The Common Ion Effect and Solubility

A common ion suppresses the solubility of an ionic substance
Calculate its solubility of AgBr in g/L ($K_{sp} = 7.7 \times 10^{-13}$) in:

(a) pure water

(b) 0.0010 M NaBr

$$\text{AgBr (s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Br}^- (aq)$$
Calculate its solubility of AgBr in g/L ($K_{sp} = 7.7 \times 10^{-13}$) in:

(a) pure water

(b) 0.0010 M NaBr

Le Chatelier’s principle: the solubility is less in a solution of NaBr than in pure water
Practice Exercise

Calculate its solubility of AgBr in g/L ($K_{sp} = 7.7 \times 10^{-13}$) in:

(a) pure water

\[ \text{AgBr} \ (s) \rightleftharpoons \text{Ag}^+ \ (aq) \ + \ \text{Br}^- \ (aq) \]

\[
K_{sp} = [\text{Ag}^+] [\text{Br}^-] = 7.7 \times 10^{-13}
\]

\[
x^2 = 7.7 \times 10^{-13}
\]

\[
x = 8.8 \times 10^{-7} \ \text{M} = 1.7 \times 10^{-4} \ \text{g/L}
\]

solubility of AgBr
**Practice Exercise**

Calculate its solubility of AgBr in g/L ($K_{sp} = 7.7 \times 10^{-13}$) in:

(b) $0.0010 \, M \, NaBr$

\[ \text{AgBr (s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Br}^- (aq) \]

\[ K_{sp} = [\text{Ag}^+] [\text{Br}^-] = 7.7 \times 10^{-13} \]

\[ [\text{Ag}^+] \ (0.0010) = 7.7 \times 10^{-13} \]

\[ [\text{Ag}^+] = 7.7 \times 10^{-10} \, M = 1.4 \times 10^{-7} \, \text{g/L} \]

solubility of AgBr
pH and Solubility
pH and Solubility

consider Mg(OH)_2

\[ K_{sp} = 1.2 \times 10^{-11} = [\text{Mg}^{2+}] \ [\text{HO}^-]^2 \]

\[ \text{Mg(OH)}_2 \leftrightarrow \text{Mg}^{2+} + 2\text{HO}^- \]

solubility decreases in basic solution because increase in [HO^-] requires decrease in [Mg^{2+}]
Calculate its molar solubility of Cr(OH)$_3$ ($K_{sp} = 3.0 \times 10^{-29}$) in a pH 10 buffer.

\[
pOH = 4
\]

\[
Cr(OH)_3 (s) \rightleftharpoons Cr^{3+} (aq) + 3OH^- (aq)
\]

\[
K_{sp} = 3.0 \times 10^{-29} = [Cr^{3+}] [OH^-]^3
\]

\[
3.0 \times 10^{-29} = [Cr^{3+}] [10^{-4}]^3
\]

\[
[Cr^{3+}] = 3 \times 10^{-17} \text{ mol/L}
\]
pH and Solubility

consider Mg(OH)$_2$

\[ K_{sp} = 1.2 \times 10^{-11} = [Mg^{2+}] \ [HO^-]^2 \]

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

solubility increases in acidic solution because [HO$^-]$ is decreased

\[ \text{H}_2\text{O} \]
In General

salts of weak acids will be more soluble in acid solution than in pure water

because the anion of a weak acid (conjugate base) is basic
BaF$_2$ is a salt of a weak acid; its anion (F-) is basic.

$$K_{sp} = 1.7 \times 10^{-6} = [\text{Ba}^{2+}] \ [\text{F}^-]^2$$

$$\text{BaF}_2 \rightleftharpoons \text{Ba}^{2+} + 2\text{F}^-$$

Solubility increases in acid because F- concentration is decreased.
Complex Ion Equilibria and Solubility

“A complex ion is an ion containing a central metal cation bonded to one or more molecules or ions.”
\[ K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}] [\text{NH}_3]^4} = 5.0 \times 10^{13} \]
• A complex ion is formed by Lewis acid-Lewis base reaction;

- Metal ion is the Lewis acid

- The neutral molecule or ion that acts as the Lewis base is called a Ligand

• The number of ligands attached to the metal ion is called the coordination number

• The bond between the Lewis acid and Lewis base is covalent

• A complex ion is characterized by the formation constant ($K_f$)
<table>
<thead>
<tr>
<th>Simple reaction</th>
<th>Complex ion</th>
<th>$K_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}^+$ + $2\text{NH}_3$</td>
<td>$\text{Ag(NH}_3)_2^+$</td>
<td>$1.5 \times 10^7$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}$ + $4\text{CN}^-$</td>
<td>$\text{Cu(CN)}_4^{2-}$</td>
<td>$1.0 \times 10^{25}$</td>
</tr>
<tr>
<td>$\text{Co}^{3+}$ + $6\text{NH}_3$</td>
<td>$\text{Co(NH}_3)_6^{3+}$</td>
<td>$5.0 \times 10^{31}$</td>
</tr>
</tbody>
</table>
The effect of complex ion formation generally is to increase the solubility of a substance.
$K_f = \frac{[\text{Ag(NH}_3\text{)}_2^+]_{\text{aq}}}{[\text{Ag}^+]_{\text{aq}} \cdot [\text{NH}_3]_\text{aq}^2} = 1.5 \times 10^7$
Practice exercise

What is the molar solubility of AgBr in a 1.0 M solution of NH₃?

\[
\text{AgBr (s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Br}^- (aq) \\
K_{sp} = 7.7 \times 10^{-13}
\]

\[
\text{Ag}^+ (aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+ (aq) \\
K_f = 1.5 \times 10^7
\]

\[
\text{AgBr (s)} + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+ (aq) + \text{Br}^- (aq) \\
K_f K_{sp} = K
\]
Practice exercise

What is the molar solubility of AgBr in a 1.0 M solution of NH₃?

$$\text{AgBr (s) } + \text{ 2NH}_3(aq) \rightleftharpoons \text{ Ag(NH}_3)_2^+(aq) + \text{ Br}^-(aq)$$

$$K_f K_{sp} = K = 12.3 \times 10^{-6}$$

$$12.3 \times 10^{-6} = \frac{x^2}{1.0} \quad x = 0.0035 \text{ M}$$

The solubility of AgBr in pure water is 9 x 10^{-7} M.
## Some typical coordination numbers

<table>
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<tr>
<td><strong>Ag</strong>&lt;sup&gt;+&lt;/sup&gt;</td>
<td>2</td>
<td><strong>Mn</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Cu</strong>&lt;sup&gt;+&lt;/sup&gt;</td>
<td>2,4</td>
<td><strong>Fe</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Au</strong>&lt;sup&gt;+&lt;/sup&gt;</td>
<td>2,4</td>
<td><strong>Co</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
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<tr>
<td><strong>Ni</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
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<tr>
<td><strong>Cu</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
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<tr>
<td><strong>Zn</strong>&lt;sup&gt;2+&lt;/sup&gt;</td>
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<tr>
<td><strong>Co</strong>&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>6</td>
<td><strong>Cr</strong>&lt;sup&gt;3+&lt;/sup&gt;</td>
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<tr>
<td></td>
<td></td>
<td><strong>Au</strong>&lt;sup&gt;3+&lt;/sup&gt;</td>
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<tr>
<td></td>
<td></td>
<td><strong>Sc</strong>&lt;sup&gt;3+&lt;/sup&gt;</td>
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</table>
Some common ligands

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{SCN}^- \\
\text{CO} & \quad \text{CN}^- \\
\text{NO} & \quad \text{I}^- \\
\text{NH}_3 & \quad \text{F}^- \\
\text{CH}_3\text{NH}_2 & \quad \text{Cl}^- \\
\text{Br}^- & \\
\end{align*}
\]