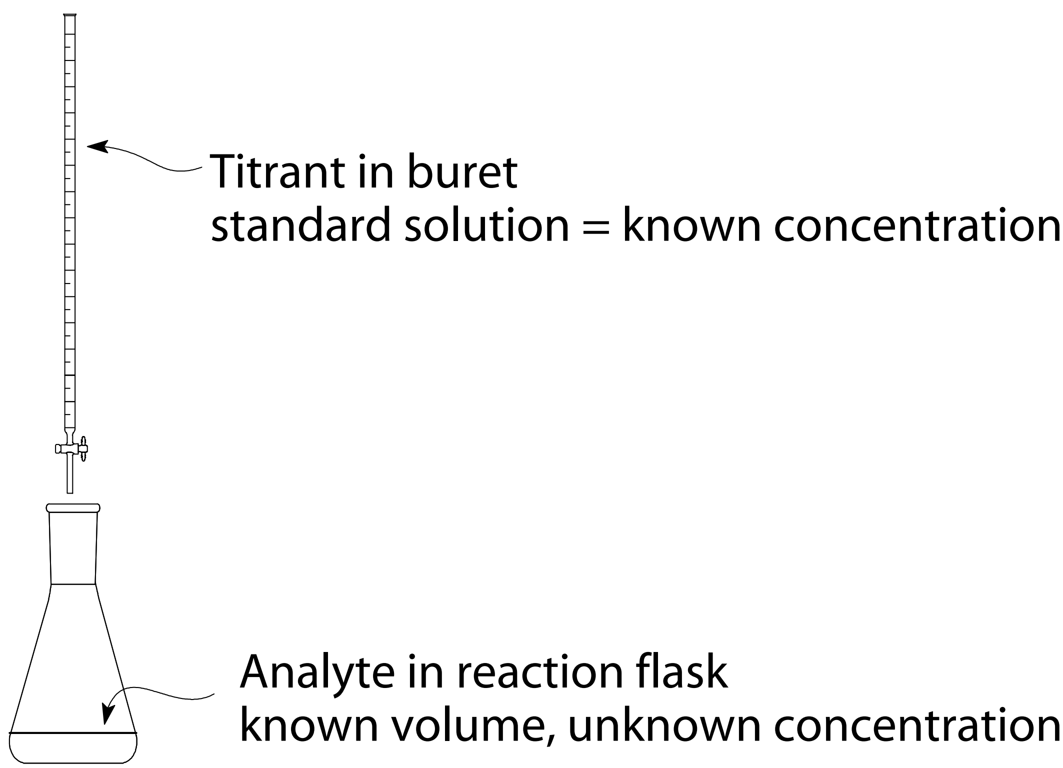
Titration

☞ Titration is the addition of a standard solution (the **titrant**) to a measured volume of a solution with unknown concentration (the **analyte)** to react according to a known stoichiometry.

$$n\ [\text{Titrant}] + m\ [\text{Analyte}] \rightarrow \text{products}$$



Titration Basic Concepts and Definitions

$$n\,[\text{Titrant}] + m\,[\text{Analyte}] \rightarrow \text{products}$$

✓ At any point in the titration, if volume is in mL,

$$\text{millimol titrant added} = \mathrm{M_t} \times V_\mathrm{t}$$

✓ **Equivalence point** - Volume of titrant necessary to achieve complete conversion of analyte into products.

☞ At the equivalence point, millimoles of analyte initially present is related to millimoles of titrant added by

$$\mathrm{M_a} \times V_\mathrm{a} = (m/n) \times \mathrm{M_t} \times V_\mathrm{t}$$

✓ **End point** - Volume of titrant added when an indicator changes color, ideally signaling the equivalence point.

Types of Acid-Base Titrations

Analyte	Titrant
Weak or strong base	Strong acid (e.g., HCl)
Weak or strong acid	Strong base (e.g., NaOH)

Examples:

strong acid - strong base (acid or base analyte; base or acid titrant)

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Weak acid (analyte) - strong base (titrant)

$$HOAc(aq) + NaOH(aq) \rightarrow NaOAc(aq) + H_2O(l)$$

Weak base (analyte) - strong acid (titrant)

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

Weak triprotic acid (analyte) - strong base (titrant)

$$H_3PO_4(aq) + 3NaOH(aq) \rightarrow Na_3PO_4(aq) + 3H_3O(l)$$

Acid-Base Titrations
Net Ionic Equations by Type

Strong Acid-Strong Base

$H_3O^+ + OH^- \rightarrow 2H_2O$

Weak Acid-Strong Base

$HA + OH^- \rightarrow A^- + H_2O$

Weak Base-Strong Acid

$B + H_3O^+ \rightarrow BH^+ + H_2O$

Acid-Base Titration
Relationships at Equivalence Point
(Monoprotic Cases)

initial millimoles analyte = millimoles titrant added

☞ $V_a M_a = V_b M_b$ ☜

Strong Acid-Strong Base

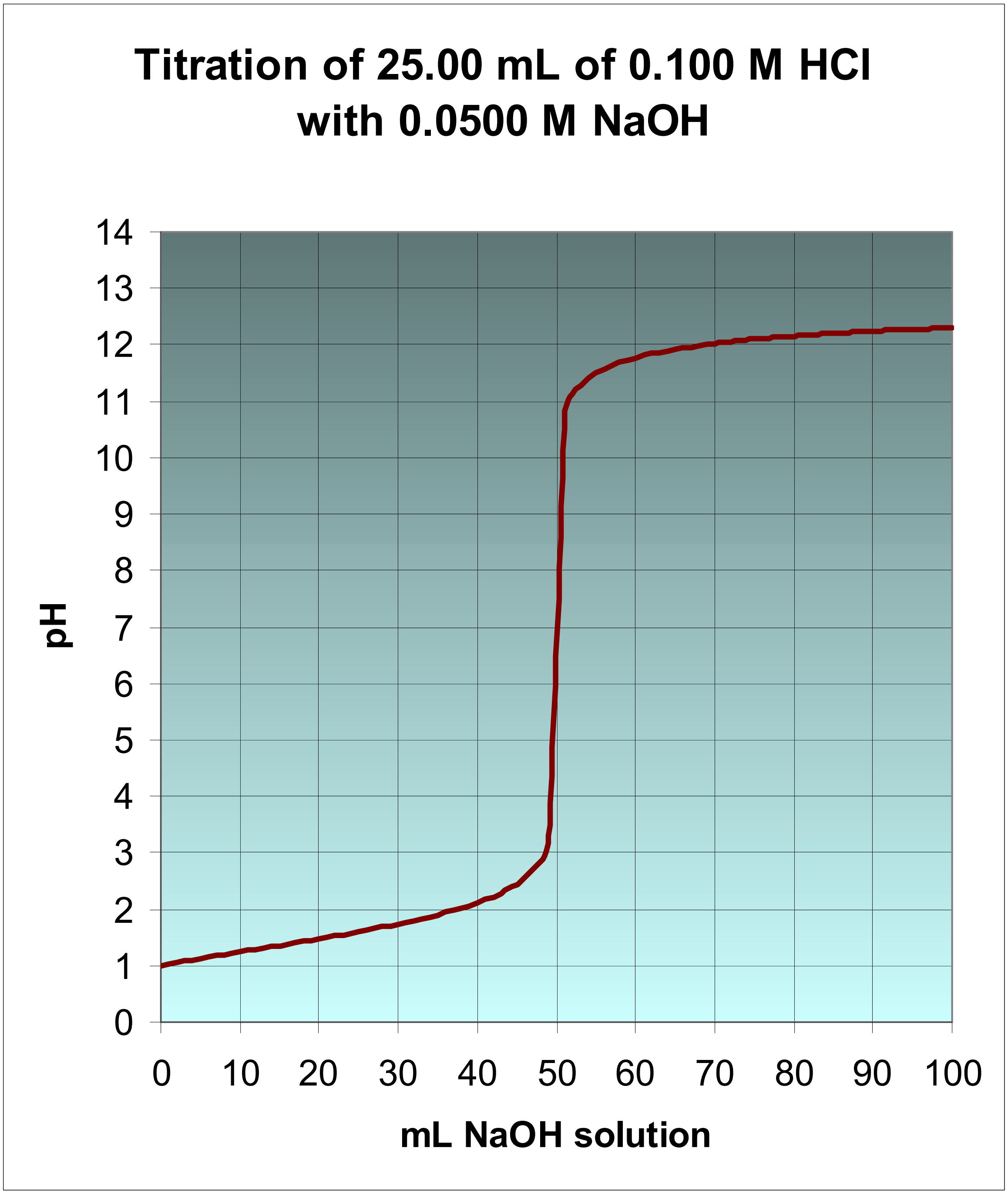
initial millimoles H_3O^+ = millimoles OH^- added
or
initial millimoles OH^- = millimoles H_3O^+ added

Weak Acid-Strong Base

initial millimoles HA = millimoles OH^- added

Weak Base-Strong Acid

initial millimoles B = millimoles H_3O^+ added



Titration of 25.00 mL of 0.100 M HCl
with 0.0500 M NaOH
pH
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
80
90
100
mL NaOH solution

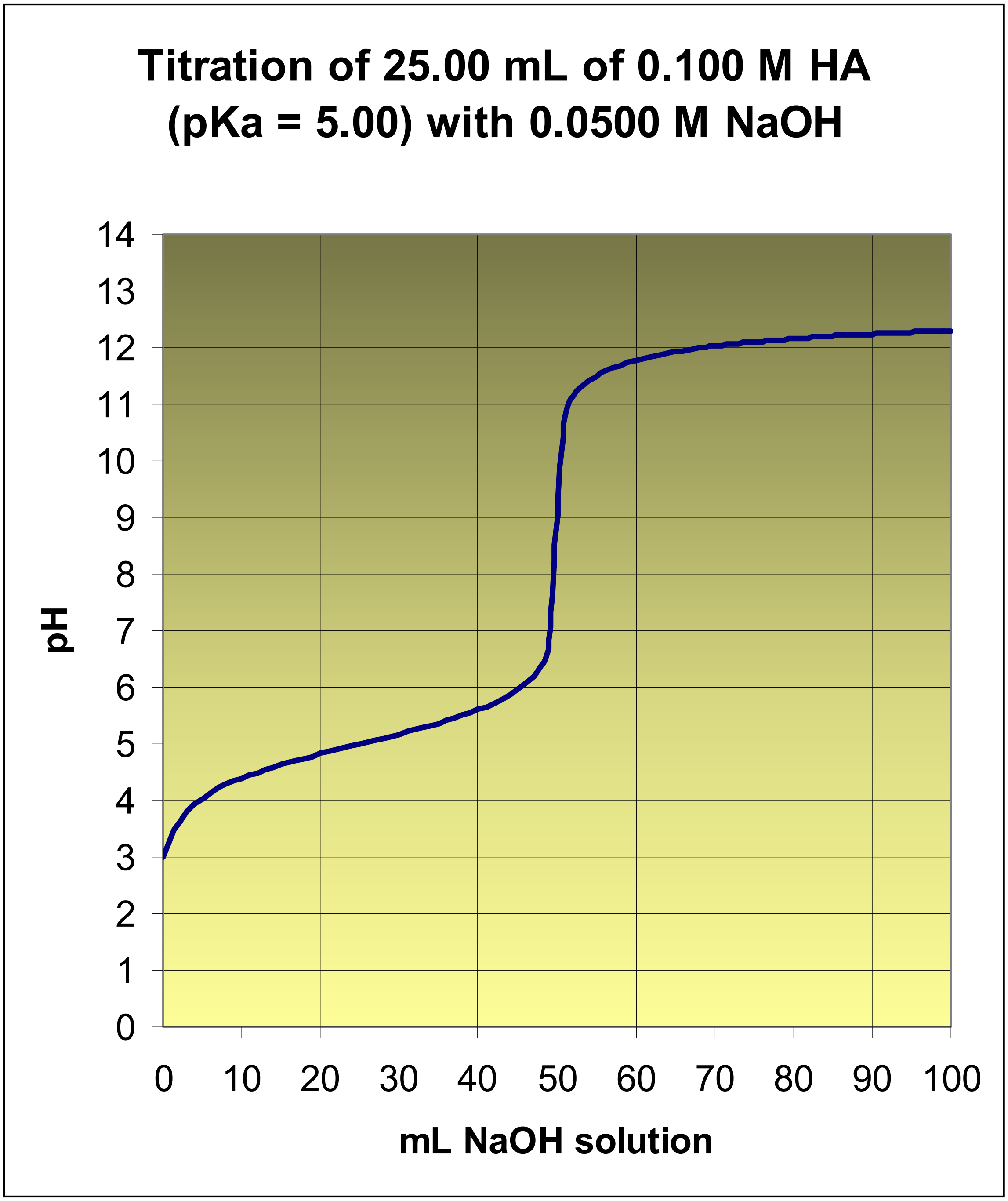
Regions in a Weak Acid Titration

1. **Initial Point** (no added titrant):
   - ✓ Pure HA in water
     - ☞ Use K_a and C_{HA} to find $[H_3O^+]$ and pH.

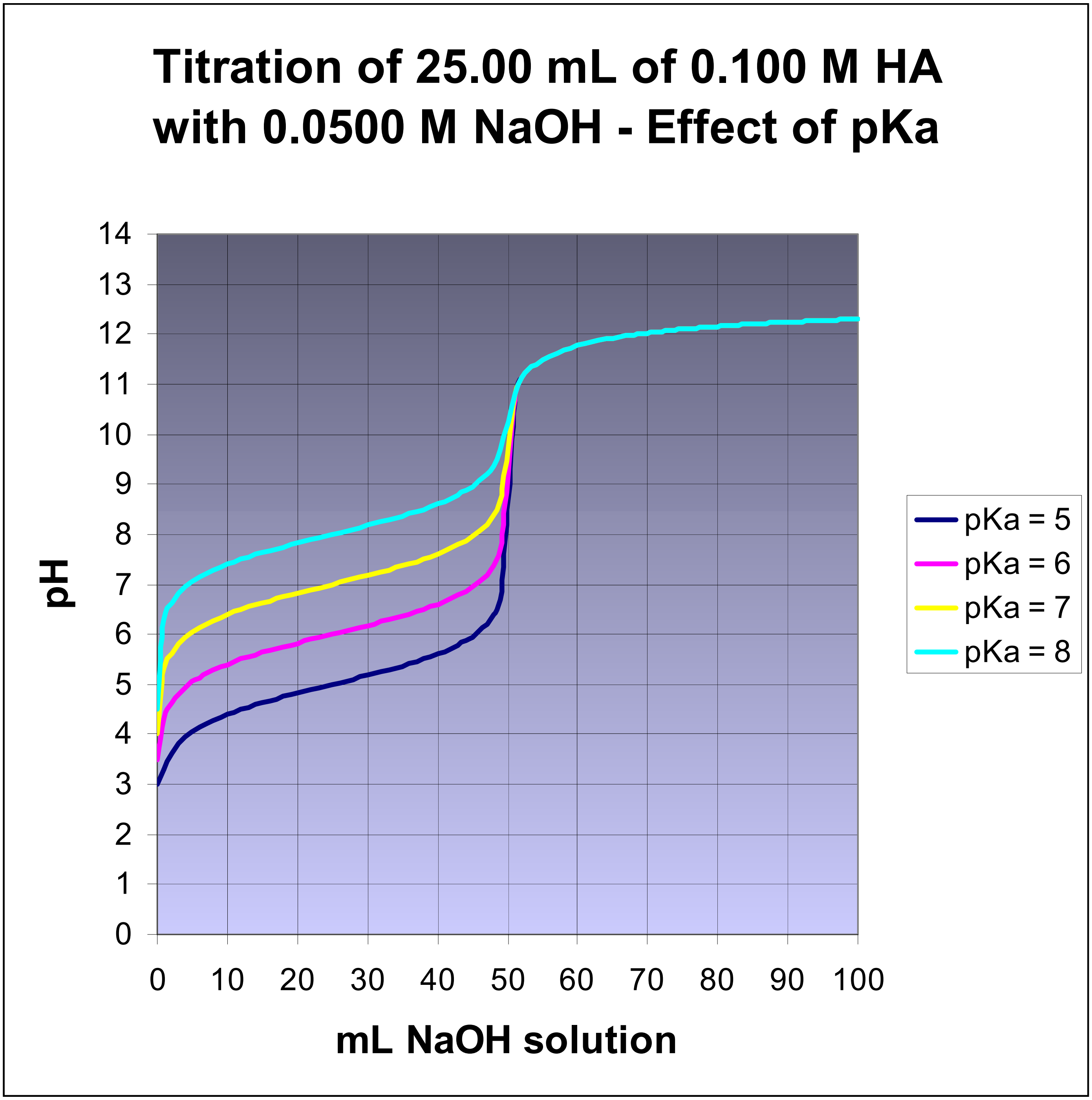
2. **Before Equivalence Point** (buffer region):
   - ✓ Significant [HA] and $[A^-]$
     - ☞ Use K_a or Henderson-Hasselbalch equation to find $[H_3O^+]$ and pH, just like a buffer.

3. **Equivalence Point**:
   - ✓ All HA converted to A^-
     - ☞ Calculate K_b for A^- as K_w/K_a^{HA}.
     - ☞ Find $[OH^-]$ and pOH as for a solution of pure A^- in water, then pH.

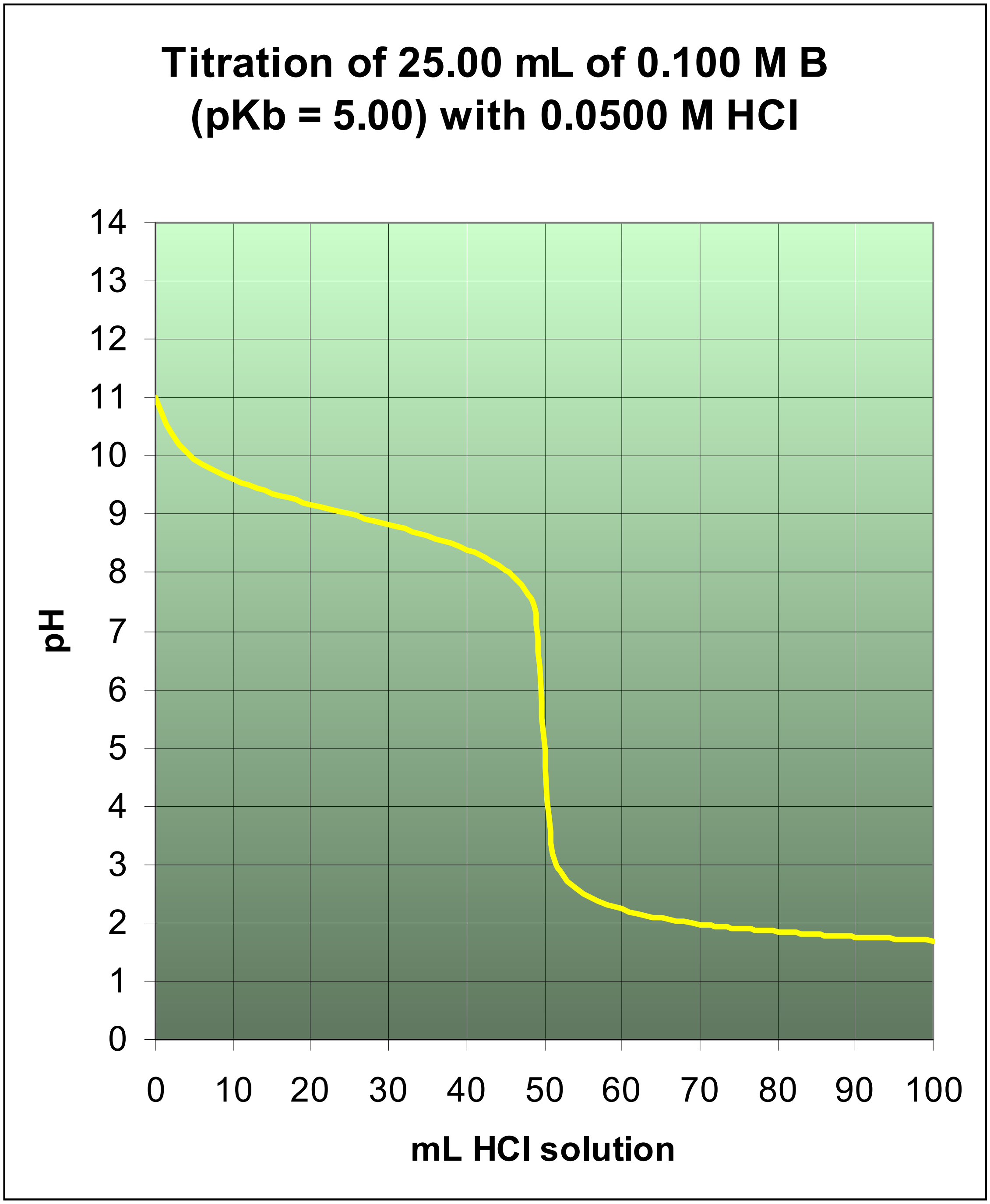
4. **Beyond Equivalence Point**:
   - ✓ Excess OH^-
     - ☞ Calculate $[OH^-]$ and pOH, then pH, as in the strong acid-base case.



Titration of 25.00 mL of 0.100 M HA
(pKa = 5.00) with 0.0500 M NaOH
pH
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
80
90
100
mL NaOH solution



Titration of 25.00 mL of 0.100 M HA
with 0.0500 M NaOH - Effect of pKa
pH
mL NaOH solution
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
0
10
20
30
40
50
60
70
80
90
100
pKa = 5
pKa = 6
pKa = 7
pKa = 8



Titration of 25.00 mL of 0.100 M B
(pKb = 5.00) with 0.0500 M HCl
pH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
0
10
20
30
40
50
60
70
80
90
100
mL HCl solution

pH at the Equivalence Point

✓ Strong acid – strong base titration:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

☞ pH = 7

✓ Weak acid – strong base titration:

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

☞ pH > 7

✓ Weak base – strong acid titration:

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

☞ pH < 7

Summary of Calculations for Weak Acid Titrations
Before Equivalence Point

Region	Calculation of $[H_3O^+]$
Initial (no added titrant)	$K_a = \frac{[H_3O^+]^2}{[HA]}$ $= \frac{[H_3O^+]^2}{C_{HA} - [H_3O^+]}$ Often, $[H_3O^+] = \sqrt{K_a C_{HA}}$
Before Equivalence Point (Buffer Region)	$K_a = \frac{[H_3O^+] C_{A^-}}{C_{HA}}$ $[H_3O^+] = K_a \times \left(\frac{\text{mmol HA}}{\text{mmol A}^-} \right)$
Half Titration Point	$[A^-] = [HA]$ $[H_3O^+] = K_a$ $pH = pK_a$

Summary of Calculations for Weak Acid Titrations
Equivalence Point and Beyond

Region	Calculation of $[OH^-]$
Equivalence Point	$K_b^{A^-} = \frac{K_w}{K_a^{HA}}$ $[OH^-] = \sqrt{K_b^{A^-} C_{A^-}}$
After Equivalence Point	$[OH^-] = \left(\frac{\text{mmol excess } OH^-}{\text{total volume}}\right)$

Summary of Calculations for Weak Base Titrations
Before Equivalence Point

Region	Calculation of $[OH^-]$
Initial (no added titrant)	$K_b = \frac{[OH^-]^2}{[B]}$ $= \frac{[OH^-]^2}{C_B - [OH^-]}$ Often, $[OH^-] = \sqrt{K_b C_B}$
Before Equivalence Point (Buffer Region)	$K_b = \frac{[OH^-]\, C_{BH^+}}{C_B}$ $[OH^-] = K_b \times \left(\frac{\text{mmol B}}{\text{mmol BH}^+} \right)$
Half Titration Point	$[BH^+] = [B]$ $[OH^-] = K_b$ $pOH = pK_b$

Summary of Calculations for Weak Base Titrations
Equivalence Point and Beyond

Region	Calculation of $[H_3O^+]$
Equivalence Point	$K_a^{BH^+} = \frac{K_w}{K_b^B}$ $[H_3O^+] = \sqrt{K_a^{BH^+} C_{BH^+}}$
After Equivalence Point	$[H_3O^+] = \left(\frac{\text{mmol excess } H_3O^+}{\text{total volume}} \right)$