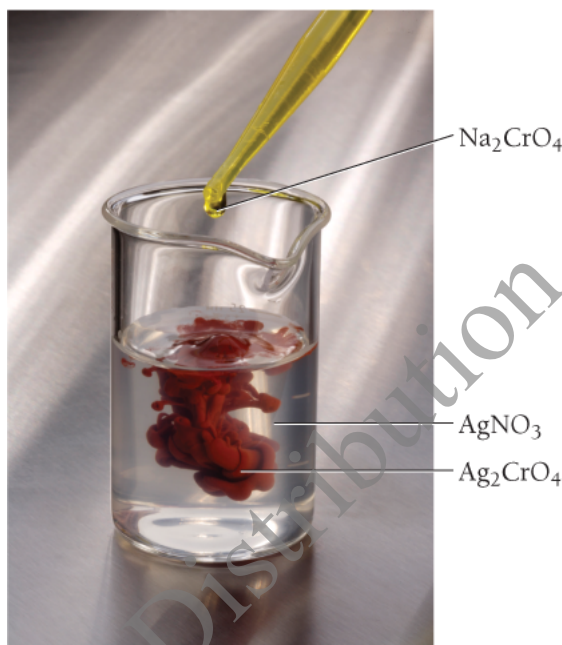


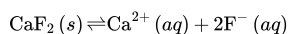
17.6: Precipitation

In [Chapter 8](#) we learned that a precipitation reaction can occur upon the mixing of two solutions containing ionic compounds when one of the possible cross products—the combination of a cation from one solution and the anion from the other—is insoluble. In this chapter, however, we have seen that the terms *soluble* and *insoluble* are extremes in a continuous range of solubility—many compounds are slightly soluble, and even those that we categorized as insoluble in [Chapter 8](#) actually have some limited degree of solubility (they have very small solubility-product constants).



Q and K_{sp}

We can better understand precipitation reactions by revisiting a concept from [Chapter 15](#)—the reaction quotient (Q). The reaction quotient for the reaction by which an ionic compound dissolves is the product of the concentrations of the ionic components raised to their stoichiometric coefficients. For example, consider the reaction by which CaF_2 dissolves:



The reaction quotient for this reaction is:

$$Q = [\text{Ca}^{2+}][\text{F}^{-}]^2$$

The difference between Q and K_{sp} is that K_{sp} is the value of this product *at equilibrium only*, whereas Q is the value of the product under any conditions. We can therefore use the value of Q to compare a solution containing any concentrations of the component ions to a solution that is at equilibrium.

Consider a solution of calcium fluoride in which Q is less than K_{sp} . Recall from [Chapter 15](#) that if Q is less than K_{sp} , the reaction will proceed to the right (toward products). Consequently, if the solution contains any solid CaF_2 , the CaF_2 will continue to dissolve. If all of the solid has already dissolved, the solution will simply remain as it is, containing less than the equilibrium amount of the dissolved ions. Such a solution is an

unsaturated solution. If more solid is added to an unsaturated solution, it will dissolve, as long as Q remains less than K_{sp} .

Now consider a solution in which Q is exactly equal to K_{sp} . In this case, the reaction is at equilibrium and will not make progress in either direction. Such a solution most likely contains at least a small amount of the solid in equilibrium with its component ions. However, the amount of solid may be too small to be visible. Such a solution is a *saturated solution*.

Finally, consider a solution in which Q is greater than K_{sp} . In this case, the reaction will proceed to the left (toward the reactants), and solid calcium fluoride will form from the dissolved calcium and fluoride ions. In other words, the solid normally precipitates out of a solution in which Q is greater than K_{sp} .

Under certain circumstances, however, Q can remain greater than K_{sp} for an unlimited period of time. Such a solution, called a *supersaturated solution*, is unstable and forms a precipitate when sufficiently disturbed. **Figure 17.14** shows a supersaturated solution of sodium acetate. When a small seed crystal of solid sodium acetate is dropped into the solution, it triggers the precipitation reaction.

Figure 17.14 Precipitation from a Supersaturated Solution

The excess solute in a supersaturated solution of sodium acetate precipitates out if a small sodium acetate crystal is added.



Summarizing the Relationship of Q and K_{sp} in Solutions Containing an Ionic Compound:

- If $Q < K_{sp}$, the solution is unsaturated, and more of the solid ionic compound can dissolve in the solution.
- If $Q = K_{sp}$, the solution is saturated. The solution is holding the equilibrium amount of the dissolved ions, and additional solid does not dissolve in the solution.
- If $Q > K_{sp}$, the solution is supersaturated. Under most circumstances, the excess solid precipitates out of a supersaturated solution.

We can use Q to predict whether a precipitation reaction will occur upon the mixing of two solutions containing dissolved ionic compounds. For example, consider mixing a silver nitrate solution with a potassium iodide solution to form a mixture that is 0.010 M in AgNO_3 and 0.015 M in KI . Will a precipitate form in the newly mixed solution? From **Chapter 8** we know that one of the cross products, KNO_3 , is soluble and will therefore not precipitate. The other cross product, AgI , may precipitate if the concentrations of Ag^+ and I^- are high enough in the newly mixed solution: We can compare Q to K_{sp} to determine whether a precipitate forms. For AgI , $K_{sp} = 8.51 \times 10^{-17}$. For the newly mixed solution, $[\text{Ag}^+] = 0.010 \text{ M}$ and $[\text{I}^-] = 0.015 \text{ M}$. We calculate Q as follows:

$$Q = [\text{Ag}^+][\text{I}^-] = (0.010)(0.015) = 1.5 \times 10^{-4}$$

The value of Q is much greater than K_{sp} ; therefore, AgI should precipitate out of the newly mixed solution.

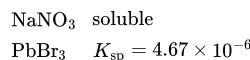
Example 17.12 Predicting Precipitation Reactions by Comparing Q and K_{sp}

A solution containing lead(II) nitrate is mixed with one containing sodium bromide to form a solution that is $\text{Pb}(\text{NO}_3)_2$ in NaBr and 0.00350 M in NaBr. Does a precipitate form in the newly mixed solution?

SOLUTION

First, determine the possible cross products and their K_{sp} values (Table 17.2). Any cross products that are soluble will *not* precipitate (see Table 8.1).

Possible cross products:



Calculate Q and compare it to K_{sp} . A precipitate only forms if $Q > K_{\text{sp}}$.

$$\begin{aligned} Q &= [\text{Pb}^{2+}] [\text{Br}^-]^2 \\ &= (0.0150)(0.00350)^2 \\ &= 1.84 \times 10^{-7} \\ Q &< K_{\text{sp}}; \text{ therefore, no precipitate forms.} \end{aligned}$$

FOR PRACTICE 17.12 If the original solutions in Example 17.12 are concentrated through evaporation and mixed again to form a solution that is 0.0600 M in $\text{Pb}(\text{NO}_3)_2$ and 0.0158 M in NaBr, does a precipitate form in the newly mixed solution?

Selective Precipitation

A solution may contain several different dissolved metal cations that we can separate by **selective precipitation**, a process involving the addition of a reagent that forms a precipitate with one of the dissolved cations but not the others. For example, seawater contains dissolved magnesium and calcium cations with the concentrations $[\text{Mg}^{2+}] = 0.059 \text{ M}$ and $[\text{Ca}^{2+}] = 0.011 \text{ M}$. We can separate these ions by adding a reagent that precipitates one of the ions but not the other. From Table 17.2, we find that $\text{Mg}(\text{OH})_2$ has a K_{sp} of 4.68×10^{-6} and that $\text{Ca}(\text{OH})_2$ has a K_{sp} of 4.68×10^{-6} , indicating that the hydroxide ion forms a precipitate with magnesium at a much lower concentration than it does with calcium. Consequently, a soluble hydroxide—such as KOH or NaOH—is a good choice for the precipitating reagent. When we add an appropriate amount of KOH or NaOH to seawater, the hydroxide ion causes the precipitation of $\text{Mg}(\text{OH})_2$ (the compound with the lowest K_{sp} but not $\text{Ca}(\text{OH})_2$). Calculations for this selective precipitation are shown in Examples 17.13 and 17.14. In these calculations, we compare Q to K_{sp} to determine the concentration that triggers precipitation.

For selective precipitation to work, K_{sp} values must differ by at least a factor of 10^3 .

Example 17.13 Finding the Minimum Required Reagent Concentration for Selective Precipitation

The magnesium and calcium ions present in seawater ($[\text{Mg}^{2+}] = 0.059 \text{ M}$ and $[\text{Ca}^{2+}] = 0.011 \text{ M}$) can be separated by selective precipitation with KOH. What minimum $[\text{OH}^-]$ triggers the precipitation of the Mg^{2+} ion?

SOLUTION The precipitation commences when the value of Q for the precipitating compound just equals the value of K_{sp} . Set the expression for Q for magnesium hydroxide equal to the value of K_{sp} , and solve for $[\text{OH}^-]$. This is the concentration above which $\text{Mg}(\text{OH})_2$ precipitates.

$$\begin{aligned}
 Q &= [\text{Mg}^{2+}] [\text{OH}^-]^2 \\
 &= (0.059) [\text{OH}^-]^2
 \end{aligned}$$

When $Q = K_{\text{sp}}$,

$$(0.059) [\text{OH}^-]^2 = K_{\text{sp}} = 2.06 \times 10^{-13}$$

$$\begin{aligned}
 [\text{OH}^-]^2 &= \frac{2.06 \times 10^{-13}}{0.059} \\
 [\text{OH}^-] &= 1.9 \times 10^{-6} \text{M}
 \end{aligned}$$

FOR PRACTICE 17.13 If the concentration of Mg^{2+} in the solution in **Example 17.13** were 0.025 M, what minimum $[\text{OH}^-]$ triggers precipitation of the Mg^{2+} ion?

Example 17.14 Finding the Concentrations of Ions Left in Solution after Selective Precipitation

You add potassium hydroxide to the solution in **Example 17.13**. When the $[\text{OH}^-]$ reaches $1.9 \times 10^{-6} \text{M}$ (as you just calculated), magnesium hydroxide begins to precipitate out of solution. As you continue to add KOH, the magnesium hydroxide continues to precipitate. At some point, the $[\text{OH}^-]$ becomes high enough to begin to precipitate the calcium ions as well. What is the concentration of Mg^{2+} when Ca^{2+} begins to precipitate?

SOLUTION First, calculate the OH^- concentration at which Ca^{2+} begins to precipitate by writing the expression for Q for calcium hydroxide and substituting the concentration of Ca^{2+} from **Example 17.13**.

$$\begin{aligned}
 Q &= [\text{Ca}^{2+}] [\text{OH}^-]^2 \\
 &= (0.011) [\text{OH}^-]^2
 \end{aligned}$$

Set the expression for Q equal to the value of K_{sp} for calcium hydroxide and solve for $[\text{OH}^-]$. $\text{Ca}(\text{OH})_2$ precipitates above this concentration.

$$\begin{aligned}
 \text{When } Q &= K_{\text{sp}}, \\
 (0.011) [\text{OH}^-]^2 &= K_{\text{sp}} = 4.68 \times 10^{-6} \\
 [\text{OH}^-]^2 &= \frac{4.68 \times 10^{-6}}{0.011} \\
 [\text{OH}^-] &= 2.06 \times 10^{-2} \text{M}
 \end{aligned}$$

Find the concentration of Mg^{2+} when OH^- reaches the concentration you just calculated by writing the expression for Q for magnesium hydroxide and substituting the concentration of OH^- that you just calculated. Then set the expression for Q equal to the value of K_{sp} for magnesium hydroxide and solve for $[\text{Mg}^{2+}]$. This is the concentration of Mg^{2+} that remains when $\text{Ca}(\text{OH})_2$ begins to precipitate.

$$\begin{aligned}
 Q &= [\text{Mg}^{2+}] [\text{OH}^-]^2 \\
 &= [\text{Mg}^{2+}] (2.06 \times 10^{-2})^2 \\
 \text{when } Q &= K_{\text{sp}}, \\
 [\text{Mg}^{2+}] (2.06 \times 10^{-2})^2 &= K_{\text{sp}} = 2.06 \times 10^{-13} \\
 [\text{Mg}^{2+}] &= \frac{2.06 \times 10^{-13}}{(2.06 \times 10^{-2})^2} \\
 [\text{Mg}^{2+}] &= 4.9 \times 10^{-10} \text{M}
 \end{aligned}$$

As you can see from the results, the selective precipitation worked very well. The concentration of Mg^{2+} dropped from 0.059 M to $4.9 \times 10^{-10} \text{M}$ before any calcium began to precipitate, which means that 99.99% of the magnesium separated out of the solution.

of the magnesium separated out of the solution.

FOR PRACTICE 17.14 A solution is 0.085 M in Pb^{2+} and 0.025 M in Ag^{+} . (a) If selective precipitation is to be achieved using NaCl, what minimum concentration of NaCl do you need to begin to precipitate the ion that precipitates first? (b) What is the concentration of each ion left in solution at the point when the second ion begins to precipitate?

Not for Distribution

Not for Distribution