

# Announcements

- Quiz 3 results posted
- Quiz 4 and 2<sup>nd</sup> HW should be up by Thurs
- New HW posted
- tutoring available at SETC  
<http://www.setc.pdx.edu>
- Exam will cover all of acids/bases and solubility
- Periodic Tables are available for new students-see me

## A quick detour back to acids

- What is the pH of 0.10M  $\text{H}_2\text{SO}_4$ ?
- Since the first ionization is strong, the solution can also be viewed as 0.10M  $\text{HSO}_4^-$  ( $K_a=1.2 \times 10^{-2}$ ) in 0.10M  $\text{H}^+$
- $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$
- $[\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-]$
- let  $x = [\text{H}^+]$  from the second ionization
- $(0.10+x)(x)/(0.10-x) = K_a = 1.2 \times 10^{-2}$
- rearranging and solving the resultant quadratic yields  $x = 0.0098$  and  $[\text{H}^+] = 0.11$  pH = 0.96

# Solubility Equilibrium

- A saturated aqueous solution of a slightly soluble salt represents an equilibrium between the solid and its product ions
  - $M_aX_b(s) \rightleftharpoons aM^{z+}(aq) + bX^{y-}(aq)$
- Like all other equilibria, it is described by a Q and a K.
  - $Q_{\text{ion}} = [M^{z+}]^a[X^{y-}]^b$  – **the ion product**
  - As with all Qs,  $Q_{\text{ion}}$  has values for all possible solutions and a unique value for the equilibrium condition. For solubility, that value is called  $K_{\text{sp}}$ , **the solubility product**.
- Just as there were seven quantities of interest in acid/base solutions, there are five in solubility:
  - $K_{\text{sp}}$
  - 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  $K_{sp}$ , 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 $K_{sp}$ , $s$ , $g_s$

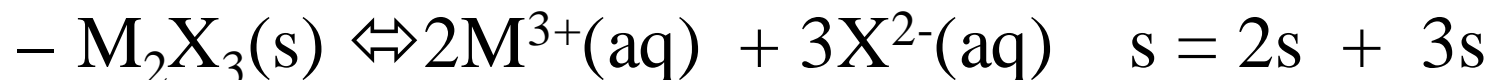
- Example 1  $MX$



- $K_{sp} = s^2 \quad \text{or} \quad s = (K_{sp})^{1/2}$

- $g_s = s * g_{fw}/10 \quad s = 10 * g_s / g_{fw}$

- Example 2  $M_2X_3$




- $K_{sp} = (2s)^2(3s)^3 = 108s^5 \quad \text{or} \quad s = (K_{sp}/108)^{1/5}$

- $g_s = s * g_{fw}/10 \quad s = 10 * g_s / g_{fw}$

# Summary Table


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

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

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molarities of the cation and anion in the saturated solution.  
will cause the correct answer to appear and you will no longer be

Compound	Ksp	Molar Sol.	Gram Sol.	[cation]	[anion]
PbCrO4			1.71e-8		
<input type="button" value="New Problem"/>	<input type="button" value="Check answer"/>	<input type="button" value="Show answer"/>			


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molarities of the cation and anion in the saturated solution.  
" will cause the correct answer to appear and you will no longer be

Compound	Ksp	Molar Sol.	Gram Sol.	[cation]	[anion]
Co(OH)2					1.48e-5
<input type="button" value="New Problem"/>	<input type="button" value="Check answer"/>	<input type="button" value="Show answer"/>			

◆ **[cation]** and **[anion]** are the molarities of the cation and anion in the saturated solution.  
will cause the correct answer to appear and you will no longer be

Compound	Ksp	Molar Sol.	Gram Sol.	[cation]	[anion]
Ag2SO3	1.50e-14				
<input type="button" value="New Problem"/>	<input type="button" value="Check answer"/>	<input type="button" value="Show answer"/>			

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molarities of the cation and anion in the saturated solution.  
will cause the correct answer to appear and you will no longer be

Compound	Ksp	Molar Sol.	Gram Sol.	[cation]	[anion]
Fe(OH)3		1.96e-10			
<input type="button" value="New Problem"/>	<input type="button" value="Check answer"/>	<input type="button" value="Show answer"/>			

# 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 DM solution of the metal nitrate are combined with E mL of FM sodium salt of X. Will ppt form?



- 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. If so, how many grams of ppt will form?
  - upon mixing  $[Ca^{2+}] = .075$  and  $[SO_4^{2-}] = 0.019$
  - $Q = 1.5 \times 10^{-3}$
  - $Q > K$  - ppt forms

# 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 A16-17 shows that fluoride forms a ppt with barium, but not with copper(II), so it could be used to separate those two ions
  - 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  $\text{Mg}^{2+}$  and  $\text{Ba}^{2+}$ , 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  $K_{sp}$ s by 0.005, This yields threshold of carbonate of  $1.6 \times 10^{-6}$  for  $\text{Ba}^{2+}$  and  $2 \times 10^{-3}$  for the  $\text{Mg}^{2+}$ . 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  $\text{Ba}^{2+} = 10^{-6}$ , the carbonate =  $8.1 \times 10^{-3}$ . This is greater than the point at which magnesium begins to ppt, so separation is not possible.

# LeChatelier Effects

- Any equilibrium discussion must include LeChatelier effects. In solubility, these take two forms:
- Chemical processes that decrease the concentration of one of the product ions thereby increasing the solubility. How can this be done?
- Addition of a soluble salt containing one of the product ions.