Applications of Aqueous Equilibria

Chapter 17
Acid Base Equilibrium & Le Chatelier’s Principle

• The Common Ion Effect
• Buffer Solutions
The Common Ion Effect

Common Ion Effect: is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.
The Common Ion Effect

• **Common Ion:** Two dissolved solutes that contain the same ion (cation or anion).

• The presence of a common ion suppresses the ionization of a weak acid or a weak base.
Calculate the \([A^- \text{aq}])\) of 0.10M acetic acid (\(K_a = 1.7 \times 10^{-5}\))

\( \text{HA(aq)} = \text{H}^+(\text{aq}) + \text{A}^-(\text{aq}) \)

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.1</th>
<th>0.00</th>
<th>0.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equil</td>
<td>0.1 - (x)</td>
<td>(x)</td>
<td>(x)</td>
</tr>
</tbody>
</table>

\[
\frac{[x][x]}{[0.1 - x]} = 1.7 \times 10^{-5} \quad x = 1.3 \times 10^{-3} = [\text{H}^+] = [\text{A}^-]\
\]
Calculate the \([A^- \text{ \textit{aq}}])\) of 0.10M acetic acid in 0.010M HCl(aq) The Common Ion Effect

\[
HA(aq) = H^+(aq) + A^-(aq)
\]

\[
\begin{array}{ccc}
\text{Initial} & 0.1 & 0.010 & 0.00 \\
\text{Change} & -x & +x & +x \\
\text{Equil} & 0.1 - x & x + 0.010 & x \\
\end{array}
\]

\[
\frac{(x + 0.010)[x]}{[0.1 - x]} = 1.7 \times 10^{-5}
\]

\[
x = 1.7 \times 10^{-4} = [A^-]
\]
Buffer Solutions

- **Buffer Solution**: is a solution of
  1. a **Weak** acid or a **Weak** base and
  2. its salt

both components must be present.

- A buffer solution has the ability to resist changes in pH
Solubility Equilibria

- **Solubility Product**: is the product of the molar concentrations of constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.

\[
MX_2(s) \leftrightarrow M^{2+} (aq) + 2X^- (aq)
\]

\[
K_{sp} = [M^{2+}][X^-]^2
\]
Solubility

Consider Barium Sulfate

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

The solubility of Barium Sulfate is the amount of \(\text{BaSO}_4(s)\) that dissolves.

The amount of \(\text{BaSO}_4\) that dissolves = \([\text{Ba}^{2+} ]\)

or \([\text{SO}_4^{2-} ]\) since they are equal.
The Solubility-Product Constant, $K_{sp}$

$$\text{BaSO}_4(s) \leftrightarrow \text{Ba}^{2+} \text{ (aq)} + \text{SO}_4^{2-} \text{ (aq)}$$

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

$$[\text{Ba}^{2+}] = [\text{SO}_4^{2-}]$$

$$K_{sp} = (s)(s) = s^2$$

where $s$ is the solubility of Barium Sulfate
Factors that Affect Solubility

The Common Ion Effect

Solubility is decreased when a common ion is added

This is an application of Le Châtelier’s principle
Factors that Affect Solubility

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

As NaF is added to the system, the solubility of CaF\(_2\) decreases.

F\(^-\) reacts with Ca\(^{2+}\) which reduces the amount of Ca\(^{2+}\) in solution.

Therefore, Solubility is decreased.
As pH decreases, $[H^+]$ increases and solubility increases. If the $F^-$ is removed, the equilibrium shifts towards the decrease and CaF$_2$ dissolves. $F^-$ can be removed by adding a strong acid:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

$$F^-(aq) + H^+(aq) \rightleftharpoons HF(aq)$$

As pH decreases, $[H^+]$ increases and solubility increases.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)₃</td>
<td>1.8x10⁻³³</td>
</tr>
<tr>
<td>BaCO₃</td>
<td>8.1x10⁻⁹</td>
</tr>
<tr>
<td>BaF₂</td>
<td>1.7x10⁻⁶</td>
</tr>
<tr>
<td>BaSO₄</td>
<td>1.1x10⁻¹⁰</td>
</tr>
<tr>
<td>Bi₂S₃</td>
<td>1.6x10⁻⁷²</td>
</tr>
<tr>
<td>CdS</td>
<td>8.0x10⁻²⁸</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>8.7x10⁻⁹</td>
</tr>
<tr>
<td>CaF₂</td>
<td>4.0x10⁻¹¹</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>8.0x10⁻⁶</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>1.2x10⁻²⁶</td>
</tr>
<tr>
<td>Cr(OH)₃</td>
<td>3.0x10⁻²⁹</td>
</tr>
<tr>
<td>CoS</td>
<td>4.0x10⁻²¹</td>
</tr>
<tr>
<td>CuBr</td>
<td>4.2x10⁻⁸</td>
</tr>
<tr>
<td>CuI</td>
<td>5.1x10⁻¹²</td>
</tr>
<tr>
<td>Cu(OH)₂</td>
<td>2.2x10⁻²⁰</td>
</tr>
<tr>
<td>CuS</td>
<td>6.0x10⁻³⁷</td>
</tr>
<tr>
<td>Fe(OH)₂</td>
<td>1.6x10⁻¹⁴</td>
</tr>
<tr>
<td>Fe(OH)₃</td>
<td>1.1x10⁻³⁶</td>
</tr>
<tr>
<td>FeS</td>
<td>6.0x10⁻¹⁹</td>
</tr>
<tr>
<td>PbCO₃</td>
<td>3.3x10⁻¹⁴</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>2.4x10⁻⁴</td>
</tr>
<tr>
<td>PbCrO₄</td>
<td>2.0x10⁻¹⁴</td>
</tr>
<tr>
<td>PbF₂</td>
<td>4.1x10⁻⁸</td>
</tr>
<tr>
<td>PbI₂</td>
<td>1.4x10⁻⁸</td>
</tr>
<tr>
<td>PbS</td>
<td>3.4x10⁻²⁸</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>4.0x10⁻⁵</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>1.2x10⁻¹¹</td>
</tr>
<tr>
<td>MnS</td>
<td>3.0x10⁻¹⁴</td>
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<tr>
<td>Hg₂Cl₂</td>
<td>3.5x10⁻¹⁸</td>
</tr>
<tr>
<td>HgS</td>
<td>4.0x10⁻⁵⁴</td>
</tr>
<tr>
<td>NiS</td>
<td>1.4x10⁻²⁴</td>
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<tr>
<td>AgBr</td>
<td>7.7x10⁻¹³</td>
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<tr>
<td>Ag₂CO₃</td>
<td>8.1x10⁻¹²</td>
</tr>
<tr>
<td>AgCl</td>
<td>1.6x10⁻¹⁰</td>
</tr>
<tr>
<td>Ag₂SO₄</td>
<td>1.4x10⁻⁵</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>6.0x10⁻⁵¹</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>1.6x10⁻⁹</td>
</tr>
<tr>
<td>SrSO₄</td>
<td>3.8x10⁻⁷</td>
</tr>
<tr>
<td>SnS</td>
<td>1.0x10⁻²⁶</td>
</tr>
<tr>
<td>Zn(OH)₂</td>
<td>1.8x10⁻¹⁴</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.0x10⁻²³</td>
</tr>
</tbody>
</table>
Use Ksp values to calculate solubility of HgS

\[ \text{HgS} = \text{Hg}^{2+} (aq) + \text{S}^{2-} (aq) \]

\[ [\text{Hg}^{2+}(aq)] = [\text{S}^{2-}(aq)] = \text{solubility} \]

\[ \text{Ksp} = [\text{Hg}^{2+}(aq)] [\text{S}^{2-}(aq)] = (s)(s) = (s)^2 \]

\[ S = (4.0 \times 10^{-54})^{1/2} = ??? \]
Use $K_{sp}$ to calculate solubility of $\text{Ca(OH)}_2$

$$\text{Ca(OH)}_2(s) \leftrightarrow \text{Ca}^{2+} (aq) + 2\text{OH}^- (aq)$$

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

$$K_{sp} = (S)(2S)^2$$

$$K_{sp} = 4S^3$$
The solubility of silver chloride (AgCl) is found experimentally to be 0.0019 g/L.

Calculate the value of $K_{sp}$

$K_{sp} = [Ag^+][Cl^-] = (s)(s) = (?)(?)$

Solubilities must be in Molarity

$s = (0.0019 \text{ g/L}) / (\text{MW}) = 1.3 \times 10^{-5} \text{ M}$

$K_{sp} = (1.3 \times 10^{-5} \text{ M})(1.3 \times 10^{-5} \text{ M})$

$K_{sp} = 1.69 \times 10^{-10} = 1.7 \times 10^{-10}$
The Common Ion Effect and Solubility

- The solubility product ($K_{sp}$) is an equilibrium constant, precipitation will occur when the ion product exceeds the $K_{sp}$ for a compound.

- If $\text{AgNO}_3$ is added to saturated $\text{AgCl}$, the increase in $[\text{Ag}^+]$ will cause $\text{AgCl}$ to precipitate.

$$Q = [\text{Ag}^+] [\text{Cl}^-] > K_{sp}$$
Le Châtelier’s Principle

• **Le Chatelier’s principle:** If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset.

• Stress may be changes in concentration, pressure, volume, or temperature that removes the system from equilibrium.
Le Châtelier’s Principle

• **Concentration Changes:**
  
  – The concentration stress of an *added* reactant or product is relieved by reaction in the direction that *consumes* the added substance.

  – The concentration stress of a *removed* reactant or product is relieved by reaction in the direction that *replenishes* the removed substance.
Factors that affect solubility

What will affect the solubility of a salt?
Calculate the solubility of silver chloride in a 0.55 M solution of NaCl.

\[ K_{SP} = 1.7 \times 10^{-10} = [Ag^+] [Cl^-] \]

\[ 1.7 \times 10^{-10} = (x) (x + 0.55) \]

if \( x \) is small \{ determined by \( K_{SP} \) \} then

\[ 1.7 \times 10^{-10} \approx (x) (0.55) \]

\[ x \approx 3.1 \times 10^{-10} \text{ M} \approx 4.5 \times 10^{-8} \text{ g/L} \]
Precipitation

When will a salt precipitate?
When will a salt precipitate?

The concentration of calcium ion in the blood plasma is 0.0025 M. If the concentration of oxalate ion is 1.0 \times 10^{-7} do you expect calcium oxalate to precipitate? Ksp for calcium oxalate is 2.3 \times 10^{-9}

\[ [Ca^{2+}][C_2O_4^{2-}] = (0.0025)(1.0 \times 10^{-7}) = 2.5 \times 10^{-10} \]

Ion Product is smaller than Ksp, so do not expect precipitation to occur.
When will a salt precipitate?

When 50.0 mL of 0.0010 M BaCl₂ is added to 50.0 mL of 0.00010 M Na₂SO₄? Ksp = 1.1 x 10⁻¹⁰ for BaSO₄

Moles \( \text{Ba}^{2+} \) = 0.0010M x 0.050L = 5 x 10⁻⁵

Moles \( \text{SO}_4^{2-} \) = 0.00010M x 0.050L = 5 x 10⁻⁶

\[ [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (5 \times 10^{-4})(5 \times 10^{-5}) = 2.5 \times 10^{-8} \]

Because the ion product is greater than Ksp, a precipitate of barium sulfate is expected.