Tutorial 13
Solutions
The Common Ion Effect and Altering Solubility

Answer to Question 1 on page 4 of Tutorial 13.

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

Refer to the following equilibrium when reading the "Reason for Effect" below:

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

Added compound	Ions		Effect on Solubility of $CaCO_{3(s)}$	Reason for effect
$Ca(NO_3)_2$	**Ca^{2+}**	**NO_3^-**	**Decrease**	**The Ca^{2+} is a common ion. Increasing the $[Ca^{2+}]$ causes the above equilibrium to shift left and decrease the solubility of $CaCO_{3(s)}$**
KNO_3	**K^+**	**NO_3^-**	**No Effect**	**Neither K^+ nor NO_3^- are common ions to the $CaCO_{3(s)}$. Neither will have an effect on the above equilibrium.**
K_2CO_3	**K^+**	**CO_3^{2-}**	**Decrease**	**The CO_3^{2-} is a common ion. Increasing the $[CO_3^{2-}]$ causes the above equilibrium to shift left and decrease the solubility of $CaCO_{3(s)}$**
$CaCO_3$	**Ca^{2+}**	**CO_3^{2-}**	**No Effect**	**Adding more of the <u>same</u> compound will have no effect on how much will dissolve. The increased surface area may have an effect on the <u>rate</u> of reaching equilibrium, but the solubility is fixed by the K_{sp} and the temperature.**

Answer to Question 2 on page 7 of Tutorial 13.

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.

Answer:

When rain hits the marble ($CaCO_3$) surface, a very small amount of the $CaCO_3$ dissolves, forming Ca^{2+} ions and CO_3^- ions and an equilibrium is established.

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

Acid rain, like any acid solution releases hydrogen (H^+) ions.

Hydrogen (H^+) ions react with carbonate (CO_3^{2-}) ions from this equilibrium, to form a solution of carbonic acid (H_2CO_3). The carbonic acid, being unstable in water solution, decomposes into water (H_2O) and carbon dioxide (CO_2):

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

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

This process decreases the $[CO_3^{2-}]$ in the original equilibrium. This, in turn causes the equilibrium to shift to the right and dissolve the solid calcium carbonate. As this happens, the statues or buildings are disfigured.

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<u>Answer to Question 3 on page 9 of Tutorial 13.</u>

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.

First, write the equilibrium equation for the dissociation of $Ca(OH)_2$.

$$Ca(OH)_{2(s)} \rightleftarrows Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

So first we could add an ion (other than OH^-) that forms a precipitate with Ca^{2+}. Looking at the solubility table, such ions could include sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), or sulphite (SO_3^{2-}).

So compounds that could be added would include any of the sodium or potassium salts of any of these ions: eg. Na_2SO_4 , Na_3PO_4 , Na_2CO_3 , Na_2SO_3 etc.

IMPORTANT NOTE: When you are writing the formula for a compound containing an ion you want to use, be really, really, <u>really</u> sure that you write the <u>*correct*</u> formula for it! Take the time necessary to look up the charges. This is a Grade 9 level skill and it looks really bad when Chemistry 12 students don't write the correct formula for a compound. I have sadly had to take marks off on tests when a student writes something like "$NaCO_3$" for a compound rather than the correct Na_2CO_3.

To explain why one of these compounds does increase the solubility of $Ca(OH)_2$ use the following example (assuming that Na_2SO_4 (SO_4^{2-}) was chosen).
(*The answer would also be correct if any of the other correct answers are substituted, eg. Na_3PO_4 etc.*)

$$Ca(OH)_{2(s)} \rightleftarrows Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

$$\downarrow +$$

SO_4^{2-} (*SO_4^{2-} ions are added*)

$$\downarrow\uparrow$$

$$CaSO_{4(s)}$$

The added sulphate (SO_4^{2-}) ions precipitate with the calcium (Ca^{2+}) ions to form solid $CaSO_4$. This <u>decreases</u> the [Ca^{2+}] in solution, causing the $Ca(OH)_2$ equilibrium to shift to the <u>right</u>, thus increasing the amount of $Ca(OH)_2$ that dissolves.

Looking at the equilibrium equation again:

$$Ca(OH)_{2(s)} \rightleftarrows Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

If we add something that forms a precipitate with hydroxide (OH^-) ions (other than Ca^{2+}), then we can decrease [OH^-] , shifting this equilibrium to the <u>right</u> and dissolving the solid $Ca(OH)_2$.

Looking at the solubility table, the following positive ions will form a precipitate with OH^- ions:

(anything <u>BUT</u> alkali ions, H^+, NH_4^+, or Sr^{2+}).

Some common positive ions that are <u>not</u> in this group are Be^{2+}, Mg^{2+}, Ag^+, Pb^{2+}, Fe^{2+} etc. etc.

It is best to use nitrate compounds of these, so some compounds that are correct could include $Be(NO_3)_2$, $Mg(NO_3)_2$, $AgNO_3$, $Pb(NO_3)_2$, $Fe(NO_3)_2$ etc.

If you chose $AgNO_3$ (Ag^+), the explanation could be like the following: (*Remember that any of the other answers, and many other possible ones could be substituted here. If you have a answer and you don't know whether it is correct, ask the teacher or another student!***)**

$$Ca(OH)_{2(s)} \rightleftarrows Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

$$\downarrow +$$

Ag^+ (*Ag^+ ions are added*)

$$\downarrow\uparrow$$

$$AgOH_{(s)}$$

(*Don't worry about the '2" on the OH^- here. We're just looking at WHAT reacts, not how much.*)

The added silver (Ag^+) ions precipitate with the hydroxide (OH^-) ions to form solid AgOH . This <u>decreases</u> the $[OH^-]$ in solution, causing the $Ca(OH)_2$ equilibrium to shift to the <u>right</u>, thus increasing the amount of $Ca(OH)_2$ that dissolves.

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<u>Answers to Self-Test starting on page 11 of Tutorial 13</u>

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 Compound	*Added Reagent*	*Effect on Solubility of Compound in Column 1*	*Explanation for Effect*
$SrSO_4$	$Ba(NO_3)_{2(aq)}$	increase	The Ba^{2+} from the barium nitrate will precipitate the SO_4^{2-} ion from the $SrSO_4$ equilibrium, forming $BaSO_4$. Decreasing the $[SO_4^{2-}]$ will cause the $SrSO_4$ equilibrium to shift to the ion side, thus dissolving the solid.
Ag_2S	$AgNO_{3(aq)}$	decrease	The Ag^+ ion from the silver nitrate is a common ion to the Ag^+ from the Ag_2S equilibrium. The increased $[Ag^+]$ causes the Ag_2S equilibrium to shift toward the solid side and decrease the solubility of Ag_2S
$SrCO_3$	$HNO_{3(aq)}$ *(nitric acid)*	increase	The H^+ ions from the acid react with the carbonate (CO_3^{2-}) ions from the $SrCO_3$ equilibrium, forming carbonic acid (H_2CO_3). The carbonic acid decomposes into carbon dioxide and water. The decreased $[CO_3^{2-}]$ in the $SrCO_3$ equilibrium causes a shift toward the ion side, thus increasing the solubility of $SrCO_3$.
AgBr	$Pb(NO_3)_{2(aq)}$	increase	The Pb^{2+} from the lead nitrate will precipitate the Br^- ion from the AgBr equilibrium, forming $PbBr_2$. Decreasing the $[Br^-]$ will cause the AgBr equilibrium to shift to the ion side, thus dissolving the solid.

$PbCl_2$	$KCl_{(aq)}$	decrease	The Cl^- ion from the potassium chloride is a common ion to the Cl^- from the $PbCl_2$ equilibrium. The increased [Cl^-] causes the $PbCl_2$ equilibrium to shift toward the solid side and decrease the solubility of $PbCl_2$
$Be(OH)_2$	$NaCl_{(aq)}$	no effect	The NaCl has no common ions to the $Be(OH)_2$ and neither the Na^+ nor the Cl^- forms any precipitates with either of the ions from $Be(OH)_2$.
$PbCO_3$	$HCl_{(aq)}$	increase	The H^+ ions from the acid react with the carbonate (CO_3^{2-}) ions from the $PbCO_3$ equilibrium, forming carbonic acid (H_2CO_3). The carbonic acid decomposes into carbon dioxide and water. The decreased [CO_3^{2-}] in the $PbCO_3$ equilibrium causes a shift toward the ion side, thus increasing the solubility of $PbCO_3$. -or- The Cl^- from the HCl will precipitate the Pb^{2+} ion from the $PbCO_3$ equilibrium, forming $PbCl_2$. Decreasing the [Pb^{2+}] will cause the $PbCO_3$ equilibrium to shift to the ion side, thus dissolving the solid.

CuI	$CaI_{2(aq)}$	decrease	The I^- ion from the calcium iodide is a common ion to the I^- from the CuI equilibrium. The increased [I^-] causes the CuI equilibrium to shift toward the solid side and decrease the solubility of CuI.
Ag_2CO_3	$Na_2S_{(aq)}$	increase	The S^{2-} from the Na_2S will precipitate the Ag^+ ion from the Ag_2CO_3 equilibrium, forming Ag_2S. Decreasing the [Ag^+] will cause the Ag_2CO_3 equilibrium to shift to the ion side, thus dissolving the solid.
$Ca_3(PO_4)_2$	$K_2SO_{4(aq)}$	increase	The SO_4^{2-} from the K_2SO_4 will precipitate the Ca^{2+} ion from the $Ca_3(PO_4)_2$ equilibrium, forming $CaSO_4$. Decreasing the [Ca^{2+}] will cause the $Ca_3(PO_4)_2$ equilibrium to shift to the ion side, thus dissolving the solid.

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.

In any water, $CaCO_3$ dissolves a slight amount, releasing Ca^{2+} ions and CO_3^{2-} ions into the solution and establishing an equilibrium:

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

Because natural rainwater is slightly acidic, it releases some H^+ ions. These H^+ ions combine with the CO_3^{2-} ions in the $CaCO_3$ equilibrium.

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

$$CO_3{}^{2-}{}_{(aq)} \xrightarrow{H^+ \textit{(from acid)}} H_2CO_{3(aq)} \xrightarrow{\textit{(decomposes)}} H_2O_{(l)} + CO_{2(g)}$$

As shown above, the H^+ ions combine with CO_3^{2-} ions to form carbonic acid (H_2CO_3), which decomposes to water and carbon dioxide.

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

After a long time, a large amount of $CaCO_3$ (limestone) will be dissolved.

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.

The equilibrium equation for the white precipitate (silver sulphate) is:

$$\mathbf{Ag_2SO_{4(s)} \rightleftarrows 2Ag^+_{(aq)} + SO_4{}^{2-}_{(aq)}}$$

Ammonium sulphide $(NH_4)_2S$) is a highly soluble compound which releases ammonium ($NH_4{}^+$) ions and sulphide (S^{2-}) ions to the solution. $NH_4{}^+$ ions are spectators in this case.

If you check the solubility table, you will see that sulphide (S^{2-}) will precipitate with silver (Ag^+) ions in the solution, forming the black precipitate silver sulphide ($Ag_2S_{(s)}$).

This will cause a decrease in the [Ag^+], shifting the above equilibrium to the right, causing the white $Ag_2SO_{4(s)}$ to dissolve.

$$\mathbf{Ag_2SO_{4(s)} \rightleftarrows 2Ag^+_{(aq)} + SO_4{}^{2-}_{(aq)}}$$

$$\downarrow$$

$$+$$

$$\mathbf{S^{2-}} \ (\textit{S}^{2-} \textit{ ions are added})$$

$$\downarrow\uparrow$$

$$\mathbf{Ag_2S_{(s)}}$$

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

Any compound that contains either Ba^{2+} ions or SO_4^{2-} ions (other than $BaSO_4$) would work.

Examples could be barium nitrate ($Ba(NO_3)_2$) or sodium sulphate (Na_2SO_4).

Looking at the equilibrium equation for $BaSO_4$ dissolving:

$$BaSO_{4(s)} \rightleftarrows Ba^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)}$$

Increasing either $[Ba^{2+}]$ or $[SO_4^{2-}]$ will cause the equilibrium to shift left and form more solid $BaSO_4$. (Thus decreasing it's solubility.)

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

The solubility equilibrium for $BeCO_3$ is:

$$BeCO_{3\,(s)} \rightleftarrows Be^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)}$$

Adding any substance which will decrease either $[Be^{2+}]$ or $[CO_3^{2-}]$ will shift this equilibrium to the right and increase the solubility of $BeCO_3$.

One way would be to find a solution which would form another precipitate with one of these ions.

Looking at the solubility table, the following ions could form a precipitate with Be^{2+} ions: OH^- , PO_4^{3-} or SO_3^{2-} . (Notice that we can't use carbonate. I hope you can see why not!)

So 3 suitable compounds could be: NaOH, Na_3PO_4 or Na_2SO_3.

As an example, the OH^- ions from NaOH would precipitate with the Be^{2+} ions in the $BeCO_3$ equilibrium, forming $Be(OH)_{2(s)}$ and decreasing the $[Be^{2+}]$. This shifts the equilibrium to the right, increasing the solubility of $Be(OH)_{2(s)}$.

There are <u>two ways</u> we could decrease the $[CO_3^{2-}]$:

One way would be to add an <u>acid</u> (eg. HCl, H_2SO_4, HNO_3). As we have found before, adding an acid to an equilibrium with carbonate (CO_3^{2-}) ions will donate H^+ ions which will join the carbonate to form carbonic acid, which will then decompose to give carbon dioxide and water:

$$* \quad BeCO_{3\,(s)} \rightleftharpoons Be^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)}$$

$$CO_3{}^{2-}_{(aq)} \xrightarrow{H^+ \ (\textit{from acid})} H_2CO_{3(aq)} \xrightarrow{(\textit{decomposes})} H_2O_{(l)} + CO_{2(g)}$$

As shown above, the H^+ ions combine with CO_3^{2-} ions to form carbonic acid (H_2CO_3), which decomposes to water and carbon dioxide.

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

Another way to decrease the $[CO_3^{2-}]$ is to add a compound with an ion which would form <u>another precipitate</u> with it.

Checking the solubility table, some ions that precipitate with <u>carbonate</u> are any ions <u>other than</u> alkali, NH_4^+ , or H^+ ions. So there are many possibilities.

They could include Ag^+ , Pb^{2+} , Cu^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} and many others.

Some possible compounds containing these ions could be:

$AgNO_3$, $Pb(NO_3)_2$, $CuNO_3$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Mg(NO_3)_2$

As an example, the Ag^+ ions from $AgNO_3$ would precipitate with the CO_3^{2-} ions in the $BeCO_3$ equilibrium, forming $Ag_2CO_{3(s)}$ and decreasing the $[CO_3^{2-}]$. This shifts the equilibrium to the right, <u>increasing</u> the solubility of $Be(OH)_{2(s)}$.

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

   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 <u>ion in common</u>) will <u>decrease</u> the solubility of the compound with low solubility.

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