Theory of indicators

Theory of Indicators

Introduction

- In **Pharmaceutical Inorganic Chemistry**, acid-base titrations and precipitation reactions are essential for the **quantitative analysis** of inorganic substances.
- To accurately detect the **end point** of these titrations, **indicators** are used.

Definition:

- An **indicator** is a chemical substance that changes color at (or near) the **equivalence point** of a titration, signaling the **completion of the reaction**.

Role in Pharmaceutical Inorganic Chemistry

- Indicators are widely used in:
  - Assay of inorganic substances
  - Volumetric analysis (acid-base, redox, complexometric, precipitation titrations)
  - Standardization of solutions
  - Quality control testing in pharmaceutical preparations

Types of Indicators (Based on Titration Type)

Titration Type	Indicator Type	Example Indicators
Acid-Base	pH indicators	Phenolphthalein, Methyl orange
Redox	Redox indicators	Starch, Diphenylamine
Complexometric	Metal ion indicators	Eriochrome Black T, Murexide
Precipitation	Adsorption indicators	Eosin, Fluorescein

Theory of Acid-Base Indicators

What is an Acid-Base Indicator?

- An **acid-base indicator** is usually a **weak acid or weak base** that changes color depending on the **pH** of the solution. It exists in two forms:
  - **HIn (acid form)** – shows one color
  - **In^- (conjugate base)** – shows a different color
- The equilibrium can be written as:

$$HIn \rightleftharpoons H^+ + In^-$$

- The color change occurs because the relative concentration of HIn and In^- changes with pH.

Henderson-Hasselbalch Equation:

- To determine the pH at which an indicator changes color:

$$pH = pKa + \log([In^-]/[HIn])$$

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- At **pH = pKa**, both forms are present equally – the solution shows an intermediate color.
- At **pH < pKa**, more HIn is present – acid color dominates.
- At **pH > pKa**, more In^- is present – basic color dominates.

Indicator Range:

- Every indicator changes color over a specific pH range, usually ±1 of its pKa.

Indicator	pH Range	Color Change
Methyl orange	3.1 – 4.4	Red (acid) → Yellow (base)
Phenolphthalein	8.2 – 10.0	Colorless (acid) → Pink (base)

Selection of Indicator:

- The choice of indicator depends on the **type of titration** and the **pH at the equivalence point**.

Titration Type	Equivalence Point (pH)	Suitable Indicator
Strong acid + Strong base	~7	Phenolphthalein or Methyl orange
Strong acid + Weak base	< 7	Methyl orange
Weak acid + Strong base	> 7	Phenolphthalein

Redox Indicators

- These indicators change color when they are oxidized or reduced during redox reactions.
- Examples:
  - **Starch**: Forms a deep blue complex with iodine; used in iodometric titrations.
  - **Diphenylamine**: Colorless in reduced form, turns violet upon oxidation.

Adsorption Indicators

- Used mainly in **precipitation titrations**, such as argentometric titrations involving silver nitrate.

Mechanism:

- The indicator is adsorbed onto the surface of the precipitate.
- At the equivalence point, a change in surface charge occurs, which alters the color of the adsorbed indicator.

Example:

- **Eosin** in chloride titration using silver nitrate (Fajans method)

Complexometric Indicators

- These are used in **complexometric titrations**, particularly with chelating agents like EDTA.
  - Indicators form weak, colored complexes with metal ions.
  - At the end point, when all metal ions are bound to EDTA, the indicator is released, causing a color change.

Example:

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- **Eriochrome Black T**: Forms a wine-red complex with calcium or magnesium ions; turns blue when metal is complexed by EDTA.

Limitations of Indicators

- Limited working pH or redox range
- Affected by temperature, ionic strength, and light
- May interfere with the analyte or titrant if not appropriately chosen
- Require clear observation of color change, which may vary between observers

Importance in Pharmaceutical Industry

- Ensures **accurate dosing** and **content uniformity** of drug substances
- Used in official **pharmacopoeial assays**
- Aids in **standardization** of solutions used in routine pharmaceutical analysis
- Crucial in **quality control labs** to confirm compliance with drug standards

Theories of acid base indicators

- Acid-base indicators are substances that change color depending on the **pH of the solution** they are in.
- They are typically **weak organic acids or bases** that exhibit different colors in their protonated and deprotonated forms.
- These indicators are crucial in **titrations** as they signal the endpoint of the reaction by undergoing a visible color change.

There are two main theories that explain the behavior of acid-base indicators:

A. Ostwald Theory (Ionization Theory)

- The Ostwald theory explains the behavior of acid-base indicators based on the **ionization equilibrium** of weak acids or bases.
- According to this theory:
  - **Ionization Equilibrium**: In the presence of a base, a weak acidic indicator (HIn) can lose a proton (H^+) to form its conjugate base (In^-).

$$HIn \leftrightarrow H^+ + In^-$$

  - **Color Change**: Both the protonated form (HIn) and the deprotonated form (In^-) have different colors due to differences in their electronic structures.
  - **pH Dependence**: The equilibrium shifts based on the pH of the solution, causing a color change as the concentration of H^+ ions changes.

Examples

1. Phenolphthalein

- **Ionization Equilibrium**:

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$$HIn\ (colorless) \leftrightarrow H^+ + In^-\ (pink)$$

- **Behavior**:
  - In **acidic solutions**, the equilibrium favors the colorless protonated form (HIn).
  - In **basic solutions**, the equilibrium shifts towards the pink deprotonated form (In^-).

2. Methyl Orange

- **Ionization Equilibrium**:

$$HIn\ (red) \leftrightarrow H^+ + In^-\ (yellow)$$

- **Behavior**:
  - In acidic solutions → red protonated form (HIn) predominates.
  - In basic solutions → yellow deprotonated form (In^-) predominates.

B. Quinonoid Theory (Resonance or Quasi-Valence Theory)

- The quinonoid theory explains the color change of indicators based on the resonance structures and electron distribution within the molecules.
- According to this theory:
  - **Resonance Structures**: Indicators can exist in two tautomeric forms—benzenoid and quinonoid structures—which have different colors.
  - **Electron Distribution**: Gaining or losing a proton changes the electron distribution, altering the absorption of light in the visible spectrum and thus the color.
  - **Color Dependence**: The color of the indicator is determined by the predominant resonance structure at a given pH.

Examples

1. Phenolphthalein

- **Structural Change**:
  - In **acidic solutions**, phenolphthalein exists in its colorless lactone (benzenoid) form.
  - In **basic solutions**, it loses a proton to form a pink-colored quinonoid structure.
- **Color Change Mechanism**: The shift from the lactone form to the quinonoid form changes the electron delocalization, resulting in a color change.

2. Methyl Orange

- **Structural Change**:
  - In **acidic conditions**, methyl orange exists in a red-colored benzenoid form.

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