Solubility Equilibria

Heretofore, we have investigated gas pressure, solution, acid-base equilibriums. Another important equilibrium that is used in the chemistry lab is that of solubility equilibriums.

For Example:

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

Like any equilibrium reaction, initially, no ions exist in solution

\[ Q < K \]

The reaction will continue to the right until

\[ Q = K \]

If more \( \text{Ca}^{2+} \) or \( \text{F}^- \) is added,

\[ Q > K \]

And the reaction would shift left

Remember, \( \text{CaF}_2 \) is a solid and has a constant concentration. However, it must be present for equilibrium to exist.

So, the equilibrium expression is written as:

\[ K_{eq} = [\text{Ca}^{2+}] [\text{F}^-]^2 = K_{sp} \]

\( K_{sp} \) = solubility product constant

It may seem strange that the amount of solid present does not affect the ratio at equilibrium.

Neither the amount of excess solid nor the size of particles present affect the solubility. It must simply be present in the most minute amount for the equilibria to exist.

<table>
<thead>
<tr>
<th>Table 18.2 • Some Common, Slightly Soluble Compounds and Their ( K_{sp} ) Values*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td>CaCO(_3)</td>
</tr>
<tr>
<td>MnCO(_3)</td>
</tr>
<tr>
<td>Fe(OH)(_3)</td>
</tr>
<tr>
<td>CaF(_2)</td>
</tr>
<tr>
<td>AgCl</td>
</tr>
<tr>
<td>AgBr</td>
</tr>
<tr>
<td>CaSO(_4)</td>
</tr>
<tr>
<td>BaSO(_4)</td>
</tr>
<tr>
<td>SrSO(_4)</td>
</tr>
<tr>
<td>Ca(H(_2)PO(_4)) (_2)</td>
</tr>
</tbody>
</table>

1. Calculate the ion concentrations in a saturated solution of calcium fluoride.

Another important connection to be made is the one between $K_{sp}$ and relative solubilities:

- “soluble” compounds are those with $K_{sp}$ values much greater than one.
  (salts containing anions and cations of strong acids or bases)
- “slightly soluble” compounds have a $K_{sp}$ value less than one.
  (salts containing anions and cations of weak acids or bases)
- “insoluble” compounds have a $K_{sp}$ value much, much, much less than one ($\sim \infty$).

The solubility product ($K_{sp}$) only describes the ratio of ions for a system at equilibrium (saturated solution), it does not describe the actual solubility.

The solubility of a substance is the quantity that dissolves to form a saturated solution.

In other words:

- Solubility product = ratio of ions in solution @ equilibrium
- Solubility = position (Q)

Example Problem:

2. What is the solubility product for a solution of $\text{Bi}_2\text{S}_3$ with a measured solubility of $1.0 \times 10^{-15}$ mol/L at 25°C?

   Just as we have been able to calculate solubility products from solubility, we can also calculate solubilities from solubility product constants (appendix D)

3. Using information from appendix D, calculate the solubility of silver chloride at 25°C

4. $1.8 \times 10^{-2}$ g of calcium fluoride are dissolved in 1 L of solution. Is this solution saturated, supersaturated, or unsaturated?
Slightly soluble compounds can be made soluble by making changes in their equilibrium according to Le Châtelier’s Principle.

Insoluble compounds generally can not be made soluble with out changing the overall chemistry of the solvent. I.e. using something other than water, or by drastically affecting the intermolecular forces in the solvation process.

Factors Affecting Solubility

- Temperature (affects $K_{sp}$)
- Common-ion Effect
- pH
- Formation of Complex Ions
- Amphoterism

Factors Affecting Solubility

- Temperature
  Generally, the solubility of solid solutes in liquid solvents increases with increasing temperature.
  The opposite is true of gases.

- Common-Ion Effect
  The addition of a strong electrolyte containing a common ion to precipitate out a weak electrolyte

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

The addition of NaF drives the equilibrium to the left

5. Calculate the solubility of solid CaF$_2$ ($K_{sp}$ 3.9x10$^{-11}$) in a 0.025 M NaF solution.
**pH and Solubility**

Adding acid or base to a solution can affect the solubility of many species (variation of common-ion effect)

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

Adding acid:

\[
\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}
\]

According to Le Chatelier’s principle, what happens to the solubility of magnesium hydroxide?

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

Notice what happens when an acid is added to the above saturated solution:

\[
2\text{F}^-(aq) + \text{H}^+(aq) \rightarrow \text{HF}(aq)
\]

Due to the basic properties of the \(\text{F}^-\) ion, the equilibrium is shifted to the right resulting in the dissociation of more \(\text{PbF}_2\).

- In general, the solubility of slightly soluble salts containing basic anions increases as the solution becomes more acidic (pH is lowered).
- The more basic the conjugate, the more the solubility is influenced by pH.

**Sample Exercise 17.13 Predicting the Effect of Acid on Solubility**

Which of these substances are more soluble in acidic solution than in basic solution: (a) \(\text{Ni(OH)}_2\), (b) \(\text{CaCO}_3\), (c) \(\text{BaF}_2\), (d) \(\text{AgCl}\)?

**Solution**

- (a) \(\text{Ni(OH)}_2\) is more soluble in acidic solution because of the basicity of \(\text{OH}^-\); the \(\text{H}^+\) reacts with the \(\text{OH}^-\) ion, forming water:

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

- (b) Similarly, \(\text{CaCO}_3\) dissolves in acid solutions because \(\text{CO}_3^{2-}\) is a basic anion:

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)
\]

The reaction between \(\text{CO}_3^{2-}\) and \(\text{H}^+\) occurs in steps, with \(\text{HCO}_3^-\) forming first and \(\text{H}_2\text{CO}_3\) forming in appreciable amounts only when the pH is sufficiently high.

- (c) The solubility of \(\text{BaF}_2\) is enhanced by lowering the pH because \(\text{F}^-\) is a basic anion:

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

- (d) The solubility of \(\text{AgCl}\) is unaffected by changes in pH because \(\text{Cl}^-\) is the anion of a strong acid and therefore has negligible basicity.

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6. Will \(\text{BaSO}_4\) be more soluble in acidic or basic solution? Show equations to defend your answer.
**Formation of Complex Ions**

We have already seen how metal ions can form complexes with water (metal Hydrates).

A characteristic property of metal ions is their ability to act as Lewis Acids.

\[
\text{Al}^{3+} + 6\text{H}_2\text{O} \rightleftharpoons \text{Al(H}_2\text{O)}_6^{3+}
\]

Lewis Acid Base

Notice that water acts as a Lewis base. Other molecules can act as Lewis bases to form complex ions as well.

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For convenience, the common practice for metal hydrates is to simplify the formulas by excluding the bound water molecules. Therefore, \(\text{Al(H}_2\text{O)}_6^{3+}\) would simply be written as:

\[
\text{Al}^{3+}
\]

However, we should know that it actually exist in its hydrated form.

---

**Complex ions** = Charged species consisting of a metal ion surrounded by ligands

**Ligands** = Lewis base molecule or ion having a lone pair of electrons that can be donated to form a coordination compound.

The number of ligands that attach to a metal ion is called the coordination number.

---

The coordination number of a metal is most often twice the oxidation number of the metal ion.

For example:

\[
\text{Ag}^+ \text{ would have a coordination number of 2}
\]

Therefore, \(\text{Ag(H}_2\text{O)}_2^{+}\)

Coordination numbers are usually 2, 4 or 6

---

Other common ligands include:

- \(\text{NH}_3\)
- \(\text{CN}^-\)
- \(\text{OH}^-\)
- \(\text{Cl}^-\)
- \(\text{SCN}^-\)

---

The formation of complex ions in a system with excess ligand is so large that it is said to go to completion.

Or, for complex ion formation \(K>>1\)

Let us investigate the effects of mixing a solution of silver nitrate with ammonia.

The major species in solution are:

\[
\text{Ag}^+, \text{NO}_3^-, \text{NH}_3, \text{NH}_4^+, \text{OH}^-
\]
1st, \[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

For this reaction, \( K_b \ll \ll 1 \)

So, very little \( \text{NH}_3 \) is consumed to produce \( \text{OH}^- \)

Even though the solution is basic due to the \( \text{OH}^- \)-present, it is still a weak equilibrium and is negligible in respect to a strong electrolyte.

2nd, \[ \text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag(NH}_3)_2^+ \]

\( K_f = 1.7 \times 10^7 \)

\( K_f \) is the formation constant for a complex ion.

\[
\begin{align*}
\text{AgCl(aq)} & \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \\
\text{Ag}^+(aq) + 2\text{NH}_3(aq) & \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) \\
\text{Overall: AgCl(aq) + 2NH}_3(aq) & \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) + \text{Cl}^-(aq)
\end{align*}
\]

Notice, \( K_f \gg 1 \). Therefore, equation favors complex ion. So much so that it can be written that:

\[ \text{Ag}^+ + 2\text{NH}_3 \rightarrow \text{Ag(NH}_3)_2^+ \]

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**Equilibrium Constants For Some Common Complex Ions**

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>( K_f )</th>
<th>Equilibrium Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(NH}_3)_2^+</td>
<td>( 1.7 \times 10^7 )</td>
<td>( \text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) )</td>
</tr>
<tr>
<td>Ag(CN)_2^-</td>
<td>( 1 \times 10^{25} )</td>
<td>( \text{Ag}^+(aq) + 2\text{CN}^-(aq) \rightleftharpoons \text{Ag(CN)}_2^-(aq) )</td>
</tr>
<tr>
<td>CdBr}_2^-</td>
<td>( 2.9 \times 10^{13} )</td>
<td>( \text{Ag}^+(aq) + 2\text{Br}^-(aq) \rightleftharpoons \text{CdBr}_2^-(aq) )</td>
</tr>
<tr>
<td>Cr(OH)_2^-</td>
<td>( 5 \times 10^3 )</td>
<td>( \text{Cr}_2^+(aq) + 4\text{OH}^-(aq) \rightleftharpoons \text{Cr(OH)}_2^+(aq) )</td>
</tr>
<tr>
<td>Co(SCN)_2^-</td>
<td>( 1 \times 10^7 )</td>
<td>( \text{Co}^{3+}(aq) + 4\text{SCN}^-(aq) \rightleftharpoons \text{Co(SCN)}_2^-(aq) )</td>
</tr>
<tr>
<td>Cu(NH}_3)_2^+</td>
<td>( 5 \times 10^{13} )</td>
<td>( \text{Cu}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Cu(NH}_3)_2^+(aq) )</td>
</tr>
<tr>
<td>Cu(CN)_2^-</td>
<td>( 1 \times 10^{13} )</td>
<td>( \text{Cu}^{2+}(aq) + 4\text{CN}^-(aq) \rightleftharpoons \text{Cu(CN)}_2^-(aq) )</td>
</tr>
<tr>
<td>Ni(NH}_3)_2^+</td>
<td>( 1.2 \times 10^9 )</td>
<td>( \text{Ni}^{2+}(aq) + 6\text{NH}_3(aq) \rightleftharpoons \text{Ni(NH}_3)_2^+(aq) )</td>
</tr>
<tr>
<td>Fe(CN)_3^-</td>
<td>( 1 \times 10^{15} )</td>
<td>( \text{Fe}^{3+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe(CN)}_3^-(aq) )</td>
</tr>
<tr>
<td>Fe(CN)_3^-</td>
<td>( 1 \times 10^{15} )</td>
<td>( \text{Fe}^{3+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe(CN)}_3^-(aq) )</td>
</tr>
</tbody>
</table>

7. Calculate the concentration of silver ions present in a solution of silver chloride at equilibrium when concentrated ammonia is added to a 0.010 M solution of silver nitrate giving an equilibrium concentration of ammonia of 0.20 M. Ignore the small volume change from the addition of ammonia.

Hint: \( \text{Ag(NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3 \quad K_{sp} = 1/k_f \)

8. Compare this value to the silver ion concentration in problem 3.

9. Calculate \([\text{Cr}^{3+}]\) in equilibrium with \( \text{Cr(OH)}_4^- \) when 0.010 mol of \( \text{Cr(NO}_3)_3 \) is dissolved in 1 L of solution buffered at pH 10.0.

Putting it all together:

We have already seen how pH affects solubility by shifting the reaction to the right or the left. The same can be done using the formation of complex ions.

Observe what happens with the addition of hydrogen cyanide to a solution containing iron (II) carbonate in equilibrium with its ions.
The reaction favors the formation of solid iron (II) carbonate. However, by adding hydrogen cyanate:

$$\text{Fe}^{2+} + 4\text{CN}^- \rightarrow [\text{Fe}((\text{CN})_4]^2- \quad K_f = 1 \times 10^{35}$$

The formation of the complex ion drives the dissolution of the iron (II) carbonate.

Some metal oxides and hydroxides that are relatively insoluble in water dissolve in strongly acidic and strongly basic solutions. This is true because these substances are capable of behaving as either an acid or a base.

Most commonly, oxides and hydroxides of Al$^{3+}$, Cr$^{3+}$, Zn$^{2+}$, and Sn$^{2+}$.

We have seen how changing the pH can increase solubility:

$$\text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$$

In this case magnesium hydroxide can only dissolve in acidic solutions. However, some hydroxides are amphoteric and can dissolve in both strongly acidic or basic solutions.

Example:

$$\text{Al(OH)}_3(s)$$

Remember, it is actually a hydrated metal ion; so:

$$\text{Al(H}_2\text{O)}_3(\text{OH})_3(s)$$

Observe:

$$\text{Al(H}_2\text{O)}_3(\text{OH})_3(s) + \text{OH}^- \rightleftharpoons \text{Al(H}_2\text{O)}_2(\text{OH})_4^{2-} + \text{H}_2\text{O}$$

Or:

$$\text{Al(H}_2\text{O)}_3(\text{OH})_3(s) + \text{H}^+ \rightleftharpoons \text{Al(H}_2\text{O)}_4(\text{OH})_2^{2+}$$

Can you think of a connection to the Qual. Scheme lab?