ANALYTICAL CHEMISTRY

Read the details of the information given below from Skoog and West's "Fundamentals of Analytical Chemistry" book, which is recommended as a reference.

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Complexation and Precipitation Reactions and Titrations

The Formation of Complexes

Titrations with Inorganic Complexing Agents

Organic Complexing Agents

Aminocarboxylic Acid Titrations

17A The Formation of Complexes

A **ligand** is an ion or a molecule that forms a covalent bond with a cation or a neutral metal atom by donating a pair of electrons, which are then shared by the two.

The number of covalent bonds that a cation tends to form with electron donors is its **coordination number**.

Titrations based on complex formation called **complexometric titrations.**

A **chelate** is produced when a metal ion coordinates with two or more donor groups of a single ligand to form a five- or six-membered heterocyclic ring.

17A-1 Complexation Equilibria

Complexation reactions involve a metal-ion M reacting with a ligand L to form a complex ML.

$$M + L \rightleftharpoons ML$$

Complexation reactions occur in a stepwise fashion and the reaction above is often followed by additional reactions:

$$ML + L \rightleftharpoons ML_2$$

$$ML_2 + L \rightleftharpoons ML_3$$

$$\vdots \qquad \vdots$$

The equilibrium constants for complex formation reactions are generally written as formation constants.

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML} \qquad \beta_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}]\,[\mathrm{L}]} = K_1$$

$$\mathrm{M} + 2\mathrm{L} \rightleftharpoons \mathrm{ML}_2 \qquad \beta_2 = \frac{[\mathrm{ML}_2]}{[\mathrm{M}]\,[\mathrm{L}]^2} = K_1 K_2$$

$$\mathrm{M} + 3\mathrm{L} \rightleftharpoons \mathrm{ML}_3 \qquad \beta_3 = \frac{[\mathrm{ML}_3]}{[\mathrm{M}]\,[\mathrm{L}]^3} = K_1 K_2 K_3$$

$$\vdots \qquad\qquad \vdots$$

17B Titrations with Inorganic Complexing Agents

Complexometric Titrations

In complexometric titrations, a metal ion reacts with a suitable ligand to form a complex, and the equivalence point is determined by an indicator or an appropriate instrumental method.

The formation of soluble inorganic complexes is not widely used for titrations, but the formation of precipitates, particularly with silver nitrate as the titrant, is the basis for many important determinations.

Precipitation Titrations

Precipitation titrations are based on reactions that yield ionic compounds of limited solubility.

The most widely used and important precipitating reagent is silver nitrate and it is used for the determination of the halogens, the halogenlike anions, mercaptans, fatty acids, and several divalent inorganic anions. Titrations with silver nitrate are sometimes called argentometric titrations.

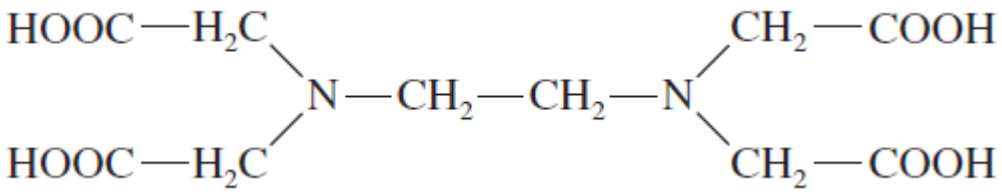
17C Organic Complexing Agents

Organic reagents are particularly useful in precipitating metals, in binding metals so as to prevent interferences, in extracting metals from one solvent to another, and in forming complexes that absorb light for spectrophotometric determinations. The most useful organic reagents form *chelate complexes* with metal ions.

17D Aminocarboxylic Acid Titrations

Ethylenediaminetetraacetic Acid (EDTA)

Ethylenediaminetetraacetic acid, which is commonly shortened to EDTA, is the most widely used complexometric titrant. EDTA has the structural formula:



Titration Methods Involving EDTA

1. Direct Titration

Many of the metals in the periodic table can be determined by titration with standard EDTA solutions. Some methods are based on indicators that respond to the analyte itself, while others are based on an added metal ion.

   i. Methods Based on Indicators for the Analyte
   ii. Methods Based on Indicators for an Added Metal Ion

2. Back-Titration Methods
3. Displacement Methods

Determination of Water Hardness

Hardness is now expressed in terms of the concentration of calcium carbonate that is equivalent to the total concentration of all the multivalent cations in the sample.

The determination of hardness is a useful analytical test that provides a measure of the quality of water for household and industrial uses.

- Water hardness is usually determined by an EDTA titration after the sample has been buffered to pH 10.

- Magnesium, which forms the least stable EDTA complex of all of the common multivalent cations in typical water samples, is not titrated until enough reagent has been added to complex all of the other cations in the sample.

- A magnesium-ion indicator, such as Calmagite or Eriochrome Black T, can serve as indicator in water-hardness titrations.