Tutorial 13

The Common Ion Effect and Altering Solubility

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 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):

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)
\]

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. (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 (CaCl\(_2\)) to the beaker. Calcium chloride is considered \textit{soluble}, so we can assume that it \textit{all dissociates} into Ca\(^{2+}\) and Cl\(^-\) ions: (Notice the single arrow!)

\[ \text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq) \]

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:

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)
\]

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 LEFT:

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)
\]

What this will do is increase the amount of CaCO$_3(s)$ and decrease the concentration of CO$_3^{2-}$.

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

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)
\]

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 CaCO₃.

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

1. Predict which compounds would **decrease** the solubility of CaCO₃ if added to a saturated solution. For each compound that does, state **why** it does.

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)
\]

<table>
<thead>
<tr>
<th>Added compound</th>
<th>Ions</th>
<th>Effect on Solubility of CaCO₃(s)</th>
<th>Reason for effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(NO₃)₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KNO₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂CO₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO₃</td>
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<td></td>
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</tbody>
</table>

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

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**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:

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)
\]

If we could somehow **decrease** either [Ca²⁺] or [CO₃²⁻], 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 \((\text{CO}_3^{2-})\) 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 \([\text{CO}_3^{2-}]\) in this equilibrium:

\[
\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})
\]

Now, focus your attention just on the carbonate:

\(\text{CO}_3^{2-}(\text{aq})\)

As you might know, when you put an acid into water, hydrogen ions \((\text{H}^+)\) are formed.

\(\text{eg. } \text{HCl}_\text{(g)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})\)

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

\[
2\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})
\]

Now, it so happens that carbonic acid \((\text{H}_2\text{CO}_3)\) is unstable in water solution. Carbonic acid is actually what is present in carbonated beverages (like pop).

In water solution, carbonic acid \((\text{H}_2\text{CO}_3)\) decomposes to form carbon dioxide gas \((\text{CO}_2(\text{g}))\) and liquid water:

\[
\text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{H}_2\text{O} (\text{l}) + \text{CO}_2 (\text{g})
\]

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 CO₂ escapes, this reaction keeps proceeding to the right.

In other words, as soon as some carbonic acid (H₂CO₃) is formed, it decomposes into CO₂(g) and water, and then the CO₂(g) escapes into the air. Because the CO₂ escapes, the reverse reaction does not have a chance to take place.

Now, recall the equilibrium on the top of page 5:

\[
CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)
\]

As was said there, something that would decrease the [CO₃²⁻] would shift this equilibrium to the right and dissolve more solid CaCO₃ (increase its solubility).

Then we learned that by adding an acid (contributing H⁺ ions), that the CO₃²⁻ is used up to make carbonic acid (H₂CO₃(aq)) which then decomposes to H₂O and CO₂(g), which escapes into the air.

This can all be summarized by the following:

\[
CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \quad H^+ (from \text{ acid})
\]

\[
H_2CO_3(aq) \quad \text{decomposes}
\]

\[
H_2O(l) + CO_2(g)
\]

So we have represented three reactions here. The ones going down the right side result in a decrease in [CO₃²⁻] in the first equilibrium (which is the one to really focus on here.)
Since the $[\text{CO}_3^{2-}]$ is decreased, the equilibrium will shift to the right, increasing the solubility of CaCO$_3$(s):

$$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$$

As a result, more CaCO$_3$(s) dissolves and the $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ goes up (to compensate for the decrease in $[\text{CO}_3^{2-}]$ caused by adding the acid.)

$$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$$

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 $[\text{CO}_3^{2-}]$ and increase the solubility of the compound.

Now, here’s a question:

2. Some buildings and statues are made of marble, which is mainly calcium carbonate (CaCO$_3$). Using the concepts in this tutorial, explain how acid rain can damage these structures.

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

\[
\text{AgCl}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq)
\]

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 (S²⁻) ions to this solution, that the S²⁻ will form a precipitate with the silver (Ag⁺) ions. This process can be represented by the following:

\[
\text{AgCl}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) + \text{S}^{2-} (S^{2-} \text{is added}) \quad \text{Ag}_2\text{S}(s)
\]

So basically, the Ag⁺ ions are being “pulled” from the AgCl equilibrium to form the precipitate Ag₂S(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 (Na₂S(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 Pb²⁺ ions precipitate Cl⁻ ions.
So you could add a solution of a compound containing Pb\(^{2+}\) (eg. Pb(NO\(_3\))\(_2\)\(\text{aq}\)) to the container with the AgCl.

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) + \text{Pb}^{2+} \quad (\text{Pb}^{2+} \text{ is added}) \\
\downarrow \\
\text{PbCl}_2(s)
\]

Now the Pb\(^{2+}\) ions react with the Cl\(^{-}\) ions from the AgCl equilibrium, forming a new precipitate (PbCl\(_2\)) and decreasing the [Cl\(^{-}\)] in the solution. Doing this causes the AgCl equilibrium to shift to the right, thus dissolving the AgCl\(_{\text{s}}\).

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.

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.

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To quickly summarize what we have shown on Tutorial 13:

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$_2$CO$_3$(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!

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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.

<table>
<thead>
<tr>
<th>Low Solubility Compound</th>
<th>Added Reagent</th>
<th>Effect on Solubility of Compound in Column 1</th>
<th>Explanation for Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrSO₄</td>
<td>Ba(NO₃)₂(aq)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag₂S</td>
<td>AgNO₃(aq)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrCO₃</td>
<td>HNO₃(aq)</td>
<td></td>
<td>(nitric acid)</td>
</tr>
<tr>
<td>AgBr</td>
<td>Pb(NO₃)₂(aq)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbCl₂</td>
<td>KCl(aq)</td>
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</tr>
<tr>
<td>Be(OH)₂</td>
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</tr>
<tr>
<td>PbCO₃</td>
<td>HCl(aq)</td>
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<td></td>
</tr>
<tr>
<td>CuI</td>
<td>CaI₂(aq)</td>
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<td></td>
</tr>
<tr>
<td>Ag₂CO₃</td>
<td>Na₂S(aq)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>K₂SO₄(aq)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2. Given that natural rainwater is slightly acidic, explain why rain will slowly dissolve limestone (CaCO$_3$) 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$_4$)$_2$S$_{(aq)}$) 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$_4$ and explain why each one of them works.

5. Name a substance (not just an ion) which could increase the solubility of BeCO$_3$. 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