Monodentate Ligands

- possess only one accessible donor group

Example
Water, $H_2O$ - most metal ions exist as aquo complexes in water

$Ag(H_2O)_2^+$  $Cu(H_2O)_4^{2+}$  $Fe(H_2O)_6^{3+}$

- charge and coordination number are NOT related
complex formed when metal ion coordinates with two or more donor groups of a single ligand to form a 5- or 6-membered ring
the disodium salt is often used since it is more soluble

EDTA

has 6 donor groups
Complexation Reaction

$M + L \rightleftharpoons ML$

$K_f = \frac{[ML]}{[M][L]}$

$K_f$ - formation constant
the denominator for each beta expression is identical

the denominator is an ascending power series in \([L]\), starting with \([L]^0\) to \([L]^n\)

\[1 + K_{f1}[L] + K_{f1}K_{f2}[L]^2 + K_{f1}K_{f2}K_{f3}[L]^3 \ldots\]
**Conditional or Effective Formation Constants**

EDTA is a weak acid, $H_6Y^{2+}$

\[
c_{EDTA} = \left[H_6Y^{2+}\right] + \left[H_5Y^+\right] + \left[H_4Y\right] + \left[H_3Y^-\right] + \left[H_2Y^{2-}\right] + \left[HY^{3-}\right] + \left[Y^{4-}\right]
\]

\[
\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{c_{EDTA}}
\]

\[
K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\alpha_{Y^{4-}}c_{EDTA}}
\]

\[
[Y^{4-}] = c_{EDTA}\alpha_{Y^{4-}}
\]

\[
K_f' = \frac{[CdY^{2-}]}{[Cd^{2+}]c_{EDTA}}
\]
Calculate the conditional formation constant of CdY$^{2-}$ for both metal and ligand at the following pH values (a) pH = 5.0 (b) = 8.0. Assume that

$$\beta_{Cd^{2+}} = 4.5 \times 10^{-4}.$$ 

EDTA ($K_{a1} = 1.0 \times 10^{-2}, K_{a2} = 2.1 \times 10^{-3}, K_{a3} = 7.8 \times 10^{-7}, K_{a4} = 6.8 \times 10^{-11}$)
At pH 5.0, \( \alpha_{Y^-} = 4.90 \times 10^{-7} \)

\[
K_f''' = K_f \times \alpha_{Y^-} \times \beta_0 = (2.9 \times 10^{16})(4.9 \times 10^{-7})(4.5 \times 10^{-4})
\]

\[
K_f''' = 6.4 \times 10^6
\]
at pH 8.0, \( \alpha_{\gamma^4^-} = 6.70 \times 10^{-3} \)

\[
K_f''' = K_f \times \alpha_{\gamma^4^-} \times \beta_0 = (2.9 \times 10^{16})(6.7 \times 10^{-3})(4.5 \times 10^{-4})
\]

\[K_f''' = 8.74 \times 10^{10}\]
Example

What is the equilibrium concentration of \( \text{Ni}^{2+} \) in a solution with an analytical \( \text{NiY}^{2-} \) concentration of 0.0150 M at pH (a) 3.0 and (b) 8.0?

\[
\text{Ni}^{2+} + \text{Y}^{4-} \rightleftharpoons \text{NiY}^{2-}
\]

\[
K_{\text{NiY}^{2-}} = \frac{[\text{NiY}^{2-}]}{[\text{Ni}^{2+}][\text{Y}^{4-}]} = 4.2 \times 10^{18}
\]

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

\[
[Y^{4-}] = \alpha_{Y^{4-}} C_T
\]
Conditional or Effective Formation Constants

\[ K_f = K_f \times \alpha_{Y^{4-}} = \frac{[NiY^{2-}]}{[Ni^{2+}]C_T} \]

\[ [Ni^{2+}]^2 = \frac{[NiY^{2-}]}{K_f \times \alpha_{Y^{4-}}} \]

\[ [Ni^{2+}] = \sqrt{\frac{[NiY^{2-}]}{K_f \times \alpha_{Y^{4-}}}} \]

at pH 3.0

\[ [Ni^{2+}] = \sqrt{\frac{0.0150}{(4.2 \times 10^{18})(2.5 \times 10^{-11})}} = 1.2 \times 10^{-5} M \]
Calculating the Conditional Constant

\[ K_{CaY^2^-} = \frac{[CaY^2^-]}{[Ca^{2+}] \alpha_{Y^4^-} C_T} \]

\[ K_f' = \alpha_{Y^4^-} \times K_{CaY^2^-} = \frac{[CaY^2^-]}{[Ca^{2+}] C_T} \]

\[ K_f' = (0.405)(5.0 \times 10^{10}) = 2.03 \times 10^{10} \]
Direct Titration

Standard EDTA solution is added to the sample until an appropriate end point signal is observed.

Example:

\[ \text{Mg}^{2+} \]

\[ \text{Mg}^{2+} + \text{H}_2\text{Y}^{2-} \rightleftharpoons \text{MgY}^{2-} + 2\text{H}^+ \]

\[ \text{MgIn}^- + \text{H}_2\text{Y}^{2-} \rightleftharpoons \text{MgY}^{2-} + \text{HIn}^{2-} \]
Prediction of Precipitation

Example

Should precipitation occur when 50.00 mL of 5.0 \times 10^{-4} \text{ M Ca(NO}_3\text{)}_2 is mixed with 50.00 mL of 2.0 \times 10^{-4} \text{ M NaF}?

\[ K_{sp} \text{ CaF}_2 = 3.9 \times 10^{-11} \]
Factors Affecting Solubility

- Common Ion Effect
- Complex Ion Formation
- pH
Factors Affecting Solubility

Common Ion Effect

\[ x = \sqrt{ \frac{K_{sp}}{0.4} } \]

\[ x = \sqrt{ \frac{2.5 \times 10^{-13}}{0.4} } = 7.91 \times 10^{-7} \text{ M} \]

\[ [\text{Pb}^{2+}] = 0.10 + x \approx 0.10 \text{ M} \]

\[ [\text{IO}_3^-] = 2x = 1.6 \times 10^{-6} \text{ M} \]
Factors Affecting Solubility

Effect of pH

1. Calculate the molar solubility of CuS in a solution in which the \([H_3O^+]\) is held constant at (a) 1.0 \(\times\) 10\(^{-1}\) M and (b) 1.0 \(\times\) 10\(^{-4}\) M. \(K_{sp} \text{ CuS} = 8.0 \times 10^{-37}\).

2. Calculate the molar solubility of PbCO\(_3\) in a solution buffered to a pH of 7.00. \(K_{sp} \text{ PbCO}_3 = 7.4 \times 10^{-14}\).
Factors Affecting Solubility

Complex Ion Formation

- solubility of ppt may increase

Example

Calculate the molar solubility of $\text{AgCl}$ in 0.010 M $\text{NH}_3$ (free uncomplexed $\text{NH}_3$).
Separating Ions by pH Control: Sulfide Separations

$[H_2S] \gg [HS^-], [H^+] \approx 0.1 M$

$K_{a1}K_{a2} = \frac{[H_3O^+][S^{2-}]}{[HS^-]}$

$0.1 = [H_2S] + [HS^-] + [S^{2-}]$

In a saturated solution of the gas $\approx 0.1 M$
Construct a titration curve for the titration of 50.00 mL of 0.0500 M Cl\(^-\) with 0.100 M Ag\(^+\). \(K_{sp\, \text{AgCl}} = 1.8 \times 10^{-10}\). Plot \(p\text{Ag}\) or \(p\text{Cl}\) against the volume of titrant.

\[
\text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)} \rightleftharpoons \text{AgCl}_{(s)}
\]

\[
K = \frac{1}{K_{sp}} = \frac{1}{1.8 \times 10^{-10}} = 5.6 \times 10^9
\]
Precipitation Titration

Before Addition of Titrant

$[Cl^-] = 0.0500 \text{ M}$

$pCl = -\log[Cl^-] = -\log 0.0500$

$pCl = 1.30$

$[Ag^+] = 0$

$pAg = \text{indeterminate}$
Addition of 10.00 mL Titrant

Precipitation Titration

\[ K_{sp} = [Ag^+][Cl^-] \]

\[
\frac{[Ag^+]}{[Cl^-]} = \frac{K_{sp}}{0.025} = \frac{1.8 \times 10^{-10}}{0.025} = 7.2 \times 10^{-9} \text{ M}
\]

\[ pAg = -\log 7.2 \times 10^{-9} = 8.14 \]
1. Calculate the conditional formation constant for the nickel(II)-EDTA complex in a solution containing 0.500 M ammonium ion and 0.500 M free (uncomplexed) ammonia.

\[ \log K_f \text{Ni(II)-EDTA} = 18.6 \]

\[ \text{Ni(NH}_3)_6^{2+} \] \[ \log K_f_1 = 2.36, \log K_f_2 = 1.90 \]
\[ \log K_f_3 = 1.55, \log K_f_4 = 1.23 \]
\[ \log K_f_5 = 0.85, \log K_f_6 = 0.42 \]

\[ pK_a \text{NH}_4^+ = 9.26 \]

2. Calculate the conditional formation constant for the mercury(II)-EDTA complex in a solution of pH 11.0 containing 0.0100 M free (uncomplexed) cyanide ion.

\[ \log K_f \text{Hg(II)-EDTA} = 21.8 \]

\[ \text{Hg(CN)}_4^{2-} \] \[ \log K_f_1 = 18.0, \log K_f_2 = 16.7 \]
\[ \log K_f_3 = 3.83, \log K_f_4 = 2.98 \]

\[ pK_a \text{EDTA} \quad pK_{a1} = 2.00, \quad pK_{a2} = 2.67, \quad pK_{a3} = 6.16, \quad pK_{a4} = 10.26 \]