Chapter 60   MORE IONIC SOLUTION EQUILIBRIA

We continue with various aspects of equilibria involving ionic solutes, now extending the coverage into scenarios with additional solutes present. As soon as you start adding things to the pot, you open up the possibility for more equilibria. This can have a large impact on 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 compounds 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.

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

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Start with an equation

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\ F^-(aq)$$
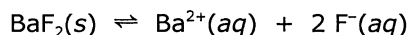
and a K_{sp} expression, whose value comes from Appendix B.

$$K_{sp} = [Ba^{2+}]\ [F^-]^2 = 1.8 \times 10^{-7}$$

Set the table.

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

The bottom line goes into K_{sp},

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

and then solve for x. You should get $x = 0.0036$, which means $[Ba^{2+}] = 0.0036$ M and $[F^-] = 0.0072$ 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 0.0036 M.

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

$$K_{sp} = 0.0036 \times 0.0072^2 = 1.9 \times 10^{-7}$$

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 the last Chapter.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$
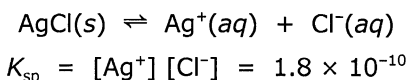
We had found the solubility of AgCl in plain water to be

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

but now let's salt things up a bit by adding NaCl to the water before adding the AgCl. What happens to the solubility of AgCl when we add it to a solution of NaCl(*aq*)? The added Na^+ cation is not involved in any equilibrium here, so it's 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 decreases $[Ag^+]$ which means less AgCl is dissolved at equilibrium. Let's see how this works out.

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Example 2. What is the solubility (in M) of AgCl in salt water which contains 0.00862 M NaCl(*aq*)?

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This starts with the same setup as in the last Chapter

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$
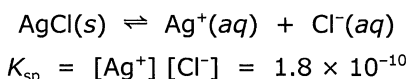
but the table begins differently. Before adding any AgCl, there is already an initial amount of Cl^- from the NaCl.

	$[Ag^+]$	$[Cl^-]$
Initial:	-0-	0.00862

Now chuck some AgCl(*s*) into the pot. Some dissolves to give $Ag^+(aq)$ and additional $Cl^-(aq)$.

	$[Ag^+]$	$[Cl^-]$
Initial:	-0-	0.00862
Changes:	+x	+x
Equilibrium:	x	0.00862 + x

The equilibrium values go into K_{sp}.

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

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

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

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 the parenthetical term (0.00862 + x) as 0.00862. This simplifies the K_{sp} expression to

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

and solving that for x gives $x = 2.1 \times 10^{-8}$. If you tried to iterate that, the parenthetical term (0.00862 + 2.1×10^{-8}) gives you 0.00862 right back, so there's no change and you're done.

Care to do a K check?

So what's the final answer for the solubility? Well, we set up x to be the concentration of Ag^+; one $Ag^+(aq)$ is produced for every formula unit of AgCl(*s*) which dissolves, so x again represents the solubility. Compare this solubility, 2.1×10^{-8} M, to the solubility in plain water which was 1.3×10^{-5} M. There is a 620-fold decrease in solubility due to the small amount of added Cl^-.

Go again.

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

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Bring back the equations from Example 1.

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\,F^-(aq)$$
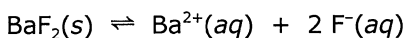
$$K_{sp} = [Ba^{2+}]\,[F^-]^2 = 1.8 \times 10^{-7}$$

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},

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

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

$$4x^3 + 0.0640\,x^2 + 2.56 \times 10^{-4}\,x - 1.8 \times 10^{-7} = 0$$

You can't do negative-b-plus-or-minus-square-root-of-whatever on this one. We'll bring in approximation/ iteration for this. We start by assuming x is small, at least small enough for $2x$ to be small compared to 0.0160.

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

Solving for x gets you 7.0×10^{-4}. Iterate:

$$(x)(0.0160 + 2x)^2 \approx (x)(0.0160 + 2 \times 7.0 \times 10^{-4})^2 = (x)(0.0174)^2 = 1.8 \times 10^{-7}$$

You get $x = 5.9 \times 10^{-4}$. Go again:

$$(x)(0.0160 + 2x)^2 \approx (x)(0.0160 + 2 \times 5.9 \times 10^{-4})^2 = (x)(0.0172)^2 = 1.8 \times 10^{-7}$$

Now $x = 6.1 \times 10^{-4}$. Keep going:

$$(x)(0.0160 + 2x)^2 \approx (x)(0.0160 + 2 \times 6.1 \times 10^{-4})^2 = (x)(0.0172)^2 = 1.8 \times 10^{-7}$$

This gives $x = 6.1 \times 10^{-4}$, which repeats the prior value. You're done and the K check is good. This is now the molarity of BaF_2 in a solution which begins with $[F^-] = 0.0160$ M. Compare this result to 0.0036 M in plain water as calculated in Example 1. The solubility went down 5.9-fold with the added F^-.

　　　Your turn.

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　　　Example 4. What is the solubility (in M) of lead(II) iodate, $Pb(IO_3)_2$, in plain water? What is the solubility (in M) in a solution of 0.00450 M KIO_3?

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Balanced equation:

K_{sp} expression:

Start off in plain water. Fill in a table:

　　　　　　Initial:

　　　　Changes:

　　　Equilibrium:

Plug these into K_{sp}.

Solve for x.

What's the solubility in plain water?

Now the solubility in the 0.00450 M KIO_3 solution. Fill in a table:

Initial:

Changes:

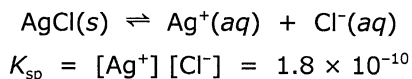Equilibrium:

Plug these into K_{sp}.

Solve for x.

What's the solubility? Clue: The solubility of $Pb(IO_3)_2$ in 0.00450 M KIO_3 is 2,500-times less than in plain water.

In all of the AgCl, BaF_2 and $Pb(IO_3)_2$ 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: the solubility is 3.0×10^{-8} M.) When you apply the Principles of Equilibrium Dynamics to the K_{sp} equation, then the presence of a common ion on the right side of the equation shifts the equilibrium to the left.

These effects have a very practical application if you want to decrease the concentration of a metal cation in solution. Reasons for doing this include economics and safety/environmental aspects. The former is associated with expensive metals such as silver or, even moreso, gold, platinum, 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 silver and copper. We'll illustrate this for a solution of $Ag^+(aq)$ and we'll use $Cl^-(aq)$ as the precipitating agent; this allows us to use the same AgCl equations as above.

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Example 5. You have an aqueous solution which contains 0.010 M $AgNO_3$. You want to reduce the concentration of Ag^+ to 5.0 μM by precipitation with NaCl. What concentration (in M) of Cl^- is necessary to give $[Ag^+]$ = 5.0 μM at equilibrium?

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Once again, we work with

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

but now we're starting with Ag^+ and adding Cl^- to produce AgCl. Note that you want $[Ag^+]$ = 5.0×10^{-6} M at equilibrium. Since that is at equilibrium, this is not a change problem and there is no table to set up. Just plug that equilibrium amount directly into K_{sp}

$$K_{sp} = [Ag^+][Cl^-] = (5.0 \times 10^{-6})[Cl^-] = 1.8 \times 10^{-10}$$

and solve to get [Cl⁻] = 3.6 × 10⁻⁵ M. At that concentration of Cl⁻(*aq*), the Ag⁺(*aq*) concentration will be at the target value of 5.0 μM at equilibrium.

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 protonate a basic anion; that decreases the concentration of the anion and that shifts the solubility product equation to the right. Consider the following equation for a generic MX(*s*), again composed of M²⁺ and X²⁻ ions.

$$K_{sp} \qquad\qquad MX(s) \rightleftharpoons M^{2+}(aq) + X^{2-}(aq)$$

The X²⁻ ion is a weak base and reacts with added strong acid.

$$K \ (= 1/K_{a2}) \qquad\qquad X^{2-}(aq) + H^+(aq) \rightleftharpoons HX^-(aq)$$
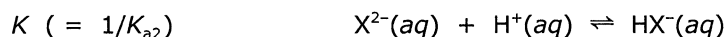
This second equation is actually the reverse of the second dissociation step for the diprotic acid, H_2X. The protonation of X²⁻ reduces its concentration, which then shifts the solubility equilibrium to the right. In this way, the solubility of MX increases. This effect can be substantial even when 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 greater for 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 discussed $CaCO_3$ in plain water as an example in the last Chapter. Now let's add some acid to the mix. Begin with simple solubility.

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$
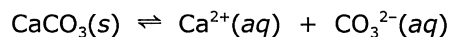
$$K_{sp} = [Ca^{2+}] [CO_3^{2-}] = 3.4 \times 10^{-9}$$

(I'm leaving out the associative effect from the last Chapter because it is insignificant to the other equilibria here.) Start adding strong acid. This will protonate carbonate.
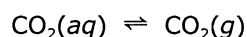
$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$$
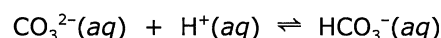
$$K = 1/K_{a2} = 2.1 \times 10^{10}$$

Note the very large K for protonation. This shifts the solubility equilibrium to the right. Add more strong acid, which can protonate bicarbonate.

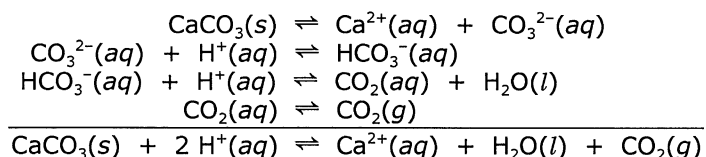$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons CO_2(aq) + H_2O(l)$$
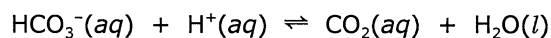
$$K = 1/K_{a1} = 2.2 \times 10^6$$

This shifts the prior equations to the right even more. CO₂ itself has a limited solubility in water and readily effervesces out of solution.

$$CO_2(aq) \rightleftharpoons CO_2(g)$$

$$K = 29.8$$

This shifts all of the prior equations to the right even more and more. Now add up all of the above equations

$$\begin{array}{r} CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \\ CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq) \\ HCO_3^-(aq) + H^+(aq) \rightleftharpoons CO_2(aq) + H_2O(l) \\ CO_2(aq) \rightleftharpoons CO_2(g) \\ \hline CaCO_3(s) + 2\,H^+(aq) \rightleftharpoons Ca^{2+}(aq) + H_2O(l) + CO_2(g) \end{array}$$

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

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

Look at the size of the overall K_{sum}; this leads 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 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 limestone or any 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 $Ca_5(PO_4)_3OH$. (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 fluorapatite, $Ca_5(PO_4)_3F$. Fluorapatite 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 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 and/or at higher concentration.

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 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 a number of ligands to one or more metal atoms or ions; for typical aqueous systems, this involves a single metal cation. The number of ligands which can bind are most commonly two, four and six. The ligands are arranged in a specific shape around the metal and some common shapes are shown, wherein L indicates a ligand. Two ligands give a linear shape, four ligands give a tetrahedral or a square planar shape, and six ligands give an 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 $Ni(CN)_4^{2-}$ is square planar although both involve four ligands on a central Ni^{2+} ion.
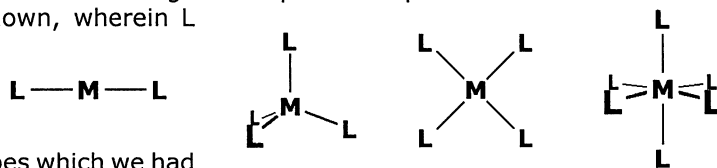
Water itself is the most common ligand and it uses a lone pair on oxygen (and not just its dipole) to bind to a metal. When dissolved in water, many metal cations form complexes with six or four water molecules. For example, Zn^{2+}, Cr^{2+}, Co^{2+}, Fe^{2+}, etc. form octahedral $M(H_2O)_6^{2+}$ complexes. Co^{2+} can actually go either way, octahedral or tetrahedral; the latter is $Co(H_2O)_4^{2+}$. 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 $M^{n+}(aq)$, without specifying the number of ligands involved. For example, $Zn^{2+}(aq)$ and $Zn(H_2O)_6^{2+}(aq)$ mean the same thing. On the other hand, not all metal cations form complexes in water; for example, $Na^+(aq)$ only involves the usual ion-dipole interactions. The metals of the *s*-block are not very good at this in general, except for Be^{2+} which 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 very 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+} and protein, which can also carry O_2 as an additional ligand. Unfortunately, since CO is such a great ligand, it will also bind to hemoglobin and it can take the place of the O_2 ligand; that's why CO is so toxic.

Complexes can contain one kind of ligand or they can contain different kinds of ligands. For example, solutions of $Al^{3+}(aq)$ and $F^-(aq)$ are a veritable hodgepodge of complexes including $Al(H_2O)_5F^{2+}$, $Al(H_2O)_4F_2^+$, $Al(H_2O)_3F_3$ 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 metal cation charge and the charges of the ligands. For example, consider $Ag(NH_3)_2^+$, $Al(H_2O)_3F_3$ and $Fe(CN)_6^{4-}$.

$Ag(NH_3)_2^+$: The ligands are ammonia molecules which are neutral by themselves. Silver ion is a constant charge cation of 1+. The sum of charges is 1+, so the charge of the complex is 1+.

$Al(H_2O)_3F_3$: The ligands include three fluorides of 1– each, and three neutral waters. Aluminum ion is a constant charge cation of 3+. The sum of all charges is zero, so the complex is neutral.

$Fe(CN)_6^{4-}$: The six ligands are cyanides, CN^-, of 1– each. Iron forms variable charge cations, so we need to determine its charge in this case from the charge on the complex. The charge of the complex is 4– overall, so the metal ion must be 2+.
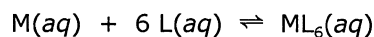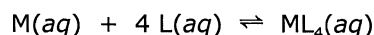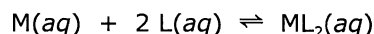
Keep the charges in mind when working with formulas for complexes. Here, you can do another one with a variable charge cation.

$AuCl_4^-$:

Let me note that it is common to put a complex's formula inside [brackets] with the charge (except zero) as a superscript after]. For example, the above formulas of complexes would be written $[Ag(NH_3)_2]^+$, $[Al(H_2O)_3F_3]$, $[Fe(CN)_6]^{4-}$ and $[AuCl_4]^-$. I won't be using brackets for the formulas of complexes because we will be using brackets for concentration terms and that could confuse things.

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. Monatomic ligands do not get parentheses. You can see this in the examples shown so far.

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

$$M(aq) + 2\,L(aq) \rightleftharpoons ML_2(aq)$$

$$M(aq) + 4\,L(aq) \rightleftharpoons ML_4(aq)$$

$$M(aq) + 6\,L(aq) \rightleftharpoons ML_6(aq)$$

These are the overall equilibria for complexes of 2, 4 or 6 ligands. Each of the above equations is a "complex formation" equation. Each complex formation equation has one $M(aq)$ and the required number of ligands on the left; there is one complex on the right. 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 $M(aq)$ 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 a specific example of a complex formation reaction, consider the equation for $Ag(NH_3)_2^+$.

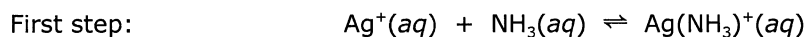$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$
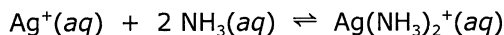
We can write an equilibrium expression in the usual manner for this reaction; the associated K is called a formation constant and is symbolized by K_f. Some values are given in Appendix B.

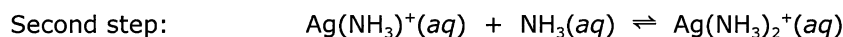$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+]\,[NH_3]^2} = 1.1 \times 10^7$$

Note the large value for K_f. In general, K_f values can be very large, and some are even greater than 10^{30}.

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.

It is possible to break up an overall complex formation reaction into separate and sequential steps, and the first two steps were mentioned in a general manner in Section 59.3. Here's the breakdown for our silver complex.

First step: $\qquad\qquad Ag^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)^+(aq)$

$$K_{f1} = \frac{[Ag(NH_3)^+]}{[Ag^+]\,[NH_3]} = 1{,}700$$

Second step: $\qquad\qquad Ag(NH_3)^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$

$$K_{f2} = \frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+]\,[NH_3]} = 6{,}500$$

As to be expected, adding the two steps together gives the overall complex formation equation for $Ag(NH_3)_2^+$, and $K_f = K_{f1} \times K_{f2}$. The single-ligand complex in this sequence, $Ag(NH_3)^+$, cancels out in the summation; it basically serves as an intermediate to the overall process of forming the final complex although it can still be present in appreciable amounts at equilibrium.

While an ML_2 complex has two steps and involves one intermediate complex, an ML_4 complex has four steps and three intermediates, and an ML_6 complex has six steps and five intermediates. This quickly becomes very tedious, especially for calculations. Depending on the system, there can be significant concentrations of any or all of the species involved. For our purposes, we limit calculations to the (overall) complex formation equation, given generically as follows.

$$M(aq) + n\,L(aq) \rightleftharpoons ML_n(aq)$$
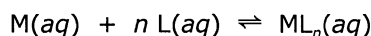
$$K_f = \frac{[ML_n]}{[M]\,[L]^n}$$

We will not cover calculations for any of the intermediate complexes. In addition, we will not do change-to-equilibrium problems because the total concentration of intermediates can be substantial. On the other hand, we can still work with calculations for systems <u>at</u> equilibrium. Keep in mind that we are heading for the effect of complex formation on solubilities. One very big point, which can be seen qualitatively right now, is that adding ligands will shift each step equation and the overall equation to the right, thereby ultimately decreasing the concentration of the metal cation in solution. The concentration of the metal cation in solution is of prime importance to a solubility product equilibrium. Given the magnitude of K_f values, the effect of ligands can be huge.

60.3 Complex calculations

Let's do some number-crunching. We'll start with the silver complex.

. . . .

Example 6. A solution at equilibrium contains 0.0053 M $Ag(NH_3)_2^+$ and 0.0018 M NH_3. What is the concentration (in M) of Ag^+?

. . . .

From above, we have

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$
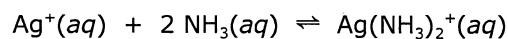
and

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

into which we plug the given concentrations of $Ag(NH_3)_2^+$ and NH_3.

$$K_f = \frac{0.0053}{[Ag^+](0.0018)^2} = 1.1 \times 10^7$$

Re-arrange and solve, and you will find $[Ag^+] = 1.5 \times 10^{-4}$ M, which is fairly small. As always in any equilibrium, dilution favors dissociation and that should favor the left side of the complex formation equation, but the large value of K_f offsets that and strongly favors the right side.

Note that there are three concentration terms in a K_f expression so, if given any two, then you can solve for the third. Here's one variation.

· ·

Example 7. A solution at equilibrium contains 6.2×10^{-5} M Ag^+ and 0.0036 M NH_3. What is the concentration (in M) of $Ag(NH_3)_2^+$?

· ·

Take the same K_f expression and plug in the different equilibrium values.

$$K_f = \frac{[Ag(NH_3)_2^+]}{(6.2 \times 10^{-5})(0.0036)^2} = 1.1 \times 10^7$$

Solve. You will get $[Ag(NH_3)_2^+] = 0.0088$ M.

These calculations are fairly straightforward. And don't forget that you can always K-check your result. You do have to be mindful of the exponent on the ligand concentration and be sure you can execute those properly on your trusty calculator.

To wit:

· ·

Example 8. A solution at equilibrium contains 0.0061 M $Fe(CN)_6^{4-}$ and 0.0016 M CN^-. What is the concentration (in M) of Fe^{2+}?

· ·

We need a new complex formation equation

$$Fe^{2+}(aq) + 6\,CN^-(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq)$$
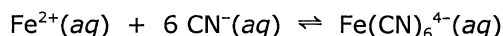
and a new K_f.

$$K_f = \frac{[Fe(CN)_6^{4-}]}{[Fe^{2+}][CN^-]^6} = 7.9 \times 10^{36}$$

Plug and chug

$$K_f = \frac{0.0061}{[Fe^{2+}](0.0016)^6} = 7.9 \times 10^{36}$$

to get $[Fe^{2+}] = 4.6 \times 10^{-23}$ M, which is an extremely small concentration, but we have an extremely large K_f.

OK, your turn.

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Example 9. A solution at equilibrium contains 0.0023 M $HgBr_4^{2-}$ and 0.0045 M Br^-. What is the concentration (in M) of Hg^{2+}?

· ·
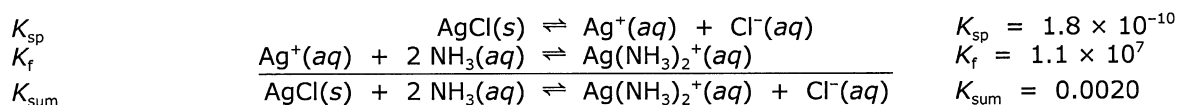
Balanced equation

K_f expression
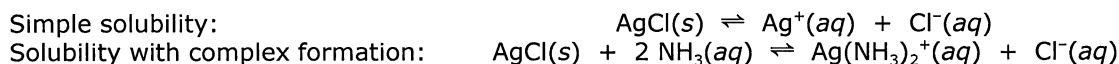
Enter your values and solve for $[Hg^{2+}]$.

You should get a value with 10^{-15}.

That's enough for the general calculations. Now let's see how this can affect the solubility of an insoluble compound. Complex formation can be an excellent way of increasing solubility, depending on the value of K_f and the concentration for the ligand. We'll discuss three Cases, each using AgCl but with different ligand conditions.

▸ Case 1. Consider again the system of AgCl and NH_3. Combine the simple solubility (K_{sp}) equation for AgCl along with the complex formation (K_f) equation for $Ag(NH_3)_2^+$.

K_{sp}	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	$K_{sp} = 1.8 \times 10^{-10}$
K_f	$\underline{Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)}$	$K_f = 1.1 \times 10^7$
K_{sum}	$AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$	$K_{sum} = 0.0020$

The sum represents solubility with complex formation, and $K_{sum} = K_{sp} \times K_f$. (We could bring in the intermediate complex, $Ag(NH_3)^+$, but its concentration is small here. The contributions from any intermediate complex here and below are less than 3% of the total. As such, we'll ignore them, just to keep things manageable.) By forming a complex, $[Ag^+]$ decreases relative to its concentration due to K_{sp} alone. This shifts the K_{sp} equilibrium to the right, allowing more of the insoluble compound to dissolve. We can relate the total solubility of AgCl to the following two equations.

Simple solubility: $\qquad\qquad\qquad\qquad\qquad AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
Solubility with complex formation: $\qquad AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$

These two equations will operate to a different extent, the latter dependent on the concentration of $NH_3(aq)$ present at equilibrium. Now the silver ion from the dissolved formula units of AgCl is divvied among $Ag^+(aq)$ and $Ag(NH_3)_2^+(aq)$; the chloride ion which is also produced remains monatomic $Cl^-(aq)$. Let's compare some numbers.

For a mixture of $AgCl(s)$ in plain water at equilibrium (as cited previously in this Chapter), we have

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

and this directly gives the solubility of AgCl in plain water as 1.3×10^{-5} M.

For a mixture of $AgCl(s)$ in $NH_3(aq)$, with $[NH_3] = 0.0075$ M at equilibrium, we have the following.

$$[Ag^+] = 5.4 \times 10^{-7} \text{ M} \qquad [Cl^-] = 3.3 \times 10^{-4} \text{ M} \qquad [Ag(NH_3)_2^+] = 3.3 \times 10^{-4} \text{ M}$$

(The manner of calculation for the concentration of the complex in these Cases is not within our coverage, and I am simply giving the final results each time.) Note the large decrease in $[Ag^+]$ relative to its concentration in plain water. Now, the total solubility of AgCl is represented by the sum of the concentrations for Ag^+ and $Ag(NH_3)_2^+$,

$$\text{solubility of AgCl} = [Ag^+] + [Ag(NH_3)_2^+] = 5.4 \times 10^{-7} \text{ M} + 3.3 \times 10^{-4} \text{ M} = 3.3 \times 10^{-4} \text{ M}$$

and this is also the value for the Cl^- concentration. Note also the large increase in total solubility of AgCl, which is now 25-times the solubility of AgCl in plain water. That's not a super-impressive increase but it is definitely significant, and we have a fairly low concentration of NH_3.

If you want to dissolve more, you can increase the concentration of ligand.

▸ Case 2. For a mixture of $AgCl(s)$ in $NH_3(aq)$, with $[NH_3] = 0.075$ M at equilibrium, we have the following results.

$$[Ag^+] = 5.4 \times 10^{-8} \text{ M} \qquad [Cl^-] = 0.0033 \text{ M} \qquad [Ag(NH_3)_2^+] = 0.0033 \text{ M}$$

The total solubility of AgCl in 0.10 M NH_3 is again represented by the sum of the dissolved silver species

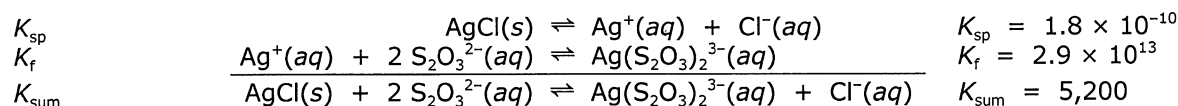$$\text{solubility of AgCl} = [Ag^+] + [Ag(NH_3)_2^+] = 5.4 \times 10^{-8} \text{ M} + 0.0033 \text{ M} = 0.0033 \text{ M}$$

and that sum again equals $[Cl^-]$. The total solubility of AgCl is now 250-times the simple solubility of AgCl in plain water.
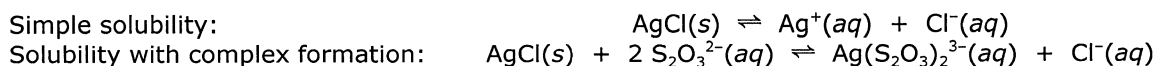
Is that enough solubility?

▸ Case 3. Another way to increase solubility is to use a better ligand. A "better" ligand is evidenced by a larger K_f for the same ML_n type of complex. Another complex of silver with two ligands is the thiosulfate

complex, $Ag(S_2O_3)_2{}^{3-}$, whose K_f is 2.9×10^{13}, which is 2.6-million times greater than the K_f for $Ag(NH_3)_2{}^+$. The relevant equations are the following.

$$K_{sp} \qquad\qquad AgCl(s) \;\rightleftharpoons\; Ag^+(aq) \;+\; Cl^-(aq) \qquad\qquad K_{sp} \;=\; 1.8 \times 10^{-10}$$
$$K_f \qquad\qquad \underline{Ag^+(aq) \;+\; 2\,S_2O_3{}^{2-}(aq) \;\rightleftharpoons\; Ag(S_2O_3)_2{}^{3-}(aq)} \qquad\qquad K_f \;=\; 2.9 \times 10^{13}$$
$$K_{sum} \qquad\qquad AgCl(s) \;+\; 2\,S_2O_3{}^{2-}(aq) \;\rightleftharpoons\; Ag(S_2O_3)_2{}^{3-}(aq) \;+\; Cl^-(aq) \qquad K_{sum} \;=\; 5{,}200$$

The K_{sum} is likewise 2.6-million times greater than the K_{sum} for $Ag(NH_3)_2{}^+$. The total solubility of AgCl is now given by the following two equations.

Simple solubility: $\qquad\qquad\qquad\qquad\qquad\qquad\qquad AgCl(s) \;\rightleftharpoons\; Ag^+(aq) \;+\; Cl^-(aq)$
Solubility with complex formation: $\qquad AgCl(s) \;+\; 2\,S_2O_3{}^{2-}(aq) \;\rightleftharpoons\; Ag(S_2O_3)_2{}^{3-}(aq) \;+\; Cl^-(aq)$

With a mere $[S_2O_3{}^{2-}] = 7.5 \times 10^{-4}$ M at equilibrium, which is 10-times lower concentration than the $[NH_3]$ in Case 1, we have

$$[Ag^+] = 3.3 \times 10^{-9}\ M \qquad [Cl^-] = 0.054\ M \qquad [Ag(S_2O_3)_2{}^{3-}] = 0.054\ M$$

which gives

$$\text{solubility of AgCl} \;=\; [Ag^+] \;+\; [Ag(S_2O_3)_2{}^{3-}] \;=\; 3.3 \times 10^{-9}\ M \;+\; 0.054\ M \;=\; 0.054\ M$$

which is now 4,100 times the solubility of AgCl in plain water, and with a very low concentration of the ligand.

These are just a few illustrations of the effects of complex formation on solubilities. In summary, the solubility of an insoluble compound increases with complex formation. The increase is greater for higher concentrations of ligand and for better ligands.

Now, a major wrap-up.

60.4 Close

With this we close on our general coverage of aqueous equilibria. This coverage has been extensive: 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 and complicated place and, in the water world of your Earth and of your own life chemistry, these equilibria can be 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

1.   True or false.

   a. The presence of a common ion in solution will always increase the solubility of a compound.

   b. The solubility of magnesium hydroxide is greater at pH 10 than at pH 4.

   c. AgCl is less soluble in 0.01 M $HNO_3(aq)$ than in 0.01 M $HCl(aq)$.

   d. $Ni(NH_3)_6{}^{2+}$ is a tetrahedral complex.

   e. The charge on the complex which is formed between a silver ion and four cyanide ligands is 2–.

   f. Ammonia can increase the solubility of some compounds by complex formation.

2.   Calculate the simple solubility (in M) for each of the following.

   a. $PbCrO_4$ $\qquad\qquad$ b. $Ag_2C_2O_4$

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.

   a. $BaSO_4$ in 0.00313 M $Ba(CH_3CO_2)_2$ $\qquad\qquad$ b. MgF_2 in 0.00443 M NaF

4. An excess of PbSO$_4$(s) is added to a solution of 4.17 × 10^{-4} M K$_2$SO$_4$, giving a heterogeneous mixture. At equilibrium, what are the concentrations (in M) of Pb^{2+}(aq) and of SO$_4^{2-}$(aq)?

5. You have 2.00 L of a solution containing Au$^+$(aq). 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 decrease [Au$^+$] to 1.0 × 10^{-6} M at equilibrium?

6. 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 CH$_3$CO$_2$H   0.01 M Na$_2$CO$_3$ 0.01 M Zn(NO$_3$)$_2$

7. Write the balanced equation for complex formation and write the K_f expression for each of the following.

    a. Cd(OH)$_4^{2-}$ b. Ni(NH$_3$)$_6^{2+}$

8. A solution of Cu^{2+}(aq) is pale blue. Adding NH$_3$ forms the deep blue complex, Cu(NH$_3$)$_4^{2+}$. For a solution which contains 0.0075 M Cu(NH$_3$)$_4^{2+}$ and 0.050 M NH$_3$ at equilibrium, what is the concentration of Cu^{2+} (in M)?

9. A solution is prepared containing 4.6 × 10^{-6} M Al^{3+} and 0.0074 M AlF$_6^{3-}$ at equilibrium. What is the concentration (in M) of F$^-$?

10. Derive the balanced equation for solubility with complex formation for copper(I) chloride using cyanide as the ligand, which forms the complex Cu(CN)$_4^{3-}$. Calculate the value of K for this equation from K_{sp} and K_f.