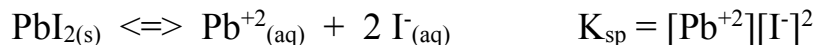# CH 223 Guide to Solubility Calculations

The extent to which an insoluble salt dissolves can be expressed in terms of the equilibrium constant. For lead(II) iodide, the expression can be written as:

$$PbI_{2(s)} \iff Pb^{+2}_{(aq)} + 2\ I^-_{(aq)} \qquad K_{sp} = [Pb^{+2}][I^-]^2$$

The equilibrium constant, K_{sp}, is called the **solubility product constant** or simply the **solubility constant**. The concentration of the solid, $PbI_{2(s)}$, is omitted from the equilibrium expression because it is a constant - all solids and liquids are removed from equilibrium constants.

The solubility of any compound can be observed graphically using the following diagram:
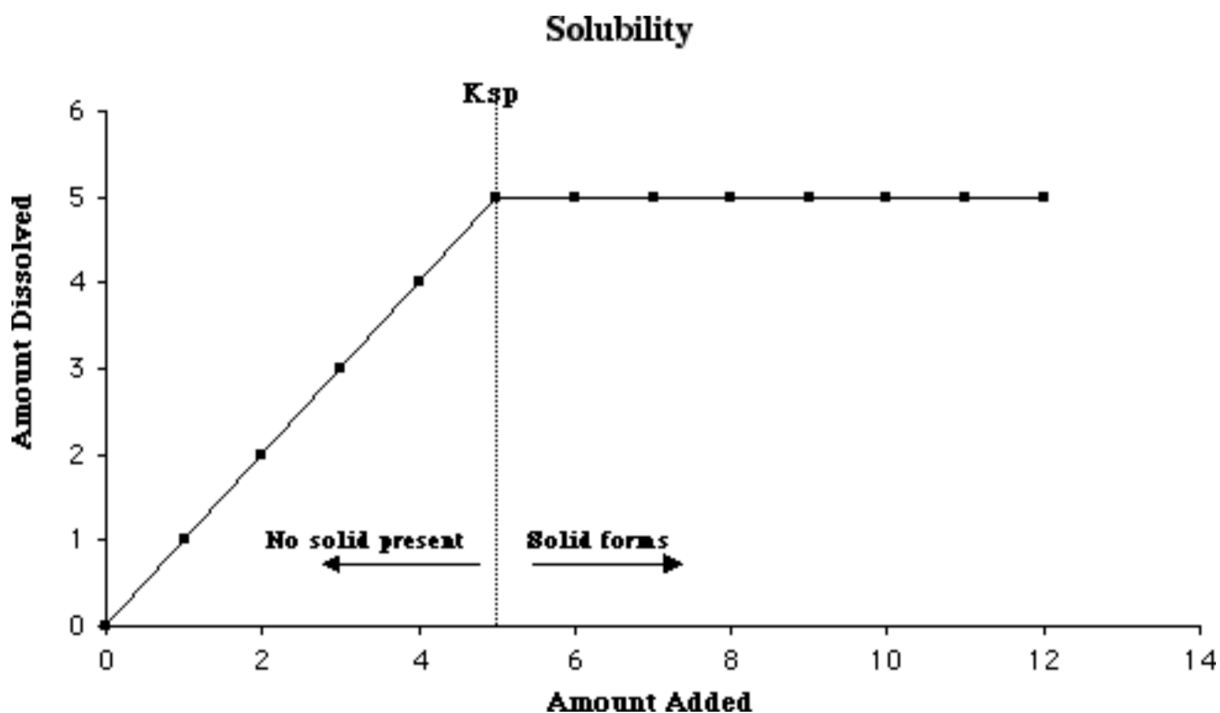
As solid is first introduced to the system, it is immediately dissolved until a certain threshold value is obtained - here referred to as "K_{sp}". Past the threshold, the solid is insoluble in the solution - no more dissolves. Each solvent has a certain capacity to dissolve solute, and the threshold value signifies the limit of the solvent to dissolve the solid solute.

Examples of typical solubility calculations follow.

1. *If 55 mg of lead(II) sulfate are placed in 250. mL of pure water, what mass of the lead compound remains undissolved?*

In a lead(II) sulfate solution, $K_{sp} = 1.8 * 10^{-8}$. The amount that dissolves, x (which is also referred to as the *solubility* of $PbSO_4$), can be expressed using K_{sp}:

$$K_{sp} = [Pb^{2+}][SO_4^{2-}] = x*x = x^2, \text{ and}$$
$$x = (K_{sp})^{0.5} = (1.8*10^{-8})^{0.5} = 1.3*10^{-4} \text{ M}$$

This is the amount that dissolves in solution; i.e. the concentration of both lead(II) ions and sulfate ions will equal $1.3*10^{-4}$ M at equilibrium.

This concentration can be converted to grams:

$$(1.3*10^{-4} \text{ mol ions / L}) * 0.250 \text{ L} * (1 \text{ mol } PbSO_4 / 1 \text{ mol ions}) * (303 \text{ g } PbSO_4 / \text{mol } PbSO_4) =$$
$$0.010 \text{ g} * (10^3 \text{ mg / g}) = \textbf{10. mg } \textbf{PbSO}_4$$

This answer means that 10. mg of lead(II) sulfate will dissolve in 250. mL of water. If 55 mg of lead(II) sulfate are placed in 250. mL of water, only 10. mg will dissolve. Therefore, at equilibrium

$$55 \text{ mg - 10. mg} = \textbf{45 mg undissolved } \textbf{PbSO}_4$$

Note that if only 7 mg of $PbSO_4$ were placed in 250. mL of water, all of it would dissolve. 10. mg is the **threshold** for the $PbSO_4$ system; if less than 10. mg is added, all of it dissolves, and if more than 10. mg is added, only 10. mg of it will dissolve and the remainder will exist as solid precipitate.

2. *A solution contains Ca^{2+} and Pb^{2+} ions, both at a concentration of 0.010 M. If sodium sulfate is added, which metal ion precipitates first? What is the concentration of the first ion to precipitate as the second more soluble ion begins to precipitate?*

The first step is to determine the salts that will be precipitating; these are **CaSO₄** ($K_{sp} = 2.4*10^{-5}$) and **PbSO₄** ($K_{sp} = 1.8*10^{-8}$). To find which one will precipitate first, we need to calculate the concentration of the sulfate ion necessary to initiate precipitation:

> For $PbSO_4$: $[SO_4^{2-}] = K_{sp} / [Pb^{2+}] = 1.8*10^{-8} / 0.010 = \textbf{1.8*10}^{-6} \textbf{ M}$
> For $CaSO_4$: $[SO_4^{2-}] = K_{sp} / [Ca^{2+}] = 2.4*10^{-5} / 0.010 = \textbf{2.4*10}^{-3} \textbf{ M}$

The concentration of sulfate required to precipitate $PbSO_4$ is *much less* than the concentration of sulfate required to precipitate $CaSO_4$; hence, **PbSO₄ will begin to precipitate** out of solution **before CaSO₄ begins to precipitate.**

To calculate the concentration of Pb^{2+} present in solution once $CaSO_4$ begins to precipitate, we need to use the concentrations of sulfate ion determined previously. $[SO_4^{2-}] = 2.4*10^{-3}$ M when $CaSO_4$ begins to precipitate, and we can use this value in the K_{sp} expression for $PbSO_4$:

$$[Pb^{2+}] = K_{sp} / [SO_4^{2-}] = 1.8*10^{-8} / 2.4*10^{-3} \text{ M} = 7.5*10^{-6} \text{ M}$$

Notice how the concentration of lead(II) ions decreased from an initial value of 0.010 M to $7.5*10^{-6}$ M once $CaSO_4$ began to precipitate.

3. *Sodium hydroxide is added dropwise to a solution containing 0.1 M concentrations of Fe^{3+}, Pb^{2+} and Al^{3+}. What is the order by which the hydroxide salts begin to precipitate?*

First, find the K_{sp} values for the relevant hydroxide complexes.

$Fe(OH)_3$: $K_{sp} = 6.3*10^{-38} = [Fe^{3+}][OH^{-1}]^3$
$Pb(OH)_2$: $K_{sp} = 2.8*10^{-16} = [Pb^{2+}][OH^{-1}]^2$
$Al(OH)_3$: $K_{sp} = 1.9*10^{-33} = [Al^{3+}][OH^{-1}]^3$

Next, calculate the concentration of hydroxide necessary to initiate precipitation in each of the salts. Remember to account for the different forms of each K_{sp} expression.

For $Fe(OH)_3$: $[OH^{-1}] = (K_{sp} / [Fe^{3+}])^{1/3} = (6.3*10^{-38} / 0.1)^{1/3} = 8.6*10^{-13}$ M
For $Pb(OH)_2$: $[OH^{-1}] = (K_{sp} / [Pb^{2+}])^{1/2} = (2.8*10^{-16} / 0.1)^{1/2} = 5.3*10^{-8}$ M
For $Al(OH)_3$: $[OH^{-1}] = (K_{sp} / [Al^{3+}])^{1/3} = (1.9*10^{-33} / 0.1)^{1/3} = 2.7*10^{-11}$ M

Fe^{3+} requires the *least* amount of OH^{-1} (only $8.6*10^{-13}$ M!) begin precipitation; hence, **$Fe(OH)_3$ will precipitate first**. The **second ion** to begin precipitating **will be $Al(OH)_3$, followed by $Pb(OH)_2$** which takes the most hydroxide ($5.3*10^{-8}$ M) to begin precipitating.