$$-\log[H^+] = -\log K_a - \log \frac{[HX]}{[X^-]}$$

$$\therefore \boxed{pH = pK_a + \log \frac{[X^-]}{[HX]}}$$

Addition of Strong Acids or Bases to Buffers

- We break the calculation into two parts: stoichiometric and equilibrium.

Addition of Strong Acids or Bases to Buffers

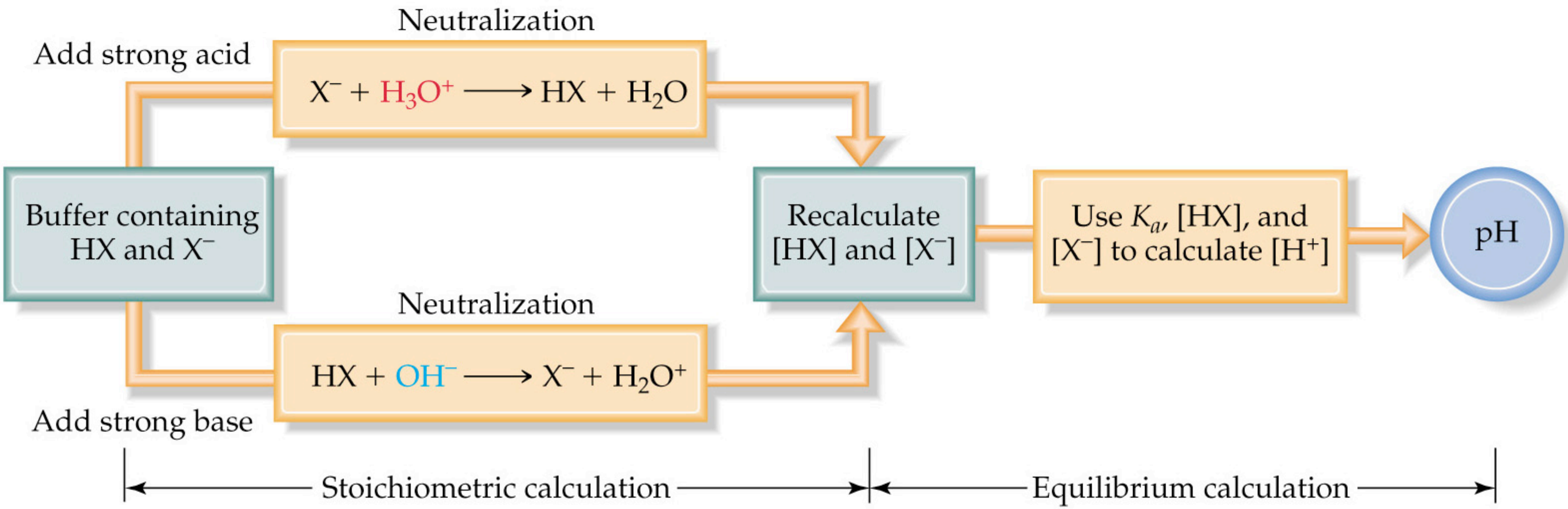
- The amount of strong acid or base added results in a neutralization reaction:

$$X^- + H_3O^+ \rightarrow HX + H_2O$$

$$HX + OH^- \rightarrow X^- + H_2O.$$

- By knowing how much H_3O^+ or OH^- was added (stoichiometry) we know how much HX or X^- is formed.
- With the concentrations of HX and X^- (note the change in volume of solution) we can calculate the pH from the Henderson-Hasselbalch equation or the original equilibrium expression (ICE chart).

$$pH = pK_a + \log \frac{\text{conjugate base}}{\text{acid}}$$



Examples

1. Consider a buffer prepared by placing 0.60 moles of HF ($K_a = 7.2 \times 10^{-4}$) and 0.48 moles of NaF in a 1.00 L solution.

    a. Calculate the pH of the buffer

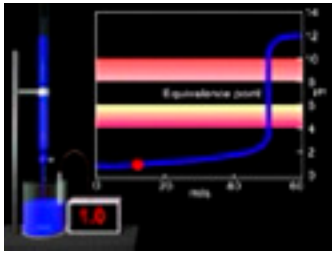
    b. Calculate the pH after the addition of 0.08 moles of HCl

    c. Calculate the pH after the addition of 0.10 moles of NaOH.

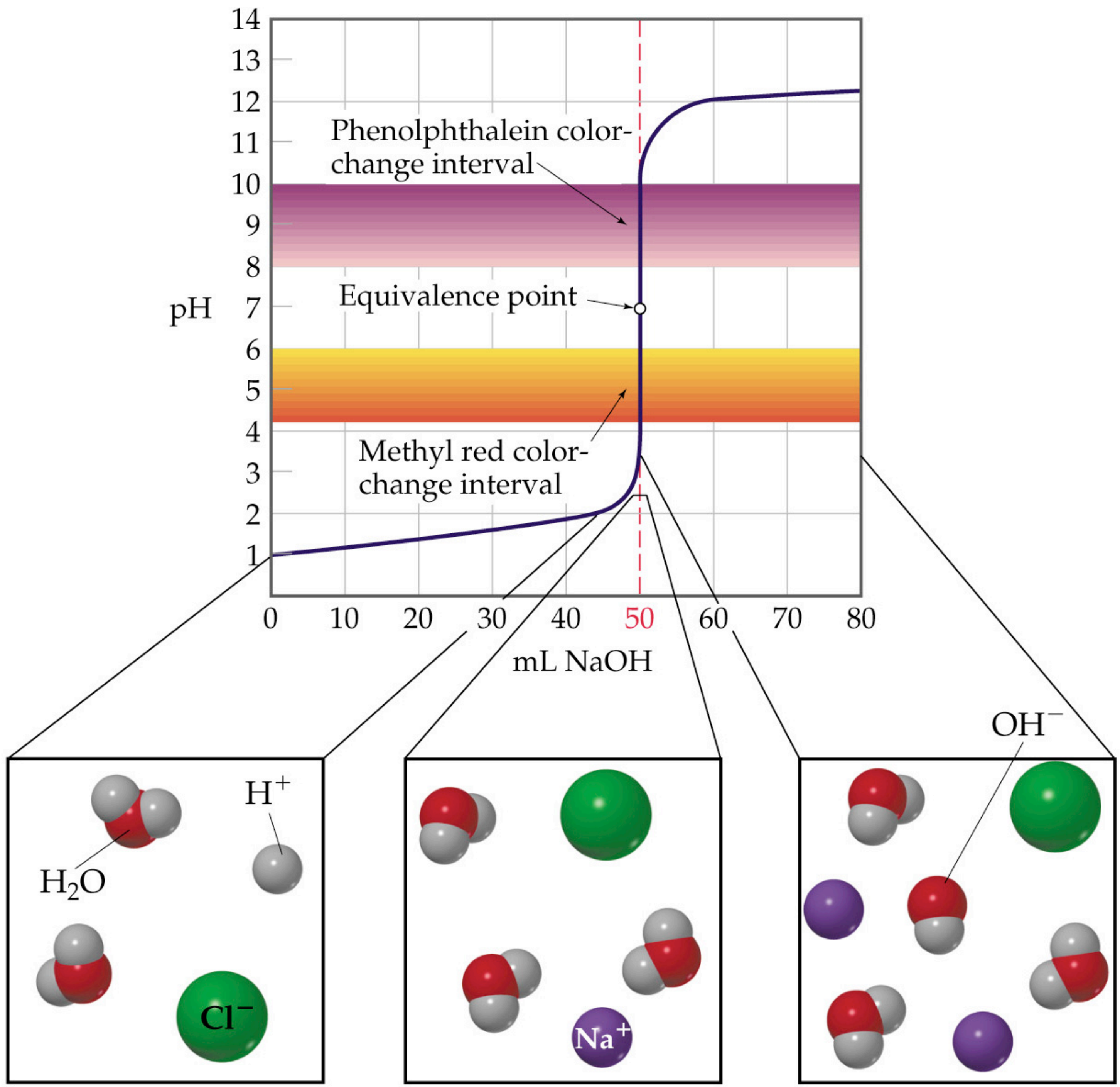
Acid-Base Titrations

Strong Acid-Strong Base Titrations

- A plot of pH versus volume of acid (or base) added is called a titration curve.
- Consider adding a strong base (e.g. NaOH) to a solution of a strong acid (e.g. HCl).
  - Before any base is added, the pH is given by the strong acid solution. Therefore, pH < 7.
  - When base is added, before the equivalence point, the pH is given by the amount of strong acid in excess. Therefore, pH < 7.



- The equivalence point in a titration is the point at which the acid and base are present in stoichiometric quantities.
- The end point in a titration is the observed point (indicator changes color)
- The difference between equivalence point and end point is called the titration error.
- Initially, the strong acid is in excess, so the pH < 7.
- As base is added, the pH increases but is still less than 7.
- At equivalence point, the pH is given by the salt solution (i.e. pH $= 7$).
- After equivalence point, the pH is given by the amount of strong base in excess.


14
13
12
11
10
9
8
pH
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
mL NaOH
Phenolphthalein color-change interval
Equivalence point
Methyl red color-change interval
H+
H2O
Cl−
Na+
OH−

Strong Acid-Strong Base Titrations

  - At equivalence point, the amount of base added is stoichiometrically equivalent to the amount of acid originally present. Therefore, the pH is determined by the salt solution. Therefore, pH = 7.

- Consider adding a strong base (e.g. NaOH) to a solution of a strong acid (e.g. HCl).
- We know the pH at equivalent point is 7.00.
- To detect the equivalent point, we use an indicator that changes color somewhere near 7.00.

Calculations

- Equivalence point: mol H^+ = mol OH^-
- pH before equivalence point:

$$[H^+] = \frac{mol\ H^+\ remaining}{total\ volume}$$

- pH at equivalence point = 7
- pH after equivalence point:

$$[OH^-] = \frac{excess\ mol\ OH^-\ added}{total\ volume}$$

Example

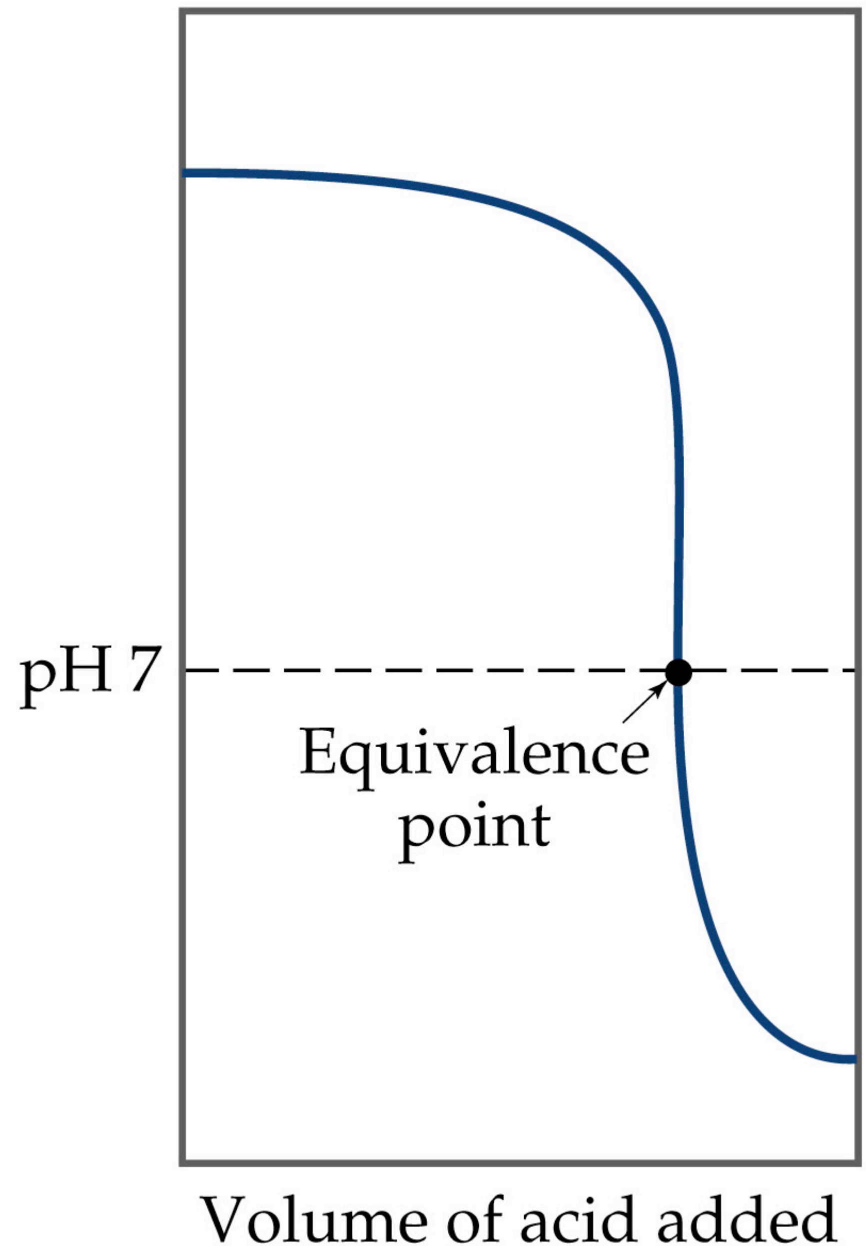
Consider the titration of 50.0 mL of 0.25 M HCl with 0.15 M NaOH

a. Calculate the volume of NaOH required to reach the equivalence point.

b. Calculate pH:

1. initially
2. after adding 25 mL NaOH
3. at the equivalence point
4. after adding 100 mL NaOH

Strong Base-Strong Acid Titrations



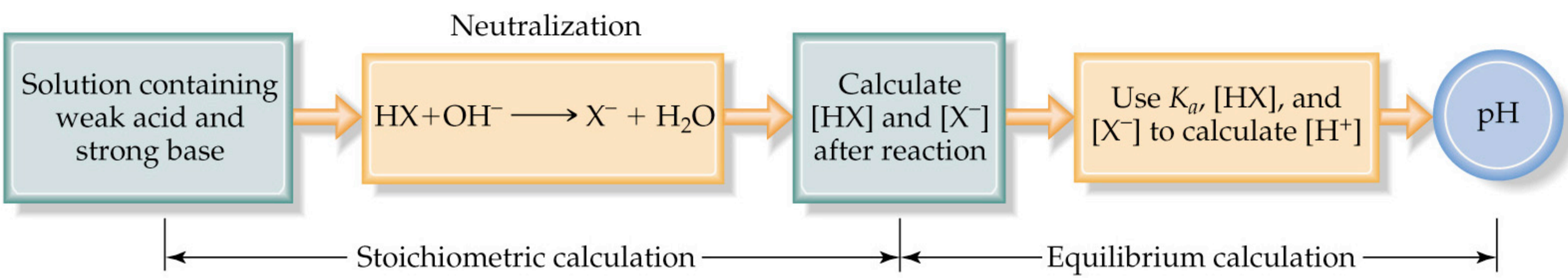
Weak Acid-Strong Base Titrations

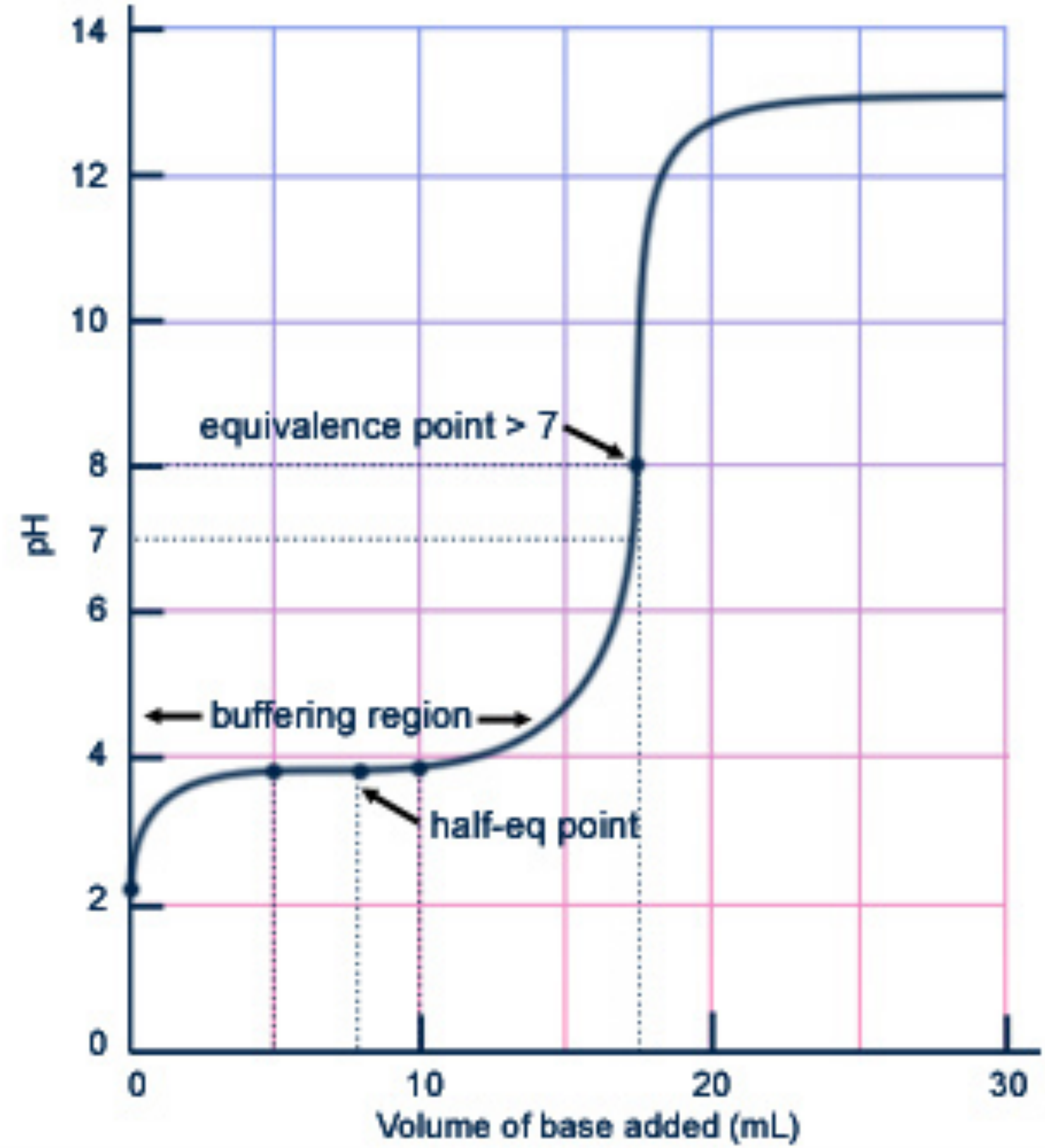
- Consider the titration of acetic acid, $HC_2H_3O_2$ and NaOH.
- Before any base is added, the solution contains only weak acid. Therefore, pH is given by the equilibrium calculation.
- As strong base is added, the strong base consumes a stoichiometric quantity of weak acid:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow C_2H_3O_2^-(aq) + H_2O(l)$$

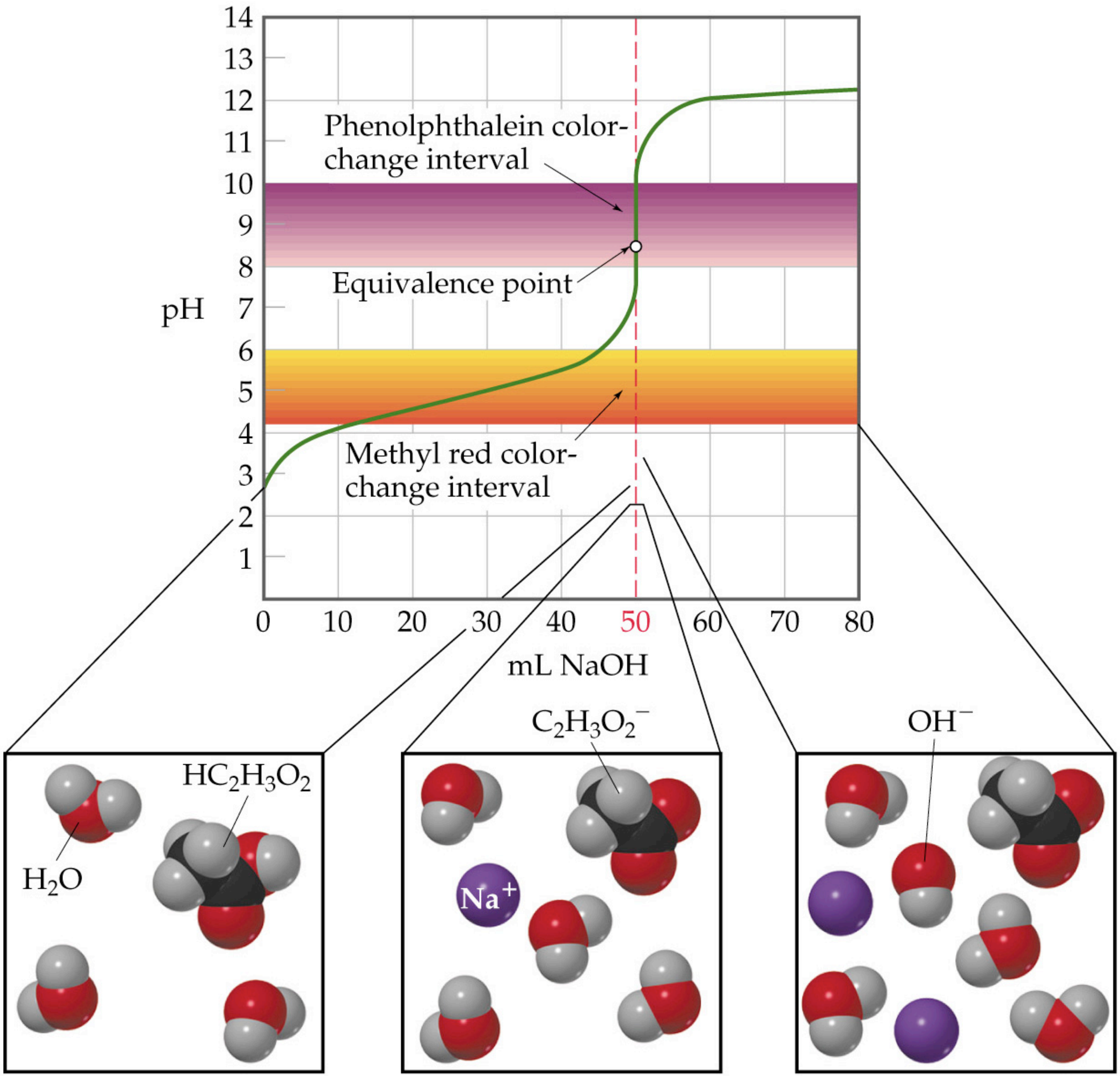
Weak Acid-Strong Base Titrations

- There is an excess of acid before the equivalence point.
- Therefore, we have a mixture of weak acid and its conjugate base.
  - The pH is given by the buffer calculation.
    - **First the amount of $C_2H_3O_2^-$ generated is calculated, as well as the amount of $HC_2H_3O_2$ consumed. (Stoichiometry.)**
    - **Then the pH is calculated using equilibrium conditions. (Henderson-Hasselbalch.)**





14
12
10
8
7
6
4
2
0
pH
equivalence point > 7
buffering region
half-eq point
0
10
20
30
Volume of base added (mL)


14
13
12
11
10
9
8
7
6
5
4
3
2
1
pH
0
10
20
30
40
50
60
70
80
mL NaOH
Phenolphthalein color-change interval
Equivalence point
Methyl red color-change interval
H_2O
$HC_2H_3O_2$
$C_2H_3O_2^-$
Na^+
OH^-

Weak Acid-Strong Base Titrations

- At the equivalence point, all the acetic acid has been consumed and all the NaOH has been consumed. However, $C_2H_3O_2^-$ has been generated.
  - Therefore, the pH is given by the $C_2H_3O_2^-$ solution.
  - This means pH > 7.
    - More importantly, pH ≠ 7 for a weak acid-strong base titration.
- After the equivalence point, the pH is given by the strong base in excess.

Calculations

- At equivalence point, moles acid = moles base
- Initial pH = pH of a weak acid solution (ICE chart)
- pH before equivalence point – Buffer Calculation

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

- pH at equivalence point – pH of a weak base solution (ICE chart)
- pH after equivalence point

$$[OH^-] = \frac{excess\ mol\ OH^-\ added}{total\ volume}$$

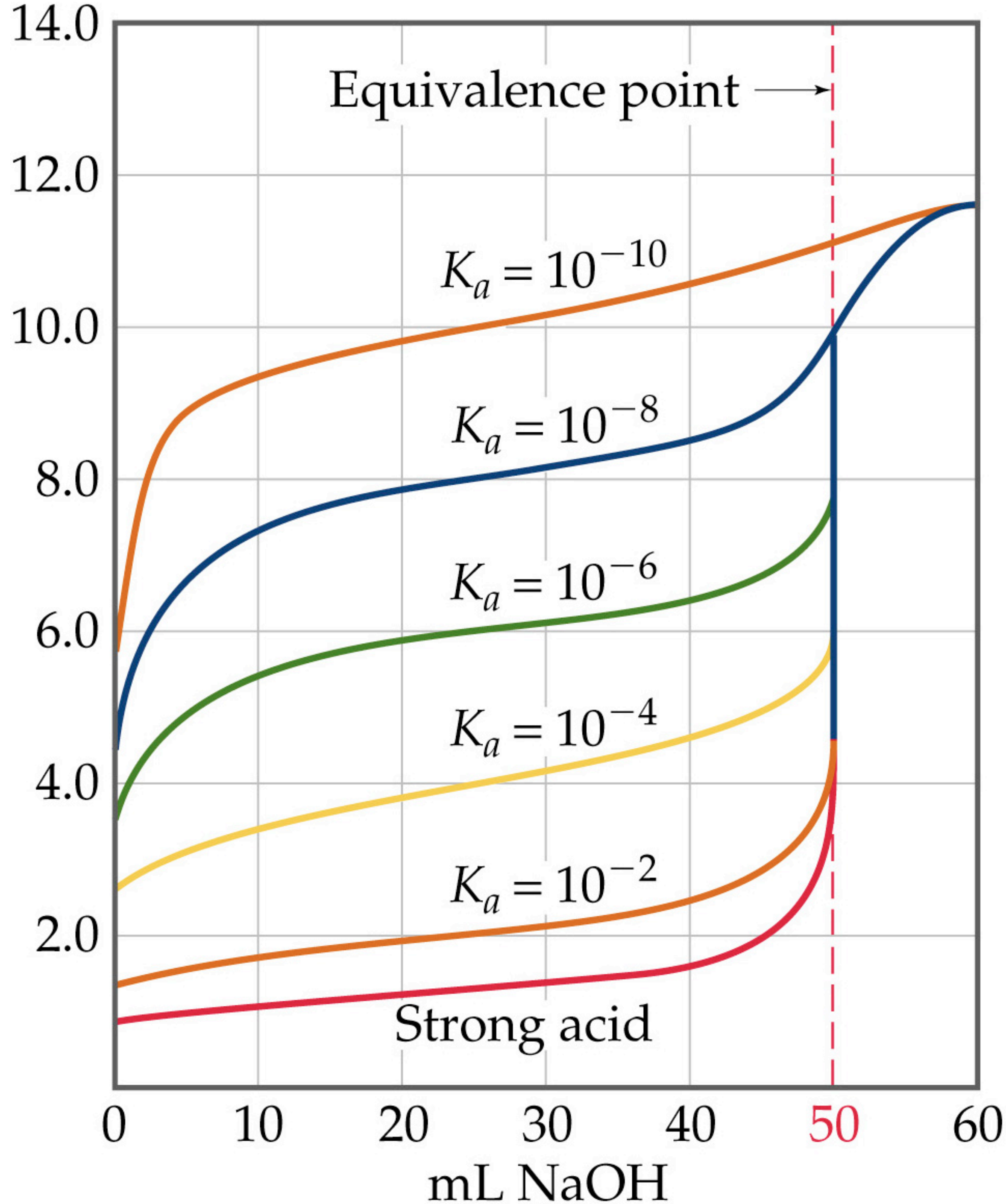
Example

Consider the titration of 50.0 mL of 0.25 M HF with 0.15 M NaOH

a. Calculate the volume of NaOH required to reach the equivalence point.

b. Calculate pH:

   1. initially
   2. after adding 25 mL NaOH
   3. at the equivalence point
   4. after adding 100 mL NaOH



14.0
12.0
10.0
8.0
6.0
4.0
2.0
Equivalence point
$K_a = 10^{-10}$
$K_a = 10^{-8}$
$K_a = 10^{-6}$
$K_a = 10^{-4}$
$K_a = 10^{-2}$
Strong acid
0
10
20
30
40
50
60
mL NaOH

Type of Titration	**pH at Equivalence Point**
Strong Acid and Strong Base	7
Strong Acid and Weak Base	<7
Strong Base and Weak Acid	>7
Weak Base and Weak Acid	If $K_a>K_b$, pH<7 If $K_a<K_b$, pH>7