Sawa University

Analytical Chemistry

REDOX TITRATIONS COMPLEXOMETRIC TITRATION

Sawa University

College of Pharmacology

First Stage

جامعـــــــة ســــــــاوة الأهلية

كلية الصيدلة

المرحلـــــــــــــة الاولى

المحاضرة السادسة : الجانب النظري

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Redox Titrations : Oxidation–Reduction Titrations–

A redox titration is a volumetric analytical method based on an oxidation–reduction reaction, in which electrons are transferred between the analyte and the titrant.

One substance undergoes oxidation (**loss of electrons**), while another undergoes reduction (**gain of electrons**).

This type of titration is widely used for the determination of **oxidizing and reducing agents**

- **Oxidation: loss of electrons**
- **Reduction: gain of electrons**

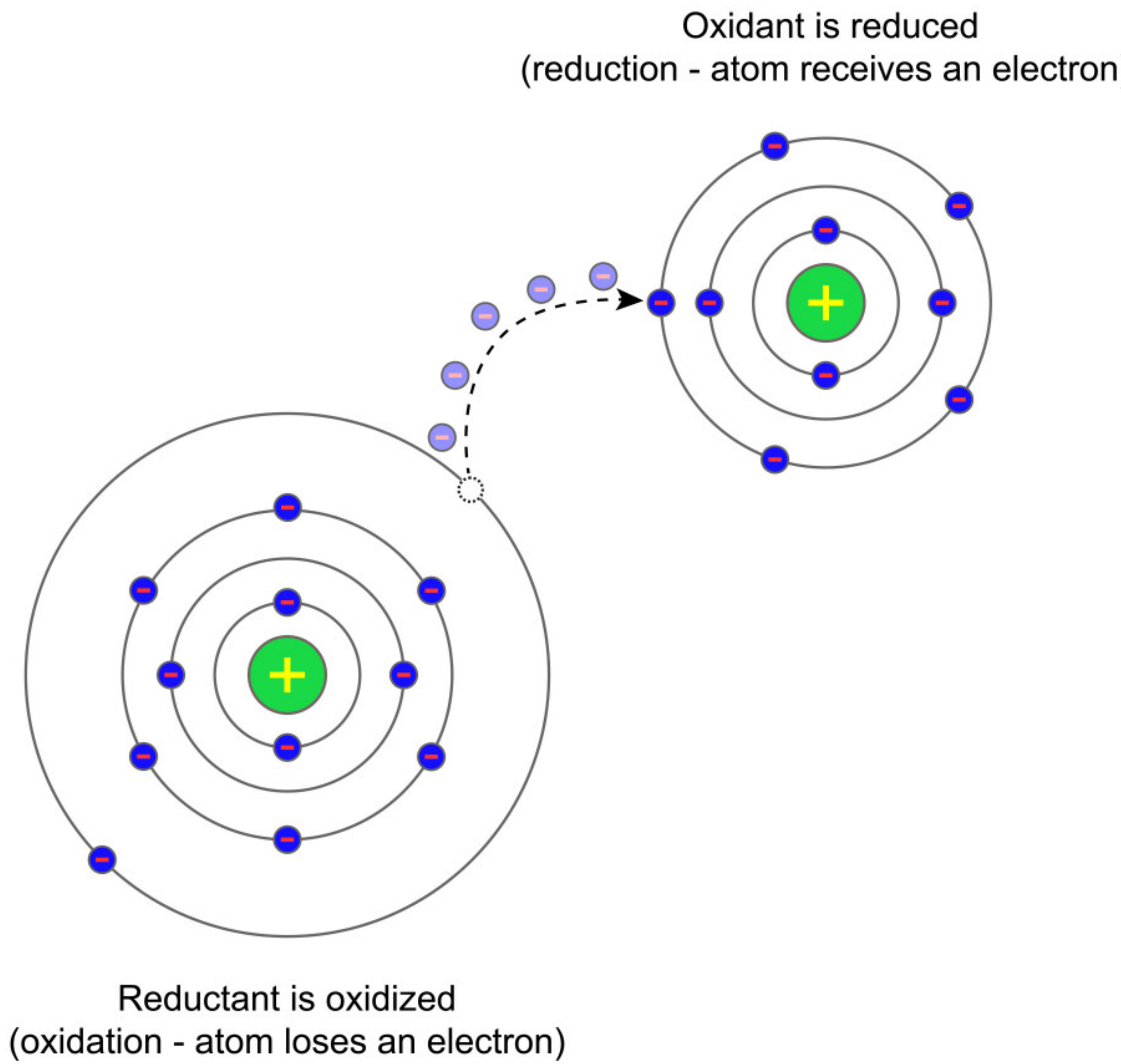
These two processes always occur together.

In redox titrations, the amount of electrons transferred **is directly related to the amount of analyte.**

Redox titrations depend on reactions that are:

- Fast Complete Stoichiometric

Redox reaction with electron transfer



End Point Detection in Redox Titrations

The end point in redox titrations can be detected by:

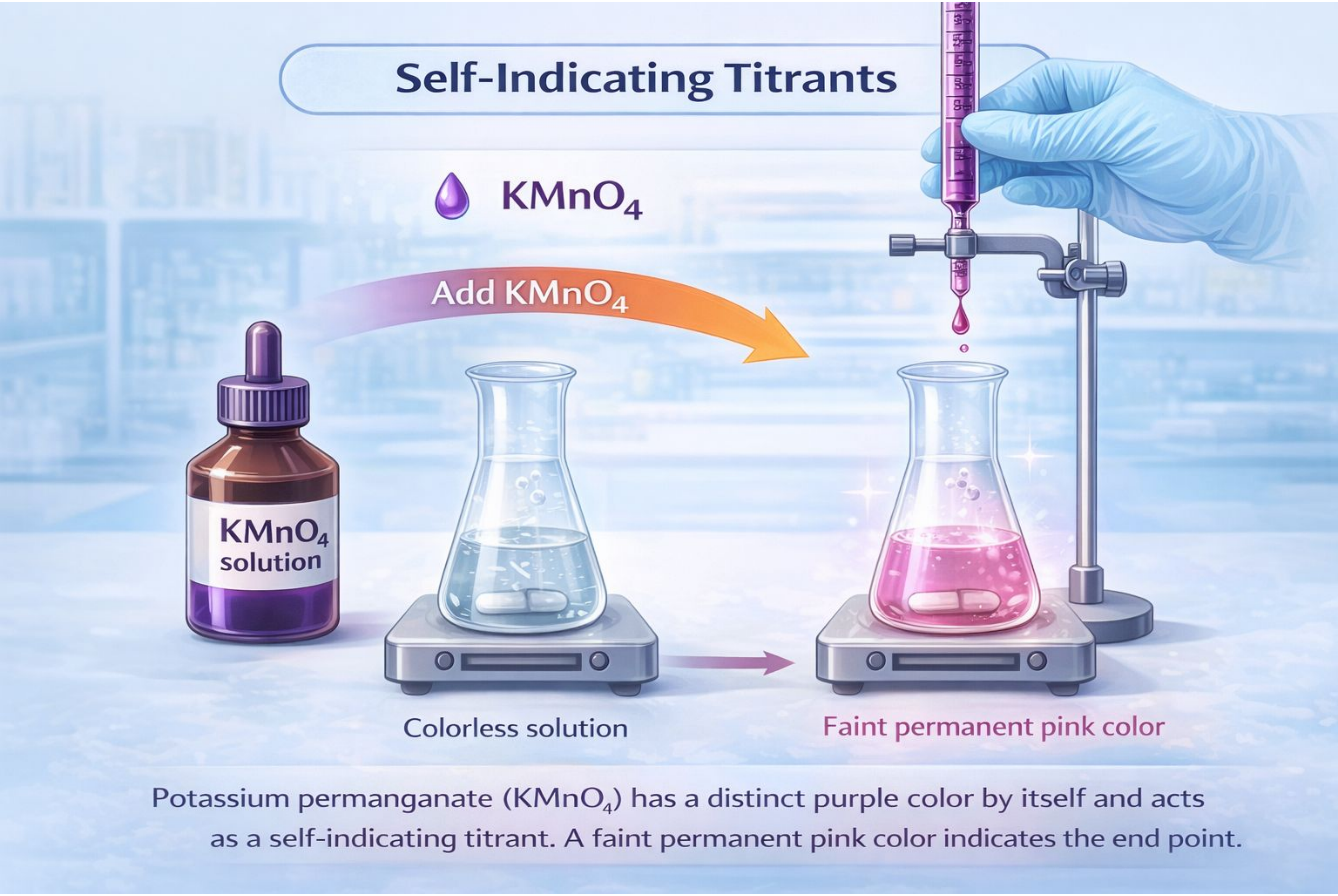
Self-indicating titrants are substances that have a distinct color by themselves, therefore no external indicator is required.

The end point is detected by the appearance of a slight excess of the titrant, which causes a permanent color change.

Example:Potassium permanganate ($KMnO_4$) A faint permanent pink color indicates the end point

External indicators are substances that are added to the titration mixture to show a color change at the end point,because the titrant or analyte does not have a visible color change on its own.

Example: Starch in iodine titrations


Self-Indicating Titrants
$KMnO_4$
Add $KMnO_4$
$KMnO_4$ solution
Colorless solution
Faint permanent pink color
Potassium permanganate ($KMnO_4$) has a distinct purple color by itself and acts as a self-indicating titrant. A faint permanent pink color indicates the end point.

Iodometric Titration

Iodometric Titration (Definition)Explanation:

Iodometric titration is an indirect redox titration in which iodine is first liberated by an oxidizing agent and then titrated with a standard reducing agent, usually sodium thiosulfate.

It is widely used for the determination of oxidizing agents and reducing substances such as vitamin C

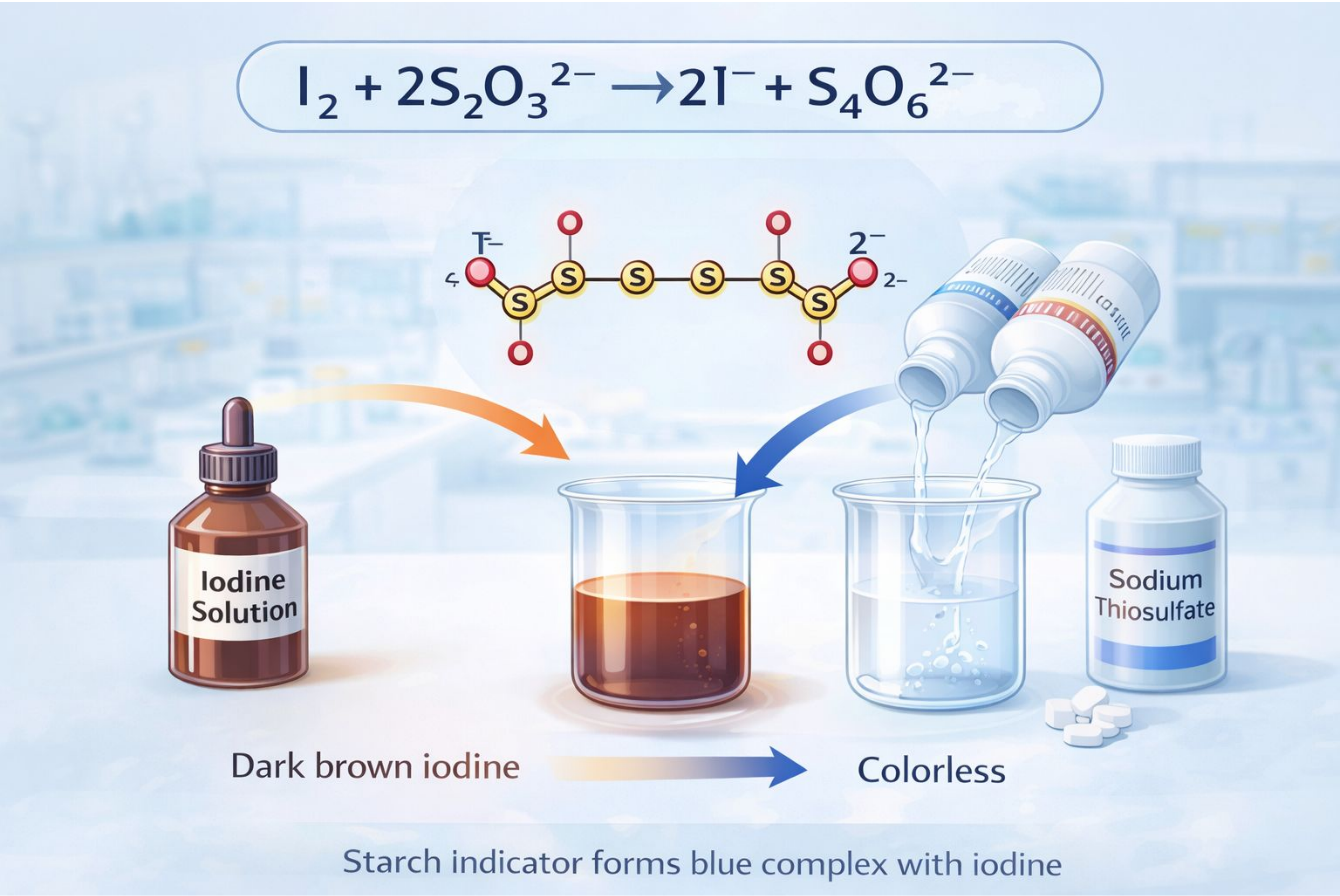
Role of Iodine and Thiosulfate

In iodometric titration:

- Iodine (I_2) acts as an oxidizing agent
- Sodium thiosulfate ($Na_2S_2O_3$) acts as a reducing agent

The titration reaction is:

$$I_2 + 2S_2O3_{2-} \rightarrow 2I^- + S_4O_6$$


$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$
Iodine Solution
Sodium Thiosulfate
Dark brown iodine
Colorless
Starch indicator forms blue complex with iodine

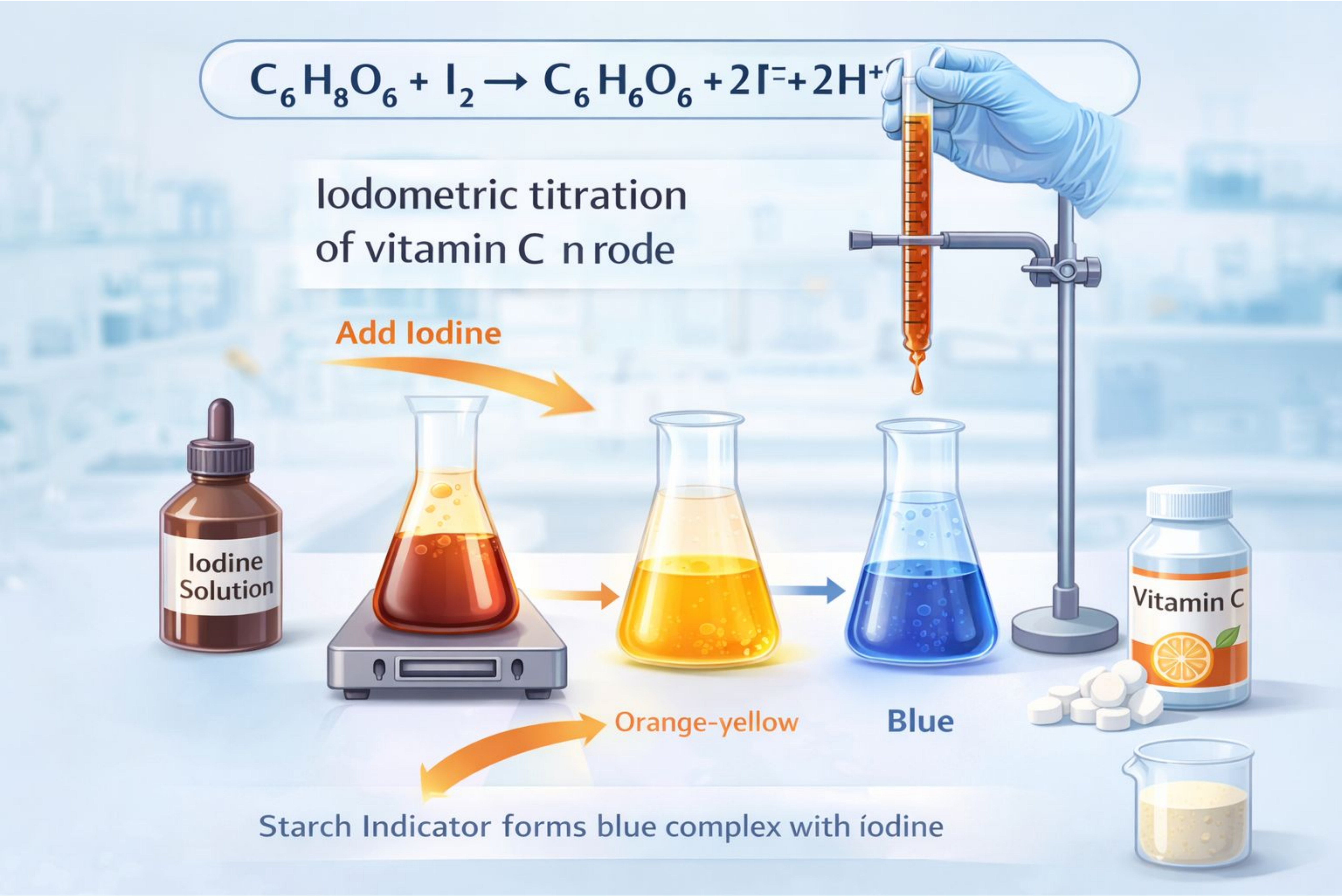
Starch Indicator (Mechanism of Action)

Starch is used as an indicator because it forms a **deep blue complex** with iodine.
As iodine is reduced to iodide during titration, the blue color disappears.
The disappearance of the blue color marks the end point.

Principle of Vitamin C Determination

Vitamin C (ascorbic acid) is a strong reducing agent.
It reduces iodine to iodide, while itself is oxidized to dehydroascorbic acid.

The amount of iodine consumed is equivalent to the


$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2I^- + 2H^+$
Iodometric titration
of vitamin C n rode
Add Iodine
Iodine Solution
Orange-yellow
Blue
Vitamin C
Starch Indicator forms blue complex with iodine

Definition of Complexometric Titration:

Complexometric titration is a volumetric analytical method based on the formation of a stable, soluble complex between a metal ion and a complexing agent (ligand).

The titration proceeds until all metal ions are completely bound to the ligand.

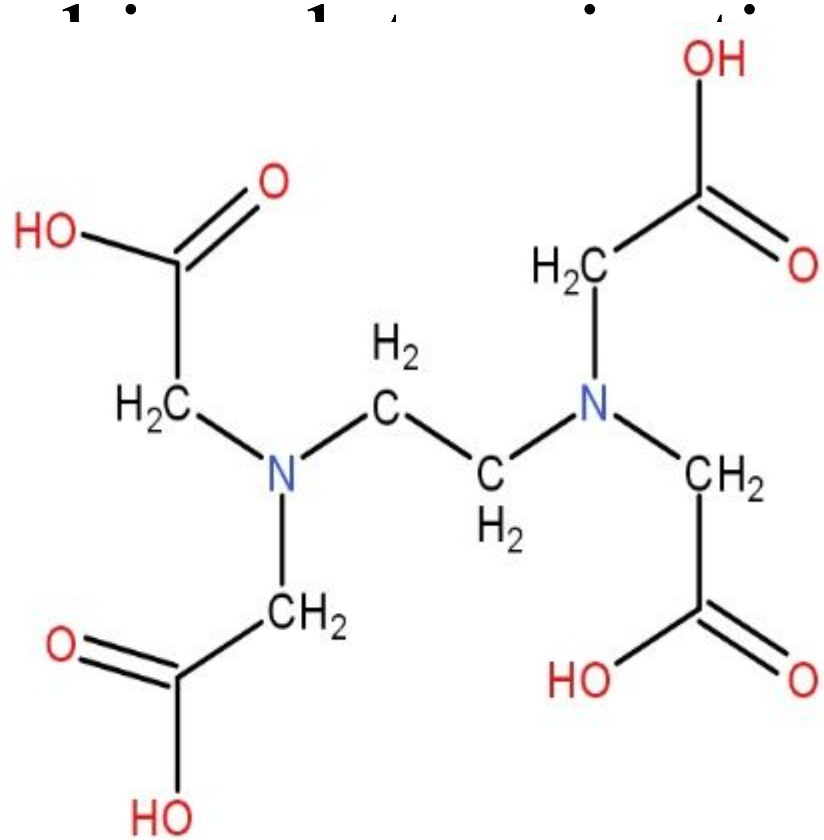
The most widely used complexing agent is **EDTA**

Principle of Complexometric Titration

- In complexometric titration, the analyte is usually a metal ion such as Ca^{2+}, Mg^{2+}, Zn^{2+}, or Fe^{3+}.
- The titrant (EDTA) reacts with the metal ion in a fixed stoichiometric ratio, usually **1:1.** General reaction:

What Is EDTA?

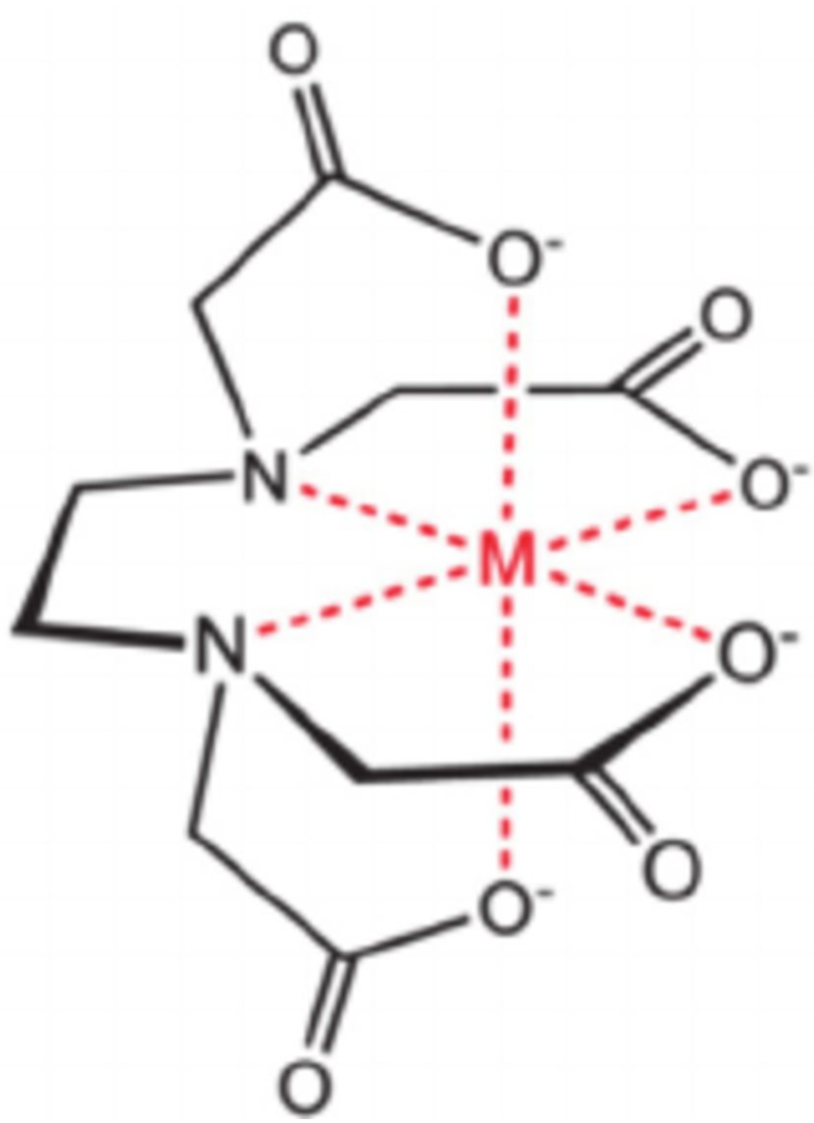
- EDTA (Ethylenediaminetetraacetic acid) is a hexadentate ligand, meaning it can bind to a metal ion through six donor atoms.
- This produces a very stable chelate complex.
- Because of its strong binding ability, EDTA is ideal for met



Ethylenediamine tetraacetic acid (EDTA)

DTA–Metal Complex FormationExplanation:

- EDTA wraps around the metal ion, forming a ring-like structure called a chelate.
- Chelation greatly increases the stability of the complex.
- This strong and s ation ensures a sharp e



Stoichiometry of EDTA TitrationsExplanation:

One important advantage of EDTA titrations is that all metal ions react with EDTA in a 1:1 molar ratio, regardless of the charge on the metal ion.

Examples:

Ca^{2+} : EDTA = 1 : 1

Mg^{2+} : EDTA = 1 : 1

Role of pH and Buffer Solutions:

The ability of EDTA to bind metal ions depends strongly on pH.

At low pH, EDTA is protonated and less effective as a ligand.

Indicators in Complexometric Titrations:

Metal ion indicators are dyes that form weak colored complexes with metal ions.

During titration, EDTA displaces the indicator from the metal ion, causing a color change at the end point.This color chan

Example Indicator: Eriochrome Black T (EBT)

Complexometric titration with EDTA is widely used to determine water hardness, which is caused mainly by Ca^{2+} and Mg^{2+} ions by using **Eriochrome Black T as indicator**

Eriochrome Black T is a commonly u

EDTA titrations of Ca^{2+} and Mg^{2+}.

Metal–indicator complex: **wine red**

Free indicator after EDTA binding: **bl**

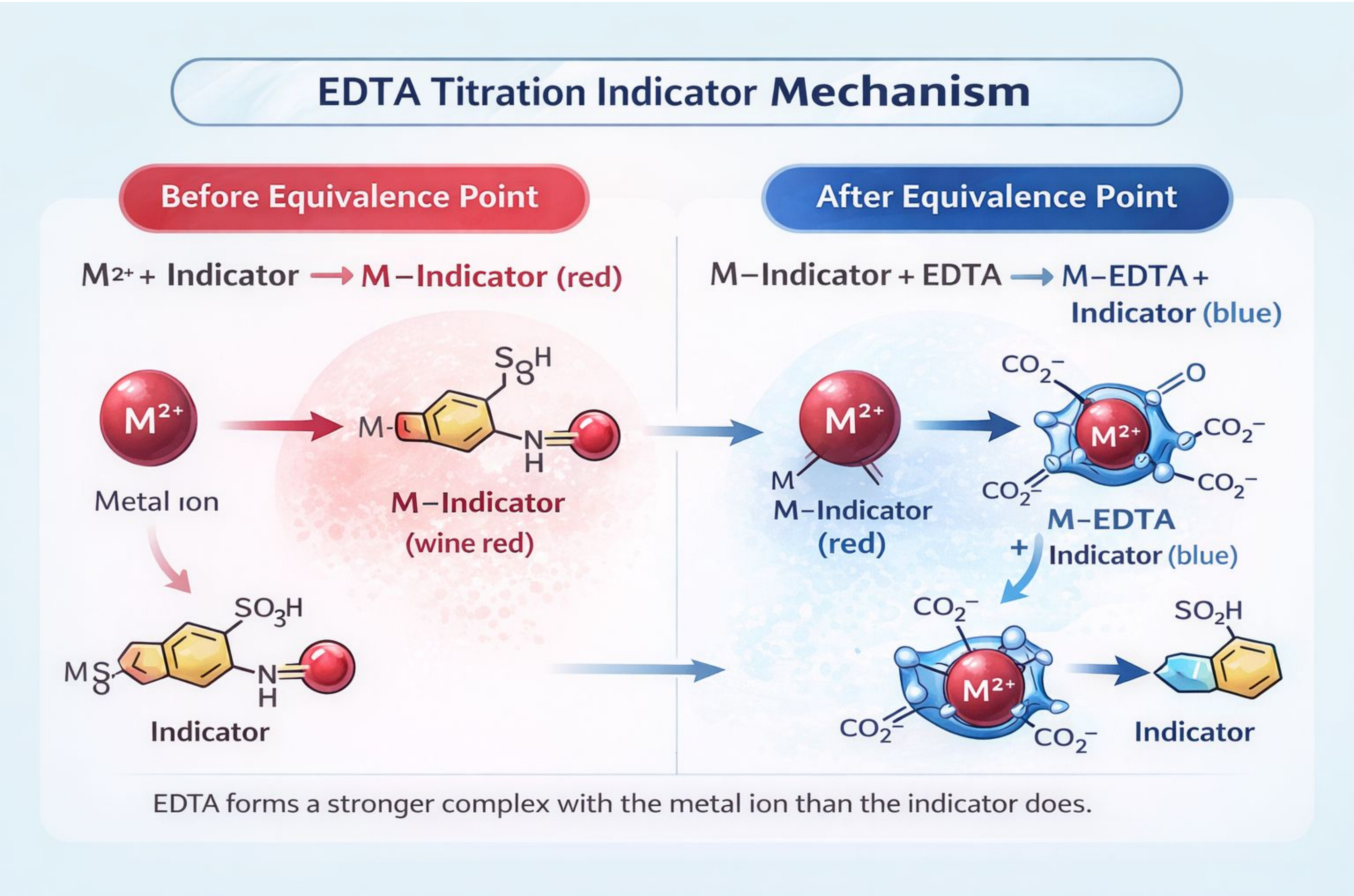
This sharp color change makes **EBT very useful**.

Mechanism of Indicator Action (EBT) :

Before equivalence point:

M2+ + Indicator →M−Indicator **(red)**

After equivalence point:


EDTA Titration Indicator Mechanism
Before Equivalence Point
After Equivalence Point
M2+ + Indicator → M−Indicator (red)
M−Indicator + EDTA → M−EDTA + Indicator (blue)
M2+
Metal ıon
M−Indicator
(wine red)
SO3H
N
H
Indicator
M−Indicator
(red)
CO2−
O
M−EDTA
+ Indicator (blue)
SO2H
Indicator
EDTA forms a stronger complex with the metal ion than the indicator does.