Complexometric Reactions and Titrations
Complexes are compounds formed from combination of metal ions with ligands (complexing agents). A metal is an electron deficient species while a ligand is an electron rich, and thus, electron donating species. A metal will thus accept electrons from a ligand where coordination bonds are formed. Electrons forming coordination bonds come solely from ligands.
A ligand is called a monodentate if it donates a single pair of electrons (like :NH₃) while a bidentate ligand (like ethylenediamine, :NH₂CH₂CH₂H₂N:) donates two pairs of electrons. Ethylenediaminetetraacetic acid (EDTA) is a hexadentate ligand. The ligand can be as simple as ammonia which forms a complex with Cu²⁺, for example, giving the complex Cu(NH₃)₄²⁺. When the ligand is a large organic molecule having two or more of the complexing groups, like EDTA, the ligand is called a chelating agent and the formed complex, in this case, is called a chelate.
The tendency of complex formation is controlled by the formation constant of the reaction between the metal ion (Lewis acid) and the ligand (Lewis base). As the formation constant increases, the stability of the complex increases.

Let us look at the complexation reaction of Ag$^+$ with NH$_3$:

\[
\begin{align*}
\text{Ag}^+ + \text{NH}_3 & \rightleftharpoons \text{Ag(NH}_3\text{)}^+ \\
\text{Ag(NH}_3\text{)}^+ + \text{NH}_3 & \rightleftharpoons \text{Ag(NH}_3\text{)}_2^+
\end{align*}
\]

\[
\begin{align*}
k_{f1} &= \frac{[\text{Ag(NH}_3\text{)}^+]}{[\text{Ag}^+][\text{NH}_3]} \\
k_{f2} &= \frac{[\text{Ag(NH}_3\text{)}_2^+]}{[\text{Ag(NH}_3\text{)}^+][\text{NH}_3]} 
\end{align*}
\]
$K_{f1} \times k_{f2} = [\text{Ag(NH}_3\text{)}_2^{+}]/[\text{Ag}^{+}][\text{NH}_3]^2$

Now look at the overall reaction:

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

$k_f = [\text{Ag(NH}_3\text{)}_2^{+}]/[\text{Ag}^{+}][\text{NH}_3]^2$

It is clear from inspection of the values of the $k_f$ that:

$K_f = k_{f1} \times k_{f2}$

For a multistep complexation reaction we will always have the formation constant of the overall reaction equals the product of all step wise formation constants
The formation constant is also called the stability constant and if the equilibrium is written as a dissociation the equilibrium constant in this case is called the instability constant.

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

\[
k_{\text{inst}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag(NH}_3\text{)}_2^+]}
\]

Therefore, we have:

\[
K_{\text{inst}} = \frac{1}{k_f}
\]
Example
A divalent metal ion reacts with a ligand to form a 1:1 complex. Find the concentration of the metal ion in a solution prepared by mixing equal volumes of 0.20 M M$^{2+}$ and 0.20 M ligand (L). $k_f = 1.0 \times 10^8$.

Solution
The formation constant is very high and essentially the metal ions will almost quantitatively react with the ligand.

The concentration of metal ions and ligand will be half that given as mixing of equal volumes of the ligand and metal ion will make their concentrations half the original concentrations since the volume was doubled.
\([\text{[M}^2+\text{]} = 0.10 \text{ M}, \text{[L]} = 0.10 \text{ M}\]

\(\text{M}^2+ + \text{L} \rightleftharpoons \text{ML}^2+\)

<table>
<thead>
<tr>
<th>Before Equilibrium</th>
<th>0</th>
<th>0</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>(\text{M}^2+)</td>
<td>(\text{L})</td>
<td>(\text{ML}^2+)</td>
</tr>
<tr>
<td>At Equilibrium</td>
<td>(x)</td>
<td>(x)</td>
<td>(0.10 - x)</td>
</tr>
</tbody>
</table>

\(K_f = \frac{(0.10 - x)}{x^2}\)

Assume \(0.10 \gg x\) since \(k_f\) is very large

\(1.0 \times 10^8 = \frac{0.10}{x^2}, \quad x = 3.2 \times 10^{-5}\)

Relative error = \((3.2 \times 10^{-5}/0.10) \times 100 = 3.2 \times 10^{-2}\%\)

The assumption is valid.

\([\text{M}^2+] = 3.2 \times 10^{-5} \text{ M}\)
Example
Silver ion forms a stable 1:1 complex with trien. Calculate the silver ion concentration at equilibrium when 25 mL of 0.010 M silver nitrate is added to 50 mL of 0.015 M trien. $K_f = 5.0 \times 10^7$

Solution
$$\text{Ag}^+ + \text{trien} \rightleftharpoons \text{Ag(trien)}^+$$

mmol Ag$^+$ added = $25 \times 0.01 = 0.25$

mmol trien added = $50 \times 0.015 = 0.75$

The reaction occurs in a 1:1 ratio

mmol trien excess = $0.75 - 0.25 = 0.50$

$[\text{Trien}] = 0.5/75 \text{ M}$

$[\text{Ag(trien)}^+] = 0.25/75 \text{ M}$
\[ K_f = \frac{0.25/75 - x}{x \times 0.50/75 + x} \]
Assume \(0.25/75 \gg x\) since \(k_f\) is very large
\[ 5.0 \times 10^7 = \frac{0.25/75}{x \times 0.50/75} \]
\[ x = 1.0 \times 10^{-8} \]
Relative error = \((1.0 \times 10^{-8}/(0.25/75)) \times 100 = 3.0 \times 10^{-4} \%
The assumption is valid.
\[ [Ag^+] = 1.0 \times 10^{-8} \text{ M} \]
The Chelon Effect

We have seen earlier that large multidentate ligands can form complexes with metal ions. These complexes are called chelates. The question is which is more stable a chelate formed from a chelating agent with four chelating groups or a complex formed from the same metal with four moles of ligand having the same donating group?
This can be simply answered by looking at the thermodynamics of the process. We know from simple thermodynamics that spontaneous processes are favored if an increase in entropy results. Now look at the dissociation of the chelate and the complex mentioned above, dissociation of the chelate will give two molecules while dissociation of the complex will give five molecules. Therefore, dissociation of the complex results in more disorder and thus more entropy. The dissociation of the complex is thus more favored and therefore the chelate is more stable as its dissociation is not favored.
EDTA Titrations

Ethylenediaminetetraacetic acid disodium salt (EDTA) is the most frequently used chelate in complexometric titrations. Usually, the disodium salt is used due to its good solubility. EDTA is used for titrations of divalent and polyvalent metal ions. The stoichiometry of EDTA reactions with metal ions is usually 1:1. Therefore, calculations involved are simple and straightforward. Since EDTA is a polydentate ligand, it is a good chelating agent and its chelates with metal ions have good stability.
EDTA Equilibria

EDTA can be regarded as $H_4Y$ where in solution we will have, in addition to $H_4Y$, the following species: $H_3Y^-$, $H_2Y^{2-}$, $HY^{3-}$, and $Y^{4-}$. The amount of each species depends on the pH of the solution where:

$$\alpha_4 = [Y^{4-}]/C_T$$

where:

$$C_T = [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

$$\alpha_4 = k_{a1}k_{a2}k_{a3}k_{a4}/([H^+]^4 + k_{a1}[H^+]^3 + k_{a1}k_{a2}[H^+]^2 + k_{a1}k_{a2}k_{a3}[H^+] + k_{a1}k_{a2}k_{a3}k_{a4})$$

The species $Y^{4-}$ is the ligand species in EDTA titrations and thus should be looked at carefully.
The Formation Constant

Reaction of EDTA with a metal ion to form a chelate is a simple reaction. For example, EDTA reacts with Ca$^{2+}$ ions to form a Ca-EDTA chelate forming the basis for estimation of water hardness. The reaction can be represented by the following equation:

$$\text{Ca}^{2+} + \text{Y}^{4-} = \text{CaY}^{2-} \quad k_f = 5.0 \times 10^{10}$$

$$K_f = [\text{CaY}^{2-}]/[\text{Ca}^{2+}][\text{Y}^{4-}]$$

The formation constant is very high and the reaction between Ca$^{2+}$ and Y$^{4-}$ can be considered quantitative. Therefore, if equivalent amounts of Ca$^{2+}$ and Y$^{4-}$ were mixed together, an equivalent amount of CaY$^{2-}$ will be formed.
The question now is how to calculate the amount of Ca\(^{2+}\) at equilibrium?

\[
\text{CaY}^{2-} \rightleftharpoons \text{Ca}^{2+} + \text{Y}^{4-}
\]

However, [Ca\(^{2+}\)] \# [Y\(^{4-}\)] at this point since the amount of Y\(^{4-}\) is pH dependent and Y\(^{4-}\) will disproportionate to form all the following species, depending on the pH.

\[
\text{C}_\text{T} = [\text{H}_4\text{Y}] + [\text{H}_3\text{Y}^-] + [\text{H}_2\text{Y}^{2-}] + [\text{HY}^{3-}] + [\text{Y}^{4-}]
\]

Where, C\(_T\) is the sum of all species derived from Y\(^{4-}\) which is equal to [Ca\(^{2+}\)].

Therefore, the [Y\(^{4-}\)] at equilibrium will be less than the [Ca\(^{2+}\)] and in fact it will only be a fraction of C\(_T\) where:

\[
\alpha_4 = \frac{[\text{Y}^{4-}]}{\text{C}_\text{T}} = \frac{\text{ka}_1 \text{ka}_2 \text{ka}_3 \text{ka}_4}{([\text{H}^+]^4 + \text{ka}_1 [\text{H}^+]^3 + \text{ka}_1 \text{ka}_2 [\text{H}^+]^2 + \text{ka}_1 \text{ka}_2 \text{ka}_3 [\text{H}^+] + \text{ka}_1 \text{ka}_2 \text{ka}_3 \text{ka}_4)}
\]
### Formation Constants for EDTA Complexes

<table>
<thead>
<tr>
<th>Cation</th>
<th>$K_{MY}$</th>
<th>Cation</th>
<th>$K_{MY}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^+$</td>
<td>$2.1 \times 10^7$</td>
<td>Cu$^{2+}$</td>
<td>$6.3 \times 10^{18}$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>$4.9 \times 10^8$</td>
<td>Zn$^{2+}$</td>
<td>$3.2 \times 10^{16}$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>$5.0 \times 10^{10}$</td>
<td>Cd$^{2+}$</td>
<td>$2.9 \times 10^{16}$</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>$4.3 \times 10^8$</td>
<td>Hg$^{2+}$</td>
<td>$6.3 \times 10^{21}$</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>$5.8 \times 10^7$</td>
<td>Pb$^{2+}$</td>
<td>$1.1 \times 10^{18}$</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>$6.2 \times 10^{13}$</td>
<td>Al$^{3+}$</td>
<td>$1.3 \times 10^{16}$</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>$2.1 \times 10^{14}$</td>
<td>Fe$^{3+}$</td>
<td>$1.3 \times 10^{25}$</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>$2.0 \times 10^{16}$</td>
<td>V$^{3+}$</td>
<td>$7.9 \times 10^{25}$</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>$4.2 \times 10^{18}$</td>
<td>Th$^{4+}$</td>
<td>$1.6 \times 10^{23}$</td>
</tr>
</tbody>
</table>
The Conditional Formation Constant

We have seen that for the reaction

\[ \text{Ca}^{2+} + \text{Y}^{4-} \rightleftharpoons \text{CaY}^{2-} \quad k_f = 5.0 \times 10^{10} \]

We can write the formation constant expression

\[ K_f = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]} \]

However, we do not know the amount of \( \text{Y}^{4-} \) at equilibrium but we can say that since \( \alpha_4 = \frac{[\text{Y}^{4-}]}{C_T} \), then we have:

\[ [\text{Y}^{4-}] = \alpha_4 C_T \]

Substitution in the formation constant expression we get:

\[ K_f = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}]} \alpha_4 C_T \]

or at a given pH we can write

\[ K'_f = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}]} C_T \]

Where \( K'_f \) is called the conditional formation constant. It is conditional since it is now dependent on pH.
Titration Curves

In most cases, a titration is performed by addition of the titrant (EDTA) to the metal ion solution adjusted to appropriate pH and in presence of a suitable indicator. The break in the titration curve is dependent on:

1. The value of the formation constant.
2. The concentrations of EDTA and metal ion.
3. The pH of the solution

As for acid-base titrations, the break in the titration curve increases as $k_f$ increases and as the concentration of reactants is increased. The pH effect on the break of the titration curve is such that sharper breaks are obtained at higher pH values.
Minimum pH for effective titrations of various metal ions with EDTA.