Solubility Product Constant

In general, when ionic compounds dissolve in 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.

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

$$\text{CaC}_2\text{O}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+} (\text{aq}) + \text{C}_2\text{O}_4^{2−} (\text{aq})$$

If we write an equilibrium expression for this situation, we obtain:

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

Note that the solid itself does not appear as a denominator in the expression since it is a it is not in the same phase as the aqueous ions.

In general, the solubility product constant ($K_{sp}$), is the equilibrium constant for the solubility equilibrium of a slightly soluble ionic compound.

Like all equilibrium constants, the $K_{sp}$ is temperature dependent, but at a given temperature it remains relatively constant.

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 $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+} (\text{aq}) + \text{CO}_3^{2−} (\text{aq})$ is

$$K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2−}]$$

but for the equation $\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+} (\text{aq}) + 2 \text{I}^{−} (\text{aq})$

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

note that the concentration of the iodide ion is squared.

Calculating $K_{sp}$ from the Solubility

Suppose the solubility of silver chloride, AgCl, is $1.9 \times 10^{-3}$ g/L. Calculate its $K_{sp}$.

$$1.9 \times 10^{-3} \text{ grams AgCl} \left(\frac{1 \text{ mole AgCl}}{143.4 \text{ grams AgCl}}\right) = 1.33 \times 10^{-5} \text{ moles AgCl}$$

So, if we were to mix solid AgCl in a liter of solution, $1.33 \times 10^{-5}$ mol will dissolve to form $1.33 \times 10^{-5}$ mol of each ion. If we substitute these equilibrium concentrations into the $K_{sp}$ expression, we obtain;

$$\text{AgCl}_\text{s} \rightleftharpoons \text{Ag}^{+} (\text{aq}) + \text{Cl}^{−} (\text{aq})$$

$$K_{sp} = [\text{Ag}^{+}] [\text{Cl}^{−}] = (1.33 \times 10^{-5}) (1.33 \times 10^{-5}) = 1.76 \times 10^{10}$$
A more complex problem is proposed when the salt we're dissolving contains more than multiples of a given ion.

For example

The solubility of Lead(II)arsenate, \( \text{Pb}_3(\text{AsO}_4)_2 \), is \( 3.0 \times 10^{-5} \) g/L. Calculate its \( K_{sp} \)

\[
3.0 \times 10^{-5} \text{ grams Pb}_3(\text{AsO}_4)_2 \left( \frac{1 \text{ mole Pb(AsO}_4)_2}{899.44 \text{ grams}} \right) = 3.34 \times 10^{-8} \text{ moles Pb(AsO}_4)_2
\]

In this case, however, the equation describing the dissolution of lead arsenate indicates that we obtain twice as many moles of the arsenate ion as we do lead ions.

\[
\text{Pb}_3(\text{AsO}_4)_2(s) \rightleftharpoons 3 \text{ Pb}^{+2} + 2 \text{ AsO}_4^{-3}
\]

So, if we were to mix solid \( \text{Pb}_3(\text{AsO}_4)_2 \) in a liter of solution, \( 3.34 \times 10^{-8} \) mol will dissolve to form

- 3 x (3.34 x 10^-8) mol of the lead ion, or \( 1.00 \times 10^{-7} \) mol of \( \text{Pb}^{+2} \)
- 2 x (3.34 x 10^-8) mol of the arsenate, or \( 6.67 \times 10^{-8} \text{ mol AsO}_4^{-3} \)

In addition to tripling the number of moles of the lead ion and doubling the number of moles of the arsenate ion, you must remember that the lead ion concentration is cubed and the arsenate concentration is squared in the \( K_{sp} \) expression. If we substitute these equilibrium concentrations into the \( K_{sp} \) expression, we obtain;

\[
K_{sp} = [\text{Pb}^{+2}]^3[\text{AsO}_4^{-3}]^2 = (1.00 \times 10^{-7})^3 (6.67 \times 10^{-8})^2 = 4.45 \times 10^{-36}
\]

**Calculating Solubility from the \( K_{sp} \)**

Calculate the solubility in g/L of calcium sulfate, \( \text{CaSO}_4 \), given that its \( K_{sp} \) is \( 2.4 \times 10^{-5} \).

The dissolution of calcium sulfate forms equal amounts of calcium ions and sulfate ions according to the following equation.

\[
\text{CaSO}_4(s) \rightleftharpoons \text{Ca}^{+2} + \text{SO}_4^{-2}
\]

If we let \([\text{Ca}^{+2}] = [\text{SO}_4^{-2}] = x\), then we can solve for the Molarity of calcium sulfate that would be soluble.

\[
K_{sp} = [\text{Ca}^{+2}][\text{SO}_4^{-2}]
\]

\[
2.4 \times 10^{-5} = (x)(x)
\]

Solving for \( x \) we get \([\text{Ca}^{+2}] = [\text{SO}_4^{-2}] = 4.90 \times 10^{-3} \text{ M}

Since the equation above shows a 1:1 mole ratio of calcium sulfate to \( \text{Ca}^{+2} \) ions, we can assume that \( 4.90 \times 10^{-3} \) moles of \( \text{CaSO}_4 \) will dissolve. Since \( \text{CaSO}_4 \) has a mass of 136.1 g/mol, this would equate to:

\[
(4.90 \times 10^{-3} \text{ mol/L}) \times (136.1 \text{ g/mol}) = 6.67 \times 10^{-1} \text{ grams/L}
\]
Solubility and the Common Ion Effect.

In the event that we would try to dissolve a salt in a solution of another salt containing the same cation or anion, this common ion has a cumulative effect on the solubility equilibrium.

For example, suppose we have a solution of Iron(II)sulfide. If we dissolve some sodium sulfide in the solution, the presence of the additional sulfide may cause the precipitation of FeS. The solution now contains less FeS. The decrease in the concentration of the FeS in a solution of Na₂S is an example of the common ion effect. In general, any ionic equilibrium is affected by a substance producing an ion involved in the equilibrium.

Calculating the solubility of a Slightly Soluble Salt in a Solution of a Common Ion

(a) Calculate the molar solubility of barium fluoride, BaF₂, in water at 25°C. The $K_{sp}$ at 25°C is $1.0 \times 10^{-6}$.

$$
\text{BaF}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2 \text{F}^-1(aq)
$$

$x$ and $2x$ (at equilibrium)

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

$1.0 \times 10^{-6} = (x)(2x)^2 = 4x^3$ solving for $x$, we get: $x = 6.30 \times 10^{-3}$ M

Since "x" represents the molarity of the Ba⁺² ion, and we get one mole of barium ions for each mole of barium fluoride that dissolves, we obtain a molar solubility for BaF₂ of $6.30 \times 10^{-3}$ M.

Now, to illustrate the common ion effect.

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

Since the solution is already 0.15 M in F⁻¹ ions, we must make an addition to our equilibrium concentrations.

$$
\text{BaF}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2 \text{F}^-1(aq)
$$

$x$ and $2x + 0.15$ (at equilibrium)

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

Because BaF₂ is only slightly soluble, you might expect "2x" to be negligible compared to 0.15. In that case

$$(2x + 0.15) \approx (0.15)$$

and substituting into the $K_{sp}$ expression, we get

$$1.0 \times 10^{-6} = (x)(0.15)^2$$

solving for $x$, we get: $x = 4.44 \times 10^{-5}$ M

Note that "x" is indeed much smaller than 0.15, so our assumption was correct. Therefore the molar solubility of barium fluoride in 0.15 M NaF is only $4.44 \times 10^{-5}$ M. In pure water, the solubility is 6.3 x $10^{-3}$ M, which is over 140 times greater.
Precipitation Calculations

The $K_{sp}$ for a salt can essentially tell you if precipitation will occur under conditions of ion concentration.

If we have a given set of concentration conditions we can calculate a solubility quotient, $Q_c$, and compare it to the $K_{sp}$. The solubility quotient (often called the ion product) has the same form as the solubility constant expression, but the concentrations of the substances are not necessarily equilibrium values. Rather, they are the concentrations at the start of the reaction. To predict the direction of the reaction, you compare $Q_c$ with $K_c$.

For example;

Suppose a solution has Ca$^{2+}$ and SO$_4^{2-}$ concentrations of 0.0052 M and 0.0041 M, respectively. If these concentrations were doubled by evaporating half the water in the solution, would precipitation of CaSO$_4$ occur given that the $K_{sp}$ for calcium sulfate is $2.4 \times 10^{-5}$?

Since the $K_{sp}$ expression for calcium sulfate is $K_{sp} = [Ca^{2+}]_{equil}[SO_4^{2-}]_{equil}$, then $Q_c = [Ca^{2+}]_{init}[SO_4^{2-}]_{init}$.

Evaporating half of the water would double the initial concentrations of Ca$^{2+}$ and SO$_4^{2-}$ to 0.0104 M and 0.0081 M, respectively. Substituting these initial conditions into the expression for $Q_c$, we obtain:

$$Q_c = (0.0104) (0.0082) = 8.53 \times 10^{-5}$$

Since this value for $Q_c$ is greater than the $K_{sp}$, you would expect precipitation to occur.

Another example

A solution of 0.00016 M lead(II)nitrate, Pb(NO$_3$)$_2$, was poured into 456 mL of 0.00023 M sodium sulfate, Na$_2$SO$_4$. Would a precipitate of lead(II)sulfate, PbSO$_4$, be expected to form if 255 mL of the lead nitrate solution were added? (The $K_{sp}$ for lead(II)sulfate is $1.7 \times 10^{-8}$)

First we must calculate the initial concentrations of Pb$^{2+}$ and SO$_4^{2-}$ in the mixture.

(0.00016 mol/L)(0.255 L) = $4.08 \times 10^{-5}$ mol Pb$^{2+}$ (from the 255 mL of Pb(NO$_3$)$_2$)

(0.00023 mol/L)(0.456 L) = $1.05 \times 10^{-4}$ mol SO$_4^{2-}$ (from the 456 mL of Na$_2$SO$_4$)

We must now divide each of these results by the cumulative volume of 255 mL + 456 mL = 711 mL

$$[Pb^{2+}] = \frac{4.08 \times 10^{-5} \text{ mol Pb}^{2+}}{0.711 \text{ L}} = 5.74 \times 10^{-5} M$$

$$[SO_4^{2-}] = \frac{1.05 \times 10^{-4} \text{ mol SO}_4^{2-}}{0.711 \text{ L}} = 1.48 \times 10^{-4} M$$

Substituting these initial concentrations into the $Q_c$ expression for PbSO$_4$, we get:

$$Q_c = [Pb^{2+}][SO_4^{2-}] = (5.74 \times 10^{-5})(1.48 \times 10^{-4}) = 8.48 \times 10^{-9}$$

Since this value is less than the $K_{sp}$, we would not expect precipitation to occur.
Completeness of Precipitation

In the real world, the concentration of certain ions in drinking water or surface water can be determined by precipitating the ion of interest, filtering it out of the solution, and simply weighing the dried solid. In order for this to be an accurate analysis, we must be assured that most of the ion of interest was precipitated and very little remained in solution.

For example, Lead chromate, PbCrO₄, is a yellow pigment used in paints. Suppose 0.50 L of a 1.0 x 10⁻⁵ M Pb(C₂H₃O₂)₂ and 0.50 L of a 1.0 x 10⁻³ M K₂CrO₄ solution are mixed. Calculate the equilibrium concentration of Pb⁺² ion remaining in the solution after PbCrO₄ precipitates. What is the percentage of Pb⁺² remaining in solution after the precipitation has occurred. (The Ksp for PbCrO₄ is 1.8 x 10⁻¹⁴)

First, let us assume a limiting reagent problem where all the lead chromate that is possible precipitates. Then using the Ksp, determine how much could redissolve.

\[
\begin{align*}
\text{Pb}^{+2} \text{(aq)} + \text{CrO}_4^{-2} \text{(aq)} & \rightarrow \text{PbCrO}_4(s) \\
\text{initial} & : 5 \times 10^{-6} \text{ mol} \quad 5 \times 10^{-4} \text{ mol} \quad 0 \\
\text{final} & : 0 \quad (5 \times 10^{-4}) - (5 \times 10^{-6}) \quad 5 \times 10^{-4} \text{ mol}
\end{align*}
\]

The cumulative volume of the two solutions is now 1.0 L, so we now have 5 x 10⁻⁴ mol solid PbCrO₄ in contact with a solution containing 4.95 x 10⁻⁴ M CrO₄⁻² ions.

Let us now calculate how much of the solid lead chromate could possibly redissolve in the presence of this excess chromate ion.

\[
\begin{align*}
\text{PbCrO}_4(s) & \rightleftharpoons \text{Pb}^{+2} \text{(aq)} + \text{CrO}_4^{-2} \text{(aq)} \\
\text{initial} & : 0 \quad 4.95 \times 10^{-4} \text{ M} \\
\text{change} & : +x \quad +x \\
\text{equilibrium} & : x \quad 4.95 \times 10^{-4} \text{ M} + x
\end{align*}
\]

Substituting into the Ksp expression for lead chromate, we obtain

\[K_{sp} = [\text{Pb}^{+2}][\text{CrO}_4^{-2}]\]

\[1.8 \times 10^{-14} = (x)(x + 4.95 \times 10^{-4}) = (x)(4.95 \times 10^{-4}) \quad \text{assuming x is negligible compared to 4.95 x 10}^{-4}\]

Solving for "x" we get

\[x = \frac{1.8\times10^{-14}}{4.95\times10^{-4}} = 3.64\times10^{-11} \text{ M Pb}^{+2} \text{ remaining in solution}\]

The number of moles of Pb⁺² in the solution prior to precipitation was 5.0 x 10⁻⁶ mol, so the percentage of Pb⁺² remaining in the solution is:

\[\frac{3.64\times10^{-11}}{5.0\times10^{-6}} \times 100\% = 7.3\times10^{-4}\%\]

and would generally be considered a complete precipitation.
Fractional Precipitation

Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.

For example, suppose a solution contains both Ba$^{+2}$ ions and Sr$^{+2}$ ions. As we slowly add a concentrated solution of potassium chromate, $K_2CrO_4$, to the solution, barium chromate precipitates first (since its $K_{sp}$ is much less than that for strontium chromate). After most of the barium chromate has precipitated, strontium chromate begins to precipitate. It is therefore possible to separate Ba$^{+2}$ ions from Sr$^{+2}$ ions from a solution by fractional precipitation.

Effect of PH on Solubility

Suppose we wish to dissolve a salt whose cation or anion may undergo hydrolysis to form $H^+$ or $OH^-$ in the solution. In this event, the pH of the solution may have a profound effect on the solubility of the salt.

For example, consider the equilibrium between solid calcium fluoride and its ions in aqueous solution.

\[ \text{CaF}_2(s) \rightleftharpoons \text{Ca}^{+2}_{(aq)} + 2 \text{F}^{-1}_{(aq)} \]

Because the fluoride ion is the conjugate base of a weak acid (HF), you would expect it to react with any $H^+$ ion that is added:

\[ \text{F}^{-1}_{(aq)} + \text{H}^{+}_{(aq)} \rightleftharpoons \text{HF}_{(aq)} \]

According to LeChatelier's Principle, as $F^{-1}$ ions are removed by the reaction with $H^+$ ion, more calcium fluoride can dissolve to replenish the fluoride ions.

Therefore you expect calcium fluoride to be more soluble in acidic solution than in pure water.

In general, salts of weak acids should be expected to be more soluble in acidic solutions.

For example,

which salt would have its solubility more affected by changes in pH, silver chloride or silver cyanide?

Looking at the two dissolution equations

\[ \text{AgCl}_{(s)} \rightleftharpoons \text{Ag}^{+}_{(aq)} + \text{Cl}^{-1}_{(aq)} \]
\[ \text{AgCN}_{(s)} \rightleftharpoons \text{Ag}^{+}_{(aq)} + \text{CN}^{-1}_{(aq)} \]

we can assume that the chloride ion will not undergo hydrolysis since it is the conjugate base of the strong acid, HCl.

However, the cyanide ion is the conjugate base of the weak acid, HCN, and consequently will react with any $H^+$ ions present to reform HCN, thus removing cyanide ions from the solution.

\[ \text{CN}^{-1}_{(aq)} + \text{H}^{+}_{(aq)} \rightleftharpoons \text{HCN}_{(aq)} \]

Based on this, one would assume that the solubility of the silver cyanide would be more affected by changes in pH.
The following problems will be collected at the second exam.

Review Questions:  1,3,5,8


### Exam Review Topics

<table>
<thead>
<tr>
<th>terms</th>
<th>skills/operations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility Product Constant</td>
<td>Writing Solubility Product Expressions</td>
</tr>
<tr>
<td>Ion Product, $Q_c$</td>
<td>Calculating $K_{sp}$ from Solubility</td>
</tr>
<tr>
<td>Fractional Precipitation</td>
<td>Calculating Solubility from $K_{sp}$</td>
</tr>
<tr>
<td>Complex Ion</td>
<td>Calculating Solubility in presence of Common Ion</td>
</tr>
<tr>
<td>Ligand</td>
<td>Predicting Precipitation</td>
</tr>
<tr>
<td>Formation Constant, $K_f$</td>
<td>Determining Effect of pH on Solubility</td>
</tr>
<tr>
<td>Dissociation Constant, $K_d$</td>
<td></td>
</tr>
</tbody>
</table>