Acid–Base Titrations

(A) Theories of Acid–Base Indicators

Indicators are weak acids or bases that change color depending on the pH.

Theories:

1. **Ostwald's Theory**
   - Indicators are weak acids/bases.
   - Their ionized and unionized forms have different colors.
   - pH changes shift ionization equilibrium → color change.

   Example:

   HIn ⇌ H++In−HIn \; \rightleftharpoons \; H^+ + In^-HIn⇌H++In−

   - **HIn** (acid form) has one color
   - **In⁻** (base form) has another color
2. **Quinonoid Theory**
   - Indicator exists in two tautomeric forms: **benzenoid** (one color) and **quinonoid** (another color).
   - Acid/base medium stabilizes one form → visible color change.

Type	Example	Indicator
Strong Acid vs Strong Base	HCl vs NaOH	Phenolphthalein, Methyl orange (both work)
Strong Acid vs Weak Base	HCl vs NH_4OH	Methyl orange (acidic end point)
Weak Acid vs Strong Base	CH_3COOH vs NaOH	Phenolphthalein (basic end point)
Weak Acid vs Weak Base	CH_3COOH vs NH_4OH	No sharp endpoint (potentiometry needed)

Acid–Base Titrations

↓

Strong Acid + Strong Base → pH 7, sharp endpoint

Strong Acid + Weak Base → pH < 7, acidic endpoint

Weak Acid + Strong Base → pH > 7, basic endpoint

Weak Acid + Weak Base → No sharp endpoint

Classification of acid base titration

1. Strong Acid vs Strong Base

- Example: **HCl vs NaOH**
- Neutralization at **pH 7** (sharp change).
- **Indicators**: Both **methyl orange** and **phenolphthalein** suitable.
- **Neutralization curve**: Vertical rise at pH 7.

2. Strong Acid vs Weak Base

- Example: **HCl vs NH_4OH**
- Salt formed hydrolyzes → medium becomes **acidic** (pH < 7).
- **Indicator**: Methyl orange (works well in acidic range).
- **Neutralization curve**: Vertical rise around pH 5.

3. Weak Acid vs Strong Base

- Example: **CH_3COOH vs NaOH**
- Salt hydrolyzes → medium becomes **basic** (pH > 7).
- **Indicator**: Phenolphthalein (works well in basic range).
- **Neutralization curve**: Vertical rise around pH 9.

4. Weak Acid vs Weak Base

- Example: **CH_3COOH vs NH_4OH**
- Salt hydrolyzes strongly; pH change is **very small** and gradual.
- **Indicators**: No sharp endpoint → conventional indicators fail.
- **Method used**: Potentiometric or conductometric titration.
- **Neutralization curve**: No sharp vertical region.

(C) Theory of Titrations

1. Strong Acid vs Strong Base

- Complete neutralization, sharp pH change near equivalence (pH ~7).

- Both methyl orange & phenolphthalein suitable.

2. Strong Acid vs Weak Base

- Salt hydrolyzes → equivalence point is **acidic (pH < 7)**.
- Use **methyl orange**.

3. Weak Acid vs Strong Base

- Salt hydrolyzes → equivalence point is **basic (pH > 7)**.
- Use **phenolphthalein**.

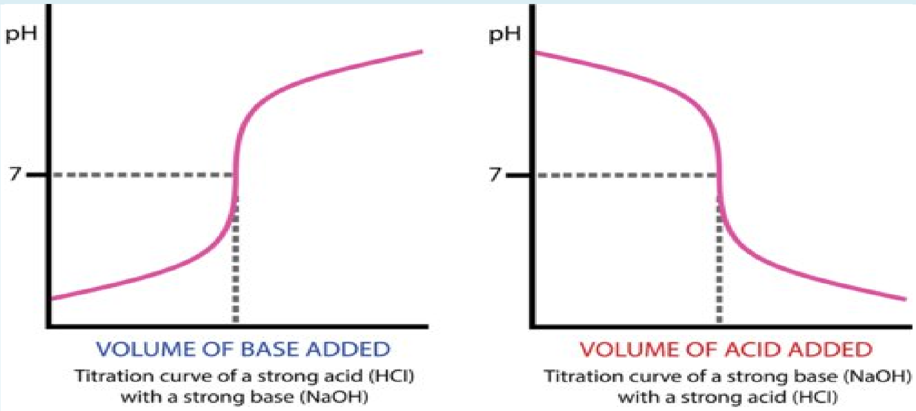
4. Weak Acid vs Weak Base

- Gradual pH change, no sharp inflection.
- Indicators fail → need **potentiometric titration**.

Neutralization Curves

☞ Flow of chart:

- **Strong acid + strong base** → S-shaped, sharp vertical rise at pH 7.
- **Strong acid + weak base** → steep rise at acidic pH (~5).
- **Weak acid + strong base** → steep rise at basic pH (~9).
- **Weak acid + weak base** → sloped curve, no clear equivalence.



Acid-base titration curves

Before we start discussing about titration and titration curves, we should quickly refresh the concept of a weak/strong acid and weak/strong base.

A strong acid dissociates (or ionizes) completely in aqueous solution to form hydronium ions (H\[_{3}\]O\[^\text{+}\])

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

A weak acid does not dissociate completely in aqueous solution to form hydronium ions (H\[_{3}\]O\[^\text{+}\])

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

A strong base dissociates completely in aqueous solution to form hydroxide ions (OH\[^\text{-}\])

$$NaOH \longrightarrow Na^+ + OH^-$$

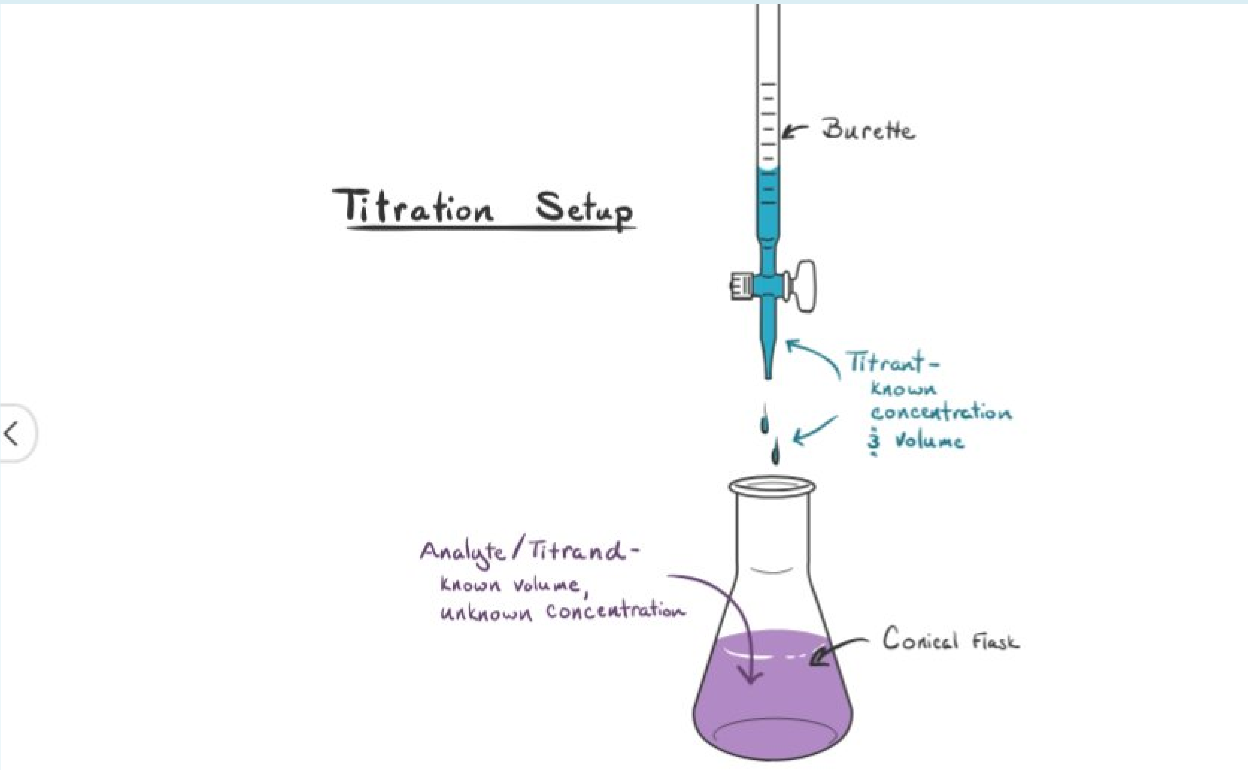
A weak base does not dissociate completely in aqueous solution to form hydroxide ions (OH\[^\text{-}\])

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$\underset{\text{acid}}{HA} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{conjugate base}}{A^-}$$

Here, HA is the acid and A\[^\text{-}\] is termed as the conjugate base of HA

$$\underset{\text{base}}{A^-} + H_2O \rightleftharpoons OH^- + \underset{\text{conjugate acid}}{HA}$$


Titration Setup
Burette
Titrant -
known
concentration
& volume
Analyte / Titrand -
known volume,
unknown concentration
Conical Flask