To this point in our examination of aqueous equilibria, we have focused almost entirely on the chemistry of acids and bases. The problem is that there are plenty of things we can dump in water which don’t particularly alter the pH of a neutral solution. In fact they don’t appear to do much of anything. An example of this is rocks. You throw a rock into water, nothing exciting seems to happen.

In truth, very often ionic equilibria are established which we can describe in a quantitative fashion which tell us that throwing a rock into water is actually a pretty exciting event from a chemical equilibrium perspective. In fact, I’m going to show you how to get rich from the knowledge.

Well let’s start off cheap: I will throw a piece of chalk into a bowl of water. While it may appear that the chalk just sinks to the bottom of the container, the following equilibrium is actually being established before your eyes.

\[
\text{chalk} = \text{CaCO}_3 (s) \leftrightarrow \text{Ca}^{++} (aq) + \text{CO}_3^{=} (aq)
\]

This expression indicates that chalk in the solid phase establishes an equilibrium with the water in which some chalk dissolves to form the ions \( \text{Ca}^{++} \) and \( \text{CO}_3^{=} \) while at the same time some ions, \( \text{Ca}^{++} \) and \( \text{CO}_3^{=} \) are reacting in the reverse direction to form a molecule of chalk that sinks to the bottom of the beaker.
Since an equilibrium expression is written, we can also write an equilibrium equation

\[ K = \frac{[\text{Ca}^{++}(\text{aq})][\text{CO}_3^{=}\text{(aq)}]}{\text{CaCO}_3(\text{s})} \]

Of course since we have a solid in the denominator, we assume an activity of one and write a simpler equilibrium expression that is referred to as the **solubility product equilibrium** with an equilibrium constant referred to as the \( K_{sp} \):

\[ K_{sp} = [\text{Ca}^{++}(\text{aq})][\text{CO}_3^{=}\text{(aq)}] \]

What would you guess would be a typical \( K_{sp} \) value? Well if you look in the water you will notice the chalk is still sitting on the bottom of the beaker as a **precipitate**—it has not dissolved much. Therefore the equilibrium rests far to the left and the concentration of ions in solution is tiny. For this reason we usually refer to ionic compounds which do not dissolve much in water as: **sparingly soluble salts.**

Here are some examples of sparingly soluble salts taken from Appendix H.

<table>
<thead>
<tr>
<th>equilibrium</th>
<th>( K_{sp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{PbS} \leftrightarrow \text{Pb}^{++} + \text{S}^{=} )</td>
<td>( 8.4 \times 10^{-28} )</td>
</tr>
<tr>
<td>( \text{MgF}_2 \leftrightarrow \text{Mg}^{++} + 2\text{F}^{-} )</td>
<td>( 6.4 \times 10^{-9} )</td>
</tr>
<tr>
<td>( \text{AgCl} \leftrightarrow \text{Ag}^{+} + \text{Cl}^{-} )</td>
<td>( 1.8 \times 10^{-10} )</td>
</tr>
<tr>
<td>( \text{NiS} \leftrightarrow \text{Ni}^{++} + \text{S}^{=} )</td>
<td>( 3 \times 10^{-21} )</td>
</tr>
<tr>
<td>( \text{CaCO}_3 \leftrightarrow \text{Ca}^{++} + \text{CO}_3^{=} )</td>
<td>( 4.8 \times 10^{-9} )</td>
</tr>
<tr>
<td>( \text{Fe(OH)}_3 \leftrightarrow \text{Fe}^{+++} + 3\text{OH}^{-} )</td>
<td>( 6.3 \times 10^{-38} )</td>
</tr>
<tr>
<td>( \text{BaSO}_4 \leftrightarrow \text{Ba}^{++} + \text{SO}_4^{=} )</td>
<td>( 1.1 \times 10^{-10} )</td>
</tr>
<tr>
<td>( \text{CuSCN} \leftrightarrow \text{Cu}^{++} + \text{SCN}^{-} )</td>
<td>( 1.6 \times 10^{-11} )</td>
</tr>
</tbody>
</table>
Note we have numbers with large negative exponents meaning we have extremely small numbers. What such a number tells us is that these compounds don’t dissolve. They are effectively insoluble.

**Soluble Salts.** Contrast these values with what you might expect for a soluble salt like NaCl. You can set up a solubility product expression for NaCl as well:

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

The problem is you won’t find a number for this \( K_{sp} \) in the back of the book. NaCl is to sparingly soluble salts what HCl is to weak acids. Remember that when working acid base problems with a strong acid we just assumed it dissociated completely. It made the calculation easier. The same idea works here for soluble salts. We don’t assign them a \( K_{sp} \), we just assume they dissolve completely. And to a good approximation this is true. Dump some salt in water, stir it up, and it dissolves completely, presumably forming \( \text{Na}^+ \) and \( \text{Cl}^- \).

Now we know that if we saturate a solution with salt, then excess salt will fall to the bottom of the beaker, so obviously we could calculate a \( K_{sp} \), but as they say, it is beyond the scope of this course to do so. We’ll just assume \( K_{sp} \) is infinite for NaCl in the same way we assume \( K_a \) for HCl is infinite.

**Solubility Rules and \( K_{sp} \)**

Not long ago in CH301, you learned about some solubility rules for common ions. I know you did. I looked it up; it is on p.124 and 125 of Davis. At that time you were given a qualitative feel for which
salts were soluble and which salts weren’t. For example, you learned that:

- alkali metals like Na\(^+\) and K\(^+\) are soluble.
- Ammonium, NH\(_4^+\), salts are soluble.
- Nitrate NO\(_3^-\), salts are soluble.
- Sulfides, S\(^-\), are generally insoluble.

Well let’s compare this partial list of rules with what we have learned from a quantitative perspective about solubility.

In establishing an equilibrium between a salt and its dissolved ions

\[
AB(s) \rightleftharpoons A^+(aq) + B^-(aq)
\]

If the salt dissolves, equilibrium rests to the right and \(K_{sp}\) is large.

If the salt is insoluble, equilibrium rests to the left and \(K_{sp}\) is small.

So with respect to the relationship between solubility products and solubility rules we can say:

Insoluble salts have small \(K_{sp}\) values

Soluble salts have big \(K_{sp}\) values.

Consistent with this, note in the table on p 115 that NiS and PbS \(K_{sp}\) values are very small which agrees with rule 4 on p 116 which states that sulfides are insoluble. Also consistent is our assumption that the \(K_{sp}\) for NaCl is (see rule 1.) Now I’m not saying you have to do this, but try comparing the qualitative rules on p 125 of Davis with the \(K_{sp}\) values in Appendix H.
Okay, enough chit chat. Let’s work some solubility problems!!

**Example. Determining solubility product constants.**

One liter of saturated silver chloride solution contains 0.00192 g of dissolved AgCl. Calculate the molar solubility of AgCl and also the $K_{sp}$.

\[
0.00192 \text{g AgCl} \\
\text{moles of dissolved AgCl} = \frac{0.00192 \text{g AgCl}}{143 \text{g/mole}} = 1.34 \times 10^{-5} \text{moles} \\
\text{in one liter, molar solubility} = \frac{1.34 \times 10^{-5} \text{moles}}{1\text{liter}} = 1.34 \times 10^{-5} \text{moles/liter} \\
\text{let } x = [\text{Ag}^+] = [\text{Cl}^-] = 1.34 \times 10^{-5} \text{M} \quad \text{note 1:1 ratio of Ag}^+ \text{ to Cl}^- \\
K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = (x)(x) = (1.34 \times 10^{-5} \text{M})^2 = 1.8 \times 10^{-10}
\]

**Example. Determining solubility product constants.**

Calculate the molar solubility and $K_{sp}$ of a one liter CaF$_2$ solution which contains 0.0167 g of CaF$_2$.

\[
\text{because one liter, } \quad \frac{0.0167 \text{g CaF}_2}{78 \text{ g/mole}} = 2.14 \times 10^{-4} \text{M} \\
\text{molar solubility} = \frac{2.14 \times 10^{-4} \text{M}}{2} = 1.07 \times 10^{-4} \text{M} \\
\text{CaF}_2 \Leftrightarrow \text{Ca}^{+2} + 2\text{F}^- \\
K_{sp} = [\text{Ca}^{+2}][\text{F}^-]^2 \\
\text{let } x = [\text{Ca}^{+2}] = 2.14 \times 10^{-4} \text{M} \\
2x = [\text{F}^-] = 4.27 \times 10^{-4} \text{M} \\
K_{sp} = (2.14 \times 10^{-4} \text{M})(4.27 \times 10^{-4} \text{M})^2 = 3.9 \times 10^{-11}
\]
A Comparison table.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar Solubility</th>
<th>Solubility Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>$1.34 \times 10^{-5}$ M</td>
<td>$1.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>$2.14 \times 10^{-4}$ M</td>
<td>$3.9 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Note that even though the solubility product constant for AgCl is larger than for CaF$_2$, the molar solubility for AgCl is smaller than for CaF$_2$. In other words, there are fewer Ag$^+$ ions in solution than Ca$^{++}$ at equilibrium. The reason for this is that there is a squared term in the CaF$_2$ equilibrium.

**Calculating solubility from $K_{sp}$.**

Just as one uses $K_a$ values to assist in calculating the pH of a solution, the most common use of a $K_{sp}$ is to estimate the solubility of an ion in solution.

**Example.** Calculate the molar solubility of BaSO$_4$ in water. How many grams of BaSO$_4$ are actually dissolved? From page 115

$$\text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_{4}^{-2} \quad K_{sp} = [\text{Ba}^{2+}][\text{SO}_{4}^{-2}] = 1.1 \times 10^{-10}$$

let $x = [\text{Ba}^{2+}] = [\text{SO}_{4}^{-2}]$

$$K_{sp} = (x)(x) = 1.1 \times 10^{-10}$$

molar solubility $= x = [\text{Ba}^{2+}] = [\text{SO}_{4}^{-2}] = (1.1 \times 10^{-10})^{1/2} = 1.05 \times 10^{-5}$ M
Common Ion Effect in Solubility Problems.

Life in solution is rarely clean. Most often there are multiple equilibria going on ALL OF WHICH must simultaneously be true.

Whenever we have an ion participating in more than one equilibrium, we have to deal with what is known as the common ion effect. Typically the common ion effect is used to allow us to suppress the solubility of an unwanted ion.

For example, note from the problem above that the solubility of Ba\(^{++}\) in solution is \(1.05 \times 10^{-5}\)M. What if we wanted to reduce that solubility, i.e. how might we remove Ba\(^{++}\) from solution? One approach is to rely upon LeChatlier’s principle which states that a system at equilibrium will shift to relieve stress on the system.

Look at the solubility expression for BaSO\(_4\).

\[
\text{BaSO}_4 \rightleftharpoons \text{Ba}^{++} + \text{SO}_4^{=} 
\]

Note that according to LeChatlier, if we increase the amount of SO\(_4^{=}\) in solution, the equilibrium must shift to the left to relieve the stress. This means that the concentration of Ba\(^{++}\) will decrease. In other words, the Ba\(^{++}\) solubility will go down as more of the BaSO\(_4\) precipitate forms.

Let’s look at this common ion effect in action from a more quantitative perspective.
Example. Common ion and solubility product equilibria.

Calculate the molar solubility of BaSO\(_4\) in a 0.01 M Na\(_2\)SO\(_4\) solution. Compare this result to the BaSO\(_4\) solubility in pure water.

First recognize that we have two equilibria going on here. One involves a sodium salt which means that we have essentially 0.1 M SO\(_4^{2-}\) in solution as a result (see the solubility rules).

\[
\text{Na}_2\text{SO}_4(s) \rightleftharpoons 2\text{Na}^+ + \text{SO}_4^{2-} \quad K_{sp} = \text{infinity}
\]

Now we dump in some BaSO\(_4\). Note it doesn’t say how much we add. This is because BaSO\(_4\) is basically insoluble and no matter how much or little we add, it is going to fall to the bottom like the rock that it is. Now a little of this BaSO\(_4\) will establish an equilibrium with Ba\(^{2+}\) and SO\(_4^{2-}\) in water

\[
\text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-} \quad K_{sp} = 1.1 \times 10^{-10}
\]

reaction is far to the left
Note that we will have two sources of SO$_4^{2-}$ in solution: that which comes from the barium salt and that which comes from the sodium salt. Obviously, the vast majority, 0.1M is coming from the sodium with just a tiny amount to satisfy the $K_{sp}$ of BaSO$_4$ coming from the barium salt. (Wow, look at all the parallels between this problem involving SO$_4^{2-}$ coming from both a strong electrolyte and a weak electrolyte, and the acid/base problem involving H$^+$ coming from both a strong acid and a weak acid. Remember that in that case as well we pretty much ignore the contribution from the weak acid.)

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2+}] = 1.1 \times 10^{-10}$$

[SO$_4^{2+}$] from Na$^+ = 0.01$M

let $x = [\text{Ba}^{2+}] = [\text{SO}_4^{2+}]$ (from BaSO$_4$)

$$K_{sp} = 1.1 \times 10^{-10} = (x)(0.01+x)$$

assume $x$ is very small

$$[\text{Ba}^{2+}] = x = 1.1 \times 10^{-10}/0.01 = 1.1 \times 10^{-8}\text{M}$$

$$[\text{SO}_4^{2+}] = 0.01\text{M}$$

Note that the answer for this problem is that the molar solubility of $1.1 \times 10^{-8}$ M in the presence of a common ion, is 900 times lower than the molar solubility of BaSO$_4$ in pure water.
Simultaneous Equilibria.

The last example we examined involved a sulfate ion coming from two sources and consequently involved simultaneously in two equilibria. However because the sodium sulfate was considered to dissociate completely, we didn’t pay any attention to quantitatively evaluating its equilibrium equation. This is not always the case. Often, there are multiple equilibria and we have to consider satisfying equilibrium equations simultaneously.

(Did what I just say sound like:

solving simultaneous equations ???)

Remember back in advanced algebra in high school how you learned to solve more than one algebraic expression involving the same variables? Well that happens to be the approach you would take in solving simultaneous equilibria problems.

Most examples you will encounter at this stage in your science career involve solubility product equilibria that also happen to be involved in acid-base equilibria. For example, looking at the solubility tables and notice that many of the anions of these insoluble salts also happen to be the conjugate bases of acids.

For example, we have a

$$\text{OH}^-, \text{S}^-, \text{and } \text{CO}_3^= $$

which are involved not only in precipitation reactions but also react with protons from the water to form the following acid/base equilibria:
\[
\begin{align*}
H^+ + OH^- & \rightarrow H_2O \\
2H^+ + S^{=} & \rightarrow H_2S \\
2H^+ + CO_3^{=} & \rightarrow H_2CO_3
\end{align*}
\]

Thus in working problems involving any salt with these anions, we would have to simultaneously address multiple equilibria.

Sadly, there isn’t time to investigate the kinds of procedures necessary to solve these problems, but be aware that multiple equilibria can exist in solution and that they must all simultaneous be satisfied.

**Selective precipitation. (A Get Rich Quick Scheme)**

Often in this world we would like to separate things from each other. There is a huge field of science known as **separation science** which includes such techniques as chromatography and electrophoresis. For example, did you know that gasoline consists of hundreds of different compounds which can be separated in time on the basis of boiling point by gas chromatography:

Similarly, what may seem like a simple compound you purchase at the supermarket, is actually made up of scores of different types of molecules. For example, when you suck on a peppermint, you are sucking on peppermint oil which actually consists of dozens of rather
nasty looking organic molecules known as terpenes, which look like this:

It is always kind of funny to watch supposedly health conscious organic new age types rage on and one about the dangerous chemicals in our environment before going home for some aroma therapy as they pour a bunch of peppermint oil into their bath water.

But I digress. Back on task we go.

These separation techniques will be discussed in some detail in your later science courses, because everyone needs ways to separate things that are mixed together.

In the mean time, we will examine an approach to separating a mixture of materials that is based upon solubility product equilibria.

Consider a solution that contains a mixture of 0.1 M of the following three ions, Cu$^+$, Ag$^+$, Au$^+$. Now if we could selectively remove at least two of these ions from solution, we could get rich.
Each of these cations has the following equilibrium with Cl⁻:

\[ \text{CuCl (s)} \rightleftharpoons \text{Cu}^+ (aq) + \text{Cl}^- (aq) \quad K_{sp} = [\text{Cu}^+][\text{Cl}^-] = 1.9 \times 10^{-7} \]

\[ \text{AgCl (s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Cl}^- (aq) \quad K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10} \]

\[ \text{AuCl (s)} \rightleftharpoons \text{Au}^+ (aq) + \text{Cl}^- (aq) \quad K_{sp} = [\text{Au}^+][\text{Cl}^-] = 1.9 \times 10^{-13} \]

Note that these three equilibria are separated by about three orders of magnitude each in terms of the equilibrium constant. Also note that they are ranked from most soluble to least soluble. In other words, if we started adding Cl⁻ in increasing amounts, the metal ions would start to precipitate but at different concentrations of Cl⁻. Basically, we can work a kind of sequential common ion problem by adding Cl⁻ in increasing concentration. Inspection of the K_{sp} values indicates that AuCl is the least soluble salt, so it stands to reason that as we add increasing amounts of Cl⁻, it will be the first to fall out of solution.

\[ K_{sp} = [\text{Au}^+][\text{Cl}^-] = 1.9 \times 10^{-13} \]

\[ [\text{Au}^+] = 1 \text{M} \]

\[ [\text{Cl}^-] = K_{sp}/[\text{Au}^+] = (1.9 \times 10^{-13})/(1 \text{M}) \]

\[ [\text{Cl}^-] = 1.9 \times 10^{-13} \text{M}, \text{ so at higher concentrations, AuCl precipitates} \]

Thus when we’ve added more than 2 \times 10^{-13} M Cl⁻, a pile of AuCl precipitate ends up on the floor of the beaker. We could stop the addition of Cl⁻ right now, decant the liquid, and collect the AuCl and head for the hills. But there is more.
We could then continue to add Cl\textsuperscript{−} until a second precipitate forms, this time with the Ag\textsuperscript{+}.

Here the precipitate falls out of solution when Cl\textsuperscript{−} exceeds 1.8 x 10\textsuperscript{-10} M.

\[ K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = 1.8 \times 10^{-10} \]

\[ [\text{Ag}^+] = 1\text{M} \]

\[ [\text{Cl}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{1\text{M}} = 1.8 \times 10^{-10} \text{M} \]
Again we decant and collect the AgCl. We are richer still. Finally we add enough Cl\(^-\) that the Cu\(^+\) falls out of solution.

\[
[Cu^+] = 1 \text{M}
\]

\[K_{sp} = [Cu^+][Cl^-]\]

\[K_{sp} = 1.9 \times 10^{-7}\]

\[= [1 \text{M}][x]\]

\[x = 1.9 \times 10^{-7} \text{M}\]

This occurs when Cl\(^-\) reaches a level in excess of 1.9 \times 10^{-7} \text{ M}.

Recall that we started this section on solubility product equilibria by recalling the set of qualitative rules we had memorized in CH301 for when precipitates form. Now, a short hour later we are working related problems, but by knowing about chemical equilibria, are able to quantitatively evaluate the precipitation process.