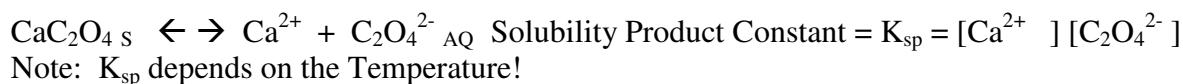


Chapter 17 Solubility and Complex Ion Equilibria

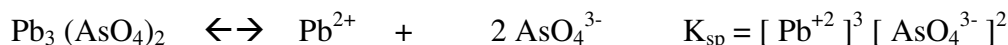
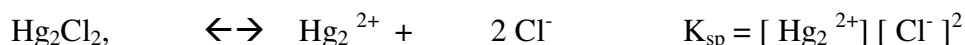
These Notes are to SUPPLEMENT the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests!

To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

17.1 The Solubility Product Constant



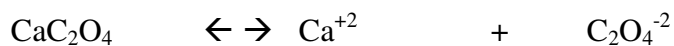
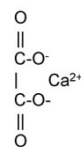
Example 17.1 Write the solubility product expression for AgCl, Hg₂Cl₂, Pb₃(AsO₄)₂



Example 17.1 Give the solubility product expression for Barium Sulfate, Iron (III) Hydroxide, Calcium Phosphate? **Class Project**

Exercise 17.2 at 25 °C, 1 L of water with CaC₂O₄ is evaporated to dryness giving 0.0061 g of CaC₂O₄. Calculate K_{sp} ?

$$\text{Moles of CaC}_2\text{O}_4 = 0.0061 \text{ g} / 128 \text{ g/mole} = 4.8 \times 10^{-5} \text{ moles}$$



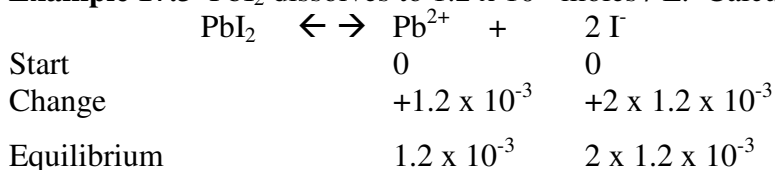
Start	0	0
Change	+4.8 x 10 ⁻⁵ moles	+4.8 x 10 ⁻⁵ moles
Equilibrium	4.8 x 10 ⁻⁵ moles	4.8 x 10 ⁻⁵ moles

$$K_{\text{sp}} = [\text{Ca}^{+2}] [\text{C}_2\text{O}_4^{-2}] = (4.8 \times 10^{-5})(4.8 \times 10^{-5}) = 2.3 \times 10^{-9}$$

Exercise 17.2 Silver Chloride has the solubility of 1.9 x 10⁻³ g/l. Calculate K_{sp} ?

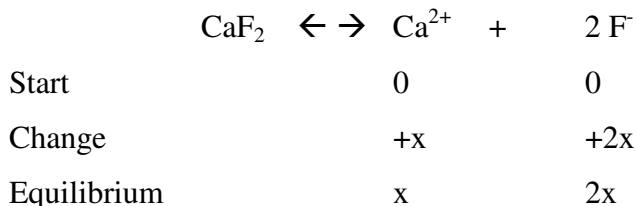
Class Project

Example 17.3 PbI_2 dissolves to 1.2×10^{-3} moles / L. Calculate K_{sp} ?



$$K_{sp} = [\text{Pb}^{2+}] [\text{I}^-]^2 = (1.2 \times 10^{-3}) (2 \times 1.2 \times 10^{-3})^2 = 6.9 \times 10^{-9}$$

Example 17.4 CaF_2 has a $K_{sp} = 3.4 \times 10^{-11}$. What is the solubility in grams / liter.



$$K_{sp} = [\text{Ca}^{2+}] [\text{F}^-]^2 = 3.4 \times 10^{-11} = x * (2x)^2$$

$$4x^3 = 3.4 \times 10^{-11} \quad x = 2.0 \times 10^{-4} = \text{solubility in moles / Liter}$$

$$2.0 \times 10^{-4} \text{ moles} * 78.1 \text{ g / mole} = 1.6 \times 10^{-2} \text{ grams / liter}$$

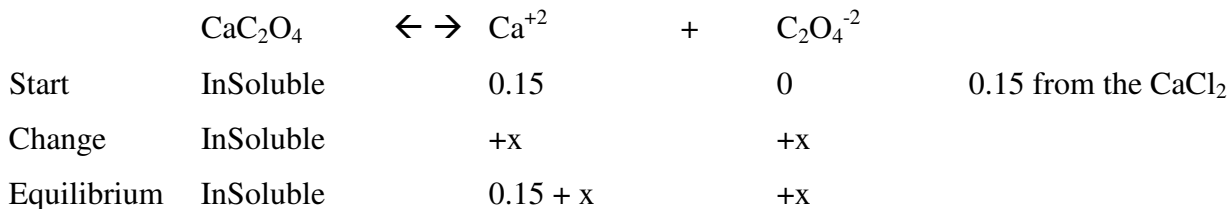
Exercise 17.4 Calcium Sulfate has a $K_{sp} = 2.4 \times 10^{-5}$. What is the solubility in grams / liter. **Class Project**

Concept Check 17.1 Lead compounds are used in paint. If PbCrO_4 with a $K_{sp} = 1.8 \times 10^{-14}$, PbSO_4 with a $K_{sp} = 1.7 \times 10^{-8}$ or PbS $K_{sp} = 2.5 \times 10^{-27}$ are added to the same quantity of water, which one will supply the largest quantity of Lead (II)? **Class Project**

17.2 Solubility and the Common Ion

Determine the solubility of a salt when a common anion from another salt is added. E.g. A soluble salt of CaCl_2 is added to a slightly soluble CaC_2O_4 [Oxalate].

Example 17.5 What is the molar solubility of CaC_2O_4 in a solution with 0.15 M CaCl_2 ? In pure water, CaC_2O_4 is soluble to 4.8×10^{-5} M. The solubility of CaC_2O_4 is 2.3×10^{-9} .



$$K_{sp} = [\text{Ca}^{+2}] [\text{C}_2\text{O}_4^{-2}] = (0.15 + x) x = 2.3 \times 10^{-9}$$

Since CaC_2O_4 is only slightly soluble, x is small. And

TEST = $[\text{CaC}_2\text{O}_4] / 2.3 \times 10^{-9} = [\text{A BIG NUMBER}] / 2.3 \times 10^{-9} = \text{MUCH GREATER THAN 100!!}$
So, below, $(0.15 + x) = 0.15$

$$x = \frac{2.3 \times 10^{-9}}{0.15 + x} = \frac{2.3 \times 10^{-9}}{0.15} = 1.5 \times 10^{-8} = \text{molar solubility of } \text{CaC}_2\text{O}_4$$

From above, the molar solubility in water is 4.8×10^{-5} moles or 3200 times more soluble!!

Exercise 17.5 What is the molar solubility of BaF_2 in water? $K_{\text{sp}} = 1.0 \times 10^{-6}$.
What is the molar solubility of BaF_2 in 0.15 NaF?

Class Project

17.3 Precipitation Calculations

Reaction Quotient = Q_c = Ion Product = same as Equilibrium Constant K_c .

1. If $Q_c < K_c$ **The reaction goes in the forward direction**
2. If $Q_c = K_c$ **The reaction is at equilibrium**
3. If $Q_c > K_c$ **The reaction goes in the reverse direction**

We add $\text{Pb}(\text{NO}_3)_2$ and NaCl to a solution to give: 0.050 M $\text{Pb}(\text{NO}_3)_2$ and 0.10 M Cl^- . Will PbCl_2 precipitate out?

$K_{\text{sp}} \text{PbCl}_2$ is 1.6×10^{-5} .



You put in the concentrations at the start of the reaction

$$\text{Ion Product} = Q_c = [\text{Pb}^{2+}] [\text{Cl}^-]^2 = (0.050)(0.10)^2 = 5.0 \times 10^{-4}$$

$K_{\text{sp}} \text{PbCl}_2$ is 1.6×10^{-5} . So Q_c is greater than K_{sp} , so the reaction goes in the reverse direction.

- or - PbCl_2 is formed – it **does precipitate out!**

Example 17.6 Calcium is 0.0025 M. If Oxalate ion is 1.0×10^{-7} , will calcium oxalate precipitate out? $K_{\text{sp}} = 2.3 \times 10^{-9}$.

$$\text{Ion Product} = Q_c = [\text{Ca}^{+2}] [\text{C}_2\text{O}_4^{-2}] = (0.0025)(1.0 \times 10^{-7}) = 2.5 \times 10^{-10}$$

$$Q_c = 2.5 \times 10^{-10} \quad K_{\text{sp}} = 2.3 \times 10^{-9}$$

Q_c is smaller than K_{sp} so the reaction goes forward – no ppt!

Exercise 17.6 A water solution is 0.0052 M in Ca^{2+} and 0.0041 M in SO_4^{2-} . Will CaSO_4 precipitate out? $K_{\text{sp}} = 2.4 \times 10^{-4}$.
Class Project

Example 17.7 Is a ppt expected from a solution of 50.0 ml of 0.0010 M BaCl_2 and 50.0 ml of 0.00010 M Na_2SO_4 ? K_{sp} for $\text{BaSO}_4 = 1.1 \times 10^{-10}$.

$$\text{Ba}^{+2} = 0.050 \text{ L} * 0.0010 \text{ M/L} = 5.0 \times 10^{-5} \text{ mol}$$

$$\text{Ba}^{+2} = \frac{5.0 \times 10^{-5} \text{ mol}}{[50.0 \text{ ml} + 50.0 \text{ ml}] * 1 \text{ L} / 1000 \text{ ml}} = 5.0 \times 10^{-4} \text{ M} \quad [\text{do same for } \text{SO}_4]$$

$$Q_c = [\text{Ba}^{+2}] [\text{SO}_4] = 1.1 \times 10^{-10} = (5.0 \times 10^{-5})(5.0 \times 10^{-5}) = 2.5 \times 10^{-8}$$

$$Q_c = 2.5 \times 10^{-8} \quad K_{\text{sp}} = 1.1 \times 10^{-10} \quad Q_c > K_{\text{sp}} \text{ The reaction goes to the reverse, yes PPT!}$$

Exercise 17.7 Will Lead (II) Sulfate precipitate out from a solution of 255 ml 0.00016 M lead (II) nitrate and 456 ml 0.00023 M sodium sulfate? K_{sp} for $\text{PbSO}_4 = 1.7 \times 10^{-8}$.
Class Project

Fractional Precipitation is a technique for separating two or more ions from a solution of a reactant that precipitates the first one ion, then another.

Start with 0.10 M Ba²⁺ and 0.10 M Sr²⁺.

Add K₂CrO₄ [Potassium Chromate] to precipitate the chromates [Ba & Sr].

K_{sp} for BaCrO₄ = 1.2 x 10⁻¹⁰. K_{sp} for SrCrO₄ = 3.5 x 10⁻⁵.

Solution: calculate at what concentration the chromate will ppt out.

$$K_{sp} = [Ba^{+2}] [CrO_4^{-}] = 1.2 \times 10^{-10}$$

$$(0.10) [CrO_4^{-}] = 1.2 \times 10^{-10} \quad [CrO_4^{-}] = 1.2 \times 10^{-10} / 0.10 = 1.2 \times 10^{-9} M$$

$$K_{sp} = [Sr^{+2}] [CrO_4^{-}] = 3.5 \times 10^{-5}$$

$$(0.10) [CrO_4^{-}] = 3.5 \times 10^{-5} \quad [CrO_4^{-}] = 3.5 \times 10^{-5} / 0.10 = 3.5 \times 10^{-4} M$$

Ba precipitates at [CrO₄⁻] = 1.2 x 10⁻⁹ M Sr precipitates at [CrO₄⁻] = 3.5 x 10⁻⁴ M

Ba ppt out first!

What % of Ba²⁺ is left when the SrCrO₄ starts to precipitate out?

$$K_{sp} = [Ba^{+2}] [CrO_4^{-}] = 1.2 \times 10^{-10}$$

When the [CrO₄⁻] = 3.5 x 10⁻⁴ SrCrO₄ will start to ppt out.

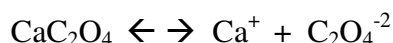
$$[Ba^{+2}] [3.5 \times 10^{-4}] = 1.2 \times 10^{-10}$$

$$[Ba^{+2}] = 1.2 \times 10^{-10} / 3.5 \times 10^{-4} = 3.4 \times 10^{-7} M \quad \text{When SrCrO}_4 \text{ will start to ppt out, this is the } [Ba^{+2}]$$

$$\text{The amount of Ba}^{+2} \text{ left} = 100 \% * 3.4 \times 10^{-7} M / 0.10 M = 3.4 \times 10^{-4} \%$$

See Figure 17.5, page 745. Silver Nitrate is in your burette for a titration. The flask contains Chloride. As you titrate, Silver Chloride will precipitate out. The flask also has some Potassium Chromate. When all of the Chloride is titrated by the Silver, the first amount of excess Silver will precipitate out Silver Chromate which is red-brown.

17.4 Effect of pH on Solubility.



The oxalate ion will react with an acid to form HC₂O₄⁻¹ [see the reverse reactions below]:



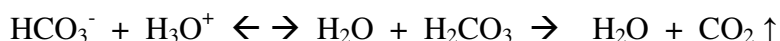
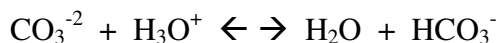
So if you add acid to a solution of Calcium Oxalate, the H⁺ will react with the C₂O₄⁻² to form HC₂O₄⁻ and H₂C₂O₄. As it does this, more CaC₂O₄ will dissolve to keep up the equilibrium of C₂O₄⁻².

So the effect is adding acid to the Calcium Oxalate solution will cause more Calcium Oxalate to dissolve!

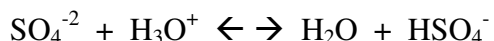
Salts of a weak acid are more soluble in an acidic solution.

Tooth decay has a similar chemical pathway. Bacteria in you mouth metabolise sugar and generate a small amount of an acidic solution. Teeth are a calcium compound: Ca₅(PO₄)₃OH. The salt of the weak acid PO₄⁻³ dissolves in the acidic solution forming cavities. Adding Fluoride to the water adds F⁻. This will replace the OH with F to form Ca₅(PO₄)₃F which is less soluble!

Example 17.8 Which salt – calcium carbonate or calcium sulfate has its solubility affected more by the addition of HCl? $K_{a2} \text{HCO}_3^- = 4.8 \times 10^{-11}$ and for HSO_4^- .



The carbon dioxide is removed from the reaction, forcing it to the right.



Based on the K_a 's above, HSO_4^- is a stronger acid than HCO_3^- so CaCO_3 is more soluble in an acidic solution than CaSO_4 .

Exercise 17.8 Which salt – silver chloride or silver cyanide has its solubility affected more by the addition of acid?

Separation of Metal Ions by Sulfide Ppt.

Most metal sulfides are insoluble in water, but slightly dissolve in acidic solutions [see above note].

Zinc and Lead (II) can be separated by adjusting the pH with the addition of Sulfide as:



Making the solution acidic drives the reaction to the left leaving only a small amount of sulfide in solution.



In an acidic solution, PbS with the lower solubility constant will ppt out first!

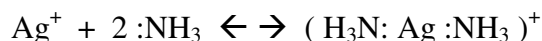
Complex Ion Equilibria

A **complex ion** is formed from a metal ion and a Lewis Base attached by a coordinate covalent bond:

Lewis Base: donates an electron pair

Covalent Bond: a bond formed when both electrons of the bond are donated by the same atom. e.g. $:\text{NH}_3$.

Ligand is the Lewis Base that bonds to the metal ion to form the complex.



The formation constant K_f of a complex ion is the equilibrium constant for the formation of the complex ion from the aqueous metal ion and the ligands.

$$K_f = \frac{[\text{H}_3\text{N: Ag :NH}_3^+]}{[\text{Ag}^+][:\text{NH}_3]^2} = 1.7 \times 10^7. \quad \text{Class Project} \quad \text{So which way will this reaction go?}$$

The dissociation constant K_d for a complex ion is the reciprocal of K_f .

$$K_d = \frac{1}{K_f} = \frac{[\text{Ag}^+][:\text{NH}_3]^2}{[\text{H}_3\text{N: Ag :NH}_3^+]} = \frac{1}{1.7 \times 10^7}$$

Example 17.9 What is the concentration of Ag^+ in 0.010 M AgNO_3 with 1.00 M NH_3 ? K_f for $\text{Ag}(\text{NH}_3)_2^+$ is 1.7×10^7 . Since K_f is large, most of the silver will go to form the Complex.

	Ag^+	+	$2 : \text{NH}_3$	$\leftarrow \rightarrow$	$(\text{H}_3\text{N} : \text{Ag} : \text{NH}_3)^+$	
Start	0.010 M					
At equilibrium	0.010 M		$1.00 \text{ M} - 2 * 0.010\text{M}$		0.010 M	
	0.010 M		0.98 M			
	$(\text{H}_3\text{N} : \text{Ag} : \text{NH}_3)^+$	$\leftarrow \rightarrow$	Ag^+	+	$2 : \text{NH}_3$	<u>DISSOCIATION</u>
Start	0.010 M		0		0.98 M	
Change	-x		+x		+2x	
At equilibrium	$0.010 - x$		x		$0.98 + 2x$	

$$K_f = \frac{[\text{H}_3\text{N} : \text{Ag} : \text{NH}_3^+]}{[\text{Ag}^+][\text{:NH}_3]^2} = 1.7 \times 10^7.$$

$$K_d = \frac{1}{K_f} = \frac{1}{1.7 \times 10^7} = \frac{[\text{Ag}^+][\text{:NH}_3]^2}{[\text{H}_3\text{N} : \text{Ag} : \text{NH}_3^+]} = \frac{x(0.98 + 2x)^2}{(0.010 - x)}$$

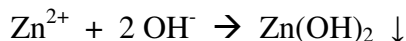
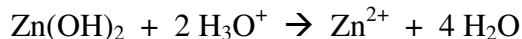
Test = $[\text{Ag}^+]/K_d = 0.010 / 1.7 \times 10^{-7} = 1.7 \times 10^{-5}$ which is greater than 100 so +2x and -x go away!

$$\frac{1}{1.7 \times 10^7} = 5.9 \times 10^{-8} = \frac{x(0.98)^2}{0.010}$$

$$x = 5.9 \times 10^{-8} * 0.010 / (0.98)^2 = 6.1 \times 10^{-10} \text{ for the } \text{Ag}^+ \text{ concentration}$$

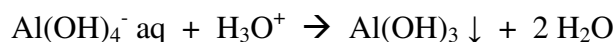
Exercise 17.9 What is the concentration of Cu^{+2} in a solution that started with 0.015 M $\text{Cu}(\text{NO}_3)_2$ and 0.100 M NH_3 ? Cu^{+2} forms $\text{Cu}(\text{NH}_3)_4^{+2}$ with a K_f of 4.8×10^{12} . **Class Project**

Amphoteric Hydroxide is a metal hydroxide that reacts with both bases and acids.



Other common Amphoteric hydroxides are Al^{3+} , Cr^{3+} , Pb^{2+} , Sn^{2+} and Sn^{4+} .

Aluminum's Amphoteric properties is used to purify it. Aluminum is dissolved in NaOH and filtered to remove the insoluble such as sand and iron oxide. Adding acid will then precipitate out the pure $\text{Al}(\text{OH})_3$.]



Using Solubility for Qualitative Metal Ion Analysis:

Group I Ag^+ , Hg_2^{2+} , Pb^{2+} Precipitated as the chloride with HCl

Group II As^{3+} , Bi^{3+} , Cd^{2+} , Cu^{2+} , Hg^{2+} , Pb^{2+} , Sb^{3+} and Sn^{4+}
Precipitated as the sulfide with acidic H_2S

Group III Co^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+}
Precipitated as the sulfide with basic $[\text{NH}_3] \text{H}_2\text{S}$

Group IV Ba^{2+} , Ca^{2+} , Mg^{2+} , Sr^{2+} Precipitated as the carbonate or phosphate

Filtrate will contain any soluble Group V – K^+ and Na^+ ions.