17.4 Solubility Equilibria for Ionic Compounds: K_{sp}

- The solubility of ionic compounds is a big deal, from kidney stones to drinking water to stalagtites and stalagmites

A. K_{sp} “Solubility Product Constant”

- In a “saturated solution,” insoluble solid is in equilibrium with aqueous ions
- Easy to write K expressions

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$ K=

I

C

E (doesn't matter, not in K!!)

B. Various K_{sp} setups, depending on Formulas and Number of Cations/Anions Produced:

1. $AgCl(s) \rightleftharpoons$ K =

2. $Zn(OH)_2(s) \rightleftharpoons$ K =

3. $ScCl_3(s) \rightleftharpoons$ K =

4. $Al_2(SO_4)_3(s) \rightleftharpoons$ K =

Points:

1. Manipulating equations with x^3 or x^4 is common!
2. While the solid itself doesn't appear in the K expression, the value of “x” does tell how many moles/L of the original solid can dissolve.
    - If you know how many moles/Liter of product solute is present, you know how many moles/Liter of parent solid actually dissolves

C. Technical note: often K_{sp} problems end up with x^3 or x^4 type terms. What does this mean and how do I solve them?

- Ex 1: $x^3 = 100$ meaning: x times x times x = 100. Or, $x = 100^{1/3}$ (x = 4.64)
  - Calculator: find your calculator's $\sqrt[x]{y}$ key, enter 100 for "y" and 3 for "x"
  - In other words, solve as $x = \sqrt[3]{100}$
  - On my Texas Instruments Calculator (yours may differ):
    - enter 100 first
    - click the $\sqrt[x]{y}$ key second
    - enter 3 third

- Ex 2: $0.26^3 = x$ meaning: 0.26 times 0.26 times 0.26 = x. (x = 0.0176)
  - Calculator: find your calculator's y^x key, enter 0.26 for "y" and 3 for "x"
  - On my Texas Instruments Calculator (yours may differ, x^y for Casio?):
    - enter 0.26 first
    - click the y^x key second
    - enter 3 third

Calculator Practice

x equals

1. $x^3=125$
   - enter 125
   - click the $\sqrt[x]{y}$ key
   - enter 3
2. $x^3=200$
3. $x^4=12.7$

x equals

4. $12^3=x$
   - enter 12
   - click the y^x key
   - enter 3
5. $8^4=x$
6. $3.2^3=x$

D. Definitions
1. "Solubility": g/L of solid that dissolves
2. "Molar solubility": mol/L of solid that dissolves

E. Interconverting Solubility and K_{sp}: Calculations

1. Working from K_{sp} to solubility:

K_{sp} $\rightleftharpoons$ moles/L of ions $\rightleftharpoons$ moles/L of solid $\rightleftharpoons$ (g/L) of solid

2. Working from solubility to K_{sp}:

Solubility of compound (g/L) $\rightleftharpoons$ Molar solubility of compound (mol/L) $\rightleftharpoons$ Molar concentration of ions $\rightleftharpoons$ K_{sp}

Working from K_{sp} to solubility:

K_{sp} $\rightleftharpoons$ moles/L of ions $\rightleftharpoons$ moles/L of solid $\rightleftharpoons$ (g/L) of solid

1. $PbCl_2$ (278 g/mol) $PbCl_2$ (s) $\rightleftharpoons$ K =
K_{sp}=1.6 x 10^{-5}

a. Calculate $[Pb^{2+}]$ and $[Cl^-]$ for a saturated solution of $PbCl_2$.

b. Calculate molar solubility (mol/L) for $PbCl_2$

c. Calculate mass solubility (g/L) for $PbCl_2$

d. What mass of $PbCl_2$ (278 g/mol) would dissolve in 140 mL?

Working from solubility to K_{sp}:

Solubility of compound (g/L) $\rightleftharpoons$ Molar solubility of compound (mol/L) $\rightleftharpoons$ Molar concentration of ions $\rightleftharpoons$ K_{sp}

1. Find K_{sp} for CaF_2 whose molar solubility is 2.1 x 10^{-4} mol/L.

Molar solubility plus stoichiometry tells us what ion concentrations are, from which K can be found.

2. $BaCO_3$ (197g/mol) has a solubility of 0.014 g/L. Find K_{sp} for $BaCO_3$.

17.5 Factors that affect Solubility of Ionic Compounds (LeChatelier's Principle)

A. pH Factor: If anion is basic, solubility increases at low pH (high $[H^+]$)

1. Via selective removal of anion (product side)
2. Many basic anions: OH^-, F^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-} etc.
3. Few non-basic anions: Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, HSO_4^-

Example 1: $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

Add acid:

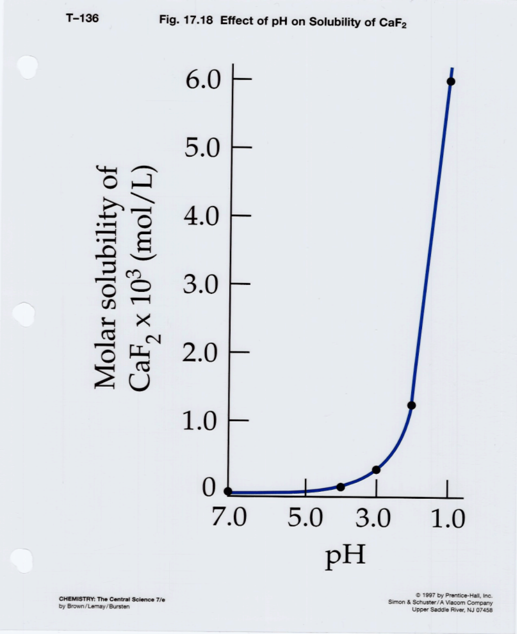
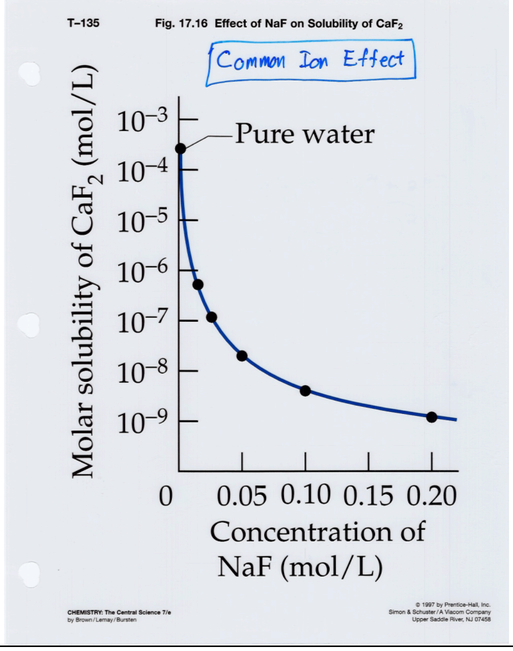
By selective removal of $[OH^-]$,
$Q < K$, so ala LeChatelier,
solid $Cu(OH)_2$ keeps dissolving,
and $[Cu^{2+}]$ keeps rising

Example 2: $PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$ $K=[Pb^{2+}][F^-]^2$

Add acid:

Example 3: $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$ $K=[Pb^{2+}][Br^-]^2$

Add acid:

pH Effect on CaF_2 (fluoride is a basic anion)	**Common Ion Effect** (fluoride from NaF is the "common ion")
	

B. Common Ion Effect: A "common ion" decreases solubility

Example: $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

Additive	Equilibrium Shift	Impact on:	Ratio of $[Ba^{2+}]$ to $[SO_4^{2-}]$		Impact on Moles of $BaSO_4$	Impact on Solubility of $BaSO_4$
1 Add $Ba^{2+}(aq)$ (for example, $Ba(NO_3)_2$)		$[SO_4^{2-}]$	$[Ba^{2+}]$	$[SO_4^{2-}]$		
2 Add SO_4^{2-} (aq) (for example, Na_2SO_4)		$[Ba^{2+}]$	$[Ba^{2+}]$	$[SO_4^{2-}]$		

Notes:

1. If Ba^{2+} or SO_4^{2-} is added as a common ion from a different source, that pushes the equilibrium to left, so solubility decreases
2. Case 1, where $Ba(NO_3)_2$ was added:
    a. The barium ion concentration $[Ba^{2+}]$ is dominated by the fully soluble $[Ba(NO_3)_2]$ source
    b. Simplifying assumption allows the contribution "x" from $BaSO_4$ to be ignored
    c. As a result, solving for $[SO_4^{2-}]$ and thus the molar solubility of $BaSO_4$ under these conditions becomes easy.

Point: When a known concentration of a common ion is present, you can easily:
1. Calculate molar concentrations of ions
2. Calculate molar solubility of the solid

Problem:

1. What is the molar solubility of $BaSO_4$ when added to regular water?

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$

2. What is the molar solubility of $BaSO_4$ in the presence of 0.10-M $Ba(NO_3)_2$?

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$

3. What is the molar solubility of $BaSO_4$ in the presence of 0.50-M Na_2SO_4?

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$

How would the solubility of the salts be affected?

Q's: 1. Is there a common ion? 2. Is there a basic anion that might be impacted by pH?

	Added $Ca(NO_3)_2$	Added NaF	Added HNO_3	More soluble at Low or High pH?
1. CaF_2				
2. $CaCO_3$				
3. $Ca(OH)_2$				
4. ZnF_2				
5. $PbCl_2$				
6. AgI				
7. $ZnSO_4$				

8. What is molar solubility of AgBr ($K_{sp}=3.3\times10^{-13}$) in a solution with 0.20 M NaBr (which of course dissolves fully)?

9. What would AgBr solubility be without NaBr present?

10. Determine molar solubility for $Mg(OH)_2$ ($K_{sp}=1.5 \times 10^{-11}$) at the following pH's:

Equation:

a. pH=12.00

b. pH=6.00

pH often can define the concentrion of hydroxide (or other basic anions whose K_a is known)

C. Complex Ion Formation (not for test, but lab relevant)

- many Lewis bases can <u>increase</u> the solubility of a solid by <u>irreversible removal</u> of a product cation
- NH_3, ^-CN common

$$\begin{tikzcd} \mathrm{CuBr(s)} \arrow[r, rightleftharpoons] & \mathrm{Cu^+(aq) + Br^-(aq)} \arrow[d, "4\ \mathrm{NH_3}"] & K = 5.3 \times 10^{-9} \\ & \mathrm{Cu(NH_3)_4^+} & \end{tikzcd}$$

- Selective, irreversible removal of the copper ion via ammonia complexation drives the equilibrium in the right direction.
    - Thus, the solubility of the original solid increases.

General pH Strategy: Finding the pH after Acid or Base is added to a solution

- Whether it be to a buffer solution, a strong acid solution, a weak acid solution, a strong base solution or a weak base solution prior to the new addition
- The strategy is similar to when we added acid or base to a buffer

6. Write out the acid-base reaction
    - It helps to recognize which species are acidic or basic or neutral, and weak or strong
7. Calculate the initial moles
    - Number of moles = molarity x volume (in Liters)
8. Use ICE to determine post-reaction ("E") moles
9. Assess the post-reaction situation, based on what's left at the end
10. Solve the pH problem from there

	Post-Reaction Situation		
1	Strong acid only	$[H^+] = [SA]$	
2	Strong acid plus weak acid	$[H^+] = [SA]$	Ignore WA, which makes insignificant contribution
3	Strong base only	$[HO^-] = [SB]$	
4	Strong base plus weak base	$[HO^-] = [SB]$	Ignore WB, which makes insignificant contribution
5	Weak acid only	$[H^+] = \sqrt{K_b x [WB]}$	Qual: pH < 7
6	Weak base only	$[HO^-] = \sqrt{K_b x [WB]}$	Qual: pH > 7 May need to find K_b from K_a
7	Weak acid plus weak base	$pH = pK_a + \log \frac{[base]}{[acid]}$	Buffer solution
8	No acid or base; only neutral salts	pH = 7.0	

- For many of these, it will be necessary to calculate molarities
- To do this, make sure that you factor in the total, combined volume

Key: Recognizing the Final Situation!!