

In Tutorial 13, 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 <u>shift</u> 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. $CaCO_{3(s)}$:

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

Let's say we have a saturated solution of calcium carbonate (CaCO₃). What this means is that we would have some solid CaCO₃ sitting on the bottom of the solution and there would be some Ca²⁺ ions and some CO_3^{2-} ions dissolved in the solution. (See the next page...)



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 (CaCb) to the beaker. Calcium chloride is considered <u>soluble</u>, so we can assume that it <u>all dissociates</u> into Ca²⁺ 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 Ct 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 CaCO₃! So what in the world will happen now?



Since there were no Ct 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:

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

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>:

$$CaCO_{3(s)} \longrightarrow Ca^{2+}(aq) + CO_{3^{2-}(aq)}$$

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



Since this results in more solid CaCO₃ in the beaker, we can say that:

Adding Ca^{2+} ions to the solution <u>decreases the solubility</u> 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 <u>the same as</u> (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 CaCO₃.

Now, it's time for you to make some predictions:

1. Predict which compounds would <u>decrease</u> the solubility of $CaCO_{3(s)}$ if added to a saturated solution. For each compound that does, state **why** it does.

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

Added		Effect on Solubility of		
compound	Ions	CaCO _{3(s)}	Reason for effect	
Ca(NO ₃) ₂				
KNO3				
K ₂ CO ₃				
CaCO ₃				

Check page 1 of Tutorial 13 - Solutions for the answers.

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:

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

If we could somehow <u>*decrease*</u> 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.

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The *carbonate* (CO_3^{2-}) ion happens to be easy to decrease. All we have to do is add some <u>acid</u> 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:

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

Now, focus your attention just on the carbonate:

CO₃²⁻(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:

 $2H^+_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow H_2CO_3_{(aq)}$



Now, it so happens that *carbonic acid* (H_2CO_3) is *unstable* 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 :

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

See the diagram on the next page.....



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 on the top of page 5:

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}(aq) + CO3^{2-}(aq)$$

As was said there, something that would <u>*decrease*</u> the $[CO_3^{2-}]$ would shift this equilibrium to the <u>*right*</u> and dissolve more solid CaCO₃ (<u>*increase*</u> it's solubility).

Then we learned that by adding an <u>acid</u> (contributing H⁺ ions), that the CO_3^{2-} is used up to make carbonic acid (H₂CO_{3(aq)}) which then decomposes to H₂O and CO_{2(g)}, which escapes into the air.

This can all be summarized by the following:

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

$$H^{+}(from acid)$$

$$H_{2}CO_{3(aq)}$$

$$decomposes$$

$$H_{2}O_{(l)} + CO_{2(g)}$$

?

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 <u>right</u>, *increasing* the solubility of $CaCO_{3(s)}$.

$$CaCO_{3(s)} \longrightarrow Ca^{2+}(aq) + CO_{3}^{2-}(aq)$$

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.)

$$c_{aCO_{3(s)}} \longrightarrow Ca^{2+}(aq) + CO_{3^{2-}(aq)}$$

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

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

Now, here's a question:

Some buildings and statues are made of marble, which is mainly *calcium carbonate* (CaCO₃).
 Using the concepts in this tutorial, explain how <u>acid rain</u> can damage these structures.

Check page 2 of Tutorial 13 - Solutions for the answers.

Increasing Solubility by Forming Another Precipitate

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

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

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

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 <u>left</u> and <u>decrease</u> 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:

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

$$+ S^{2-} (S^{2-} is added)$$

$$\downarrow Ag_2S(s)$$

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 (S²⁻) 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.

AgCl_(s)
$$Ag^+(aq) + Cl^-(aq)$$

+ $Pb^{2+} (Pb^{2+} is added)$
 $\downarrow \land$
 $PbCl_{2(s)}$

Now the Pb²⁺ ions react with the Cl⁺ ions from the AgCl equilibrium, forming a new precipitate (PbCb_{2(s)}) and <u>*decreasing*</u> the [Cl⁺] in the solution. Doing this causes the AgCl equilibrium to shift to the <u>*right*</u>, thus <u>*dissolving*</u> 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 <u>positive ion</u> that is needed, putting the negative ion <u>nitrate</u> (NO₃⁻) with it is always a safe bet as NO₃⁻ will not form any unwanted precipitates and compound with NO₃⁻ 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.

Okay, get out your solubility table and try the following question:

3. Suggest two different compounds which could be added to a saturated solution of calcium hydroxide $(Ca(OH)_{2(s)})$ in order to **increase** it's solubility. Show with **equilibrium equations** how each one works.

(There is more room on the next page)

Check page 3 of Tutorial 13 - Solutions for the answers.

To quickly summarize what we have shown on Tutorial 13:

- 1. The solubility of a compound is **<u>decreased</u>** 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 <u>carbonate</u> (CO_3^{2-}) ion can be <u>increased</u> by adding an <u>acid</u>. 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.

Read through this tutorial again, and you should be ready for the Self-Test. Make sure you have your periodic table and solubility table with you!

Self-Test on Tutorial 13

1. The following table shows some compounds with low solubility in the left column. In column 2, a solution (reagent) is added. In column 3, indicate whether the solubility of the compound on the left will be increased, decreased or not affected. In column 4 give a brief explanation for your answer. You don't need to include equilibrium equations in your explanations in this case.

Low Solubility	Added Reagent	Effect on Solubility of Compound in	
Compound		Column 1	Explanation for Effect
SrSO ₄	Ba(NO ₃) _{2(aq)}		
Ag ₂ S	AgNO _{3(aq)}		
SrCO ₃	HNO _{3(aq)} (nitric acid)		
AgBr	Pb(NO ₃) _{2(aq)}		
PbCb	KCl _(aq)		
Be(OH) ₂	NaCl _(aq)		
PbCO ₃	HCl _(aq)		
CuI	CaI _{2(aq)}		
Ag ₂ CO ₃	Na ₂ S _(aq)		
Ca ₃ (PO ₄) ₂	K ₂ SO _{4(aq)}		

2. Given that natural rainwater is slightly acidic, explain why rain will slowly dissolve limestone $(CaCO_{3(s)})$ over a period of time. Give a full explanation including relevant equilibrium equations.

3. Silver sulphate is a white precipitate with low solubility. When a solution of ammonium sulphide $((NH_4)_2S_{(aq)})$ is added, the white precipitate slowly dissolves and a black precipitate forms on the bottom. Using **equilibrium equations** and clear explanations, indicate what happened here.

4. Name two compounds (not just ions) that can *decrease* the solubility of $BaSO_{4(s)}$ and explain <u>why</u> each one of them works

5. Name a substance (not just an ion) which could *increase* the solubility of BeCO_{3(s)}. Explain why this substance works.

6. Briefly explain what is meant by the *common ion effect*.

Check the answers to the Self-Test starting on page 5 of Tutorial 13 - Solutions

Tutorial 13 - The Common Ion Effect and Altering Solubility