Chapter 59 IONIC SOLUBILITY EQUILIBRIA

We now return to solubility, a notion which we have previously examined in a variety of forms. Way back in Chapters 10 - 12, we had gotten into solubility and precipitation reactions. At that time, we were primarily concerned with identifying products, balancing equations and doing stoichiometry. We did discuss some aspects behind the reasons for soluble and insoluble, but we were limited to an enthalpy approach (although we didn't call it enthalpy at that time) and we only considered ionic solutes. Quite a bit later in Chapters 39 - 41, we discussed more of the equilibrium of solubility, covering the full range of solutes including gases, liquids, molecular solids and ionic solids. We were able to delve deeper into both the enthalpy and entropy aspects, although only qualitatively for the latter. We got quantitative with entropy in Chapter 44, we combined it with enthalpy to give free energy in Chapter 45, and we did some calculations with ΔG in Chapters 46 and 47; a number of illustrations and examples in those Chapters dealt with solubility, although mostly for molecular solutes. Molecular solutes are fairly straightforward, regardless of whether their native phase is gas, liquid or solid. Many simply dissolve and that's it, although acids and bases do dissociate, at least to some extent. On the other hand, ionic solutes dissociate into separate ions, and that dissociation may or may not be complete. Furthermore, the separate ions can then be involved in other equilibria at the same time. As we have already seen, some individual cations and anions undergo weak acid or weak base dissociation on their own. As we will see here, cations and anions can do other equilibria also.

At this time, we go further into the equilibria of solubility in aqueous solutions. Solubility remains vastly important to a wide range of applications in your world. Chapter 10:

> ❝ You are able to be here because Earth has suitable conditions for liquid phase water. Importantly, water is liquid phase under these conditions because it has strange and unusual properties. There is one thing that water can do better than just about any other solvent at these conditions: it can dissolve many ionic compounds. Water can also dissolve many covalent compounds, too, but so can many other solvents. Why is this important? The ability to dissolve ionics opens up entirely different worlds of chemistry. On the one hand, water can dissolve many ionics, but not all. The oceans contain massive amounts of dissolved compounds, mostly simple ionics. On the other hand, rocks are also primarily ionic compounds and these don't dissolve readily in water. Much of this is important for shaping Earth. It's also important for shaping biology. The chemistry of life is inextricably associated with the ability of water to dissolve some ionics but not others. Like the sea, your blood is a soup of dissolved ions. Yet, your bones and teeth are also ionic compounds, although these don't dissolve. ❞

Chapter 39:

> ❝ From the discussion so far, we see that any phase can participate in forming a mixture. Nevertheless, our primary focus here will be liquid solutions. Furthermore, our primary focus will involve this planet's most important solvent, H_2O. Water's role in natural processes on Earth cannot be overstated, biologically or nonbiologically. All of life on Earth and all of surface Earth itself depend critically on the ability of water to dissolve or not to dissolve. These things are part of your world. They are an absolutely critical part of your world. And in your world, <u>what is soluble is just as important as what is insoluble</u>. The ions and sugars in your blood need to be soluble; your bones and cell membranes need to be insoluble. ❞

We now expand on the equilibria which are connected to the solubility of ionic compounds. There's actually more to the meaning of "solubility" in many cases. We will see these things as we go, but we will first discuss a molecular solute for illustration purposes.

59.1 Solubility

There are some technicalities to the term solubility which we will now examine.

For some molecular compound A of gas, liquid or solid native phase, simple solubility in water is represented by the equilibrium with its aqueous solute phase, A(*aq*).

$$\begin{aligned} A(g) &\rightleftharpoons A(aq) \\ A(l) &\rightleftharpoons A(aq) \\ A(s) &\rightleftharpoons A(aq) \end{aligned}$$

For solutes which do not engage in any other equilibria, their solubility can be calculated based on the *K* for the above equations as was illustrated in Chapter 47. A problem arises, however, if A(*aq*) gets significantly involved in other equilibria. If so, the total solubility of A needs to include the simple solubility shown above and also those other equilibria. I will illustrate this using the molecular compound SO_2 since we have worked quite a bit with different equilibria for this compound. Now we'll see how these affect total solubility. We did a calculation of its gas and aqueous equilibrium in Section 41.2.

> ❝ Let's say you have a solution of SO_2 dissolved in water. You pour this into a fresh container, evacuate the air, and then close off the container while leaving a gas space inside. Some $SO_2(aq)$ will escape to the gas phase, eventually giving a dynamic equilibrium.
>
> $$SO_2(g) \rightleftharpoons SO_2(aq)$$
>
> If $[SO_2(aq)] = 0.064$ M at equilibrium, what is the pressure of $SO_2(g)$ in the gas space of the container?
>
> To do this, start with your solubility equation.
>
> $$[SO_2(aq)] = k_H \times P$$
>
> Enter the given concentration and the k_H.
>
> $$0.064 \text{ M} = 1.4 \frac{\text{M}}{\text{atm}} \times P$$
>
> Rearrange and solve for P: you get 0.046 atm for the pressure of $SO_2(g)$ in the gas space. ❞

Back then in Chapter 41 we had used the Henry constant, k_H, for the solubility of gases but later, in Section 47.1, we related k_H to K from $\Delta G°$.

SO_2 is a fairly soluble gas and we now know that it is also a weak acid with a fairly high K_{a1}.

$$SO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \qquad K_{a1} = 0.014$$

There is also a second dissociation but K_{a2} is much smaller.

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \qquad K_{a2} = 6.7 \times 10^{-8}$$

By the rationale in Section 55.3, we will ignore this second dissociation for the present illustration.

So what does acid dissociation have to do with solubility?

Given the simple solubility equation,

$$SO_2(g) \rightleftharpoons SO_2(aq)$$

then some dissolved $SO_2(aq)$ can react with $H_2O(l)$ and dissociate into $H^+(aq)$ and $HSO_3^-(aq)$. By the Principles of Equilibrium Dynamics, that would decrease the amount of $[SO_2(aq)]$ in solution and that would shift the simple solubility equilibrium to the right. This means more $SO_2(g)$ dissolves to reach equilibrium. We can also look at this as follows. Combine the simple solubility equation with the first acid dissociation. Watch your phases for SO_2.

$$\begin{array}{ll} K(\text{simple solubility}) & SO_2(g) \rightleftharpoons SO_2(aq) \\ K_{a1} & \underline{SO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq)} \\ K_{sum} & SO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \end{array}$$

The sum connects $SO_2(g)$ directly with $HSO_3^-(aq)$; this equation represents solubility with acid dissociation. We can now envision that the total solubility of $SO_2(g)$ derives from two processes.

$$\begin{array}{lr} \text{Simple solubility:} & SO_2(g) \rightleftharpoons SO_2(aq) \\ \text{Solubility with acid dissociation:} & SO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \end{array}$$

These two equations in particular show directly what happens to $SO_2(g)$: some $SO_2(g)$ dissolves and forms $SO_2(aq)$ and some $SO_2(g)$ dissolves and forms $HSO_3^-(aq)$. Chemically, all of the above equilibria are connected and ongoing. The total amount of dissolved SO_2 is therefore represented by the amounts of $SO_2(aq) + HSO_3^-(aq)$. Let's calculate this total for the conditions in the problem from Section 41.2. We were given $[SO_2(aq)] = 0.064$ M at equilibrium. We can use this to find $[HSO_3^-(aq)]$ via K_{a1}.

$$K_{a1} = \frac{[H^+(aq)]\,[HSO_3^-(aq)]}{[SO_2(aq)]} = 0.014$$

The original problem gave $[SO_2(aq)] = 0.064$ M at equilibrium, so this is not a problem which involves a change in amounts. The 0.064 M is the final value and this goes into K_{a1} directly.

$$K_{a1} = \frac{[H^+(aq)]\,[HSO_3^-(aq)]}{0.064} = 0.014$$

Note that acid dissociation gives equal amounts of H^+ and HSO_3^-, so we can write

$$K_{a1} = \frac{[HSO_3^-(aq)]^2}{0.064} = 0.014$$

and from this, $[HSO_3^-(aq)] = 0.030$ M at equilibrium. The grand total of all sulfur species in the entire system at equilibrium is therefore the following.

$$[SO_2(aq)] = 0.064 \text{ M} \qquad [HSO_3^-(aq)] = 0.030 \text{ M} \qquad P(SO_2(g)) = 0.046 \text{ atm}$$

Now imagine that the problem was worded differently: if the pressure of $SO_2(g)$ is 0.046 atm at equilibrium, then what's the solubility of SO_2? This is where the term itself can take different meaning. It can be represented by the simple solubility equilibrium involving only $SO_2(aq)$, in which case the answer is 0.064 M. But, on a practical side, more SO_2 will physically dissolve although it ends up as $HSO_3^-(aq)$. That leads to the total solubility which includes all of the SO_2 which actually dissolved. In that case, the solubility is 0.094 M, which is the total of $[SO_2(aq)] + [HSO_3^-(aq)]$. Notice that having another equilibrium occurring simultaneously can have a very large effect on total solubility.

As you can see, there are a few subtleties to the term "solubility", so you need to watch the meaning for a given application or problem. Again, if the solute does not engage in any other process to any significant extent, then the simple solubility equation will give the total solubility. If, however, other equilibria are operating to a significant extent, then the simple solubility equation will be inadequate for calculating total solubility. Although inadequate, the calculation does give a minimum solubility; if simultaneous equilibria are involved, then they will always increase the total solubility of a compound in plain water. Regardless, the simple solubility equilibrium is still the common starting point for the consideration of solubility.

On a quantitative note, solubility always refers to the amount of some compound which is dissolved per amount of solution or per amount of solvent at saturation condition. In other words, solubility is an equilibrium amount. At equilibrium, the system will involve a heterogeneous mixture of the compound in its native form ((*s*) or (*l*) or (*g*)) in contact with a solution of that compound at some steady concentration. For gases, this also requires a specific gas pressure. Units of solubility can take a variety of forms such as those described in Chapter 42. In addition, a traditional unit used in many solubility tables is grams of solute per 100 mL of water, a unit which we have used off and on since Chapter 10. For dilute solutions, the volume of water used will be the same as the volume of solution, so this will be the same as grams of solute per 100 mL solution.

I have presented the SO_2 example here as a lead into some of the subtleties of "solubility". I chose SO_2 for this introduction because it is a molecular solute and a bit simpler than many ionic solutes. Plus, we've already covered the relevant equilibria for this compound in prior Chapters. At this time, we head into the solubility equilibria of ionic solutes. These can get more involved than molecular solutes.

59.2 K_{sp}

The general equation for simple solubility of an ionic compound, A(*s*), is the following.

$$A(s) \rightleftharpoons \text{cations}(aq) + \text{anions}(aq)$$

This equation is written based on full dissociation of the ions, which is how we have been dealing with ionic solutes over the long term. There are issues with this and we will finally be getting into some of these in this Chapter. Regardless of the extent of dissociation, let me note that our emphasis will lie with insoluble compounds and not with soluble compounds. This emphasis will limit the coverage to ionic compounds whose cation is a metal ion. Ionic compounds whose cation is not a metal cation, such as NH_4^+ or a protonated amine, tend to give soluble compounds so they would not be included here. Thus, we will be dealing with insoluble, ionic compounds of generic form MX, M_2X, MX_2, MX_3, etc., where M is a metal cation and X is an anion.

It is important to remember that insoluble is associated with insignificant solubility. Technically, the solubility is not absolutely zero, but it's between that and very small. Chapter 10:

> ❝ There are actually two phenomena which are critically important to the total aqueous picture. The two phenomena are <u>solubility</u> and <u>dissociation</u>. Solubility is the more general of the two: you can have solubility without dissociation, but you cannot have dissociation without solubility.

Both of these can apply to solutes which are ionic compounds and to solutes which are covalent compounds. So don't think that we're leaving out covalents. These are still very important to the total picture. And don't think that solubility and dissociation are easy to do, because they are not. This is where water's weirdness really comes to light: the ability to dissolve and to dissociate many different kinds of compounds.

For our present purposes, solubility refers to whether a compound does or does not dissolve to a significant extent. The underlined part is very important to understanding solubility, and I will explain this further in the next Chapter. For now, I give two simple examples.

You know sodium chloride, NaCl, as the primary component of table salt. You know this dissolves very well in water. We say that sodium chloride is "soluble".

You may not know barium sulfate, $BaSO_4$, from experience, but we did use it last Chapter as the product of an aqueous reaction and we said at the time that it was not soluble and it formed a white powder. We can now state that barium sulfate does not dissolve to a significant extent and we therefore consider it "insoluble". ❞

As we proceed in the here and now, we limit our coverage to insolubles because our approach and calculations won't work for soluble cases. We cannot do a solubility calculation for NaCl because its equilibrium solubility is so high. As noted previously on several occasions, moderate concentrations of ions lead to numerous complications which can throw off a calculation. On the other hand, for insoluble compounds, the ion concentrations are very low and our approach and calculations will remain fairly ideal.

We now start in. Let's consider the simple solubility equilibrium for $BaSO_4$.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

This type of solubility equation is specifically called a solubility product equation. Solubility product equations can be written for any ionic compound, regardless of soluble or insoluble. They always involve one mole of solid on the left and the fully dissociated ions on the right. The K expression for this process is specifically designated as K_{sp} and this is called a solubility product or a solubility product constant.

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

As always, a solid has unity activity and does not appear in K. Here's another example, using AgCl.

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

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

These two are easy cases because the ion ration is 1:1. Try a different ratio: here it is for $Ca_3(PO_4)_2$.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3\ Ca^{2+}(aq) + 2\ PO_4^{3-}(aq)$$

$$K_{sp} = [Ca^{2+}]^3\,[PO_4^{3-}]^2$$

Values of K_{sp} are known for many compounds and some values are given in Appendix B. For example, the solubility product for AgCl is 1.8×10^{-10}. If you take a pinch of AgCl and throw it into one liter of water, then a very, very small amount dissolves and dissociates upon going to equilibrium. To the human eye, the amount which does dissolve would not be perceptible. Each formula unit of AgCl which dissolves and dissociates gives one Ag^+ ion and one Cl^- ion. Thus, the amount of AgCl which does dissolve will correspond to $[Ag^+]$ or $[Cl^-]$ in solution at equilibrium. Neither of these ions engages in any other equilibrium process to a significant extent, so the simple solubility equation is the only one we need. We can calculate $[Ag^+]$ and $[Cl^-]$ at equilibrium by the general methods for any equilibrium. We would start by setting up a table. For initial conditions, there is only AgCl(*s*) before dissolving and dissociating; there are no ions yet. AgCl(*s*) does not appear in the table because it remains unity activity.

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

Change will occur as a very, very small amount of AgCl(*s*) dissolves and dissociates. This will give some Ag^+ and some Cl^-.

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

This leads to the equilibrium amounts.

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

These go to into K_{sp}

$$K_{sp} = [Ag^+]\,[Cl^-] = (x)\,(x) = x^2 = 1.8 \times 10^{-10}$$

and square-rooting gives $x = 1.3 \times 10^{-5}$. Thus, $[Ag^+] = 1.3 \times 10^{-5}$ M and $[Cl^-] = 1.3 \times 10^{-5}$ M at saturation equilibrium. Now, remember what I said earlier:

> On a quantitative note, solubility always refers to the amount of some compound which is dissolved per amount of solution or per amount of solvent at saturation condition.

For ionic compounds, solubility refers to the amount of formula units which are dissolved. This will connect somehow to a cation concentration and/or to an anion concentration, although this can get complicated if other equilibria are operating. For the present AgCl example, each ion is formed 1:1 for each formula unit of dissolved AgCl, so at equilibrium we can write

$$\text{solubility of AgCl} = [Ag^+] = [Cl^-]$$

which means the solubility of AgCl in water is 1.3×10^{-5} M. With suitable conversions, you can put this into other units. For example, with the molar mass, you can convert this to g/100 mL.

$$\text{solubility of AgCl} = \frac{1.3 \times 10^{-5}\text{ mol AgCl}}{\text{L}} \times \frac{143.4\text{ g AgCl}}{\text{mol AgCl}} \times \frac{0.100\text{ L}}{100\text{ mL}} = \frac{0.00019\text{ g}}{100\text{ mL}}$$

That's only 190 μg dissolved in 100 mL, and that's very small. (BTW: When you do a calculation like this, do not enter the "100" into the calculator because the "100 mL" actually remains as part of the final unit.)

Values of K_{sp} range over many exponents and solubilities will also range broadly. There is a hitch, however, in how the relative values of K_{sp} between different compounds reflect the relative solubilities. In prior Chapters for acids and bases with coefficients of one in the balanced equation and powers of one in the K expressions, we could use the magnitude of K_a or of K_b to compare weak, weaker or not so weak. This kind of simple comparison will now be conditional for K_{sp} because the coefficients and powers can differ. The condition is that you can only do this between ionic compounds with the same total number of ions in the formula unit. You cannot make this assessment between ionic compounds of different numbers of ions without getting into calculations. Let me illustrate why.

Consider ionic compounds of formulas MX, M_2X, MX_2 and MX_3 and assume that each compound has a solubility of 1.0×10^{-4} M. To keep this illustration simple, we will assume the compounds have no other equilibria operating. Keep in mind that solubility refers to formula units dissolved per volume. We will now calculate K_{sp} for each of these.

- The simple solubility of MX is represented by

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

and the given value of 1.0×10^{-4} mol of formula units per L leads to $[M^+] = 1.0 \times 10^{-4}$ M and $[X^-] = 1.0 \times 10^{-4}$ M at equilibrium. The value of K_{sp} is then determined by those.

MX: $K_{sp} = [M^+]\,[X^-] = (1.0 \times 10^{-4})\,(1.0 \times 10^{-4}) = 1.0 \times 10^{-8}$

- M_2X is represented by

$$M_2X(s) \rightleftharpoons 2\,M^+(aq) + X^{2-}(aq)$$

for which the given solubility leads to $[M^+] = 2.0 \times 10^{-4}$ M and $[X^{2-}] = 1.0 \times 10^{-4}$ M. The value of K_{sp} is then determined as follows.

M_2X: $K_{sp} = [M^+]^2\,[X^{2-}] = (2.0 \times 10^{-4})^2\,(1.0 \times 10^{-4}) = 4.0 \times 10^{-12}$

Note that the K_{sp} is different compared to the MX case, even though the solubilities are the same. The K_{sp} is different because there are different numbers of ions in the formula unit.

▸ Likewise, for MX_2 we get

$$MX_2(s) \rightleftharpoons M^{2+}(aq) + 2\,X^{-}(aq)$$

$$[M^{2+}] = 1.0 \times 10^{-4}\ M \qquad [X^{-}] = 2.0 \times 10^{-4}\ M$$

$$MX_2\!: \quad K_{sp} = [M^{2+}]\,[X^{-}]^2 = (1.0 \times 10^{-4})\,(2.0 \times 10^{-4})^2 = 4.0 \times 10^{-12}$$

This is the same value for K_{sp} as for M_2X because MX_2 and M_2X have the same total number of ions.

▸ Finally for MX_3 we get

$$MX_3(s) \rightleftharpoons M^{3+}(aq) + 3\,X^{-}(aq)$$

$$[M^{3+}] = 1.0 \times 10^{-4}\ M \qquad [X^{-}] = 3.0 \times 10^{-4}\ M$$

$$MX_3\!: \quad K_{sp} = [M^{3+}]\,[X^{-}]^3 = (1.0 \times 10^{-4})\,(3.0 \times 10^{-4})^3 = 2.7 \times 10^{-15}$$

This one has a different number of ions than the above cases and K_{sp} is again different.

Although all of these cases have the same solubility of 1.0×10^{-4} M, they have a large spread in the value of K_{sp}. Thus, numbers for K_{sp} do not give us a quick, qualitative way of comparing relative solubility among different compounds unless the compounds have the same number of ions in the formula unit. Thus, M_2X and MX_2 can be directly compared but no others in this list can be directly compared. For example, I could look up $K_{sp} = 5.4 \times 10^{-12}$ for $Ag_2C_2O_4$ and $K_{sp} = 4.9 \times 10^{-17}$ for $Fe(OH)_2$ and correctly say that $Ag_2C_2O_4$ is more soluble because it has a larger K_{sp}. On the other hand, I cannot look at $K_{sp} = 1.8 \times 10^{-10}$ for AgCl and directly say how its solubility compares to that of either $Ag_2C_2O_4$ or $Fe(OH)_2$. I would need to do a calculation. (The actual solubilities are $Ag_2C_2O_4$ > AgCl > $Fe(OH)_2$ although the K_{sp} values run AgCl > $Ag_2C_2O_4$ > $Fe(OH)_2$.) Thus and overall, you need to be careful with how to interpret the magnitude of K_{sp} with respect to comparing actual solubilities among different compounds.

Again, the calculations so far assume no other equilibria are significant, but we're about to change that.

59.3 Other equilibria in ionic solutions

The prior SO_2 example illustrated how total solubility can be affected by another equilibrium operating simultaneously in the system. As we now get into ionic solids, I will point out that one or both ions of most insoluble compounds will engage in other equilibria and those other equilibria will often increase the total solubility. Since solubility is so vastly important to a wide range of compounds and their solution applications, then these other equilibria can be an important aspect. We will consider the following types of equilibria:

Acid-base effects
Associative equilibria
  Ion pairing
  Complex formation

For the present discussion, I will use a generic compound MX(*s*) which is composed of M^{2+} and X^{2-} ions. For simple solubility, we have the following solubility product equation.

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

The impact of other equilibria will depend on how those affect the concentrations of M^{2+} and/or X^{2-}. Any equilibrium which uses M^{2+} and/or X^{2-} would decrease the concentration of M^{2+} and/or X^{2-} in the above equation and that would shift the above equation further to the right. Shifting the above equation to the right causes more solid to dissolve. In this way, the solubility increases.

- ACID-BASE EFFECTS

As has been seen, some metal cations are acidic

$$K_a(M^{2+}) \qquad M^{2+}(aq) + H_2O(l) \rightleftharpoons M(OH)^{+}(aq) + H^{+}(aq)$$

while some anions are basic.

$$K_b(X^{2-}) \qquad X^{2-}(aq) + H_2O(l) \rightleftharpoons HX^{-}(aq) + OH^{-}(aq)$$

Although there are some acidic anions, those are limited to hydrogen anions (most of which are actually amphoteric). There are a few hydrogen anions which can form insoluble compounds (HPO_4^{2-} being one example) but we will exclude those from our coverage here.

As some $M^{2+}(aq)$ forms some $M(OH)^{+}(aq)$, then the K_{sp} equation shifts to the right. Likewise, as some $X^{2-}(aq)$ forms some $HX^{-}(aq)$, this also shifts the K_{sp} equation to the right. Either of these causes more $MX(s)$ to dissolve, and this increases the solubility of MX. These effects will not be significant until K_a or K_b becomes appreciably large. How large is that? Well, the overall effect will also depend on the specific insoluble compound and its K_{sp}. Not many common metal cations are acidic enough for a significant effect so we will simply exclude those from further considerations. On the other hand, there are many common anions which are basic enough to have a significant effect. Let's develop this picture a bit more for these cases. Combine the K_{sp} equation with the K_b equation.

$$\begin{array}{ll} K_{sp} & MX(s) \rightleftharpoons M^{2+}(aq) + X^{2-}(aq) \\ K_{b} & \underline{X^{2-}(aq) + H_2O(l) \rightleftharpoons HX^{-}(aq) + OH^{-}(aq)} \\ K_{sum} & MX(s) + H_2O(l) \rightleftharpoons M^{2+}(aq) + HX^{-}(aq) + OH^{-}(aq) \end{array}$$

The sum represents solubility with base dissociation. We can now express the total solubility of a compound which contains a basic anion by the following two equations.

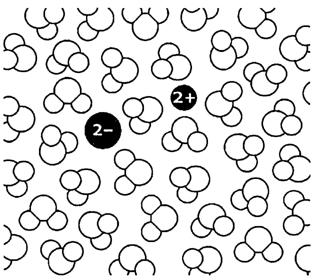
$$\begin{array}{lr} \text{Simple solubility:} & MX(s) \rightleftharpoons M^{2+}(aq) + X^{2-}(aq) \\ \text{Solubility with base dissociation:} & MX(s) + H_2O(l) \rightleftharpoons M^{2+}(aq) + HX^{-}(aq) + OH^{-}(aq) \end{array}$$

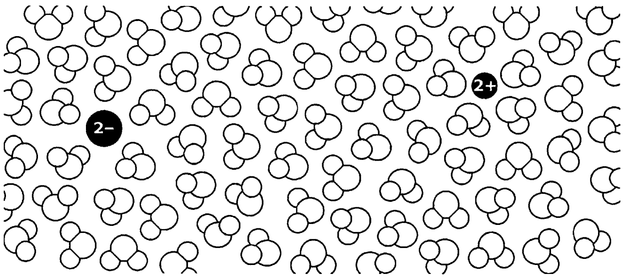
Although all of these equations are interconnected, these two equations in particular show a direct connection to the formula units of $MX(s)$ which are dissolved. These two equations will operate to a different extent and one or both can be significant. For basic anions, the sum equation will be more significant when the K_b is larger. PO_4^{3-} is one of the best for this, with a K_b of 0.022; this will impact the solubility of many phosphate compounds. Other examples of fairly high K_b include arsenate, carbonate, cyanide, etc. Again, whether base dissociation is significant to solubility will also depend on the K_{sp} of the compound involved. The most drastic cases of basic anions are oxide and sulfide ions. Both O^{2-} and S^{2-} are strongly basic; as such, base dissociation of the anion drastically increases the solubility of all metal oxides and sulfides. For these, the simple solubility equilibrium is no longer significant; the equilibrium for solubility with base dissociation becomes much more important.

- ASSOCIATIVE EQUILIBRIA

We have assumed since Chapter 10 that an ionic compound dissociates completely into separated cations and anions, but now we are going to see how dissociation is not necessarily complete. We now consider association, which is the opposite of dissociation. Associative equilibria are very general in many processes, not just aqueous solutions. For the present context, these will refer to some kind of equilibrium between a cation and an anion in which all parties remain dissolved. These associative equilibria can operate simultaneously along with simple solubility, thereby again increasing the total solubility of a compound. We will consider two types of associative equilibria: ion pairing and complex formation.

1. ION PAIRING. Ion pairing involves a pairing of a cation and an anion in close proximity in solution. The pairing results primarily from simple +/− attraction; the ions simply hang together, attracted by their opposite charges. Each ion can still be hydrated by water molecules, or the two ions can shed some or all of the water molecules between them and get into closer proximity (as shown at left) or be in direct contact. Due to the pairing, the ions are not truly independent and they are not truly dissociated. Compare this to true, full dissociation, below right, in which the ions are so far apart that they have no sense of or interaction with each other. Ion pairing is yet another example of dynamic equilibrium: the ions can separate and wonder off until eventually finding another opposite to pair with. In an ion pair, if the cation and anion are of the same charge number, then the pairing is neutral. If the ions do not have the same charge number, then the pairing is not neutral: for example, a Mg^{2+} cation can pair with a Cl^{-} anion to give a $MgCl^{+}$ ion pair.





There are several factors which affect the extent of ion pairing in solution. Charge density of the ions can be very important: higher charge density tends to favor ion pairing. Concentration of the ions is important: higher concentration favors more pairing. Note that this concentration effect runs opposite to the effect for dissociative equilibria, such as weak acid or weak base dissociation: dilution favors dissociation, while higher concentration favors association. Besides charge density and concentration, other factors can also be involved. Additionally, beyond simple pairs, larger clusters or chains can even occur, but we will not deal with those here.

A general equilibrium for ion pairing between M^{2+} and X^{2-} can be written as follows.

$$K(\text{ion pair}) \qquad M^{2+}(aq) + X^{2-}(aq) \rightleftharpoons MX(aq)$$

$MX(aq)$ designates the soluble ion pair. Combine this with the simple solubility equation (K_{sp}).

$$\begin{array}{ll} K_{sp} & MX(s) \rightleftharpoons M^{2+}(aq) + X^{2-}(aq) \\ K(\text{ion pair}) & \underline{M^{2+}(aq) + X^{2-}(aq) \rightleftharpoons MX(aq) \qquad\qquad\qquad} \\ K_{sum} & MX(s) \rightleftharpoons MX(aq) \end{array}$$

The sum equation represents solubility with ion pairing. Note the distinction between $MX(s)$ and $MX(aq)$ in the sum equation: $MX(s)$ refers to one formula unit of the undissolved ionic solid, while $MX(aq)$ is one specific ion pair which is dissolved but associated. $MX(s)$ and $MX(aq)$ are different chemical identities. This distinction can be subtle, so watch the phases. Ion pairing equilibria will have their own K's which tend to be modest, in the 10^1 - 10^3 range. You can get into calculations with them but we will not do so. Our interest is in the qualitative effect of ion pairing on solubility and that effect is to increase the total solubility. The equations above give two connections to the formula units of $MX(s)$ which are dissolved.

$$\begin{array}{ll} \text{Simple solubility:} & MX(s) \rightleftharpoons M^{2+}(aq) + X^{2-}(aq) \\ \text{Solubility with ion pairing:} & MX(s) \rightleftharpoons MX(aq) \end{array}$$

These two equilibria will operate to a different extent. Notice that, when $MX(aq)$ ion pairs are present in solution along with $M^{2+}(aq)$ and $X^{2-}(aq)$, then dissociation is not complete.

2. COMPLEX FORMATION. In normal everyday usage and even within chemistry itself, the word complex can mean different things in different applications, as a noun or as an adjective. In the current context, it specifically refers to a metal complex, also called a coordination complex. These complexes are specific polyatomic chemical units which are formed between a metal center and various groups called ligands. The ligands provide electrons for the interaction; usually this involves a lone pair. This interaction is not simple +/− electrical attraction between ions anymore, and it's not a simple ion-dipole interaction either. The metal and ligand are in a direct connection; this gives a type of chemical bond, referred to as a coordinate bond, and these can include covalent character. We had actually hinted at complexes back in Section 39.4 when discussing the enthalpy of ion-dipole interactions in water.

> ❝ The grand total in energy for all water molecules which are interacting with ions is now in the hundreds and even thousands of kJ's per mol range; thus, the total ion-dipole interaction can now compete with chemical bond energies. Some of the strongest cases actually lead into a whole different ballgame associated with "complexes", but we're going to wait until later in Chapter 59 to get into those. ❞

Later is now. I am only giving a brief introduction to complexes at this time as it relates to the solubility of a compound in plain water. More of the ballgame will be discussed in the next Chapter when we generalize the discussion for solutions with other solutes present.

Many anions can serve as ligands and this enables a metal cation and its anion to set up a complex formation equilibrium. In forming a complex, one metal cation can often bind more than one anion, and this can set up multiple steps of complex formation. This has some parallel to polyprotic acid dissociations which can likewise be written as separate steps. Here is the equation which depicts the first step of complex formation between M^{2+} and a single X^{2-} ligand.

$$K(\text{complex, first step}) \qquad M^{2+}(aq) + X^{2-}(aq) \rightleftharpoons MX(aq)$$

A second step can be written as follows.

$$K(\text{complex, second step}) \qquad MX(aq) + X^{2-}(aq) \rightleftharpoons MX_2^{2-}(aq)$$

For now we will limit to the first step only. I am trying to illustrate the general, qualitative effects on solubility without getting into all the details, and the first step will suffice for now. We'll do all steps in the fuller discussion in the next Chapter when we have more solutes present; that will make a huge difference.

Notice that the equation for the first step is the same as the equation written upstairs for ion pairing, but now $MX(aq)$ refers to a complex. The equilibrium aspects of the two processes are similar, and this simplifies matters considerably since we can use "MX(*aq*)" as either an ion pair or a complex. *K* values for complex formation do tend to be much larger than *K* values for ion pairing and there are several factors involved in those; we will look more at *K* values for complexes in the next Chapter. Since the balanced equations are the same for the two processes, we will adopt the ones shown previously for ion pairing and now generalize them for both types of associative effects. The result is that we can relate the solubility of MX(*s*) to two outcomes.

Simple solubility: $MX(s) \rightleftharpoons M^{2+}(aq) + X^{2-}(aq)$
Solubility with association: $MX(s) \rightleftharpoons MX(aq)$

These two processes will again operate to a different extent and, again, the presence of MX(*aq*) indicates that dissociation is not complete.

OK, we've now got a number of equilibria which are possible for ions in solution. Now peel open those eyeballs so we can see how all of this can play out.

59.4 Eye on ions

In the grand generality of any aqueous solution containing any ionic solute, dissociation and association equilibria are very common and the effects can range from very large down to insignificant. It just depends on the system. It can apply to solubility and it can apply to insolubility. By their nature, insolubles have very low concentrations of ions in solution at equilibrium, and one or more simultaneous equilibria can have a sizeable effect on such small numbers. We will now summarize the possible effects, still using a generic MX compound of M^{2+} and X^{2-} charges. The concepts are similar for other formulas such as M_2X, MX_2, MX_3, etc., but the equations will have different numbers of M's and X's.

Return to the solubility product equation.

Simple solubility: $MX(s) \rightleftharpoons M^{2+}(aq) + X^{2-}(aq)$

For a basic anion, bring in base dissociation.

Solubility with base dissociation: $MX(s) + H_2O(l) \rightleftharpoons M^{2+}(aq) + HX^-(aq) + OH^-(aq)$

For association, bring in that also.

Solubility with association: $MX(s) \rightleftharpoons MX(aq)$

Each of these equations can contribute to total solubility and all of them can be operating to a different extent. For total solubility, we would have to add up the amount of MX(*s*) which dissolves from each type of equilibrium. Those calculations can be very tedious for a particular compound unless we can rule out one or more processes as not significant. As you can see, solubility is not always simple.

Although not always simple, you can still do an initial calculation for solubility based only on K_{sp} for an ionic compound, but you have to understand that the result will be a minimum. If no simultaneous equilibria are operating to a significant extent, then that gives the actual solubility. If one or more other equilibria are operating, then the total solubility can be higher and even many times higher. Let's now look at a specific case quantitatively.

Carbonate compounds are of tremendous importance mineralogically, biologically and in many human applications. We've previously looked at the weak acid/base chemistry associated with CO_3^{2-} and its related members including HCO_3^-, H_2CO_3, $CO_2(aq)$ and even $CO_2(g)$. Now we look at the solubility of a carbonate compound. Although carbonates tend to be insoluble compounds, their equilibria can be extremely important. For illustration purposes, I'll highlight calcium carbonate, which is one of the most important carbonate compounds. $CaCO_3$ is globally abundant in limestone and marble, and it is abundantly used in a wide range of applications. It sees use in construction, ceramics, paper making, paints and adhesives, to name a few. It also finds use in human health and nutrition in the form of antacids and calcium supplements, although too much calcium can kill. $CaCO_3$ is regarded as the most important biomineral, appearing in a wide variety of biological systems such as eggshells, seashells, the teeth of sea urchins, corals, the nacre of pearls, etc. It even brings balance to humans and to other vertebrates by its vestibular role.

$CaCO_3$ actually has several different crystal forms which can arise through variations in conditions such as temperature, pressure, other solutes present, etc. We won't get into that level of detail. For our purposes here and now, we pose a fundamental question: if $CaCO_3(s)$ is added to pure water at standard conditions, how much dissolves and what chemical species are present at equilibrium?

We begin with simple solubility.

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

You can calculate a solubility based on K_{sp} by the same method as shown earlier for AgCl. Starting from

$$K_{sp} = [Ca^{2+}]\,[CO_3^{2-}]$$

you would set up your table.

	$[Ca^{2+}]$	$[CO_3^{2-}]$
Initial:	-0-	-0-
Changes:	$+x$	$+x$
Equilibrium:	x	x

Those equilibrium amounts go into K_{sp}

$$K_{sp} = [Ca^{2+}]\,[CO_3^{2-}] = (x)\,(x) = 3.4 \times 10^{-9}$$

and that gives $x = 5.8 \times 10^{-5}$. Based only on this equilibrium, the solubility of $CaCO_3$ would be 5.8×10^{-5} M. That is at least a minimum.

Is that everything?

Carbonate is appreciably basic

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^{-}(aq) + OH^{-}(aq) \qquad K_b = 2.1 \times 10^{-4}$$

and this does affect the solubility for this compound. Summing this and the prior equation gives the equation for solubility with base dissociation.

$$CaCO_3(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + HCO_3^{-}(aq) + OH^{-}(aq) \qquad K = K_{sp} \times K_b = 7.1 \times 10^{-13}$$

Despite the very small K, this contribution turns out to be substantial relative to the amount of $CaCO_3$ dissolved. At equilibrium, you would have the following total amounts from the two equilibria so far.

$$[Ca^{2+}] = 1.11 \times 10^{-4}\text{ M} \qquad [CO_3^{2-}] = 3.1 \times 10^{-5}\text{ M} \qquad [HCO_3^{-}] = [OH^{-}] = 8.0 \times 10^{-5}\text{ M}$$

(Whencesoever came these numbers? The calculations to derive these concentrations are beyond our coverage here, so I am only showing the final results.) Notice that the amount of bicarbonate actually exceeds the amount of carbonate. This may seem unusual but remember that dilution favors dissociation. In this case, the percent dissociation of carbonate is very high (72%) due to the very low concentrations involved.

So what's the solubility now? We can express the total solubility of $CaCO_3$ so far in terms of Ca^{2+}

$$\text{solubility of } CaCO_3 = [Ca^{2+}] = 1.11 \times 10^{-4}\text{ M}$$

or in terms of CO_3^{2-} and HCO_3^{-}.

$$\text{solubility of } CaCO_3 = [CO_3^{2-}] + [HCO_3^{-}] = 3.1 \times 10^{-5}\text{ M} + 8.0 \times 1.0^{-5}\text{ M} = 1.11 \times 10^{-4}\text{ M}$$

Either way is fine. Notice that this solubility is nearly double what is calculated based only on simple solubility.

Is that everything?

The associative equilibrium for $CaCO_3$ (ion-pairing in this case) is the following

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(aq) \qquad K_{assoc} = 1{,}400$$

and when that is added to the K_{sp} equation, you get the following sum for solubility with association.

$$CaCO_3(s) \rightleftharpoons CaCO_3(aq) \qquad K = K_{sp} \times K_{assoc} = 4.8 \times 10^{-6}$$

This contribution turns out to be of small effect, and the K expression directly gives $[CaCO_3(aq)] = 4.8 \times 10^{-6}$ M.

Now the totals at equilibrium are the following.

$$[Ca^{2+}] = 1.11 \times 10^{-4}\text{ M} \qquad [CO_3^{2-}] = 3.1 \times 10^{-5}\text{ M} \qquad [HCO_3^{-}] = [OH^{-}] = 8.0 \times 10^{-5}\text{ M}$$

$$[CaCO_3(aq)] = 4.8 \times 10^{-6}\text{ M}$$

So what's the solubility now? All of the calcium ions from the dissolved formula units of $CaCO_3(s)$ have ended up as separated Ca^{2+} cations and as associated $CaCO_3(aq)$.

$$\text{solubility of } CaCO_3 = [Ca^{2+}] + [CaCO_3] = 1.11 \times 10^{-4}\text{ M} + 4.8 \times 10^{-6}\text{ M} = 1.16 \times 10^{-4}\text{ M}$$

All of the carbonate ions from the dissolved $CaCO_3(s)$ have ended up as CO_3^{2-}, HCO_3^- and $CaCO_3(aq)$.

$$\begin{aligned}\text{solubility of } CaCO_3 &= [CO_3^{2-}] + [HCO_3^-] + [CaCO_3] \\ &= 3.1 \times 10^{-5}\text{ M} + 8.0 \times 1.0^{-5}\text{ M} + 4.8 \times 10^{-6}\text{ M} = 1.16 \times 10^{-4}\text{ M}\end{aligned}$$

Again, either way of calculating the final total solubility is fine.

Is that everything?

Technically, we could consider the base dissociation of $HCO_3^-(aq)$ to give $CO_2(aq)$ but that additional dissociation step is not significant and it can be ignored. Also technically, we could even include some loss of $CO_2(aq)$ from solution to give $CO_2(g)$ but we're keeping a lid on things and assuming no gas space in the system. (We'll open this up to more solutes and more possibilities in the next Chapter.) So, yes, this is everything for now. Although we won't be covering how to do some of the calculations used above, I wanted to illustrate how total solubility is the grand sum of the various equilibria which can enter into the picture.

This was only one example of one compound, and these effects can vary widely for other compounds. K_b will be a big factor in the base effects. Charge density will be a big factor in the associative effects. Ionic MX compounds with 1+/1− ions are not big players in these effects (as noted for the AgCl example earlier), although there are exceptions. M_2X or MX_2 compounds with 1+/2− or 2+/1− ions and MX with 2+/2− ions (e.g., $CaCO_3$) will often show these effects. As soon as you get to any combination with a 3+ or 3− ion, then the effects will be substantial. Overall, depending on the ionic compound, some will have solubilities close to those calculated by K_{sp} alone, whereas others will have solubilities which are several times greater or even hundreds or thousands of times greater. We will be avoiding the extreme cases.

Problems

1. True or false.
    a. Associative equilibria will lead to a decrease in the total solubility of a compound.
    b. Ion pairing will not occur between two anions.
    c. Potassium nitrate has stronger ion pairing in solution than calcium carbonate.
    d. All ion pairs are neutral.

2. Write the balanced equation for the solubility product and write the K_{sp} expression for each of the following.
    a. $Fe(OH)_3$ b. $CuCrO_4$

3. Write the balanced equation for the solubility product and write the K_{sp} expression for each of the following.
    a. lead(II) bromide b. nickel(II) phosphate

4. Consider three hypothetical compounds of formulas MX, MX_2 and MX_3, all having the same numerical value of $K_{sp} = 1.0 \times 10^{-10}$. Based only on simple solubility (K_{sp}), calculate the solubility (in M) of each. Rank these from least soluble to most soluble.

5. Using free energies of formation, calculate $\Delta G°$ (in kJ) for the solubility product equation for magnesium hydroxide and use this value to calculate K_{sp} at 25 °C.

6. Derive the balanced equation for solubility with base dissociation for $Ag_2C_2O_4$. Calculate the value of K for this equation from K_{sp} and K_b.