Solubility Equilibrium & Ksp Notes

Solubility Refresher:
- **Solute**: substance that is dissolved into something else. The minor component of a solution.
- **Solvent**: substance that makes of the major component of a solution. (water generally)
- **Saturated Solution**: solution that has the maximum amount of solute dissolved in it.

Solubility:
- Refers to the quantity that will dissolve to form a saturated solution.
- Typical units: grams of solute per Liter of solution
- **Molar solubility** is the maximum molarity of a solute.

\[ Molar \ solubility = Maximum \ molarity \]

Factors Affecting Solubility:
1. "**Common Ion Effect**" (LeChatelier’s Principle)

\[ \text{NaCl (s)} \rightleftharpoons \text{Na}^{+} (aq) + \text{Cl}^{-} (aq) \]

Addition of either Na\(^{+}\) (aq) or Cl\(^{-}\) (aq) shifts equilibrium to the left, reducing solubility. This can be done with aqueous HCl because it dissociates to form H\(^{+}\) and Cl\(^{-}\) ions. Can also be done with aqueous Na\(_2\)SO\(_4\) since it exists as separate Na\(^{+}\) and SO\(_4^{2-}\) ions.

**BIG IDEA**: Adding a “common ion” decreases the solubility of a salt.

2. **Solubility and pH**

\[ \text{Mg(OH)\(_2\)} (s) \rightleftharpoons \text{Mg}^{2+} (aq) + 2 \text{OH}^{-} (aq) \]

Addition of H\(^{+}\) to this will shift this equilibrium to the right. The H\(^{+}\) will react with the OH\(^{-}\) to produce to water. Thus, the equilibrium will shift to the right to produce more OH\(^{-}\), increasing the solubility. Mg(OH)\(_2\) is essentially insoluble in cold water \( \ldots \ldots \ldots \ldots \ldots \text{0.0009 grams per 100 mL} \)
Consider the following process:

\[
\text{BaSO}_4 (s) \rightleftharpoons \text{Ba}^{2+} (aq) + \text{SO}_4^{2-} (aq)
\]

\[K = \]

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

\[K = \]

**Solubility Product:** (Ksp)
Equals the product of the concentration of the ions involved in the equilibrium raised to the power of their coefficients in the equilibrium expression.

Ksp is the equilibrium constant for the equilibrium that exists between a solid ionic solute and its ions in a *saturated* aqueous solution.

**The smaller the Ksp value, the lower the solubility.**

Precipitation of Ions:

\[
\text{BaSO}_4 (s) \rightleftharpoons \text{Ba}^{2+} (aq) + \text{SO}_4^{2-} (aq)
\]

\[Ksp = [\text{Ba}^{2+} (aq)] [\text{SO}_4^{2-} (aq)]\]

Q = initial reaction conditions

\[Q = [\text{Ba}^{2+} (aq)] [\text{SO}_4^{2-} (aq)]\]

If Q > Ksp  “solvent cannot dissolve that many ions” so precipitate forms until Q = Ksp
If Q = Ksp  “equilibrium achieved”….we have a perfectly saturated solution
If Q < Ksp  “still able to dissolve more ions” so solid dissolves until Q = Ksp
Types of Ksp Problems

I. Dissolving the solid ionic compound into pure water. Solving for a missing variable in a mathematical expression.

The Ksp for CaF$_2$ is $3.9 \times 10^{-11}$. What is the molar solubility (max molarity) of a CaF$_2$ solution?

$$K_{sp} = [Ca^{2+}][F^-]^2$$

A saturated solution of sodium chloride has a molarity of 5.65 M. What is the Ksp for NaCl?

II. Dissolving the solid ionic compound into a “Common-Ion” Solution

Picture this as trying to dissolve a compound into a pre-existing solution containing one of the ions.

What will be the molar solubility of AgCl solution that already contains 0.75 M NaCl? $K_{sp} = 1.8 \times 10^{-10}$.

What is the molar solubility of CaF$_2$ in a 0.50 M KF solution? The Ksp of CaF$_2$ is $3.9 \times 10^{-11}$. 
III. Will a precipitate form when two substances are mixed? Compare Q to Ksp.

Throw all of the ions into a beaker of pure water. Are the concentrations of the ions high enough to “find each other” to make a precipitate? Must calculate the molarities of each ion and then plug the ion molarities into the Ksp math expression.

A person mixes 100.0 mL of 0.0016 M CaCl\(_2\) and 50.0 mL of 0.0081 M K\(_2\)SO\(_4\).

If the Ksp for CaSO\(_4\) is 2.4 \times 10^{-5}, will a CaSO\(_4\) precipitate be observed?

Compare this value (Q) to the Ksp textbook value. If Q > Ksp, a ppt will form. If Q < Ksp then no precipitate forms. If Q = Ksp, the solution is fully saturated. “On the brink of a precipitate!”

IV. Selective Precipitation: Which sparingly soluble solid will form a precipitate first?

A beaker contains 250 mL of a mixture that is labeled as 0.10 M Sr(NO\(_3\))\(_2\) and 0.00050 M Pb(NO\(_3\))\(_2\). A person slowly adds solid Na\(_2\)CO\(_3\) to the beaker until a precipitate starts to form.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Ksp Value</th>
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<tbody>
<tr>
<td>SrCO(_3)</td>
<td>9.3 \times 10^{-10}</td>
</tr>
<tr>
<td>PbCO(_3)</td>
<td>7.4 \times 10^{-14}</td>
</tr>
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Given these conditions, what substance (SrCO\(_3\) or PbCO\(_3\)) starts to precipitate first? What is the concentration of the [CO\(_3^{2-}\)] when the first precipitate starts to form?