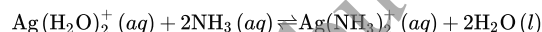




17.7: Complex Ion Equilibria

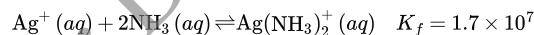
We have discussed several different types of equilibria so far, including acid–base equilibria and solubility equilibria. We now turn to equilibria of another type, which primarily involve transition metal ions in solution. Transition metal ions tend to be good electron acceptors (good Lewis acids). In aqueous solutions, water molecules can act as electron donors (Lewis bases) to hydrate transition metal ions. For example, silver ions are hydrated by water in solution to form $\text{Ag}(\text{H}_2\text{O})_2^+$ (aq). Chemists often write Ag^+ (aq) as a shorthand notation for the hydrated silver ion, but the bare ion does not really exist by itself in solution.

Species such as $\text{Ag}(\text{H}_2\text{O})_2^+$ are known as *complex ions*. A **complex ion** contains a central metal ion bound to one or more *ligands*. A **ligand** is a neutral molecule or ion that acts as a Lewis base with the central metal ion. In $\text{Ag}(\text{H}_2\text{O})_2^+$, water is the ligand. If we put a stronger Lewis base into a solution containing $\text{Ag}(\text{H}_2\text{O})_2^+$, the stronger Lewis base displaces the water in the complex ion. For example, ammonia reacts with $\text{Ag}(\text{H}_2\text{O})_2^+$ according to the following reaction:



We cover complex ions in more detail in [Chapter 22](#). Here, we focus on the equilibria associated with their formation.

For simplicity, we often leave water out of the equation:



The equilibrium constant associated with the reaction for the formation of a complex ion, such as the one just shown, is the **formation constant** (K_f). We determine the expression for K_f by the law of mass action, like any equilibrium constant. For $\text{Ag}(\text{NH}_3)_2^+$, the expression for K_f is:

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

Notice that the value of K_f for $\text{Ag}(\text{NH}_3)_2^+$ is large, indicating that the formation of the complex ion is highly favored. [Table 17.3](#) lists the formation constants for some common complex ions. In general, values of K_f are very large, indicating that the formation of complex ions is highly favored in each case. [Example 17.15](#) illustrates the use K_f in calculations.

Table 17.3 Formation Constants of Selected Complex Ions in Water at 25 °C

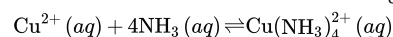
Complex Ion	K_f	Complex Ion	K_f
$\text{Ag}(\text{CN})_2^-$	1×10^{21}	$\text{Cu}(\text{NH}_3)_4^{2+}$	1.7×10^{13}
$\text{Ag}(\text{NH}_3)_2^+$	1.7×10^7	$\text{Fe}(\text{CN})_6^{4-}$	1.5×10^{35}
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	2.8×10^{13}	$\text{Fe}(\text{CN})_6^{3-}$	2×10^{43}

AlF_6^{3-}	7×10^{19}	$\text{Hg}(\text{CN})_4^{2-}$	1.8×10^{41}
$\text{Al}(\text{OH})_4^-$	3×10^{33}	HgCl_4^{2-}	1.1×10^{16}
CdBr_4^{2-}	5.5×10^3	HgI_4^{2-}	2×10^{30}
CdI_4^{2-}	2×10^6	$\text{Ni}(\text{NH}_3)_6^{2+}$	2.0×10^8
$\text{Cd}(\text{CN})_4^{2-}$	3×10^{18}	$\text{Pb}(\text{OH})_3^-$	8×10^{13}
$\text{Co}(\text{NH}_3)_6^{3+}$	2.3×10^{33}	$\text{Sn}(\text{OH})_3^-$	3×10^{25}
$\text{Co}(\text{OH})_4^{2-}$	5×10^9	$\text{Zn}(\text{CN})_4^{2-}$	2.1×10^{19}
$\text{Co}(\text{SCN})_4^{2-}$	1×10^3	$\text{Zn}(\text{NH}_3)_4^{2+}$	2.8×10^9
$\text{Cr}(\text{OH})_4^-$	8.0×10^{29}	$\text{Zn}(\text{OH})_4^{2-}$	2×10^{15}
$\text{Cu}(\text{CN})_4^{2-}$	1.0×10^{25}		

Example 17.15 Complex Ion Equilibria

You mix a 200.0-mL sample of a solution that is 1.5×10^{-3} M in $\text{Cu}(\text{NO}_3)_2$ with a 250.0-mL sample of a solution that is 0.20 M in NH_3 . After the solution reaches equilibrium, what concentration of $\text{Cu}^{2+}(\text{aq})$ remains?

SOLUTION Write the balanced equation for the complex ion equilibrium that occurs and look up the value of K_f in Table 17.3. Since this is an equilibrium problem, you have to create an ICE table, which requires the initial concentrations of Cu^{2+} and NH_3 in the combined solution. Calculate those concentrations from the given values.

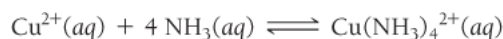


$$K_f = 1.7 \times 10^{13}$$

$$[\text{Cu}^{2+}]_{\text{initial}} = \frac{0.200 \text{ L} \times \frac{1.5 \times 10^{-3} \text{ mol}}{\text{L}}}{0.200 \text{ L} + 0.250 \text{ L}} = 6.7 \times 10^{-4} \text{ M}$$

$$[\text{NH}_3]_{\text{initial}} = \frac{0.250 \text{ L} \times \frac{0.20 \text{ mol}}{\text{L}}}{0.200 \text{ L} + 0.250 \text{ L}} = 0.11 \text{ M}$$

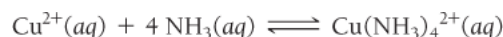
Construct an ICE table for the reaction and write down the initial concentrations of each species.



	$[\text{Cu}^{2+}]$	$[\text{NH}_3]$	$[\text{Cu}(\text{NH}_3)_4^{2+}]$
Initial	6.7×10^{-4}	0.11	0.0
Change			
Equil			

Since the equilibrium constant is large and the concentration of ammonia is much larger than the concentration of Cu^{2+} , you can assume that the reaction will be driven to the right so that most of the Cu^{2+} is consumed. Unlike in previous ICE tables, where you let x represent the change in concentration in going to equilibrium, here you let x represent the small amount of Cu^{2+} that remains when equilibrium is reached.

remains when equilibrium is reached.



	$[\text{Cu}^{2+}]$	$[\text{NH}_3]$	$[\text{Cu}(\text{NH}_3)_4^{2+}]$
Initial	6.7×10^{-4}	0.11	0.0
Change	$\approx (-6.7 \times 10^{-4})$	$\approx 4(-6.7 \times 10^{-4})$	$\approx (+6.7 \times 10^{-4})$
Equil	x	0.11	6.7×10^{-4}

Substitute the expressions for the equilibrium concentrations into the expression for K_f and solve for x .

Confirm that x is indeed small compared to the initial concentration of the metal cation.

The remaining Cu^{2+} is very small because the formation constant is very large.

$$\begin{aligned}
 K_f &= \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} \\
 &= \frac{6.7 \times 10^{-4}}{x(0.11)^4} \\
 x &= \frac{6.7 \times 10^{-4}}{K_f(0.11)^4} \\
 &= \frac{6.7 \times 10^{-4}}{1.7 \times 10^{13}(0.11)^4} \\
 &= 2.7 \times 10^{-13}
 \end{aligned}$$

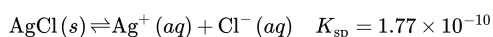
Since $x = 2.7 \times 10^{-13} \ll 6.7 \times 10^{-4}$, the approximation is valid. The remaining $[\text{Cu}^{2+}] = 2.7 \times 10^{-13} \text{M}$

FOR PRACTICE 17.15 You mix a 125.0-mL sample of a solution that is 0.0117 M in NiCl_2 with a 175.0-mL sample of a solution that is 0.250 M in NH_3 . After the solution reaches equilibrium, what concentration of $\text{Ni}^{2+}(\text{aq})$ remains?

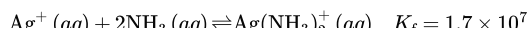
The Effect of Complex Ion Equilibria on Solubility

Recall from Section 17.5 that the solubility of an ionic compound with a basic anion increases with increasing acidity because the acid reacts with the anion and drives the reaction to the right. Similarly, the solubility of an ionic compound containing a metal cation that forms complex ions increases in the presence of Lewis bases that form complex ions with the cation. The most common Lewis bases that increase the solubility of metal cations are NH_3 , CN^- , and OH^- .

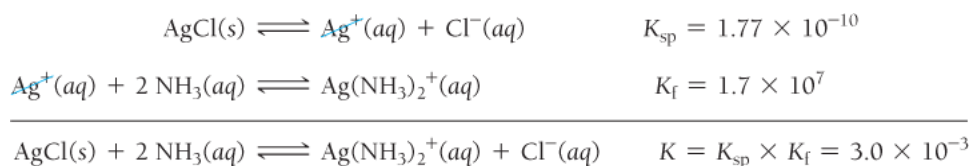
For example, silver chloride is only slightly soluble in pure water:



However, adding ammonia increases its solubility dramatically because, as we saw previously in this section, the ammonia forms a complex ion with the silver cations:



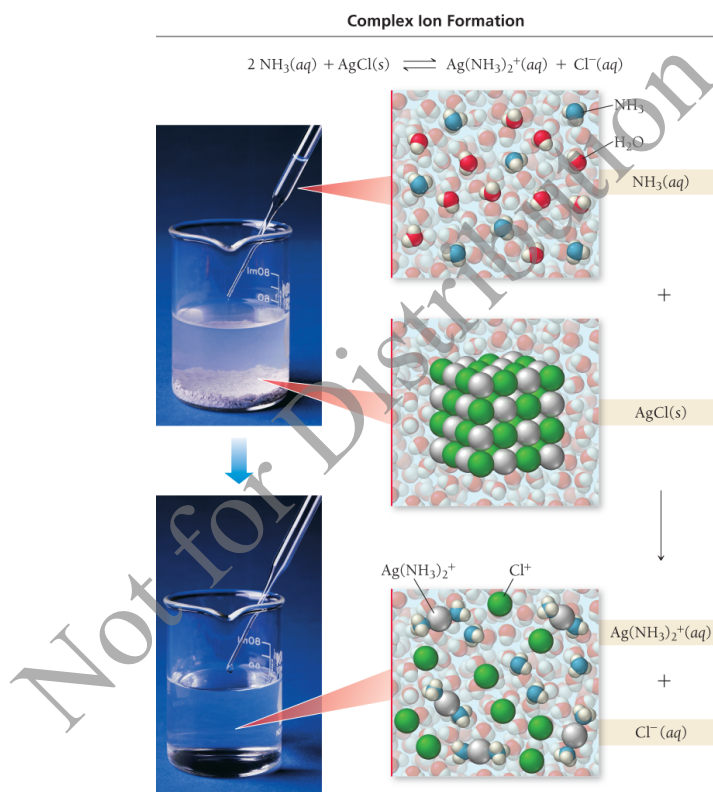
The large value of K_f significantly lowers the concentration of $\text{Ag}^+(aq)$ in solution and therefore drives the dissolution of $\text{AgCl}(s)$. The two previous reactions can be added together:



As we learned in Section 15.3, the equilibrium constant for a reaction that is the sum of two other reactions is the product of the equilibrium constants for the two other reactions. Adding ammonia changes the equilibrium constant for the dissolution of $\text{AgCl}(s)$ by a factor of $3.0 \times 10^{-3} / 1.77 \times 10^{-10} = 1.7 \times 10^7$ (17 million), which makes the otherwise relatively insoluble $\text{AgCl}(s)$ quite soluble, as shown in Figure 17.15.

Figure 17.15 Complex Ion Formation

Normally insoluble AgCl is made soluble by the addition of NH_3 which forms a complex ion with Ag^+ and dissolves the AgCl .



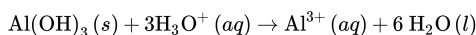
Conceptual Connection 17.11 Solubility and Complex Ion Equilibria

The Solubility of Amphoteric Metal Hydroxides

Many metal hydroxides are insoluble or only very slightly soluble in pH-neutral water. For example, $\text{Al}(\text{OH})_3$ has $K_{sp} = 2 \times 10^{-32}$, which means that if we put $\text{Al}(\text{OH})_3$ in water, the vast majority of it will settle to the bottom as an undissolved solid. All metal hydroxides, however, have a basic anion (OH^-) and therefore become more soluble in acidic solutions (see the previous subsection and Section 17.5).

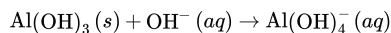
The metal hydroxides become more soluble because they can act as a base and react with $\text{H}_3\text{O}^+(aq)$. For

example, $\text{Al}(\text{OH})_3$ dissolves in acid according to the reaction:



$\text{Al}(\text{OH})_3$ acts as a base in this reaction.

Interestingly, some metal hydroxides can also act as acids—they are *amphoteric*. The ability of an amphoteric metal hydroxide to act as an acid increases its solubility in basic solution. For example, $\text{Al}(\text{OH})_3(s)$ dissolves in basic solution according to the reaction:

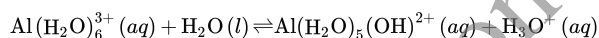


$\text{Al}(\text{OH})_3$ acts as an acid in this reaction.

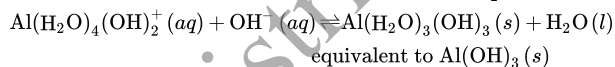
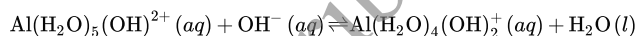
$\text{Al}(\text{OH})_3$ is soluble at high pH and soluble at low pH but *insoluble* in a pH-neutral solution.

Recall from Section 16.3 that a substance that can act as either an acid or a base is said to be amphoteric.

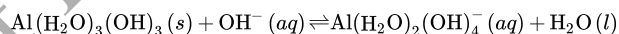
We can observe the whole range of the pH-dependent solubility behavior of Al^{3+} by considering a hydrated aluminum ion in solution, beginning at an acidic pH. We know from Section 16.9 that Al^{3+} in solution is inherently acidic because it complexes with water to form $\text{Al}(\text{H}_2\text{O})_6^{3+}(aq)$. The complex ion then acts as an acid by losing a proton from one of the complexed water molecules according to the reaction:



Addition of base to the solution drives the reaction to the right and continues to remove protons from complexed water molecules:



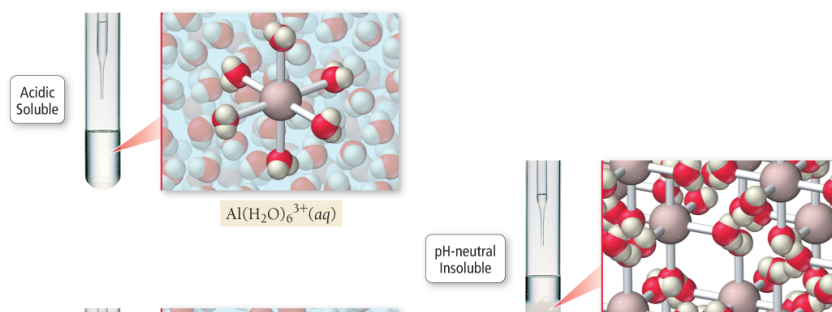
The result of removing three protons from $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is the solid white precipitate $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3(s)$ which is more commonly written as $\text{Al}(\text{OH})_3(s)$. The solution is now pH-neutral, and the hydroxide is insoluble. Addition of more OH^- makes the solution basic and dissolves the solid precipitate:

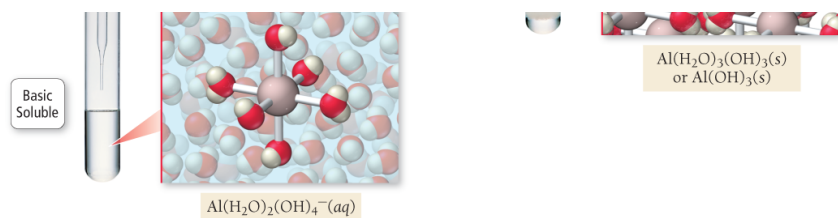


As the solution goes from acidic to neutral to basic, the solubility of Al^{3+} changes accordingly, as illustrated in Figure 17.16.

Figure 17.16 Solubility of an Amphoteric Hydroxide

Because aluminum hydroxide is amphoteric, its solubility is pH-dependent. At low pH, the formation of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ drives the dissolution. At neutral pH, insoluble $\text{Al}(\text{OH})_3$ precipitates out of solution. At high pH, the formation of $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^-$ drives the dissolution.





The extent to which a metal hydroxide dissolves in both acid and base depends on the degree to which it is amphoteric. Cations that form amphoteric hydroxides include Al^{3+} , Cr^{3+} , Zn^{2+} , Pb^{2+} , and Sn^{2+} . Other metal hydroxides, such as those of Ca^{2+} , Fe^{2+} , and Fe^{3+} , are not amphoteric—they become soluble in acidic solutions but not in basic ones.

Not for Distribution

Not for Distribution