Chapter 16
More Equilibria in Aqueous Solution
Slightly Soluble Salts
&
Complex Ions
Hill, Petrucci, McCreary & Perry 4th Ed.
The Solubility Product Expression

Solubility Equilibria are Heterogeneous Equilibria.

Calcium Oxalate:

\[ \text{CaC}_2\text{O}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \]

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

Lead Iodide:

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

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

The exponents are equal to the coefficients
Write the $K_{sp}$ Expression from the Chemical Equation!

$$\text{Hg}_2\text{Cl}_2(s) \rightleftharpoons \text{Hg}_2^{2+}(aq) + 2 \text{Cl}^-_{(aq)}$$

$$K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2$$

Mercury (I) is a dimeric ion!

$$\text{HgCl}_2(s) \rightleftharpoons \text{Hg}^{2+}(aq) + 2 \text{Cl}^-_{(aq)}$$

$$K_{sp} = [\text{Hg}^{2+}][\text{Cl}^-]^2$$

Mercury (II) is a monomeric ion!
Calculating $K_{sp}$ from Solubility

Silver Chloride, AgCl, has a solubility of 1.9 x $10^{-3}$ g/L calculate the solubility product.
Calculating $K_{sp}$ from Solubility
Lead Iodide, PbI$_2$, has a solubility of $1.2 \times 10^{-3}$ mol/L calculate the solubility product.
Calculating Solubility from Ksp

Calculate the molar solubility of Calcium Fluoride, CaF₂, from its Ksp of $3.4 \times 10^{-11}$.

CaF₂(s) $\rightleftharpoons$ Ca²⁺(aq) + 2 F⁻(aq)

Ksp = [Ca²⁺][F⁻]²

solve the Ksp expression for x!
Solubility and the Common Ion Effect

The dissociation/dissolution of Calcium Oxalate.

In pure water: \( K_{sp} = 2.7 \times 10^{-9} \)

\[
\text{CaC}_2\text{O}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq)
\]

\[ \text{eq1} \quad -x \approx 0 \quad +x \quad +x \]

Adding a soluble calcium salt such as \( \text{CaCl}_2 \) so \([\text{Ca}^{2+}] = 0.15 \text{ M}\) we will shift the equilibrium to the left. Calcium oxalate will become less soluble in the solution of \( \text{Ca}^{2+} \).

\[ \text{eq2} \quad -z \quad 0.15 + z \quad +z \]

\[ \approx 0 \quad \approx 0.15 \text{ M} \]

It should be clear that \( z < x \ll 0.15 \), i.e. both are near zero compared to the much larger concentration of calcium ion.
Solubility and the Common Ion Effect

Calculate the solubility of calcium oxalate in pure water:

\[
\text{CaC}_2\text{O}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq)
\]

\[
[\text{eq1}] \quad -x \approx 0 +x +x
\]

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

Now in 0.15 M CaCl$_2$:

\[
[\text{eq2}] \quad -z 0.15 + z +z
\]

\[
\approx 0 \approx 0.15 \text{ M}
\]

\[
K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]
\]
Knowing When a Precipitate will Form

- Precipitation occurs when $Q_{sp}$ the ion concentration product exceeds $K_{sp}$.

\[ Q_{sp} < K_{sp} \Rightarrow \text{Unsaturated} \]
\[ Q_{sp} = K_{sp} \Rightarrow \text{Saturated} \]
\[ Q_{sp} > K_{sp} \Rightarrow \text{Supersaturated} \]

A “supersaturated” solution is not at equilibrium but is “metastable” and will form a precipitate on initiation.
Will a Precipitate Form?

A solution containing 0.0052 M Calcium ion and 0.0041 M sulfate ion in solution was evaporated to half its original volume. Will a precipitate form? \( \text{K}_{\text{sp}} = 2.4 \times 10^{-5} \)

\[
\text{Ca}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{CaSO}_4_{(s)}
\]

Concentrations before evaporation! Concentrations after evaporation?

\[ \text{K}_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 2.4 \times 10^{-5} \] At equilibrium!
Will a Precipitate Form?

255 mL of 0.00016 M lead nitrate solution and 456 mL of 0.00023 M sodium sulfate solution are combined. Will a precipitate form?

\[ \text{K}_{sp} = 1.7 \times 10^{-8} \]

\[ \text{Pb}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{PbSO}_4_{(s)} \]

\[ \text{K}_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = 1.7 \times 10^{-8} \]

\[ [\text{Pb}^{2+}] = \]

Calculating these concentrations is a dilution problem!

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

\[ Q_{sp} = ? \]
Determining Completeness of Precipitation

• Usually one ion is added, as a soluble salt, to another ion to cause precipitation. The amount of precipitate is usually a problem in reaction stoichiometry.

• It is often necessary to determine the residual ion concentration and the percent removed as the precipitate which formed. This requires use of the solubility product expression to determine concentration of the residual ion.
Determining Completeness of Precipitation

500 mL of $1.0 \times 10^{-3}$ M potassium chromate solution and 500 mL of $1.0 \times 10^{-5}$ M lead acetate solution are combined. Calculate amount of precipitate formed?

$$K_{sp} = 1.8 \times 10^{-15}$$

$$\text{Pb}^{2+}_{(aq)} + \text{CrO}_4^{2-}_{(aq)} \rightleftharpoons \text{PbCrO}_4(s)$$

$$K_{sp} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = 1.8 \times 10^{-15}$$

The quantity of lead ion is clearly the limiting reactant! Use stoichiometry to calculate the quantity of lead which will precipitate! Assume 100% precipitation!

Use the concentration of excess chromate ion to calculate the concentration of residual lead ion in the solution!

Can we approximate $[\text{CrO}_4^{2-}]$? Don't forget the effect of dilution on the concentrations here!
The Effect of pH on Solubility

• If a salt is a slightly soluble metal hydroxide lowering the pH (reducing the hydroxide concentration) makes it more soluble; dissolve; and conversely.

• If a slightly soluble salt has the anion of a weak acid, lowering the pH will make it more soluble; dissolve; and conversely.

• If a slightly soluble salt has the cation of a weak base, raising the pH will make it more soluble; dissolve; and conversely.
pH and Solubility

Calculate the pH of a saturated solution of Magnesium Hydroxide, Mg(OH)$_2$.

\[ K_{sp} = 1.8 \times 10^{-11} \]

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

\[ K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 \]
pH and Solubility

Calculate the maximum pH a 0.010 M solution of Magnesium Chloride, MgCl_2, a very soluble salt can be kept in solution.

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

\[-x \quad +x \quad +2x\]

\[K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.8 \times 10^{-11}\]

The only ions present are Mg^{2+}, Cl^-, H^+ and OH^-.

What is the only possible precipitate?

Write the chemical equation and the $K_{sp}$ expression.
pH & Solubility of Metal Sulfides

Qualitative treatment of Principles of Qualitative Analysis.

\[
\begin{align*}
H_2S_{(aq)} & \rightleftharpoons H^{+}_{(aq)} + HS^-_{(aq)} \quad K_{a1} = 8.9 \times 10^{-8} \\
HS^-_{(aq)} & \rightleftharpoons H^{+}_{(aq)} + S^{2-}_{(aq)} \quad K_{a2} = 1.2 \times 10^{-13}
\end{align*}
\]

Control of sulfide ion concentration

\[
\begin{align*}
H_2S_{(aq)} & \rightleftharpoons 2 H^{+}_{(aq)} + S^{2-}_{(aq)} \\
K_{a1,2} &= \frac{[H^+]^2[S^{2-}]}{[H_2S]} = K_{a1} \times K_{a2} = (8.9 \times 10^{-8})(1.2 \times 10^{-13}) \\
[S^{2-}] &= \frac{[H_2S] K_{a1,2}}{[H^+]^2} \\
[S^{2-}] &= \frac{1.1 \times 10^{-21}}{[H^+]^2}
\end{align*}
\]

Saturation water at 25°C:

\[
[H_2S] = 0.10 \text{ M}
\]

The [S^{2-}] can be varied over a wide range by control of pH.

\[
pH = 10 \quad 7 \quad 2 \\
[S^{2-}] = 0.11 \quad 1 \times 10^{-7} \quad 1 \times 10^{-17}
\]

Most HS^- salts of metal ions are relatively soluble.
pH & Solubility of Metal Sulfides

The solubility of iron(II) sulfide is pH dependent.

\[
\text{FeS}(s) \rightleftharpoons \text{Fe}^{2+}(aq) + \text{S}^{2-}(aq) \quad K_{sp} = 6 \times 10^{-18} \\
K_{sp} = [\text{Fe}^{2+}][\text{S}^{2-}] = 6 \times 10^{-18}
\]

Assuming [H₂S] is a 25°C saturated solution = 0.10 M

\[
[S^{2-}] = \frac{1.1 \times 10^{-21}}{[H^{+}]^2}
\]

Solubility at pH 1:

\[
[\text{Fe}^{2+}] = \frac{6 \times 10^{-18}}{1 \times 10^{-19}} \quad [\text{Fe}^{2+}] = 60 \text{ M} \\
\text{Very soluble!}
\]

Solubility at pH 7:

\[
[\text{Fe}^{2+}] = \frac{6 \times 10^{-18}}{1 \times 10^{-7}} \quad [\text{Fe}^{2+}] = 6 \times 10^{-11} \text{ M} \\
\text{Very insoluble!}
\]

Since the [S²⁻] can be varied over a wide range by control of pH the solubility of most slightly soluble metal sulfides can be drastically changed.
**pH & Solubility – Selective Precipitation**

Find a pH where only one of the two metals will precipitate when \([\text{Fe}^{2+}]\) and \([\text{Cu}^{2+}]\) have concentrations of 0.050 M.

\[
\text{FeS}(s) \quad K_{sp} = 6 \times 10^{-18} \quad \text{CuS}(s) \quad K_{sp} = 6 \times 10^{-36}
\]

Relatively much more soluble!  Relatively very insoluble!

Find a pH which will cause the relatively more soluble salt to just become saturated.

This will not actually cause it to precipitate, only reach its maximum limit of solubility.

The very insoluble salt will have precipitated and it is possible to calculate its residual ion concentration.
Can barium, $\text{Ba}^{2+}$, and strontium, $\text{Sr}^{2+}$, be separated by precipitation when both have concentrations of 0.100 M?

One needs to choose a precipitating anion that has a large $K_{\text{sp}}$ difference between the two cations, i.e. chromate!

$\text{BaCrO}_4(\text{s})$  \( K_{\text{sp}} = 1.2 \times 10^{-10} \)  \hspace{1cm}  $\text{SrCrO}_4(\text{s})$  \( K_{\text{sp}} = 3.5 \times 10^{-5} \)

Relatively very insoluble!  \hspace{1cm}  Relatively much more soluble!

The experimental procedure is to titrate the solution with chromate ion from a buret until the less soluble salt is precipitated.

If the $K_{\text{sp}}$ difference is large enough there will be a pause of a few drops as the concentration builds to saturate the more soluble salt.

The titration is stopped at this point and the precipitate is filtered.

The more soluble salt can now be precipitated without contamination.  The salts are now separated.

Mathematically one calculates the concentration of chromate ion which will saturate the more soluble strontium ion.  Then calculates the residual barium ion remaining in solution at that concentration.