Learning Objectives

- Define and use the relevant terminologies of complex ion equilibria
- Compare and contrast between complex ion and Lewis acid-base equilibria
- Describe and explain the concept of complex equilibria and stepwise equilibrium reactions.
- Use the concept of chemical equilibria in complexometric titrations and calculations.
- Distinguish among the various types of EDTA titrations and their uses.
- Carry out complexometric titrations and related calculations.

In this unit, the concept of complex ion formation and associated stepwise equilibrium reactions will be examined and discussed. Particular emphasis will be given to the application of the complex ion reactions in complexometric titrations, *titrimetric methods based upon complex formation*, as a means to quantitative analysis of metal ions in solution. The emphasis will be on how complex ion formation can be used as a basis of a titrimetric method to quantify metal ions in solution. Here, ethylenediamine tetraacetic acid (EDTA) will be studied as an analytical reagent or titrant that forms very stable complexes with many metal ions in complexometric titration. EDTA (a tertiary amine that also contains carboxylic acid groups) is the most widely used polyaminocarboxylic acid. A discussion of the factors that influence the stability of metal-EDTA complexes and their significance as well as the types of EDTA titrations will also be covered.

Key Concepts

- **Acid-base indicators**: acids or bases which exhibits a visual change on neutralization by the basic or acidic *titrant* at or near the *equivalence point*.
- **Chelation**: the process involved in formation of a chelate.
- **Chemical stoichiometry**: measurement based on exact knowledge of chemical combination
- **Colorimetric indicator**: intensely coloured substances in at least one form (bound or unbound to a metal) and do change colour when the metal ion analyte binds with it.
- **Complex**: a substance composed of two or more components capable of an independent existence.
- **Complexation**: the *association of two or more chemical species that are capable of independent existence by sharing one or more pairs of electrons*.
- **Complexometric indicator**: water soluble organic molecules that undergoes definite colour change in the presence of specific metal ions and are used in complexometric titrations.
- **Complexometric titration**: A titration based on the formation of coordination complexes between a metal ion and complexing agent (or chelating agent) to form soluble complexes.
- **Complexing agent or ligand**: molecules and/or anions with one or more donor atoms that each donate a lone pair of electrons to the metal ion to form a covalent bond.
- **Coordination complex**: a complex in which a central atom or ion is joined to one or more ligands through what is formally a coordinate covalent bond in which both of the bonding electrons are supplied by a ligand.
- **Metal chelate**: a species that is simultaneously bound to two or more sites on a ligand.
- **Monodentate (or Unidentate) ligand**: A ligand that shares a single pair of electrons with a central metal ion in a complex.
- **Multidentate ligand**: A ligand which shares more than one pair of electrons with a central metal ion in a complex. Those ligands which share 2, 3, 4, 5, or 6 are referred to as bidentate, tridentate, tetradeutate (or quadridentate),
pentadentate (or quinqui dentate), and hexadentate, respectively.

- **Stability constant of a complex**: a measure of the extent of formation of the complex at equilibrium.

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**Introduction**

Complex-forming reactions involving many metal ions can serve as a basis for accurate and convenient titrations for such metal ions. These kinds of complex ion titration procedures referred to as complexometric titrations, have high accuracies and offer the possibility of determinations of metal ions at the millimole levels. They have their applications in many chemical and biological processes. The processes involved in the formation of complex ions are basically acid-base type reactions in which the metal ion acts as an acid and the anions or molecules as the base (see unit 2 that deals with acids and bases). In this activity, the theory and applications of complex ion formation, and specifically complexometric titrations in quantifying metal ions in solution will be examined. In addition, the significance of using a reagent that forms a chelate over one that merely forms a complex with a metal ion in volumetric analysis will be explained. Since much attention has recently been focused on the use of ethylenediamine tetraacetic acid (EDTA) in titrimetry, its various applications will be highlighted in this unit.

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**Introduction to Complexation Equilibria and Processes**

In this introduction, important terminologies that will be encountered when dealing with the topic of complexation titration are provided. Also included is a brief description of what a complex is and how their very nature contrast Lewis acid-base systems.

In the broadest sense, **complexation** is the association of two or more chemical species that are capable of independent existence by sharing one or more pairs of electrons. Although this type of a chemical reaction can be classified as a Lewis acid-base reaction, it is more commonly known as a **complexation reaction**. As applied to chemical analysis, this definition is generally taken to mean the bonding of a central metal ion, capable of accepting an unshared pair of electrons with a ligand that can donate a pair of unshared electrons.

Consider the addition of anhydrous copper (II) perchlorate to water. The salt dissolves readily according to the reaction,

\[
\text{Cu(ClO}_4\text{)}_2 \text{(s)} \rightarrow \text{Cu(H}_2\text{O)}_4^{2+} \text{(aq)} + 2\text{ClO}_4^-\]

in which a pair of electrons on the oxygen atom of each H₂O molecule forms a **coordinate covalent bond**, a bond in which both electrons originate from one atom (in this case one oxygen atom of H₂O), to Cu²⁺ ion. In this reaction, Cu²⁺ acts as a **Lewis acid** and H₂O as a **Lewis base**. Such binding of solvent molecules to a metal ion is called **solvation** or, in the special case of solvent water, **hydration**. The Cu(H₂O)⁴²⁺ ion is called an **aquo complex**.

In a complexation reaction, the product of the reaction is termed a **complex**. The species which donates the electron pairs by acting as a Lewis base is known as a **complexing agent or ligand**, and the ion which accepts the donated electrons, the Lewis acid, is called the **central ion or central atom**. Central ions are generally metallic cations. The ligand can be either a neutral molecule such as water or ammonia; or an ion such as chloride, cyanide, or hydroxide. The complex can have either a positive or a negative charge, or it can be neutral.
For most analytical applications, complexation occurs between a dissolved metal ion and a dissolved ligand capable of displacing water from the metal ion. This is illustrated for the reaction between a hydrated copper (II) ion and dissolved NH₃ ligand below.

\[
\left[ \mathrm{ Cu \left( H_2O \right)_4 } \right]^ { 2 + } + \mathrm{ NH}_3 \underset{\text{water}}{\longrightarrow} \left[ \mathrm{ CuNH_3 } \left( H_2O \right)_3 \right]^ { 2 + } + \mathrm{ H}_2\mathrm{O}
\]

Normally for reactions that occur in water, \(\text{H}_2\text{O}\) is omitted and the complexation reaction is written simply as

\[
\ce{Cu^{2+} + NH3 <=> [CuNH3]^{2+}}
\]

### Classification of Ligands

Ligands are classified according to the number of pairs of electrons which they can share with the central metal or metal ion. A ligand that shares a single pair of electrons (such as ammonia, water, cyanide, F⁻, Cl⁻, Br⁻, I⁻, CN⁻, SCN⁻, NO₂⁻, NH₃, H₂O, N(CH₂CH₃)₃, CH₃COCH₃, etc.) is a monodentate or unidentate ligand; a ligand, which shares more than one pair of electrons, is a multidentate ligand. A multidentate ligand, which shares two (such as NH₂CH₂CH₂NH₂, C₂O₄²⁻, etc.), three, four, five, or six pairs of electrons is a bidentate, tridentate (or terdentate), tetradentate (or quadridentate), pentadentate (or quindentate), or hexadentate (or sexadentate) ligand, respectively. The maximum number of electron pair donor groups that a metal ion can accommodate in complexation reaction is known as its coordination number. Typical values are 2 for Ag⁺, as in Ag(CN)₂⁻, 4 for Zn²⁺, as in Zn(NH₃)₄²⁺; and 6 for Cr³⁺, as in Cr(NH₃)₆³⁺.

### Nature of Linkage in complex ions

A central metal ion can form a single bond with a ligand which is able to donate a pair of electrons from one of its atoms only, as in the examples given above for the formation of Zn(NH₃)₄²⁺, Cr(NH₃)₆³⁺ etc. However, with multidentate (or sometimes known as polydentate) ligands, it can form a bond in more than one location to form a ring structure. Generally, ring formation results in increased stability of the complex. A species that is simultaneously bonded to two or more sites on a ligand is called a metal chelate, or simply a chelate and the process of its formation is called chelation.

A chelate is formed if two or more donor atoms is coordinated by the simultaneous use of two or more electron pairs to the same metal atom. An example of a metal-EDTA complex is provided in the figure below.

Note that, all types of bidentate, tridentate, tetradentate, pentadentate and hexadentate ligands can act as chelating ligands and their complexes with metals are therefore known as chelates.
Here, EDTA behaves as a hexadentate ligand since six donor groups are involved in bonding the divalent metal cation.

Importance of Chelates

Chelates find application both in industry and in the laboratory where fixing of metal ions is required. In analytical chemistry, chelates are used in both qualitative and quantitative analysis. For example, Ni^{2+}, Mg^{2+}, and Cu^{2+} are quantitatively precipitated by chelating agents. In volumetric analysis, chelating agents (such as ethylenediamine tetraacetic acid, EDTA) are often used as reagents or as indicators for the titration of some metal ions. Because of the stability of chelates, polydentate ligands (also called chelating agents) are often used to sequester or remove metal ions from a chemical system. Ethylenediamine tetraacetic acid (EDTA), for example, is added to certain canned foods to remove transition-metal ions that can catalyze the deterioration of the food. The same chelating agent has been used to treat lead poisoning because it binds Pb^{2+} ions as the chelate, which can then be excreted by the kidneys.

In the subsequent sections that follow, the application of the fundamentals of complex ion formation is demonstrated in complexometric titration. This is achieved after briefly considering the subtopic of complex equilibria.

Complex ion Equilibria

*Stability constant* of a complex is defined as a *measure of the extent of formation of the complex at equilibrium*. Stability of a complex depends on the strength of the linkage between the central metal ion and the ligands (i.e., the bond) and therefore, the stronger the metal ligand bond, the more stable the complex.

Metal complexes are formed by replacement of molecules in the solvated shell of a metal ion in aqueous solution with the ligands by *stepwise reaction* as shown below:
\([\text{M(H}_2\text{O})_2]+L\rightleftharpoons[\text{M(H}_2\text{O})_2\text{L}]+\text{H}_2\text{O}\)

\([\text{M(H}_2\text{O})_{n-1}L]+L\rightleftharpoons[\text{M(H}_2\text{O})_{n-1}\text{L}_2]+\text{H}_2\text{O}\)

\([\text{M(H}_2\text{O})_{n-2}\text{L}_2]+L\rightleftharpoons[\text{M(H}_2\text{O})_{n-2}\text{L}_3]+\text{H}_2\text{O}\)

Overall reaction is:

\([\text{M(H}_2\text{O})_n]+nL\rightleftharpoons[\text{ML}_n]+n\text{H}_2\text{O}\)

where \(L\) stands for the ligand and \(n\) refers to the number of molecules of a particular species. If we ignore the water molecules in the above equations, one can then write the above equations and their corresponding equilibrium constants as follows:

\[\text{M}+L\rightleftharpoons[\text{ML}];\quad \text{K}_1=\frac{[\text{ML}]}{[\text{M}][L]}\]

\[\text{ML}+L\rightleftharpoons[\text{ML}_2];\quad \text{K}_2=\frac{[\text{ML}_2]}{[\text{ML}][L]}\]

\[\text{ML}_2+L\rightleftharpoons[\text{ML}_3];\quad \text{K}_3=\frac{[\text{ML}_3]}{[\text{ML}_2][L]}\]

\[\text{ML}_{n-1}+L\rightleftharpoons[\text{ML}_n];\quad \text{K}_n=\frac{[\text{ML}_n]}{[\text{ML}_{n-1}][L]}\]

The equilibrium constants, \(\text{K}_1\), \(\text{K}_2\), \(\text{K}_3\), ..., and \(\text{K}_n\) are known as the stepwise formation constants or stepwise stability constants or consecutive stability constants.

Note that the values of the stepwise stability constants decrease in the order:

\[\text{K}_1>\text{K}_2>\text{K}_3>...>\text{K}_n\]

because a previously metal ion-coordinated ligand tends to repel any incoming ligand of a similar kind.

The products of the stepwise stability constants is known as overall stability or cumulative stability constant and is designated as \(\beta\), i.e.,

\[\beta=\text{K}_1 \times \text{K}_2 \times \text{K}_3 \times ... \times \text{K}_n\]

As previously mentioned, multidentate ligands which form five- or six-member red rings with central metal ions, generally have unusually high stability. To be useful in a titration, the complexation reaction must occur rapidly as compared with the rate of addition of the titrant. Complexes which are formed rapidly are called labile complexes and those which are formed slowly are called nonlabile or inert complexes. Generally, only titration reactions which form labile complexes
are useful.

Consider the simple complexation of copper (II) ion by the unidentate ligand NH3 in water. The reaction between these two species is:

\[
\text{Cu}^{2+} + \text{NH}_3 \leftrightarrow [\text{CuNH}_3]^{2+}
\]

(the H2O is omitted for simplicity). In aqueous solution the copper (II) ion is actually hydrated and NH3 replaces H2O. The equilibrium constant for this reaction is the stepwise formation constant, \(K_1\), is expressed as:

\[
\begin{align*}
K_1 &= \frac{[\text{CuNH}_3]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]} = 2.0 \times 10^4
\end{align*}
\]

The equilibrium of the addition of a second ammonia molecule,

\[
[\text{CuNH}_3]^{2+} + \text{NH}_3 = [\text{Cu(NH}_3)_2]^{2+}
\]

is described by a second stepwise formation constant, \(K_2\),

\[
\begin{align*}
K_2 &= \frac{[\text{Cu(NH}_3)_2]^{2+}}{[\text{CuNH}_3]^{2+}[\text{NH}_3]} = 5.0 \times 10^3
\end{align*}
\]

The overall process for the addition of the two NH3 molecules to a Cu2+ ion and the equilibrium constant for that reaction are given by the following:

\[
\begin{align*}
\text{Cu}^{2+} + 2\text{NH}_3 &= [\text{Cu(NH}_3)_2]^{2+}
\end{align*}
\]

\[
\begin{align*}
K &= \frac{[\text{Cu(NH}_3)_2]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^2} = 2.0 \times 10^7
\end{align*}
\]
\( \beta_2 = \frac{[\text{Cu}^{2+}][\text{NH}_3]^2}{[\text{Cu}^{2+}][\text{NH}_3]^2} = K_1 \times K_2 = 1.0 \times 10^8 \)

The formation constant \( \beta_2 = K_1 K_2 \) is called an overall formation constant. Recall that the equilibrium constant of a reaction obtained by adding two other reactions is the product of the equilibrium constants of these two reactions, \( \beta_2 \).

Similarly, the stepwise and overall formation constant expressions for the complexation of a third and fourth molecule of \( \text{NH}_3 \) to copper (II) are given by the following:

\[
\begin{align*}
\text{Cu(NH}_3\text{)}^2_2 + \text{NH}_3 & \rightleftharpoons \text{Cu(NH}_3\text{)}^3_2 \quad (K_3) = \frac{[\text{Cu(NH}_3\text{)}^3_2]}{[\text{Cu(NH}_3\text{)}^2_2][\text{NH}_3]} \\
\text{Cu(NH}_3\text{)}^3_2 + \text{NH}_3 & \rightleftharpoons \text{Cu(NH}_3\text{)}^4_2 \quad (K_4) = \frac{[\text{Cu(NH}_3\text{)}^4_2]}{[\text{Cu(NH}_3\text{)}^3_2][\text{NH}_3]} \\
\text{Cu}^{2+} + 4\text{NH}_3 & \rightleftharpoons [\text{Cu(NH}_3\text{)}^4_2]^{2+}
\end{align*}
\]

\( \beta_3 = \frac{[\text{Cu(NH}_3\text{)}^3_2]}{[\text{Cu}^{2+}][\text{NH}_3]^3} = K_1 K_2 \)

\( \beta_4 = \frac{[\text{Cu(NH}_3\text{)}^4_2]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = K_1 K_2 K_3 K_4 \)

The values of \( K_3 \) and \( K_4 \) are 1.0 x 10\(^3\) and 2.0 x 10\(^2\), respectively. Therefore, the values of \( \beta_3 \) and \( \beta_4 \) are 1.0 x 10\(^{11}\) and 2.0 x 10\(^{13}\), respectively.

The stepwise formation constants of the amine complexes of copper (II) are relatively close together. This means that over a wide range of \( \text{NH}_3 \) concentrations, there will exist at the same time, at least two (normally more), copper (II) amine complexes in solution at significant concentrations relative to each other. This is generally true of unidentate ligands and hence limits their use as titrants for the determination of metal ions (save for a few specialized cases, which is beyond the scope of this module).

A major requirement for titration is a single reaction that goes essentially to completion at the equivalence point. This requirement is generally not met by unidentate ligands because of the fact that their formation constants are not very high.
Dissociation of Complexes

A given complex behaves as a weak electrolyte and dissociates to a small degree. The equilibrium constant for the dissociation of a complex is simply the inverse of its formation constant, \( K_{\text{form}} \), and is known as the instability constant, \( K_{\text{ins}} \). For example, the complex ion \( \text{Ag(NH}_3\text{)}_2^+ \) dissociates according to the equilibrium reaction:

\[
[\text{Ag(NH}_3\text{)}_2^+] \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3
\]

and its instability constant is given by,

\[
K_{\text{ins}} = \frac{1}{K_{\text{form}}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag(NH}_3\text{)}_2^+]}
\]

In actual practice, the dissociation of a complex ion, just like the ionization of a polyprotic acid, occurs in steps as shown below:

\[
\text{Ag(NH}_3\text{)}_2^+ \rightleftharpoons \text{Ag(NH}_3\text{)}^+ + \text{NH}_3
\]

\[
K_1 = \frac{[\text{Ag(NH}_3\text{)}^+][\text{NH}_3]}{[\text{Ag(NH}_3\text{)}_2^+]}
\]

\[
\text{Ag(NH}_3\text{)}^+ \rightleftharpoons \text{Ag}^+ + \text{NH}_3
\]

\[
K_2 = \frac{[\text{Ag}^+][\text{NH}_3]}{[\text{Ag(NH}_3\text{)}^+]}
\]

The overall instability constant, \( K_{\text{ins}} = K_1 \times K_2 \)

Exercise (PageIndex(1))

Calculate the percent dissociation of a 0.10 M \( \text{Ag(NH}_3\text{)}_2^+ \) solution if its instability constant, \( K_{\text{ins}} = 6.3 \times 10^{-8} \).

Answer

Application of Complex Equilibria in Complexation Titration:

The concept behind formation of complexes can be used as stated earlier (see section on importance of chelates), in
quantitative analysis of either metal ions or other anions of interest.

An example to illustrate the use of complex titration exercise is in the determination of cyanide present in a solution via the titration of cyanide with silver nitrate solution given below.

When a solution of silver nitrate is added to a solution containing cyanide ion (alkali cyanide), a white precipitate is formed when the two ligands first come into contact with each other. On stirring, the precipitate re-dissolves due to the formation of an alkali stable salt of silver-cyanide complex, i.e.,

\[ \text{Ag}^+ + 2\text{CN}^- = [\text{Ag(CN)}_2]^-
\]

When the above reaction is complete (following attainment of an equivalence point), further addition of the silver nitrate solution now yields an insoluble silver cyanoargentate (sometimes termed insoluble silver cyanide). The end point of the reaction is indicated by the formation of a permanent precipitate or turbidity. Such a titration experiment can be used to quantify the amount of cyanide present in a solution. Here cyanide is an example of a complexone; another term for a complexing agent.

Note that the formation of a single complex species in contrast to a stepwise production of complex species simplifies complexation titration (i.e., complexometric titrations) and facilitates the detection of end points.

The chelate most commonly used for complexometric titrations is ethylenediamine tetraacetic acid (EDTA); an aminopolycarboxylic acid which is an excellent complexing agent. It is normally represented by either of the following two structures:

![Structure of EDTA](image)

Its greatest advantage is that it is inexpensive, chemically inert, and it reacts with many metals with a simple stoichiometry

\[ \text{EDTA}^{4-} + \text{M}^{n+} \rightarrow [\text{M}-\text{EDTA}]^{n-4} \]

where \( n \) is the charge on the metal ion, \( M \).

This complexing agent has four (4) ionizable acid groups with the following \( pK_a = -\log K_a \) where \( K_a \) is the acid dissociation constant) values: \( pK_{a1} = 2 \), \( pK_{a2} = 2.7 \), \( pK_{a3} = 6.6 \) and \( pK_{a4} = 10.3 \) at 20°C. These values suggest that the complexing agent behaves as a dicarboxylic acid with two strongly acidic groups and that there are two ammonium protons of which the first ionizes in the pH region of about 6.3 and the second at pH of about 11.5.

If \( \text{M}^{n+} \) is the metal ion and \( \text{Y}^{4-} \) stands for the completely ionized form of EDTA, then the metal-EDTA complex can be represented as \( \text{MY}^{(n-4)+} \). The stability of such a complex is often dependent on a number of factors, that need due consideration as one investigates the application of EDTA titration experiments in quantification of metal ions in solution. These factors affect the various multiple equilibria shown above, which in turn influences how
complexometric titration is carried out. The next section looks at the two important factors that are true for all complexometric titrations.

Factors affecting Stability of Metal-EDTA complexes

- **Effect of pH on stability of metal-EDTA complexes**

The concentration of each of the complexes shown, say in examples above, will depend on the pH of the solution. So to have any properly defined equilibria, the pH of the solution mixture will have to be buffered. Equally important, the concentration of protons, $H^+$, which would otherwise compete with the $M^{n+}$ ions, must be held rigorously constant. For instance, at low pH values protonation (the act of transferring or donating a proton, a hydrogen ion, $H^+$, to a species) of $Y^{4-}$ species occurs and the species $HY^{3-}$, $H_2Y^{2-}$, $H_3Y^-$ and even undissociated $H_4Y$ may well be present. (The abbreviations $H_4Y$, $H_3Y^-$, $H_2Y^{2-}$, $HY^{3-}$, and $Y^{4-}$ are often used to refer to EDTA and its ions.) Thus, the act of lowering the pH of the solution will decrease the concentration of $Y^{4-}$. On the other hand, increasing the pH of the solution will cause tendency to form slightly soluble metallic hydroxides owing to the reaction below:

\[
(MY)^{(n-4)}^+ + nOH^- \rightleftharpoons M(OH)_n^{n+} + Y^{4-}
\]

The extent of hydrolysis (meaning the splitting of water in a reaction such as)

\[
OAc^- + H_2O \rightleftharpoons HOAc + OH^-
\]

de $(MY)^{(n-4)}$ depends upon the characteristic of the metal ion and is largely controlled by the solubility product of the metallic hydroxide and the stability constant of the complex. The larger the stability constant of the complex, the lesser the tendency of the metal hydroxide to form.

- **The effect of other complexing agents**

If another complexing agent (other than $Y^{4-}$) is also present in the solution, then the concentration of $M^{n+}$ in solution will be reduced owing to its ability to further complex with the interfering complexing agent. The relative proportions of the complexes will be dependent on the stability constants of the two types of metal-complexing agent complexes.

EDTA titration has been traditionally used in quantitating calcium ions in water, in a process referred to as determining water hardness. Water hardness is customarily referred to as concentration of calcium in the form of calcium carbonate.

In the following section, we shall use the $Ca^{2+}$-EDTA titration to illustrate the method of complexometric titration. In this method, a colorimetric indicator, [these are intensely coloured substances in at least one form (bound or unbound to the metal) and do change colour when the metal-ion analyte binds with it], is used.

The reaction between $Ca^{2+}$ and EDTA proceeds according to the stoichiometry shown below:

\[
Ca^{2+} + EDTA^{4-} \rightleftharpoons Ca - EDTA^{2-}
\]
with a corresponding equilibrium constant for *formation* expressed as

\[
\text{K}_f \left( \text{Ca} - \text{EDTA}^{2-} \right) = \frac{[\text{Ca} - \text{EDTA}^{2-}]}{[\text{Ca}^+][\text{EDTA}^{4-}]}
\]

Note that, whereas the equilibrium constants for acids and bases are often tabulated as dissociation constants, equilibrium constants for complex formation are tabulated as *formation constants*.

### Titration Curves

In the former unit, we learnt that in the titration of a strong acid versus a strong base, a plot of pH against the volume of the solution of the strong base added yields a point of inflexion at the equivalence point. Similarly, in an EDTA versus metal ion titration, if \( pM = -\log[M^{n+}] \), where \( M^{n+} \) signifies the metal ion whose concentration is required) is plotted against the volume of EDTA solution added, a point of inflexion occurs at the equivalence point. The general shape of a titration curve obtained following the titration of 100 mL of a 0.1 mol/L solution of \( \text{Ca}^{2+} \) ion with a 0.1 mol/L Na-EDTA solution at two separate pH conditions is shown below.

![Titration Curves](image)

### Chemistry of EDTA Titrations

EDTA is used to titrate many ions. For instance, EDTA has been used successfully over the years for the determination of water hardness (a measure of the total \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) ions in water). Water hardness is often conveniently determined by titration of total \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) ions with EDTA. In this subsection, we shall look at the chemistry of EDTA titrations in general.

In the presence of Eriochrome Black T (EBT) as an indicator, a minor difficulty is usually encountered. Note that metal complexes of EBT are generally red in colour. Therefore, if a colour change is to be observed with EBT indicator, the pH of the solution must be between 7 and 11 so that the blue form of the indicator dominates when the titrant breaks up the red metal-EBT complex at the end point. At a pH of 10, the endpoint reaction is:
EDTA is normally standardized against a solution of Ca\(^{2+}\) ions. In the early stages of the EDTA titration with EBT as indicator, the Ca\(^{2+}\)-EBT complex does not dissociate appreciably due to a large excess of the untitrated Ca\(^{2+}\) ions in solution (i.e., Ca\(^{2+}\) ions is plenty in solution). As the titration progresses further and more Ca\(^{2+}\) ions is complexed with the titrant, the equilibrium position shifts to the left (i.e., previously complexed Ca-EBT complex, which is red in colour, begins to dissociate to give back more Ca\(^{2+}\) ions for complexation with the titrant EDTA), causing a gradual change in colour from the red Ca-EBT complex.

To avoid this problem of gradual change in colour, a small amount of 1:1 EDTA:Mg is often added to the titration flask (this does not affect the stoichiometry of the titration reaction because the quantities of EDTA and Mg are equimolar) because MgIn complex is sufficiently stable that it will not dissociate appreciably prior to attainment of the equivalence point. (Note that at pH 10, Ca-EDTA complex is more stable than Mg-EDTA complex and also, MgIn-complex is more stable than CaIn-complex.)

Note that when 1:1 EDTA:Mg is added to the Ca\(^{2+}\) analyte-containing indicator solution, the following reactions take place:

\[
\begin{align*}
\text{MgY}^{-2} + \text{Ca}^{2+} & \rightarrow \text{Mg}^{2+} + \text{CaY}^{-2} \quad \text{(more stable)} \\
\text{Mg}^{2+} + \text{CaIn}^{-} & \rightarrow \text{Ca}^{2+} + \text{MgIn}^{-} \quad \text{(more stable)}
\end{align*}
\]

**Explanation:**

When EDTA titrant is added, it first binds all the Ca\(^{2+}\) as per the reaction shown below (Note that at pH 10, the predominant species of EDTA is HY\(^{3-}\)):

\[
\text{Ca}^{2+} + \text{HY}^{3-} \rightarrow \text{CaY}^{2-} + \text{H}^{+}
\]

Upto and including the end point, EDTA replaces the less strongly bound Eriochrome Black T from the Mg\(^{2+}\)-EBT complex (represented as MgIn\(^{-}\)) as shown below:

\[
\text{MgIn}^{-} + \text{HY}^{3-} \rightarrow \text{HIn}^{2-} + \text{MgY}^{2-}
\]

### Types of EDTA Titrations

Important metal ions-EDTA titration experiments fall into the following categories:

A. Direct Titration
In **direct titration**, the solution containing the metal ion to be determined is buffered to the desired pH and titrated directly with a standard EDTA solution. It may be necessary to prevent precipitation of the hydroxide of the metal ion (or a basic salt) by the addition of an **auxiliary complexing agent** (or sometimes called **masking agent**), since they form stable complexes with potential interference, such as tartarate or citrate.

**At start (i.e., before addition of titrant):**

\[
M^{n+} + Ind \rightleftharpoons [M\text{ind}]^{n+}
\]

where \( Ind \) is representing the indicator.

**During titration:**

\[
M^{n+} + [H_2Y]^{2-} \rightleftharpoons [MY]^{n+} + 2H^+ + \text{Ind}
\]

where \([H_2Y]^{2-}\) is representing EDTA titrant

**At Endpoint:**

\[
[M\text{ind}]^{n+} + [H_2Y]^{2-} \rightleftharpoons [MY]^{n+} + \text{Ind} + 2H^+
\]

Note that the **complexed** ([\(M\text{ind}\)]^{n+}) and **free indicator** (\(\text{ind}\)) have different colours.

At the **equivalence point** the magnitude of the concentration of the metal ion being determined decreases abruptly. This **equivalence point** is generally determined by the change in color of a **metal indicator** that responds to changes in pM.

Example \(\PageIndex{1}\): Titration of 100 mL of a water sample at pH 13 in the presence of a calcium specific indicator such as Eriochrome Black T required 14.0 mL of 0.02M EDTA solution. Calculate the hardness of the water sample as CaCO_3 in mg L\(^{-1}\).

**Solution**

Important information to note:

- Molecular weight for CaCO_3 is 100g

- The stoichiometry for the reaction between Ca\(^{2+}\) and EDTA at pH 13 is given by:

\[
Ca^{2+} + EDTA^{4-} \rightleftharpoons Ca - EDTA^{2-}
\]

- Both Mg\(^{2+}\) and Ca\(^{2+}\) contribute to water hardness. Both metal ions have the same stoichiometry with EDTA, hence the titration includes the sum of Mg and Ca ions in the water sample.

- The \(14.0\text{mL of }0.02\text{MEDTA}\) contains \(\left(\frac{14.0\text{ mL}}{1000\text{ mL/L}}\right) \times 0.02\text{ moles/L}) = 2.80 \times 10^{-4}\) moles of EDTA.
From the above 1:1 stoichiometry, the number of Ca$^{2+}$ ions present in the 100 mL water sample (equivalent to the combined Ca$^{2+}$ and Mg$^{2+}$ ions responsible for water hardness) should be equal to the number of moles of the titrant, EDTA.

Hence, number of moles of Ca$^{2+}$ ions present in the 100 mL water sample = $2.80 \times 10^{-4}$ moles.

$2.80 \times 10^{-4}$ moles of Ca$^{2+}$ is equivalent to $(2.80 \times 10^{-4} \text{ moles}) \times 100 \text{ g mole}^{-1} \text{CaCO}_3 = 2.80 \times 10^{-2} \text{ g} \times 1000 \text{ mg g}^{-1} = 28.0 \text{ mg of Ca (as CaCO}_3)$. 

Therefore, the hardness of the water is $28.0 \text{ mg present in the 100 mL of water} = \frac{28.0 \text{ mg}}{100 \text{ mL} / 1000 \text{ mL}^{-1}} = 280 \text{ mg L}^{-1}$ hardness.

Exercise (\PageIndex{2})

A 50.00 mL water sample required 21.76 mL of 0.0200 mol/L EDTA to titrate water hardness at pH 13.0. What was the hardness in mg L$^{-1}$ of CaCO$_3$?

Answer

B. Back titration

This is for the determination of metal ions that cannot be titrated directly with EDTA, say in alkaline solution (e.g., Mn$^{2+}$ and Al$^{3+}$) due to precipitation of their hydroxides).

In back titration, an excess known amount of a standard EDTA solution is added to the solution of the analyte. The resulting solution mixture is then buffered to the desired pH, and the excess EDTA titrated with a standard solution of a second metal ion. Examples of metal ions often used as the second metal include solutions of; ZnCl$_2$, ZnSO$_4$, MgCl$_2$ or MgSO$_4$. The end point is then detected with the aid of an appropriate metal indicator that responds to the second metal ion introduced in the back titration.

The following steps apply:

\[
\text{Mn}^+ + [\text{H}_2\text{Y}]^{2-} \rightleftharpoons [\text{MY}]^{n-4} + 2\text{H}^+ \\
\text{where [H}_2\text{Y}]^{2-} \text{ is representing EDTA titrant}
\]

\[
\text{Zn}^{2+} + [\text{H}_2\text{Y}]^{2-} \rightleftharpoons [\text{ZnY}]^{2-} + 2\text{H}^+
\]

At Endpoint:

\[
\text{Zn}^{2+} + \text{ind} + \rightarrow [\text{Znind}]^{2+}
\]

Back titration becomes necessary if analyte:
• precipitates in the absence of EDTA,
• reacts too slowly with EDTA, or
• blocks the indicator.

Example \(\PageIndex{2}\):

A 3208 g sample of nickel ore was processed to remove interferences and 50.00 ml of 0.1200 mol L\(^{-1}\) EDTA was added in excess to react with Ni\(^{2+}\) ions in solution. The excess EDTA was titrated with 24.17 mL of 0.0755 mol L\(^{-1}\) standard Mg\(^{2+}\). Calculate the %Ni in the ore.

**Solution**

• The stoichiometry for the reaction between Ni\(^{2+}\) (or Mg\(^{2+}\)) and EDTA can be represented as: \(\text{Ni}^{2+} + \text{EDTA}^{4-} = \text{Ni} - \text{EDTA}^{2-}\)

• The stoichiometry represents a 1:1, i.e., for every mole of EDTA present, an equivalent number of moles of Ni\(^{2+}\) is used up.

• Total number of moles of EDTA initially available in the 50.00 mL (=0.050 L) solution of 0.1200 mol L\(^{-1}\) EDTA = 0.1200 moles L\(^{-1}\) x 0.050 L = 6.0 x 10\(^{-3}\) moles.

• Number of moles of the titrant Mg\(^{2+}\) ions present in the 24.17 mL (= 0.02417 L) of 0.0755 mol L\(^{-1}\) = 0.02417 L x 0.0755 moles L\(^{-1}\) = 1.82 x 10\(^{-3}\) moles

• Therefore, the moles of EDTA that must have reacted with the available Ni\(^{2+}\) ions originally present = (6.0 x 10\(^{-3}\) - 1.82 x 10\(^{-3}\)) moles = 4.18 x 10\(^{-3}\) moles.

• Hence, number of moles of Ni\(^{2+}\) ions originally present in the 50.00 mL (= 0.050 L) solution = 4.18 x 10\(^{-3}\) moles.

• This is = 4.18 x 10\(^{-3}\) moles x 58.7g/mol (Atomic weight for Ni = 58.7g) = 0.245366 g

• Therefore, \%Ni in the ore \(\dfrac{0.245366 \text{ g}}{3208 \text{ g}} \times 100\% = 0.00765\%

**C. Replacement or substitution titration**

Substitution titration may be used for the metal ions that do not react (or react unsatisfactorily) with a metal indicator (e.g., Ca\(^{2+}\), Pb\(^{2+}\), Hg\(^{2+}\), Fe\(^{3+}\)), or for metal ions that form EDTA complexes that are more stable than those of other metals such as magnesium and calcium.

In this, there is quantitative displacement of the second metal (Mg\(^{2+}\) or Zn\(^{2+}\)) from a complex by the analyte metal. Usually, the determination of the metal ions that form weak complexes with the indicator and the colour change is unclear and vague.
The metal cation $M^{n+}$ to be determined may be treated with the magnesium complex of EDTA leading to the following reaction:

$$M^{n+} + MgY^{2-}\rightarrow (MY)^{(n-4)+} + Mg^{2+}$$

The amount of magnesium ion set free is equivalent to the cation present and can be titrated with a standard solution of EDTA.

The following steps apply:

1. **Replacement step:**
   $$Ca^{2+} + [MgY]^{2-} \rightarrow [CaY]^{2-} + Mg^{2+}$$

2. **$Mg^{2+}$ + Ind $\rightarrow [Mg\text{ Ind}]^{2+}$**
   $$Mg^{2+} + [H_2Y]^{2-} \rightarrow [MgY]^{2-} + 2H^+$$
   $$[Mg\text{ Ind}]^{2+} + [H_2Y]^{2-} \rightarrow [MgY]^{2-} + \text{Ind} + 2H^+$$

**D. Alkalimetric Titration**

When a solution of $Na_2H_2Y$ is added to a solution containing metallic ions, complexes are formed with the liberation of two equivalents of hydrogen ion, i.e.,

$$M^{n+} + H_2Y^{2-} \rightarrow (MY)^{(n-4)+} + 2H^+$$

The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid-base indicator or potentiometric end point. Alternatively, an iodate-iodide mixture is added as well as the EDTA solution and the liberated iodine is titrated with a standard thiosulphate solution.

Note that the solution of the metal to be determined must be accurately neutralized before titration; this is often a difficult matter on account of the hydrolysis of many salts, and constitutes a weak feature of alkalimetric titration.

**Example \(\PageIndex{3}\):**

A 10.00 mL solution of $FeSO_4$ was added to 50.00 mL of 0.05 mol L$^{-1}$ $Na_2H_2Y$. The $H^+$ released required 18.03 mL of 0.080 mol L$^{-1}$ NaOH for titration. What was the molar concentration of the $FeSO_4$ solution?

**Solution**

- The stoichiometry for the reaction between $Fe^{2+}$ and $Na_2H_2Y$ can be represented as: $Fe^{2+} + Na_2H_2Y = Na_2FeY + 2H^+$. Here 1 mole of $Fe^{2+}$ ions yields 2 moles of $H^+$ ions.
- The stoichiometry for the acid-base neutralization reaction between the released $H^+$ ions and NaOH in the titration
process can be represented as:

\[ H^+ + OH^- = H_2O \].  This is 1:1 reaction (i.e., for every 1 mole of H\(^+\) ions released, an equivalent moles of hydroxide is needed for neutralization.

- Therefore, number of moles of H\(^+\) released = number of moles of OH\(^-\) ions present in the 18.03 mL (= 0.01803 L) of the 0.080 mol L\(^-1\) NaOH solution = 0.01803 L x 0.080 mol L\(^-1\) = 1.4424 x 10\(^{-3}\) moles.

- Since for every mole of Fe\(^{2+}\) ions consumed, twice as many moles of H\(^+\) ions are released, then the number of moles of Fe\(^{2+}\) ions consumed = \(\frac{1}{2}\) x 1.4424x10\(^{-3}\) moles = 7.212x10\(^{-4}\) moles.

- Therefore, 7.212 x 10\(^{-4}\) moles of Fe\(^{2+}\) ions were present in the original 10.00 mL (= 0.010 L) solution of FeSO\(_4\). Thus, Molar concentration of the FeSO\(_4\) solution = \(\frac{7.212 \times 10^{-4} \text{ moles}}{0.010 \text{ L}}\) = 0.07212 M.