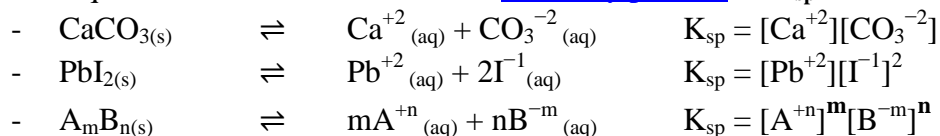


Ch 17 Solubility and Complex Ion Equilibria

For an ionic compound which dissolves into H₂O, there is a reaction with an equilibrium.

The equilibrium constant is called the **solubility product** or **K_{sp}**.



Ex 17.01 a.) For Mg(OH)₂ K_{sp} = [Mg⁺²][OH⁻¹]² b.) For Pb₃(PO₄)₂, K_{sp} = [Pb⁺²]³[PO₄⁻³]²

The **molar solubility (molsol)** is the saturated molarity of the compound.

- For solutions with no other compounds present, A_mB_n has **molsol** = [A]/m = [B]/n
- In these solutions, molsol can be used to calculate K_{sp} and vice-versa.

Ex 17.02 Find molsol and K_{sp} if 0.00934 g CaCO₃ are dissolved in 1.00 L of water at saturation.

- MolSol = [Ca⁺²] = [CO₃⁻²] = (0.00934 g/L) ÷ (100.09 g/mol) = 9.33 × 10⁻⁵ M
- K_{sp} = [Ca⁺²][CO₃⁻²] = (**molsol**)² = (9.33 × 10⁻⁵)² = 8.7 × 10⁻⁹

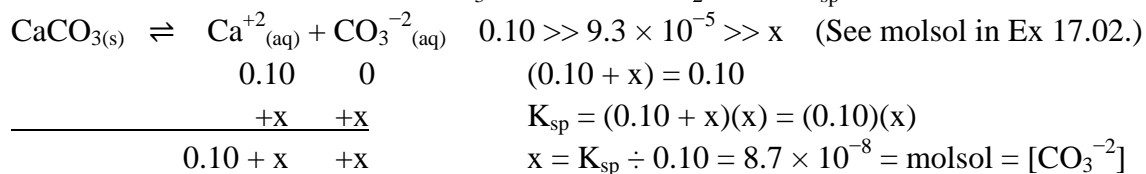
Ex 17.03 PbI_{2(aq)} has molsol = 1.5 × 10⁻³ mol/L. Find K_{sp}.

- [Pb⁺²] = molsol [I⁻¹] = 2 × molsol
- K_{sp} = [Pb⁺²][I⁻¹]² = (molsol)(2 × molsol)² = 4 × (molsol)³ = 4 × (1.5 × 10⁻³)³ = 1.4 × 10⁻⁸
- **K_{sp} = 4 × (molsol)³ and molsol = $\sqrt[3]{K_{\text{sp}}/4}$**

Common Ion Effect

- **K_{sp}** is a **constant** at a given T. Therefore, increasing the concentration of one ion, by adding a 2nd compound which contains it, will have to **reduce the concentration of the other ion**.
- **MolSol** will still be directly related to the concentration of the other ion, and its value be **reduced** as well.
- The concentration of the added common ion is no longer directly related to molsol. This common ion concentration is approximately constant if the amount added from the 2nd compound far exceeds the amount which dissociates from the molsol of the 1st compound.
- If CaCO_{3(s)} is at equilibrium with a solution where CaCl₂ was also dissolved, then the Ca⁺² from CaCl₂ decreased the amount of CO₃⁻² that can be dissolved.
- K_{sp} does not change, but [Ca⁺²] will be larger (and approximately constant) due to the CaCl₂. So, molsol and [CO₃⁻²] will both decrease.

Ex 17.05 Determine the molsol of CaCO₃ in 0.10 M CaCl₂ where K_{sp} = 8.7 × 10⁻⁹



Precipitation Calculations

- With K_c , the reaction quotient Q_c took the same form, but with interim (i) concentrations.
- With K_{sp} , the Q_c is called the **ion product**. Q_c is interim and not necessarily at equilibrium.
- $Q_c = K_{sp}$ at equilibrium, when the solution is saturated and at its solubility.
- If two solutions are combined, then Q_c can be used to predict whether or not precipitation will occur.
- $Q_c > K_{sp}$ **results in ppt.** (The reaction goes in reverse.)
- If $Q_c < K_{sp}$, the solution is not saturated, more can dissolve, and there is no ppt. (The reaction can go forward.)

Ex 17.06 Predict whether precipitation occurs for CaCO_3 ($K_{sp} = 8.7 \times 10^{-9}$)

- $[\text{Ca}^{+2}]_i$ is 0.00025 M and $[\text{CO}_3^{-2}]_i$ is 1.2×10^{-7} M.
- Ion Product is $Q_c = [\text{Ca}^{+2}]_i[\text{CO}_3^{-2}]_i = (2.5 \times 10^{-4})(1.2 \times 10^{-7}) = 3.0 \times 10^{-11}$
- $Q_c < K_{sp}$ No ppt occurs and more CaCO_3 can dissolve.

Ex 17.07 Predict whether precipitation occurs for BaSO_4 ($K_{sp} = 1.1 \times 10^{-10}$)

- Use this equation for dilution: $M_2 = M_1 \left(\frac{V_1}{V_2} \right)$, where V_2 is the total combined volume.
- $[\text{Ba}^{+2}]_i = (0.00015 \text{ M}) \left(\frac{0.050\text{L}}{0.100\text{L}} \right) = 0.000075 \text{ M} = 7.5 \times 10^{-5} \text{ M}$
- $[\text{SO}_4^{-2}]_i = (0.0015 \text{ M}) \left(\frac{0.050\text{L}}{0.100\text{L}} \right) = 0.00075 \text{ M} = 7.5 \times 10^{-4} \text{ M}$
- $Q_c = [\text{Ba}^{+2}]_i[\text{SO}_4^{-2}]_i = (7.5 \times 10^{-5})(7.5 \times 10^{-4}) = 5.6 \times 10^{-8}$
- $Q_c > K_{sp}$ The reaction goes in reverse and a solid ppt forms.

Fractional Precipitation

- Fractional precipitation is a technique for separating two or more ions from a solution by adding a counter-ion that sequentially ppts one ion completely, then another (and so forth).
- This can be accomplished if there is a large difference between the K_{sp} 's for the different compounds of the ions with the added counter-ion.
- The desired result is that one ion **completely ppts** before the next ion begins to ppt.
- For example, suppose we add CrO_4^{-2} to a solution with $[\text{Ba}^{+2}] = [\text{Sr}^{+2}] = 0.10 \text{ M}$.
 $K_{sp1} = 8.5 \times 10^{-11}$ for BaCrO_4 and $K_{sp2} = 3.6 \times 10^{-5}$ for SrCrO_4 , so BaCrO_4 will ppt first.

$$[\text{CrO}_4^{-2}] = \frac{K_{sp1}}{[\text{Ba}^{+2}]} = \frac{(8.5 \times 10^{-11})}{(0.10)} = 8.5 \times 10^{-10} \text{ M when } \text{BaCrO}_4 \text{ begins to ppt.}$$

$$[\text{CrO}_4^{-2}] = \frac{K_{sp2}}{[\text{Sr}^{+2}]} = \frac{(3.6 \times 10^{-5})}{(0.10)} = 3.6 \times 10^{-4} \text{ M when } \text{SrCrO}_4 \text{ begins to ppt.}$$

$$\text{When } \text{SrCrO}_4 \text{ begins to ppt, } [\text{Ba}^{+2}] = \frac{K_{sp1}}{[\text{CrO}_4^{-2}]} = \frac{8.5 \times 10^{-11}}{3.6 \times 10^{-4}} = 2.4 \times 10^{-7} \text{ M}$$

$$\frac{2.4 \times 10^{-7}}{0.10} \times 100\% = 2.4 \times 10^{-4} \%$$

Only 0.00024% of the Ba^{+2} is left in the solution when SrCrO_4 begins to ppt.

This means that 99.99976% of the Ba^{+2} has precipitated before the Sr^{+2} even begins to ppt.

Effect of pH on Solubility

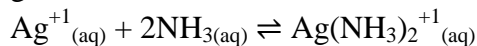
- Oxalate salts are basic and have low solubility. $\text{BaC}_2\text{O}_4(\text{s}) \rightleftharpoons \text{Ba}^{+2}(\text{aq}) + \text{C}_2\text{O}_4^{-2}(\text{aq})$
- Suppose a strong acid is added: $\text{C}_2\text{O}_4^{-2}(\text{aq}) + \text{H}_3\text{O}^{+1}(\text{aq}) \rightleftharpoons \text{HC}_2\text{O}_4^{-1}(\text{aq}) + \text{H}_2\text{O}(\text{L})$
- The strong acid removes $[\text{C}_2\text{O}_4^{-2}]$. This makes Q_c less than K_c in the first reaction.
- This causes the equilibrium of that reaction to shift to the right, so that $\text{BaC}_2\text{O}_4(\text{s})$ dissolves.
- Salts like BaC_2O_4 which contain the **conjugate base anion (A^{-n})** of a weak acid can be expected to be **more soluble in acidic solutions**.
- Salts like $(\text{C}_5\text{H}_5\text{NH})\text{Cl}$ which contain the **conjugate acid cation (BH^{+1})** of a weak base can be expected to be **more soluble in basic solutions**.

Ex 17.08 Determine which Salt Solubility is more affected by Acidification: CaCO_3 vs. CaSO_4

- **The salt with the stronger base anion will react most strongly with the acid.**
- Look at the conjugate acids of the ions. **The weaker acid has the stronger base anion.**
- [Figure 14.8](#) shows that HCO_3^{-1} is a weaker acid than HSO_4^{-1} .
- The table also shows that CO_3^{-2} is a stronger base than SO_4^{-2} .
- Therefore, the solubility of CaCO_3 would be more improved by acid than that of CaSO_4 .

Complex Ion Equilibria

- A **complex ion** is formed from a **metal cation (Lewis acid)** and a **ligand (Lewis base)**.
- They are connected together by a coordinate covalent bond (one atom donates both e^{-1} 's).
- A ligand is a Lewis base because it has a nonbonding e^{-1} pair that it can donate (like $:\text{NH}_3$).



- **Formation Constant:** $K_f = \frac{[\text{Ag}(\text{NH}_3)_2^{+1}]}{[\text{Ag}^{+1}][\text{NH}_3]^2} = 1.7 \times 10^{+7}$ K_f is a very large number!

Refer to [Appendix K](#) and [here](#) for K_f values of other complex ions.

- The reverse reaction has a very small equilibrium constant as it is heavily unfavored.
- **Dissociation Constant:** $K_d = \frac{1}{K_f} = \frac{[\text{Ag}^{+1}][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^{+1}]} = 5.9 \times 10^{-8}$ $\text{Ag}(\text{NH}_3)_2^{+1} \rightleftharpoons \text{Ag}^{+1} + 2\text{NH}_3$

Ex 17.09 Determine Free $[\text{Ag}^{+1}]$ in a Complex Ion Solution (1.00 M NH_3 and 0.050 M AgNO_3)

- First, assume the formation reaction between Ag^{+1} and NH_3 goes 100% forward.
- Essentially all Ag^{+1} is converted to complex ion: $[\text{Ag}(\text{NH}_3)_2^{+1}]_{\text{eqm}} = [\text{Ag}^{+1}]_o = 0.050 \text{ M}$
- This removes 2NH_3 's for each Ag^{+1} : $[\text{NH}_3]_{\text{eqm}} = [\text{NH}_3]_o - 2[\text{Ag}^{+1}]_o$
 $[\text{NH}_3]_{\text{eqm}} = 1.00 - (2 \times 0.050) = 0.90 \text{ M}$
- Then, determine the extent of the reverse reaction (dissociation), using the values from the formation reaction (above) to set up the dissociation reaction's equilibrium table.



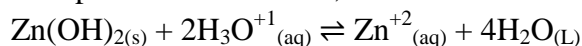
$$\begin{array}{ccc} 0.050 & 0 & 0.90 \\ -x & +x & +2x \\ \hline 0.050 - x & +x & 0.90 + 2x \end{array} \quad [\text{Ag}^{+1}] = x = \frac{K_d(0.050)}{(0.90)^2} = 3.6 \times 10^{-9} \text{ M}$$

Very little silver has separated from the complex ion.
Only a tiny amount of the complex ion has dissociated.

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

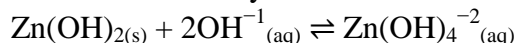
- $\text{Zn(OH)}_{2(s)}$ reacts with either 2OH^{-1} 's or $2\text{H}_3\text{O}^{+1}$'s.

- The compound can be a base, so that it reacts with acids:



- The compound can also be an acid, so that it reacts with more hydroxides.

It combines with the hydroxides to create a complex ion:



- Hydroxides of Al, Cr(III), Pb(II), Sn(II), and Sn(IV) have similar reactions.

- Al is removed from bauxite ore ($\text{Al}_2\text{O}_{3(s)}$ and $\text{Fe}_2\text{O}_{3(s)}$) with $\text{OH}^{-1}_{(aq)}$.

This forms the soluble complex ion $\text{Al(OH)}_4^{-1}_{(aq)}$, while $\text{Fe}_2\text{O}_{3(s)}$ remains insoluble.

Add one equivalent of acid to the complex ion in solution to get $\text{Al(OH)}_{3(s)}$ as a precipitate.

Complex Ions and Solubility

- A precipitate can be dissolved by a ligand that forms a soluble complex with the metal ion.

An example of this would be the formation of $\text{Ag(NH}_3)_2^{+1}_{(aq)}$ from $\text{AgCl}_{(s)}$ and $\text{NH}_{3(aq)}$.

- The ion product (Q_c) for a slightly soluble salt (AgCl) can be **reduced below its K_{sp}** by adding a ligand (NH_3) to remove the cation (Ag^{+1}) and form its complex ion ($\text{Ag(NH}_3)_2^{+1}$).

- As a result, the precipitate can be **dissolved** by adding the **ligand**.

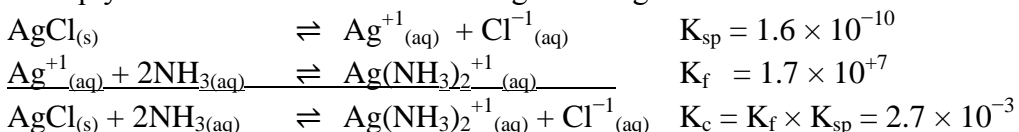
- The ligand removes the cation by combining with it to create the complex ion.

- The K_{sp} reaction which dissolves $\text{AgCl}_{(s)}$ will shift to the right, and this shift can be predicted from LeChatelier's principle because the removed Ag^{+1} cation is the product of this reaction.

- The two reactions involved, dissolving the precipitate (K_{sp}) and forming the complex ion (K_f), can be added together into one sum reaction that has its own equilibrium constant (K_c).

- Multiply the two component K expressions together to get the sum reaction's K_c expression.

- Multiply the two numerical K values together to get the sum reaction's numerical K_c value.



Ex 17.10 Effect of a Ligand on Solubility in a Solution with 0.050 M AgNO_3 and 0.010 M NaCl

a) If no ligand is present, then substitute both concentrations into the Q_c expression.

$$Q_c = [\text{Ag}^{+1}]_i[\text{Cl}^{-1}]_i = (0.050)(0.010) = 5.0 \times 10^{-4} \quad \text{and} \quad K_{sp} = 1.6 \times 10^{-10}$$

$Q_c \gg K_{sp}$ AgCl precipitates.

b) In Ex 17.09, 0.90 M NH_3 is present as a ligand, so that most of the Ag^{+1} is complexed as $\text{Ag(NH}_3)_2^{+1}_{(aq)}$. If NH_3 is present along with Ag^{+1} and Cl^{-1} , then $[\text{Ag}^{+1}]$ will be small.

The amount of free Ag^{+1} ion was reduced to $[\text{Ag}^{+1}] = 3.6 \times 10^{-9}$ in Ex 17.09.

$$Q_c = [\text{Ag}^{+1}]_i[\text{Cl}^{-1}]_i = (3.6 \times 10^{-9})(0.010) = 3.6 \times 10^{-11}$$

$Q_c < K_{sp}$ AgCl does not precipitate.

Ex 17.11 Effect of a Ligand on MolSol in a Saturated Solution of AgCl with 1.00 M NH₃

- MolSol of AgCl is not equal to [Ag⁺] because Ag⁺ has been removed by NH₃.
- MolSol of AgCl is still equal to [Cl⁻].
- Determine [Cl⁻] in 1.00 M NH₃ where K_c = 2.7 × 10⁻³ for the combined sum reaction.



1.00 M	0	0
<hr style="width: 100%; border: 0.5px solid black;"/>	<hr style="width: 100%; border: 0.5px solid black;"/>	<hr style="width: 100%; border: 0.5px solid black;"/>
- 2x	+x	+x
1.0 - 2x	x	x

$$K_c = 2.7 \times 10^{-3} = \frac{(x)^2}{(1 - 2x)^2}$$

$$\sqrt{K_c} = 0.052 = \frac{x}{1 - 2x}$$

$$\text{molSol of AgCl} = [\text{Cl}^{-1}] = x = 0.047 \text{ M}$$

Qualitative Analysis

- A qualitative analysis determines the identities of the substances present in a mixture.
- For example, the metal cations present in a solution can be identified based on the **solubilities** of their chlorides and sulfides. Each of the cations could be sequentially isolated by fractional precipitation and then analyzed for in their precipitates.
- For example, Cl⁻ will **precipitate** Ag⁺, Hg₂⁺², Hg⁺², and Pb⁺² ions.
All of the other cations, though, will remain **dissolved** in solution.
The precipitate can then be separated from the solution and analyzed for the three metals.
- The remaining solution can be treated with H₂S and H₃O⁺ to precipitate the acid-insoluble sulfides.
This precipitate can be analyzed for metals such as Cu⁺² and Bi⁺³.
- Next, H₂S and NH₃ will precipitate the base-insoluble sulfides.
This precipitate can be analyzed for metals such as Ni⁺² and Al⁺³.
- Phosphates and carbonates of alkali earth metals (Group II-A), such as Ca⁺² and Mg⁺², can then be precipitated for analysis as well.
- **Flame tests** can identify metal cations remaining in the solution, typically alkali metals (Group I-A) such as Na⁺¹ (yellow flame) and K⁺¹ (violet flame), which rarely precipitate.