

Chapter 60 MORE IONIC SOLUTION EQUILIBRIA

© 2012 Mark E. Noble
noblereaction.org

We continue with various aspects of equilibria involving ionic solutes, now extending the coverage into scenarios with multiple solutes present. As soon as you start adding things to the pot, you open up the possibility for more equilibria. This can give big changes in solubility, sometimes increasing and sometimes decreasing. It also enables the formation of new types of complexes. As we proceed, we will be getting more into the types of calculations which can be involved.

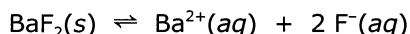
60.1 More of solubility

Let's do another example of simple solubility and then we will get into the effects of, and some calculations for, other solutes present in the solution. To keep our solubility calculations at least somewhat in reasonable range, we will impose a few limitations. We will work primarily with M^+/X^- , M^+/X^{2-} , M^{2+}/X^- and M^{2+}/X^{2-} combinations. We will use K_{sp} alone to calculate an approximate (and minimum) solubility for these compounds in plain water. We will assume that acid/base effects and associative effects are not significant for an insoluble compound in plain water. We will exclude oxides and sulfides completely, since those anions are strongly basic and because the resultant OH^- and HS^- ions engage in associative equilibria very strongly. On the other hand, when we add another solute to the solution, then we will bring in additional effects if they apply. The limitations given here are for calculations; for strictly qualitative considerations without any calculation, we can work with any type of compound.

The basics were set up in the illustration in the last Chapter for the solubility of $AgCl$ in plain water. For a new Example, consider barium fluoride in plain water.

Example 1. What is the solubility of BaF_2 in water?

Start with an equation



and a K_{sp} expression which you can fill in. The value is 1.8×10^{-7} .

$$K_{sp} = 1.8 \times 10^{-7} =$$

Here's the whole table.

	$[Ba^{2+}]$	$[F^-]$
Initial:	-0-	-0-
Changes:	+x	+2x
Equilibrium:	x	2x

These go to into K_{sp} , which you can do

$$K_{sp} = 1.8 \times 10^{-7} =$$

and you can solve for x . You should get $x = 3.6 \times 10^{-3}$, which means $[Ba^{2+}] = 3.6 \times 10^{-3} M$ and $[F^-] = 7.2 \times 10^{-3} M$. Since we set up x to be the concentration of Ba^{2+} and because one $Ba^{2+}(aq)$ is produced for every formula unit of $BaF_2(s)$ which dissolves, then x is also the measure of solubility. The solubility of BaF_2 in water is $3.6 \times 10^{-3} M$.

By the way, a K -check remains useful to confirm your work. Here,

$$K_{sp} = (3.6 \times 10^{-3}) \times (7.2 \times 10^{-3}) = 1.9 \times 10^{-7}$$

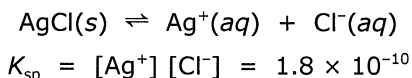
and that's close enough.

Now let's start adding things and see how that affects solubilities.

The easiest thing to add which will affect solubility is a soluble compound which contains the same cation or the same anion which is present in the insoluble compound itself. The cation or the anion which is common to both sources is called a common ion. The term common ion is actually general and not

limited to solubility considerations; it simply means any ion in an equilibrium system which derives from more than one source.

To illustrate, we return to the AgCl example from last Chapter.



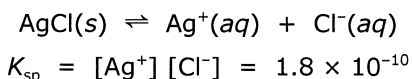
We had found that the solubility of AgCl in plain water is

$$\text{solubility of AgCl} = [\text{Ag}^+] = [\text{Cl}^-] = 1.3 \times 10^{-5} \text{ M}$$

Now let's salt things up a bit by adding NaCl. What happens to the solubility of AgCl when we add it to a solution of NaCl? The Na^+ cation is not involved in any equilibrium here and it is a spectator. On the other hand, Cl^- is part of the equilibrium and it will have an effect on solubility: the additional Cl^- shifts the simple solubility equation to the left. This means less AgCl is dissolved at equilibrium. Let's see how this works out.

.....
Example 2. What is the solubility of AgCl in salt water with $[\text{Cl}^-] = 0.00862 \text{ M}$?

This starts with the same setup as in the last Chapter



but the table begins differently. You have an initial amount of Cl^- from the NaCl.

	$[\text{Ag}^+]$	$[\text{Cl}^-]$
Initial:	-0-	0.00862
Changes:	+x	+x
Equilibrium:	x	0.00862 + x

The equilibrium values go into K_{sp} .

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (x)(0.00862 + x) = 1.8 \times 10^{-10}$$

How would you like to solve that? You could re-arrange the above equation

$$x^2 + 0.00862x - 1.8 \times 10^{-10} = 0$$

and then use the quadratic equation to get $x = 2.1 \times 10^{-8}$. Can we use approximation/iteration? Well, this is an insoluble compound in the presence of an added amount of a common ion, so x should be extremely small. Let's approximate $(0.00862 + x)$ as 0.00862. This simplifies the K_{sp} expression to

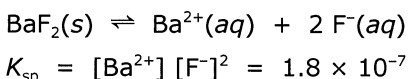
$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (x)(0.00862 + x) \approx (x)(0.00862) = 1.8 \times 10^{-10}$$

which also gives $x = 2.1 \times 10^{-8}$. If you tried to iterate that, you would be adding 2.1×10^{-8} to 0.00862 which gives you 0.00862 right back. That won't change anything, so you're done. So, what's the final answer for the solubility? Well, we set up x to be the concentration of Ag^+ ; one $\text{Ag}^+(aq)$ is produced for every formula unit of $\text{AgCl}(s)$ which dissolves, so x again represents the solubility. Compare this solubility, $2.1 \times 10^{-8} \text{ M}$, to the solubility in plain water which was $1.3 \times 10^{-5} \text{ M}$. There is a 620-fold decrease in solubility due to the small amount of added Cl^- .

Go again.

.....
Example 3. What is the solubility of BaF_2 in a solution of 0.0160 M KF?

Bring back the equations from Example 1.



Here's the full table; note the initial F^- .

	[Ba ²⁺]	[F ⁻]
Initial:	-0-	0.0160
Changes:	+x	+2x
Equilibrium:	x	0.0160 + 2x

These go into K_{sp} ,

$$K_{sp} = [\text{Ba}^{2+}] [\text{F}^{-}]^2 = (x) (0.0160 + 2x)^2 = 1.8 \times 10^{-7}$$

and then you solve for x . Well, that's easier said than done. This one becomes a cubic equation.

$$4x^3 + 0.0640x^2 + 0.000256x - 1.8 \times 10^{-7} = 0$$

You can't do negative- b -plus-or-minus-square-root of whatever on this one. Unless you're into cubics, approximation/iteration is the way to go. We start by assuming x is small, at least small enough for $2x$ to be small compared to 0.0160.

$$K_{sp} = [\text{Ba}^{2+}] [\text{F}^{-}]^2 = (x) (0.0160 + 2x)^2 \approx (x) (0.0160)^2 = 1.8 \times 10^{-7}$$

Solving for x gets you 0.00070. Iterate:

$$(x) (0.0160 + 2x)^2 \approx (x) (0.0160 + 2(0.00070))^2 = (x) (0.0174)^2 = 1.8 \times 10^{-7}$$

You get $x = 0.00059$. Again:

$$(x) (0.0160 + 2x)^2 \approx (x) (0.0160 + 2(0.00059))^2 = (x) (0.0172)^2 = 1.8 \times 10^{-7}$$

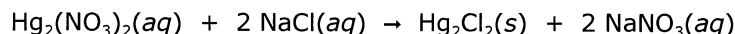
Now $x = 0.00061$. Keep going:

$$(x) (0.0160 + 2x)^2 \approx (x) (0.0160 + 2(0.00061))^2 = (x) (0.0172)^2 = 1.8 \times 10^{-7}$$

Same answer, $x = 0.00061$. You're done. This is now the solubility of BaF_2 in a solution which begins with $[\text{F}^{-}] = 0.0160 \text{ M}$. Compare this result to $3.6 \times 10^{-3} \text{ M}$ in plain water as calculated in Example 1. The solubility went down with the added F^{-} .

In both of the AgCl and BaF_2 cases, the presence of the anion from a second source decreased the solubility of the compound compared to its solubility in plain water. This will always be true as long as there are no other significant equilibria. It will also be true if the cation is a common ion instead of the anion. For example, the solubility of AgCl in a solution of 0.00600 M AgNO_3 is less than the solubility of AgCl in plain water. (You can calculate this: it's $3.0 \times 10^{-8} \text{ M}$.) When you apply the Principles of Equilibrium Dynamics to the K_{sp} equation, then the presence of a common ion shifts the equilibrium to the left, toward more solid.

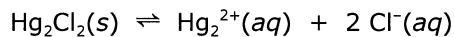
These effects have a very practical application if you want to decrease the concentration of a metal cation in solution. Why would you want to? Two big reasons include economics and safety/environmental aspects. The former is associated with expensive metals such as silver or, even moreso, gold, platinum, or etc. If you work with soluble compounds of these, then you can recover their remaining amounts in a solution by precipitating them until their residual concentration drops to some very low level. You then filter off the precipitate and recover your metal from the precipitate. The safety and environmental aspects involve the very toxic and hazardous metal cations such as lead, mercury, cadmium and even some of the not-so-bad such as copper. Again, you can often precipitate them from solution until their remaining solution concentration drops to an acceptable level. For an example, consider the preparation of mercury(I) chloride using a simple precipitation method.



After filtering the solid Hg_2Cl_2 from the mixture, there will be a small residual amount of $\text{Hg}_2^{2+}(aq)$ due to its solubility equilibrium; this residual amount will be in the original solution and it will be in any water which was used to wash the solid. In plain water, the simple solubility of Hg_2Cl_2 is $7.0 \times 10^{-7} \text{ M}$ which corresponds to 280 ppb of Hg_2^{2+} . (You could calculate these values.) What if you want that concentration to be even smaller?

.....
Example 4. What concentration of Cl^{-} is necessary to drop the concentration of Hg_2^{2+} in water to 1.0 ppb? 1.0 ppb Hg_2^{2+} corresponds to $2.5 \times 10^{-9} \text{ M}$.

Set up your equilibrium



and your K_{sp} expression.

$$K_{\text{sp}} = [\text{Hg}_2^{2+}] [\text{Cl}^-]^2 = 1.4 \times 10^{-18}$$

You want $[\text{Hg}_2^{2+}] = 2.5 \times 10^{-9}$ M at final equilibrium. Just plug that in and solve for $[\text{Cl}^-]$.

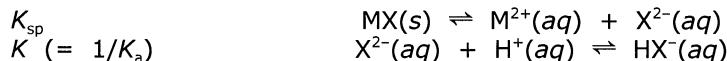
$$(2.5 \times 10^{-9}) [\text{Cl}^-]^2 = 1.4 \times 10^{-18}$$

You will get 2.4×10^{-5} M. That's all you need for this problem. In order to decrease $[\text{Hg}_2^{2+}]$ from 280 ppb in plain water down to 1.0 ppb using Cl^- , you need to have 2.4×10^{-5} M Cl^- in the solution.

OK, let's change gears.

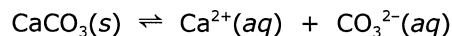
We now consider a different aspect, one which increases solubility. You can increase solubility by decreasing an amount of one of the ions on the right side of the simple solubility equation. The simultaneous equilibria discussion in the last Chapter actually did this same thing, but now we are going to extend some of those aspects by adding another solute. We will limit our coverage to base effects and complex formation.

As noted in the last Chapter for a compound in plain water, base effects will only be significant when K_{b} is big enough. Now, let's change the circumstances by adding a strong acid to the solution. The strong acid will react with the basic anion; that decreases the concentration of the anion and that shifts the solubility equation to the right. Consider the following equations for a generic $\text{MX}(s)$, again composed of M^{2+} and X^{2-} ions.



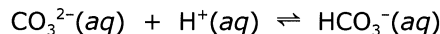
The second equation is not the usual base dissociation but instead it is written for the reaction of a weak base X^{2-} with a strong acid. In doing so, X^{2-} is protonated to form HX^- ; this equation is actually the reverse of an acid dissociation step. The protonation of X^{2-} reduces its concentration which then shifts the solubility equilibrium to the right. Thus, the solubility of MX increases. This effect can be substantial even when the K_{b} of the anion is not so great. For example, the solubility of BaF_2 will increase with addition of strong acid even though the K_{b} of F^- is only 1.5×10^{-11} . The impact is even bigger on compounds with an anion of appreciable K_{b} such as phosphate, arsenate, carbonate, cyanide, etc. For oxides or sulfides with their strong base anion, then the solubilities will skyrocket upon addition of strong acid; in fact, this is one of the best ways to get those types of compounds to dissolve.

Carbonates warrant special mention because they are so common, so important, and because they can involve a number of equilibria which we have covered. We used CaCO_3 in plain water as an example in the last Chapter. Let's take another look. Begin with simple solubility.



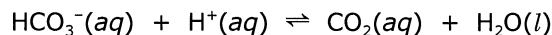
$$K_{\text{sp}} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] = 3.4 \times 10^{-9}$$

Add a very small amount of strong acid.



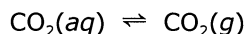
$$K = 1/K_{\text{a}2} = 2.1 \times 10^{10}$$

Note the very large K for protonation. This shifts the solubility equilibrium to the right. Add more strong acid.



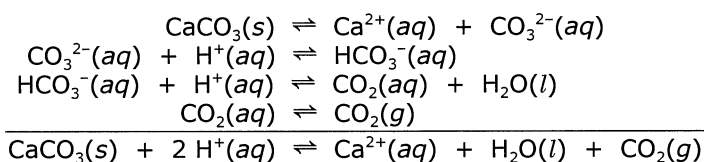
$$K = 1/K_{\text{a}1} = 2.2 \times 10^6$$

This shifts the prior equations to the right even more. CO_2 itself has only limited solubility in water.



$$K = 29.8$$

$\text{CO}_2(g)$ can then bubble out of solution. This shifts all of the prior equations to the right even more and more. Now add up all of the above equations



and multiply the individual K 's to get the overall K_{sum} .

$$K_{\text{sum}} = 3.4 \times 10^{-9} \times 2.1 \times 10^{10} \times 2.2 \times 10^6 \times 29.8 = 4.7 \times 10^9$$

Look at the size of the overall K_{sum} ; this represents a very high solubility for CaCO_3 in acid solution. For carbonates in general, protonation of CO_3^{2-} and of HCO_3^- overwhelmingly drives the entire process to the right. If you drip acid solution onto marble or limestone or chalk or a sea shell or anything else which contains CaCO_3 , then you will get bubbling and dissolving of the solid. This is typical of all carbonates. Technically, you can also use a weak acid, in which case you don't drive the equilibria as far to the right unless you use a generous excess. Acid rain will also work, and the above reactions typify the degradation of carbonate-containing statues and other materials over time. These series of reactions represent the actual equilibria which are behind the gas-forming reactions for carbonates, way back in Section 12.3. All of these things are connected.

Another example is in your mouth, specifically your teeth. Tooth enamel is an extremely resistant substance composed primarily of a mineral called hydroxyapatite which has the cumbersome formula of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. (The "apatite" part is pronounced like appetite.) Your enamel is constantly dissolving and reforming, and those processes must be in balance to keep a hard, protective surface on your teeth. If you lower the pH, however, the higher concentration of H^+ leads to more reaction with the OH^- ; that can lead to enhanced dissolving of the hydroxyapatite which can then lead to tooth decay (caries). Oral bacteria are major culprits in this decay, since their waste products include weak acids. Now bring in F^- . Fluoride treatments, fluoride toothpastes and fluoridation of municipal water supplies are all intended to provide added protection by forming fluoroapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Fluoroapatite is more resistant to the weak acids because F^- is a weak base. But that's still not a guarantee, so be sure to brush up on your oral hygiene. You can't just increase the total amount of F^- in order to achieve higher protection; the amount of fluoride added in these applications is very small and must be kept low due to its harmful effects elsewhere in the body.

Overall, remember: an acid will increase the solubility of any insoluble compound which has a basic anion. The effect is greater for anions which are better bases and for acids which are stronger.

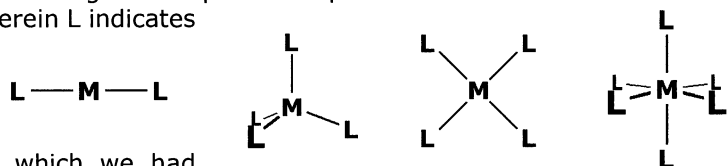
In addition to acid effects, complex formation will also increase solubility. We now discuss this topic more as its own type of solution equilibrium.

60.2 Complex formation

Complexes were introduced in the last Chapter very briefly, in the context of the solubility of a compound by itself in plain water. In those cases, the complex could only form between the cation and the anion of the insoluble compound. We now expand and generalize the discussion of complex formation, beginning with homogeneous equilibria and then finally returning to the effects on solubility. Now the ligands can vary since they can come from other solutes which are added to the solution. This opens up many more possibilities for the kinds of complexes which can form.

Complexes form through the binding of ligands to a metal atom or ion; for typical aqueous systems, this involves a metal cation. More than one ligand can bind, and cases of two, four and six ligands are among the most common. The ligands are arranged in a specific shape around the metal

and some common shapes are shown, wherein L indicates a generic ligand. Two ligands give a linear shape, four ligands give tetrahedral or square planar shape, and six ligands give octahedral shape.



These shapes are some of the shapes which we had covered for VSEPR (Chapters 28 and 29) but the shapes for transition metal complexes commonly involve other factors which are not contained within VSEPR. Thus, variations are possible. For example, NiCl_4^{2-} is tetrahedral while $\text{Ni}(\text{CN})_4^{2-}$ is square planar although both involve four ligands on Ni^{2+} .

Water itself is one of the most common ligands and it uses a lone pair on oxygen (and not just its dipole) to bind to a metal. When dissolved in water, many metal cations form complexes with six or four water molecules. For example, Zn^{2+} , Cr^{2+} , Co^{2+} , Fe^{2+} , etc. form octahedral $\text{M}(\text{H}_2\text{O})_6^{2+}$ complexes. Co^{2+}

can actually go either way, octahedral or tetrahedral; the latter is $\text{Co}(\text{H}_2\text{O})_4^{2+}$. These complexes are all polyatomic cations of their own identity, and they are then hydrated by additional water molecules by the usual ion-dipole and hydrogen bonding interactions. (There is some overlap here with the discussion for metal acidity in Section 56.4, but metal acidity is not limited to complexes.) Although many metal cations form specific complexes with water ligands, it remains common to use a generic notation for them such as $\text{M}^{n+}(\text{aq})$ without specifying the number of ligands involved. For example, $\text{Zn}^{2+}(\text{aq})$ and $\text{Zn}(\text{H}_2\text{O})_6^{2+}(\text{aq})$ mean the same thing. On the other hand, not all metal cations form complexes in water; for example, $\text{Na}^+(\text{aq})$ only involves the usual ion-dipole interactions. The metals of the *s*-block are simply not good at this except for Be^{2+} ; Be^{2+} actually forms complexes quite well.

The importance of complexes extends far beyond water as ligand. There are many different kinds of ligands in general, but our emphasis here involves those ligands which are important to aqueous systems. Those will include any ligand which can compete against water to bind to a metal cation. Many such ligands are known. Simple halide anions such as F^- , Cl^- , etc. can be good ligands. NH_3 is a good ligand. CO and CN^- are outstanding ligands and this is what makes them so toxic; they will form the wrong kind of complex with many essential metal ions in your body and that can kill. Speaking of metals in your body, many of the metal cations in biological systems are bonded to extremely complicated ligands involving large proteins. Hemoglobin is one such example; this involves a complex with Fe^{2+} which carries O_2 through your bloodstream. In that complex, the O_2 acts as one of the ligands.

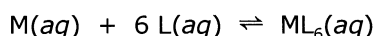
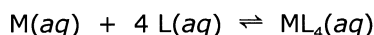
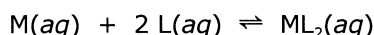
Complexes can contain one kind of ligand or they can contain different kinds of ligands. For example, solutions of AlF_3 in water are a hodgepodge of complexes including $\text{Al}(\text{H}_2\text{O})_5\text{F}^{2+}$, $\text{Al}(\text{H}_2\text{O})_4\text{F}_2^+$, $\text{Al}(\text{H}_2\text{O})_3\text{F}_3$ and others, all involving various equilibria. Complexes can also come in a variety of charges, and some are cationic, some are neutral and some are anionic. The actual charge of the complex is the sum of the M^{n+} cation charge and the charges of the ligands. Examples include $\text{Ag}(\text{NH}_3)_2^+$, $\text{Al}(\text{H}_2\text{O})_3\text{F}_3$ and $\text{Ni}(\text{CN})_4^{2-}$ which can be broken down as follows.

$\text{Ag}(\text{NH}_3)_2^+$:	The ligands are ammonia molecules which are neutral by themselves. The complex is 1+, so the metal cation must be 1+, namely Ag^+ .
$\text{Al}(\text{H}_2\text{O})_3\text{F}_3$:	The ligands include three fluorides, F^- , and three neutral waters. The complex is neutral, so the metal ion must be 3+ to offset the ligand charges. The cation is Al^{3+} .
$\text{Ni}(\text{CN})_4^{2-}$:	The four ligands are cyanides, CN^- . The complex is 2-, so the metal ion must be 2+. The cation is Ni^{2+} .

Keep the charges in mind when working with formulas for complexes.

Speaking of formulas for complexes, let me add another point. When the ligand itself is polyatomic, then it is placed in parentheses in the complex's formula. Just glance up at the examples shown so far. Monatomic ligands do not get parentheses.

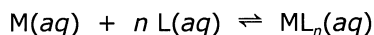
The formation of ML_2 , ML_4 and ML_6 complexes can be represented by the following equilibria. The charges for M, L and the complex, ML_n , are left out for simplicity.



It is possible to break up each of these into separate and sequential steps, and the first two steps were mentioned in Section 59.3. Nevertheless, the equilibrium constants tend to be large and that drives the system to the final complexes shown as ML_2 , ML_4 or ML_6 . It is therefore customary to work with the overall equilibria as given above for these cases. How do you know if a particular M/L combination will give ML_2 , ML_4 or ML_6 ? That depends on a number of factors which we will not go into; for our purposes, the final number of ligands in a particular complex will simply be indicated. Keep in mind that the designation $\text{M}(\text{aq})$ can already include water ligands. The presence of water ligands does not affect our approach here and we can continue to leave them out of a formula for simplicity.

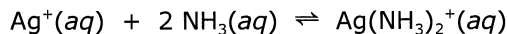
As an aside, let me point out that complex formation is a totally different type of formation than the thermodynamic formation reactions introduced in Chapter 19. Although both of these types are referred to as formation reactions, they are totally different. Don't confuse them.

Equilibrium constants for complex formation are specifically designated as K_f . For a complex of formula ML_n , we can generalize these as follows.



$$K_f = \frac{[ML_n]}{[M] [L]^n}$$

As an example, consider $Ag(NH_3)_2^+$ which is a linear complex. If you start with a solution of $Ag^+(aq)$ and then add NH_3 to the solution, a complex formation equilibrium will result.



$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+] [NH_3]^2} = 1.1 \times 10^7$$

Notice the large value for K_f . In general, K_f values can be very large, even moreso than here. Some values are listed in Appendix B.

The calculation methods used for complex formation equilibria can be a bit different from the methods used for most aqueous systems covered in this and the prior five Chapters. The reason is that the calculations often cannot be solved directly due to unusually high power terms in the K_f expression. For example, the K_f expression for an ML_6 complex will have an $[L]^6$ term. This forces us into approximation/iteration. That's nothing new, of course, and we have already done numerous examples of this for problems which could not be solved directly. What makes it different now is that we are dealing with large numbers for the value of K itself. This changes the approach for approximation/iteration, although it only amounts to adding one step. I'll show you this for the $Ag(NH_3)_2^+$ example.

Example 5. Consider 1.00 L of a solution which contains 0.0100 mol Ag^+ . 0.0200 mol NH_3 is added. Calculate $[Ag^+]$, $[NH_3]$ and $[Ag(NH_3)_2^+]$ at equilibrium.

The equilibrium equation and the K_f expression are from above.



$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+] [NH_3]^2} = 1.1 \times 10^7$$

We have 1.00 L solution, so the numbers for moles and molarities are the same. Initial amounts are given for Ag^+ and NH_3 ; these will change. Start a table.

	$[Ag^+]$	$[NH_3]$	$[Ag(NH_3)_2^+]$
Initial:	0.0100	0.0200	-0-

Change happens as the complex forms.

	$[Ag^+]$	$[NH_3]$	$[Ag(NH_3)_2^+]$
Initial:	0.0100	0.0200	-0-
Changes:	-x	-2x	+x

This leads to the final equilibrium amounts.

	$[Ag^+]$	$[NH_3]$	$[Ag(NH_3)_2^+]$
Initial:	0.0100	0.0200	-0-
Changes:	-x	-2x	+x
Equilibrium:	0.0100 - x	0.0200 - 2x	x

Plug into K_f .

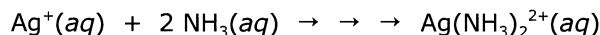
$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+] [NH_3]^2} = \frac{x}{(0.0100 - x)(0.0200 - 2x)^2} = 1.1 \times 10^7$$

OK, this is heading for a cubic equation in the denominator and we need to be thinking about approximation/iteration. But what would you approximate? Would you assume x is small compared to 0.0100? Unfortunately, the large value of K_f says that the change to equilibrium will be very large, and

x will be very large compared to 0.0100. The same consideration applies to $2x$ versus 0.0200. This is not a small x anymore, and approximation/iteration won't work. You can try it if you'd like.

So what do we do? Punt? No, we bring in a knuckleball.

There is a math trick to play for this type of problem. We cannot use iteration by the above route because the change from left to right is way too large. But we can arithmetically reset the problem to the right side of the equation, and then calculate its change backwards to the left. The change back to the left will be small, and that will allow us to do iteration. The reset trick involves treating the problem first as a simple stoichiometry problem: calculate the amount of complex which can form based only on the stoichiometry for the balanced equation. In other words, assume no equilibrium and just do the reaction all the way to product.



We were given 0.0100 mol Ag^+ and 0.0200 mol NH_3 ; these are stoichiometric amounts for the reaction and neither is in excess. Assuming full stoichiometric reaction to the right, this will give us 0.0100 mol $\text{Ag}(\text{NH}_3)_2^+$ with no reactants left over. This now is your reset point. Redo the table with this reset to the right.

	$[\text{Ag}^+]$	$[\text{NH}_3]$	$[\text{Ag}(\text{NH}_3)_2^+]$
Initial:	-0.0100-	-0.0200-	-0-
Reset Right:	-0-	-0-	0.0100

Now, from the reset point, we consider the system to change back to the left to a small extent in order to go to equilibrium.

	$[\text{Ag}^+]$	$[\text{NH}_3]$	$[\text{Ag}(\text{NH}_3)_2^+]$
Initial:	-0.0100-	-0.0200-	-0-
Reset Right:	-0-	-0-	0.0100
Change Left:	+ x	+ $2x$	- x

That gives the final equilibrium amounts.

	$[\text{Ag}^+]$	$[\text{NH}_3]$	$[\text{Ag}(\text{NH}_3)_2^+]$
Initial:	-0.0100-	-0.0200-	-0-
Reset Right:	-0-	-0-	0.0100
Change Left:	+ x	+ $2x$	- x
Equilibrium:	x	$2x$	0.0100 - x

Those plug into K_f .

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{(0.0100 - x)}{(x)(2x)^2} = 1.1 \times 10^7$$

Now we can do some assuming. There will be little change backwards, so we assume x to be small compared to 0.0100 in the numerator.

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{(0.0100 - x)}{(x)(2x)^2} \approx \frac{0.0100}{(x)(2x)^2} = 1.1 \times 10^7$$

Re-arrangement gives the following.

$$\frac{0.0100}{1.1 \times 10^7} = 4x^3$$

$$x = 6.1 \times 10^{-4}$$

Is that a final answer? Iterate.

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{(0.0100 - 0.00061)}{(x)(2x)^2} \approx \frac{0.0094}{(x)(2x)^2} = 1.1 \times 10^7$$

$$\frac{0.0094}{1.1 \times 10^7} = 4x^3$$

$$x = 6.0 \times 10^{-4}$$

That's close. Iterate again.

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{(0.0100 - 0.00060)}{(x)(2x)^2} \approx \frac{0.0094}{(x)(2x)^2} = 1.1 \times 10^7$$

$$\frac{0.0094}{1.1 \times 10^7} = 4x^3$$

$$x = 6.0 \times 10^{-4}$$

Same result. We end with the following.

$$[\text{Ag}^+] = 6.0 \times 10^{-4} \text{ M}$$

$$[\text{NH}_3] = 1.2 \times 10^{-3} \text{ M}$$

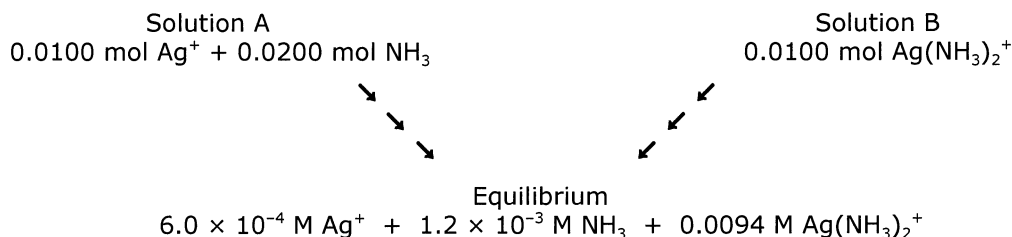
$$[\text{Ag}(\text{NH}_3)_2^+] = 9.4 \times 10^{-3} \text{ M}$$

K-check.

$$K_f = \frac{0.0094}{(0.00060)(0.0012)^2} = 1.1 \times 10^7$$

Done.

By incorporating the reset step, we were able to change an undoable problem into a doable problem. Again, it was just a math trick. The math trick does not change the chemistry of the system whatsoever. If you start some Solution A with 0.0100 mol Ag^+ + 0.0200 mol NH_3 and start some Solution B with 0.0100 mol $\text{Ag}(\text{NH}_3)_2^+$, then both solutions will separately go to the same point of equilibrium balance.



The two solutions will go to the same point of equilibrium balance as long as the starting amounts are stoichiometrically equivalent. The math trick simply provides a way of doing the calculation. In essence, after reset, we are simply running the equilibrium in reverse. For the reverse process, $K = 1/K_f = 5.9 \times 10^{-8}$ which is now small enough for iteration to work.

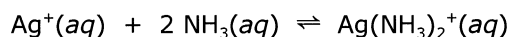
OK, pause for a moment. You might want to go back over this Example so that you understand the reset business better. This Example is the most basic type of complex formation problem to consider. We will do more with this type and we will be getting into excesses as we continue.

60.3 More complex equilibria

As a practical matter in complex formation applications, the ligand is usually added in excess to drive the equilibrium even further to the right. We'll illustrate this with a spinoff to the above problem, now quadrupling the amount of NH_3 at the start.

Example 6. Consider 1.00 L of a solution which contains 0.0100 mol Ag^+ . 0.0800 mol NH_3 is added. Calculate $[\text{Ag}^+]$, $[\text{NH}_3]$ and $[\text{Ag}(\text{NH}_3)_2^+]$ at equilibrium.

Same equations.

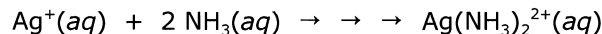


$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.1 \times 10^7$$

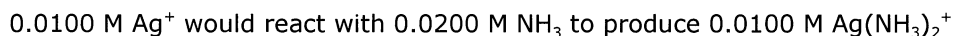
Again, we have 1.00 L solution, so the numbers for moles and molar are the same. (Don't expect that all the time.) Start a table.

	[Ag ⁺]	[NH ₃]	[Ag(NH ₃) ₂ ⁺]
Initial:	0.0100	0.0800	-0-

We will now reset this to the right.



You were given an excess amount of NH₃ and you have a limiting amount of Ag⁺. As always, the limiting reagent sets the amount of product possible. Stoichiometrically, the balanced equation says



and that would leave 0.0600 M NH₃ in excess at the end. After reset, you have 0.0100 M complex and you also have the 0.0600 M excess amount of ligand.

	[Ag ⁺]	[NH ₃]	[Ag(NH ₃) ₂ ⁺]
Initial:	0.0100	0.0800	0
Reset Right:	-0-	0.0600	0.0100

We now consider the system to change backwards to the left, to a small extent.

	[Ag ⁺]	[NH ₃]	[Ag(NH ₃) ₂ ⁺]
Initial:	0.0100	0.0800	0
Reset Right:	-0-	0.0600	0.0100
Change Left:	+x	+2x	-x

This leads to the final equilibrium amounts.

	[Ag ⁺]	[NH ₃]	[Ag(NH ₃) ₂ ⁺]
Initial:	0.0100	0.0800	0
Reset Right:	-0-	0.0600	0.0100
Change Left:	+x	+2x	-x
Equilibrium:	x	0.0600 + 2x	0.0100 - x

Those plug into K_f .

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{(0.0100 - x)}{(x)(0.0600 + 2x)^2} = 1.1 \times 10^7$$

Now, we approximate x as small compared to 0.0100 and $2x$ as small compared to 0.0600.

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{(0.0100 - x)}{(x)(0.0600 + 2x)^2} \approx \frac{0.0100}{(x)(0.0600)^2} = 1.1 \times 10^7$$

Re-arrangement gives

$$\frac{0.0100}{(0.0600)^2 \times (1.1 \times 10^7)} = x$$

$$x = 2.5 \times 10^{-7}$$

Iterate? This value of x will not change 0.0100 in the numerator of K_f and $2x$ will not change 0.0600 in the denominator. You will get the same number. You're done. We end with the following.

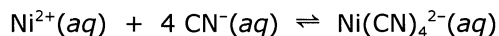
$$\begin{aligned} [\text{Ag}^+] &= 2.5 \times 10^{-7} \text{ M} \\ [\text{NH}_3] &= 0.0600 \text{ M} \\ [\text{Ag}(\text{NH}_3)_2^+] &= 0.0100 \text{ M} \end{aligned}$$

Compare this result using excess ligand to the prior result in Example 5 using a stoichiometric amount. The excess ligand knocked the final [Ag⁺] from 6.0×10^{-4} M down to 2.5×10^{-7} M.

Let's repeat these types of problems, now with different complexes. By the way, let me give you a tip here. The amount of ligand which is provided by the problem will be a stoichiometric amount or it will be in excess; usually, the ligand is not the limiting reagent. That means, for our coverage, the amount of metal cation will be a stoichiometric amount or it will be a limiting amount. Keep this in mind when doing the reset: base the stoichiometry part on the metal cation.

Example 7. A 500. mL solution of the complex $\text{Ni}(\text{CN})_4^{2-}$ is prepared using 0.00830 mol $\text{Ni}(\text{NO}_3)_2$ and 0.0332 mol KCN. What are the concentrations of Ni^{2+} , CN^- and $\text{Ni}(\text{CN})_4^{2-}$ at equilibrium?

Set up an equation. As described upstairs earlier, the formula of the complex breaks down into a Ni^{2+} cation and four CN^- ligands; balance the equation based on that. NO_3^- and K^+ are not part of the complex and they are spectating.



$$K_f = \frac{[\text{Ni}(\text{CN})_4^{2-}]}{[\text{Ni}^{2+}] [\text{CN}^-]^4} = 1.7 \times 10^{30}$$

We need some initial concentrations. Watch your volume this time.

	$[\text{Ni}^{2+}]$	$[\text{CN}^-]$	$[\text{Ni}(\text{CN})_4^{2-}]$
Initial:	0.0166	0.0664	-0-

Go for the reset. What's the stoichiometry for the given amount of the metal cation? The balanced equation says

0.0166 M Ni^{2+} would react with 0.0664 M CN^- to produce 0.0166 M $\text{Ni}(\text{CN})_4^{2-}$

and we can see that the given amount of ligand is the stoichiometric amount.

	$[\text{Ni}^{2+}]$	$[\text{CN}^-]$	$[\text{Ni}(\text{CN})_4^{2-}]$
Initial:	-0.0166-	-0.0664-	-0-
Reset Right:	-0-	-0-	0.0166

Now change back to the left.

	$[\text{Ni}^{2+}]$	$[\text{CN}^-]$	$[\text{Ni}(\text{CN})_4^{2-}]$
Initial:	-0.0166-	-0.0664-	-0-
Reset Right:	-0-	-0-	0.0166
Change Left:	+x	+4x	-x

Final.

	$[\text{Ni}^{2+}]$	$[\text{CN}^-]$	$[\text{Ni}(\text{CN})_4^{2-}]$
Initial:	-0.0166-	-0.0664-	-0-
Reset Right:	-0-	-0-	0.0166
Change Left:	+x	+4x	-x
Equilibrium:	x	4x	0.0166 - x

Plug into K_f .

$$K_f = \frac{[\text{Ni}(\text{CN})_4^{2-}]}{[\text{Ni}^{2+}] [\text{CN}^-]^4} = \frac{(0.0166 - x)}{(x)(4x)^4} = 1.7 \times 10^{30}$$

Approximate x as small compared to 0.0166.

$$K_f = \frac{[\text{Ni}(\text{CN})_4^{2-}]}{[\text{Ni}^{2+}] [\text{CN}^-]^4} = \frac{(0.0166 - x)}{256x^5} \approx \frac{0.0166}{256x^5} = 1.7 \times 10^{30}$$

Re-arrangement gives

$$\frac{0.0166}{256 \times (1.7 \times 10^{30})} = x^5$$

$$x = 1.3 \times 10^{-7}$$

Iterate? This value for x will not affect the 0.0166 in the numerator. You will get the same number if you do iterate, so you're done. We end with the following.

$$[\text{Ni}^{2+}] = 1.3 \times 10^{-7} \text{ M}$$

$$[\text{CN}^-] = 5.2 \times 10^{-7} \text{ M}$$

$$[\text{Ni}(\text{CN})_4^{2-}] = 0.0166 \text{ M}$$

The K -check is right on the money.

OK, your turn.

.....
Example 8. 1.00 L of 0.00565 M Hg^{2+} is treated with 0.0343 moles of NaBr to form the complex HgBr_4^{2-} . What are the concentrations of Hg^{2+} , Br^- and HgBr_4^{2-} at equilibrium?

Set up your balanced equation.

Here's your K_f expression.

$$K_f = \frac{[\text{HgBr}_4^{2-}]}{[\text{Hg}^{2+}] [\text{Br}^-]^4} = 1.0 \times 10^{21}$$

Plug in some initial concentrations.

	$[\text{Hg}^{2+}]$	$[\text{Br}^-]$	$[\text{HgBr}_4^{2-}]$
Initial:			

Go for the reset. What's the stoichiometry for the given amount of metal cation?

_____ M Hg^{2+} would react with _____ M Br^- to produce _____ M HgBr_4^{2-}

I will tell you that Br^- is in excess and the excess amount is 0.0117 M. Check and be sure that you can get that. Plug in the amounts after reset.

	$[\text{Hg}^{2+}]$	$[\text{Br}^-]$	$[\text{HgBr}_4^{2-}]$
Reset Right:			

Change back to the left.

Change Left:

Final equilibrium.

Equilibrium:

Put these into K_f .

$$K_f = 1.0 \times 10^{21} = \frac{[\text{HgBr}_4^{2-}]}{[\text{Hg}^{2+}] [\text{Br}^-]^4} =$$

Approximate x . With the approximation, it should be looking like this:

$$K_f \approx \frac{0.00565}{x(0.0117)^4} = 1.0 \times 10^{21}$$

Re-arrangement gives the following.

$$x = \frac{0.00565}{(0.0117)^4 \times (1.0 \times 10^{21})} = 3.0 \times 10^{-16}$$

Should you iterate? You won't need to. We end with the following.

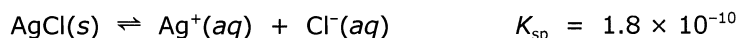
$$\begin{aligned} [\text{Hg}^{2+}] &= 3.0 \times 10^{-16} \text{ M} \\ [\text{Br}^-] &= 0.0117 \text{ M} \\ [\text{HgBr}_4^{2-}] &= 0.00565 \text{ M} \end{aligned}$$

OK?

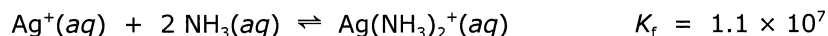
That's enough calculations. This completes the general discussion for complex formation. As you can see, these can have very high K_f values, giving equilibrium conditions which are overwhelmingly towards the complex. Now let's see how this affects solubility.

Complex formation is an excellent way of increasing solubility due to the high values of K_f which can be involved. By forming a complex, the metal cation concentration decreases relative to K_{sp} alone, shifting the simple solubility equilibrium far to the right. Thus, more of the compound dissolves. I will illustrate this with AgCl and NH_3 since we've worked with these already. Silver compounds are good examples of this behavior anyway, because silver forms many insoluble compounds and silver also forms a variety of complexes with different ligands.

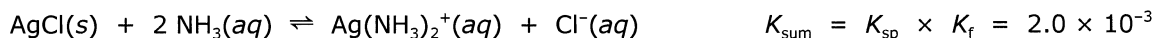
The simple solubility for AgCl is



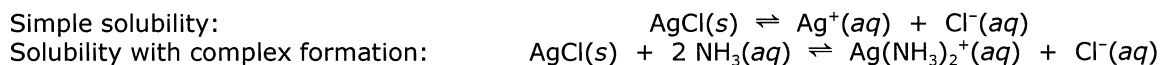
and complex formation between Ag^+ and NH_3 gives the following.



The large K_f means that most (by far) of the Ag^+ which dissolved will end up as complex and not as $\text{Ag}^+(aq)$. This shifts the simple solubility equilibrium far to the right. At equilibrium, $[\text{Ag}(\text{NH}_3)_2^+]$ is much, much greater than $[\text{Ag}^+]$. We can sum the above two equations to get the following.



The total solubility of AgCl is given by the first equation and by this third equation.



These two equations will operate to a different extent. Since $[\text{Ag}(\text{NH}_3)_2^+]$ is much, much greater than $[\text{Ag}^+]$, then the last equation dominates the outcome. The total solubility can be even further enhanced by having an excess of the ligand present in the solution. Furthermore, you could also select a better ligand with a larger K_f for a particular metal cation. This shifts the complex formation equilibria further to the right, giving even more and more solubility. Overall, remember: the solubility of a compound increases with complex formation. The increase is greater for better ligands and for higher concentrations of ligand.

60.4 Close

With this we close on our general coverage of aqueous equilibria. This coverage has been extensive, now involving seven Chapters. We've covered the equilibria of acids and bases, solubilities, complexes, and even more subtle effects such as ion pairing. A solution can be a busy place and, in the water world of your Earth and of your own life chemistry, these equilibria are vastly important. Balance remains essential, and the things which can shift that balance can have major impact.

Although we close presently on equilibrium aspects, we continue our studies of aqueous reactions. The difference between where we've been and where we're going lies in the type of reactions which are involved. Our emphasis will no longer be on the point of equilibrium, but instead on the drive to get there. As you will see, it is an electrifying topic.

Problems

- True or false.
 - The presence of a common ion in solution will always increase the solubility of a compound.
 - $\text{Ni}(\text{NH}_3)_6^{2+}$ is tetrahedral.
 - The charge on the complex which is formed between a silver ion and four cyanide ligands is 2-.
 - Ammonia can increase the solubility of some compounds by complex formation.
- Based only on simple solubility and K_{sp} , calculate the solubility (in M) for each of the following.
 - PbCrO_4
 - Ag_2CO_3
- Based only on simple solubility and K_{sp} , calculate the solubility (in M) for each of the following compounds in the given (initial) solutions.
 - BaSO_4 in 0.00313 M $\text{Ba}(\text{CH}_3\text{CO}_2)_2$
 - MgF_2 in 0.00443 M NaF
- An excess of $\text{PbSO}_4(s)$ is added to a solution of 0.000417 M K_2SO_4 . At equilibrium, what are the concentrations (in M) of $\text{Pb}^{2+}(aq)$ and of $\text{SO}_4^{2-}(aq)$?
- You have 2.00 L of a solution containing Au^+ . In order to recover most of the gold(I) as an insoluble compound, you add NaCl, which precipitates AuCl. What concentration (in M) of Cl^- is needed to lower $[\text{Au}^+]$ to 1.0×10^{-6} M?
- Consider pure water versus the separate solutions as given below. Which will give the highest solubility for ZnCO_3 ?
pure water 0.01 M HNO_3 0.01 M $\text{CH}_3\text{CO}_2\text{H}$ 0.01 M Na_2CO_3 0.01 M $\text{Zn}(\text{NO}_3)_2$
- Write the balanced equation for complex formation and write the K_f expression for each of the following.
 - $\text{Cd}(\text{OH})_4^{2-}$
 - $\text{Ni}(\text{NH}_3)_6^{2+}$
- $\text{Cu}^{2+}(aq)$ is pale blue. Adding NH_3 forms the deep blue complex, $\text{Cu}(\text{NH}_3)_4^{2+}$. For each set of initial conditions below, calculate the concentrations (in M) of Cu^{2+} , of NH_3 and of $\text{Cu}(\text{NH}_3)_4^{2+}$ at equilibrium.
 - The system begins with 0.00365 mol Cu^{2+} and 0.0146 mol NH_3 in 1.00 L total volume.
 - The system begins with 0.00365 mol Cu^{2+} and 0.0266 mol NH_3 in 1.00 L total volume.
- A 250. mL solution is prepared using 0.000700 mol Al^{3+} and 0.00580 mol F^- , producing the complex AlF_6^{3-} . What are the concentrations (in M) of Al^{3+} , of F^- and of AlF_6^{3-} at equilibrium?
- Derive the equation for solubility with complex formation for copper(I) chloride using cyanide as the ligand, to form the complex $\text{Cu}(\text{CN})_4^{3-}$. Calculate the value of K for this equation.