

Solubility and solubility equilibria

Key terms and concepts

- Solubility of ionic compounds
- Solubility product expression, K_{sp}
- Calculations involving K_{sp} and solubility
- Predicting precipitation formation
- Factors affecting solubility
 - ✓ The common ion effect
 - ✓ pH
 - ✓ Complex ion formation

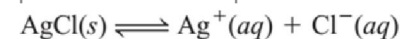
- When a solid is placed into water and dissolves, the process is known as **dissolution**. The process of dissolved constituents leaving solution and forming a solid is known as **precipitation** and the solid that forms is called a **precipitate**
- How can we **predict whether a precipitate** will form when a compound is added to a solution or when two solutions are mixed?
- Formation of precipitate depends on the solubility of the solute, which is defined as the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature. Table 4.2 classifies a number of common ionic compounds as soluble or insoluble in water

TABLE 4.2 Solubility Rules for Common Ionic Compounds in Water at 25°C

Soluble Compounds	Exceptions
Compounds containing alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and the ammonium ion (NH_4^+)	
Nitrates (NO_3^-), bicarbonates (HCO_3^-), and chlorates (ClO_3^-)	
Halides (Cl^- , Br^- , I^-)	Halides of Ag^+ , Hg_2^{2+} , and Pb^{2+}
Sulfates (SO_4^{2-})	Sulfates of Ag^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+}
Insoluble Compounds	Exceptions
Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), and sulfides (S^{2-})	Compounds containing alkali metal ions and the ammonium ion
Hydroxides (OH^-)	Compounds containing alkali metal ions and the Ba^{2+} ion

Solubility Product

- Consider a saturated solution of silver chloride that is in contact with solid silver chloride. The solubility equilibrium can be represented as



Thus, we can write the equilibrium constant for the dissociation of AgCl as

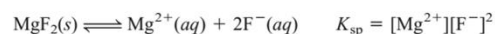
$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

in which K_{sp} is called the **solubility product constant** or simply the solubility product.

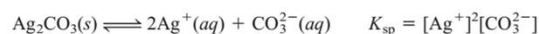
- In general, the solubility product of a compound is the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.

Examples of K_{sp} expressions:

- MgF_2



- Ag_2CO_3



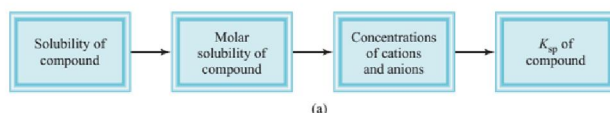
- $Ca_3(PO_4)_2$



Solubility product calculations

- The value of K_{sp} indicates the solubility of an ionic compound- **the smaller the value, the less soluble the compound in water**. However, in using K_{sp} values to compare solubilities, you should choose compounds that have similar formulas, such as $AgCl$ and ZnS , or CaF_2 and $Fe(OH)_2$.
- There are two other quantities that express a substance's solubility: **Molar solubility**, which is the number of moles of solute in 1 Liter of a saturated solution, and **Solubility**, which is the number of grams of solute in 1 L of a saturated solution.

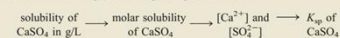
- The following figure shows the relationships among solubility, molar solubility, and K_{sp} . Both molar solubility and solubility are convenient to use in the laboratory. We can use them to determine K_{sp} by following the steps outlined in Figure (a).



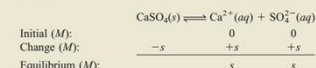
Example 17.6

The solubility of calcium sulfate ($CaSO_4$) is found to be 0.67 g/L. Calculate the value of K_{sp} for calcium sulfate.

Strategy We are given the solubility of $CaSO_4$ and asked to calculate its K_{sp} . The sequence of conversion steps, according to Figure 17.9(a), is



Solution Consider the dissociation of $CaSO_4$ in water. Let s be the molar solubility (in mol/L) of $CaSO_4$.



The solubility product for $CaSO_4$ is

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = s^2$$

First we calculate the number of moles of $CaSO_4$ dissolved in 1 L of solution

$$\frac{0.67 \text{ g } CaSO_4}{1 \text{ L soln}} \times \frac{1 \text{ mol } CaSO_4}{136.2 \text{ g } CaSO_4} = 4.9 \times 10^{-3} \text{ mol/L} = s$$

From the solubility equilibrium we see that for every mole of $CaSO_4$ that dissolves, 1 mole of Ca^{2+} and 1 mole of SO_4^{2-} are produced. Thus, at equilibrium

$$[Ca^{2+}] = 4.9 \times 10^{-3} \text{ M} \quad \text{and} \quad [SO_4^{2-}] = 4.9 \times 10^{-3} \text{ M}$$

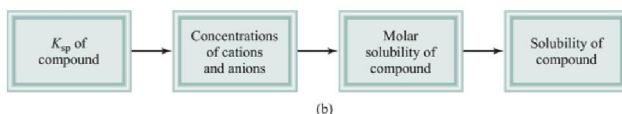
Now we can calculate K_{sp} :

$$\begin{aligned} K_{sp} &= [Ca^{2+}][SO_4^{2-}] \\ &= (4.9 \times 10^{-3})(4.9 \times 10^{-3}) \\ &= 2.4 \times 10^{-5} \end{aligned}$$

Practice Exercise The solubility of lead chromate ($PbCrO_4$) is 4.5×10^{-5} g/L. Calculate the solubility product of this compound.

Calculation of molar solubility from K_{sp}

- To calculate a compound's molar solubility from the value of K_{sp} , we must follow the following steps.

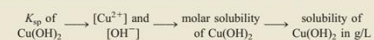


Example

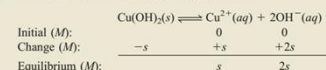
Calculate the solubility of copper(II) hydroxide $[\text{Cu}(\text{OH})_2]$ in g/L.

K_{sp} for $\text{Cu}(\text{OH})_2$ is 2.2×10^{-20} . The molar mass of $\text{Cu}(\text{OH})_2$ is 97.57 g/mol.

Strategy We are given the K_{sp} of $\text{Cu}(\text{OH})_2$ and asked to calculate its solubility in g/L. The sequence of conversion steps, according to Figure 17.9(b), is



Solution Consider the dissociation of $\text{Cu}(\text{OH})_2$ in water:



Note that the molar concentration of OH^- is twice that of Cu^{2+} . The solubility product of $\text{Cu}(\text{OH})_2$ is

$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2 = (s)(2s)^2 = 4s^3$$

From the K_{sp} value in Table 17.2, we solve for the molar solubility of $\text{Cu}(\text{OH})_2$ as follows:

$$2.2 \times 10^{-20} = 4s^3$$

$$s^3 = \frac{2.2 \times 10^{-20}}{4} = 5.5 \times 10^{-21}$$

$$s = 1.8 \times 10^{-7} \text{ M}$$

Hence

Finally, from the molar mass of $\text{Cu}(\text{OH})_2$ and its molar solubility, we calculate the solubility in g/L:

$$\text{solubility of } \text{Cu}(\text{OH})_2 = \frac{1.8 \times 10^{-7} \text{ mol-Cu}(\text{OH})_2}{1 \text{ L soln}} \times \frac{97.57 \text{ g Cu}(\text{OH})_2}{1 \text{ mol-Cu}(\text{OH})_2} = 1.8 \times 10^{-5} \text{ g/L}$$

Practice Exercise Calculate the solubility of silver chloride (AgCl) in g/L.

Predicting precipitation reactions

- From a knowledge of the **solubility rules** and the **solubility products**, we can **predict whether a precipitate will form** when we mix two solutions or add a soluble compound to a solution
- We use **Q** called the **ion product**, to represent the product of the molar concentrations of the ions raised to the power of their stoichiometric coefficients and compared to K_{sp} values to predict if a precipitate will form.

For the dissociation of an ionic solid in water, the following conditions may exist:

- 1) The solution is unsaturated
- 2) The solution is saturated
- 3) The solution is supersaturated

The following relationships are useful in making predictions on when a precipitate might form.

$Q < K_{sp}$: no precipitate forms

$Q = K_{sp}$: no precipitate forms

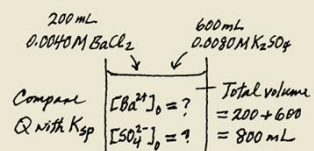
$Q > K_{sp}$: a precipitate forms

Example 17.8

Exactly 200 mL of 0.0040 M BaCl_2 are added to exactly 600 mL of 0.0080 M K_2SO_4 . Will a precipitate form?

Strategy Under what condition will an ionic compound precipitate from solution? The ions in solution are Ba^{2+} , Cl^- , K^+ , and SO_4^{2-} . According to the solubility rules listed in Table 4.2 (p. 98), the only precipitate that can form is BaSO_4 . From the information given, we can calculate $[\text{Ba}^{2+}]$ and $[\text{SO}_4^{2-}]$ because we know the number of moles of the ions in the original solutions and the volume of the combined solution. Next we calculate the reaction quotient Q ($Q = [\text{Ba}^{2+}]_0[\text{SO}_4^{2-}]_0$) and compare the value of Q

with K_{sp} of BaSO_4 to see if a precipitate will form, that is, if the solution is supersaturated. It is helpful to make a sketch of the situation.



Solution The number of moles of Ba^{2+} present in the original 200 mL of solution is

$$200 \text{ mL} \times \frac{0.0040 \text{ mol Ba}^{2+}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 8.0 \times 10^{-4} \text{ mol Ba}^{2+}$$

The total volume after combining the two solutions is 800 mL. The concentration of Ba^{2+} in the 800 mL volume is

$$[\text{Ba}^{2+}] = \frac{8.0 \times 10^{-4} \text{ mol}}{800 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} = 1.0 \times 10^{-3} \text{ M}$$

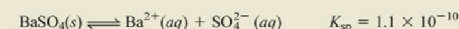
The number of moles of SO_4^{2-} in the original 600 mL solution is

$$600 \text{ mL} \times \frac{0.0080 \text{ mol SO}_4^{2-}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 4.8 \times 10^{-3} \text{ mol SO}_4^{2-}$$

The concentration of SO_4^{2-} in the 800 mL of the combined solution is

$$[\text{SO}_4^{2-}] = \frac{4.8 \times 10^{-3} \text{ mol}}{800 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}} = 6.0 \times 10^{-3} \text{ M}$$

Now we must compare Q with K_{sp} . From Table 17.2,



As for Q ,

$$Q = [\text{Ba}^{2+}]_0[\text{SO}_4^{2-}]_0 = (1.0 \times 10^{-3})(6.0 \times 10^{-3}) = 6.0 \times 10^{-6}$$

Therefore,

$$Q > K_{sp}$$

The solution is supersaturated because the value of Q indicates that the concentrations of the ions are too large. Thus, some of the BaSO_4 will precipitate out of solution until

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$$

Practice Exercise If 2.00 mL of 0.200 M NaOH are added to 1.00 L of 0.100 M CaCl_2 , will precipitation occur?

Predict whether a precipitate will form when each of the following is added to 650 mL of 0.080 M K_2SO_4 : (a) 250 mL of 0.0040 M BaCl_2 ; (b) 175 mL of 0.15 M AgNO_3 ; (c) 325 mL of 0.25 M $\text{Sr}(\text{NO}_3)_2$. (Assume volumes are additive.)

Factors that affect solubility

Several factors exist that affect the solubility of ionic compounds. In this section we examine three factors that affect the solubility of ionic compounds:

- Presence of common ions
- Solution pH
- Presence of complexing agents or formation of complex ions

The common ion effect and solubility

- Precipitation of an ionic compound from solution occurs **whenever the ion product exceeds K_{sp}** for that substance.

- Suppose we study a solution containing two dissolved substances that share a common ion, say, AgCl and AgNO_3 . In addition to the dissociation of AgCl , the following process also contributes to the total concentration of the common silver ions in solution:



- If AgNO_3 is added to a saturated AgCl solution, the increase in $[\text{Ag}^+]$ will make the ion product greater than the solubility product:

$$Q = [\text{Ag}^+]_0[\text{Cl}^-]_0 > K_{sp}$$

- To reestablish equilibrium, some AgCl will precipitate out of the solution, as LeChâtelier's principle would predict, until the ion product is once again equal to K_{sp} . The effect of **adding a common ion, then, is a decrease in the solubility of the salt (AgCl) in solution**. Note that in this case $[Ag^+]$ is no longer equal to $[Cl^-]$ at equilibrium; rather, $[Ag^+] > [Cl^-]$.

Calculating the effect of a common ion on solubility

Example 17.9

Calculate the solubility of silver chloride (in g/L) in a $6.5 \times 10^{-3} M$ silver nitrate solution.

Strategy This is a common-ion problem. The common ion here is Ag^+ , which is supplied by both AgCl and $AgNO_3$. Remember that the presence of the common ion will affect only the solubility of AgCl (in g/L), but not the K_{sp} value because it is an equilibrium constant.

Step 4: At equilibrium,

$$[Ag^+] = (6.5 \times 10^{-3} + 2.5 \times 10^{-8}) M \approx 6.5 \times 10^{-3} M$$

$$[Cl^-] = 2.5 \times 10^{-8} M$$

and so our approximation was justified in Step 3. Because all the Cl^- ions must come from AgCl, the amount of AgCl dissolved in $AgNO_3$ solution also is $2.5 \times 10^{-8} M$. Then, knowing the molar mass of AgCl (143.4 g), we can calculate the solubility of AgCl as follows:

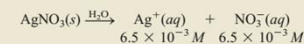
$$\text{solubility of AgCl in } AgNO_3 \text{ solution} = \frac{2.5 \times 10^{-8} \text{ mol AgCl}}{1 \text{ L soln}} \times \frac{143.4 \text{ g AgCl}}{1 \text{ mol AgCl}} = 3.6 \times 10^{-6} \text{ g/L}$$

Check The solubility of AgCl in pure water is $1.9 \times 10^{-3} \text{ g/L}$ (see the Practice Exercise in Example 17.7). Therefore, the lower solubility ($3.6 \times 10^{-6} \text{ g/L}$) in the presence of $AgNO_3$ is reasonable. You should also be able to predict the lower solubility using Le Châtelier's principle. Adding Ag^+ ions shifts the solubility equilibrium to the left, thus decreasing the solubility of AgCl.

Practice Exercise Calculate the solubility in g/L of AgBr in (a) pure water and in (b) $0.0010 M$ NaBr.

Solution Step 1: The relevant species in solution are Ag^+ ions (from both AgCl and $AgNO_3$) and Cl^- ions. The NO_3^- ions are spectator ions.

Step 2: Because $AgNO_3$ is a soluble strong electrolyte, it dissociates completely:



Let s be the molar solubility of AgCl in $AgNO_3$ solution. We summarize the changes in concentrations as follows:

	$AgCl(s)$	\rightleftharpoons	$Ag^+(aq)$	+	$Cl^-(aq)$
Initial (M):			6.5×10^{-3}		0.00
Change (M):	$-s$		$+s$		$+s$
Equilibrium (M):			$(6.5 \times 10^{-3} + s)$		s

Step 3:

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

$$1.6 \times 10^{-10} = (6.5 \times 10^{-3} + s)(s)$$

Because AgCl is quite insoluble and the presence of Ag^+ ions from $AgNO_3$ further lowers the solubility of AgCl, s must be very small compared with 6.5×10^{-3} . Therefore, applying the approximation $6.5 \times 10^{-3} + s \approx 6.5 \times 10^{-3}$, we obtain

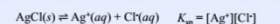
$$1.6 \times 10^{-10} = (6.5 \times 10^{-3})s$$

$$s = 2.5 \times 10^{-8} M$$

Calculate the molar solubility of silver chloride in a solution that is $6.5 \times 10^{-3} M$ in silver nitrate.

Strategy Silver nitrate is a strong electrolyte that dissociates completely in water. Therefore, the concentration of Ag^+ before any AgCl dissolves is $6.5 \times 10^{-3} M$. Use the equilibrium expression, the K_{sp} for AgCl, and an equilibrium table to determine how much AgCl will dissolve.

Solution The dissolution equilibrium and the equilibrium expression are



	$AgCl(s)$	\rightleftharpoons	$Ag^+(aq)$	+	$Cl^-(aq)$
Initial concentration (M)			6.5×10^{-3}		0
Change in concentration (M)			$+s$		$+s$
Equilibrium concentration (M)			$6.5 \times 10^{-3} + s$		s

Solution Substituting these concentrations into the equilibrium expression gives

$$1.6 \times 10^{-10} = (6.5 \times 10^{-3} + s)(s)$$

We expect s to be very small, so

$$6.5 \times 10^{-3} + s \approx 6.5 \times 10^{-3}$$

and

$$1.6 \times 10^{-10} = (6.5 \times 10^{-3})(s)$$

Thus

$$s = \frac{1.6 \times 10^{-10}}{6.5 \times 10^{-3}} = 2.5 \times 10^{-8} M$$

Therefore, the molar solubility of AgCl in $6.5 \times 10^{-3} M$ $AgNO_3$ is $2.5 \times 10^{-8} M$.

Think About It The molar solubility of AgCl in water is $\sqrt{1.6 \times 10^{-10}} = 1.3 \times 10^{-5} M$. The presence of $6.5 \times 10^{-3} M$ $AgNO_3$ reduces the solubility of AgCl by a factor of ~500.

The effect of pH on solubility

The pH of a solution affects the solubility of any substance whose anion is basic. Consider $\text{Mg}(\text{OH})_2$, for which the solubility equilibrium is



A saturated solution of $\text{Mg}(\text{OH})_2$ has a calculated pH of 10.52 and its Mg^{2+} concentration is $1.7 \times 10^{-4} \text{ M}$. Now suppose that solid $\text{Mg}(\text{OH})_2$ is equilibrated with a solution buffered at pH 9.0. The pOH, therefore, is 5.0, so $[\text{OH}^-] = 1.0 \times 10^{-5}$. Inserting this value for $[\text{OH}^-]$ into the solubility-product expression, we have

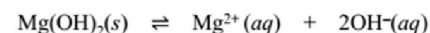
$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.8 \times 10^{-11}$$

$$[\text{Mg}^{2+}](1.0 \times 10^{-5})^2 = 1.8 \times 10^{-11}$$

$$[\text{Mg}^{2+}] = \frac{1.8 \times 10^{-11}}{(1.0 \times 10^{-5})^2} = 0.18 \text{ M}$$

Thus, the $\text{Mg}(\text{OH})_2$ dissolves until $[\text{Mg}^{2+}] = 0.18 \text{ M}$. It is apparent that $\text{Mg}(\text{OH})_2$ is much more soluble in this solution.

- If were reduced further by making the solution even more acidic, the concentration would have to increase to maintain the equilibrium condition. Thus, a sample of $\text{Mg}(\text{OH})_2(s)$ dissolves completely if sufficient acid is added.
- The solubility of almost any ionic compound is affected if the solution is made sufficiently acidic or basic. The effects are noticeable, however, only when one (or both) ions in the compound are at least moderately acidic or basic. The metal hydroxides, such as $\text{Mg}(\text{OH})_2$, are examples of compounds containing a strongly basic ion, the hydroxide ion.



$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.2 \times 10^{-11}$$

$$(s)(2s)^2 = 4s^3 = 1.2 \times 10^{-11}$$

$$s = 1.4 \times 10^{-4} \text{ M}$$

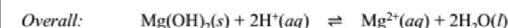
At equilibrium:

$$[\text{OH}^-] = 2(1.4 \times 10^{-4} \text{ M}) = 2.8 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log(2.8 \times 10^{-4}) = 3.55$$

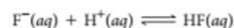
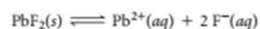
$$\text{pH} = 14.00 - 3.55 = 10.45$$

In a solution with a pH of less than 10.45, the solubility of $\text{Mg}(\text{OH})_2$ increases.



If the pH of the medium were higher than 10.45, $[\text{OH}^-]$ would be higher and the solubility of $\text{Mg}(\text{OH})_2$ would decrease because of the common ion (OH^-) effect.

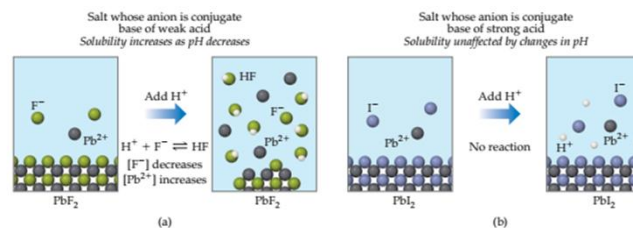
- In general, the solubility of a compound **containing a basic anion** (that is, the anion of a weak acid) **increases as the solution becomes more acidic**. As we have seen, the solubility of $\text{Mg}(\text{OH})_2$ greatly increases as the acidity of the solution increases.
- The **solubility of PbF_2 increases as the solution becomes more acidic**, too, because is a weak base (it is the conjugate base of the weak acid HF). As a result, the solubility equilibrium of PbF_2 is shifted to the right as the concentration of F^- is reduced by protonation to form HF. Thus, the solution process can be understood in terms of two consecutive reactions:



The equation for the overall process is



- Other salts that contain basic anions, such as CO_3^{2-} , PO_4^{3-} , CN^- , or S^{2-} , behave similarly. These examples illustrate a general rule: **The solubility of slightly soluble salts containing basic anions increases as $[\text{H}^+]$ increases** (as pH is lowered).
- The more basic the anion, the more the solubility is influenced by pH. The solubility of salts with anions of negligible basicity (the anions of strong acids), such as Cl^- , Br^- , I^- and NO_3^- , is unaffected by pH changes.



▲ FIGURE 17.19 Response of two ionic compounds to addition of a strong acid. (a) The solubility of PbF_2 increases on addition of acid. (b) The solubility of PbI_2 is not affected by addition of acid. The water molecules and the anion of the strong acid have been omitted for clarity.

Predicting the effect of acid on solubility

SAMPLE EXERCISE 17.13 Predicting the Effect of Acid on Solubility

Which of these substances are more soluble in acidic solution than in basic solution: (a) $\text{Ni}(\text{OH})_2(s)$, (b) $\text{CaCO}_3(s)$, (c) $\text{BaF}_2(s)$, (d) $\text{AgCl}(s)$?

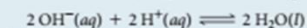
SOLUTION

Analyze The problem lists four sparingly soluble salts, and we are asked to determine which are more soluble at low pH than at high pH.

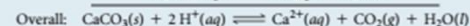
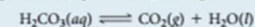
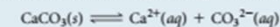
Plan Ionic compounds that dissociate to produce a basic anion are more soluble in acid solution.

Solve

(a) $\text{Ni}(\text{OH})_2(s)$ is more soluble in acidic solution because of the basicity of OH^- ; the H^+ reacts with the OH^- ion, forming water:

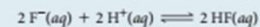
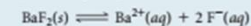


(b) Similarly, $\text{CaCO}_3(s)$ dissolves in acid solutions because CO_3^{2-} is a basic anion:



The reaction between CO_3^{2-} and H^+ occurs in steps, with HCO_3^- forming first and H_2CO_3 forming in appreciable amounts only when $[\text{H}^+]$ is sufficiently high.

(c) The solubility of BaF_2 is enhanced by lowering the pH because F^- is a basic anion:



(d) The solubility of AgCl is unaffected by changes in pH because Cl^- is the anion of a strong acid and therefore has negligible basicity.

PRACTICE EXERCISE

Write the net ionic equation for the reaction between an acid and (a) CuS , (b) $\text{Cu}(\text{N}_3)_2$.

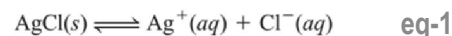
Answers: (a) $\text{CuS}(s) + \text{H}^+(aq) \rightleftharpoons \text{Cu}^{2+}(aq) + \text{HS}^-(aq)$

(b) $\text{Cu}(\text{N}_3)_2(s) + 2 \text{H}^+(aq) \rightleftharpoons \text{Cu}^{2+}(aq) + 2 \text{HN}_3(aq)$

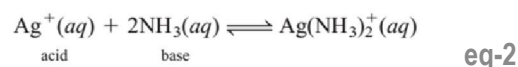
Effect of complexation on solubility

- One method for increasing a precipitate's solubility is to add a ligand that forms soluble complexes with one of the precipitate's ions.

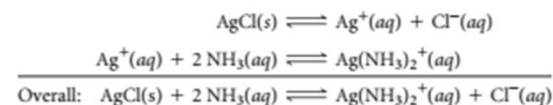
Consider, for example, the solubility of AgCl



What is the effect of adding a ligand that forms a stable, soluble complex with Ag⁺? Ammonia, for example, reacts with Ag⁺ as shown here



- Adding NH₃ decreases the concentration of Ag⁺ as the Ag(NH₃)₂⁺ complex forms. In turn, decreasing the concentration of Ag⁺, increases the solubility of AgCl as reaction 1 reestablishes its equilibrium position. This process can be viewed as the sum of two reactions. Thus, adding together reaction 1 and reaction 2 clarifies the effect of NH₃ on the solubility of AgCl, by showing NH₃ as a reactant.



- The presence of NH₃ drives the reaction, the dissolution of AgCl, to the right as Ag⁺ is consumed to form Ag(NH₃)₂⁺.

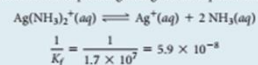
SAMPLE EXERCISE 17.14 Evaluating an Equilibrium Involving a Complex Ion

Calculate the concentration of Ag⁺ present in solution at equilibrium when concentrated ammonia is added to a 0.010 M solution of AgNO₃ to give an equilibrium concentration of [NH₃] = 0.20 M. Neglect the small volume change that occurs when NH₃ is added.

SOLUTION

Analyze Addition of NH₃(aq) to Ag⁺(aq) forms Ag(NH₃)₂⁺, as shown in Equation 17.22. We are asked to determine what concentration of Ag⁺(aq) remains uncombined when the NH₃ concentration is brought to 0.20 M in a solution originally 0.010 M in AgNO₃.

Plan We assume that the AgNO₃ is completely dissociated, giving 0.010 M Ag⁺. Because *K_f* for the formation of Ag(NH₃)₂⁺ is quite large, we assume that essentially all the Ag⁺ is converted to Ag(NH₃)₂⁺ and approach the problem as though we are concerned with the dissociation of Ag(NH₃)₂⁺ rather than its formation. To facilitate this approach, we need to reverse Equation 17.22 and make the corresponding change to the equilibrium constant:



Solve If [Ag⁺] is 0.010 M initially, [Ag(NH₃)₂⁺] will be 0.010 M following addition of the NH₃. We construct a table to solve this equilibrium problem. Note that the NH₃ concentration given in the problem is an equilibrium concentration rather than an initial concentration.

	Ag(NH ₃) ₂ ⁺ (aq)	Ag ⁺ (aq)	+	2 NH ₃ (aq)
Initial	0.010 M	0 M		
Change	-x M	+x M		
Equilibrium	0.010-x M	x M		0.20 M

Because [Ag⁺] is very small, we can ignore x, so that 0.010 - x ≈ 0.010 M. Substituting these values into the equilibrium-constant expression for the dissociation of Ag(NH₃)₂⁺, we obtain

$$\frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{(x)(0.20)^2}{0.010} = 5.9 \times 10^{-8}$$

$$x = 1.5 \times 10^{-8} \text{ M} = [\text{Ag}^+]$$

Formation of the Ag(NH₃)₂⁺ complex drastically reduces the concentration of free Ag⁺ ion in solution.

PRACTICE EXERCISE

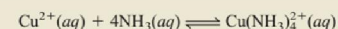
Calculate [Cr³⁺] in equilibrium with Cr(OH)₄⁻ when 0.010 mol of Cr(NO₃)₃ is dissolved in 1 L of solution buffered at pH 10.0.

Answer: 1 × 10⁻¹⁶ M

Example 17.10

A 0.20-mole quantity of CuSO₄ is added to a liter of 1.20 M NH₃ solution. What is the concentration of Cu²⁺ ions at equilibrium?

Strategy The addition of CuSO₄ to the NH₃ solution results in complex ion formation



From Table 17.4 we see that the formation constant (K_f) for this reaction is very large; therefore, the reaction lies mostly to the right. At equilibrium, the concentration of Cu^{2+} will be very small. As a good approximation, we can assume that essentially all the dissolved Cu^{2+} ions end up as $\text{Cu}(\text{NH}_3)_4^{2+}$ ions. How many moles of NH_3 will react with 0.20 mole of Cu^{2+} ? How many moles of $\text{Cu}(\text{NH}_3)_4^{2+}$ will be produced? A very small amount of Cu^{2+} will be present at equilibrium. Set up the K_f expression for the preceding equilibrium to solve for $[\text{Cu}^{2+}]$.

Solution The amount of NH_3 consumed in forming the complex ion is 4×0.20 mol, or 0.80 mol. (Note that 0.20 mol Cu^{2+} is initially present in solution and four NH_3 molecules are needed to form a complex ion with one Cu^{2+} ion.) The concentration of NH_3 at equilibrium is therefore $(1.20 - 0.80)$ mol/L soln or 0.40 M , and that of $\text{Cu}(\text{NH}_3)_4^{2+}$ is 0.20 mol/L soln or 0.20 M , the same as the initial concentration of Cu^{2+} . [There is a 1:1 mole ratio between Cu^{2+} and $\text{Cu}(\text{NH}_3)_4^{2+}$.] Because $\text{Cu}(\text{NH}_3)_4^{2+}$ does dissociate to a slight extent, we call the concentration of Cu^{2+} at equilibrium x and write

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

$$5.0 \times 10^{13} = \frac{0.20}{x(0.40)^4}$$

Solving for x and keeping in mind that the volume of the solution is 1 L, we obtain

$$x = [\text{Cu}^{2+}] = 1.6 \times 10^{-13} M$$

Practice Exercise If 2.50 g of CuSO_4 are dissolved in 9.0×10^2 mL of 0.30 M NH_3 , what are the concentrations of Cu^{2+} , $\text{Cu}(\text{NH}_3)_4^{2+}$, and NH_3 at equilibrium?

Thank you

