

# M O D U L E

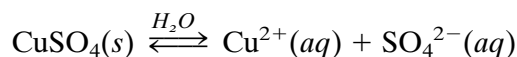
## 3

# COMPLEX ION EQUILIBRIA

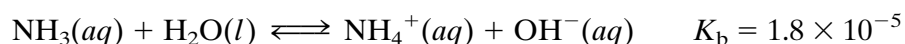
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## COM.1 COMPLEX IONS

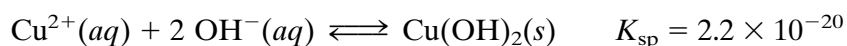
The basic assumption behind the discussion of solubility equilibria is the idea that salts dissociate into their ions when they dissolve in water. Copper sulfate, for example, dissociates into the  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$  ions in water.



If we add 2 M  $\text{NH}_3$  to the solution, the first thing we notice is the formation of a light blue, almost bluish-white, precipitate. This can be explained by combining what we know about acid–base and solubility equilibria. Ammonia acts as a base toward water to form a mixture of the ammonium and hydroxide ions.



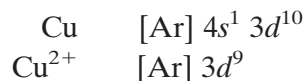
The  $\text{OH}^-$  ions formed in the reaction combine with  $\text{Cu}^{2+}$  ions in the solution to form an insoluble  $\text{Cu}(\text{OH})_2$  precipitate.



In theory, the  $\text{OH}^-$  ion concentration should increase when more ammonia is added to the solution. As a result, more  $\text{Cu}(\text{OH})_2$  should precipitate from the solution. At first, this is exactly what happens. In the presence of excess ammonia, however, the  $\text{Cu}(\text{OH})_2$  precipitate dissolves, and the solution turns deep blue. This raises an important question: “Why does the  $\text{Cu}(\text{OH})_2$  precipitate that forms in dilute ammonia dissolve in excess ammonia?”

The first step toward answering the question involves writing the electron configuration of copper metal and its  $\text{Cu}^{2+}$  ion.

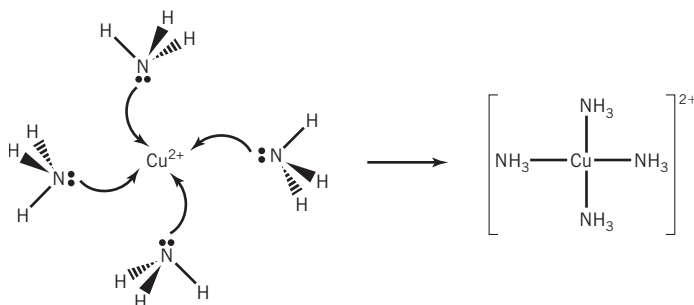
## 2 COMPLEX ION



It is sometimes useful to think about the electron configuration of the  $\text{Cu}^{2+}$  ion in terms of the entire set of valence-shell orbitals. In addition to the nine electrons in the  $3d$  subshell, the  $\text{Cu}^{2+}$  ion has an empty  $4s$  orbital and a set of three empty  $4p$  orbitals.

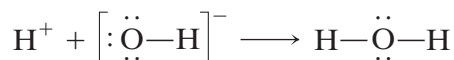


The empty  $4s$  and  $4p$  orbitals on the  $\text{Cu}^{2+}$  ion are used to pick up pairs of nonbonding electrons from four  $\text{NH}_3$  molecules to form a  $\text{Cu}(\text{NH}_3)_4^{2+}$  ion, as shown in Figure COM.1.



**FIGURE COM.1** The  $\text{Cu}^{2+}$  ion has four empty valence-shell orbitals that can accept a pair of nonbonding electrons from an  $\text{NH}_3$  molecule to form a covalent  $\text{Cu}-\text{N}$  bond.

G. N. Lewis was the first to recognize the similarity between this reaction and the acid–base reaction in which an  $\text{H}^+$  ion combines with an  $\text{OH}^-$  ion to form a water molecule.



Both reactions involve the transfer of a pair of nonbonding electrons from one atom to an empty orbital on another atom to form a covalent bond. Both reactions can therefore be interpreted in terms of an electron pair acceptor combining with an electron pair donor.

Lewis suggested that we could expand our definition of acids by assuming that an acid is any substance that acts like the  $\text{H}^+$  ion to accept a pair of nonbonding electrons. *A Lewis acid is therefore an electron pair acceptor.* A Lewis base, on the other hand, is any substance that acts like the  $\text{OH}^-$  ion to donate a pair of nonbonding electrons. *A Lewis base is therefore an electron pair donor.*

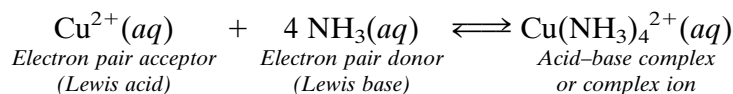
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### Checkpoint

Use Lewis structures to predict which of the following can act as an electron pair donor, or Lewis base.

- (a)  $\text{H}_2\text{O}$     (b)  $\text{CO}$     (c)  $\text{O}_2$     (d)  $\text{H}^-$     (e)  $\text{BH}_3$
- 

The product of the reaction of a Lewis acid with a Lewis base is an **acid–base complex**. When the  $\text{Cu}^{2+}$  ion reacts with four  $\text{NH}_3$  molecules, the product of the reaction is called a **complex ion**.



Any atom or molecule with at least one empty valence-shell orbital can be a Lewis acid. Any atom or molecule that contains at least one pair of nonbonding electrons is a Lewis base. All of the substances whose Lewis structures are shown in Figure COM.2, for example, can act as Lewis bases to form complex ions.

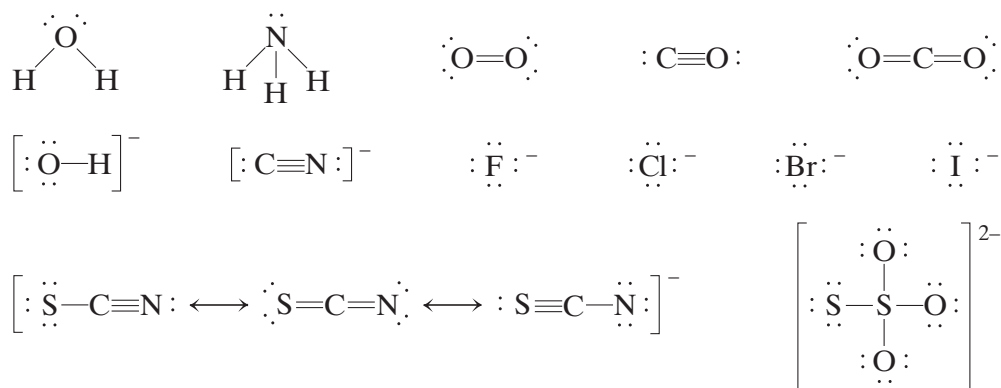
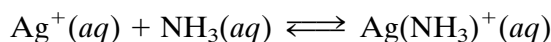


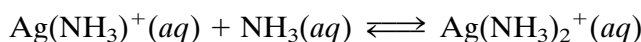
FIGURE COM.2 Lewis structures of some potential Lewis bases.

## COM.2 THE STEPWISE FORMATION OF COMPLEX IONS

When a transition metal ion binds one or more Lewis bases to form an acid–base complex, it picks up the Lewis bases one at a time. The  $\text{Ag}^+$  ion, for example, combines with  $\text{NH}_3$  in a two-step reaction. It first picks up one  $\text{NH}_3$  molecule to form a one-coordinate complex.



This intermediate then picks up a second  $\text{NH}_3$  molecule in a separate step.

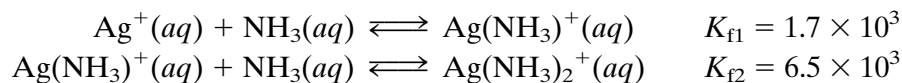


It is possible to write equilibrium constant expressions for each step in these complex ion formation reactions. The **complex formation equilibrium constant ( $K_f$ )** expressions for the two steps in the formation of the  $\text{Ag}(\text{NH}_3)_2^+$  complex ion are written as follows.

$$K_{f1} = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]}$$

$$K_{f2} = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]}$$

The difference between  $K_{f1}$  and  $K_{f2}$  for the complexes between  $\text{Ag}^+$  and ammonia is only a factor of 4.



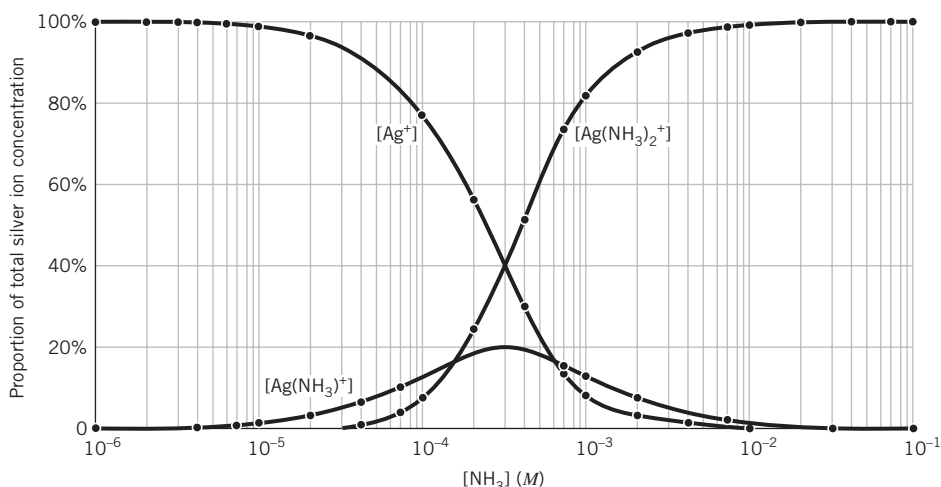
This means that most of the  $\text{Ag}^+$  ions that pick up an  $\text{NH}_3$  molecule to form the one-coordinate  $\text{Ag}(\text{NH}_3)^+$  complex ion are likely to pick up a second  $\text{NH}_3$  molecule to form

the two-coordinate  $\text{Ag}(\text{NH}_3)_2^+$  complex ion. Table COM.1 summarizes the concentrations of the  $\text{Ag}^+$ ,  $\text{Ag}(\text{NH}_3)^+$ , and  $\text{Ag}(\text{NH}_3)_2^+$  ions over a range of  $\text{NH}_3$  concentrations.

**TABLE COM.1** Effect of Changes in the  $\text{NH}_3$  Concentration on the Fraction of Silver Present as the  $\text{Ag}^+$ ,  $\text{Ag}(\text{NH}_3)^+$ , and  $\text{Ag}(\text{NH}_3)_2^+$  Ions

$[\text{NH}_3]$ (M)	$\text{Ag}^+$ (%)	$\text{Ag}(\text{NH}_3)^+$ (%)	$\text{Ag}(\text{NH}_3)_2^+$ (%)
$10^{-6}$	99.8	0.2	0.001
$10^{-5}$	98.2	1.7	0.1
$10^{-4}$	78.1	13.3	8.6
$10^{-3}$	7.3	12.4	80.4
$10^{-2}$	0.09	1.5	98.4
$10^{-1}$	0.0009	0.2	99.8

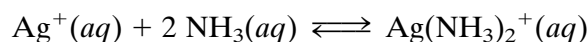
Data from Table COM.1 are plotted in Figure COM.3. Essentially all of the silver is present as the  $\text{Ag}^+$  ion at very low concentrations of  $\text{NH}_3$ . As the  $\text{NH}_3$  concentration increases, the dominant species soon becomes the two-coordinate  $\text{Ag}(\text{NH}_3)_2^+$  ion. Even at  $\text{NH}_3$  concentrations as small as  $0.0010\text{ M}$ , most of the silver is present as the  $\text{Ag}(\text{NH}_3)_2^+$  ion.



**FIGURE COM.3** The effect of changes in the  $\text{NH}_3$  concentration on the proportion of the total silver ion concentration present as  $\text{Ag}^+$ ,  $\text{Ag}(\text{NH}_3)^+$ , and  $\text{Ag}(\text{NH}_3)_2^+$  ions.

The concentration of the one-coordinate  $\text{Ag}(\text{NH}_3)^+$  intermediate is never very large. Either the  $\text{NH}_3$  concentration is so small that most of the silver is present as the  $\text{Ag}^+$  ion, or it is large enough that essentially all of the silver is present as the two-coordinate  $\text{Ag}(\text{NH}_3)_2^+$  complex ion.

If the only important components of the equilibrium are the free  $\text{Ag}^+$  ion (at low  $\text{NH}_3$  concentrations) and the two-coordinate  $\text{Ag}(\text{NH}_3)_2^+$  complex ion (at moderate to high  $\text{NH}_3$  concentrations), we can collapse the individual steps in the reaction into the following overall equation.



The overall complex formation equilibrium constant expression for the reaction is written as follows.

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

This expression is equal to the product of the equilibrium constant expressions for the individual steps in the reaction.

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

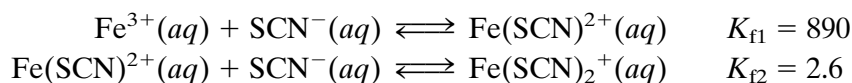
The overall complex formation equilibrium constant is therefore equal to the product of the  $K_f$  values for the individual steps.

$$K_f = K_{f1} \times K_{f2} = 1.1 \times 10^7$$

Overall complex formation equilibrium constants for common complex ions can be found in Appendix B.1.

### Exercise COM.1

Calculate the complex formation equilibrium constant for the two-coordinate  $\text{Fe}(\text{SCN})_2^+$  complex ion from the following data.

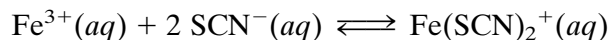


### Solution

The difference between the stepwise formation equilibrium constants for the complex is relatively small.

$$\begin{aligned} K_{f1} &= \frac{[\text{Fe}(\text{SCN})^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} = 890 \\ K_{f2} &= \frac{[\text{Fe}(\text{SCN})_2^+]}{[\text{Fe}(\text{SCN})^{2+}][\text{SCN}^-]} = 2.6 \end{aligned}$$

Solutions of these complex ions are therefore best described in terms of an overall complex formation equilibrium when there is an excess of the ligand.



The equilibrium constant expression for the overall reaction is equal to the product of the expressions for the individual steps in the reaction.

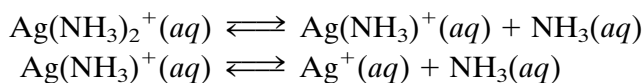
$$\frac{[\text{Fe}(\text{SCN})_2^+]}{[\text{Fe}^{3+}][\text{SCN}^-]^2} = \frac{[\text{Fe}(\text{SCN})^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} \times \frac{[\text{Fe}(\text{SCN})_2^+]}{[\text{Fe}(\text{SCN})^{2+}][\text{SCN}^-]}$$

The overall equilibrium constant is therefore the product of  $K_{f1}$  and  $K_{f2}$ .

$$K_f = K_{f1} \times K_{f2} = 2.3 \times 10^3$$

### COM.3 COMPLEX DISSOCIATION EQUILIBRIUM CONSTANTS

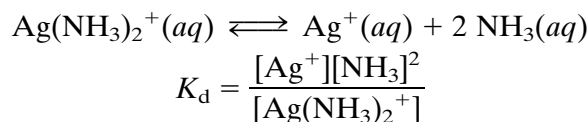
Complex ions can also be described in terms of complex dissociation equilibria. We can start by assuming, for example, that most of the silver ions in an aqueous solution of ammonia are present as the two-coordinate  $\text{Ag}(\text{NH}_3)_2^+$  complex ion. We then assume that some of the ions dissociate to form  $\text{Ag}(\text{NH}_3)^+$  complex ions and then eventually  $\text{Ag}^+$  ions.



A **complex dissociation equilibrium constant ( $K_d$ )** expression can be written for each of the reactions.

$$\begin{aligned} K_{d1} &= \frac{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]}{[\text{Ag}(\text{NH}_3)_2^+]} \\ K_{d2} &= \frac{[\text{Ag}^+][\text{NH}_3]}{[\text{Ag}(\text{NH}_3)^+]} \end{aligned}$$

Alternatively, the individual steps in the reaction can be collapsed into an overall equation, which can be described by an overall equilibrium constant expression.



#### Exercise COM.2

Calculate the complex dissociation equilibrium constant for the  $\text{Cu}(\text{NH}_3)_4^{2+}$  ion from the value of  $K_f$  for the complex. [For  $\text{Cu}(\text{NH}_3)_4^{2+}$ ,  $K_f = 2.1 \times 10^{13}$ .]

#### Solution

The equilibrium expression for the complex formation reaction is written as follows.

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

The equilibrium constant expression for the complex dissociation reaction is nothing more or less than the inverse of the complex formation equilibrium expression.

$$K_d = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}]}$$

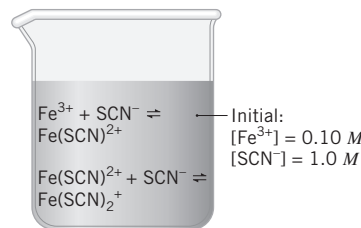
The value of  $K_d$  is therefore equal to the inverse of  $K_f$ .

$$K_d = \frac{1}{K_f} = 4.8 \times 10^{-14}$$

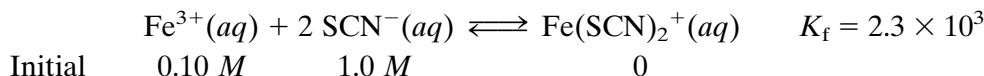
#### COM.4 APPROXIMATE COMPLEX ION CALCULATIONS

Complex formation equilibria provide another example of the general rule that it is useful to begin equilibrium calculations by comparing the reaction quotient for the initial conditions with the equilibrium constant for the reaction. Consider, for example, the following question:

*What fraction of the total iron(III) concentration is present as the  $Fe^{3+}$  ion in a solution that was initially 0.10 M  $Fe^{3+}$  and 1.0 M  $SCN^-$ ? [For  $Fe(SCN)_2^+$ ,  $K_f = 2.3 \times 10^3$ .]*



The initial conditions for the reaction can be summarized as follows.

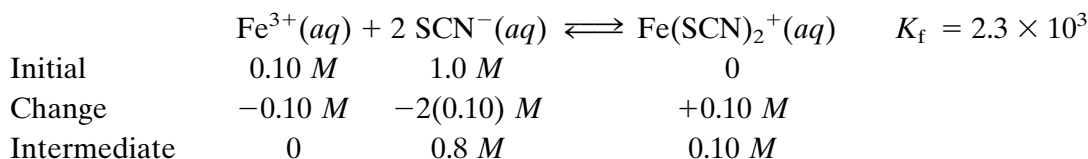


$\Delta(SCN^-) = 2\Delta(Fe^{3+})$   
as we form the  $Fe(SCN)_2^+$  complex

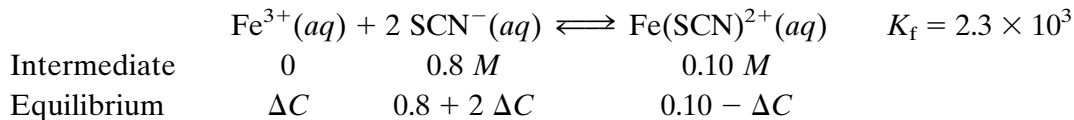
The initial value of the reaction quotient is therefore equal to zero.

$$Q_f = \frac{(Fe(SCN)_2^+)}{(Fe^{3+})(SCN^-)^2} = \frac{(0)}{(0.10)(1.0)^2} = 0 \ll 2.3 \times 10^3$$

Because the reaction quotient is very much smaller than the equilibrium constant for the reaction, it would be absurd to assume that the reaction is close to equilibrium. We therefore define a set of intermediate conditions in which we drive the reaction as far as possible toward the right.



We then assume that the reaction comes to equilibrium from the intermediate conditions.



Substituting the information into the equilibrium expression for the reaction gives the following equation.

$$\frac{[0.10 - \Delta C]}{[\Delta C][0.8 + 2 \Delta C]^2} = 2.3 \times 10^3$$

## 8 COMPLEX ION

Because we defined the intermediate condition so that it was reasonably close to equilibrium, we are now ready to assume that  $\Delta C$  is relatively small.

$$\frac{[0.10]}{[\Delta C][0.8]^2} \approx 2.3 \times 10^3$$

Solving the approximate equation gives the following result.

$$\Delta C \approx 6.8 \times 10^{-5}$$

The assumption that  $\Delta C$  is relatively small is valid because the problem was defined so that it would be valid. We can now use the value of  $\Delta C$  to answer the original question.

$$[\text{Fe}^{3+}] = 6.8 \times 10^{-5} \text{ M}$$

Even though the complex formation equilibrium constant is not very large, essentially all of the iron in the solution is present as the  $\text{Fe}(\text{SCN})_2^+$  complex ion. Only a negligible fraction is present as the  $\text{Fe}^{3+}$  ion.

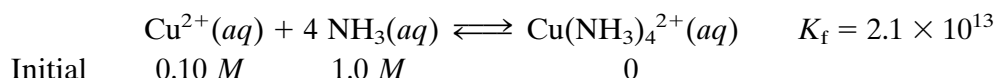
$$\frac{6.8 \times 10^{-5}}{0.10} \times 100 = 0.068\%$$

### Exercise COM.3

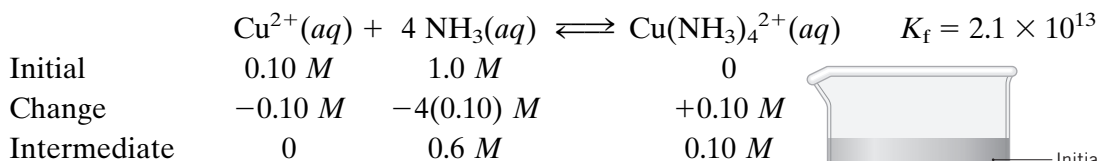
Calculate the concentration of the  $\text{Cu}^{2+}$  ion in a solution that is initially  $0.10 \text{ M Cu}^{2+}$  and  $1.0 \text{ M NH}_3$ . [For  $\text{Cu}(\text{NH}_3)_4^{2+}$ ,  $K_f = 2.1 \times 10^{13}$ .]

#### Solution

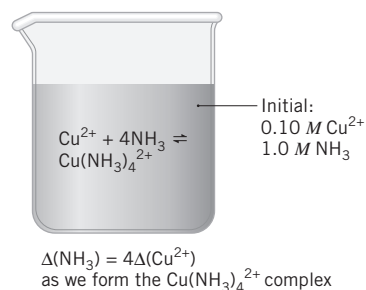
We can set up the calculation as follows.



Because there is no  $\text{Cu}(\text{NH}_3)_4^{2+}$  ion in the solution when we start, the initial value of  $Q_f$  for the reaction is zero and  $Q_f$  is very much smaller than  $K_f$  for the reaction. Because  $K_f$  for the complex is very large, essentially all of the  $\text{Cu}^{2+}$  ions should form  $\text{Cu}(\text{NH}_3)_4^{2+}$  ions at equilibrium. We therefore define a set of intermediate conditions in which we shift the reaction to the right until all of the  $\text{Cu}^{2+}$  ion is converted into  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex ions.



We then let the reaction come to equilibrium from the intermediate conditions.



	$\text{Cu}^{2+}(\text{aq}) + 4 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$	$K_f = 2.1 \times 10^{13}$
Intermediate	0                      0.6 M                      0.10 M	
Equilibrium	$\Delta C$ $0.6 + 4 \Delta C$ $0.10 - \Delta C$	

The next step in solving the problem involves writing the equilibrium constant expression for the reaction.

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

We then substitute what we know about the equilibrium concentrations of the three components of the reaction into the equation.

$$\frac{[0.10 - \Delta C]}{[\Delta C][0.6 + 4 \Delta C]^4} = 2.1 \times 10^{13}$$

The value of  $K_f$  is so large that very little  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex ion dissociates as the reaction comes to equilibrium. It is therefore reasonable to assume that  $\Delta C$  is relatively small.

$$\frac{[0.10]}{[\Delta C][0.6]^4} \approx 2.1 \times 10^{13}$$

Solving the approximate equation gives the following result.

$$\Delta C \approx 3.7 \times 10^{-14}$$

The assumption that  $\Delta C$  is small is valid. We can therefore use the results of the calculation to determine the concentration of the free (uncomplexed)  $\text{Cu}^{2+}$  ion in the solution.

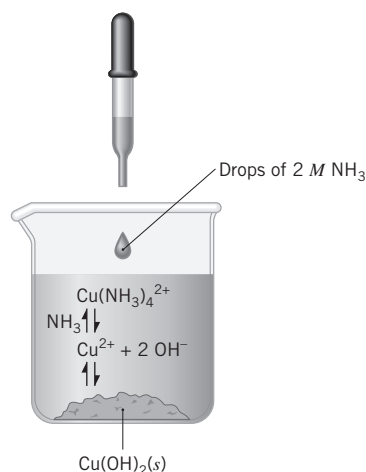
$$[\text{Cu}^{2+}] = 3.7 \times 10^{-14} \text{ M}$$

The results of the preceding exercise can be used to explain why  $\text{Cu}(\text{OH})_2$  dissolves in excess ammonia. Before we can do this, however, we need to understand why  $\text{Cu}(\text{OH})_2$  precipitates in the first place. Ammonia acts as a base toward water.

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

Even fairly dilute solutions of the  $\text{OH}^-$  ion have more than enough  $\text{OH}^-$  ion to precipitate  $\text{Cu}(\text{OH})_2$  from a 0.10 M  $\text{Cu}^{2+}$  ion solution. As the amount of  $\text{NH}_3$  added to the solution increases, the concentration of the  $\text{OH}^-$  ion increases. But it doesn't become very much larger. The  $\text{OH}^-$  ion concentration in a 0.001 M  $\text{NH}_3$  solution is  $1.3 \times 10^{-4}$  M. By the time the  $\text{NH}_3$  concentration reaches 0.10 M, the  $\text{OH}^-$  ion concentration has increased by only a factor of 10, to  $1.3 \times 10^{-3}$  M.

As the amount of  $\text{NH}_3$  added to the solution increases, the concentration of  $\text{Cu}^{2+}$  ions rapidly decreases because the



ions are tied up as  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex ions. According to the preceding exercise, the  $\text{Cu}^{2+}$  ion concentration in  $1.0\text{ M}$   $\text{NH}_3$  is only  $3.7 \times 10^{-14}\text{ M}$ . Thus, the ion product for  $\text{Cu}(\text{OH})_2$  under these conditions is about the same size as the solubility product for the compound.

$$Q_{\text{sp}} = (\text{Cu}^{2+})(\text{OH}^-)^2 = (3.7 \times 10^{-14})(1.3 \times 10^{-3})^2 = 6.3 \times 10^{-20} \approx K_{\text{sp}}$$

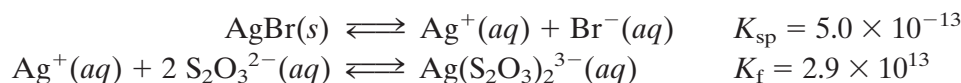
As soon as the  $\text{NH}_3$  concentration exceeds  $1\text{ M}$ , the  $\text{Cu}^{2+}$  ion concentration becomes so small that the ion product for  $\text{Cu}(\text{OH})_2$  is smaller than  $K_{\text{sp}}$ , and the  $\text{Cu}(\text{OH})_2$  precipitate dissolves.

## COM.5 USING COMPLEX ION EQUILIBRIA TO DISSOLVE AN INSOLUBLE SALT

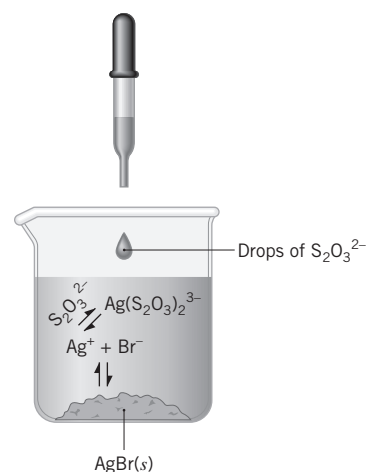
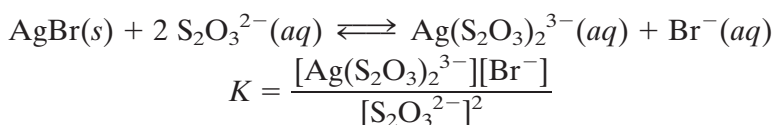
The key to using complex ion equilibria to dissolve an insoluble salt is simple: Choose a complex for which  $K_f$  is large enough that the concentration of the uncomplexed metal ion is too small for the ion product to exceed the solubility product. To show how this is done, let's examine the step in the processing of photographic film in which the  $\text{AgBr}$  crystals that don't capture light are washed from the film. Because this step permanently fixes the image onto the film, the reagent used to achieve it is called a "fixer."

We can decide whether a particular complexing agent is strong enough to be used as a fixer by calculating the solubility of  $\text{AgBr}$  in an aqueous solution of the reagent. Consider, for example, the following question.

*Use the following equilibria to decide whether the thiosulfate ion ( $\text{S}_2\text{O}_3^{2-}$ ) is a reasonable choice for the complexing agent for washing unreacted  $\text{AgBr}$  from photographic film.*



$\text{AgBr}$  will dissolve if the  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  complex is strong enough to reduce the  $\text{Ag}^+$  ion concentration to the point at which the product of the  $\text{Ag}^+$  and  $\text{Br}^-$  ion concentrations at equilibrium is smaller than the  $K_{\text{sp}}$  for  $\text{AgBr}$ . One way of deciding whether  $K_f$  for the complex is large enough to overcome the solubility product equilibrium involves combining the equilibria in the solution to give the following overall equation.



The equilibrium constant for the reaction is equal to the product of  $K_f$  times  $K_{\text{sp}}$ .

$$K = K_f \times K_{\text{sp}} = (2.9 \times 10^{13})(5.0 \times 10^{-13}) = 15$$

Because the equilibrium constant is larger than 1, a significant amount of  $\text{AgBr}$  should dissolve in the solution. Let's see how much  $\text{AgBr}$  can dissolve in a liter of a  $1.0\text{ M}$   $\text{S}_2\text{O}_3^{2-}$  solution.

When AgBr dissolves in pure water, the concentration of the  $\text{Ag}^+$  and  $\text{Br}^-$  ions must be the same.

$$\text{In pure water} \quad [\text{Ag}^+] = [\text{Br}^-] = \Delta C$$

In 1.0 M  $\text{S}_2\text{O}_3^{2-}$  essentially all of the silver ion will be present as the two-coordinate  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  ion.

$$\text{In 1.0 M } \text{S}_2\text{O}_3^{2-} \quad [\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] = [\text{Br}^-] = \Delta C$$

The concentration of the  $\text{S}_2\text{O}_3^{2-}$  ion at equilibrium will be equal to the initial concentration of the ion minus the amount consumed when the  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  complex is formed.

$$[\text{S}_2\text{O}_3^{2-}] = 1.0 - 2 \Delta C$$

Substituting the information into the equilibrium constant expression for the overall reaction gives the following equation.

$$\frac{[\Delta C][\Delta C]}{[1.0 - 2 \Delta C]^2} = 15$$

Solving the equation with the quadratic formula gives the following result.

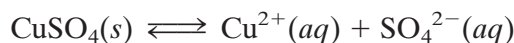
$$\Delta C = 0.44 \text{ M}$$

The  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  complex ion is strong enough to dissolve up to 0.44 moles of AgBr per liter of solution. Thus, it isn't surprising that the thiosulfate ion is used as the fixer in the processing of virtually all commercial photographic films.

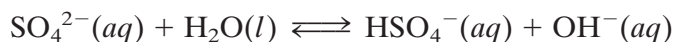
## COM.6 A QUALITATIVE VIEW OF COMBINED EQUILIBRIA

Most of the discussion so far has focused on individual equilibria. This section will examine how Le Châtelier's principle can be applied to systems in which many chemical equilibria exist simultaneously.

Consider what happens when solid  $\text{CuSO}_4$  dissolves in an aqueous  $\text{NH}_3$  solution. If we start with enough copper sulfate to form a saturated solution, the following solubility product equilibrium will exist in the solution.



The  $\text{SO}_4^{2-}$  ion formed when  $\text{CuSO}_4$  dissolves in water is a weak Brønsted base that can pick up an  $\text{H}^+$  ion to form the hydrogen sulfate and hydroxide ions.

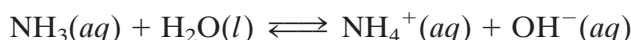


There are other sources of the  $\text{OH}^-$  ion in the solution. Water, of course, dissociates to some extent to form the  $\text{OH}^-$  ion.

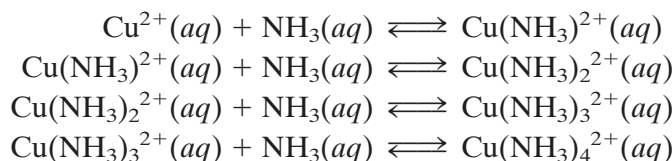


## 12 COMPLEX ION

Ammonia also reacts with water, to some extent, to form the  $\text{NH}_4^+$  and  $\text{OH}^-$  ions.



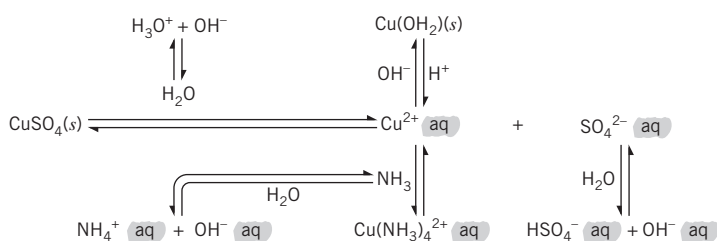
The  $\text{Cu}^{2+}$  ion released into solution when  $\text{CuSO}_4$  dissolves reacts with ammonia to form a series of complex ions.



If the concentration of the  $\text{OH}^-$  ion is large enough, a second solubility product equilibrium will exist in the solution.



The simple process of dissolving copper(II) sulfate in aqueous ammonia therefore can involve nine simultaneous equilibria. In theory, we must consider each of the reactions if we want to predict what will happen under a particular set of experimental conditions. In practice, we can make at least one simplifying assumption. We can assume that the complex ion equilibria in the system can be represented by a single equation in which the  $\text{Cu}^{2+}$  ion combines with four  $\text{NH}_3$  molecules to form the four-coordinate  $\text{Cu}(\text{NH}_3)_4^{2+}$  ion. We can therefore construct a fairly complete model of what happens in the solution if we take into account the equilibria summarized in Figure COM.4.



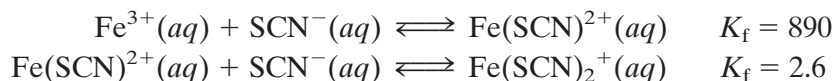
**FIGURE COM.4** Relationships among the equilibria that exist in a saturated solution of  $\text{CuSO}_4$  in ammonia.

Let's now apply Le Châtelier's principle to the model in Figure COM.4 to predict the effect of adding various substances to a saturated solution of  $\text{CuSO}_4$  in aqueous  $\text{NH}_3$ .

- **Solid  $\text{CuSO}_4$ :** Adding excess  $\text{CuSO}_4$  to a saturated solution has no effect on any of the equilibria shown in Figure COM.4 because it has no effect on the concentration of either the  $\text{Cu}^{2+}$  or  $\text{SO}_4^{2-}$  ions.
- **Nitric acid:** Nitric acid is a strong acid that should convert most of the  $\text{NH}_3$  into  $\text{NH}_4^+$  ions. Anything that removes  $\text{NH}_3$  from the solution tends to destroy the  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex ion. Adding nitric acid therefore tends to increase the  $\text{Cu}^{2+}$  ion concentration, which should cause  $\text{CuSO}_4$  to precipitate from solution. We don't expect  $\text{Cu}(\text{OH})_2$  to precipitate, however, because the concentration of the  $\text{OH}^-$  ion in a strong acid solution is much too small.
- **Sodium hydroxide:** Sodium hydroxide is a strong base. In theory, it should react with the  $\text{NH}_4^+$  ion in the solution to form more  $\text{NH}_3$ . In practice, there isn't very much  $\text{NH}_4^+$  ion in the solution to begin with, so adding  $\text{NaOH}$  has little effect on most of the equilibria in the solution. The presence of excess  $\text{OH}^-$  ion, however, is likely to precipitate some of the  $\text{Cu}^{2+}$  ion in solution as  $\text{Cu}(\text{OH})_2$ .

- **Aqueous ammonia:** Any increase in the  $\text{NH}_3$  concentration should increase the amount of the  $\text{Cu}^{2+}$  ion tied up as  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex ions. This reduces the concentration of the free  $\text{Cu}^{2+}$  ion, which makes the ion product for  $\text{CuSO}_4$  smaller than the solubility product. As a result, adding more  $\text{NH}_3$  can cause more  $\text{CuSO}_4$  to dissolve. It is also likely to dissolve any residual  $\text{Cu}(\text{OH})_2$  that might be present.

Another example of combined equilibria revolves around the aqueous chemistry of the  $\text{Fe}^{3+}$  ion. Dilute solutions of the ion prepared by dissolving an iron(III) salt in perchloric acid are essentially colorless. In the presence of the thiocyanate ion, however, a blood-red solution is formed. The solution contains a pair of complex ions.



The  $\text{Fe}^{3+}$  ion also forms a complex with the citrate ion ( $\text{Cit}^{3-}$ ).



Different colors are observed for the following aqueous solutions shown in Figure COM.5.

- A dilute aqueous solution of the  $\text{Fe}^{3+}$  ion is colorless.
- A solution formed by mixing the  $\text{Fe}^{3+}$  and  $\text{SCN}^{-}$  ions is blood-red.
- A solution formed by adding a strong acid to a mixture of the  $\text{Fe}^{3+}$  and  $\text{SCN}^{-}$  ions is blood-red.
- A solution formed by mixing the  $\text{Fe}^{3+}$  and  $\text{Cit}^{3-}$  ions is yellow.
- A solution formed by adding a strong acid to a mixture of the  $\text{Fe}^{3+}$  and  $\text{Cit}^{3-}$  ions is colorless.
- A solution formed by mixing the  $\text{Fe}^{3+}$ ,  $\text{SCN}^{-}$ , and  $\text{Cit}^{3-}$  ions is yellow.
- A solution formed by adding a strong acid to a mixture of the  $\text{Fe}^{3+}$ ,  $\text{SCN}^{-}$ , and  $\text{Cit}^{3-}$  ions is blood-red.



FIGURE COM.5 (Photo by Andy Washnik.)

The color (or lack thereof) tells us something about each of the solutions.

- For solution (a), the color of dilute solutions of the  $\text{Fe}^{3+}$  ion is so weak they are essentially colorless.
- For (b), when the  $\text{SCN}^{-}$  ion is added to an aqueous solution of the  $\text{Fe}^{3+}$  ion, the  $\text{Fe}(\text{SCN})^{2+}$  and  $\text{Fe}(\text{SCN})_2^{+}$  complex ions are formed, and the solution turns a blood-red color.
- For (c), nothing happens when a strong acid is added to a mixture of the  $\text{Fe}^{3+}$  and  $\text{SCN}^{-}$  ions. This tells us something about the strength of the conjugate acid of the  $\text{SCN}^{-}$  ion—thiocyanic acid,  $\text{HSCN}$ . If  $\text{HSCN}$  were a weak acid, adding a strong acid to the solution would tie up the  $\text{SCN}^{-}$  ion as  $\text{HSCN}$ . If that happened, the  $\text{SCN}^{-}$

ion would no longer be free to form a complex with the  $\text{Fe}^{3+}$  ion. This would decrease the amount of the  $\text{Fe}(\text{SCN})^{2+}$  and  $\text{Fe}(\text{SCN})_2^+$  complex ions in solution, thereby decreasing the intensity of the color of the solution. Since this is not observed, HSCN must be a relatively strong acid. This conclusion is consistent with the  $K_a$  for thiocyanic acid found in Appendix B.

- For (d), mixing the  $\text{Fe}^{3+}(\text{aq})$  and  $\text{Cit}^{3-}(\text{aq})$  ions forms the  $\text{Fe}(\text{Cit})$  complex, which has a pale yellow color.
- For (e), because citric acid is a relatively weak acid, the  $\text{Cit}^{3-}$  ion is a reasonably good base. Adding a strong acid therefore destroys the  $\text{Fe}(\text{Cit})$  complex by converting the citrate ion into its conjugate acid—citric acid ( $\text{H}_3\text{Cit}$ ). When this happens, the pale yellow color disappears.
- For (f), the  $K_f$  for the  $\text{Fe}(\text{Cit})$  complex is much larger than  $K_f$  for the  $\text{Fe}(\text{SCN})_2^+$  complex ion. Given a choice between  $\text{SCN}^-$  and  $\text{Cit}^{3-}$  ions, the  $\text{Fe}^{3+}$  ions form complexes with  $\text{Cit}^{3-}$  ions. A solution containing a mixture of the three ions therefore has the characteristic color of the  $\text{Fe}(\text{Cit})$  complex.
- For (g), when a strong acid is added to a mixture of the  $\text{Fe}^{3+}$ ,  $\text{Cit}^{3-}$ , and  $\text{SCN}^-$  ions, the  $\text{Cit}^{3-}$  ions are converted to citric acid ( $\text{H}_3\text{Cit}$ ). When the  $\text{Cit}^{3-}$  ions are removed from solution, the only complexing agent left in the solution is the  $\text{SCN}^-$  ion. The solution therefore turns the color of the  $\text{Fe}(\text{SCN})^{2+}$  and  $\text{Fe}(\text{SCN})_2^+$  complex ions.

## COM.7 A QUANTITATIVE VIEW OF COMBINED EQUILIBRIA

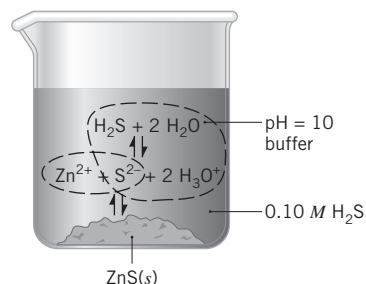
We can perform quantitative calculations for solutions of combined equilibria if we keep in mind how these equilibria are coupled. Consider, for example, the following question.

*What is the solubility of zinc sulfide in a 0.10 M  $\text{H}_2\text{S}$  solution buffered at pH 9.00?*

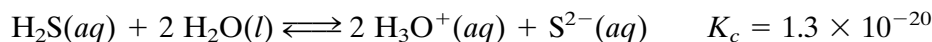
We might start by building a representation of the equilibria that must be considered in order to do the calculation, such as the one shown in the diagram.

We then calculate the  $\text{H}_3\text{O}^+$  ion concentration in the buffer solution.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-10.00} = 1.0 \times 10^{-10} \text{ M}$$



We then ask, What effect does this pH have on the dissociation of  $\text{H}_2\text{S}$ ?



Because it is a weak acid, we can assume that the concentration of  $\text{H}_2\text{S}$  at equilibrium is more or less equal to its initial concentration.

$$[\text{H}_2\text{S}] \approx 0.10 \text{ M}$$

We now know the  $\text{H}_2\text{S}$  and  $\text{H}_3\text{O}^+$  concentrations at equilibrium, which means that we can calculate the concentration of the  $\text{S}^{2-}$  ion at equilibrium before any  $\text{ZnS}$  dissolves.

$$\frac{[\text{H}_3\text{O}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]} \approx \frac{[1.0 \times 10^{-9}]^2[\text{S}^{2-}]}{[0.10]} \approx 1.3 \times 10^{-20}$$

$$[\text{S}^{2-}] \approx 1.3 \times 10^{-3} M$$

When ZnS dissolves, we get more  $\text{S}^{2-}$  ion. The amount of ZnS that dissolves can be calculated from the following equation, where  $C_s$  is the solubility of ZnS.

$$[\text{Zn}^{2+}][\text{S}^{2-}] = K_{\text{sp}}$$

$$[\Delta C][\Delta C + 1.3 \times 10^{-3}] = 1.6 \times 10^{-24}$$

If we have to, we can always solve the equation with the quadratic formula. Before we do this, however, we might look for an assumption that makes the problem easier to solve. In this case, it seems reasonable to assume that the solubility of ZnS is so small that most of the  $\text{S}^{2-}$  ion at a pH of 9.00 comes from the dissociation of  $\text{H}_2\text{S}$ .

$$\Delta C \ll 1.3 \times 10^{-3} M$$

When that assumption is made, we get the following approximate equation.

$$[\Delta C][1.3 \times 10^{-3}] \approx 1.6 \times 10^{-24}$$

When we solve the equation, we get a solubility of ZnS that is so small that we have to conclude that the assumption used to generate the equation is valid.

$$\Delta C \approx 1.2 \times 10^{-21}$$

There is no magic formula that can help us divide problems such as this into steps, or decide the order in which steps should be handled. The following general rules, however, might guide us through these problems.

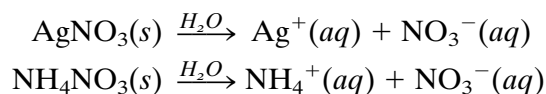
- Identify the equilibria that must be included in the model of the solution.
- Draw a figure that shows how the equilibria are coupled.
- Find the simplest equilibrium—the one for which all of the necessary data are available—and solve that part of the problem.
- Ask, “Where did this get me?” “What can I do with the information?”
- Never lose track of what was accomplished in a previous step.
- Use the results of one step to solve another until all of the equilibria have been solved.

#### Exercise COM.4

Predict whether AgOH will precipitate from a solution buffered at pH 9.00 that is initially 0.010 M AgNO<sub>3</sub> and 1.00 M NH<sub>4</sub>NO<sub>3</sub>. (For AgOH,  $K_{\text{sp}} = 2.0 \times 10^{-8}$ ; for NH<sub>3</sub>,  $K_{\text{b}} = 1.8 \times 10^{-5}$ ; for Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>,  $K_{\text{f}} = 1.1 \times 10^7$ ; for H<sub>2</sub>O,  $K_{\text{w}} = 1.0 \times 10^{-14}$ .)

#### Solution

We might start by noting that silver nitrate and ammonium nitrate are both soluble salts.



We then build a representation of the equilibria present in the solution such as the one in the accompanying drawing.

We can solve some problems by looking at the initial conditions and working toward the final answer. Others, such as this, are so complex it is useful to look at the goal and then work backwards. The goal in this problem is to decide whether  $\text{AgOH}$  precipitates from the solution. In order to make that decision, we need two pieces of information: the  $\text{Ag}^+$  and  $\text{OH}^-$  ion concentrations at equilibrium. We can therefore divide the problem into two parts whose goals consist of determining the values of the  $[\text{Ag}^+]$  and  $[\text{OH}^-]$  terms when all other reactions in the system are at equilibrium.

It seems reasonable to start with the goal that is easiest to achieve: finding the  $\text{OH}^-$  ion concentration. Because we know the pH of the buffered solution, we can calculate the  $\text{H}_3\text{O}^+$  ion concentration at equilibrium.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.00} = 1.0 \times 10^{-9} \text{ M}$$

We can then use the  $\text{H}_3\text{O}^+$  ion concentration to calculate the  $\text{OH}^-$  ion concentration in the buffer solution.

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-9}} = 1.0 \times 10^{-5} \text{ M}$$

We now turn to the second part of the problem, finding the concentration of the  $\text{Ag}^+$  ion at equilibrium. We know that the  $\text{Ag}^+$  ion is in equilibrium with the  $\text{Ag}(\text{NH}_3)_2^+$  complex ion.

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

If we knew the concentrations of  $\text{NH}_3$  and the  $\text{Ag}(\text{NH}_3)_2^+$  complex ion, we could calculate the  $\text{Ag}^+$  ion concentration at equilibrium. This gives us two new subgoals: determining the  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{NH}_3$  concentrations.

Determining the  $\text{Ag}(\text{NH}_3)_2^+$  ion concentration is relatively easy. We know that the initial concentration of the  $\text{Ag}^+$  ion in this solution is  $0.010 \text{ M}$ . We also know that the ion forms a strong complex with  $\text{NH}_3$ . We can therefore assume that essentially all of the silver ions in the solution will be present as  $\text{Ag}(\text{NH}_3)_2^+$  complex ions.

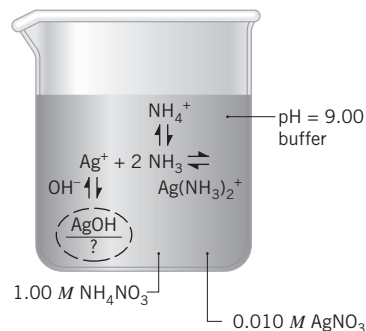
$$[\text{Ag}(\text{NH}_3)_2^+] \approx 0.010 \text{ M}$$

Now all we need is the  $\text{NH}_3$  concentration. We know that ammonia is in equilibrium with the  $\text{NH}_4^+$  ion.

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

Substituting the known  $\text{OH}^-$  ion concentration gives the following equation.

$$K_b = \frac{[\text{NH}_4^+][1.0 \times 10^{-5}]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$



Rearranging the equation gives the following result.

$$\frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 1.8$$

The concentration of the  $\text{NH}_4^+$  ion at equilibrium is therefore 1.8 times the concentration of  $\text{NH}_3$ .

$$[\text{NH}_4^+] = 1.8[\text{NH}_3]$$

We also know that the solution was initially 1.00 *M* in  $\text{NH}_4^+$  ions. Those ions are now present as  $\text{NH}_3$  molecules, as  $\text{NH}_4^+$  ions, or as part of the  $\text{Ag}(\text{NH}_3)_2^+$  complex ions.

$$[\text{NH}_3] + [\text{NH}_4^+] + 2[\text{Ag}(\text{NH}_3)_2^+] = 1.00 \text{ M}$$

We can ignore the last term in the equation because the concentration of the  $\text{Ag}(\text{NH}_3)_2^+$  ion can't be larger than the initial concentration of the  $\text{Ag}^+$  ion: 0.010 *M*. We can therefore assume that only a negligibly small fraction of the  $\text{NH}_4^+$  that was added to the solution is present in the  $\text{Ag}(\text{NH}_3)_2^+$  complex ion.

$$[\text{NH}_3] + [\text{NH}_4^+] \approx 1.00 \text{ M}$$

We now have two equations in two unknowns.

$$\begin{aligned} [\text{NH}_4^+] &= 1.8[\text{NH}_3] \\ [\text{NH}_3] + [\text{NH}_4^+] &= 1.00 \text{ M} \end{aligned}$$

Substituting the first of the equations into the second allows us to solve for the  $\text{NH}_3$  and  $\text{NH}_4^+$  concentrations at equilibrium.

$$\begin{aligned} [\text{NH}_3] &= 0.36 \text{ M} \\ [\text{NH}_4^+] &= 0.64 \text{ M} \end{aligned}$$

We can now return to the complex formation equilibrium.

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

and substitute into the equation the approximate values for the concentrations of  $\text{NH}_3$  and the  $\text{Ag}(\text{NH}_3)_2^+$  complex ion at equilibrium.

$$\frac{[0.010]}{[\text{Ag}^+][0.36]^2} \approx 1.1 \times 10^7$$

We can then solve the equation for the  $\text{Ag}^+$  ion concentration at equilibrium.

$$[\text{Ag}^+] \approx 7.0 \times 10^{-9} \text{ M}$$

We can now look at the product of the  $\text{Ag}^+$  and  $\text{OH}^-$  ion concentrations when the system is at equilibrium.

$$[\text{Ag}^+][\text{OH}^-] = [7.0 \times 10^{-9}][1.0 \times 10^{-5}] = 7.0 \times 10^{-14}$$

The ion product for the solution ( $7.0 \times 10^{-14}$ ) is very much smaller than the solubility product for AgOH ( $2.0 \times 10^{-8}$ ), which means that AgOH won't precipitate from solution.

## KEY TERMS

Acid–base complex

Complex ion

Complex dissociation  
equilibrium constant,  
 $K_d$

Complex formation  
equilibrium constant,  
 $K_f$

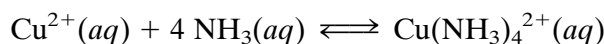
## PROBLEMS

### Complex Ion Equilibria

- Define the following terms: *Lewis acid*, *Lewis base*, *complex ion*, and *coordination number*.
- Use examples to explain the difference between Lewis acids and Brønsted acids, and between Lewis bases and Brønsted bases.
- Which of the following is a Lewis acid?  
(a) CO (b) C<sub>2</sub>H<sub>2</sub> (c) BeF<sub>2</sub> (d) CH<sub>4</sub> (e) NF<sub>3</sub>
- Which of the following is a Lewis acid?  
(a) CH<sub>3</sub><sup>+</sup> (b) CH<sub>4</sub> (c) NH<sub>3</sub> (d) BF<sub>4</sub><sup>−</sup> (e) O<sup>2−</sup>
- Which of the following is not a Lewis acid?  
(a) H<sup>+</sup> (b) BF<sub>3</sub> (c) CO (d) Cu<sup>2+</sup> (e) Fe<sup>3+</sup>
- Which of the following is not a Lewis base?  
(a) NH<sub>4</sub><sup>+</sup> (b) OH<sup>−</sup> (c) Cl<sup>−</sup> (d) O<sub>2</sub> (e) SCN<sup>−</sup>
- Which of the following Lewis acids is not a Brønsted acid?  
(a) HF (b) HOAc (c) H<sub>3</sub>PO<sub>4</sub> (d) NH<sub>3</sub> (e) BF<sub>3</sub>
- Explain why the charges on the Fe(SCN)<sup>2+</sup> and Fe(SCN)<sub>2</sub><sup>+</sup> ions are +2 and +1, respectively.
- Calculate the charge on the transition metal ions in the Zn(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>, Fe(SCN)<sub>2</sub><sup>+</sup>, Sn(OH)<sub>3</sub><sup>−</sup>, Co(SCN)<sub>4</sub><sup>2−</sup>, and Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub><sup>3−</sup> complex ions.

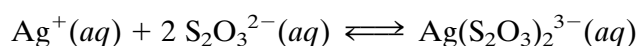
### The Stepwise Formation of Complex Ions

- Explain the difference between polyprotic acids and complex ions that allows us to assume that polyprotic acids dissociate in steps, whereas the dissociation of complex ions can be collapsed into a single overall reaction.
- Cu<sup>2+</sup> forms a four-coordinate complex with ammonia.

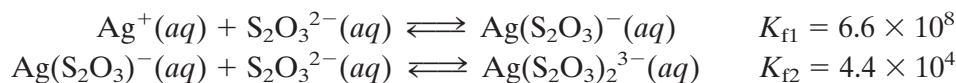


What is the relationship between the overall complex formation equilibrium constant for the reaction,  $K_f$ , and the stepwise formation constants,  $K_{f1}$ ,  $K_{f2}$ ,  $K_{f3}$ , and  $K_{f4}$ ?

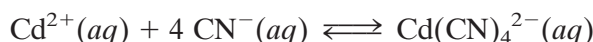
- Calculate the complex formation equilibrium constant,  $K_f$ , for the following overall reaction



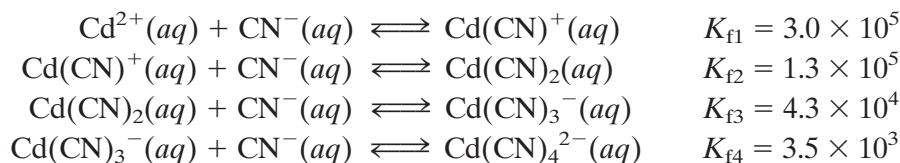
from the values of the stepwise formation constants.



13. Calculate the complex formation equilibrium constant,  $K_f$ , for the following overall reaction



from the values of the stepwise formation constants.



14. Which of the following solutions has the smallest concentration of the  $\text{Ag}^+$  ion?  
 (a) 0.10 M  $\text{Ag}^+$  and 1.0 M  $\text{Cl}^-$  (for  $\text{AgCl}_2^-$ ,  $K_f = 1.1 \times 10^5$ )  
 (b) 0.10 M  $\text{Ag}^+$  and 1.0 M  $\text{NH}_3$  (for  $\text{Ag}(\text{NH}_3)_2^+$ ,  $K_f = 1.1 \times 10^7$ )  
 (c) 0.10 M  $\text{Ag}^+$  and 1.0 M  $\text{S}_2\text{O}_3^{2-}$  (for  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ ,  $K_f = 2.9 \times 10^{13}$ )  
 (d) 0.10 M  $\text{Ag}^+$  and 1.0 M  $\text{CN}^-$  (for  $\text{Ag}(\text{CN})_2^-$ ,  $K_f = 1.3 \times 10^{21}$ )
15. Which of the following solutions has the largest concentration of the  $\text{Hg}^{2+}$  ion?  
 (a) 0.10 M  $\text{Hg}^{2+}$  and 1.0 M  $\text{Cl}^-$  (for  $\text{HgCl}_4^{2-}$ ,  $K_f = 1.2 \times 10^{15}$ )  
 (b) 0.10 M  $\text{Hg}^{2+}$  and 1.0 M  $\text{Br}^-$  (for  $\text{HgBr}_4^{2-}$ ,  $K_f = 1 \times 10^{21}$ )  
 (c) 0.10 M  $\text{Hg}^{2+}$  and 1.0 M  $\text{I}^-$  (for  $\text{HgI}_4^{2-}$ ,  $K_f = 6.8 \times 10^{29}$ )  
 (d) 0.10 M  $\text{Hg}^{2+}$  and 1.0 M  $\text{CN}^-$  (for  $\text{Hg}(\text{CN})_4^{2-}$ ,  $K_f = 3 \times 10^{41}$ )

### Complex Dissociation Equilibrium Constants

16. Which of the following equations describes the relationship between the complex formation equilibrium constant,  $K_f$ , and the complex dissociation equilibrium constant,  $K_d$ , for the  $\text{Fe}(\text{CN})_6^{3-}$  complex ion?  
 (a)  $K_f = K_d$  (b)  $K_f = K_w/K_d$  (c)  $K_f = K_d/K_w$  (d)  $K_f = K_w \times K_d$  (e)  $K_f = 1/K_d$
17. Derive the relationships among  $K_{f1}$ ,  $K_{f2}$ ,  $K_{d1}$ , and  $K_{d2}$  for the  $\text{Fe}(\text{SCN})_2^{2+}$  and  $\text{Fe}(\text{SCN})_2^+$  complex ions.

### Approximate Complex Ion Calculations

18. Calculate the  $\text{Fe}^{3+}$  ion concentration at equilibrium in a solution prepared by adding 0.100 mole of  $\text{SCN}^-$  to 250 mL of 0.0010 M  $\text{Fe}(\text{NO}_3)_3$ .



19. Calculate the  $\text{Cu}^{2+}$  ion concentration at equilibrium in a solution that is initially 0.10 M in  $\text{Cu}^{2+}$  and 4.0 M in  $\text{NH}_3$ . [For  $\text{Cu}(\text{NH}_3)_4^{2+}$ ,  $K_f = 2.1 \times 10^{13}$ .]  
 20. Calculate the  $\text{Zn}^{2+}$  ion concentration at equilibrium in a solution prepared by dissolving 0.220 mole of  $\text{ZnCl}_2$  in 500 mL of 2.0 M ammonia. [For  $\text{Zn}(\text{NH}_3)_4^{2+}$ ,  $K_f = 2.9 \times 10^9$ .]  
 21. Calculate the  $\text{Sb}^{3+}$  ion concentration at equilibrium in a 0.10 M  $\text{Sb}^{3+}$  ion solution that has been buffered at pH 8.00. [For  $\text{Sb}(\text{OH})_4^-$ ,  $K_f = 2 \times 10^{38}$ .]

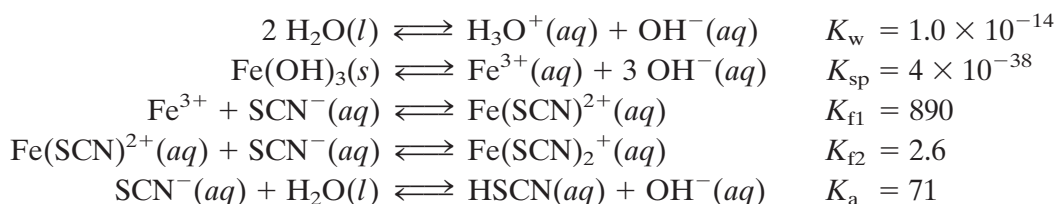
22. Calculate the  $\text{Sb}^{3+}$  ion concentration at equilibrium in a solution that is initially  $0.10\text{ M}$  in  $\text{Sb}^{3+}$  and  $6.0\text{ M}$  in  $\text{HCl}$ . (For  $\text{SbCl}_4^-$ ,  $K_f = 5.2 \times 10^4$ .)
23. Calculate the  $\text{Co}^{3+}$  ion concentration at equilibrium in a solution that is initially  $0.10\text{ M}$  in  $\text{Co}^{3+}$  and  $1.0\text{ M}$  in  $\text{SCN}^-$ . [For  $\text{Co}(\text{SCN})_4^-$ ,  $K_f = 1 \times 10^3$ .]
24. Calculate the  $\text{Cd}^{2+}$  ion concentration at equilibrium in a solution prepared by adding  $10.0\text{ mL}$  of  $15\text{ M}$  aqueous ammonia to  $100\text{ mL}$  of a solution of  $7.00 \times 10^{-3}$  grams of  $\text{CdCl}_2$  in water. [For  $\text{Cd}(\text{NH}_3)_4^{2+}$ ,  $K_f = 1.3 \times 10^7$ .]

### Using Complex Ion Equilibria to Dissolve an Insoluble Salt

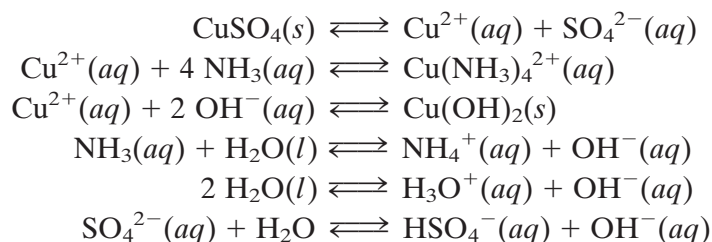
25.  $\text{AgCl}$  is virtually insoluble in water, but it is reasonably soluble in  $4.0\text{ M}$   $\text{NH}_3$ . How many moles of  $\text{AgCl}$  will dissolve in  $1.00$  liter of  $4.00\text{ M}$   $\text{NH}_3$ ? [For  $\text{AgCl}$ ,  $K_{\text{sp}} = 1.8 \times 10^{-10}$ ; for  $\text{Ag}(\text{NH}_3)_2^+$ ,  $K_f = 1.1 \times 10^7$ .]
26.  $\text{AgBr}$  is less soluble than  $\text{AgCl}$ , so we need to raise the concentration of ammonia in the solution in order to get a reasonable amount to dissolve. How many grams of  $\text{AgBr}$  will dissolve in  $250\text{ mL}$  of  $6.0\text{ M}$   $\text{NH}_3$ ? [For  $\text{Ag}(\text{NH}_3)_2^+$ ,  $K_f = 1.1 \times 10^7$ ; for  $\text{AgBr}$ ,  $K_{\text{sp}} = 5.0 \times 10^{-13}$ .]
27.  $K_f$  for the  $\text{Ag}(\text{NH}_3)_2^+$  complex ion is not large enough to allow silver bromide to dissolve in  $4.0\text{ M}$   $\text{NH}_3$ . How many moles of  $\text{AgBr}$  will dissolve in  $1.0$  liter of  $15\text{ M}$   $\text{NH}_3$ ? [For  $\text{AgBr}$ ,  $K_{\text{sp}} = 5.0 \times 10^{-13}$ ; for  $\text{Ag}(\text{NH}_3)_2^+$ ,  $K_f = 1.1 \times 10^7$ .]
28.  $K_f$  for the thiosulfate complex is not large enough to allow silver iodide to dissolve in  $\text{S}_2\text{O}_3^{2-}$  solutions, but the value of  $K_f$  for the cyanide complex ion,  $\text{Ag}(\text{CN})_2^-$ , is much larger. How many moles of  $\text{AgI}$  will dissolve in  $1.0$  liter of  $4.0\text{ M}$   $\text{CN}^-$ ? [For  $\text{AgI}$ ,  $K_{\text{sp}} = 8.3 \times 10^{-17}$ ; for  $\text{Ag}(\text{CN})_2^-$ ,  $K_f = 1.3 \times 10^{21}$ .]

### A Qualitative View of Combined Equilibria

29.  $\text{Fe}^{3+}$  forms blood-red complexes with the thiocyanate ion,  $\text{SCN}^-$ . What is the best way to increase the concentration of these complex ions in a solution that contains the following equilibria?



- (a) Add  $\text{HNO}_3$ . (b) Add  $\text{NaOH}$ . (c) Add  $\text{NaSCN}$ . (d) Add  $\text{Fe}(\text{OH})_3$ .
30. What is the effect of adding a strong acid to a solution that contains the  $\text{Zn}(\text{CN})_4^{2-}$  complex ion if  $\text{HCN}$  is a weak acid ( $K_a = 6 \times 10^{-10}$ )?
- (a) The  $\text{Zn}^{2+}$  ion concentration increases.  
 (b) The  $\text{Zn}^{2+}$  ion concentration decreases.  
 (c) The  $\text{Zn}^{2+}$  ion concentration remains the same.  
 (d) The  $\text{Zn}^{2+}$  and  $\text{CN}^-$  ion concentrations both increase.  
 (e) There is no way of predicting what will happen to the  $\text{Zn}^{2+}$  ion concentration.
31. What is one way to increase the concentration of the  $\text{Cu}^{2+}$  ion in a saturated solution of  $\text{CuSO}_4$  in ammonia in which the following equilibria occur?



- Add an acid, such as  $\text{HNO}_3$ .
- Add a base, such as  $\text{NaOH}$ .
- Increase the ammonia concentration.
- Add more  $\text{CuSO}_4$ .
- None of these increases the  $\text{Cu}^{2+}$  ion concentration in the solution.

### Integrated Problems

- What concentration of  $\text{NH}_3$  must be present in a  $0.10 \text{ M}$   $\text{AgNO}_3$  solution to prevent  $\text{AgCl}$  from precipitating when  $4.0$  grams of sodium chloride is added to  $250 \text{ mL}$  of the solution? [For  $\text{Ag}(\text{NH}_3)_2^+$ ,  $K_f = 1.1 \times 10^7$ ; for  $\text{AgCl}$ ,  $K_{sp} = 1.8 \times 10^{-10}$ .]
- Will  $\text{Co}(\text{OH})_3$  precipitate from a solution that is initially  $0.10 \text{ M}$  in  $\text{Co}^{3+}$  and  $1.0 \text{ M}$  in  $\text{SCN}^-$  if the solution is buffered at  $\text{pH } 7.00$ ? [For  $\text{Co}(\text{OH})_3$ ,  $K_{sp} = 1.6 \times 10^{-44}$ ; for  $\text{Co}(\text{SCN})_4^-$ ,  $K_f = 1 \times 10^3$ .]
- It is possible to keep  $\text{Co}(\text{OH})_3$  from precipitating from a  $0.010 \text{ M}$   $\text{CoCl}_3$  solution by buffering the solution at  $\text{pH } 9.10$  with a buffer that contains  $\text{NH}_3$  and the  $\text{NH}_4^+$  ion. How much  $6.0 \text{ M}$   $\text{NH}_3$  and  $6.0 \text{ M}$   $\text{HCl}$  must be added per liter of the solution to prevent  $\text{Co}(\text{OH})_3$  from precipitating? [For  $\text{NH}_3$ ,  $K_b = 1.8 \times 10^{-5}$ ; for  $\text{Co}(\text{OH})_3$ ,  $K_{sp} = 1.6 \times 10^{-44}$ ; for  $\text{Co}(\text{NH}_3)_6^{3+}$ ,  $K_f = 2 \times 10^{35}$ .]
- Calculate the  $\text{CO}_3^{2-}$  ion concentration in a  $0.10 \text{ M}$   $\text{HCO}_3^-$  solution buffered with equal numbers of moles of  $\text{NH}_3$  and  $\text{NH}_4^+$ . Is this  $\text{CO}_3^{2-}$  concentration large enough to precipitate  $\text{BaCO}_3$  when the solution is mixed with an equal volume of a  $0.10 \text{ M}$   $\text{Ba}^{2+}$  ion solution? (For  $\text{BaCO}_3$ ,  $K_{sp} = 5.1 \times 10^{-9}$ ; for  $\text{H}_2\text{CO}_3$ ,  $K_{a1} = 4.5 \times 10^{-7}$ ,  $K_{a2} = 4.7 \times 10^{-11}$ ; for  $\text{NH}_3$ ,  $K_b = 1.8 \times 10^{-5}$ .)
- Research has shown that enough  $\text{CO}_3^{2-}$  ion can be leached out of clay to buffer groundwater at a  $\text{pH}$  of about  $8$ . Assume that the total concentration of the  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions in the solution is  $0.10 \text{ M}$ . Calculate the maximum concentration of  $^{60}\text{Co}$  that could leach into the groundwater if clay were used as a barrier to store the radioactive isotope. [For  $\text{CoCO}_3$ ,  $K_{sp} = 1.4 \times 10^{-13}$ ; for  $\text{Co}(\text{OH})_3$ ,  $K_{sp} = 1.6 \times 10^{-44}$ ; for  $\text{H}_2\text{CO}_3$ ,  $K_{a1} = 4.5 \times 10^{-7}$ ,  $K_{a2} = 4.7 \times 10^{-11}$ .]