

Titrimetric Analysis

(Chemistry-DSE-1002E2: **Organic & Analytical Chemistry**,
Section-II)

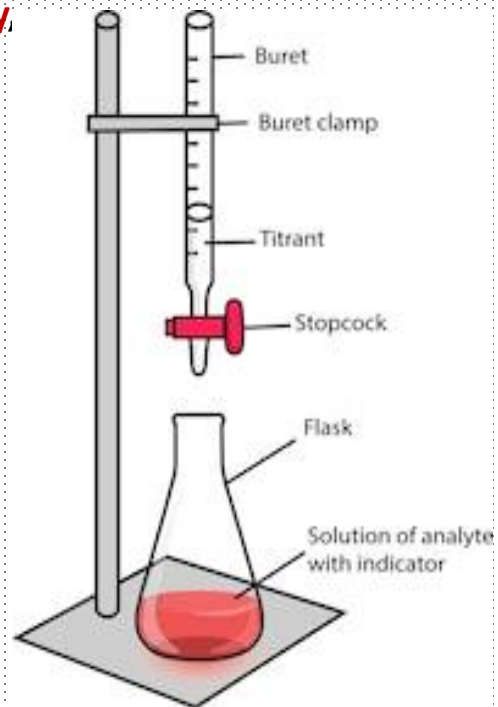
BY

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General Introduction, types of titrations, Imp terms used,

Acid-Base titrations: *Neutralization Indicators (Acid-Base Indicators), Theory of indicators w. r. t. Ostwald's color change interval and Ostwald's Quinoid theory, Construction of titration curves and choice of indicators in the titration of: (i) strong acid and strong base (ii) strong acid and weak base (iii) weak acid and strong base (iv) weak acid and weak base.*

Complexometric titrations: *General introduction, types of EDTA titrations, metallochromic indicators w. r. t. Eriochrome Black-T.*

Redox titrations: *General introduction, theory of redox indicators, Use of diphenyl amine and ferroin as redox indicators.*

General Introduction

- ❑ **Chemical Analysis:** *It is the study of chemical composition and structure of substances.*
- ❑ **Qualitative Analysis:** *It is a method used for identification of ions or compounds in a sample.*
- ❑ **Quantitative Analysis:** *It deals with determination of amt. of chemical substance present either alone or in a simple or complex mixture.*
- ❑ **Volumetric Analysis:** *It is type of Quantitative analysis. It is carried out by determining the volume of solution of accurately known concentration which is required to react with the solⁿ of the substance to be determined.*

Important Terms Used

- **Standard Solution:** *Solution of accurately known concentration.*
- **Titrant:** *Reagent of known concentration.*
- **Titrand:** *Solution of substance to be titrated with titrant.*
- **Mole:** *Amt of sub whose wt. in gms is numerically equal to m.w. of substance.*
- **Molar Solution:** *A solution containing 1M of substance In 1 litre.*
- **Molarity:** *Number of moles of solute per litre solution.*
- **Gram equivalent wt.:** *Wt. of substance in gms which is chemically equivalent to one gram atom of H or 35.5 gm of Cl or 8 gm of oxygen in a given reaction.*
- **Normal Solution:** *A solution containing 1 gm eq. wt of substance In 1 litre.*

- **Normality:** No. of gm equivalent wt. of solute present in 1 litre of soln.
- **Titration:** The process of determining the volume of std. solution that is required to complete a reaction with analyte.
- **Neutralization Reaction:** H^+ ion from acid reacts with OH^- from base to form water molecules.
- **Acidimetric Titration:** Standard acid solution is used for quantitative determination of alkali.
- **Alkalimetric Titration:** Standard alkali solution is used for quantitative determination of acid.
- **Indicator:** A chemical substance changes colour in accordance with pH of solution & thereby determines end point of titration.

- **Equivalence/ Stoichiometric/Theoretical End point:** *The point at which just adequate reagent is added to react completely with substance.*
- **End Point:** *Color change of indicator becomes apparent to the eye.*
- **End Point Error:** *Difference between end point and equivalence point*
- **Titration Exponent:** *pH at which titration in presence of given indicator is ended.*
- **Colour Change interval:** *Color of neutralization indicator changes in a definite narrow range of pH is called as.....*

Theory of Acid-base Indicators

- An indicator is a substance which is used to determine the end point in a titration.
- In acid-base titrations, organic substances (weak acids or weak bases) are generally used as indicators.
- They change their color within a certain pH range.

The color change and the pH range of some common indicators are tabulated below

| Indicator | pH range | Colour change |
|------------------------|-----------------|---------------------------|
| Methyl orange | 3.2-4.5 | Pink to yellow |
| Methyl red | 4.4-6.5 | Red to yellow |
| Litmus | 5.5-7.5 | Red to blue |
| Phenol red | 6.8-8.4 | Yellow to red |
| Phenolphthalein | 8.3-10.5 | Colourless to pink |

Ostwald's Colour change interval theory

According to this theory:

(a) The color change is due to ionization of the acid base indicator.

The unionized form has different color than the ionized form.

(b) The ionization of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base.

In case, the indicator is a weak acid, its ionization is very much low in acids due to common H^+ ions while it is fairly ionized in alkalies.

Similarly if the indicator is a weak base, its ionization is large in acids and low in alkalies due to common OH^- ions.

Ostwald's Quinoid theory

Table 1.1 : Colour changes and pH range of certain indicators

| Indicator | Chemical name | Nature of indicator | pH range | Acid medium | Alkaline medium | (Titration exponent) pK_{in} |
|--------------------|---|---------------------|----------|-------------|-----------------|--------------------------------|
| Cresol red (acid) | 1-Cresolsulphone-phthalein | Acid | 0.2-1.8 | Red | Yellow | - |
| | 1-p-Dimethyl-amino-phenyl ethylene)-quinoline ethiodide | Acid | 1.5-2.5 | Colourless | Red | - |
| Thymol blue (acid) | Thymol-sulphone-phthalein | Acid | 1.2-2.8 | Red | Yellow | 1.7 |
| Tropeoline oo | Diphenylamino-p-benzene sodium sulphonate | Basic | 1.3-3.0 | Red | Yellow | - |
| Bromophenol blue | Tetra bromo-phenol-sulphone-phthalein | Acid | 3.0-4.6 | Yellow | | 4.1 |
| Methyl orange | Dimethylamino-azo-benzene-sodium sulphonate | Basic | 2.9-4.6 | Red | Yellow | 3.7 |
| Methyl red | o-carboxy-benzene-azodimethyl aniline | Basic | 4.2-6.3 | Red | Yellow | 5.0 |
| Litmus (Azolitmin) | - | Acid | 5.0-8.0 | Red | Blue | - |
| Bromo-thymol blue | Dibromothymol sulphate phthalein | Acid | 6.0-7.5 | Yellow | Blue | 7.1 |
| Neutral red | Amino-dimethyl amino-tolu-phenazonium chloride | Basic | 6.8-8.0 | Red | Yellow | - |
| Phenolphthalein | phenolphthalein | Acid | 8.3-10.0 | Colourless | Red | 9.6 |

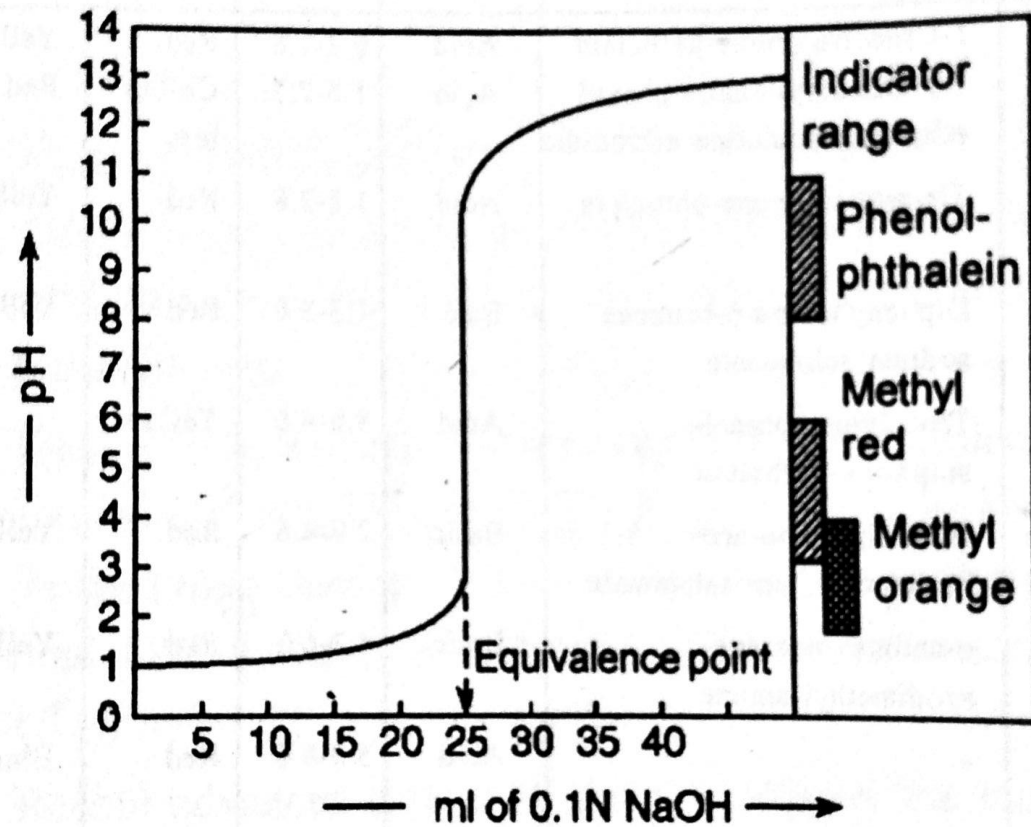


Fig. 1.1 : Neutralisation curve of 25 ml 0.1N HCl with 0.1N NaOH.

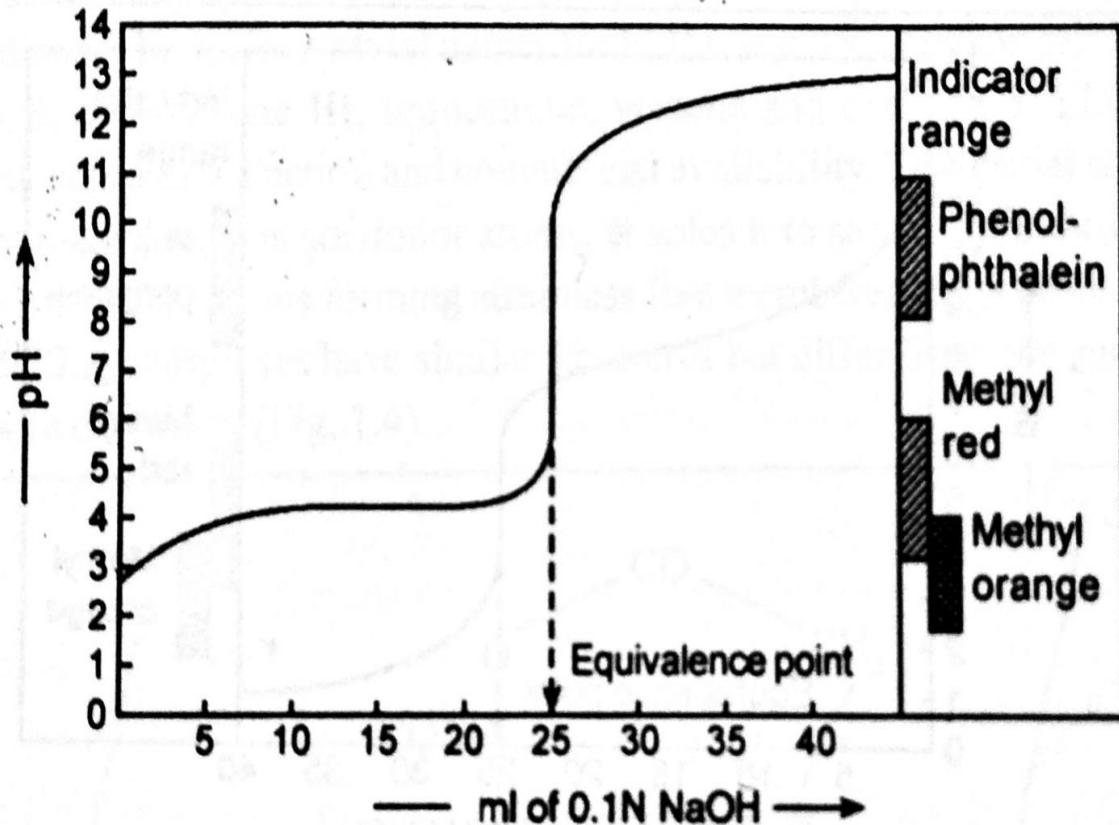


Fig. 1.2 : Neutralisation curve of 25 ml 0.1N CH₃COOH with 0.1N NaOH.

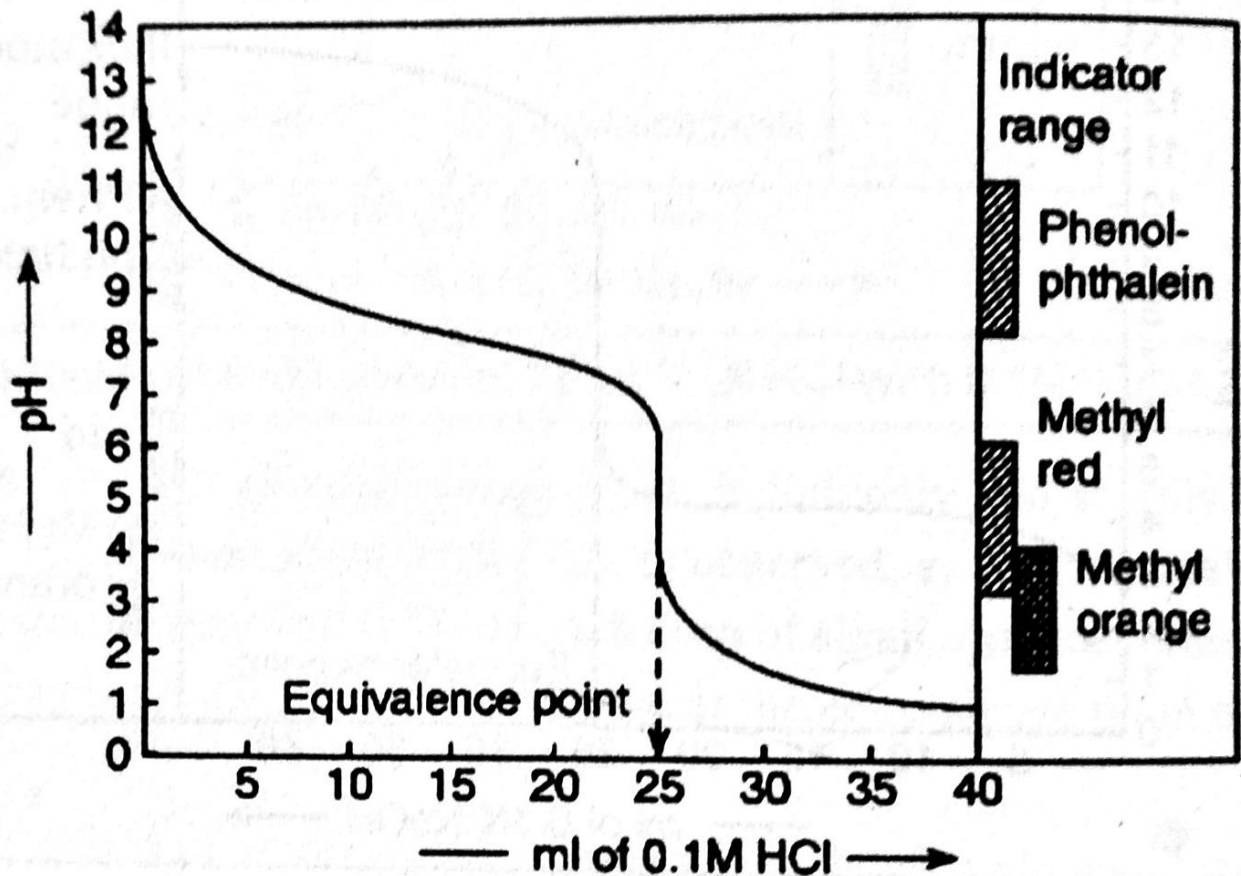
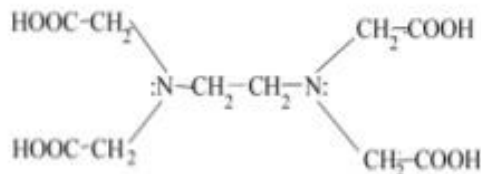


Fig. 1.3 : Neutralisation curve of 25 ml 0.1M Ammonia solution with 0.1M HCl.

COMPLEXOMETRIC TITRATIONS

- Complexometric titrations are based on the formation of a complex between the analyte and the titrant. The chelating agent EDTA is commonly used to titrate metal ions in solution.
- *Example : EDTA Titrations*



structure of EDTA

EDTA (Ethylenediaminetetraacetic acid) One of the most common chelating agents used for complexometric titrations in analytical chemistry.

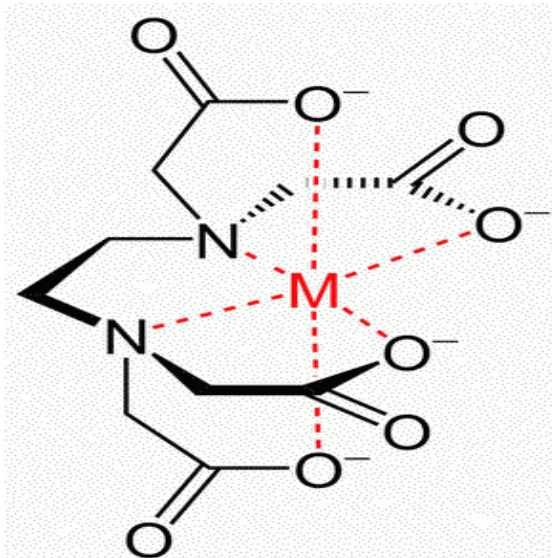
Types of Complexometric Titrations

A. Titrations involving Unidentate Ligands: Liebig Method



at equiv. pt. solid will appear

B. Titrations involving Unidentate Ligands: e.g. EDTA Titrations



Types of EDTA titration

- 1- Direct titration
- 2- Back titration
- 3- Displacement titration
- 4- Alkalimetric titration
- 5- Indirect titration
- 6- Masking titration

1. Direct Titrations

- ❖ The analyte solution is buffered to an appropriate pH and titrated with standard EDTA:
- ❖ Stability of metal-EDTA complex is large enough to produce a sharp end point.
- ❖ To the analyte solution, an auxiliary complexing agent (ammonia, tartarate, citrate, or triethanolamine) is added: Prevent the metal ion from precipitating in the absence of EDTA (Metal—ACA is less stable than Metal—EDTA).
- ❖ **Note:** At high pH M-OH is ppt. Ex: Pb^{2+} .

Direct titration of Pb^{2+} : is carried at pH 10 (ammonia) – add auxiliary complexing agent (tartaric acid) → Pb-tartarate complex less stable than Pb-EDTA.

2. Back Titrations

A known excess of EDTA is added to the analyte. The excess EDTA is then titrated with a standard solution of a second metal ion.

❖ It is used for when:

- 1- The analyte precipitates in the absence of EDTA.
- 2- The analyte reacts too slowly with EDTA under titration conditions.
- 3- The analyte blocks the indicator.

N.B. The titrant metal (Mg) should not displace the analyte or its EDTA complex.

2. Back Titrations

Ex1: Determination of Al^{3+} :

- Excess EDTA is added, pH is adjusted to 7-8, boil, cool, add Erio—T, & back titrate with standard Zn^{2+} :
- Avoid precipitation of Al^{3+} as $\text{Al}(\text{OH})_3$ at pH 7 in the absence of EDTA.
- Avoid indicator blocking as Al^{3+} —EDTA complex is stable in solution at this pH.

Ex₂: Ni^{2+} form slow dissociate complex with Ind. (pyridylazonaphthol) PNA (blocked) and metal cannot dissociate and react with EDTA.

➤ ∴ $\text{Ni} + \text{excess EDTA} \neq \text{st Cu}^{2+}$.

3. Displacement Titrations

- For metal that don't have suitable indicator.
- For metal not complexed easily with EDTA



Determination of Hg^{2+} :

Ex₁: Hg^{2+} has no suitable indicator



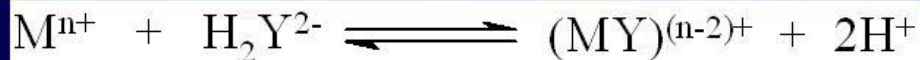
K ($(\text{Hg—EDTA})^{2+}$ is greater than **K** ($\text{Mg—EDTA})^{2+}$)

Determination of Ca^{2+} :

Ex₂: Ca^{2+} ion by direct titration by EDTA using Erio-T

∴ Poor E.P. by direct Titration because Ca-Ind complex is very weak.

4- Alkalimetric Titration



1- H^+ is titrated with standard NaOH using Acid-Base Indicator or EP detected by potentiometry.

2- Alternative way: IO_3^- / I^- mix is added + EDTA iodine is liberated then titrate I_2 by $S_2O_3^{2-}$

There are difficulties:

a) Neutralize solution of metal \rightarrow may be hydrolyze salts

b) No buffer can be used in this titration.

5- Indirect Titration: (Anions titration)

For anions that can form ppt with metals



then excess metal titrated by EDTA

Ex₁: SO_4^{2-} :



2) Filter-wash:



4) xx EDTA # st Mg^{2+} using suitable indicator.

Ex₂: PO_4^{3-}



2) $\text{MgNH}_4\text{PO}_4 \downarrow\downarrow + \text{Excess st EDTA} \rightarrow \text{Mg-EDTA}$

3) Excess EDTA # Zn^{2+} ion using suitable Ind.

Ex₃: CN⁻



2) Excess Ni # (st) EDTA.

Ex₄: Halides (X⁻)



3) Ni²⁺ # EDTA

(Ag⁺ replace Ni²⁺ ion cyanide in complex)

Ex₅: F⁻



2) $\text{CaF}_2 \downarrow \downarrow + \text{Excess EDTA} \dots \dots \dots$

Ex₆: CO₃²⁻, Cr₂O₄²⁻, SO₃²⁻, S²⁻ - indirect.

6- Masking

□ **Def.:** Process in which some component of analyte is protected from reaction with EDTA without being physically separated from medium.

□ There are 3 methods:

(1) Masking agent

(2) Kinetic masking

(3) Masking by adjustment of oxidation state of element F^- mask Al^{3+} form stable complex.

(1) Masking agent:

Ex₁: F^-

Mix of Al^{3+} + Mg^{2+} : mask Al^{3+} with F^- leave Mg^{2+}
 Mg^{2+} # EDTA.

Metallochromic Indicators

- *It is organic substance capable of forming intense coloured complex with metal ion having different colour from itself.*
- *E.g. Eriochrome black-T*

Theory of Metal ion Indicator

- *Metal ion indicators are represented as In, when added to metal ion*
- $M + In \longrightarrow M-In$ *(water soluble & characteristic colour)*
- *Titration: Complexing agent first combines with free metal ion. At last when all metal ions are complexed then it replaces indicator as,*
- $M-In + EDTA \longrightarrow M-EDTA + In$ *(shows own color)*

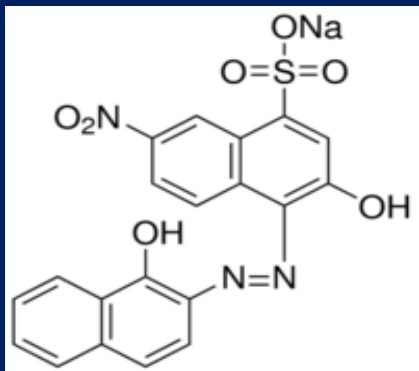
Color change of an Indicator depends on pH

$$K_{In} \text{ (Indicator Const)} = \frac{[M-In]}{[M] [In]}$$

□ *Indicator const. changes with pH therefore it is called as Conditional indicator (K'_{In})*

□ *E.g. Eriochrome black-T or Solochrome black*

□ *1-(1-hydroxy-2-naphthylazo)-6-nitro-2-Naphthol-4-sulfonate*



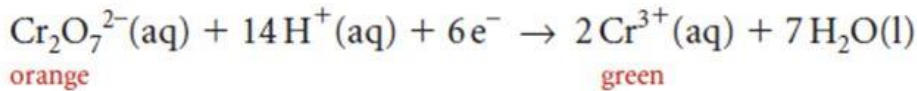
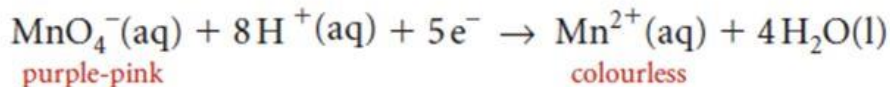
- *pH range 7-11*
- *Metal ions like Cu, Ni, Co, Al, Fe(III), Ti(IV), Pt forms very stable complex with indicator.*
- *Therefore, their titrations not possible (blocks indicator)*

REDOX TITRATIONS

- REDOX TITRATIONS are based on an oxidation-reduction reaction between the analyte and titrant. Redox titrations are carried out by using a potentiometer or a redox indicator to determine the endpoint.

Redox Titration

- In redox titration, no indicator is required because the titrant is a strong oxidizing agent that has a very significant colour change when it undergoes reduction.
- Common OA's used in redox titration are MnO_4^- (aq) and $\text{Cr}_2\text{O}_7^{2-}$ (aq) , both in acidified solutions.



- In a redox titration, it is often necessary to standardize the titrant. Due to the reactive nature of the oxidizing agents used as the titrant, they often react with themselves in their storage container.
- Standardizing involves performing an initial titration with a solution prepared from a solid (so the exact concentration is known) to determine the exact concentration of the titrant.

Redox reactions are of three types:

- (i) Intermolecular redox reactions.
- (ii) Intramolecular redox reactions,
- (iii) Auto redox reactions

OR

Disproportionation reactions.

Redox reactions are divided into two main types:

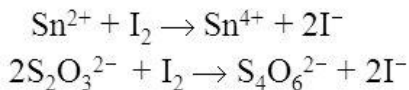
- (i) Chemical redox reactions,
- (ii) Electrochemical redox reactions which either produce or consume electricity

Oxidation and reduction process takes place in a reaction simultaneously.

Which among the following acts as oxidising as well as reducing agent?

Iodimetry: Direct titration of reducing substances with iodine

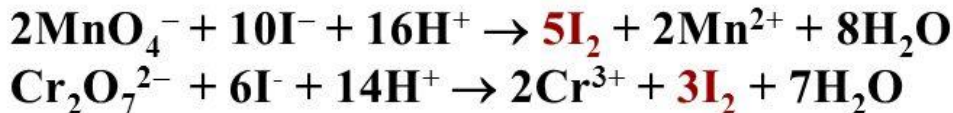
The reducing substances ($E^{\circ} < + 0.54 \text{ V}$) are directly titrated with iodine.



(Self indicator or starch as indicator)

Iodometry: Back titration of oxidizing substances

The oxidizing substance ($E^{\circ} > + 0.54 \text{ V}$) is treated with excess iodide salt:



The liberated iodine is titrated with standard sodium thiosulphate (starch as indicator)

Example 11-13

Dichromate ions oxidize iron (II) ions to iron (III) ions and are reduced to chromium (III) ions in **acidic** solution. Write and balance the net ionic equation for the reaction.



Mass balance the half-reaction



Charge balance the half reaction



This is the **oxidation half-reaction**

Mass balance the half-reaction



Charge balance the half reaction



This is the **reduction half-reaction**

Add the two half-reaction





::::Thank You::::

::::Keep Learning::::