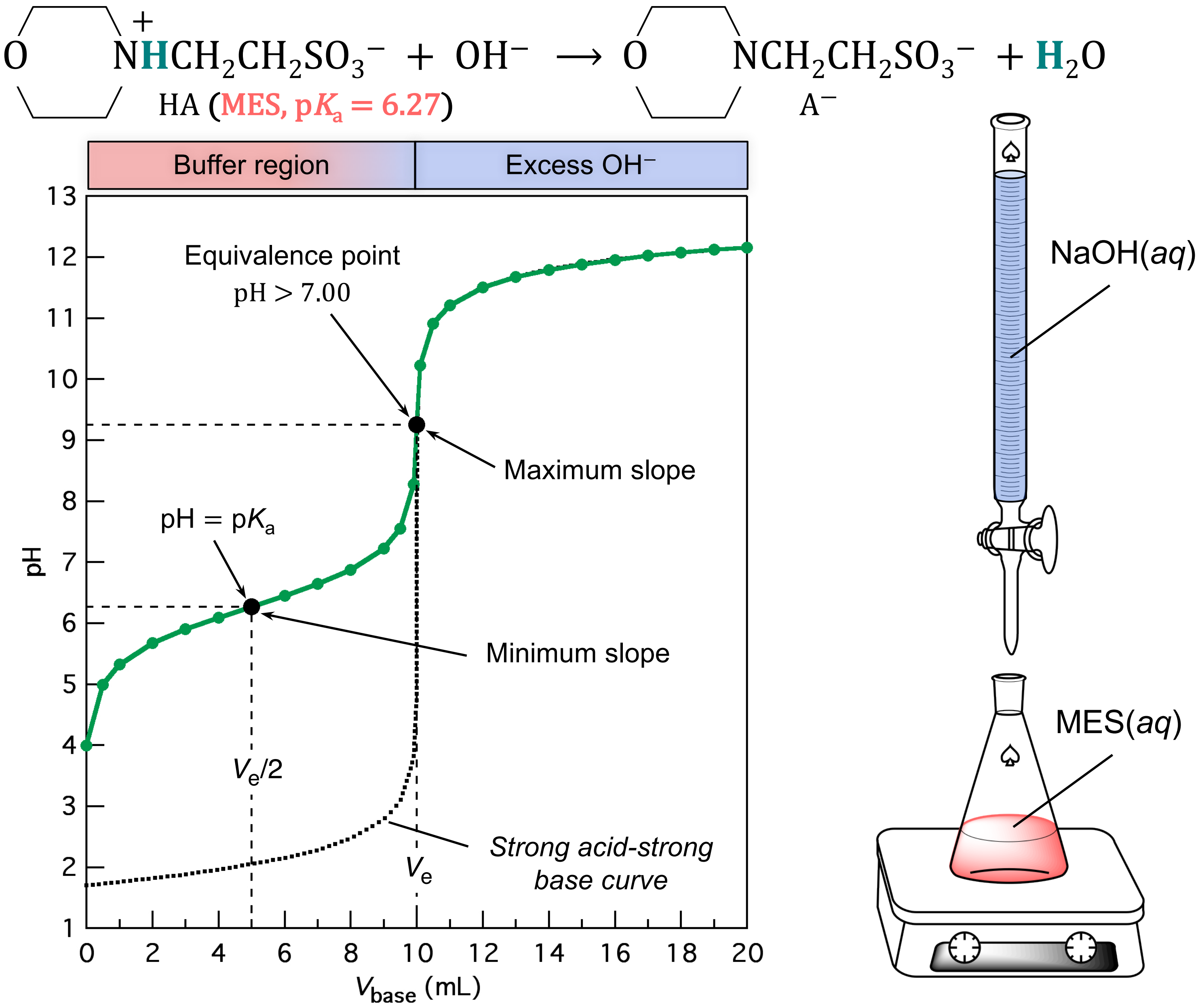
4. Excess OH^-
$\text{pH} = -\log(K_w/[OH^-])$

$V_e = (M_a V_a)/M_b$

10-2 Titration of Weak Acid with Strong Base

FIGURE 10-2 **Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH**

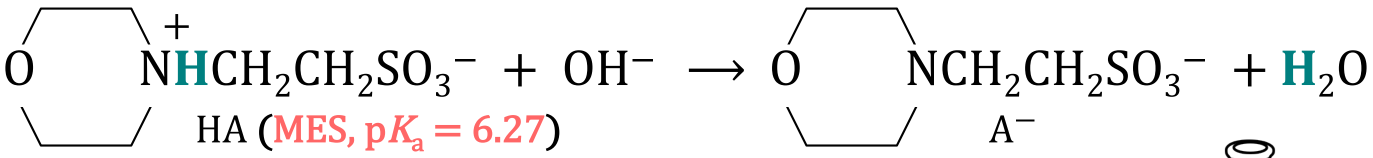
Titration reaction:



10-2 Titration of Weak Acid with Strong Base

FIGURE 10-2 **Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH**

Titration reaction:

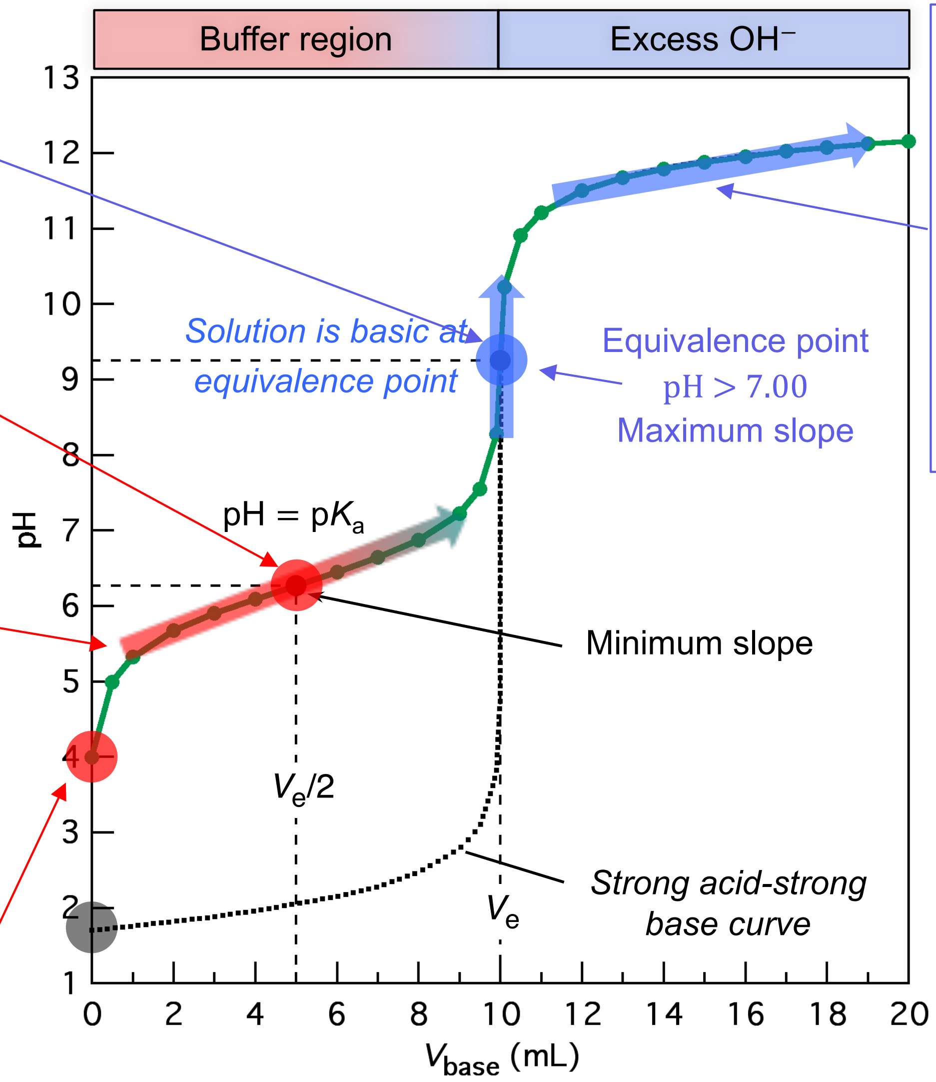


pH > 7 at the V_e point because the weak base A^- reacts with water to produce OH^-.

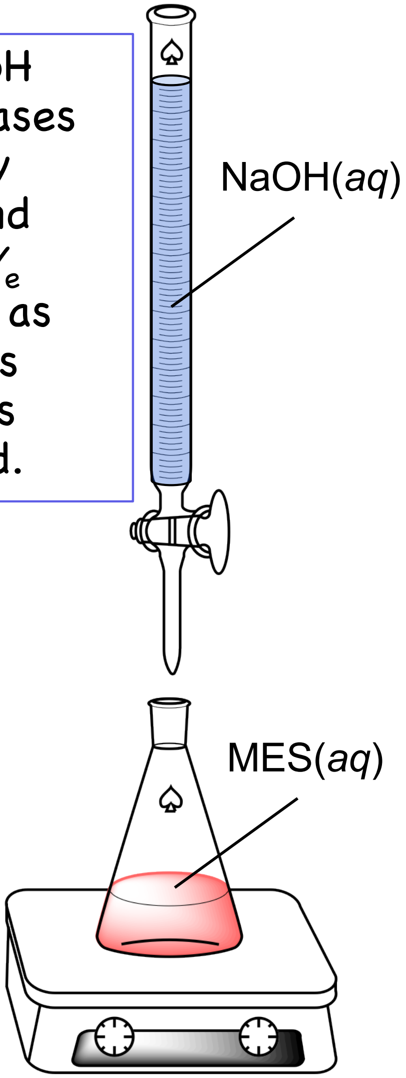
pH = pK_a at the midpoint of the buffer region.

The curve rises gradually in the buffer region prior the steep rise to the V_e point.

The initial pH is higher than for the strong acid solution because the weak acid supplies much less H_3O^+ than does the strong acid.



The pH increases slowly beyond the V_e point as excess OH^- is added.



10-2 Titration of Weak Acid with Strong Base

Calculating the pH During This Titration

- First we write the **titration (*neutralization*) reaction**:

$$\underset{\text{Weak acid}}{HA(aq)} + \underset{\text{Strong base}}{OH^-(aq)} \xrightarrow{100\%} H_2O(l) + \underset{\text{Weak base}}{A^-(aq)} \qquad K_c = \frac{1}{K_b} = \frac{K_a}{K_w}$$

- The equilibrium constant is so large that we can say that the reaction "goes to completion" after each addition of OH^-.

- To calculate the pH, we must consider *partial dissociation of HA, the presence of an HA/A^- buffer, and the reaction of A^- with water*.

- A useful starting point is to calculate the volume of NaOH (V_e) needed to reach the equivalence point:

$$\underbrace{(V_e\ \text{mL})(0.1000\ \text{M})}_{\substack{\text{mmol of NaOH}\\ \text{at equivalence point}}} = \underbrace{(50.00\ \text{mL})(0.02000\ \text{M})}_{\substack{\text{mmol of HA}\\ \text{being titrated}}} \implies V_e = 10.00\ \text{mL}$$

- Besides calculating V_e, there are **four** kinds of pH calculations during weak acid–strong base titrations.

10-2 Titration of Weak Acid with Strong Base

Region 1: Before Base Is Added

1. Before any base is added, the solution contains just HA in H_2O—a *weak-acid problem*:

$$\underset{F - x}{HA(aq)} \rightleftharpoons \underset{x}{A^-(aq)} + \underset{x}{H^+(aq)} \qquad K_a = 10^{-pK_a}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{F - x}$$

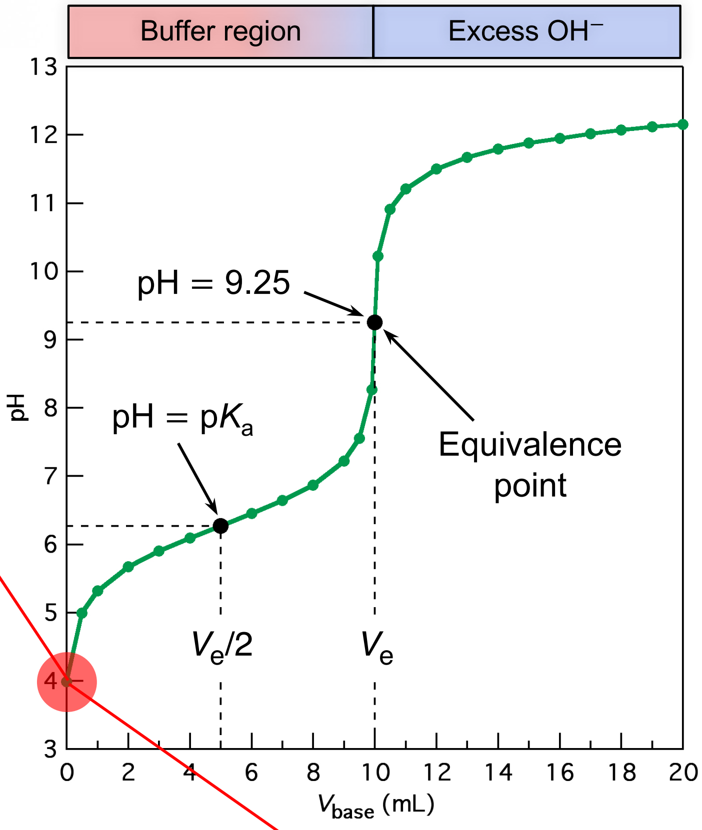
$$x = [H_3O^+];\ pH = -\log x$$

Before we add any NaOH from the buret, the flask of acid contains 0.1000 M MES with pK_a = 6.27, so:

$$\frac{x^2}{0.02000 - x} = 10^{-6.27} \implies x = 1.03 \times 10^{-4} = [H^+]$$

$$pH = -\log x = -\log(1.03 \times 10^{-4}) = 3.99$$

Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH



50 + 0 = 50 mL
Weak acid MES
(acidic)

pH = 3.99

10-2 Titration of Weak Acid with Strong Base

Region 2: Before the V_e Point

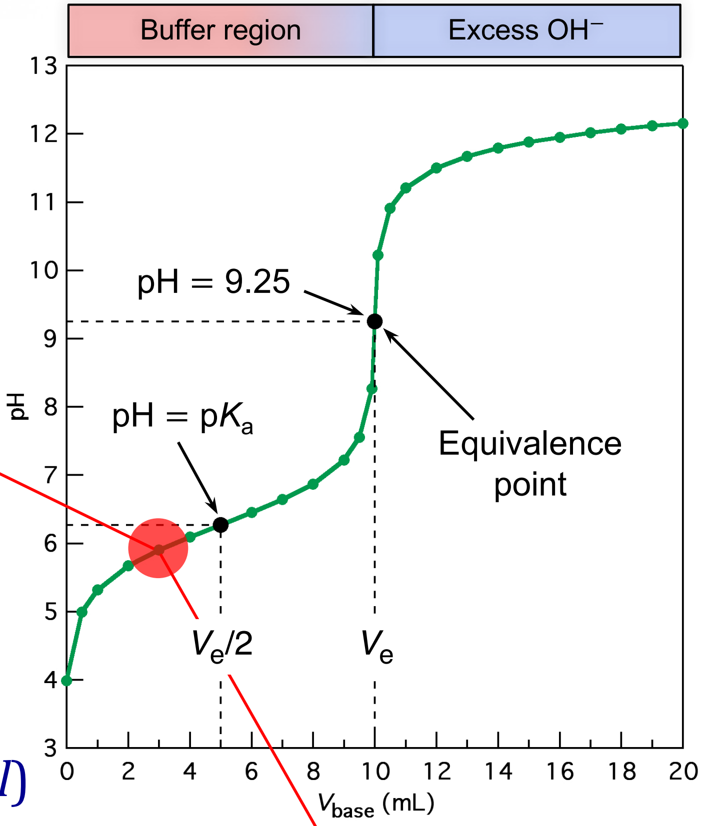
2. Before the equivalence point, there is a mixture of HA and A⁻, a **buffer** (*Aha! A buffer!*), which is created by the titration reaction:

$$HA(aq) + OH^-(aq) \longrightarrow A^-(aq) + H_2O(l)$$

The *Henderson-Hasselbalch equation* can be used to find pH once we know the quotient [A⁻]/[HA]:

$$pH = pK_a + \log([A^-]/[HA])$$

Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH



50 + 3 = 53 mL
[HA] > [A⁻]
(acidic)

pH = 5.90

For example, after adding 3.00 mL of NaOH:

Titration rxn	$HA(aq)$	+	$OH^-(aq)$	$\longrightarrow$	$A^-(aq) + H_2O(l)$
	0.02000 M		0.1000 M		
	× 50.00 mL		× 3.00 mL		
Initial moles	1.000 mmol		0.300 mmol		—
Final moles	0.700 mmol		—		0.300 mmol

$$pH = pK_a + \log([A^-]/[HA]) = 6.27 + \log(0.300/0.700) = 5.90$$

The H-H equation needs only mol because V_{total} cancels in the quotient [A⁻]/[HA].

10-2 Titration of Weak Acid with Strong Base

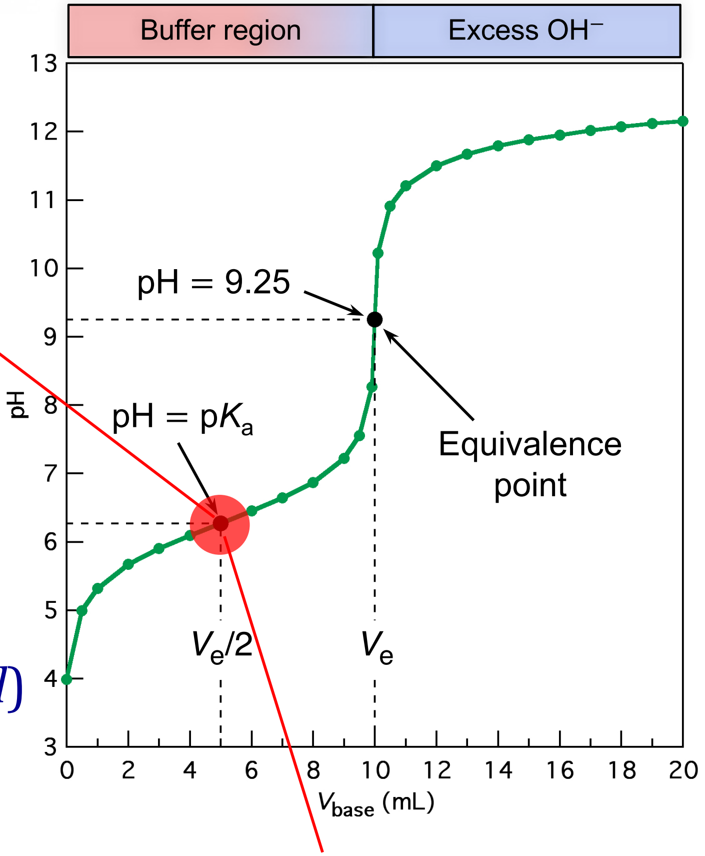
Region 2: Landmark Point at $V_e/2$

2a. When the **volume of titrant is ½V_e**, $[A^-] = [HA]$ and **pH = pK_a** for the acid HA:

$$pH = pK_a + \log([A^-]/[HA]) = pK_a + \log(1) = pK_a$$

Advice. *As soon as you recognize that you are half-way to the equivalence point,* ***no*** *pH calculation is needed!*

Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH



After adding 5.00 mL of NaOH to the flask of acid, half of HA will be converted to A^-:

Titration rxn	$HA(aq)$ +	$OH^-(aq)$ $\longrightarrow$	$A^-(aq) + H_2O(l)$
	0.02000 M × 50.00 mL	0.1000 M × 5.00 mL	
Initial moles	1.000 mmol	0.500 mmol	—
Final moles	0.500 mmol	—	0.500 mmol

$$pH = pK_a + \log(0.500/0.500) = 6.27$$

50 + 5 = 55 mL
$[HPr] = [Pr^-]$
($pK_a < pK_b$, so acidic)

pH = 6.27

NOTE: *Having the experimental titration curve allows to find the pK_a by reading the pH when V_{base} = ½V_e, where V_{base} is the volume of added base.*

10-2 Titration of Weak Acid with Strong Base

Region 3: At the Equivalence Point

3. At the equivalence point, the solution contains "just" A^- in H_2O. This is a *weak-base* problem:

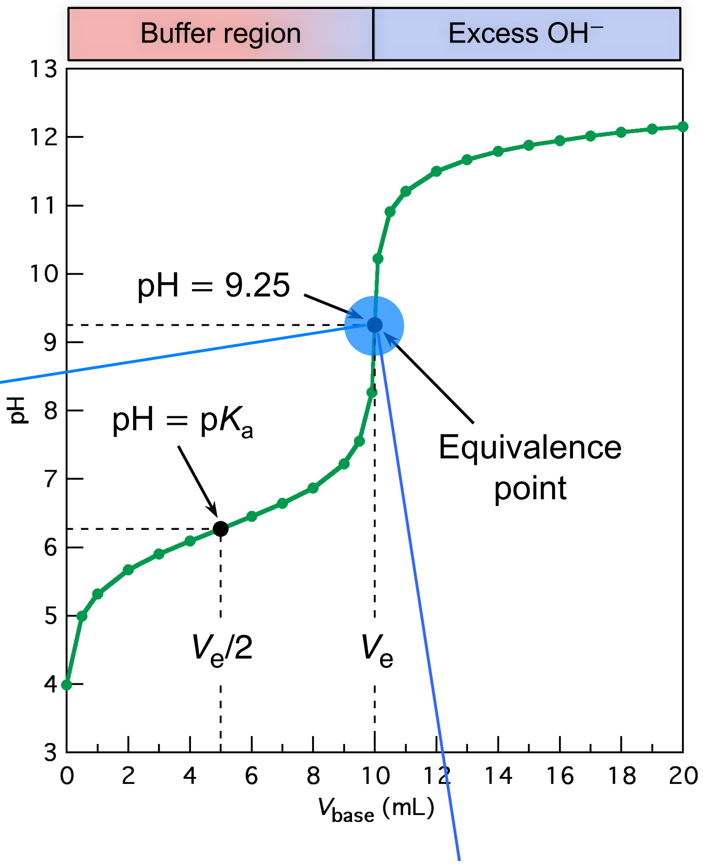
$$\underset{F' - x}{A^-(aq)} + H_2O(l) \rightleftharpoons \underset{x}{HA(aq)} + \underset{x}{OH^-(aq)}$$

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2}{F' - x} = \frac{K_w}{K_a}$$

$$\text{where} \quad F' = [A^-]_{\text{diluted}} = \frac{\text{mol of HA}_{\text{init}}}{\text{total volume}}$$

$$\text{pH} = -\log(K_w/x)$$

Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH



50 + 10 = 60 mL

Weak base A^-

(basic)

(a) Calculating K_b of A^- from $pK_a = 6.27$ of HA:

$$K_b = 10^{-pK_b} = 10^{-(pK_w - pK_a)} = 10^{-(14.00 - 6.27)} = 1.8_6 \times 10^{-8}$$

10-2 Titration of Weak Acid with Strong Base

Region 3: At the Equivalence Point

(b) Calculating $[A^-]_{dil}$ after all HA_{init} has reacted:

$$[A^-]_{dil} = \frac{(0.02000\ \text{M})(50.00\ \text{mL})}{(50.00 + 10.00)\ \text{mL}} = 0.01667\ \text{M} = F'$$

(c) Solving for $[OH^-]$ and calculating the pH:

$$\frac{x^2}{F' - x} = \frac{x^2}{0.01667 - x} = K_b = 1.8_6 \times 10^{-8}$$

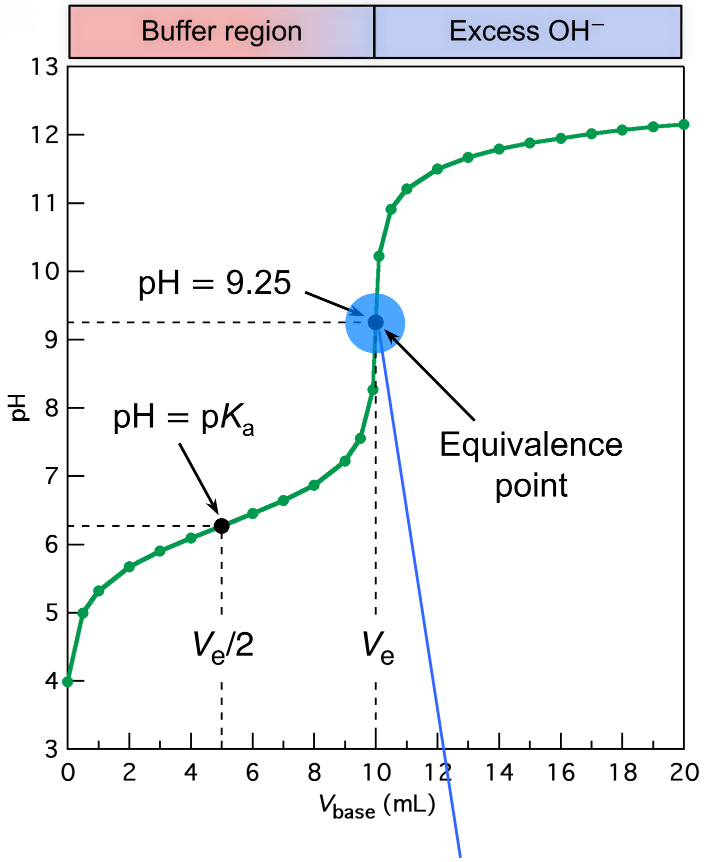
$$x = 1.76 \times 10^{-5}\ \text{M} = [OH^-]$$

$$\text{pH} = -\log\frac{K_w}{x} = -\log\frac{1.00 \times 10^{-14}}{1.76 \times 10^{-5}} = 9.25$$

or $$\text{pOH} = -\log x = -\log(1.76 \times 10^{-5}) = 4.75$$

$$\text{pH} = \text{p}K_w - \text{pOH} = 14.00 - 4.75 = 9.25$$

Titration of 50.00 mL of 0.02000 M MES
with 0.1000 M NaOH



50 + 10 = 60 mL
Weak base A^-
(basic)

pH = 9.25

- *The pH is higher than 7 at the equivalent point in the titration of weak acid with a strong base.*

10-2 Titration of Weak Acid with Strong Base

Region 4: After the V_e Point

4. After the equivalence point, the pH is determined by excess OH⁻ in the solution:

$$\text{initial mol } H^+ = M_{\text{acid}} \times V_{\text{acid}}$$

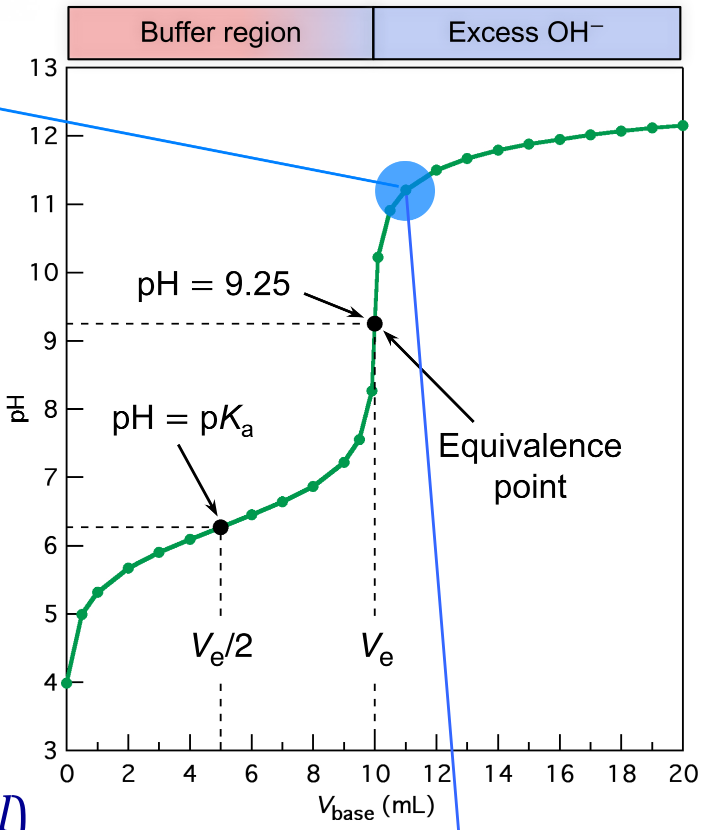
$$\text{mol } OH^- \text{ added} = M_{\text{base}} \times V_{\text{base}}$$

$$\text{mol } OH^-_{\text{excess}} = \text{mol } OH^-_{\text{added}} - \text{mol } H^+_{\text{init}}$$

$$[OH^-] = (\text{mol } OH^-_{\text{excess}})/(V_{\text{acid}} + V_{\text{base}})$$

$$pH = -\log(K_w/[OH^-])$$

Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH



50 + 11 = 61 mL
$[OH^-] >> [H^+]$
(basic)

For example, after adding 11.00 mL of NaOH:

Titration rxn	$HA(aq)$	+	$OH^-(aq)$	$\longrightarrow A^-(aq) + H_2O(l)$
	0.02000 M		0.1000 M	
	× 50.00 mL		× 11.00 mL	
Initial moles	1.000 mmol		1.100 mmol	
Final moles	—		0.100 mmol	

pH = 11.21

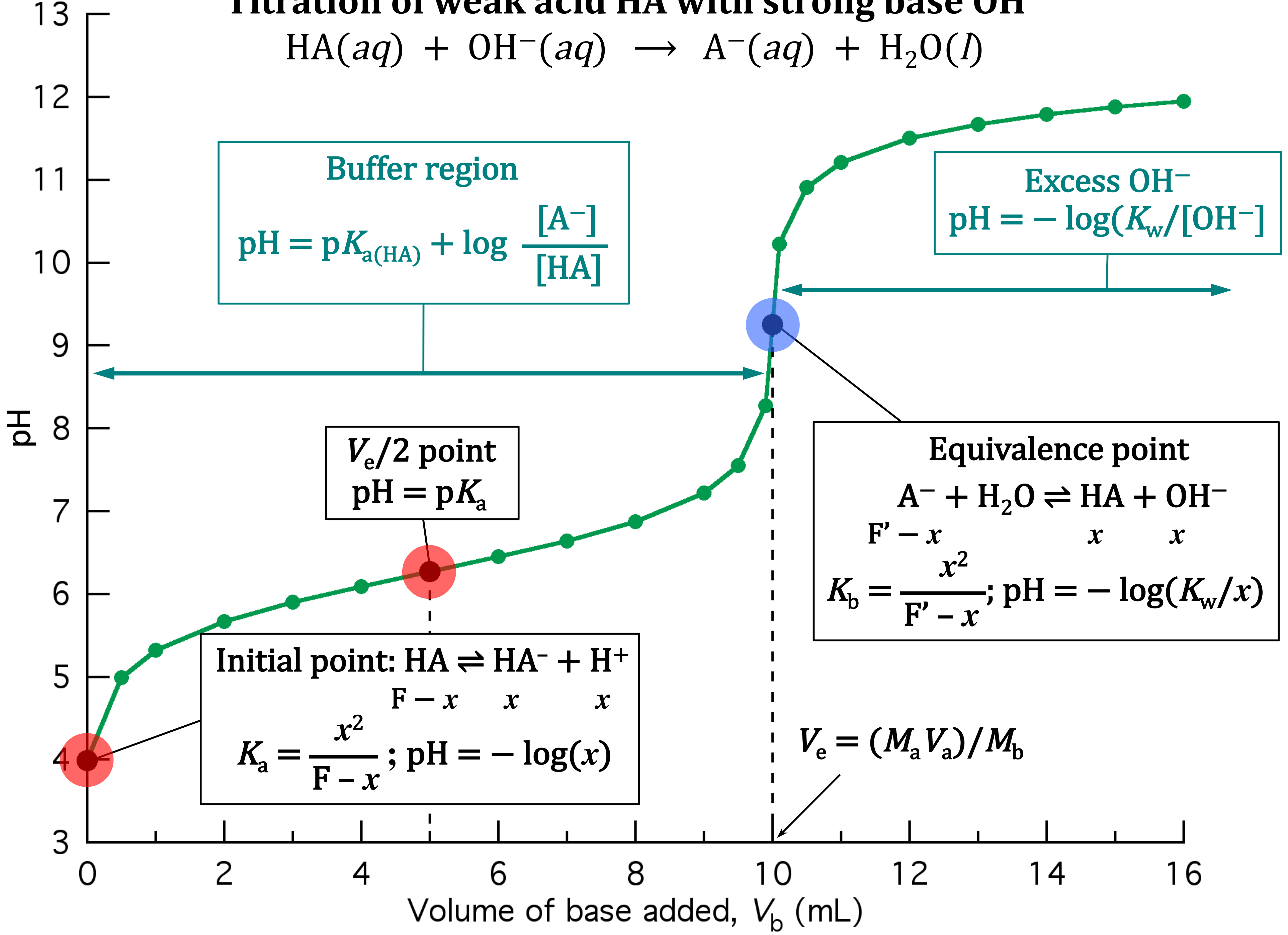
$$pOH = -\log[0.01639] = 2.79$$

$$pH = 14.00 - 2.79 = 11.21$$

$$[OH^-] = (0.100 \text{ mmol})/(61.00 \text{ mL}) = 0.01639 \text{ M}$$

Titration of weak acid HA with strong base OH^-

$$HA(aq) + OH^-(aq) \longrightarrow A^-(aq) + H_2O(l)$$



Buffer region

$$pH = pK_{a(HA)} + \log \frac{[A^-]}{[HA]}$$

Excess OH^-

$$pH = -\log(K_w/[OH^-])$$

$V_e/2$ point

$$pH = pK_a$$

Equivalence point

$$\begin{array}{cccc} A^- + H_2O & \rightleftharpoons & HA & + \; OH^- \\ F' - x & & x & x \end{array}$$

$$K_b = \frac{x^2}{F' - x}; \; pH = -\log(K_w/x)$$

Initial point: $HA \rightleftharpoons HA^- + H^+$

$$\begin{array}{ccc} F - x & x & x \end{array}$$

$$K_a = \frac{x^2}{F - x}; \; pH = -\log(x)$$

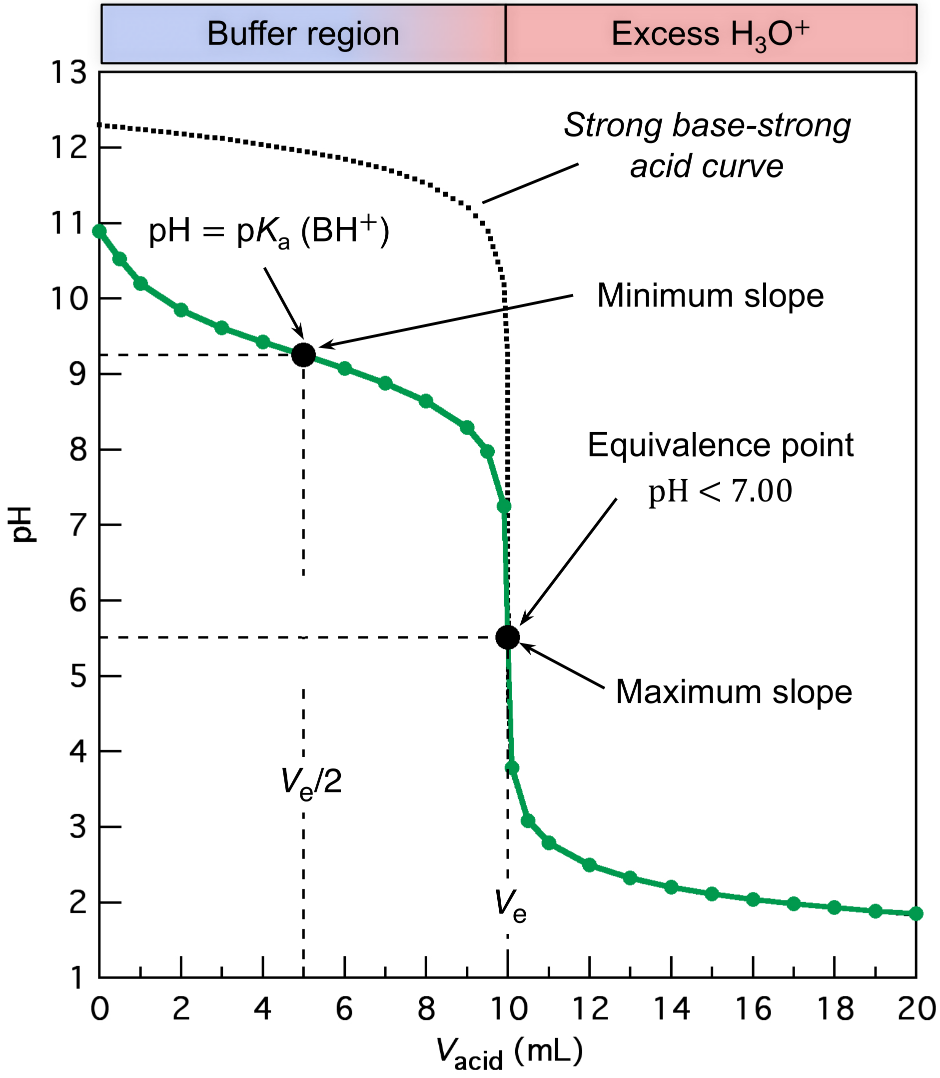
$$V_e = (M_a V_a)/M_b$$

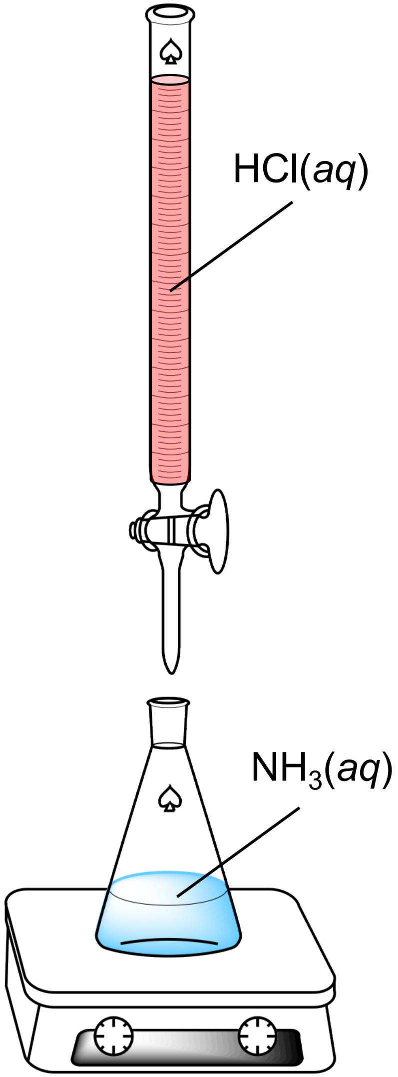
10-3 Titration of Weak Base with Strong Acid

Titration of 50.00 mL of 0.02000 M NH_3 with 0.1000 M HCl

Titration reaction: $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

$pK_a = 9.245$





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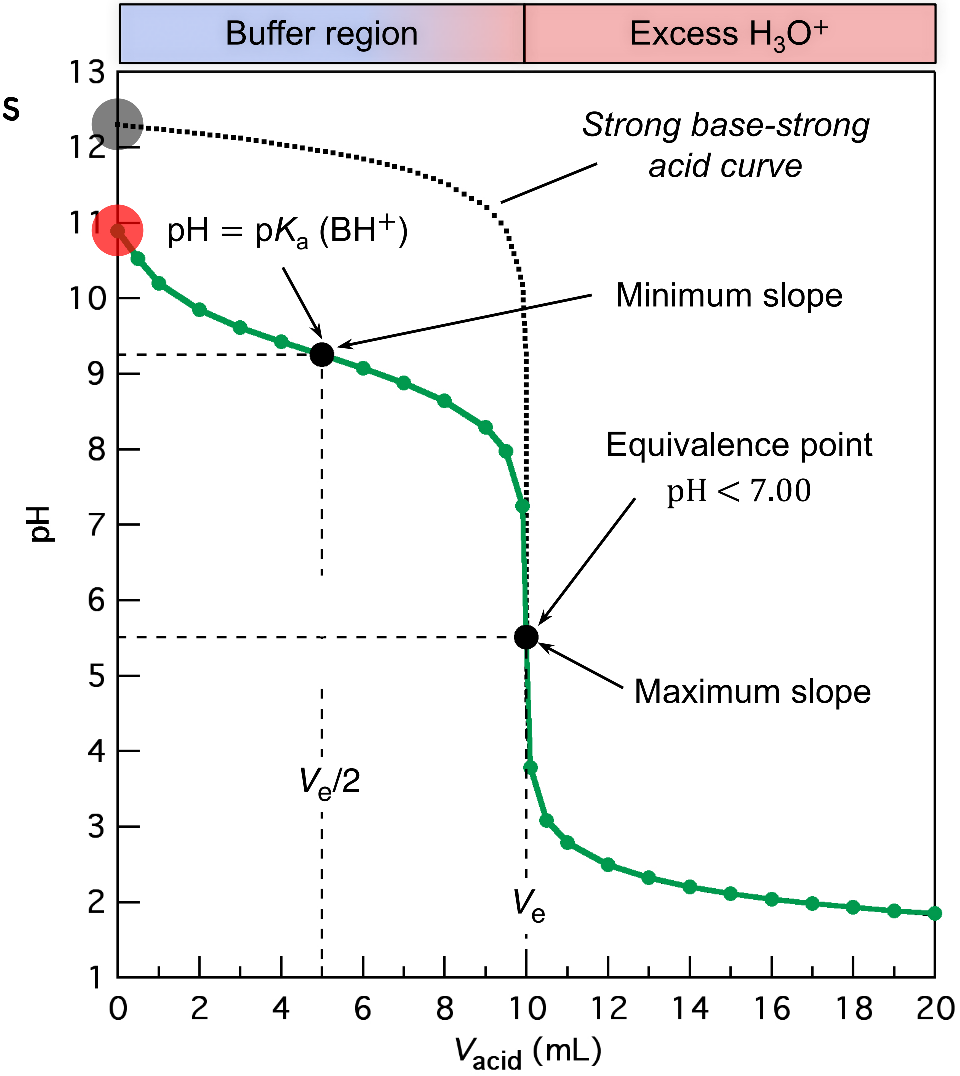
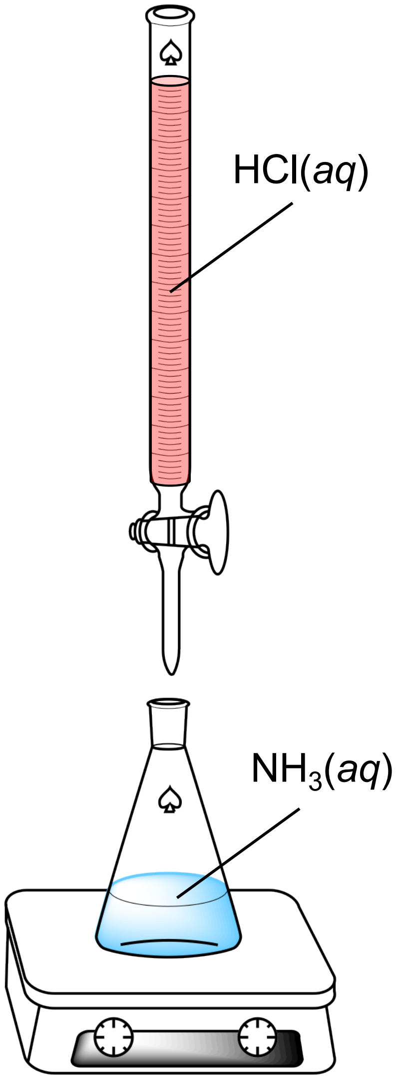
Titration of 50.00 mL of 0.02000 M NH_3 with 0.1000 M HCl

Titration reaction: $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

$pK_a = 9.245$

The initial pH is lower than for the strong base solution because the weak base supplies much less OH^- than does the strong base.





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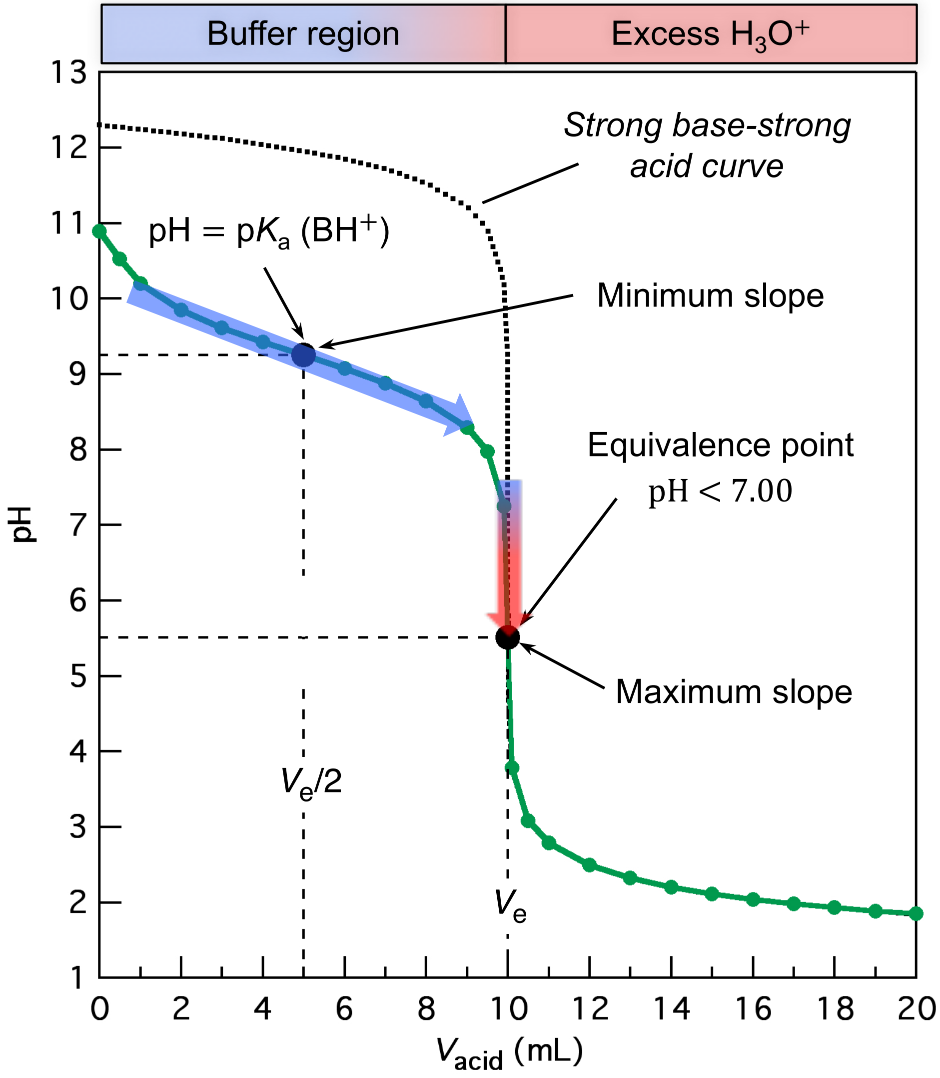
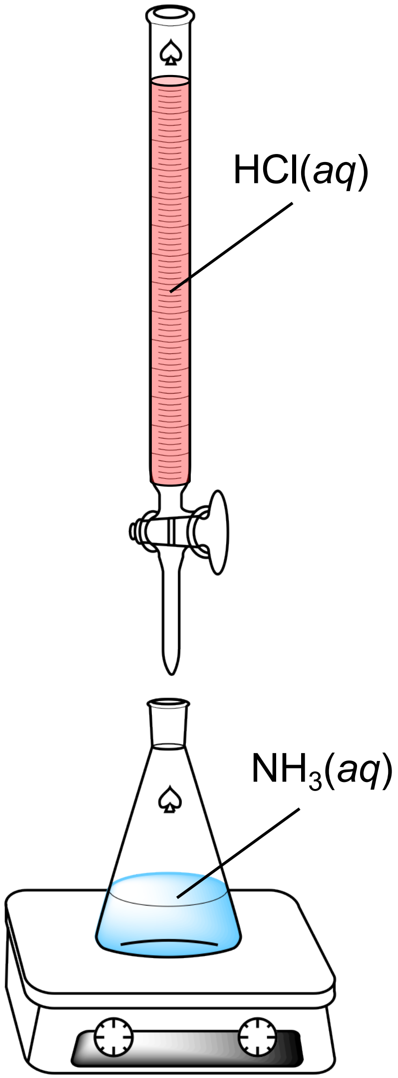
Titration of 50.00 mL of 0.02000 M NH_3 with 0.1000 M HCl

Titration reaction: $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

$pK_a = 9.245$

The curve drops gradually in the buffer region prior the steep drop to the V_e point.





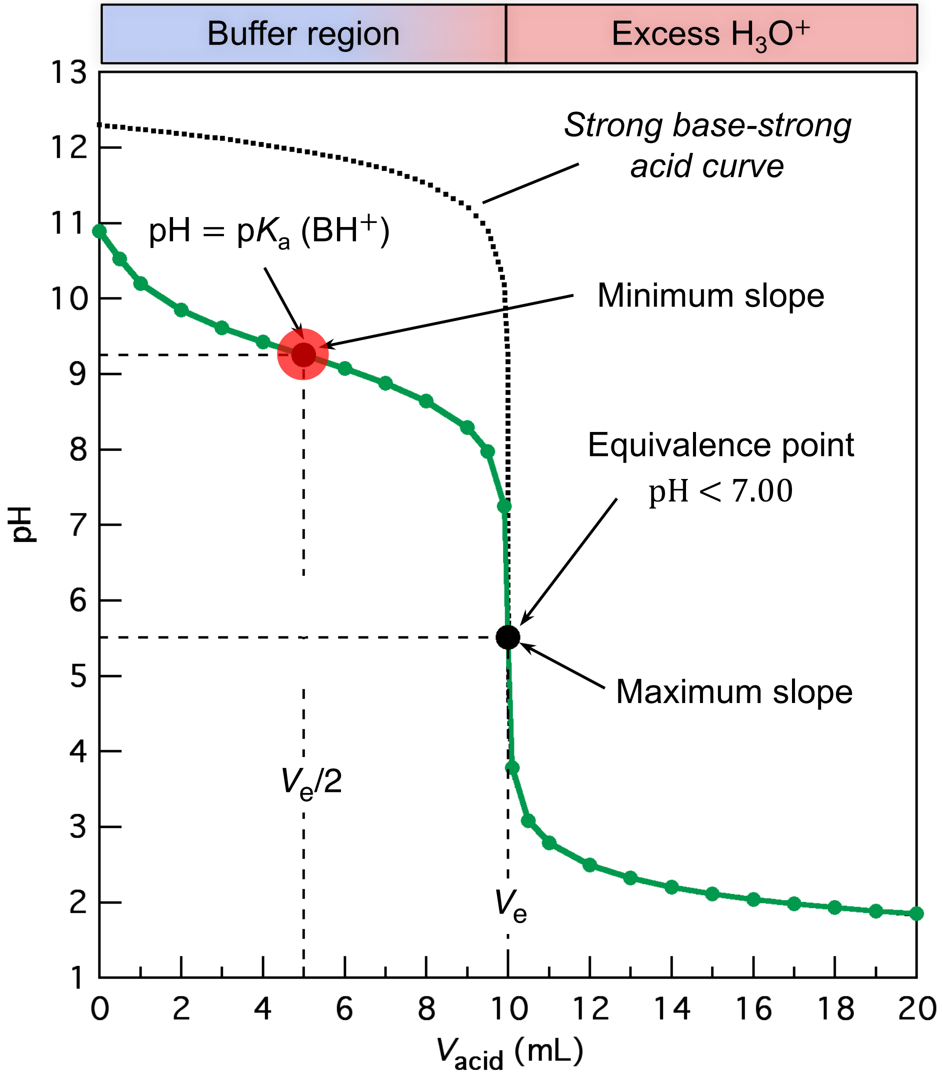
10-3 Titration of Weak Base with Strong Acid

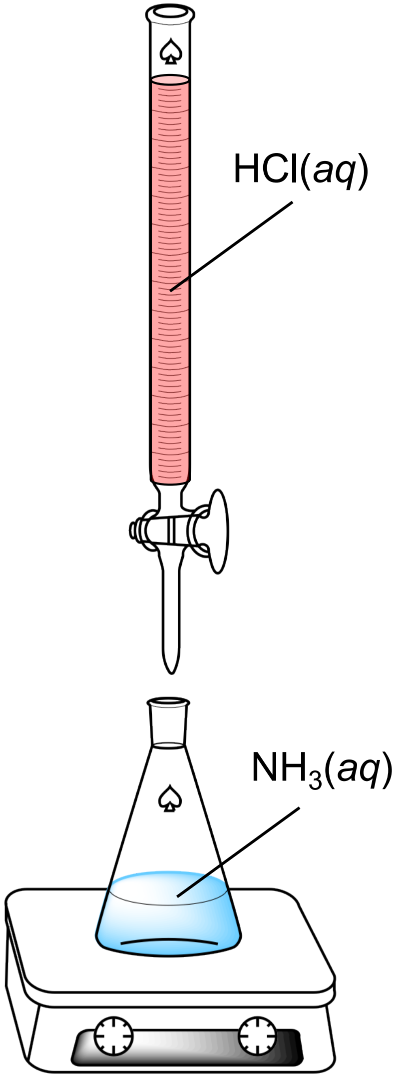
Titration of 50.00 mL of 0.02000 M NH_3 with 0.1000 M HCl

Titration reaction: $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

$pK_a = 9.245$

pH = pK_a of BH^+
at the midpoint of
the buffer region.





10-3 Titration of Weak Base with Strong Acid

Titration of 50.00 mL of 0.02000 M NH_3 with 0.1000 M HCl

Titration reaction: $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

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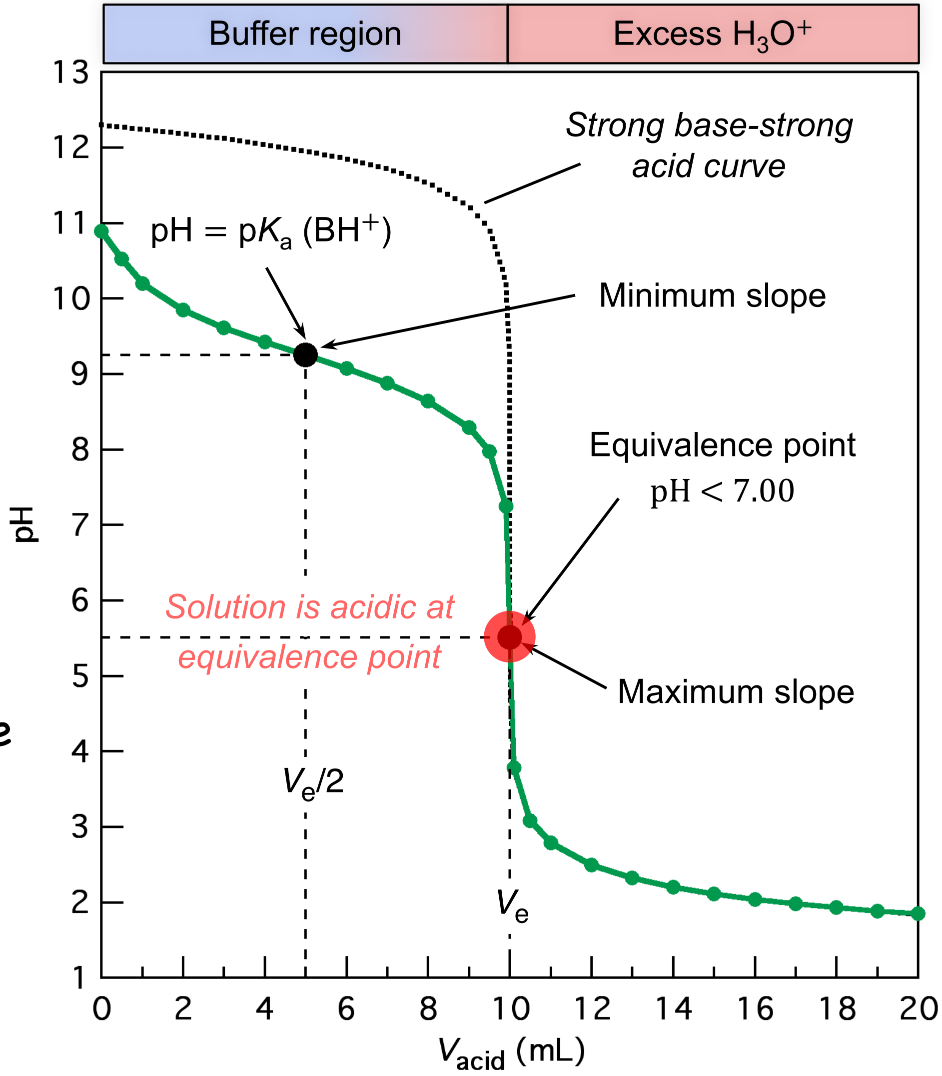
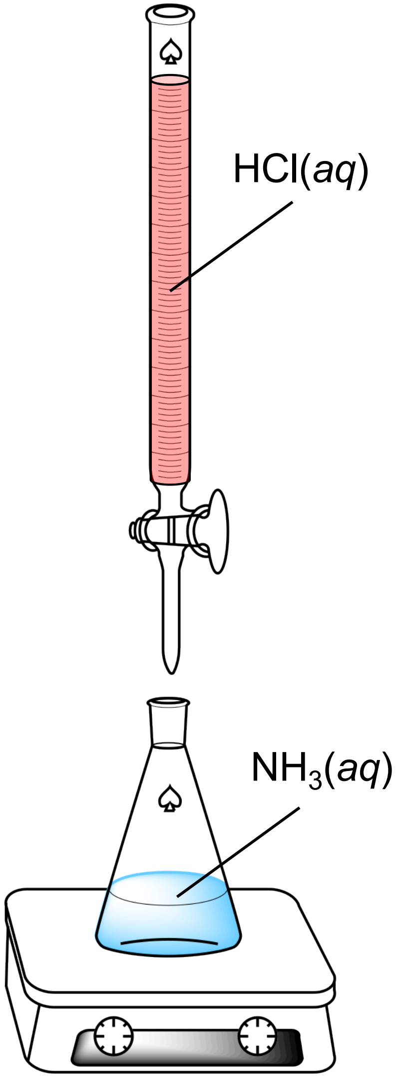




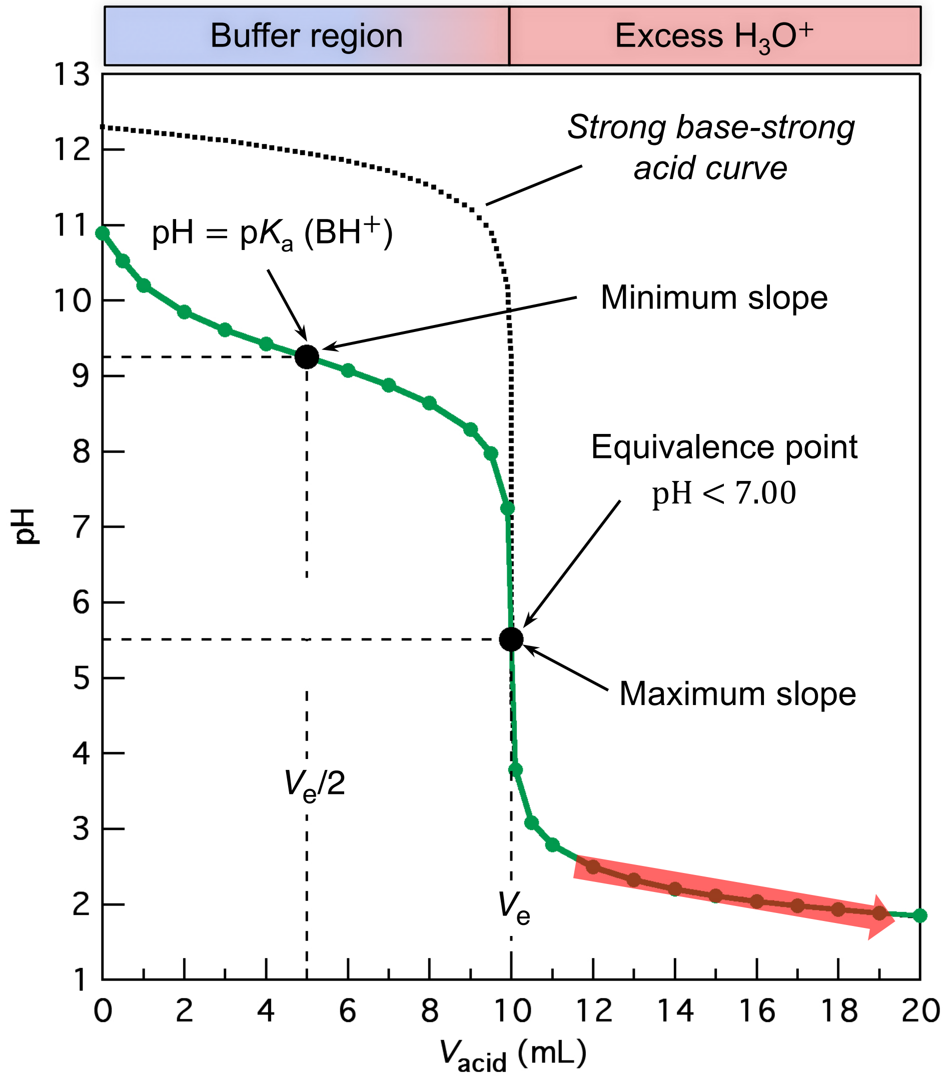
pH < 7 at the V_e point because the weak acid BH^+ reacts with water to produce H^+.

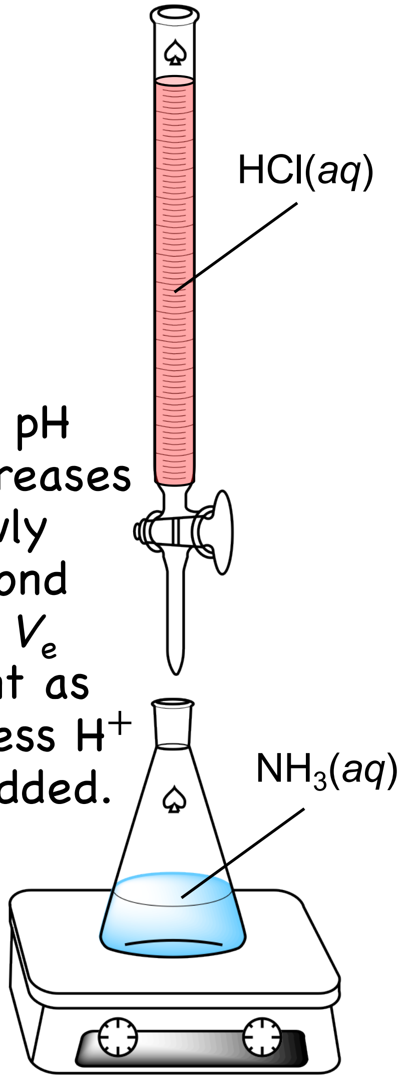
10-3 Titration of Weak Base with Strong Acid

Titration of 50.00 mL of 0.02000 M NH_3 with 0.1000 M HCl

Titration reaction: $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

$pK_a = 9.245$

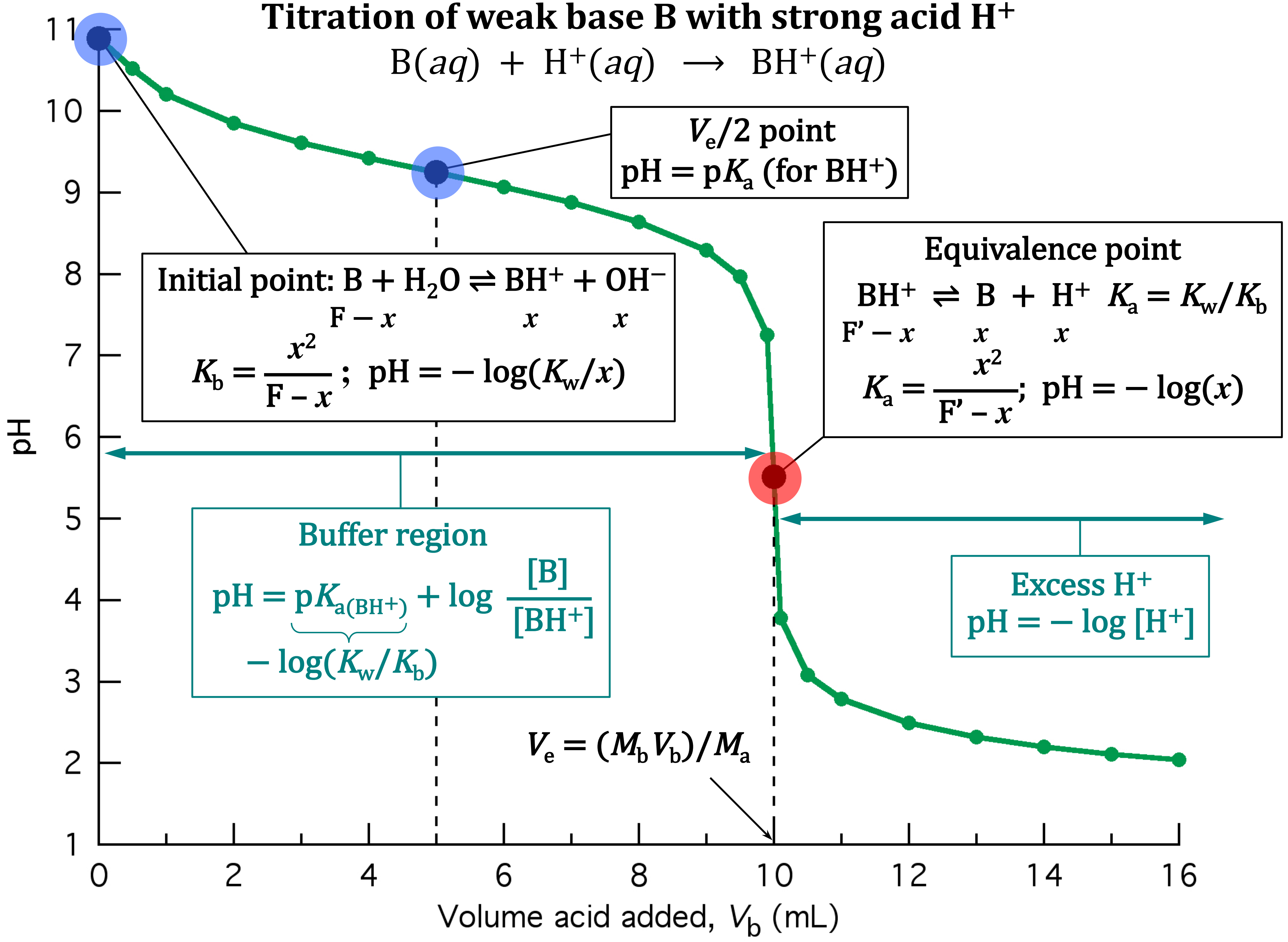




The pH decreases slowly beyond the V_e point as excess H^+ is added.

Titration of weak base B with strong acid H^+

$$B(aq) + H^+(aq) \longrightarrow BH^+(aq)$$



$V_e/2$ point
pH = pK_a (for BH^+)

Initial point: $B + H_2O \rightleftharpoons BH^+ + OH^-$

$$\underset{F-x}{B} + H_2O \rightleftharpoons \underset{x}{BH^+} + \underset{x}{OH^-}$$

$$K_b = \frac{x^2}{F-x}; \quad pH = -\log(K_w/x)$$

Equivalence point

$$\underset{F'-x}{BH^+} \rightleftharpoons \underset{x}{B} + \underset{x}{H^+} \quad K_a = K_w/K_b$$

$$K_a = \frac{x^2}{F'-x}; \quad pH = -\log(x)$$

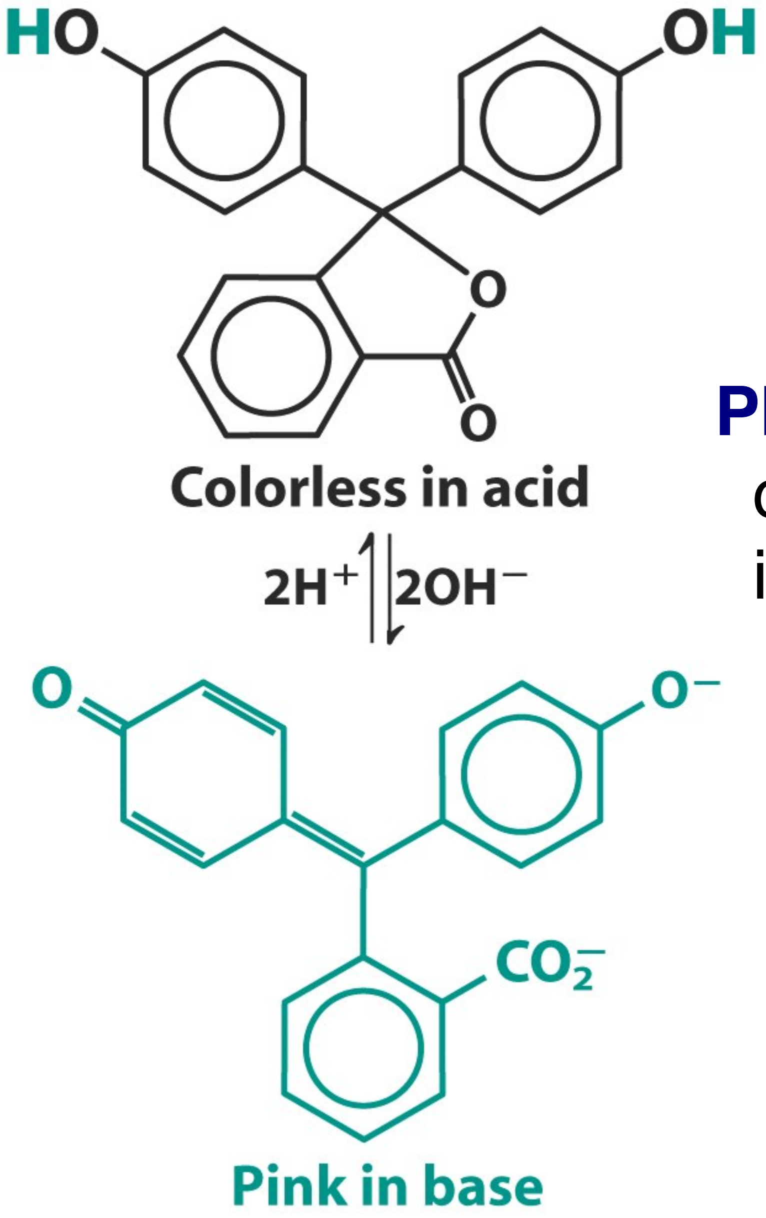
Buffer region

$$pH = \underbrace{pK_{a(BH^+)}}_{-\log(K_w/K_b)} + \log\frac{[B]}{[BH^+]}$$

Excess H^+
$pH = -\log[H^+]$

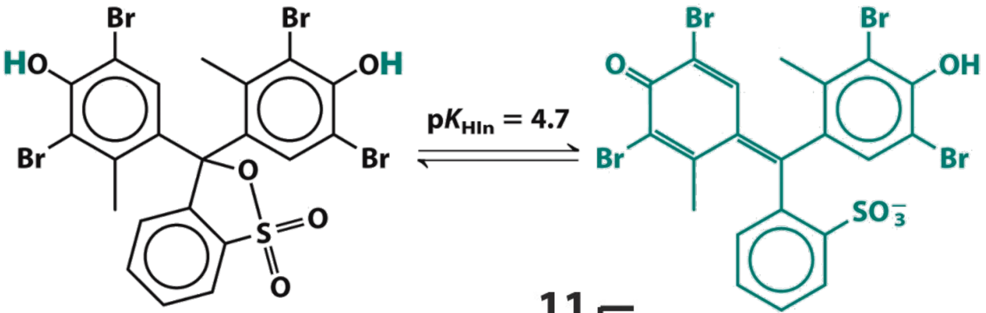
$$V_e = (M_b V_b)/M_a$$

10-4 Using Indicators to Find the End Point



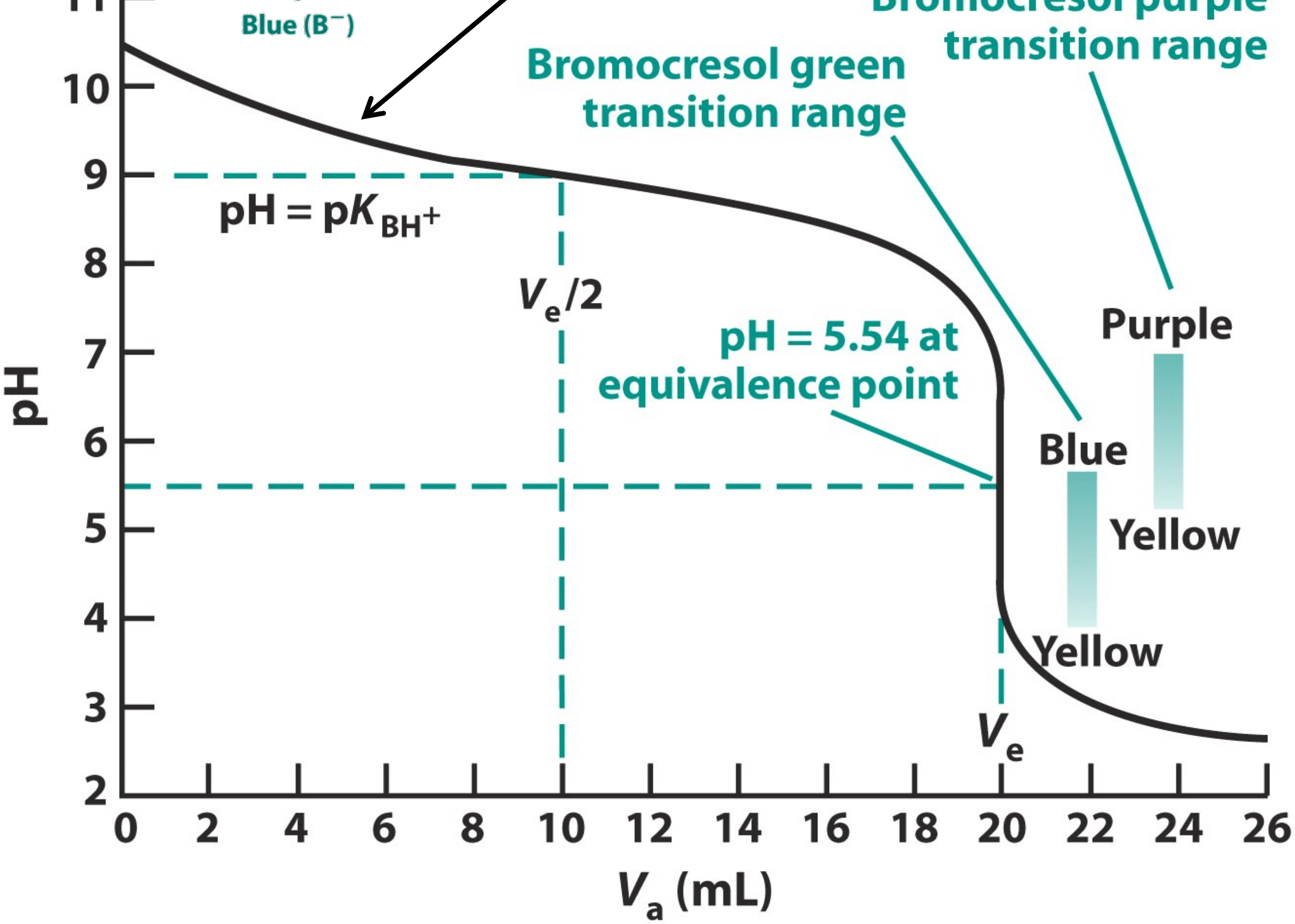
Phenolphtalein **(pK_a = 9.7 @ 25° C)**
one of the most commonly used indicators

10-4 Using Indicators to Find the End Point

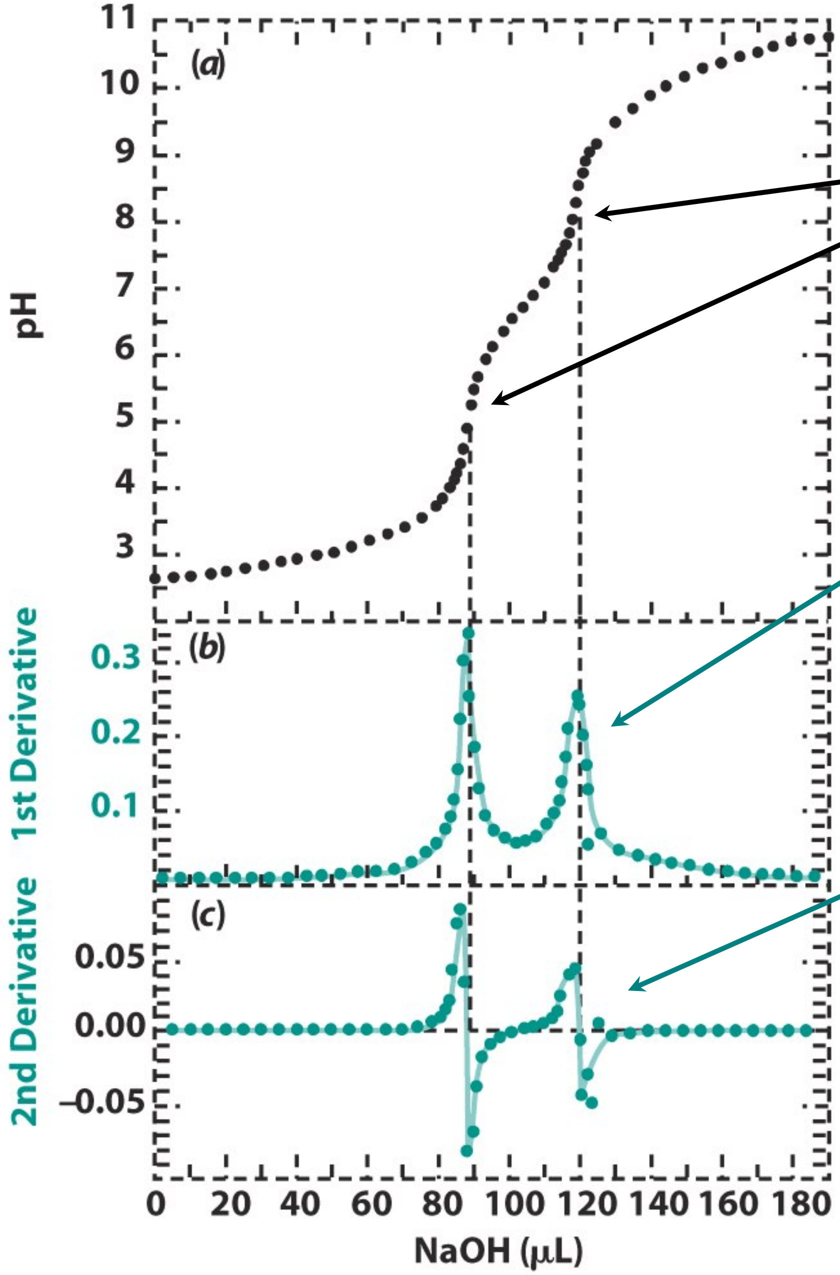


Choose an indicator whose color change occurs as close as possible to the theoretical pH of the equivalence point.

Base (pK_b = 5.00, 100 mL, 0.0100 M) titrated with 0.0500 M HCl.



10-4 Using a pH Electrode to Find the End Point



The end point has maximum slope (*first derivative*),

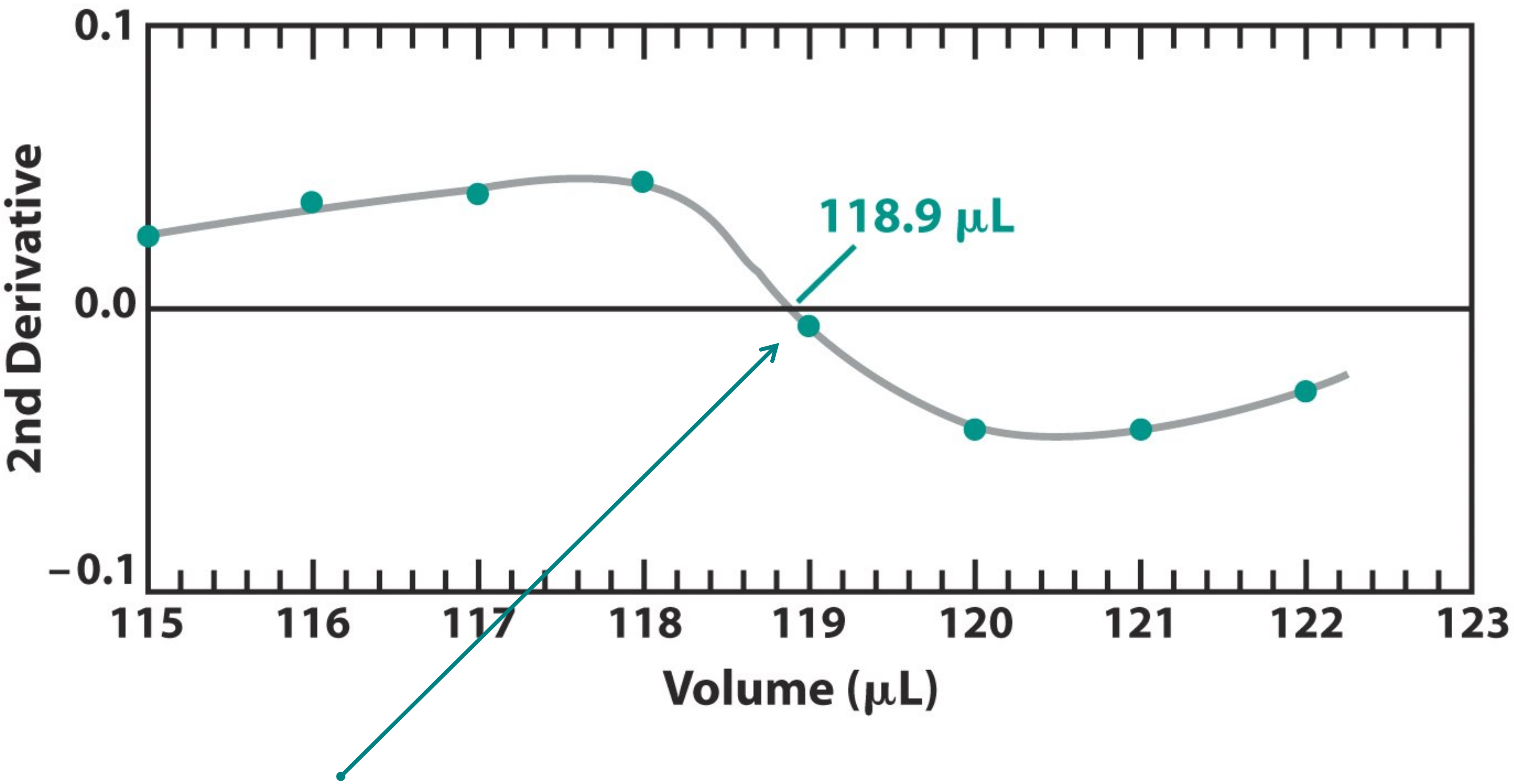
$$\text{slope} = \frac{\Delta\text{pH}}{\Delta V}$$

and zero slope of the slope (*second derivative*)

$$\frac{\Delta(\text{slope})}{\Delta V} = \frac{\Delta(\Delta\text{pH}/\Delta V)}{\Delta V}$$

End points are taken as maxima in the first derivative curve and zero crossings of the second derivative.

10-4 Using a pH Electrode to Find the End Point



The slope of the slope (*the second derivative*) is 0 at the end point.