

UNIT 2

Acid-Base Titration: Theories of Acid-Base Indicators

Introduction

Acid-base titration is a type of volumetric analysis used to determine the concentration of an acid or base by neutralizing it with a base or acid of known concentration. To detect the endpoint of the titration, **acid-base indicators** are used.

Indicators are **weak organic acids or bases** that change color depending on the pH of the solution. The choice of a suitable indicator depends on the **pH range** over which the color change occurs.

Theories of Acid-Base Indicators

There are two primary theories that explain how acid-base indicators work:

1. Ostwald's Theory (Ionization Theory)

Proposed by: Wilhelm Ostwald

Basic concept:

According to Ostwald, indicators are **weak acids or weak bases**. The color change is due to a shift in the equilibrium between the **ionized and unionized forms** of the indicator, which are **different in color**.

Let the indicator be a weak acid: $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$

- HIn = one color (e.g., red)
- In^- = different color (e.g., yellow)

When:

- **$[\text{H}^+]$ is high (acidic medium):** Equilibrium shifts to the left \rightarrow more $\text{HIn} \rightarrow$ one color
- **$[\text{H}^+]$ is low (basic medium):** Equilibrium shifts to the right \rightarrow more $\text{In}^- \rightarrow$ another color

pH range of indicator:

The indicator changes color within the pH range:

$$\text{pH} = \text{pK}_{\text{In}} \pm 1$$

Where K_{a} is the dissociation constant of the indicator.

Example:

- Methyl orange:
 - Red in acidic medium (HIn)
 - Yellow in basic medium (In^-)
 - pH range: 3.1 to 4.4
 - Phenolphthalein: Colorless in acid (HIn) and Pink in base (In^-) " pH range: 8.3 to 10.0

2. Quinonoid Theory

Proposed by: F. Koelsch (for phenolphthalein-type indicators)

Basic concept:

This theory is based on **structural changes** in the indicator molecules. Indicators exist in two tautomeric forms:

- **Benzenoid form:** Colorless or one color
- **Quinonoid form:** Colored form

The indicator undergoes a structural transformation in response to pH changes.

Example: Phenolphthalein

- In acidic medium → benzenoid structure → colorless
- In basic medium → quinonoid structure → pink

This theory explains color changes better for complex organic indicators like phenolphthalein, which do not fit well under Ostwald's theory alone.

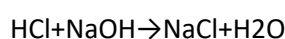
Classification of Acid-Base Titrations

Acid-base titrations are analytical procedures used to determine the concentration of an acidic or basic substance by reacting it with a base or acid of known strength. These are **neutralization reactions**, and they are classified based on the **strength of the acid and base involved**.

1. Strong Acid vs Strong Base

Example: HCl vs NaOH

Reaction:



- Sharp and clear endpoint
- Equivalence point at $\text{pH} \approx 7$
- **Suitable indicators:**
 - Phenolphthalein (colorless → pink)
 - Methyl orange (red → yellow)

2. Strong Acid vs Weak Base

Example: HCl vs NH_4OH

Reaction:

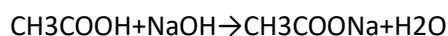


- Salt formed (ammonium chloride) undergoes hydrolysis
- **Suitable indicator:**
 - Methyl orange (acidic range)

3. Weak Acid vs Strong Base

Example: CH_3COOH vs NaOH

Reaction:



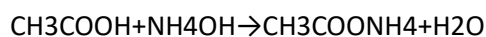
Equivalence point at $\text{pH} > 7$ (alkaline)

- Salt (sodium acetate) hydrolyzes to give basic solution
- **Suitable indicator:**
 - Phenolphthalein

4. Weak Acid vs Weak Base

Example: CH_3COOH vs NH_4OH

Reaction:



No sharp endpoint due to very gradual pH change

- Equivalence point around $\text{pH} \approx 7$, but transition is not sharp
- **No suitable indicator**
- Rarely used in titrimetric analysis

Summary Table

Titration Type	Equivalence Point pH	Suitable Indicator
Strong acid vs Strong base	~ 7	Methyl orange, phenolphthalein
Strong acid vs Weak base	< 7	Methyl orange
Weak acid vs Strong base	> 7	Phenolphthalein
Weak acid vs Weak base	~ 7 (no sharp change)	No suitable indicator

Theory Involved in Titrations of Strong, Weak, and Very Weak Acids and Bases

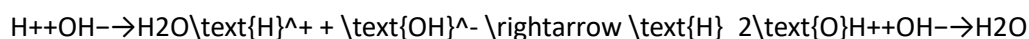
Acid-base titrations are based on the principle of **neutralization**, where an acid reacts with a base to form salt and water. The nature of the acid and base (whether strong or weak) influences the **pH change**, **titration curve**, and **choice of indicator**. Understanding the theoretical basis is essential for accurate endpoint determination.

1. Titration of Strong Acid with Strong Base

Example: HCl vs NaOH

Theory:

- Both acid and base are **completely ionized** in solution.
- The reaction goes to completion:



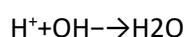
- The pH at the **equivalence point** is **7**.
 - Sharp and steep pH change occurs near equivalence point.
 - Any indicator with a pH range between **4 to 10** (like phenolphthalein or methyl orange) can be used.
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2. Titration of Strong Acid with Weak Base

Example: HCl vs NH_4OH

Theory:

- Acid is **strong and completely dissociated**, but the base is **weak and partially ionized**.
- The reaction:



However, the OH^- comes from a **partially ionized weak base**.

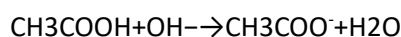
- The salt formed (NH_4Cl) **undergoes hydrolysis**, producing H^+ ions.
- The pH at the **equivalence point** is **< 7** (acidic).
- The titration curve shows a **gradual pH rise**, not very steep.
- Methyl orange** is suitable due to its acidic transition range (3.1–4.4).

3. Titration of Weak Acid with Strong Base

Example: CH_3COOH vs NaOH

Theory:

- The acid is **weak and partially dissociated**, while the base is **strong and fully ionized**.
- Reaction:



The conjugate base (CH_3COO^-) of the weak acid is formed.

- The solution at equivalence point is **basic (pH > 7)** due to hydrolysis of the acetate ion.
- The titration curve shows a **slow initial rise** in pH, followed by a **steep increase near equivalence**.
- Phenolphthalein** is suitable (pH range: 8.3–10.0).

4. Titration of Weak Acid with Weak Base

Example: CH_3COOH vs NH_4OH

Theory:

- Both acid and base are **weak and partially ionized**.
- Reaction is incomplete and does not yield a sharp equivalence point.
- The salt ($\text{CH}_3\text{COONH}_4$) undergoes hydrolysis, leading to a nearly **neutral or slightly acidic/basic solution**.
- The **pH change around equivalence is very small**, making it hard to detect the endpoint visually.
- **No suitable indicator** gives a clear endpoint.
- Not preferred for titrimetric analysis unless **instrumental methods (e.g., potentiometry)** are used.

5. Titration of Very Weak Acid or Very Weak Base

Theory:

- **Very weak acids** (like boric acid) or **very weak bases** (like aniline) ionize to a very small extent in water.
- They **do not react completely** with titrants under normal conditions.
- Their titrations require:
 - Use of **non-aqueous solvents** (e.g., glacial acetic acid or ethanol)
 - Use of **modified titration techniques**
- **Special indicators** or instrumental methods are essential.

Key Factors Influencing Titration Behavior

- **Dissociation constant (K_a or K_b):** Stronger acid/base \rightarrow sharper curve
- **Salt hydrolysis:** Affects pH at equivalence point
- **Buffer formation:** Occurs in weak acid/base titrations
- **Titration curve slope:** Determines indicator choice
- **Indicator selection:** Based on expected pH at equivalence point

Neutralization Curves (Titration Curves)

A **neutralization curve** (also called a **titration curve**) is a plot of **pH versus volume of titrant added** during an acid-base titration. It reflects the change in pH as the titration progresses and helps in identifying the **equivalence point**, selecting the **appropriate indicator**, and understanding the acid-base behavior.

Titration curves differ based on the strength of the acid and base involved. Four main types are discussed below.

1. Strong Acid vs Strong Base

Example: HCl titrated with NaOH

Initial pH: Very low (~ 1), due to complete dissociation of strong acid.

As base is added: pH increases gradually.

Near equivalence point: Rapid and steep rise in pH.

Equivalence point: Occurs at $\text{pH} = 7$.

After equivalence point: pH increases more slowly due to excess OH^- .

Key characteristics:

- Sharp and vertical curve near equivalence point.
- Suitable indicators: Phenolphthalein, Methyl orange.

2. Weak Acid vs Strong Base

Example: Acetic acid titrated with NaOH

Initial pH: Moderately low ($\sim 3\text{--}4$), because acetic acid is weak and partially ionized.

As base is added: Gradual increase in pH due to buffer formation.

Buffer region: Significant pH stability due to $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ system.

Equivalence point: Occurs at $\text{pH} > 7$ (typically ~ 8.7) due to basic nature of salt.

After equivalence point: pH rises sharply, then levels out.

Key characteristics:

- Curved slope before and after equivalence.
- Buffering effect visible.
- Suitable indicator: Phenolphthalein.

3. Strong Acid vs Weak Base

Example: HCl titrated with NH_4OH

Initial pH: Low (~ 1), due to strong acid.

As base is added: pH rises slowly due to weak base.

Equivalence point: Occurs at $\text{pH} < 7$ (typically ~ 5.5) due to acidic salt NH_4Cl .

After equivalence point: pH levels off slowly.

Key characteristics:

- Gradual pH rise.
- No steep inflection.
- Suitable indicator: Methyl orange.

4. Weak Acid vs Weak Base

Example: Acetic acid titrated with Ammonium hydroxide

Initial pH: ~4.5

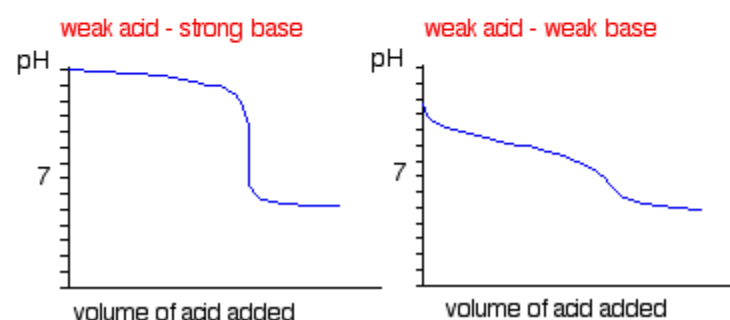
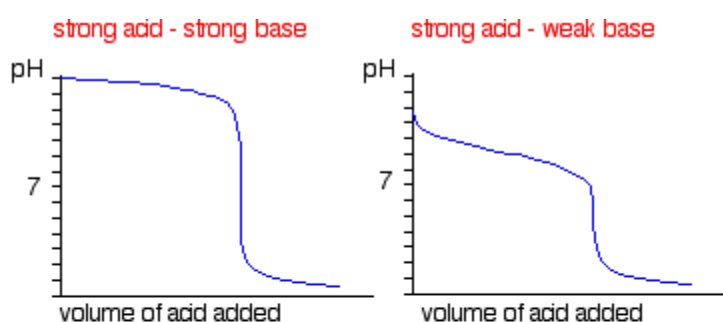
As titration proceeds: pH rises slowly.

Equivalence point: Near neutral (pH ~6–7), but the change is very gradual.

Overall curve: Flat with no sharp vertical region.

Key characteristics:

- No distinct equivalence point.
- Not suitable for manual titration with visual indicators.
- Requires instrumental methods like potentiometric titration.



Non-Aqueous Titration – Solvents

Introduction:

Non-aqueous titration is a titrimetric method in which the titration is carried out in a **solvent other than water**. It is used for analyzing **weakly acidic or basic substances** that do not dissolve well or do not ionize completely in aqueous media. This method improves solubility and enhances the strength of weak acids or bases by using appropriate non-aqueous solvents.

Role of Solvents in Non-Aqueous Titration:

The **solvent system** is the most critical component of non-aqueous titration. Solvents affect the **dissociation** of analytes and the **sharpness** of the end point. Depending on their nature, solvents are classified into four major types:

1. Aprotic Solvents:

- These are **neutral and non-ionizing** solvents.
- They do **not donate or accept protons**.
- Often used as diluents in titrations to **increase solubility**.
- **Examples:**
 - Benzene
 - Chloroform
 - Carbon tetrachloride
 - Toluene

These solvents are **inert** and do not interfere with the titration reaction, but they do not enhance ionization either.

2. Protophilic Solvents:

- These are **basic solvents** that **accept protons (H^+)**.
- They help in ionizing **acidic substances**, making them suitable for titration of weak acids.
- **Examples:**
 - Dimethylformamide (DMF)
 - Ethylenediamine
 - Pyridine
 - Triethylamine

These solvents improve the ionization of **weak acids** by stabilizing the proton donated by the acid.

3. Protogenic Solvents:

- These are **acidic solvents** that **donate protons (H^+)**.
- They are suitable for **basic substances**, as they help in their ionization by supplying protons.
- **Examples:**
 - Glacial acetic acid
 - Sulfuric acid
 - Formic acid

These solvents are used to **titrate weak bases** like antihistamines, alkaloids, etc., in the pharmaceutical field.

4. Amphiprotic Solvents:

- These solvents can both **donate and accept protons**, depending on the situation.
- They behave like **water** to some extent in their ability to support both acid and base titrations.
- **Examples:**
 - Alcohols (ethanol, methanol)
 - Acetic acid (in some conditions)

These are used for titrations involving compounds of **moderate acid-base character**.

Key Considerations in Solvent Selection:

- **Solubility** of analyte in the chosen solvent
- **Ionizing power** of the solvent (high for strong titrations)
- **Inertness** – solvent must not react with titrant or analyte
- Solvent's ability to **support indicator color change**
- Volatility and safety (some are toxic or flammable)

Acidimetry and Alkalimetry in Non-Aqueous Titrations

Introduction

In **non-aqueous titrations**, **acidimetry** and **alkalimetry** involve the estimation of acidic or basic drug substances **in solvents other than water**, especially when these substances are **insoluble** or **weakly ionized** in water. The use of appropriate **non-aqueous solvents** enhances solubility and ionization, allowing accurate titration.

These methods are particularly useful in **pharmaceutical analysis**, where many drug substances are **weak bases (e.g., alkaloids)** or **weak acids (e.g., barbiturates)** and are not titratable in aqueous media.

Non-Aqueous Acidimetry

Definition:

Titration of **basic substances** with a **standard non-aqueous acid solution** (like perchloric acid) in a suitable **non-aqueous solvent**.

Purpose:

To analyze **weak bases** which do not give a sharp endpoint in aqueous titrations.

Common titrants:

- **Perchloric acid** in glacial acetic acid

Common solvents:

- **Glacial acetic acid** (protogenic solvent)
- Acetic anhydride
- Dioxane (co-solvent)

Indicators used:

- Crystal violet
- 1-naphthol benzene
- Quinaldine red

Example:

- Estimation of **ephedrine hydrochloride** using **0.1 N HClO₄** in glacial acetic acid

Non-Aqueous Alkalimetry

Definition:

Titration of **acidic substances** with a **standard non-aqueous base solution** (like sodium methoxide) in a suitable **non-aqueous solvent**.

Purpose:

To analyze **weak acids** that do not ionize fully in water.

Common titrants:

- **Sodium methoxide** in methanol
- Potassium methoxide

Common solvents:

- **Dimethylformamide (DMF)** (protophilic solvent)
- Pyridine
- Methanol

Indicators used:

- Thymol blue

- Thymolphthalein
- Azoviolet
- Phenolphthalein (in some systems)

Example:

- Estimation of **barbiturates** (e.g., phenobarbital) using **sodium methoxide** in **DMF**

Key Considerations

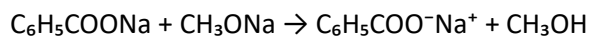
- **Solvent selection** is based on the nature of the analyte (acidic or basic).
- **Titrants and indicators** must be compatible with the solvent and analyte.
- **Dry conditions** are essential to prevent reaction with atmospheric moisture, especially when using titrants like sodium methoxide or perchloric acid in acetic acid.
- Non-aqueous titration provides **sharper endpoints** and better **accuracy** for poorly water-soluble or weakly ionizing drugs.

1. Estimation of Sodium Benzoate

Principle:

Sodium benzoate is a weak acid salt that can be titrated in a **non-aqueous medium** using a **standard base** such as **sodium methoxide**. The carboxylic acid group of benzoic acid reacts with methoxide ion to form its salt in an **aprotic solvent** like **dimethylformamide (DMF)**.

Reaction:



Solvent:

- Dimethylformamide (DMF)

Titrant:

- 0.1 N Sodium methoxide in methanol

Indicator:

- Thymolphthalein or phenolphthalein (color change from colorless to blue)

Procedure:

1. Accurately weigh about 0.2 g of sodium benzoate.
2. Dissolve in 25 mL of DMF.
3. Add 2–3 drops of thymolphthalein indicator.
4. Titrate with 0.1 N sodium methoxide until a permanent blue color appears.

Calculation:

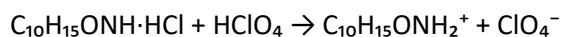
1 mL of 0.1 N sodium methoxide \equiv 0.01442 g of $\text{C}_6\text{H}_5\text{COONa}$

2. Estimation of Ephedrine Hydrochloride

Principle:

Ephedrine hydrochloride is a **weak organic base**, titrated by **non-aqueous acidimetry** using **perchloric acid** in **glacial acetic acid**. The nitrogen atom of ephedrine accepts a proton from perchloric acid in a non-aqueous medium.

Reaction:



Solvent:

- Glacial acetic acid

Titrant:

- 0.1 N Perchloric acid in glacial acetic acid

Indicator:

- Crystal violet (color change from violet to green)

Procedure:

1. Accurately weigh about 0.3 g of ephedrine hydrochloride.
2. Dissolve in 25 mL of glacial acetic acid.
3. Add 1–2 drops of crystal violet.
4. Titrate with 0.1 N perchloric acid until the violet color turns to green.

Calculation:

1 mL of 0.1 N perchloric acid \equiv 0.01651 g of ephedrine hydrochloride