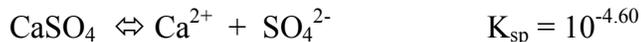


## Mineral Solubility Questions

The solubility product ( $K_{sp}$ ) of a solid has an important function: it tells us whether the solid will dissolve, and if so the resulting concentrations, or precipitate. If we know the solid is present and in contact with a water body, we can use the solubility product to determine the dissolved concentration of the solid's constituents assuming it has reached equilibrium. Conversely, if we want to know whether that specific mineral might form (precipitate) from a solution, we can measure the dissolved concentration of the solid's components and, with the correct stoichiometries, determine if the solid is expected to form (precipitate).

In the examples below we will assume the activities (a) equal concentrations [C]. Note, however, that this is incorrect except for very dilute solutions and that we need to calculate activity coefficients ( $\gamma$ ) to move between activity and concentration.

**Example Question 1, Gypsum Solubility.** Gypsum (formally  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , but written below simply as  $\text{CaSO}_4$ ) is a common solid found in salty irrigation water. If gypsum was the primary Ca solid in contact with a water body (a pond, for example), what concentration of calcium would be in the water?

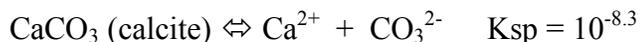


**Example Question 2a, Cinnabar Dissolution.** What would be the expected concentration of mercury in a pond if cinnabar were the controlling solid phase.



**Example Question 2b, Cinnabar Dissolution.** What would be the concentration of mercury in the pond if sulfide were introduced from multiple sources (bacterial production, for example) and had a measured concentration of  $[\text{S}^{2-}] = 1 \times 10^{-12} \text{ M}$ .

**Example Question 4, Calcite Precipitation.** You are interested in whether calcium carbonate, as calcite, will form on your facet as a result of the water composition. After having the water tested, you find that  $(\text{Ca}^{2+}) = 10^{-3} \text{ M}$  and  $(\text{CO}_3^{2-}) = 10^{-4} \text{ M}$ . Determine with you would expect calcite to precipitate in this water given the reaction



## Mineral Solubility Answer Sheet

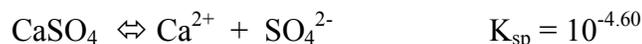
The solubility product ( $K_{sp}$ ) of a solid has an important function: it tells us whether the solid will dissolve, and if so the resulting concentrations, or precipitate. If we know the solid is present and in contact with a water body, we can use the solubility product to determine the dissolved concentration of the solid's constituents assuming it has reached equilibrium. Conversely, if we want to know whether that specific mineral might form (precipitate) from a solution, we can measure the dissolved concentration of the solid's components and, with the correct stoichiometries, determine if the solid is expected to form (precipitate).

In the examples below we will assume the activities ( ) equal concentrations [ ]. Note, however, that this is incorrect except for very dilute solutions and that we need to calculate activity coefficients ( $\gamma$ ) to move between activity and concentration.

**Example Question 1, Gypsum Solubility.** Gypsum (formally  $\text{CaSO}_4\cdot\text{H}_2\text{O}$ , but written below simply as  $\text{CaSO}_4$ ) is a common solid found in salty irrigation water. If gypsum was the primary Ca solid in contact with a water body (a pond, for example), what concentration of calcium would be in the water?

Solution:

First, we need to write the reaction for gypsum dissolution/precipitation (note that solubility products are usually expressed as a solid dissociation reaction).



Now we can write the mass action expression.

$$K_{sp} = \frac{(\text{Ca}^{2+})(\text{SO}_4^{2-})}{(\text{CaSO}_4)_{gyp}}$$

The activity of a solid is unity, by convention, and thus we have only two variables. Without any other source of calcium or sulfate, we will have congruent dissolution and equal amounts of each ion dissolving from the solid.

As a result, we have

$$\begin{aligned} (\text{Ca}^{2+}) &= (\text{SO}_4^{2-}) \\ (\text{Ca}^{2+})^2 &= 10^{-4.60} \end{aligned}$$

And we can now solve the question.

$$\begin{aligned} (\text{Ca}^{2+}) &= 5.01 \times 10^{-3} \\ \text{and } (\text{SO}_4^{2-}) &= 5.01 \times 10^{-3} \end{aligned}$$

(The concentration of calcium, expressed as square brackets, would be  $[Ca^{2+}] = (Ca^{2+})/\gamma^2$ , where  $\gamma^2$  is the activity coefficient for a divalent ion.)

**Example Question 2a, Cinnabar Dissolution.** What would be the expected concentration of mercury in a pond if cinnabar were the controlling solid phase.

Solution:

Again, starting with the dissolution/precipitation reaction



And then moving to the mass action expression.

$$K_{sp} = (Hg^{2+})(S^{2-})$$

Because the activity of the solid is 1, it was omitted from the mass action expression.

And, again, with no other ions in solution we have the relationship

$$\begin{aligned} (Hg^{2+}) &= (S^{2-}) \\ (Hg^{2+})^2 &= 1 \times 10^{-53} \\ (Hg^{2+}) &= 3.16 \times 10^{-27} = (S^{2-}) \text{ right?} \end{aligned}$$

**Example Question 2b, Cinnabar Dissolution.** What would be the concentration of mercury in the pond if sulfide were introduced from multiple sources (bacterial production, for example) and had a measured concentration of  $[S^{2-}] = 1 \times 10^{-12}$  M.

We can skip directly to the mass action expression, with

$$(Hg^{2+})(1 \times 10^{-12}) = 10^{-53}$$

Thus,

$$(Hg^{2+}) = 1 \times 10^{-41}$$

The example above demonstrates the extremely low concentration of  $Hg^{2+}$  that results from cinnabar dissolution. However, it gives us a misleading picture of the total dissolved mercury that may reside in a water because it ignores other forms of dissolved mercury. Aqueous complexes (cation-anion associations) of mercury may be the dominant species in many water bodies and thus need to be accounted for.

**Example 3, Contribution of Ion Complexes.** What would be the concentration of mercury in the form of  $HgS_2H^-$  within a marine systems having cinnabar present and  $(HS^-) = 2 \times 10^{-4}$  M (at pH 8, this is the dominant form of sulfide). The reaction of bisulfide with cinnabar is:



Solution:

From the reaction, we derive the mass action express,

$$K_2 = \frac{(HgSH^-)}{(HS^-)(HgS)}$$

Again, the activity of a solid is set at 1, simplifying the expression.

$$K_2 = \frac{(HgSH^-)}{(HS^-)}$$

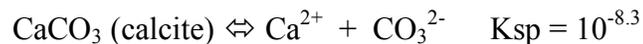
This leads to

$$\begin{aligned} (HgS_2H^-) &= (2 \times 10^{-4}) (10^{-4.82}) \\ &= 3.03 \times 10^{-9} \end{aligned}$$

Note the wildly different concentration of mercury species resulting between questions 2 and 3.

One last example question, now turning to mineral precipitation.

**Example Question 4, Calcite Precipitation.** You are interested in whether calcium carbonate, as calcite, will form on your facet as a result of the water composition. After having the water tested, you find that  $(Ca^{2+}) = 10^{-3}$  M and  $(CO_3^{2-}) = 10^{-4}$  M. Determine with you would expect calcite to precipitate in this water given the reaction



Solution:

From the mass action expression, we write

$$K_{sp} = (Ca^{2+}) (CO_3^{2-})$$

If we measure the activity of calcium and carbonate, we can find the ion activity product (IAP) for calcite (this is simply the expression of the current conditions relative to that expected at equilibrium)

$$\begin{aligned} \text{IAP} &= (\text{Ca}^{2+}) (\text{CO}_3^{2-}) \\ &= (10^{-3}) (10^{-4}) \\ &= 10^{-7} \end{aligned}$$

The  $K_{sp}$  represents the concentrations that result if the water is in equilibrium with the solid. If the IAP is less than the  $K_{sp}$ , the mineral should dissolve. If the IAP is greater than the  $K_{sp}$ , then the concentrations must decrease via mineral precipitation. In the present case, the IAP ( $10^{-7}$ ) >  $K_{sp}$  ( $10^{-8.3}$ ) and so calcite can, indeed, precipitate.