Complexation equilibra

Key terms and concepts

➢ Complex ion; ligands; central metal ions; coordination number

➢ Monodentate, bidentate, multidentate ligands

➢ Chelates and chelating agents

➢ Stepwise ($K_{f,i}$) and cumulative (K_f) stability (formation) constants

➢ Complex ions and solubility of precipiates

➢ Instability (dissociation) constants

Complexation equilibra

➢ Complexes are ions or neutral molecules in solution that are comprised of components that are capable of existing independently in solution.

➢ All complexes consist of **a central metal ion,** which acts as **a Lewis acid** (an electron acceptor), and one or more **ligands,** which act **as Lewis bases** (electron donors).

➢ The central metal ion is characterized by **its positive charge and its coordination number**, CN, i.e., the number of ligands with which it is able to form bonds.

➢ Ligands are quite diverse in character, but they all **include an electronegative atom** that has one or more pairs of electrons available to form bonds with metal ions.

➢ Types of ligands include **simple monoatomic anion**s (e.g., Cl^-, Br^-), **multiatomic inorganic ions** (e.g., OH^-, CO_23^-, CN^-), **neutral molecules** (e.g., NH_3), and **organic bases and anions** (e.g., amines and carboxylic acid anions).

➢ The most common ligand is water itself, which has oxygen as its electronegative ion.

➢ Ligands are also classified by **the number of binding sites** they contain. **Monodentate ligands** have one atom with a pair of electrons available to share with a metal ion; **bidentate ligands** have two sites; and **multidentate ligands** have an unspecified number greater than one.

➢ Ligands with two or more sites **form ringed structures** (Figure 1) with metal ions that are called chelates (after the Greek word for claw), and such multidentate ligands are called **chelating agents.**
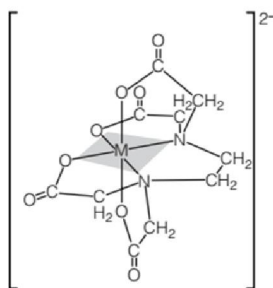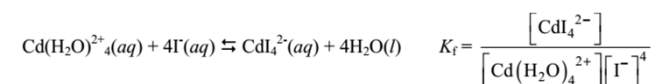
Fig. 1. The structure of a metal-EDTA chelate showing its octahedral geometry.

➢ In general, the binding strength of chelating agents increases with the number of binding sites on the agent because the agent is able to fill a greater number of bonding orbitals on a metal ion as the number of ligand atoms increases.
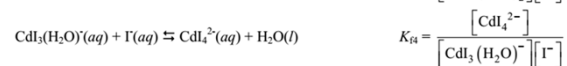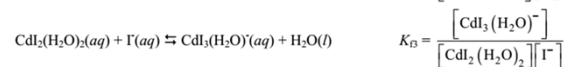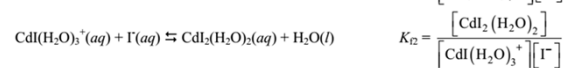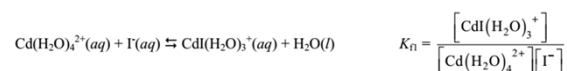
Complexation equilibrium constants

➢ Equilibrium constants for complexation reactions usually are written as formation constants (also called stability or association constants)

➢ Considering the formation of the complex ion CdI_4^{2-}(aq) from cadmium ion and iodide. The equilibrium constant expression for the formation of the complex according to the formation reaction is given below

$$Cd(H_2O)^{2+}_4(aq) + 4I^-(aq) \leftrightarrows CdI_4^{2-}(aq) + 4H_2O(l) \qquad K_f = \frac{\left[CdI_4^{2-}\right]}{\left[Cd(H_2O)_4^{2+}\right]\left[I^-\right]^4}$$

K_f is referred to as the **overall formation (or stability) constant**

➢ In reality, the metal cation, M^{n+}, is hydrated by several water molecules and the ligand, L, gradually replaces them one at a time in stepwise manner. We can write four stepwise reactions for the formation of CdI_4^{2-}

$$Cd(H_2O)_4^{2+}(aq) + I^-(aq) \leftrightarrows CdI(H_2O)_3^+(aq) + H_2O(l) \qquad K_{f1} = \frac{\left[CdI(H_2O)_3^+\right]}{\left[Cd(H_2O)_4^{2+}\right]\left[I^-\right]}$$

$$CdI(H_2O)_3^+(aq) + I^-(aq) \leftrightarrows CdI_2(H_2O)_2(aq) + H_2O(l) \qquad K_{f2} = \frac{\left[CdI_2(H_2O)_2\right]}{\left[CdI(H_2O)_3^+\right]\left[I^-\right]}$$

$$CdI_2(H_2O)_2(aq) + I^-(aq) \leftrightarrows CdI_3(H_2O)^-(aq) + H_2O(l) \qquad K_{f3} = \frac{\left[CdI_3(H_2O)^-\right]}{\left[CdI_2(H_2O)_2\right]\left[I^-\right]}$$

$$CdI_3(H_2O)^-(aq) + I^-(aq) \leftrightarrows CdI_4^{2-}(aq) + H_2O(l) \qquad K_{f4} = \frac{\left[CdI_4^{2-}\right]}{\left[CdI_3(H_2O)^-\right]\left[I^-\right]}$$

➢ Where $K_{f1}, K_{f2}, K_{f3}, K_{f4}$ are referred to as the stepwise formation constant.

➢ And the **overall formation constant**, K_f is simply equal to the product of the stepwise formation constants:
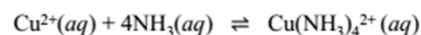
$$K_f = \frac{\left[CdI(H_2O)_3^+\right]}{\left[Cd(H_2O)_4^{2+}\right]\left[I^-\right]} \times \frac{\left[CdI_2(H_2O)_2\right]}{\left[CdI(H_2O)_3^+\right]\left[I^-\right]} \times \frac{\left[CdI_3(H_2O)^-\right]}{\left[CdI_2(H_2O)_2\right]\left[I^-\right]} \times \frac{\left[CdI_4^{2-}\right]}{\left[CdI_3(H_2O)^-\right]\left[I^-\right]}$$

$$= K_{f1} \times K_{f2} \times K_{f3} \times K_{f4}$$

➢ Complexes between good Lewis acids (such as highly charged and transition metal cations) and good Lewis bases (such as NH_3, CN^-, OH^-, …) are extremely stable

➢ Their K_f values are very large ($>10^5$)

➢ If enough ligand is present in the solution, almost the entire amount of the cation is converted to the complex

➢ So $\quad C_M \approx [M(L)_m^{n+}]$

➢ For example considering the formation of copper complexes formed from hydroxide and ammonia.

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$$

$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) + 2OH^-(aq)$$
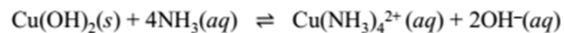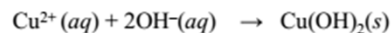
The formation of the $Cu(NH_3)_4^{2+}$ ion can be expressed as

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$

$$K_f = \frac{\left[Cu(NH_3)_4^{2+}\right]}{\left[Cu^{2+}\right]\left[NH_3\right]^4} = 5.0 \times 10^{13}$$

Q. Write the stepwise reactions for the formation of the above complexes.

Example: What is the concentration of Fe^{3+} after mixing of **25 mL 0.020 M** $Fe(NO_3)_3$ solution with **25 mL 1.0 M** KCN solution? ($K_f = 4.0 \times 10^{43}$ for the complex $Fe(CN)_6^{3-}$)

→ 0.020 M $Fe(NO_3)_3$ → 0.020 M Fe^{3+}

→ 1.0 M KCN → 1.0 M CN^-
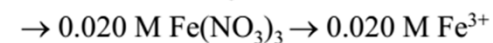
→ After mixing, the total volume is 25 + 25 = 50 mL

⇒ C_{Fe} = (0.020 M×25 mL/50 mL) = 0.010 M

⇒ C_{CN} = (1.0 M ×25 mL/50 mL) = 0.50 M

	Fe^{3+}	+ 6CN^-	↔ $Fe(CN)_6^{3-}$
i	0.010	0.50	0
c	-x	-6x	+x
e	0.010 - x	0.50 - 6x	x
e'	y	0.44	0.010

$$K_f = \frac{[Fe(CN)_6^{3-}]}{[Fe^{3+}][CN^-]^6}$$

$$K_f = \frac{0.010}{y(0.44)^6}$$

→ K_f is very large so almost the entire amount of Fe^{3+} is converted to the complex

⇒ $x \approx C_{Fe}$ ⇒ $x \approx 0.010$

⇒ $(0.50 - 6x) \approx (0.50 - 6 \times 0.010) = 0.44$

→ Define a new variable, $y = 0.010 - x = [Fe^{3+}]$

$$K_f = \frac{0.010}{y(0.44)^6} \quad \Rightarrow \quad y = \frac{0.010}{K_f(0.44)^6}$$

$$y = \frac{0.010}{4.0 \times 10^{43}(0.44)^6} = \boxed{3.4 \times 10^{-44} \text{ M} = [Fe^{3+}]}$$

Complex Ions and Solubility of Precipitates

➤ The solubility of some ionic solids in water can be improved by the addition of an appropriate ligand (such as NH_3, CN^-, …)

   – The ligand (L) forms a complex with the cation of the slightly soluble salt and the solubility equilibrium shifts toward further dissolution
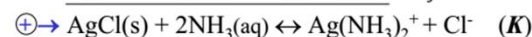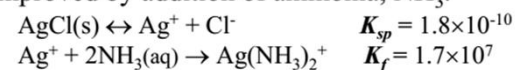
$$MA(s) \leftrightarrow M^{n+} + A^{n-} \qquad M^{n+} + mL \leftrightarrow M(L)_m^{\,n+}$$

➤ Consider the dissolution of AgCl in a 0.1 M NH_3 solution. We consider the solubility equilibrium as well as the complexation equilibrium.

$$AgCl(s) \leftrightarrow Ag^+ + Cl^- \qquad K_{sp} = 1.8\times10^{-10}$$
$$Ag^+ + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+ \qquad K_f = 1.7\times10^7$$
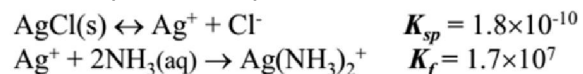
➤ As the NH_3 complexes Ag+, more AgCl must dissolve in order to maintain the concentration of Ag+ at the level required by the first equilibrium. Note that both of these equilibria must be satisfied simultaneously.

Example: The solubility of AgCl can be improved by addition of ammonia, NH_3.

$$AgCl(s) \leftrightarrow Ag^+ + Cl^- \qquad K_{sp} = 1.8\times10^{-10}$$
$$Ag^+ + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+ \qquad K_f = 1.7\times10^7$$
$$\oplus \rightarrow \; AgCl(s) + 2NH_3(aq) \leftrightarrow Ag(NH_3)_2^+ + Cl^- \quad (K)$$

$\rightarrow K = K_{sp}\times K_f = 1.8\times10^{-10}\times1.7\times10^7 = \boxed{3.1\times10^{-3}}$

$\rightarrow$ The overall equilibrium constant, K, is much larger than K_{sp}

$\Rightarrow$ The addition of NH_3 shifts the equilibrium to the right and the **solubility increases**

Example: Calculate the molar solubility of AgCl in **0.10 M** NH_3 solution.

	$AgCl(s) + 2NH_3(aq) \leftrightarrow Ag(NH_3)_2^+ + Cl^-$			
i	excess	0.10	0	0
c	$-s$	$-2s$	$+s$	$+s$
e	excess	$0.10 - 2s$	s	s

$$K = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = \frac{s^2}{(0.10-2s)^2}$$

$$\frac{s}{0.1-2s} = \sqrt{K} \quad \Rightarrow \quad s = \frac{0.10\sqrt{K}}{1+2\sqrt{K}} = \frac{0.10\sqrt{3.1\times10^{-3}}}{1+2\sqrt{3.1\times10^{-3}}}$$

$$\Rightarrow \boxed{s = 5.0\times10^{-3}}$$

**Note:** The solubility of AgCl in 0.10 M NH_3 is higher than that in **pure water** which is:

$$s = (K_{sp})^{1/2} = (1.8\times10^{-10})^{1/2} = 1.3\times10^{-5}\,M$$

Problem

Given the above formation constant for $Ag(NH_3)_2^+$ and the K_{sp} value for AgBr of 5.0×10^{-13}, calculate the molar solubility of AgBr in (a) water, and (b) 0.10 M NH_3.
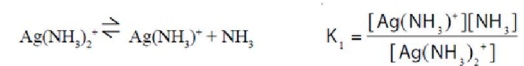
Dissociation of Complexes

➤ 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_{form}, and is known as the **instability constant, K_{ins}.**

➤ For example, the complex ion $Ag(NH_3)_2^+$ dissociates according to the equilibrium reaction:

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$
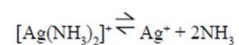
and its *instability constant* is given by,

$$K_{ins} = \frac{1}{K_{form}} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

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

$$Ag(NH_3)_2^+ \rightleftharpoons Ag(NH_3)^+ + NH_3 \qquad K_1 = \frac{[Ag(NH_3)^+][NH_3]}{[Ag(NH_3)_2^+]}$$

$$Ag(NH_3)^+ \rightleftharpoons Ag^+ + NH_3 \qquad K_2 = \frac{[Ag^+][NH_3]}{[Ag(NH_3)^+]}$$

The *overall instability constant*, $K_{ins} = K_1 \times K_2$