Tutorial 7
The Common Ion Effect and Altering Solubility

In Tutorial 7, you will be shown:

1. What the Common Ion Effect is and how it can be used.
2. How we can increase or decrease the solubility of a compound by adding other materials.

The Common Ion Effect

To understand the Common Ion Effect, you must first review LeChatelier's Principle.

Remember, it goes something like this:

Le Chatelier's Principle:

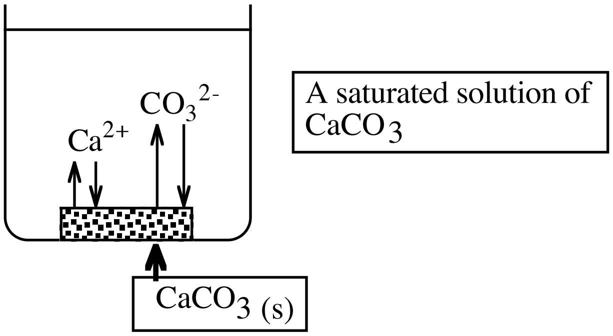
When a stress is applied to a system at equilibrium, the equilibrium will shift so as to partially counteract the imposed stress.

Let's see how this might apply to solubility.

We can start by looking at the equilibrium equation for a compound of low solubility, eg. $CaCO_{3(s)}$:

$$\mathbf{CaCO_{3(s)} \rightleftarrows Ca^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)}}$$

Let's say we have a saturated solution of calcium carbonate ($CaCO_3$). What this means is that we would have some solid $CaCO_3$ sitting on the bottom of the solution and there would be some Ca^{2+} ions and some $CO_3{}^{2-}$ ions dissolved in the solution.



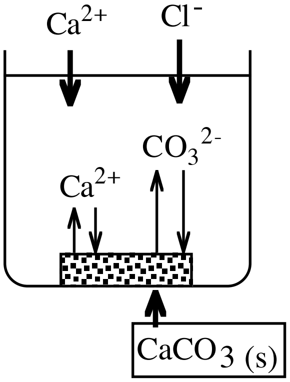
Since this solution is at equilibrium, the concentration of dissolved Ca^{2+} and CO_3^{2-} ions in solution will stay constant. (*Even though ions are dissolving and precipitating all the time--at rates which just balance each other.*) This situation would remain constant through eternity ***unless*** we do something.

Let's say we add a small amount of Calcium Chloride ($CaCl_2$) to the beaker. Calcium chloride is considered ***soluble***, so we can assume that it *all dissociates* into Ca^{2+} and Cl^- ions: (*Notice the single arrow!*)

$$CaCl_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

So what we would be doing is adding some Ca^{2+} ions and some Cl^- ions to the solution in the beaker.

But remember, the solution in the beaker was already saturated with Ca^{2+} and CO_3^{2-} ions from the $CaCO_3$! So what in the world will happen now?



Since there were no Cl^- ions in the solid or in the solution before, they will not affect anything. They can be regarded as spectator ions in this case.

But you can see by the diagram that we are adding Ca^{2+} ions to a saturated solution of $CaCO_3$.

Looking at the equilibrium equation for $CaCO_{3(s)}$ dissolving:

$$\mathbf{CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)}}$$

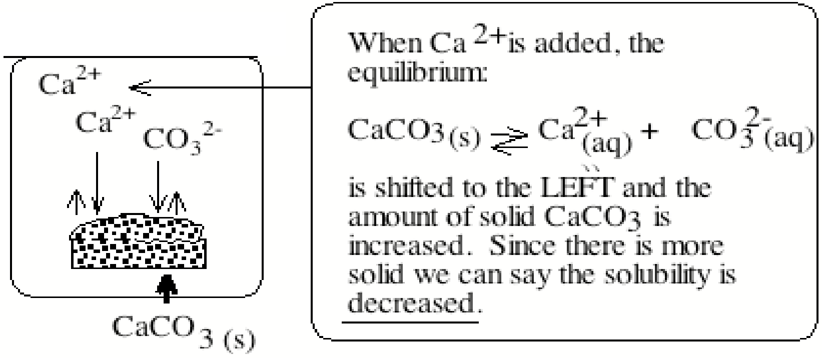
What we are actually doing is increasing the $[Ca^{2+}]$ in this equilibrium. This, of course is imposing a **stress** on the system at equilibrium.

By LeChatelier's Principle, increasing the $[Ca^{2+}]$ can be counteracted by the equilibrium shifting to the <u>LEFT</u>:

$$\mathbf{CaCO_{3(s)} \rightleftharpoons \Large{Ca^{2+}_{(aq)}} + CO_3{}^{2-}_{(aq)}}$$

What this will do is ***<u>increase the amount of CaCO</u>***$_{3(s)}$ and ***<u>decrease</u>*** the concentration of CO_3^{2-}.

$$\mathbf{\Large{CaCO_{3(s)}} \rightleftharpoons Ca^{2+}_{(aq)} + \small{CO_3{}^{2-}_{(aq)}}}$$



When Ca^{2+} is added, the equilibrium:

$$CaCO_{3(s)} \rightleftarrows Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

is shifted to the LEFT and the amount of solid $CaCO_3$ is increased. Since there is more solid we can say the solubility is decreased.

Since this results in more solid $CaCO_3$ in the beaker, we can say that:

Adding Ca^{2+} ions to the solution decreases the solubility of $CaCO_3$.

Now, hopefully you can see where the name "Common Ion Effect" fits in.

The ion Ca^{2+} that was added to the saturated $CaCO_3$ solution is the same as (common to) one of the ions in the original solution.

We can now generalize a little bit:

A compound of low solubility forms two ions in a saturated solution. The addition of either of these two ions (from a compound or solution with an ion in common) will decrease the solubility of the compound with low solubility.

Using this concept, we can see that many compounds could decrease the solubility of $CaCO_3$.

Increasing Solubility

We can use LeChatelier's Principle for increasing the solubility of a compound as well as for decreasing it (as we did with the Common Ion Effect).

Let's look at this equilibrium again:

$$CaCO_{3(s)} \rightleftarrows Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

If we could somehow ***decrease*** either $[Ca^{2+}]$ or $[CO_3^{2-}]$, then this equilibrium would shift to the ***right*** and the amount of solid would decrease. (ie. the solubility would ***increase***.)

But, how do we decrease the concentration of an ion? We can't just reach in and pull ions out of a solution! But, there IS a way.

The ***carbonate*** (CO_3^{2-}) ion happens to be easy to decrease. All we have to do is add some ***acid*** to the container. The following sequence of reactions will (hopefully) help you understand how this works. Just remember, what we are trying to do is ***decrease*** the $[CO_3^{2-}]$ in this equilibrium:

$$CaCO_{3(s)} \rightleftarrows Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

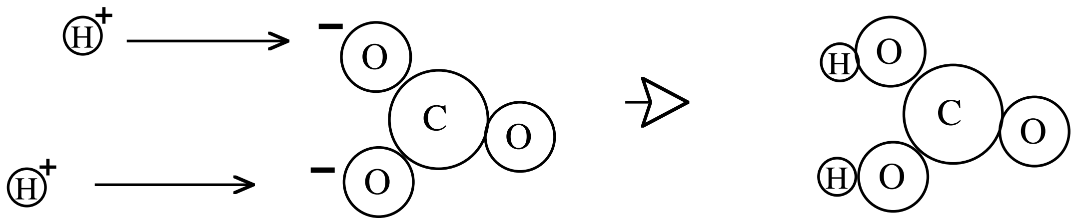
Now, focus your attention just on the carbonate:

$$CO_3^{2-}{}_{(aq)}$$

As you might know, when you put an ***acid*** into water, hydrogen ions (H^+) are formed.
(eg. $HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$)

Well, when these hydrogen ions collide with carbonate, they temporarily form a compound called ***carbonic acid***. Let's see:

$$2H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow H_2CO_{3\,(aq)}$$



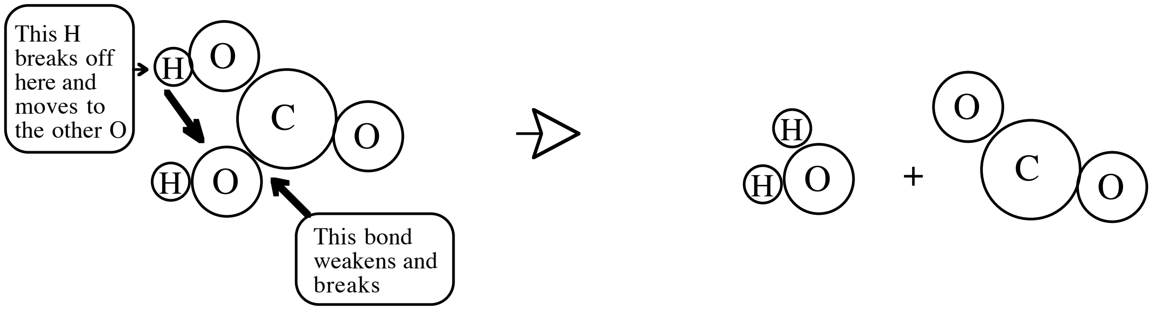
$$2\,H^+ \quad + \quad CO_3^{2-} \longrightarrow H_2CO_3$$

hydrogen ions (from acid) *carbonate ion* *carbonic acid*

Now, it so happens that ***carbonic acid*** (H_2CO_3) is ***<u>unstable</u>*** in water solution. Carbonic acid is actually what is present in ***carbonated*** beverages (like pop).

In water solution, carbonic acid (H_2CO_3) ***<u>decomposes</u>*** to form carbon dioxide gas ($CO_{2(g)}$) and liquid water :

$$H_2CO_{3\,(aq)} \rightarrow H_2O_{\,(l)} + CO_{2\,(g)}$$



$$H_2CO_{3(aq)} \xrightarrow{\text{decomposes}} H_2O_{(l)} + CO_{2(g)}$$

What happens now is the carbon dioxide gas escapes (in the form of bubbles) from the solution. Because the CO_2 escapes, this reaction ***keeps proceeding to the right***.

In other words, as soon as some carbonic acid (H_2CO_3) is formed, it decomposes into $CO_{2(g)}$ and water, and then the $CO_{2(g)}$ escapes into the air. Because the CO_2 escapes, the reverse reaction does not have a chance to take place.

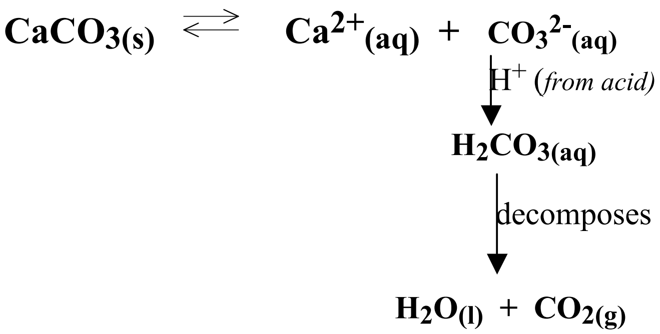
Now, recall the equilibrium:

$$\mathbf{CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}}$$

As was said there, something that would ***decrease*** the $[CO_3^{2-}]$ would shift this equilibrium to the ***right*** and dissolve more solid $CaCO_3$ (*increase* it's solubility).

Then we learned that by adding an ***acid*** (contributing H^+ ions), that the CO_3^{2-} is used up to make carbonic acid ($H_2CO_{3(aq)}$) which then decomposes to H_2O and $CO_{2(g)}$, which escapes into the air.

This can all be summarized by the following:



$$\mathbf{CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}}$$
$$CO_3^{2-}{}_{(aq)} \xrightarrow{H^+ \text{ (from acid)}} H_2CO_{3(aq)} \xrightarrow{\text{decomposes}} H_2O_{(l)} + CO_{2(g)}$$

So we have represented three reactions here. The ones going down the right side result in a ***decrease*** in $[CO_3^{2-}]$ in the first equilibrium (which is the one to really focus on here.)

Since the $[CO_3^{2-}]$ is decreased, the equilibrium will shift to the right, ***increasing*** the solubility of $CaCO_{3(s)}$.

$$\mathbf{CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}}$$

As a result, more $CaCO_{3(s)}$ dissolves and the $[Ca^{2+}]$ and $[CO_3^{2-}]$ goes up (to compensate for the decrease in $[CO_3^{2-}]$ caused by adding the acid.)

$$\mathbf{CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}}$$

As long as more acid is added, this process will continue until all the solid $CaCO_3$ has been dissolved.

It is important to realize here that this reaction is ***specific*** to compounds with the ***carbonate*** ion. Adding an acid may work with a few other ions like sulphite (SO_3^{2-}), but ***not*** all of them ! In Chem. 12, it is important to remember that:

Adding an acid to a low solubility compound with carbonate, will decrease the [CO_3^{2-}] and increase the solubility of the compound.

Increasing Solubility by Forming Another Precipitate

Remember, if we decrease the concentration of an ion in a solubility equilibrium, the equilibrium will shift ***right*** and *increase the solubility* of the solid:

For example, if in the following equilibrium, [Ag^+] is *decreased*, the equilibrium will shift ***right*** and some of the solid AgCl will dissolve:

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

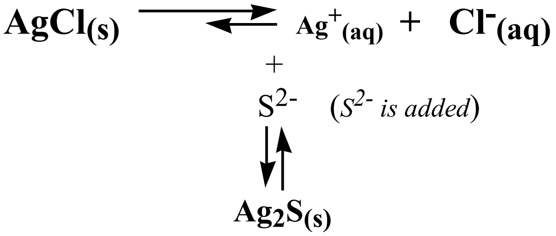
Well, now we will show you another way to decrease the concentration of a specific ion (like Ag^+).

What you can do is add something that will form a precipitate with Ag^+. This will decrease the [Ag^+] in the solution.

So what you are really doing is forming one precipitate to dissolve another one.

Firstly, it would be a mistake to add chloride ions (Cl^-), as this would just make this equilibrium shift ***left*** and *decrease* the solubility of AgCl. We are trying to do the opposite!

It is found that if you add sulphide (S^{2-}) ions to this solution, that the S^{2-} will form a precipitate with the silver (Ag^+) ions. This process can be represented by the following:



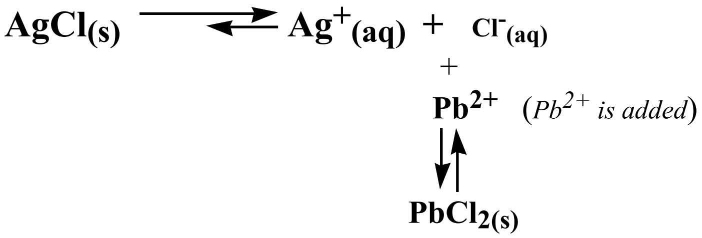
$$\begin{array}{ccccc} AgCl_{(s)} & \rightleftharpoons & Ag^+_{(aq)} & + & Cl^-_{(aq)} \\ & & + & & \\ & & S^{2-} & & (S^{2-}\text{ is added}) \\ & & \downarrow\uparrow & & \\ & & Ag_2S_{(s)} & & \end{array}$$

So basically, the Ag^+ ions are being "pulled" from the AgCl equilibrium to form the precipitate $Ag_2S_{(s)}$.

Of course, you can't just add sulphide (S^{2-}) ions by themselves. You would have to add a solution containing a soluble compound of sulphide. A soluble compound of sulphide is sodium sulphide ($Na_2S_{(aq)}$).

You could consult your "Solubility Table" to find an ion (other than $Ag^{+)}$ that would form a precipitate with Cl^-. Our table says that Pb^{2+} ions precipitate Cl^- ions.

So you could add a solution of a compound containing Pb^{2+} (eg. $Pb(NO_3)_{2(aq)}$) to the container with the AgCl.



$$\begin{array}{ccccc} AgCl_{(s)} & \rightleftharpoons & Ag^{+}_{(aq)} & + & Cl^{-}_{(aq)} \\ &&&& + \\ &&&& Pb^{2+} \quad (\mathit{Pb^{2+}\ is\ added}) \\ &&&& \downarrow\uparrow \\ &&&& PbCl_{2(s)} \end{array}$$

Now the Pb^{2+} ions react with the Cl^- ions from the AgCl equilibrium, forming a new precipitate ($PbCl_{2(s)}$) and ***decreasing*** the $[Cl^-]$ in the solution. Doing this causes the AgCl equilibrium to shift to the ***right***, thus *dissolving* the $AgCl_{(s)}$.

You can always use your solubility table to find a compound that will precipitate a certain ion from solution. Remember, the table gives you just ions.

For any ***positive ion*** that is needed, putting the negative ion ***nitrate*** (NO_3^-) with it is always a safe bet as NO_3^- will not form any unwanted precipitates and compound with NO_3^- are all soluble, so they will be readily break up to supply the ions you want.

For any negative ion that you need, it is safe to use the sodium (Na^+) or potassium (K^+) salt of the ion, since these would always be soluble and Na^+ or K^+ will not form any unwanted precipitates.

To quickly summarize what we have shown on Tutorial 7:

1. The solubility of a compound is **decreased** when an ion which is the same as one of the ions in the compound (***common ion***) is present or added.

2. The solubility of compounds containing the **carbonate** (CO_3^{2-}) ion can be **increased** by adding an **acid**. The H^+ ions from the acid react with the carbonate (CO_3^{2-}) forming carbonic acid $H_2CO_{3(aq)}$) which decomposes into water and $CO_{2(g)}$. In this way the $[CO_3^{2-}]$ is decreased in the solubility equilibrium for the original compound, the equilibrium shifts toward the side with the ions, and the solid dissolves more.

3. The solubility of a compound can be **increased** by adding a solution that will form a precipitate with one of the ions in the compound. This will decrease the concentration of that ion, causing the equilibrium to shift to the ion side and dissolve the solid.