SOLUBILITY EQUILIBRIA (\(K_{sp}\), THE SOLUBILITY PRODUCT)

- Saturated solutions of salts are another type of chemical equilibria. Remember those solubility rules? The fine print said that “soluble” is defined as 3.0 g salt dissolving in 100 g water. What if 2.9 g dissolves? We call it “insoluble”, but a good bit does actually dissolve. So, “insoluble” is not an absolute term.
  - Slightly soluble salts establish a dynamic equilibrium with the hydrated cations and anions in solution.
    - When the solid is first added to water, no ions are initially present.
    - As dissolution proceeds, the concentration of ions increases until equilibrium is established. This occurs when the solution is saturated.
  - The equilibrium constant, the \(K_{sp}\), is no more than the product of the ions in solution. (Remember, solids do not appear in equilibrium expressions.)
  - For a saturated solution of AgCl, the equation would be:
    \[ \text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \]

- The solubility product expression would be:
  \[ K_{sp} = [\text{Ag}^+] [\text{Cl}^-] \]
- The AgCl(s) is left out since solids are left out of equilibrium expressions (constant concentrations).

<table>
<thead>
<tr>
<th>Ionic Solid</th>
<th>(K_{sp}) (at 25°C)</th>
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\(^{a}\) Contains Hg₂⁺⁺ ions. \(K = [\text{Hg}_2^{2+}] [X^{-}]^2\) for Hg₂X₂ salts, for example.
You can find loads of $K_{sp}$ values on tables contained in any text. Look up a table of $K_{sp}$ values in your text and write the $K_{sp}$ expression and value for the following salts:

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{+2} + 2 \text{F}^- \quad K_{sp} =$$

$$\text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2 \text{Ag}^+ + \text{SO}_4^{2-} \quad K_{sp} =$$

$$\text{Bi}_2\text{S}_3(s) \rightleftharpoons 2 \text{Bi}^{+3} + 3 \text{S}^2- \quad K_{sp} =$$

**DETERMINING $K_{sp}$ FROM EXPERIMENTAL MEASUREMENTS**

In practice, $K_{sp}$ is determined by careful laboratory measurements using various spectroscopic methods.

- Remember STOICHIOMETRY!!
- Example: Lead(II) chloride dissolves to a slight extent in water according to the equation:

$$\text{PbCl}_2 \rightleftharpoons \text{Pb}^{+2} + 2 \text{Cl}^-$$

- Calculate the $K_{sp}$ if the lead ion concentration has been found to be $1.62 \times 10^{-2} M$.
- *If the lead ion concentration is “$x$” then chloride’s concentration is “$2x$”. Also note that the “molar solubility” is equal to “$x$” since the coefficient on the salt is “1” (think stoichiometry!). So….*

$$K_{sp} = (1.62 \times 10^{-2})(3.24 \times 10^{-2})^2 = 1.70 \times 10^{-5}$$

**Exercise 1**  **Calculating $K_{sp}$ from Solubility I**

Copper(I) bromide has a measured molar solubility of $2.0 \times 10^{-4}$ mol/L at 25°C. Calculate its $K_{sp}$ value.

$$K_{sp} = 4.0 \times 10^{-8}$$
Exercise 2  Calculating $K_{sp}$ from Solubility II

Calculate the $K_{sp}$ value for bismuth sulfide (Bi$_2$S$_3$), which has a molar solubility of $1.0 \times 10^{-15}$ mol/L at 25°C.

\[ K_{sp} = 1.1 \times 10^{-73} \]

ESTIMATING SALT SOLUBILITY FROM $K_{sp}$

- Example: The $K_{sp}$ for CaCO$_3$ is $3.8 \times 10^{-9}$ @ 25°C. Calculate the molar solubility of calcium carbonate in pure water in a) moles per liter & b) grams per liter:

  - The relative solubilities can be deduced by comparing values of $K_{sp}$ BUT, BE CAREFUL!
  - These comparisons can only be made for salts having the same ION:ION ratio.
  - Please don’t forget solubility changes with temperature! Some substances become less soluble in cold while some become more soluble!

Exercise 3  Calculating Solubility from $K_{sp}$

The $K_{sp}$ value for copper(II) iodate, Cu(IO$_3$)$_2$, is $1.4 \times 10^{-7}$ at 25°C. Calculate its solubility at 25°C.

\[ = 3.3 \times 10^{-3} \text{ mol/L} \]
SOLUBILITY AND THE COMMON ION EFFECT

The presence of a common ion will cause the equilibrium to shift so that even less of the substance with the smaller $K_{sp}$ value will dissolve.

- Experiment shows that the solubility of any salt is always less in the presence of a “common ion”. WHY?
- LeChatelier’s Principle, that’s why! Be reasonable and use approximations when you can!!
- pH can also affect solubility. Evaluate the equation to see who would want to “react” with the addition of acid or base.
- Would magnesium hydroxide be more soluble in an acid or a base? Why?

$$\text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+} \text{(aq)} + 2 \text{OH}^- \text{(aq)}$$  
(milk of magnesia)

Exercise 4  
Solubility and Common Ions

Calculate the solubility of solid CaF$_2$ ($K_{sp} = 4.0 \times 10^{-11}$) in a 0.025 $M$ NaF solution.

$$= 6.4 \times 10^{-8} \text{ mol/L}$$

- $K_{sp}$ AND THE REACTION QUOTIENT, Q

- With some knowledge of the reaction quotient, we can decide
  - whether a ppt will form at the conditions given AND
  - calculate the concentrations of ions required to begin the ppt. of an insoluble salt

1. $Q < K_{sp}$, the system is not at equil. (unsaturated)
2. $Q = K_{sp}$, the system is at equil. (saturated)
3. $Q > K_{sp}$, the system is not at equil. (supersaturated)

Precipitates form when the solution is supersaturated!!!
- Precipitation of insoluble salts
  - Metal-bearing ores often contain the metal in the form of an insoluble salt, and, to complicate matters, the ores often contain several such metal salts.
  - Dissolve the metal salts to obtain the metal ion, concentrate in some manner, and ppt. selectively only one type of metal ion as an insoluble salt.

**Exercise 5** Determining Precipitation Conditions

A solution is prepared by adding 750.0 mL of $4.00 \times 10^{-3} \, M \, \text{Ce(NO}_3\text{)}_3$ to 300.0 mL of $2.00 \times 10^{-2} \, M \, \text{KIO}_3$. Will Ce(IO$_3$)$_3$ ($K_{sp} = 1.9 \times 10^{-10}$) precipitate from this solution?

**Exercise 6** Precipitation

A solution is prepared by mixing 150.0 mL of $1.00 \times 10^{-2} \, M \, \text{Mg(NO}_3\text{)}_2$ and 250.0 mL of $1.00 \times 10^{-1} \, M \, \text{NaF}$. Calculate the concentrations of Mg$^{2+}$ and F$^{-}$ at equilibrium with solid MgF$_2$ ($K_{sp} = 6.4 \times 10^{-9}$).

$[\text{Mg}^{2+}] = 2.1 \times 10^{-6} \, M$

$[\text{F}^{-}] = 5.50 \times 10^{-2} \, M$
QUALITATIVE ANALYSIS (a favorite lab question topic on the AP Exam!)

- A Qualitative Analysis Scheme introduces you to the basic chemistry of various ions
- It also illustrates how the principles of chemical equilibria can be applied.

**Objective:** Separate the following metal ions: silver, lead, cadmium and nickel

- Adding HCl causes silver and lead to ppt. (Aren’t you glad you now know your solubility rules?) while nickel and cadmium will stay in solution.
- Separate nickel and cadmium by filtration.
- Add HOT water to the ppts and filter while HOT and the lead(II) chloride will redissolve.
- Separate the chloride ppts by filtration.
- Separating Cd and Ni is more subtle. We use their sulfide $K_{sp}$ values to determine which sulfide precipitates first!

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**Exercise 7**

**Selective Precipitation**

A solution contains $1.0 \times 10^{-4} \, M \, Cu^+$ and $2.0 \times 10^{-3} \, M \, Pb^{2+}$. If a source of $I^-$ is added gradually to this solution, will PbI$_2$ ($K_{sp} = 1.4 \times 10^{-8}$) or CuI ($K_{sp} = 5.3 \times 10^{-12}$) precipitate first? Specify the concentration of $I^-$ necessary to begin precipitation of each salt.

**CuI will precipitate first**

**Concentration in excess of $5.3 \times 10^{-8} \, M$ required**
ACID BASE AND PPT. EQUILIBRIA OF PRACTICAL SIGNIFICANCE

SOLUBILITY OF SALTS IN WATER AND ACIDS

- the solubility of PbS in water:
  \[ \text{PbS (s)} \rightleftharpoons \text{Pb}^{2+} + \text{S}^{2-} \]
  \[ K_{sp} = 8.4 \times 10^{-28} \]

- the hydrolysis of the S\(^{2-}\) ion in water:
  \[ \text{S}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HS}^- + \text{OH}^- \]
  \[ K_b = 0.077 \]

Overall process:
\[ \text{PbS + H}_2\text{O} \rightleftharpoons \text{Pb}^{2+} + \text{HS}^- + \text{OH}^- \]
\[ K_{total} = K_{sp} \times K_b = 6.5 \times 10^{-29} \]

- May not seem like much but it can increase the environmental lead concentration by a factor of about 10,000 over the solubility of PbS calculated from simply \( K_{sp} \)!

- Any salt containing an anion that is the conjugate base of a weak acid will dissolve in water to a greater extent than given by the \( K_{sp} \).

- This means salts of sulfate, phosphate, acetate, carbonate, and cyanide, as well as sulfide can be affected. If a strong acid is added to water-insoluble salts such as ZnS or CaCO\(_3\) then hydroxide ions from the anion hydrolysis is removed by the formation of water. This shifts the anion hydrolysis further to the right; the weak acid is formed and the salt dissolves.

- Carbonates and many metal sulfides along with metal hydroxides are generally soluble in strong acids.

- The only exceptions are sulfides of mercury, copper, cadmium and a few others.

- Insoluble inorganic salts containing anions derived from weak acids tend to be soluble in solutions of strong acids.

- Salts are not soluble in strong acid if the anion is the conjugate base of a strong acid!!