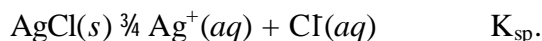


Solubility and Complex Ion Formation

Solubility

Solubility is the limit to which something will dissolve. When we think of something as being soluble we think of substances like Sodium Chloride or sugar. Most substances that we think of as being insoluble, according to the solubility rules from Chapter 4, are really only slightly soluble. For instance, Silver Chloride, which is generally thought to be insoluble, is actually in equilibrium with the ions when in water



The equilibrium constant here is K_{sp} , which stands for **solubility product constant**. The equilibrium expression for the above is

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

Remember that solids are absorbed into the equilibrium constant and as a result do not appear explicitly in the equilibrium expression.

Knowing the K_{sp} of a substance allows us to calculate the molar solubility of that substance. We can set up our table as always

	$\text{AgCl}(s)$	\rightleftharpoons	$\text{Ag}^+(aq)$	+	$\text{Cl}^-(aq)$
Initial []			0		0
Δ			+x		+x
Final []			x		x

Plugging this information into the equilibrium expression gives

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (x)(x) = x^2 = 1.9 \times 10^{-10}$$

Solving for x, which is the molar solubility, gives

$$x^2 = 1.9 \times 10^{-10}$$

$$x = \sqrt{1.9 \times 10^{-10}} = 1.4 \times 10^{-5}$$

The molar solubility of Silver Chloride is 1.4×10^{-5} M.

Usually the solubility is given in units of g of solute per 100 mL of water (solution). How do we convert between molar solubility and this unit? What is the solubility of Silver Chloride in g AgCl/100 mL water?

$$\frac{1.4 \times 10^{-5} \text{ mol AgCl}}{L} \times \frac{143.3 \text{ g AgCl}}{1 \text{ mol AgCl}} \times \frac{1 \text{ L}}{10(100 \text{ mL})} = 2.0 \times 10^{-4} \text{ g AgCl} / 100 \text{ mL}$$

Let's look at another, slightly more complicated, problem.

What is the molar solubility of Calcium Phosphate ($K_{sp} = 1 \times 10^{-26}$)?

	$\text{Ca}_3(\text{PO}_4)_2(s)$ $\frac{3}{4}$	$3 \text{ Ca}^{2+}(aq)$ +	$2 \text{ PO}_4^{3-}(aq)$
Initial []		0	0
Δ		+3x	+2x
Final		3x	2x

$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (3x)^3 (2x)^2 = 108x^5 = 1 \times 10^{-26}$$

$$x = \sqrt[5]{\frac{1 \times 10^{-26}}{108}} = 2 \times 10^{-6}$$

The molar solubility of Calcium Phosphate is 2×10^{-6} M.

Common Ion Effect

When we try to dissolve a slightly soluble compound into a solution that already contains one of the ions, the net result is that the compound does not dissolve to as great an extent as it would if that ion were not present. This is an application of LeChâtelier's Principle. The concentration of the ion not originally present in the solution will be much lower than it would be in pure water.

What is the concentration of Calcium ions when solid Calcium Phosphate is added to a 0.25 M solution of Sodium Phosphate?

	$\text{Ca}_3(\text{PO}_4)_2(s)$ $\frac{3}{4}$	$3 \text{ Ca}^{2+}(aq)$ +	$2 \text{ PO}_4^{3-}(aq)$
Initial []		0	0.25
Δ		+3x	+2x
Final		3x	0.25+2x

$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (3x)^3 (0.25 + 2x)^2 \approx (3x)^3 (0.25)^2 = 1.6875x^3 = 1 \times 10^{-26}$$

$$x = \sqrt[3]{\frac{1 \times 10^{-26}}{1.6875}} = 2 \times 10^{-9}$$

The concentration of Calcium ions is 3 times this amount or 6×10^{-9} M. This is approximately 1000 times smaller than it would have been in pure water.

Precipitation Calculations

All compounds whether they are considered soluble or slightly soluble have a solubility limit. That limit depends on the concentration of the species present in the solution. The compound will precipitate if the concentrations are such that the reaction quotient, Q , is greater than the K_{sp} .

Therefore, in order to determine when a compound will precipitate or not, we need to calculate Q . Then if:

$Q > K$	A precipitate will result
$Q = K$	The solution is at equilibrium
$Q < K$	No precipitate, any solids will dissolve until $Q = K$.

Examples:

- A solution contains 1.5×10^{-4} M Hydrochloric acid and 1.2×10^{-3} M Lead(II) Nitrate. Is there a precipitate?

$$Q = [\text{Pb}^{2+}][\text{Cl}^-]^2 = (1.2 \times 10^{-3})(1.5 \times 10^{-4})^2 = 2.7 \times 10^{-11}$$

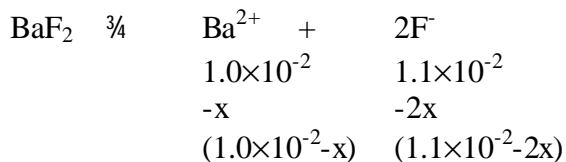
This is less than the K_{sp} for Lead(II) Chloride (1.6×10^{-5}) so there is no precipitate.

- A 1.0×10^{-2} M solution of Barium Acetate also contains 1.1×10^{-2} M Sodium Fluoride. Is there a precipitate?

$$Q = [\text{Ba}^{2+}][\text{F}^-]^2 = (1.0 \times 10^{-2})(1.1 \times 10^{-2})^2 = 1.2 \times 10^{-6}$$

This is more than the K_{sp} (1.0×10^{-6}) so there will be a precipitate.

- What mass of Barium Fluoride will precipitate from 100.0 mL of the above solution?



$$K_{sp} = (1.0 \times 10^{-2} - x)(1.1 \times 10^{-2} - 2x)^2$$

This is a third order polynomial. IT can be solved by an approximation method. We can guess a value for x and check the result. We then adjust the value for x up or down until it agrees with the K_{sp} (within the significant figures in the problem). We can also use electronic methods of solving it. Some graphing

calculators can do this. We can also use PC programs such as Mathematica or MathCad. MathCad gives the following results:

$$\left[(1.0 \cdot 10^{-2} - x) (1.1 \cdot 10^{-2} - 2 \cdot x)^2 = 1.0 \cdot 10^{-6} \right] \text{ solve } , x \rightarrow \left[\begin{array}{c} 3.9754796305938003210 \cdot 10^{-4} \\ 1.0301226018470309984 \cdot 10^{-2} - 5.0935527556977365920 \cdot 10^{-3} \cdot i \\ 1.0301226018470309984 \cdot 10^{-2} + 5.0935527556977365920 \cdot 10^{-3} \cdot i \end{array} \right]$$

Here we take the only real value as the answer 4.0×10^{-4} . The mass of Barium Fluoride can then be calculated.

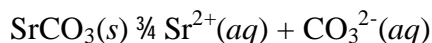
$$100.0 \text{ mL} \times \frac{10^{-3} \text{ L}}{1 \text{ mL}} \times \frac{4.0 \times 10^{-4} \text{ mol BaF}_2}{1 \text{ L}} \times \frac{175.34 \text{ g BaF}_2}{1 \text{ mol BaF}_2} = 7.0 \times 10^{-3} \text{ g BaF}_2$$

pH dependence of solubility

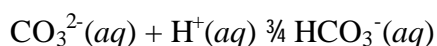
Some slightly soluble compounds have a solubility that is dependent on the pH of the solution. If the anion in the compound comes from a weak acid the compound will be more soluble in an acidic solution than in a neutral solution.

Most metal ions precipitate in basic solutions as the metal hydroxide (the exceptions to this are the group IA and IIA metals which form soluble hydroxides). Some compound will be more soluble in a solution of aqueous ammonia because the metal will form a complex ion with the ammonia, which results in the compound having a higher solubility than in neutral solutions.

If we examine this qualitatively (without numbers) we can see why some slightly soluble compounds are more soluble in acidic solutions. Consider the following equilibrium:



If we add hydrogen ions to this solution the carbonate will be involved in a second equilibrium:



The hydrogen ion will remove the carbonate ion from the solution (converting it into bicarbonate). This will result in more Strontium Carbonate dissolving.

We can take advantage of this pH dependence to effect the separation of metal ions. Most metal will precipitate with the Sulfide ion (S^{2-}). This ion is the conjugate base of the weak acid H_2S (actually HS^-). This means that the pH will affect the solubility of metal sulfides. We can, sometimes, find a pH that causes one ion precipitate but not the

other. If we then buffer the solution to that pH, one ion will precipitate out but the other will not.

Example:

What pH range is required to precipitate one of the ion in a mixture that contains 0.10 M Zinc ions and 0.10 M Iron(II) ions?

First we must determine what the Sulfide ion concentration must be to precipitate these ions.

Fe²⁺:

$$K_{sp} = [Fe^{2+}][S^{2-}] = 6 \times 10^{-18}$$
$$[S^{2-}] = \frac{K_{sp}}{[Fe^{2+}]} = \frac{6 \times 10^{-18}}{0.10} = 6 \times 10^{-17}$$

Zn²⁺:

$$K_{sp} = [Zn^{2+}][S^{2-}] = 1.1 \times 10^{-21}$$
$$[S^{2-}] = \frac{K_{sp}}{[Zn^{2+}]} = \frac{1.1 \times 10^{-21}}{0.10} = 1.1 \times 10^{-20}$$

We need the sulfide ion concentration to be between 6×10^{-17} M and 1.1×10^{-20} M. This can be accomplished by adjusting the pH. What pH values are needed? We must look at the equilibrium for Hydrogen Sulfide:



If we saturate a solution with Hydrogen Sulfide, the concentration of Hydrogen Sulfide will be 0.10 M. Knowing this and the combined K for the above reaction (1.1×10^{-20}) we can calculate the concentration of the Hydrogen ion needed, and from that the pH.

$$K = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = 1.1 \times 10^{-20}$$
$$[H^+] = \sqrt{\frac{K[H_2S]}{[S^{2-}]}}$$

For Fe²⁺ this gives:

$$[H^+] = \sqrt{\frac{K[H_2S]}{[S^{2-}]}} = \sqrt{\frac{(1.1 \times 10^{-20})(0.10)}{(6 \times 10^{-17})}} = 4.2 \times 10^{-3}$$

$$pH = 2.39$$

For Zn^{2+} this gives:

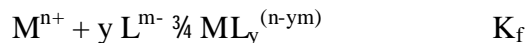
$$[H^+] = \sqrt{\frac{K[H_2S]}{[S^{2-}]}} = \sqrt{\frac{(1.1 \times 10^{-20})(0.10)}{(1.1 \times 10^{-20})}} = 0.316$$

$$pH = 0.50$$

If we can buffer the pH to somewhere between 0.50 and 2.39 we will precipitate out the Zinc and not the Iron (because the Zinc requires a lower Sulfide ion concentration).

Complex Ion Formation

Metal ions can react with Lewis Bases to form complex ions. The equilibrium for this looks like:

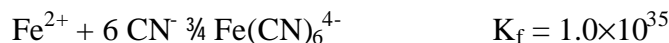


Here M is the metal ion and L is the ligand. K_f is called the **formation constant**. Formation constants tend to be very large number ($>10^7$). This means that the equilibrium lies primarily on the right side of the above equation. In order to solve this type of problem we generally need to assume the reaction goes all the way to completion and then returns to equilibrium. We do this because it simplifies the mathematics. With the aid of computers and programs like MathCad or Mathematica we can sometimes solve these equilibria directly. We will get the same answer either way.

Example:

Calculate the concentration of Iron(II) ions in a solution that contains 0.10 M $Fe(NO_3)_2$ and 1.00 M NaCN.

The equilibrium we are looking at here is:



We start by setting up our table and assuming a complete reaction:

	Fe^{2+}	+	6CN^-	$\frac{3}{4}$	$\text{Fe}(\text{CN})_6^{4-}$
initial []	0.10		1.00		0.00
Δ	-0.10		-0.60		+0.10
final []	0		0.40		0.10

Now we set up the table for the equilibrium calculation.

	Fe^{2+}	+	6CN^-	$\frac{3}{4}$	$\text{Fe}(\text{CN})_6^{4-}$
initial []	0		0.40		0.10
Δ	+x		+6x		-x
final []	x		0.40+6x		0.10-x

These numbers get plugged into our equilibrium calculation.

$$K_f = \frac{[\text{Fe}(\text{CN})_6^{4-}]}{[\text{Fe}^{2+}][\text{CN}^-]^6} = \frac{(0.10 - x)}{(x)(0.40 + 6x)^6}$$

This is a seventh order polynomial. In order to solve it we need to make some approximations. We are going to assume, because the reaction has such a large K and the equilibrium is mostly on the right of the reaction, that $-x$ and $+6x$ are negligible. This gives us

$$K_f \approx \frac{(0.10)}{(x)(0.40)^6}$$

$$x \approx \frac{0.10}{K(0.40)^6} = 2.44 \times 10^{-33}$$

We must check our assumptions. When we do we find that they are valid, 10^{-33} is negligible compared to 0.10 or 0.40. This means that the Iron(II) ion concentration in the solution is 2.4×10^{-33} M. This is an extremely small number. In 1.0 L of solution there will be $\sim 10^{-10}$ ions in solution. Obviously this cannot be the case so the reaction is complete.

Complex ions and solubility

As mentioned earlier some metal will form complexes with ammonia (or other ions like CN^-). This will affect the solubility of the compounds formed by these metals. The metals will go into the complexes fairly readily, because of the very large values for K. This means that the ions are taken out of solution so more of the compound will dissolve. There are two ways of looking at this. First, we can examine whether or not a precipitate will form in a solution in which a complex also forms. Second, we can calculate the solubility of a compound in a solution such as aqueous ammonia.

Examples:

Will a precipitate form in a solution that contains 0.0010 M Ni(NO₃)₂, 1.00 M NaOH and 1.00 M NaCN? What will be the Nickel(II) ion concentration when the solution comes to equilibrium?

We examine the complex ion formation first because of the large K. The equilibrium table for this is:

	Ni ²⁺ +	4 CN ⁻ ^{3/4}	Ni(CN) ₄ ²⁻
initial []	0.0010	1.00	0.00
Δ	-0.0010	-0.0040	+0.0010
final []	0	0.996	0.0010

This then comes to equilibrium:

	Ni ²⁺ +	4 CN ⁻ ^{3/4}	Ni(CN) ₄ ²⁻
initial []	0	0.996	0.0010
Δ	+x	+4x	-x
final []	x	0.996+4x	0.0010-x

This gives a Nickel(II) ion concentration of

$$K_f = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4} = \frac{0.0010 - x}{x(0.996 + 4x)^4} \approx \frac{0.0010}{x \cdot 0.996^4}$$

$$x \approx 1.016 \times 10^{-34} = [Ni^{2+}]$$

The Nickel(II) ion concentration from this is 1.0×10⁻³⁴. This gets plugged into the equilibrium for the Nickel(II) Hydroxide equilibrium.

	Ni(OH) ₂ ^{3/4}	2 OH ⁻ ^{3/4}	Ni ²⁺
initial []	0	1.00	1.0×10 ⁻³⁴

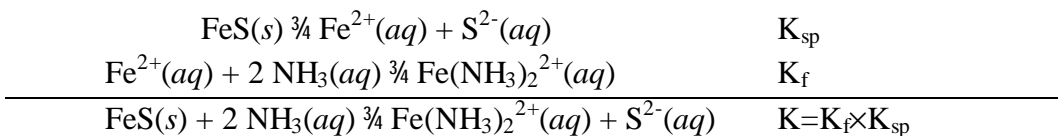
We first must calculate Q to determine if there is a precipitate.

$$Q = [Ni^{2+}][OH^-]^2 = 1.0 \times 10^{-34} < 2.0 \times 10^{-15} = K_{sp}$$

Because Q is less than K_{sp} no precipitate forms and the Nickel(II) ion concentration is equal to the concentration calculate from the complex ion formation (1.0×10⁻³⁴).

What is the molar solubility of Iron(II) Sulfide in 1.00 M $\text{NH}_3(aq)$?

In order to solve this type of problem we must find the equation for the solubility of Iron(II) Sulfide in NH_3 . This is done by adding the equilibrium reactions together.



$$K = 3.98 \times 10^3 \times 6 \times 10^{-18} = 2.4 \times 10^{-14}$$

First we set up the table:

	FeS	+	2 NH ₃	\rightleftharpoons	Fe(NH ₃) ₂ ²⁺	+	S ²⁻
initial []			1.00		0.00		0.00
Δ			-2x		+x		+x
final []			1.00-2x		x		x

Then we setup the equilibrium calculation:

$$\begin{aligned}
 K &= \frac{[\text{Fe}(\text{NH}_3)_2^{2+}][\text{S}^{2-}]}{[\text{NH}_3]^2} = 2.4 \times 10^{-14} \\
 &= \frac{x^2}{(1.00 - 2x)^2}
 \end{aligned}$$

To solve this we can make an approximation or realize that we can take the square root of both sides, which gives:

$$\begin{aligned}
 2.4 \times 10^{-14} &= \frac{x^2}{(1.00 - 2x)^2} \\
 \sqrt{2.4 \times 10^{-14}} &= \sqrt{\frac{x^2}{(1.00 - 2x)^2}} \\
 1.5 \times 10^{-7} &= \frac{x}{(1.00 - 2x)} \\
 1.5 \times 10^{-7} - 3.0 \times 10^{-7} x &= x \\
 x &= 1.5 \times 10^{-7}
 \end{aligned}$$

Here, just as in any other solubility problem, x is the molar solubility. So the molar solubility of Iron(II) Sulfide is 1.5×10^{-7} M.