

## 7.4: Criteria for Precipitation and its Completeness

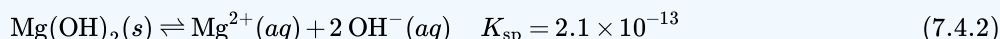
The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:



We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient ( $Q = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$ ) is equal to the solubility product ( $K_{\text{sp}} = 4.8 \times 10^{-9}$ ). If we mix a solution of calcium nitrate, which contains  $\text{Ca}^{2+}$  ions, with a solution of sodium carbonate, which contains  $\text{CO}_3^{2-}$  ions, the slightly soluble ionic solid  $\text{CaCO}_3$  will precipitate, provided that the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions are such that  $Q$  is greater than  $K_{\text{sp}}$  for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of  $Q$  equals  $K_{\text{sp}}$ . A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that  $Q$  is less than  $K_{\text{sp}}$ , then the solution is not saturated and no precipitate will form.

We can compare numerical values of  $Q$  with  $K_{\text{sp}}$  to predict whether precipitation will occur, as Example 7.4.7 shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

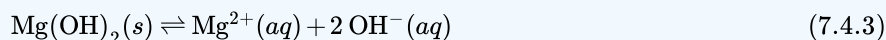
The first step in the preparation of magnesium metal is the precipitation of  $\text{Mg}(\text{OH})_2$  from sea water by the addition of lime,  $\text{Ca}(\text{OH})_2$ , a readily available inexpensive source of  $\text{OH}^-$  ion:



The concentration of  $\text{Mg}^{2+}(aq)$  in sea water is 0.0537 M. Will  $\text{Mg}(\text{OH})_2$  precipitate when enough  $\text{Ca}(\text{OH})_2$  is added to give a  $[\text{OH}^-]$  of 0.0010 M?

### Solution

This problem asks whether the reaction:



shifts to the left and forms solid  $\text{Mg}(\text{OH})_2$  when  $[\text{Mg}^{2+}] = 0.0537 \text{ M}$  and  $[\text{OH}^-] = 0.0010 \text{ M}$ . The reaction shifts to the left if  $Q$  is greater than  $K_{\text{sp}}$ . Calculation of the reaction quotient under these conditions is shown here:

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8} \quad (7.4.4)$$

Because  $Q$  is greater than  $K_{\text{sp}}$  ( $Q = 5.4 \times 10^{-8}$  is larger than  $K_{\text{sp}} = 2.1 \times 10^{-13}$ ), we can expect the reaction to shift to the left and form solid magnesium hydroxide.  $\text{Mg}(\text{OH})_2(s)$  forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of  $Q$  is equal to  $K_{\text{sp}}$ .

### ? Exercise 7.4.1

Use the solubility products in Appendix J to determine whether  $\text{CaHPO}_4$  will precipitate from a solution with  $[\text{Ca}^{2+}] = 0.0001 \text{ M}$  and  $[\text{HPO}_4^{2-}] = 0.001 \text{ M}$ .

### Answer

No precipitation of  $\text{CaHPO}_4$ ;  $Q = 1 \times 10^{-7}$ , which is less than  $K_{\text{sp}}$

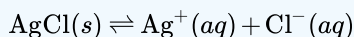
### ✓ Precipitation of AgCl upon Mixing Solutions

Does silver chloride precipitate when equal volumes of a  $2.0 \times 10^{-4} \text{ M}$  solution of  $\text{AgNO}_3$  and a  $2.0 \times 10^{-4} \text{ M}$  solution of  $\text{NaCl}$  are mixed?

(Note: The solution also contains  $\text{Na}^+$  and  $\text{NO}_3^-$  ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

### Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:



The solubility product is  $1.8 \times 10^{-10}$  (see Appendix J).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of AgNO<sub>3</sub> and NaCl is greater than  $K_{sp}$ . The volume doubles when we mix equal volumes of AgNO<sub>3</sub> and NaCl solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing, [Ag<sup>+</sup>] and [Cl<sup>-</sup>] are both equal to:

$$\frac{1}{2}(2.0 \times 10^{-4}) M = 1.0 \times 10^{-4} M$$

The reaction quotient,  $Q$ , is *momentarily* greater than  $K_{sp}$  for AgCl, so a supersaturated solution is formed:

$$Q = [\text{Ag}^+][\text{Cl}^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sp}$$

Since supersaturated solutions are unstable, AgCl will precipitate from the mixture until the solution returns to equilibrium, with  $Q$  equal to  $K_{sp}$ .

### ? Exercise 7.4.2

Will KClO<sub>4</sub> precipitate when 20 mL of a 0.050-M solution of K<sup>+</sup> is added to 80 mL of a 0.50-M solution of ClO<sub>4</sub><sup>-</sup>? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

**Answer**

No,  $Q = 4.0 \times 10^{-3}$ , which is less than  $K_{sp} = 1.07 \times 10^{-2}$

In the previous two examples, we have seen that Mg(OH)<sub>2</sub> or AgCl precipitate when  $Q$  is greater than  $K_{sp}$ . In general, when a solution of a soluble salt of the M<sup>m+</sup> ion is mixed with a solution of a soluble salt of the X<sup>n-</sup> ion, the solid, M<sub>p</sub>X<sub>q</sub> precipitates if the value of  $Q$  for the mixture of M<sup>m+</sup> and X<sup>n-</sup> is greater than  $K_{sp}$  for M<sub>p</sub>X<sub>q</sub>. Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

### ✓ Precipitation of Calcium Oxalate

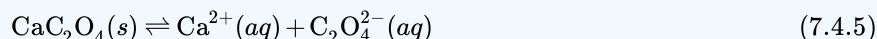
Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, for this purpose (Figure 7.4.4). At sufficiently high concentrations, the calcium and oxalate ions form solid, CaC<sub>2</sub>O<sub>4</sub>•H<sub>2</sub>O (which also contains water bound in the solid). The concentration of Ca<sup>2+</sup> in a sample of blood serum is  $2.2 \times 10^{-3} M$ . What concentration of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ion must be established before CaC<sub>2</sub>O<sub>4</sub>•H<sub>2</sub>O begins to precipitate?



Figure 7.4.4: Anticoagulants can be added to blood that will combine with the Ca<sup>2+</sup> ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

**Solution**

The equilibrium expression is:



For this reaction:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2.27 \times 10^{-9} \quad (7.4.6)$$

(see Appendix J)

$\text{CaC}_2\text{O}_4$  does not appear in this expression because it is a solid. Water does not appear because it is the solvent.

Solid  $\text{CaC}_2\text{O}_4$  does not begin to form until  $Q$  equals  $K_{\text{sp}}$ . Because we know  $K_{\text{sp}}$  and  $[\text{Ca}^{2+}]$ , we can solve for the concentration of  $\text{C}_2\text{O}_4^{2-}$  that is necessary to produce the first trace of solid:

$$\begin{aligned} Q = K_{\text{sp}} &= [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2.27 \times 10^{-9} \\ (2.2 \times 10^{-3})[\text{C}_2\text{O}_4^{2-}] &= 2.27 \times 10^{-9} \\ [\text{C}_2\text{O}_4^{2-}] &= \frac{2.27 \times 10^{-9}}{2.2 \times 10^{-3}} = 1.0 \times 10^{-6} \end{aligned}$$

A concentration of  $[\text{C}_2\text{O}_4^{2-}] = 1.0 \times 10^{-6} \text{ M}$  is necessary to initiate the precipitation of  $\text{CaC}_2\text{O}_4$  under these conditions.

### ? Exercise 7.4.3

If a solution contains 0.0020 mol of  $\text{CrO}_4^{2-}$  per liter, what concentration of  $\text{Ag}^+$  ion must be reached by adding solid  $\text{AgNO}_3$  before  $\text{Ag}_2\text{CrO}_4$  begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer:

$$7.0 \times 10^{-5} \text{ M}$$

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of  $K_{\text{sp}}$  and the concentration of one ion in solution, we can calculate the concentration of the second ion remaining in solution. The calculation is of the same type as that in Example—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

### ✓ Concentrations Following Precipitation

Clothing washed in water that has a manganese  $[\text{Mn}^{2+}(aq)]$  concentration exceeding 0.1 mg/L ( $1.8 \times 10^{-6} \text{ M}$ ) may be stained by the manganese upon oxidation, but the amount of  $\text{Mn}^{2+}$  in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide,  $\text{Mn}(\text{OH})_2$ , what pH is required to keep  $[\text{Mn}^{2+}]$  equal to  $1.8 \times 10^{-6} \text{ M}$ ?

**Solution** The dissolution of  $\text{Mn}(\text{OH})_2$  is described by the equation:



We need to calculate the concentration of  $\text{OH}^-$  when the concentration of  $\text{Mn}^{2+}$  is  $1.8 \times 10^{-6} \text{ M}$ . From that, we calculate the pH. At equilibrium:

$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{OH}^-]^2 \quad (7.4.8)$$

or

$$(1.8 \times 10^{-6})[\text{OH}^-]^2 = 4.5 \times 10^{-14} \quad (7.4.9)$$

so

$$[\text{OH}^-] = 1.6 \times 10^{-4} \text{ M} \quad (7.4.10)$$

Now we calculate the pH from the pOH:

$$\begin{aligned}\text{pOH} &= -\log[\text{OH}^-] = -\log(1.6 \times 10^{-4}) = 3.80 \\ \text{pH} &= 14.00 - \text{pOH} = 14.00 - 3.80 = 10.20\end{aligned}$$

If the person doing laundry adds a base, such as the sodium silicate ( $\text{Na}_4\text{SiO}_4$ ) in some detergents, to the wash water until the pH is raised to 10.20, the manganese ion will be reduced to a concentration of  $1.8 \times 10^{-6} \text{ M}$ ; at that concentration or less, the ion will not stain clothing.

### ? Exercise 7.4.4

The first step in the preparation of magnesium metal is the precipitation of  $\text{Mg}(\text{OH})_2$  from sea water by the addition of  $\text{Ca}(\text{OH})_2$ . The concentration of  $\text{Mg}^{2+}(\text{aq})$  in sea water is  $5.37 \times 10^{-2} \text{ M}$ . Calculate the pH at which  $[\text{Mg}^{2+}]$  is diminished to  $1.0 \times 10^{-5} \text{ M}$  by the addition of  $\text{Ca}(\text{OH})_2$ .

### Answer

11.09

Due to their light sensitivity, mixtures of silver halides are used in fiber optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though  $\text{AgCl}$  ( $K_{\text{sp}} = 1.6 \times 10^{-10}$ ),  $\text{AgBr}$  ( $K_{\text{sp}} = 7.7 \times 10^{-13}$ ), and  $\text{AgI}$  ( $K_{\text{sp}} = 8.3 \times 10^{-17}$ ) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding  $\text{Ag}^+$  to a solution of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ; essentially all of the  $\text{AgI}$  will precipitate before any of the other solid halides form because of its smaller value for  $K_{\text{sp}}$ . However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  to a solution of  $\text{Ag}^+$ .

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller  $K_{\text{sp}}$ ) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the  $K_{\text{sp}}$  values of the two compounds differ by two orders of magnitude or more (e.g.,  $10^{-2}$  vs.  $10^{-4}$ ), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of selective precipitation, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.



Determining if a Precipitate forms (The Ion Product): <https://youtu.be/Naf7PoHPz8Y>

### Summary

A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product. A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution. The common ion effect can also play a role in precipitation reactions. In the presence of an ion in common with one of the ions in the solution, Le Chatelier's principle applies and more precipitate comes out of solution so that the molar solubility is reduced.

## Glossary

**common ion effect**

effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

**molar solubility**

solubility of a compound expressed in units of moles per liter (mol/L)

**selective precipitation**

process in which ions are separated using differences in their solubility with a given precipitating reagent

**solubility product ( $K_{sp}$ )**

equilibrium constant for the dissolution of a slightly soluble electrolyte

## Contributors and Attributions

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