

Units 3 – K_{sp} – Solubility Product constant – How well does a compound dissolve?

Part II: Equilibrium

- ✓ What is equilibrium in terms of physical and chemical systems?
- ✓ Writing Equilibrium law expressions from a balanced chemical equation (mass action expressions)
- ✓ What is K_{eq} and relate how K_{eq} provides information on a system achieving equilibrium.
- ✓ Determining the equilibrium constant via lab
- ✓ Le Chatelier's Principle to predict shifts in equilibrium.
- ✓ Concentration vs time graphs in systems achieving and have reached equilibrium
- ✓ K_{sp} expressions from balanced chemical equations for salts with low solubility
- ✓ Solve problems with K_{sp} including common ions
- ✓ Predicting whether a precipitate will form.

Part II: Equilibrium

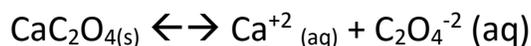
Solubility Product (K_{sp}) & Common Ion effect Notes

- ✓ K_{sp} expressions from balanced chemical equations for salts with low solubility
 - ✓ Solve problems with K_{sp} including common ions
 - ✓ Q_{sp} and K_{sp} – Predicting precipitates

Solubility Product

In general, when ionic compounds dissolve in **pure water**, they go into solution as ions. When the solution becomes **saturated** with ions, that is, unable to hold any more, the excess solid settles to the bottom of the container and an equilibrium is established between the undissolved solid and the dissolved ions. Remember, a saturated solution is the maximum amount of the compound that a solution can hold, it does not necessarily mean that the compound will be completely dissociated into solution.

For example, when enough calcium oxalate is introduced into pure water solution for it to become saturated, the following equilibrium is established.



The K_{sp} (**S**olubility **P**roduct constant) is written as:

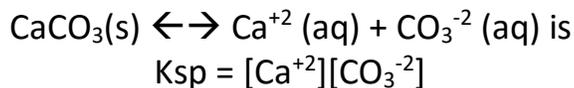
$$K_{\text{sp}} = [\text{Ca}^{+2}][\text{C}_2\text{O}_4^{-2}]$$

Notice that the expression is very similar to the K_{eq} (Law of Mass action) expression that it is a ratio between products and reactants. There are no units, nor a denominator because solids are not included in the K_{sp} expression. K_{sp} expression is simply the **concentration** of the dissociated ions *multiplied* to each other.

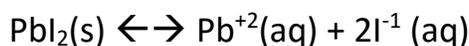
In general, the **Solubility Product, K_{sp}** , is the *equilibrium constant for the solubility equilibrium of a slightly soluble compound*. In other words, how well a compound will dissociate will depend on the K_{sp} constant. A **larger** K_{sp} will represent a **larger** number of ions dissociated, or a very **soluble** compound, while a **small** K_{sp} value would mean a very **insoluble** or **slightly soluble** compound (two small concentrations multiplied to each other).

It also noteworthy, that, just like any equilibrium expression, each ion concentration in the expression is raised to the power of its coefficient in the solubility equation.

For example, the K_{sp} expression for:



but for the equation:



$$K_{sp} = [\text{Pb}^{+2}][\text{I}^{-1}]^2$$

Note that the concentration of the iodide ion is squared.

Calculations for K_{sp} :

Calculations involving K_{sp} are simpler than for previous equilibrium calculations because the reactant is a solid and therefore omitted from the equilibrium expression. There are really only two types of problems that need to be solved:

- a) calculating K_{sp} from solubility data or
- b) calculating solubility from K_{sp}

1) Calculating K_{sp} from solubility data (solubility)

Ex. 100 mL of a saturated PbI_2 solution was found to contain $5.23 \times 10^{-2}\text{g PbI}_2(\text{s})$.

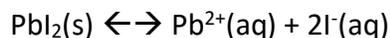
Calculate K_{sp}

1. Notice you are provided with the mass of the precipitate formed in the solution, hence the solid measured in grams.
2. The first step is to calculate the molarity of the compound. But since molarity is $M = n/L$, we need to calculate for moles first.
 - a. Moles of $\text{PbI}_2 = 1.29 \times 10^{-4}\text{mol}$
 - b. Molarity of $\text{PbI}_2 = 1.29 \times 10^{-4}\text{mol}/0.1\text{L} = 1.29 \times 10^{-3}\text{M}$
3. Now write the K_{sp} expression:



$$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2 \quad \text{*Notice the exponent and the 2 in front of the iodide ion}$$

4. In order to calculate the concentrations of the ion, use stoichiometry to find the concentrations of the ions.



$$[\text{PbI}_2] = [\text{Pb}^{2+}] = 1.29 \times 10^{-3}\text{M}$$

$$[\text{I}^{-}] = 2 \times [\text{Pb}^{2+}] = 2 (1.29 \times 10^{-3}\text{M}) = 2.58 \times 10^{-3} \text{ M} \quad \text{*Use stoichiometry to calculate I}^{-}\text{ ion.}$$

5. Now plug into the Ksp expression:

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^{-}]^2$$

$$K_{\text{sp}} = (1.29 \times 10^{-3}\text{M}) (2.58 \times 10^{-3} \text{ M})^2 \quad \text{(Remember the [I}^{-}\text{] was multiplied by 2)}$$

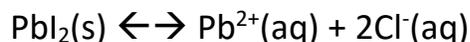
$$K_{\text{sp}} = 8.59 \times 10^{-9}\text{M of PbI}_2$$

What does this number mean? Since it is an extremely small number, the concentration of the ions is very small, thus, it is *not* a very soluble compound.

Ex. 2. What is the molar solubility of PbCl_2 if the K_{sp} of PbCl_2 is 1.8×10^{-4} ?

In this question, you are given the K_{sp} , and asked to calculate the molar solubility, which is the molarity (concentration) of the solution.

1. Write out the Ksp expression:



$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 \quad \text{*Don't forget to multiply by 2 for the Cl}^{-}$$

Since we are not given any concentration and in fact are asked to calculate for the concentrations, use "x" be the unknown molarity concentration.

$$K_{\text{sp}} [\text{x}][2\text{x}]^2 \quad \text{*Don't forget to multiply by 2 for the Cl}^{-}$$

Substitute equilibrium values into Ksp expression.

$$1.8 \times 10^{-4} = 4\text{x}^3$$

Solve for x (you will have to take the cube root)

$$\text{x} = 0.0356 \text{ M}$$

Therefore, the molar solubility of PbCl_2 is **0.0356M**. This is the concentration of PbCl_2 found in a 1L solution.

Ex 3. What is the $[Ag^+]$ in a saturated solution of Ag_2CO_3 ?

In this question, you are provided with a compound but with no K_{sp} . This is when you have to look up the value from the K_{sp} table.

1. First, the K_{sp} is needed so lookup the value of K_{sp} :

$$K_{sp} \text{ of } Ag_2CO_3 = 8.5 \times 10^{-12}$$

Now with the K_{sp} value, we can calculate the molarity.

2. Next, write out the dissociation equation and the K_{sp} expression:



$$K_{sp} = [Ag^+]^2 [CO_3^{2-}]$$

3. Let x be the molar solubility of Ag_2CO_3

$$[Ag^+] = 2x \text{ and } [CO_3^{2-}] = x$$

Substitute equilibrium values into K_{sp} expression.

$$K_{sp} = (2x)^2(x)$$

$$K_{sp} = 4x^3 = 8.5 \times 10^{-12}$$

$x = 1.29 \times 10^{-4} \text{ mol/L}$ At this step, this is the same as the previous example but since this question is asking for the concentration of Silver ion, we need to substitute the x value back into Ag^+ .

$$[Ag^+] = 2x = 2(1.29 \times 10^{-4} \text{ mol/L}) = \mathbf{2.57 \times 10^{-4} \text{ mol/L for Silver ion.}}$$

Try these:

The molar solubility (Molarity) of Ag_2S is $1.3 \times 10^{-17} \text{ M}$. What is the K_{sp} for Ag_2S ?

$$\text{Ans: } K_{sp} = 4(1.3 \times 10^{-17})^3 = 8.8 \times 10^{-51}$$

The value of K_{sp} for $AgCl$ is 1.8×10^{-10} . What is the molar solubility of $AgCl$?

$$\text{Ans: } X = 1.3 \times 10^{-5} \text{ M}$$

Common Ion Effect!

What is it?

Here's a scenario, you decided to make a solution of BaF_2

Net ionic equation: $\text{BaF}_{2(s)} \rightleftharpoons \text{Ba}^{2+}_{(aq)} + 2\text{F}^{-}_{(aq)}$

We know from Le Chatelier's principle that if we were to add more Fluoride ions, it will shift the reaction to the left to make more of the solid.

What if we were to add **NaF** into the same solution? How does the addition of **NaF** affect the solution? Since NaF will dissociate into Na^+ and F^- , it will add more F^- ions into the solution, thus affecting the equilibrium. The F^- is the *common ion* because it is the same ion that is already in the solution.

As a result, adding NaF into the solution will ultimately affect the equilibrium by adding more stress to the product side, and shifting the equilibrium to the left.

Here is an example of a basic K_{sp} calculation and the effects of bringing in a common ion.

Ex1a.

Calculate the molar solubility (M) of barium fluoride, BaF_2 , in water at 25C. The K_{sp} at 25C is 1.0×10^{-6} .



$$K_{sp} = [\text{Ba}^{2+}][\text{F}^{-}]^2 \quad \text{Use } x \text{ for the concentrations}$$

$$1.0 \times 10^{-6} = (x)(2x)^2$$

$$1.0 \times 10^{-6} = 4x^3$$

$$\text{Solve for } x: \quad x \text{ is } 6.30 \times 10^{-3} \text{ M}$$

$6.30 \times 10^{-3} \text{ M}$ is the concentration of BaF_2 AND Ba^{2+} since their molar coefficients are the same.

Now what happens when we dissolve NaF into the SAME solution?

Ex1b.

What is the molar solubility (M) of barium fluoride in a solution that is 0.15 M NaF at 25C

So in this question, you are asked to calculate the molarity of BaF_2 in a solution with 0.15M of NaF. The F^- in this case will be the common ion.

Since we already have a 0.15M of F^- ions, we must add the concentration into our equilibrium concentrations:



“x” “2x + 0.15” Add the 0.15M from NaF
(at equilibrium)

$$K_{sp} = [\text{Ba}^{2+}] [\text{F}^{-}]^2$$

Here is the trick to common ion problems:

Since Barium Fluoride (BaF_2) is slightly soluble (small k_{sp} compared to 0.15M), so we can neglect the 2x. We have to do this in order to make the calculations easier.

$$K_{sp} = [\text{Ba}^{2+}] [\text{F}^{-}]^2$$

$$1.0 \times 10^{-6} = (x) (0.15)^2 \quad \text{We neglect the 2x because that is the common ion concentration.}$$

$$x = 4.44 \times 10^{-5} \text{ M} \quad \text{You can see that 'x' is a lot smaller than 0.15M, so our assumption was safe.}$$

What did we just solve?

The concentration of BaF_2 is $4.44 \times 10^{-5} \text{ M}$ in the presence of NaF.

However, in pure water solution, the concentration of BaF_2 is $6.3 \times 10^{-3} \text{ M}$ (from calculation ex.1a).

Does this make sense?

Yes it does! When NaF is added, the common F^- ion is the added stress to the equilibrium, to alleviate the stress, Le Chatelier suggests that the reaction will shift to the reactants making more of the solid BaF_2 . This would make more solid and less dissociation!

So would it be better to dissolve it pure water or in NaF solution?

Another example:

Calculate the molarity of silver chloride in a 1.5×10^{-3} mol/L silver nitrate solution. K_{sp} for AgCl is 1.6×10^{-10} .

Step 1: Recognize that the question is asking for AgCl. Always solve for the one with the K_{sp} provided. Don't get confused with Silver nitrate. We only need silver nitrate for its concentration. Silver in this case is the common ion.



Step 2: Write the K_{sp} expression for Silver chloride:

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

Step 3: Identify the concentrations of Ag^{+} and Cl^{-}

$[\text{Ag}^{+}] = 1.5 \times 10^{-3} \text{M}$ from silver nitrate but because AgCl is being added, there is an unknown amount of Ag^{+} , which we will call "x".

Therefore, $[\text{Ag}^{+}] = 1.5 \times 10^{-3} \text{M} + x$

$$[\text{Cl}^{-}] = "x"$$

Step 4: Write the K_{sp} expression

$$\begin{aligned} 1.6 \times 10^{-10} &= [1.5 \times 10^{-3} \text{M} + x][x] \\ &\text{(ignore the x from Ag}^{+}\text{)} \\ x &= 1.1 \times 10^{-7} \text{M} \end{aligned}$$

$$[\text{AgCl}] = 1.1 \times 10^{-7} \text{M}$$

The molar solubility of silver chloride in a $1.5 \times 10^{-3} \text{M}$ silver nitrate solution is $1.1 \times 10^{-7} \text{M}$.