Announcements

- Homework due date changed to this Thurs. A new assignment will also be posted on Thurs.
- Make certain you come to lab prepared this week as you are really going to be on your own.
- Today we will be finishing up acids/bases and possibly starting solubility. Thus, refer to last week's notes for Tuesday's discussions.
- Review the solubility rules-Table 4.1 on p.144

Solubility Equilibrium

- A saturated aqueous solution of a slightly soluble salt represents an equilibrium between the solid and its product ions
  - $M_aX_b(s) \Leftrightarrow aM^{z+}(aq) + bX^{y-}(aq)$
- Like all other equilibria , it is described by a Q and a K.
  - $Q_{ion} = [M^{z+}]^a[X^{y-}]^b$ – **the ion product**
  - As with all Qs, Q_{ion} 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}
  - gs-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)
  - $[M^{z+}]$-cation concentration in the sat'd solution
  - $[X^{y-}]$-anion concentration in the sat'd solution

Things to ponder

- Is there some real standard that makes a material soluble or insoluble?
- Does the Ksp, by itself, give a good description of the solubility characteristics of a salt? Why is this different from the Ks 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?

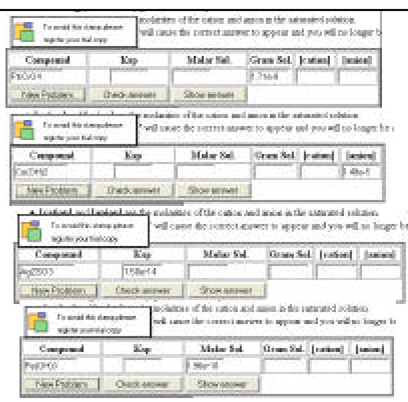
Relating Ksp,s,gs

- Example 1 MX
  - $MX(s) \Leftrightarrow M^{+}(aq) + X^{-}(aq)$ s = s + s
  - $Ksp = s^2$ or $s = (Ksp)^{1/2}$
  - gs=s*gfw/10 s=10*gs/gfw
- Example 2 M_2X_3
  - $M_2X_3(s) \Leftrightarrow 2M^{3+}(aq) + 3X^{2-}(aq)$ s = 2s + 3s
  - $Ksp = (2s)^2(3s)^3 = 108s^5$ or $s = (Ksp/108)^{1/5}$
  - gs=s*gfw/10 s=10*gs/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)

a:b	[M]	[X]	Ksp	s
1:1	s	s	s^2	$\sqrt{Ksp}$
1:2	s	2s	$4s^3$	$\sqrt[3]{(Ksp/4)}$
2:1	2s	s	$4s^3$	$\sqrt[3]{(Ksp/4)}$
2:2	2s	2s	$16s^4$	$\sqrt[4]{(Ksp/16)}$
3:1	3s	s	$27s^4$	$\sqrt[4]{(Ksp/27)}$
1:3	s	3s	$27s^4$	$\sqrt[4]{(Ksp/27)}$
2:3	2s	3s	$108s^5$	$\sqrt[5]{(Ksp/108)}$
3:2	3s	2s	$108s^5$	$\sqrt[5]{(Ksp/108)}$



Saturated solution described other ways

1. The molar solubility of cobalt(II) sulfide is $2.3*10^{-14}$ M. Provide a complete treatment.
2. A saturated solution of barium carbonate has an carbonate concentration of $3.4*10^{-3}$ M. Provide a complete treatment.
3. The Ksp of manganese (III) sulfate is $1.5*10^{-31}$. 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. For solubility:
  - 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 D M solution of the metal nitrate are combined with E mL of F M 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 Ksp for CuCl is $1.0*10^{-6}$. If equal volumes of 0.0010M copper(I) nitrate and 0.0030M sodium chloride are combined, will ppt form?
  - Upon mixing $[Cu^+]=5*10^{-4}$ and $[Cl^-]=1.5*10^{-3}$
  - $Q=7.5*10^{-7}$
  - Q<Ksp-no ppt
- **Example 2:** The Ksp for $CaSO_4$ is $2.4*10^{-5}$. If 30.0mL of 0.20M calcium nitrate are combined with 50mL of 0.030M potassium sulfate, will ppt form. upon mixing $[Ca^{2+}]=.075$ and $[SO_4^{2-}]=0.019$
  - $Q=1.5*10^{-3}$
  - Q>K-ppt forms

A few more

- For each of the following, assume equal volumes are combined. Identify the possible ppt and then determine if pption will occur.
- 0.0050M ammomnium carbonate and 0.0010M strontium nitrate
- 0.0010M silver(I) nitrate and 0.0020M potassium phosphate
- $2.2*10^{-4}$M potassium nitrate and 0.020M iron(III) chloride
- $1.2*10^{-5}$ M potassium sulfide and $2.0*10^{-3}$ 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-]=$1.3*10^{-3}$M?
- A solution of zinc nitrate has $[Zn^{2+}]$=0.025M. 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, these take two forms:
- Chemical processes that decrease the concentration of one of theproduct 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 NH_3 solutions
   - $AgCl \Leftrightarrow Ag^+ + Cl^-$ (Ksp) then $Ag^+ + 2NH_3 \Rightarrow Ag(NH_3)_2^+ (K_f)$
   - what type of compound is $Ag(NH_3)_2^+$
   - $AgCl + 2NH_3 \Leftrightarrow Ag(NH_3)_2^+ + Cl^-$ $K = K_f * K_{sp}$
   - 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^{3+} ,which, as base is added first ppts and then redissolves due to the formation of $Al(OH)_4^-$
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 the $[Cl^-]=1.7*10^{-7}/0.010=1.7*10^{-5}$ which would be the molar solubility,s, of the CuCl
- How does this compare with the molar solubility of CuCl in water?
- What is the solubility of calcium fluoride in 0.050M calcium nitrate?
- $Ksp=[Ca^{2+}][F^-]^2=4.0*10^{-11}$
- if $[Ca^{2+}]=0.050$ then $[F^-]=(4.0*10^{-11}/0.050)^{1/2}=2.8*10^{-5}$
- Unlike the case of the CuCl, this is not the solubility, but 2s, so $s=1.4*10^{-5}$
- 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 $ZnCO_3=2.0*10^{-10}$
- $[Zn^{2+}]_i=25*0.01/100=2.5*10^{-3}$
- $[CO_3^{2-}]i=75*.02/100=0.015$
- $Qion=(2.5*10^{-3})(0.015)=3.75*10^{-5}$
- Q>K ppt forms
- To determine the quantity of ppt, begin by assuming complete pption limited by the limiting ion, in this case the Zn^{2+}. After this step $[Zn^{2+}]=0.00$ and $[CO_3^{2-}]=0.015-0.0025=0.0125$.
- Next, check the amount of ppt that would "redissolve" to establish the saturated solution: $2.0*10^{-10}=[Zn^{2+}]*0.0125$; $[Zn^{2+}]=1.6*10^{-8}$. This small amount is due to the very large excess of carbonate
- moles of ppt=0.0025M*.10L=.00025moles-resulting from Zn ion
- grams=0.00025*125.4=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 those two ion.
- If there is an anion which ppts 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-at what carbonate concentration would each solid form-in this case, since the salts are 1:1,divide the Ksps by 0.005, This yields threshold of carbonate of $3.2*10^{-7}$ for Ba^{2+} and $2*10^{-3}$ for the Mg^{2+}. Thus, the barium ion will ppt first
  - To determine whether full separation is possible, we set 10^{-6} M as the point at which all of the barium is considered to be removed. This is somewhat arbitrary, but also seems reasonable.
  - When $Ba^{2+}=10^{-6}$, the carbonate $=1.6*10^{-3}$. 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 concentrations, respectively.
  - Ksps: $Sn(OH)_2=5.4*10^{-27}$ $Cr(OH)_3=6.7*10^{-31}$
- Analyze the potential of hydroxide ion to separate the two ions at the 99.5% level
- At what $[OH^-]$ would each ion ppt?
  - Sn: $[OH^-]=(5.4*10^{-27}/.020)^{1/2}=5.2*10^{-13}$
  - Cr^{3+}: $[OH^-]=(6.7*10^{-31}/.001)^{1/3}=8.7*10^{-10}$
  - Sn^{2+} ppts first
- 99.5% removal of Sn^{2+} would result in the $[Sn^{2+}]=1*10^{-4}$
- when $[Sn^{2+}]=1*10^{-4}$ then $[OH^-]=(6.7*10^{-31}/1*10^{-4})^{1/2}$ $=8.2*10^{-14}$. 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 Pb2+ 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^{+},Ba^{2+} , copper(II) and Mg^{2+} be separated? Describe the process used as a sequence of anions added to the solution and list the ptt at each stage.
- If the solution also contained Pb^{2+} is separation still possible?