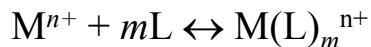


19.4 Equilibria Involving Complex Ions

- **Complex ions** – consist of a metal cation surrounded by anions or neutral molecules called ligands
- Complex ions are **Lewis acid-base complexes** (adducts)
 - The **metal cation** is a **Lewis acid**
 - The **ligands** are **Lewis bases**

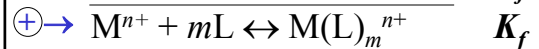
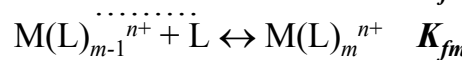
Formation of Complex Ions

➤ For a metal cation, M^{n+} , and a neutral ligand, L , the complex formation is given by the equilibrium:



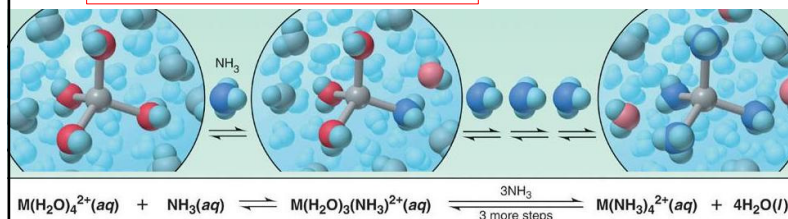
$$K_f = \frac{[M(L)_m^{n+}]}{[M^{n+}][L]^m} \quad K_f \rightarrow \text{formation constant of the complex}$$

➤ 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



$$K_f = K_{f1} \times K_{f2} \times \dots \times K_{fm}$$

Note: Water has been omitted from the expressions



- 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 ($>10^5$)
 \Rightarrow If enough ligand is present in the solution, almost the entire amount of the cation is converted to the complex $\rightarrow C_M \approx [M(L)_m^{n+}]$

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 $Fe(CN)_6^{3-}$)

$\rightarrow 0.020 \text{ M } Fe(NO_3)_3 \rightarrow 0.020 \text{ M } Fe^{3+}$

$\rightarrow 1.0 \text{ M } KCN \rightarrow 1.0 \text{ M } CN^-$

\rightarrow After mixing, the total volume is $25 + 25 = 50 \text{ mL}$

$$\Rightarrow C_{Fe} = (0.020 \text{ M} \times 25 \text{ mL} / 50 \text{ mL}) = 0.010 \text{ M}$$

$$\Rightarrow C_{CN} = (1.0 \text{ M} \times 25 \text{ mL} / 50 \text{ mL}) = 0.50 \text{ M}$$

	$Fe^{3+} + 6CN^- \leftrightarrow Fe(CN)_6^{3-}$			$K_f = \frac{[Fe(CN)_6^{3-}]}{[Fe^{3+}][CN^-]^6}$
<i>i</i>	0.010	0.50	0	
<i>c</i>	-x	-6x	+x	$K_f = \frac{0.010}{y(0.44)^6}$
<i>e</i>	0.010 - x	0.50 - 6x	x	
<i>e'</i>	y	0.44	0.010	

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

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

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

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

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

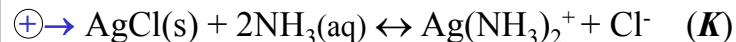
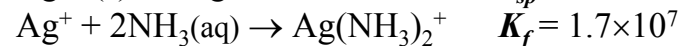
$$y = \frac{0.010}{4.0 \times 10^{43} (0.44)^6} = \boxed{3.4 \times 10^{-44} \text{ M} = [\text{Fe}^{3+}]}$$

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



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



$$\rightarrow K = K_{sp} \times K_f = 1.8 \times 10^{-10} \times 1.7 \times 10^7 = \boxed{3.1 \times 10^{-3}}$$

→ The overall equilibrium constant, K , is much larger than K_{sp}

⇒ 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.

	$\text{AgCl(s)} + 2\text{NH}_3(\text{aq}) \leftrightarrow \text{Ag(NH}_3)_2^+ + \text{Cl}^-$			
<i>i</i>	excess	0.10	0	0
<i>c</i>	-s	-2s	+s	+s
<i>e</i>	excess	0.10 - 2s	s	s

$$K = \frac{[\text{Ag(NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = \frac{s^2}{(0.10 - 2s)^2}$$

$$\frac{s}{0.1 - 2s} = \sqrt{K} \Rightarrow s = \frac{0.10\sqrt{K}}{1 + 2\sqrt{K}} = \frac{0.10\sqrt{3.1 \times 10^{-3}}}{1 + 2\sqrt{3.1 \times 10^{-3}}}$$

$$\Rightarrow \boxed{s = 5.0 \times 10^{-3}}$$

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

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

Complex Ions of Amphoteric Hydroxides

➤ Metals that form amphoteric oxides also form **amphoteric hydroxides** which react with both acids and bases

➤ Have low solubility in pure water

➤ Dissolve well in aqueous acids or bases

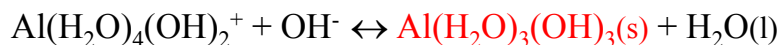
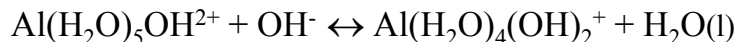
→ The solubility in acids is due to a reaction with H_3O^+ which shifts the solubility equilibrium toward dissolution (as discussed in 19.3)

→ The solubility in bases is due to the formation of soluble complexes of the metal ions with OH^-

- The solubility of amphoteric hydroxides can be explained as a complex formation process

Example: $\text{Al}(\text{OH})_3$

- In acidic solution OH^- ions are scarce so Al^{3+} is completely hydrated as $\text{Al}(\text{H}_2\text{O})_6^{3+}$
- As the solution becomes less acidic and more basic, the OH^- ions gradually accept H^+ from the hydrating water molecules



→ The neutral complex of **Al** is insoluble

⇒ A precipitate forms → $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3(\text{s})$ → usually written without the water as $\text{Al}(\text{OH})_3(\text{s})$

→ As the solution becomes even more basic, the OH^- ions accept H^+ from one of the 3 remaining water molecules



⇒ The precipitate dissolves due to the formation of the soluble negative complex ion

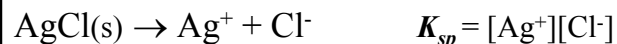
- Zn^{2+} , Sn^{2+} , Pb^{2+} , ... exhibit similar behavior
- Other metals such as Fe^{2+} , Fe^{3+} , ... only form the neutral insoluble hydroxide complex which can not be dissolved in basic solution

19.5 Applications of Ionic Equilibria

Selective Precipitation

- Mixtures of cations can be separated by selective precipitation with an anion if the solubilities of the precipitates are significantly different
- The concentration of the anion is selected in a way so that Q_{sp} is above K_{sp} for the less soluble ion and just below K_{sp} for the more soluble ion

Example: What is the maximum concentration of Cl^- that would precipitate only one of the ions in a solution that is **0.0010 M** in Ag^+ and **0.020 M** in Pb^{2+} ? $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$; $K_{sp}(\text{PbCl}_2) = 1.7 \times 10^{-5}$



→ Calculate the concentrations of Cl^- at which precipitation of each ion begins:

$$[\text{Cl}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{0.0010} = 1.8 \times 10^{-7} \text{ M}$$

$$[\text{Cl}^-] = \sqrt{\frac{K_{sp}}{[\text{Pb}^{2+}]}} = \sqrt{\frac{1.7 \times 10^{-5}}{0.020}} = 2.9 \times 10^{-2} \text{ M}$$

→ AgCl will precipitate first at $[\text{Cl}^-] > 1.8 \times 10^{-7} \text{ M}$

→ If $[\text{Cl}^-] < 2.9 \times 10^{-2} \text{ M}$, PbCl_2 will not precipitate

⇒ The maximum $[\text{Cl}^-]$ is just below **$2.9 \times 10^{-2} \text{ M}$**

Note: The concentration of unprecipitated Ag^+ is:

$$[\text{Ag}^+] = K_{sp}/[\text{Cl}^-] = 1.8 \times 10^{-10}/2.9 \times 10^{-2} = 6.2 \times 10^{-9} \text{ M}$$