Solubility Equilibrium

You should review the solubility rules in chapter 4.

A saturated aqueous solution of a slightly soluble salt represents an equilibrium between the solid and its product ions:

- $\text{MX}_s(s) \rightleftharpoons \text{M}^{z+}(aq) + \text{X}^{y-}(aq)$

- Like all other equilibria, it is described by a $Q$ and a $K$.
- $Q = [\text{M}^{z+}][\text{X}^{y-}]$ - the ion product.
- As with all $Q$s, $Q$ has values for all possible solutions and a unique value for the equilibrium condition. For solubility, that value is called $K_{sp}$, the solubility product.
- Why does neither of these have a denominator?

- Just as there were seven quantities of interest in acid/base solutions, there are five in solubility:
  - $K_{sp}$
  - $g_{s}$ - the gram solubility (mass of solute which will dissolve in 100g of water)
  - $s$ - molar solubility (moles of solute per liter in the saturated solution)
  - $[\text{M}^{z+}]$ - cation concentration in the sat'd solution
  - $[\text{X}^{y-}]$ - anion concentration in the sat'd solution

Things to ponder

- Is there some real standard that makes a material soluble or insoluble?
- Does the $K_{sp}$, by itself, give a good description of the solubility characteristics of a salt? Why is this different from the $K$s in acid/base chemistry?
- From a practical standpoint, which of the previously noted measures should we use when trying to understand the degree to which a salt dissolves?
- How are the five quantities related?

Relating $K_{sp}$, $s$, $g_{s}$

- Example 1  $\text{MX}$
  - $\text{MX}(s) \rightleftharpoons \text{M}^{z+}(aq) + \text{X}^{y-}(aq)$
  - $s = s + s$
  - $K_{sp} = s$ or $s = (K_{sp})^{1/2}$
  - $g_{s} = s \times gfw/10 \quad s = 10^6 \times g_{s}/gfw$

- Example 2  $\text{M}_2\text{X}_3$
  - $\text{M}_2\text{X}_3(s) \rightleftharpoons 2\text{M}^{z+}(aq) + 3\text{X}^{y-}(aq)$
  - $s = 2s + 3s$
  - $K_{sp} = (2s)(3s)^3 = 108s^4$ or $s = (K_{sp}/108)^{1/5}$
  - $g_{s} = s \times gfw/10 \quad s = 10^6 \times g_{s}/gfw$
Summary Table

- gs and s are always related as shown previously. The table below relates s, Ksp, and the ion concentrations for the common salt types (a and b as defined earlier)

<table>
<thead>
<tr>
<th>a:b</th>
<th>[M]</th>
<th>[X]</th>
<th>Ksp</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>s</td>
<td>s</td>
<td>( s^{2} )</td>
<td>( \frac{1}{K_{sp}} )</td>
</tr>
<tr>
<td>1:2</td>
<td>s</td>
<td>2s</td>
<td>( 4s^{3} )</td>
<td>( \frac{1}{(K_{sp}^{1/2})} )</td>
</tr>
<tr>
<td>2:1</td>
<td>2s</td>
<td>s</td>
<td>( 4s^{3} )</td>
<td>( \frac{1}{(K_{sp}^{1/2})} )</td>
</tr>
<tr>
<td>2:2</td>
<td>2s</td>
<td>2s</td>
<td>( 16s^{4} )</td>
<td>( \frac{1}{(K_{sp}^{1/3})} )</td>
</tr>
<tr>
<td>3:1</td>
<td>3s</td>
<td>s</td>
<td>( 27s^{4} )</td>
<td>( \frac{1}{(K_{sp}^{1/3})} )</td>
</tr>
<tr>
<td>1:3</td>
<td>s</td>
<td>3s</td>
<td>( 27s^{4} )</td>
<td>( \frac{1}{(K_{sp}^{1/3})} )</td>
</tr>
<tr>
<td>2:3</td>
<td>2s</td>
<td>3s</td>
<td>( 108s^{5} )</td>
<td>( \frac{1}{(K_{sp}^{1/4})} )</td>
</tr>
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<td>3s</td>
<td>2s</td>
<td>( 108s^{5} )</td>
<td>( \frac{1}{(K_{sp}^{1/4})} )</td>
</tr>
</tbody>
</table>

Saturated solution described other ways

1. The molar solubility of cobalt(II) sulfide is \( 2.3 \times 10^{-14} \) M. Provide a complete treatment.

2. A saturated solution of barium carbonate has an carbonate concentration of \( 3.4 \times 10^{-3} \) M. Provide a complete treatment.

3. The Ksp of manganese (III) sulfate is \( 1.5 \times 10^{-31} \). Provide a complete treatment.
Precipitation

- Solubility, like all equilibria, can be approached from either direction. If one prepares the solution by starting with the insoluble salt and adding it to water, that’s dissolution. If one combines initially homogenous solutions, each containing only one of the product ions, and forms solid in that manner—that’s termed precipitation.

- All equilibria are described by the comparison of \( Q \) and \( K \).
  - \( Q < K \): solution is below saturation point and more solute will dissolve
  - \( Q = K \): solution is saturated
  - \( Q > K \): solution is supersaturated and precipitate should form

The general description of the ppt of the salt \( M_aX_b \) is as follows:

- \( C \) mL of \( DM \) solution of the metal nitrate are combined with \( E \) mL of \( FM \) sodium salt of \( X \). Will ppt form?

- Why does the question use the nitrate and sodium salts?

- What are the issues?
  - Identification of the possible ppt
  - Concentrations of the ions on mixing with careful note made of the dilution and the composition of the soluble salts
  - Calculation of \( Q \)
  - Comparison of \( Q \) with \( K \) to determine ppt or no ppt

- **Example 1:** The \( K_{sp} \) for \( CuCl \) is \( 1.0 \times 10^{-6} \). If equal volumes of \( 0.0010M \) copper(I) nitrate and \( 0.0030M \) sodium chloride are combined, will ppt form?
  - Upon mixing \( [Cu^{+}] = 5 \times 10^{-4} \) and \( [Cl^{-}] = 1.5 \times 10^{-3} \)
  - \( Q = 7.5 \times 10^{-7} \)
  - \( Q < K_{sp} \)- no ppt

- **Example 2:** The \( K_{sp} \) for \( CaSO_4 \) is \( 2.4 \times 10^{-5} \). If \( 30.0mL \) of \( 0.20M \) calcium nitrate are combined with \( 50mL \) of \( 0.030M \) potassium sulfate, will ppt form?
  - Upon mixing \( [Ca^{2+}] = 0.075 \) and \( [SO_4^{2-}] = 0.019 \)
  - \( Q = 1.5 \times 10^{-3} \)
  - \( Q > K_{sp} \)- ppt forms

A few more

- For each of the following, assume equal volumes are combined. Identify the possible ppt and then determine if precipitation will occur.
  - \( 0.0050M \) ammonium carbonate and \( 0.0010M \) strontium nitrate
  - \( 0.0010M \) silver(I) nitrate and \( 0.0020M \) potassium phosphate
  - \( 2.2 \times 10^{-5}M \) potassium nitrate and \( 0.020M \) iron(III) chloride
  - \( 1.2 \times 10^{-5}M \) potassium sulfide and \( 2.0 \times 10^{-5}M \) sodium carbonate
  - \( 0.0040M \) manganese(II) nitrate and water with a pH=9.20
**Uses of Ksp-beyond simple dissolution**

- As the discussion of pption has shown, use of the Ksp extends beyond simply preparing a saturated solution by dissolution of a salt. It is critical to remember that the ion concentrations are only stoichiometrically related if the sat'd solution is prepared by direct dissolution of the salt.
- In general, the generic statement: “For a saturated solution of the salt, $M_aX_b$, what would the $[M^+]/[X^-]$ be if the $[X^-]/[M^+]$ equals…” describes the general application of Ksp to saturated solutions.
- For a saturated solution of AgBr, what is the $[Ag^+]$ if $[Br^-]=1.3 \times 10^{-3}$M?
- A solution of zinc nitrate has $[Zn^{2+}]=0.025$M. At what pH would ppt form?

**Quick summary of Basic Solubility**

- Nomenclature and writing out the “dissolving reaction” are both very important.
- When dissolving a salt to the saturation limit - stoichiometry is central and the relationships between the five variables are straightforward. Care must be taken in doing the actual calculations.
- When precipitation is the issue
  - Begin with identification of possible ppt. There may not be one.
  - Don’t forget the dilution factor.
  - Stoichiometric links between concentrations don’t exist
  - Qion vs Ksp

**LeChatelier Effects**

- Any equilibrium discussion must include LeChatelier effects. In solubility, there take two forms.
- Chemical processes that decrease the concentration of one of the product ions thereby increasing the solubility. How can this be done?
  1. Adding acid to some salts increases the solubility – explain this in general LeChatelier terms and with also in specific chemical terms
     - ex: carbonates are more soluble in acidic solution
     - ex: the solubility of AgCl is not affected by adding $H^+$
  2. Complexation of the cation by a Lewis base
     - Ex: AgCl is soluble in NH₃ solutions
     - $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2Cl$ (Kf)
     - AgCl is $Ag(NH_3)_2Cl + Cl^- \rightarrow Ag(NH_3)_2Cl^-$(Kf)
     - $K_{f} = K_{sp} * K_{f}$
     - What requirements are there for a Lewis base to increase the solubility of a salt?
  3. Certain hydroxides are amphoteric. That is, they are capable of accepting as well as donating a hydroxide ion. The key example of this behavior is $Al(OH)_3$ which, as base is added first ppt and then redissolves due to the formation of $Al(OH)_3$.
  4. There are no LeChatelier volume effects in solubility equilibria - can you think of a simple reason why?
The Common Ion Effect

- Combining a soluble salt and an insoluble salt which have an ion in common is analogous to mixing a weak and a strong acid. As expected, the presence of the soluble material decreases the solubility of the insoluble salt, just as the strong acid decreases the % ion of the weak acid.
- What is the solubility of CuCl in 0.010M copper(I) nitrate?
  - Ksp = [Cu⁺][Cl⁻] = 1.7*10⁻⁷
  - if [Cu⁺]=0.010 then [Cl⁻]=1.7*10⁻⁷/0.010=1.7*10⁻⁵
  - How does this compare with the molar solubility of CuCl in water?
  - What is the solubility of calcium fluoride in 0.050M calcium nitrate?
  - Ksp = [Ca²⁺][F⁻] = 4.0*10⁻¹¹
  - if [Ca²⁺]=0.050 then [F⁻]=4.0*10⁻¹¹/0.050=8.0*10⁻¹²
  - Unlike the case of the CuCl, this is not the solubility, but 2s, so s=4.0*10⁻¹³
  - What is s for calcium fluoride in water?

How much precipitate?

- If you combine 25mL of 0.01M zinc nitrate with 75mL of 0.020M sodium carbonate, how many grams of ppt form?
  - Ksp for ZnCO₃=2.0*10⁻¹⁰
  - [Zn²⁺]=25*0.01/100=2.5*10⁻⁴
  - [CO₃²⁻]=75*0.02/100=0.015
  - Q=2.5*10⁻⁴*0.015=3.75*10⁻⁶
  - Q>K ppt forms
  - To determine the quantity of ppt, begin by assuming complete ppt formation limited by the limiting ion, in this case the Zn²⁺. After this step [Zn²⁺]=0.00 and [CO₃²⁻]=0.015-0.0025=0.0125.
  - Next, check the amount of ppt that would "redissolve" to establish the saturated solution: 2.0*10⁻¹⁰ = [Zn²⁺][CO₃²⁻], [Zn²⁺]=1.6*10⁻⁷. This small amount is due to the very large excess of carbonate
  - moles of ppt=0.0025*125=0.031g

- How much ppt would form if you combined 25mL of 0.0010M magnesium nitrate with 50mL of .0015M sodium fluoride?
Solubility as a separation method

- Solubility can be used to separate two cations by two methods
- If there is an anion which forms a ppt with only one of the two cations, adding it to the mixture will result in a straightforward separation.
  - For example, your solubility table on page A24 shows that fluoride forms a ppt with barium, but not with copper(II), so it could be used to separate these two ions.
- If there is an anion which precipitates both cations, it may still be used to separate them, if the resultant salts differ sufficiently in their solubilities. This is a more complex situation and requires detailed calculations.
  - Assume you had a mixture of Mg\(^{2+}\) and Ba\(^{2+}\), both at 0.005M. Can they be separated using carbonate? Assume that the carbonate can be added very slowly at low concentration.
  - Step 1: What carbonate concentration would each solid form in this case, since the salts are 1:1 and the Ksp for Ba\(^{2+}\) is 5.0杭0. This yields a threshold of carbonate of 5.0杭0 for Mg\(^{2+}\) and 2杭10 for the Mg\(^{2+}\). Thus, the barium ion will ppt first.
  - To determine whether full separation is possible, we set 1杭0 M as the point at which all of the barium is considered to be removed. This is somewhat arbitrary, but also seems reasonable.
  - When Ba\(^{2+}\)=1杭0, the carbonate =1杭0. This is less than the point at which magnesium begins to ppt so separation is possible.

- A solution contains Sn\(^{2+}\) and Cr\(^{3+}\) at concentrations of 0.020M and 0.0010M, respectively.
  - Ksp: Sn(OH)\(^2+\)=5.4杭0, Cr(OH)\(^3+\)=6.7杭0
- Analyze the potential of hydroxide ion to separate the two ions at the 99.5% level.
  - At what [OH\(^-\)] would each ion ppt?
    - Sn: [OH\(^-\)]=5.4杭0\(\times\)0.020\(\times\)5杭1
    - Cr\(^{3+}\): [OH\(^-\)]=6.7杭0\(\times\)0.001\(\times\)8.7杭1
  - Sn\(^{2+}\) ppts first

  - 99.5% removal of Sn\(^{2+}\) would result in the [Sn\(^{2+}\)]=1杭0
  - when [Sn\(^{2+}\]=1杭0 then [OH\(^-\)]=6.7杭0\(\times\)1杭0\(\times\)8.7杭1
    - This is below the point at which the Cr\(^{3+}\) will begin to ppt so separation at the 99.5% level is possible.

- Can sulfate ion be used to separate Pb\(^{2+}\) and Ag\(^{+}\) from a solution where both cations are initially 0.010M? If not, what level of separation is possible for each ion?
Qualitative Analysis

• Using only the information in your solubility table, can a mixture of Ag⁺, Ba²⁺, copper(II) and Mg²⁺ be separated? Describe the process used as a sequence of anions added to the solution and list the pH at each stage.

• If the solution also contained Pb²⁺ is separation still possible?