> ## Chemistry 12
> ## Tutorial 11
> ## Predicting Precipitates and
> ## Maximum Ion Concentration

In Tutorial 11 you will be shown:

1. How to tell if a precipitate will form when two solutions of known concentration are mixed.

2. How to tell if a precipitate will form when a given mass of a solid is added to a solution.

3. How to calculate the maximum possible concentration of an ion in solution, given the concentration of another ion and the Ksp .

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Predicting Precipitates When Two Solutions Are Mixed

Your solubility table tells you when precipitates form, right? NOT ALWAYS! It tells you which combinations of ions have a solubility of > 0.1 mol/Litre! (*See bottom of the solubility table*.)

That is, if the table, for example predicts a precipitate between Ca^{2+} ions and SO_4^{2-} ions, if we mix Ca^{2+} ions and SO_4^{2-} ions ***in low enough concentrations***, a precipitate might not form.

The quantity which determines the concentrations of ions allowed before a precipitate will form is the good old Ksp !

Let's look at an example:

The Ksp for $CaCO_3$ is 5.0×10^{-9} . The expression for Ksp of $CaCO_3$ is:

$$Ksp = [Ca^{2+}] [CO_3^{2-}]$$

This means, that in a ***saturated*** solution (just on the verge of precipitating), that

$$5.0 \times 10^{-9} = [Ca^{2+}] [CO_3^{2-}]$$

The 5.0×10^{-9} is the ***most*** the product of the concentrations of these two ions can be. If we put any more Ca^{2+} or CO_3^{2-} in at this point, *the solution can't hold any more*, and a ***precipitate*** will form.

In this Tutorial, we will be looking at adding the two ions, Ca^{2+} and CO_3^{2-} from *different* sources.

In other words, we will mix one solution containing Ca^{2+} with another solution containing CO_3^{2-}.

There's nothing that says the $[Ca^{2+}]$ has to equal the $[CO_3^{2-}]$!

All we know is that if the product, $[Ca^{2+}]$ $[CO_3^{2-}]$, becomes $> 5.0 \times 10^{-9}$, a precipitate **_will_** form.

Example:

   We mix solutions of Ca^{2+} and CO_3^{2-}, so that $[Ca^{2+}] = 2.3 \times 10^{-4}$ M and the $[CO_3^{2-}] = 8.8 \times 10^{-2}$ M. The Ksp for $CaCO_3$ is 5.0×10^{-9}. Will a precipitate form?

What we calculate at this time is called a "trial ion product (TIP)" or "trial Ksp". We substitute the values of $[Ca^{2+}]$ and $[CO_3^{2-}]$ into the Ksp expression:

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

$$\text{Trial Ksp} = [Ca^{2+}] \quad [CO_3^{2-}]$$

$$\text{Trial Ksp} = (2.3 \times 10^{-4}) \; (8.8 \times 10^{-2})$$

$$\text{Trial Ksp} = 2.024 \times 10^{-5}$$

Now we compare the Trial Ksp with the real value for Ksp:

$$\text{Trial Ksp} = 2.024 \times 10^{-5}$$

$$\text{The real Ksp} = 5.0 \times 10^{-9}$$

Since 10^{-5} is greater than 10^{-9}, the Trial Ksp $>$ Ksp

Now, the Ksp (5.0×10^{-9}) told us the maximum the product could be without precipitating.

In this case the product of the ion concentrations (2.024×10^{-5}) would be much greater than the Ksp (5.0×10^{-9})

The solution can't hold this many ions, so the excess ones will precipitate.

So, to summarize:

When $\text{Trial Ksp} > \text{Ksp}$, a precipitate <u>will</u> form.


When $\text{Trial Ksp} < \text{Ksp}$, a precipitate <u>will NOT</u> form.

Now, when two solutions are mixed together the following things happen:

1. In the mixture you have <u>4 different ions</u> immediately after the solutions mix. Some of these ions might form a compound with *low solubility*. That is, they might form a *<u>precipitate</u>*.

2. Both solutions become *diluted* in each other. The volume of the mixture is the sum of the volumes of the two separate solutions.

Let's do an example to show you how all this can be worked out:

50.0 mL of 0.0035 M $Ca(NO_3)_2$ solution is mixed with 150 mL of 2.0 x 10^{-5} M Na_2CO_3 solution. Will a precipitate form?
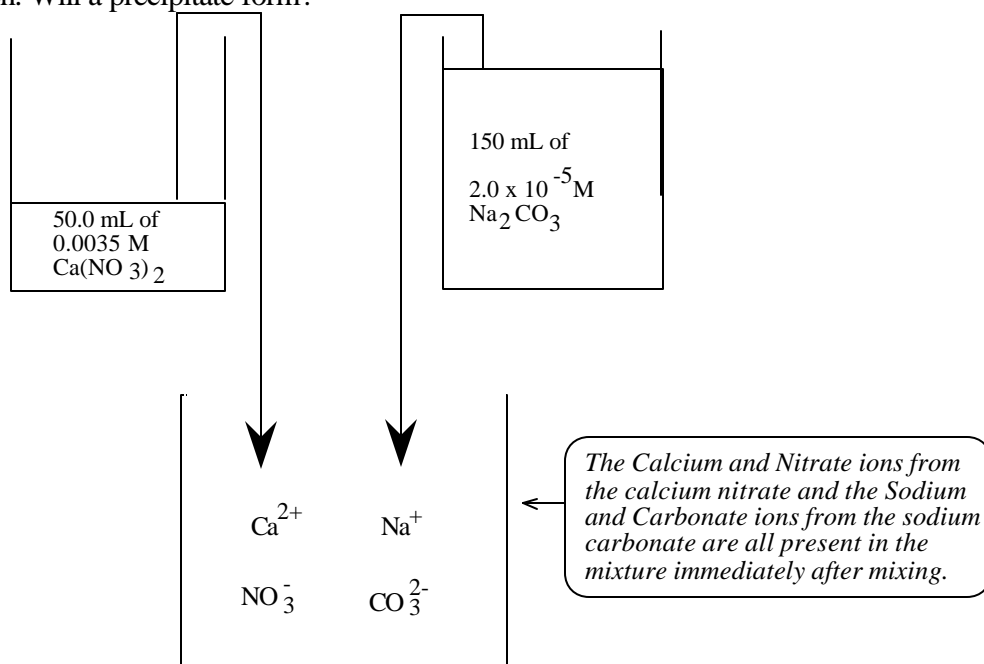

The first thing to do here is to consider the four ions which will be in the mixture immediately after mixing. *<u>Don't forget to look these up on the ion chart to make sure you have the correct formulas and charges!</u>* In this case, the ions appear in the bottom beaker on the diagram above.

Now, consider the possible new combinations of these ions:

$$Ca^{2+} \quad Na^{+}$$
$$\times$$
$$NO_3^{-} \quad CO_3^{2-}$$
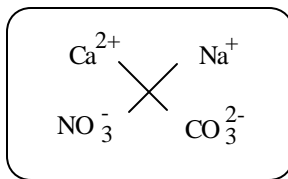
The new combinations could give $CaCO_3$ or $NaNO_3$. Looking on the Solubility Table, we find that $NaNO_3$ is *soluble*, so it will **_not_** form a precipitate.

$$Ca^{2+} \quad Na^{+}$$
$$\times$$
$$NO_3^{-} \quad CO_3^{2-}$$
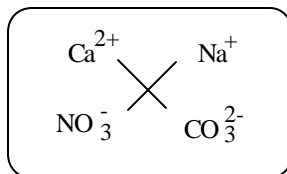
According to the Solubility Table, the other compound $CaCO_3$ has *Low Solubility.*

This means that it *might* form a precipitate if the $[Ca^{2+}]$ and the $[CO_3^{2-}]$ are high enough.

The net-ionic equation for dissolving of $CaCO_{3(s)}$ is:

$$CaCO_{3(s)} \rightleftarrows Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)}$$
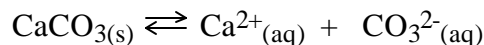
This means that the Ksp expression for $CaCO_3$ is the following:

$$Ksp = [Ca^{2+}] \ [CO_3^{2-}]$$

Look up the Ksp for $CaCO_3$ on the Ksp table. The Ksp tells us that the product of the $[Ca^{2+}]$ and the $[CO_3^{2-}]$ cannot be greater than 5.0×10^{-9}.

If that product is *greater than* 5.0×10^{-9} the moment the solutions are mixed, the Ca^{2+} ions and the CO_3^{2-} ions will very quickly react with each other to form the precipitate $CaCO_{3(s)}$. In other words, a *precipitate* will form. This will continue to happen until the product of $[Ca^{2+}]$ and $[CO_3^{2-}]$ is again equal to 5.0×10^{-9}.
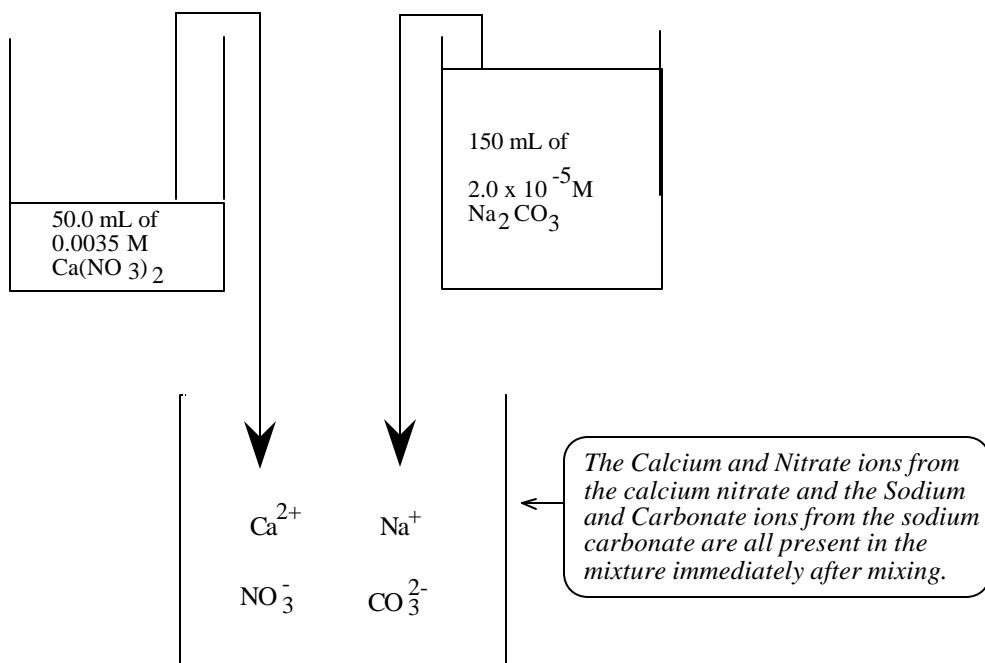
If the product of $[Ca^{2+}]$ and $[CO_3^{2-}]$ is *less than* 5.0×10^{-9} the moment the solutions are mixed, they will *not* react with each other and a precipitate will *NOT* form.

The product of $[Ca^{2+}]$ and $[CO_3^{2-}]$ *the moment the solutions are mixed*, is called the

Trial Ksp (or the Trial Ion Product (TIP))

The Trial K_{sp} would have the same expression as the real K_{sp} , only we would use the $[Ca^{2+}]$ and the $[CO_3{}^{2-}]$ that were in the beaker right after mixing:

$$\text{Trial } K_{sp} = \quad [Ca^{2+}] \ [CO_3{}^{2-}]$$

(Right after mixing)

50.0 mL of
0.0035 M
$Ca(NO_3)_2$

150 mL of

$2.0 \times 10^{-5} M$
Na_2CO_3

Ca^{2+} Na^+

$NO_3{}^-$ $CO_3{}^{2-}$

The Calcium and Nitrate ions from the calcium nitrate and the Sodium and Carbonate ions from the sodium carbonate are all present in the mixture immediately after mixing.

Now, if we look at the diagram again, we find that the original $[Ca^{2+}]$ in the beaker on the top left is 0.0035 M. When this solution is poured into the lower beaker it is diluted. Remember the Dilution Formula? If you don't, here it is!

FC x FV = IC x IV   (where F=final, I=initial, C=concentration and V=volume)

or   FC = IC x $\dfrac{IV}{FV}$

Since 50.0 mL of the $Ca(NO_3)_2$ solution is being mixed with 150.0 mL of the other solution, the total final volume in the lower beaker will be 50.0 + 150.0 = 200.0 mL.

So to find the $[Ca^{2+}]$ right after mixing, we use:

FC =   IC   x $\dfrac{IV}{FV}$

FC =   0.0035 x $\dfrac{50.0}{200.0}$ = 8.75 x 10^{-4} M

so right after mixing, the $[Ca^{2+}]$ = 8.75 x 10^{-4} M

Now, looking at the diagram again, you can see that the original $[CO_3^{2-}]$ in the beaker on the top right is 2.0×10^{-5} M. (*The $[CO_3^{2-}]$ is the same as the $[Na_2CO_3]$ because each Na_2CO_3 produces one CO_3^{2-}*).

The initial volume of this solution is 150.0 mL, and when it is mixed, the total volume (FV) is 200.0 mL. (bottom beaker)

So to find the $[CO_3^{2-}]$ right after mixing, we use:

$$FC = IC \times \frac{IV}{FV}$$

$$FC = 2.0 \times 10^{-5} \text{ M} \times \frac{150.0}{200.0} = 1.50 \times 10^{-5} \text{ M}$$

so right after mixing, the $[CO_3^{2-}] = 1.50 \times 10^{-5}$ M

Now, since we have the $[Ca^{2+}]$ and the $[CO_3^{2-}]$ right after mixing, we can calculate the Trial K_{sp}! Wow! We're almost there!

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

(Right after mixing)

$$\text{Trial } K_{sp} = (8.75 \times 10^{-4}) (1.50 \times 10^{-5})$$

$$\text{Trial } K_{sp} = 1.3 \times 10^{-8}$$

Looking way back at the beginning of the problem on page 3, we see that:

$$\text{The real } K_{sp} \text{ for } CaCO_3 \text{ is } 5.0 \times 10^{-9}$$

$$\text{Since } 1.3 \times 10^{-8} > 5.0 \times 10^{-9}$$

$$\text{Trial } K_{sp} > K_{sp}$$

So $\underline{\text{YES}}$, a precipitate will form!

That seems like an awful lot of work just to get a yes or no answer! On a test question of this type, you never get full marks for just the answer (after all you have a 50% chance just by guessing!). You must show all your work. Even on a multiple choice question, you will have to know the Trial K_{sp} and the yes/no answer

Now it's time for you to try a problem like this on your own! Do this problem and check on **Tutorial 11 -Solutions** for the solution and the answer.

1. 250.0 mL of 3.0 x 10^{-4} M $Ba(NO_3)_2$ is mixed with 350.0 mL of 0.0020 M Na_2SO_4 solution.
    a) Determine which product could possibly be a precipitate.

    b) Write the equilibrium dissociation equation for the possible precipitate in (a).

    _____
    c) Calculate the [Ba^{2+}] right after mixing

                                                        Answer _____

    d) Calculate the [SO_4^{2-}] right after mixing

                                                        Answer _____

    e) Calculate the *trial K$_{sp}$* .

                                                        Answer _____

    d) Which is greater, the trial K$_{sp}$ or the real K$_{sp}$?

                                                        Answer _____

    e) Would a precipitate form in this case?   Answer _____

<u>Check your answers in **Tutorial 11 - Solutions**</u>

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You will get more examples of this type of question on worksheets and tests, so don't worry, you will have more practice!

The next type of question we will look at is predicting a precipitate when a small amount of a solid is added to a solution:

Predicting Precipitates When a Solid is Added to a Solution

Let's do this with an example. Follow through this very carefully and make sure you understand all the points as you go along.

Will a precipitate form if 2.6 grams of K_2CO_3 is added to 200.0 mL of a 2.0 x 10^{-3} M solution of $Mg(NO_3)_2$?

SOLUTION:

Use a quick little ion box to decide what your products will be and which one (or ones) have low solubility.

$$
\boxed{\begin{array}{cc}
K^+ & Mg^{2+} \\
\times & \\
CO_3^{2-} & NO_3^-
\end{array}}
$$
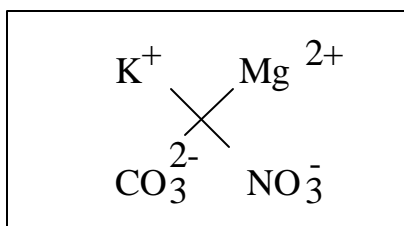
The two possible products are KNO_3 and $MgCO_3$. KNO_3 is soluble so that will <u>not</u> form a precipitate.

The only possible precipitate is $MgCO_3$ (*which has low solubility.*)

So, like in the previous type of question, we would find the Trial K_{sp} for $MgCO_3$ and compare it to the real K_{sp}.

To do this, we must find the $[Mg^{2+}]$ and $[CO_3^{2-}]$ immediately after mixing.

The initial $[Mg(NO_3)_2]$ is 2.0 x 10^{-3} M and the volume of the solution is 200.0 mL.

200 mL of 2.0 x 10^{-3}M
$Mg(NO_3)_2$
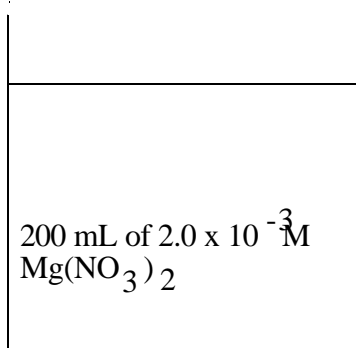
Now, *here's an important point! Adding a small amount of a solid to a large volume (eg. 200 mL) of a liquid solution will not significantly affect the total volume or the initial concentration of the solution until a reaction occurs.*

2.6 grams of solid K_2CO_3 is only about a spoonful and we can assume that the 200.0 mL volume of the solution will not change enough to worry about. (*See the diagram on the top of the next page.*)

We can also assume that the $[Mg^{2+}]$ (which is equal to the $[Mg(NO_3)_2]$) does not change.

So the $[Mg^{2+}]$ after mixing is 2.0 x 10⁻³ M.

This is the same as it was before mixing because there was <u>no liquid</u> added to the original solution, only a small amount of a solid, which would not affect the volume or the original amount of Mg^{2+}.

2.6 g of K_2CO_3

200 mL of 2.0 x 10^{-3}M
$Mg(NO_3)_2$
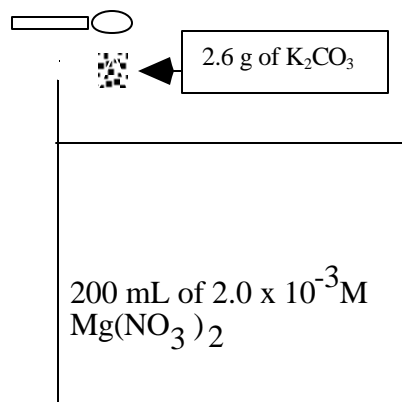
So now we know that the $[Mg^{2+}]$ after mixing is 2.0 x 10^{-3} M. What we need to find now is the $[CO_3^{2-}]$ immediately after mixing. We can then put these into the K_{sp} expression and calculate the Trial K_{sp}.

So far, all we know about the CO_3^{2-} is that we have added 2.6 grams of solid K_2CO_3 to 200.0 mL of the $Mg(NO_3)_2$ solution and that this little bit of solid does <u>not</u> significantly affect the volume of the solution. (*Nothing like repetition to drive a point home!*)

So, basically, we have the grams of K_2CO_3 and we have to find $[CO_3^{2-}]$.

Remembering some Chemistry 11, we can use the following flow chart:

$$x \ \frac{1 \ mole}{MM \ grams} \qquad\qquad M = \frac{moles}{L}$$

Grams → **Moles** → **Molar Concentration**
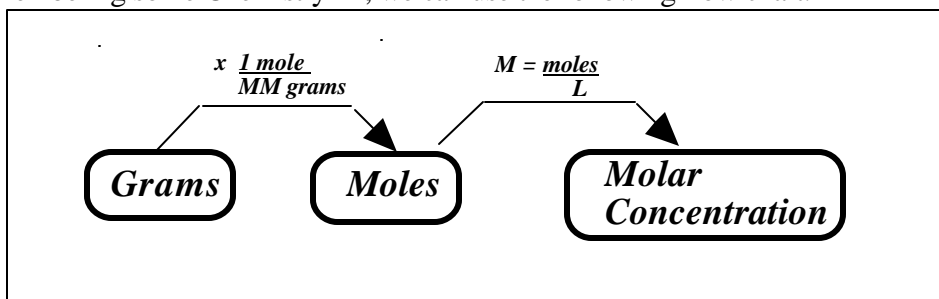
Remember the fun you used to have finding Molar Mass (MM) while socializing with the rest of the Chemistry 11 class. This should bring back some memories. You need your Periodic Table with atomic masses. (Unless, of course you have memorized them all since last year!)

$$K_2CO_3$$

$$MM = 2(39.1) \ + \ 12.0 \ + \ 3(16.0) = \underline{138.2}$$
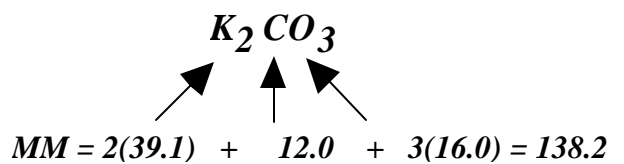
We can now do the first step of the process and change from grams to moles:

$$2.6 \text{ grams } \times \ \underline{\frac{1 \text{ mol}}{138.2 \text{ g}}} \ = \ \underline{0.0188} \text{ moles}$$

The next step will be to use the equation : $M = mol/L$ to find the Molar Concentration of K_2CO_3.

Remember, the volume of the solution we are putting the little bit of solid into is 200.0 mL and we can assume the volume does not change when the solid is added:


| 2.6 g of K_2CO_3 | $=$ | 0.0188 moles |

200 mL of 2.0×10^{-3}M $Mg(NO_3)_2$
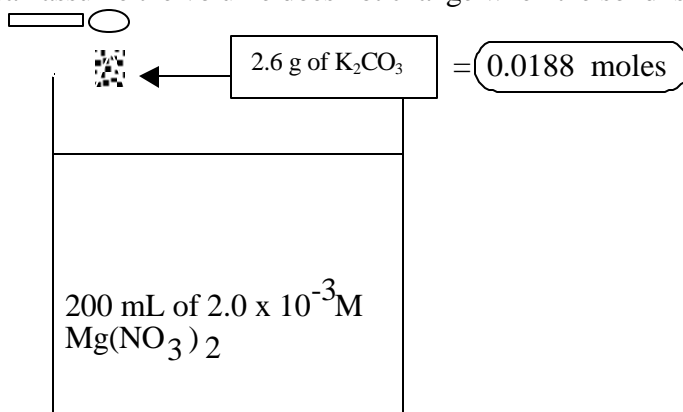
Again, with our solid basis in Chemistry 11, we remember that $200.0 \text{ mL} = 0.2000 \text{ L}$

(*NOTE: We don't worry that the liquid is a solution of $Mg(NO_3)_2$ instead of pure water. This doesn't matter until the reaction actually occurs (if it does).*)

So we can now calculate the $[K_2CO_3]$

$$M = \frac{mol}{L} = \frac{0.0188 \text{ mol}}{0.2000 \text{ L}} = \ 0.0940 \text{ M}$$

Now, because each mole of K_2CO_3 gives 1 mole of CO_3^{2-}

$$(K_2CO_{3(s)} \rightarrow \ 2K^+_{(aq)} \ + \ CO_3^{2-}_{(aq)})$$
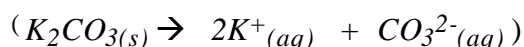
we know that

$$[CO_3^{2-}] = [K_2CO_3] \ = \ 0.0940 \text{ M}$$

We can now plug the $[Mg^{2+}]$ and the $[CO_3^{2-}]$ after mixing into the K_{sp} expression and obtain the Trial K_{sp}. (*Remember on the top of page 9, we found that the $[Mg^{2+}]$ was 2.0×10^{-3}M.*)

$$\text{Trial K}_{sp} = [Mg^{2+}] \quad [CO_3^{2-}]$$

$$= (2.0 \times 10^{-3}) \ (0.0940)$$

$$\text{Trial K}_{sp} = \underline{1.9 \times 10^{-4}}$$

Now, we compare the Trial K_{sp} (1.9×10^{-4}) with the real K_{sp} (6.8×10^{-6}):

(The K_{sp} for $MgCO_3$ is 6.8×10^{-6}. This was on the Ksp Table!)

Trial K_{sp} > K_{sp} , therefore a precipitate DOES form!

Now, let's try one of these on your own!

2.   Will a precipitate form if 3.8 grams of $Ca(NO_3)_2$ is added to 250.0 mL of
      0.0050 M Na_2SO_4 solution? Calculate the Trial K_{sp} first.
      (It would be good at this point to use the last example (starting on page 7) as a guide in doing
      this question.)

Trial K_{sp} = _____

Is there a precipitate? _____

Check your answers in Tutorial 11 Solutions.

Calculating the Maximum Possible Concentration of an Ion in Solution

This section of this tutorial deals with finding out how much of *one* ion can be present in solution if there is a certain amount of *another* one.

This probably doesn't make too much sense until we look at an example:
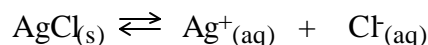
Imagine a saturated solution of AgCl.
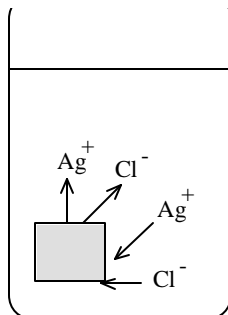
A Saturated Solution of AgCl

You can see by the diagram that in a saturated solution, for every Ag^+ or Cl^- which leaves the solid, another one goes back to the solid.

The equation which represents this equilibrium is:

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

Once the solution is saturated (at equilibrium), there is a limited number of Ag^+ and Cl^- ions which can exist dissolved in the solution.

What do you think tells us this limit?

You may have guessed it; **the K_{sp} !**

The K_{sp} for AgCl is 1.8×10^{-10}.

The K_{sp} expression is:

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

What this tells us is that:

The maximum product of the concentrations : [Ag⁺] x [Cl⁻] cannot exceed 1.8 x 10⁻¹⁰.

So what do you think might happen if we tried to test this "rule" by adding more Ag^+ or Cl^- ions to the solution?

Would it blow up and kill us all (that would teach us a lesson!) or what?

Well, if we added some Ag^+ or Cl^- ions, the product $[Ag^+]$ x $[Cl^-]$ **would** be higher than 1.8 x 10^{-10} for a very short time. (*At this point it would not be at equilibrium any more!*)

But what would happen then is the excess Ag^+ or Cl^- ions in solution would precipitate onto the crystal (solid), until the product $[Ag^+]$ x $[Cl^-]$ in the solution was again equal to 1.8 x 10^{-10}, and equilibrium was again established.

Now, here's something to ponder:

You know that if you just put some solid AgCl in water at 25 °C, that some of it will dissociate until the product $[Ag^+]$ x $[Cl^-]$ is equal to K_{sp} (1.8 x 10^{-10}).

$$AgCl_{(s)} \rightleftarrows Ag^+_{(aq)} + Cl^-_{(aq)}$$
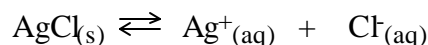
From the equation above, you can see that for every Ag^+ ion, you get **one** Cl^- ion.

So in this particular case, $[Ag^+] = [Cl^-]$

But, let's say that to some water at 25 °C, we add some Ag^+ ions and some Cl^- ions *__from different sources__*!

Let's say, for example that we add some $AgNO_3$. This is **soluble**, so it forms Ag^+ and NO_3^- ions. Now let's say, we add some NaCl. This is also soluble, so it forms Na^+ and Cl^- ions. In this case the Na^+ and the NO_3^- ions are spectators, so we'll forget about them and concentrate on the others: Ag^+ and Cl^- .

NOTE: The Na^+ and the NO_3^- ions have brackets because they are spectators.
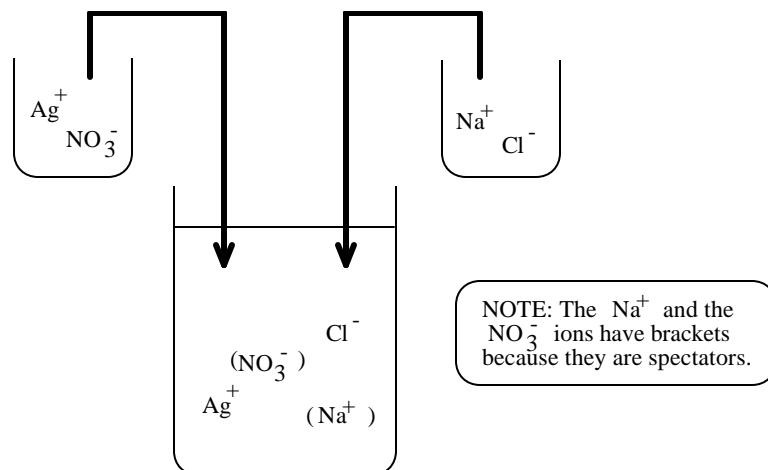
Now, here's an extremely important point:

> **When they are coming from different sources, there's <u>nothing</u> that says that the [Ag⁺] and the [Cl⁻] have to be equal.**

For example, you might have a little bit of $AgNO_3$ solution and a lot of the NaCl solution or vise versa.

What <u>does</u> matter is:

> **Once the product of the concentrations [Ag⁺] x [Cl⁻] exceeds the K_{sp} (1.8×10^{-10}), a precipitate of $AgCl_{(s)}$ will form until the product is again equal to 1.8×10^{-10}.**
> (***This is equilibrium.***)

So, hopefully you can see that it is the <u>PRODUCT</u> of their concentrations that matters. If [Ag⁺] is relatively high, then [Cl⁻] would have to be low enough so that their product did not exceed K_{sp}. If you tried to put any more in, it would just precipitate and form more solid AgCl.

So in this way, the **maximum possible concentration of one ion** (eg. Cl⁻) depends on the concentration of the other ion (eg. Ag⁺).

There are several types of problems which can be solved with an understanding of the concepts that you just read about. Let's do some examples:

Example:
Calculate the maximum possible [I⁻] in a solution in which [Ag⁺] is 1.0×10^{-5} M.

Solution:

The solution to this problem is incredibly easy! First, write the equilibrium equation and the K_{sp} expression:

$$AgI_{(s)} \; \rightleftarrows \; Ag^+_{(aq)} \; + \; I^-_{(aq)}$$

$$K_{sp} \; = \; [Ag^+] \; [I^-]$$

Next, realize that when [I⁻] is at it's **<u>maximum</u>**, you will be at **<u>equilibrium</u>**. So the product [Ag⁺] x [I⁻] will just be equal to the K_{sp}.

You know what K_{sp} is and you know what [Ag⁺] is, so just substitute these in to the K_{sp} expression and solve for [I⁻].

Look up the Ksp for AgI on the Ksp table. It is 8.5×10^{-17}

$$\mathbf{K_{sp}} \quad = \quad [\mathbf{Ag^+}] \ \ [\mathbf{I^-}]$$

$$\mathbf{8.5x\ 10^{-17}} \quad = \quad (\mathbf{1.0 \times 10^{-5}}) \ \times \ [\mathbf{I^-}]$$

So:
$$[\mathbf{I^-}] = \frac{\mathbf{8.5 \times 10^{-17}}}{\mathbf{1.0 \times 10^{-5}}}$$

$$[\mathbf{I^-}] = \mathbf{8.5 \times 10^{-12}} \ M$$

Now, looking at the results of this problem, you know that:

- if $[I^-]$ in this solution is *less than* 8.5×10^{-12} M, the solution will be **_unsaturated_**.

- if the $[I^-]$ is just *equal to* 8.5×10^{-12} M, the solution will be **_saturated_**.

- if more I^- is added, if will react with some Ag^+ and some $AgI_{(s)}$ precipitate will form.

Notice, that in this case $[Ag^+]$ is 1.0×10^{-5} M and $[I^-]$ is 8.5×10^{-12} M. They are NOT equal. That is because they came from different sources. They didn't just come from solid AgI dissolving.

Yes, I've STILL got more to say about this problem!

Notice, this was NOT a problem where you had to use "s" and find the solubility like you did in a previous type of problem. Some students get these two types of problems confused. Don't you!
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Here's one for you to try. (Be careful with the Ksp expression and the algebra!)

3.   Calculate the maximum possible $[Cl^-]$ in a solution in which $[Pb^{2+}]$ is 1.0×10^{-3} M.

Answer _____

Check your answer in **Tutorial 11 Solutions.**

The same type of problem can be worded in different ways. Here's another example for you to try:

4. Calculate the [Pb^{2+}] necessary to just start the precipitation of $PbBr_2$ from a solution in which the [Br^-] is 0.0030 M.
    (*If you are adding Pb^{2+} ions to a solution containing Br^- ions, precipitation will start immediately after the K_{sp} has been reached. So just calculate the [Pb^{2+}] necessary to form a saturated solution. A drop more will result in a precipitate starting. (Don't worry about the drop.)*)

Answer _____

Check your answer in <u>**Tutorial 11 Solutions**</u>.

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Sometimes precipitation reactions are used to remove certain ions from solutions. This may be done as a form of pollution control. We can use K_{sp} to find out how much of a certain ion might still be left in solution. Read through the next example:

Example:

A waste solution from a certain industrial process contains 0.050 M Cu^{2+} ions. In order to collect the Cu^{2+} from the solution for recycling, some OH^- ions are added to produce a precipitate of $Cu(OH)_2$. OH^- ions are added until the excess $[OH^-]$ is 2.0×10^{-3} M. Calculate the $[Cu^{2+}]$ remaining in the solution. The Ksp for $Cu(OH)_2$ is 1.6×10^{-19}.

Solution:

Don't be concerned about the word "excess". It just means that the $[OH^-]$ at the end of the procedure was 2.0×10^{-3} M.

You might think that ALL the Cu^{2+} ions will be used up if an excess of OH^- is added to precipitate them. But remember that ANY precipitate has *some* solubility, even if it is very low.

The first thing we do is write the equilibrium equation for the dissolving of $Cu(OH)_2$. This seems strange as the $Cu(OH)_2$ is actually being formed rather than dissolved. But the K_{sp} is <u>always</u> based on the equation written as dissolving (ie. the ions are on the right side of the equation!)

$$Cu(OH)_{2\ (s)} \ \rightleftharpoons \ Cu^{2+}_{(aq)} \ + \ 2OH^-_{(aq)}$$
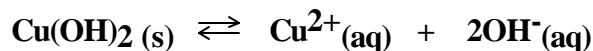
Next, we write out the K_{sp} expression. (*Of course, being careful to make the coefficient "2", an* <u>*exponent!*</u>)

$$K_{sp} = [Cu^{2+}] \ [OH^-]^2$$

The original concentration of the Cu^{2+} (which is 0.050 M) is interesting but it is not really needed to answer this problem.

You have the $[OH^-]$ at the end and you have the K_{sp}. That's all you need to calculate the $[Cu^{2+}]$ at the end. Just substitute the $[OH^-]$ and the K_{sp} into the K_{sp} expression and solve for the $[Cu^{2+}]$:

$$K_{sp} \ = \ [Cu^{2+}] \ [OH^-]^2$$

$$1.6 \times 10^{-19} \ = \ [Cu^{2+}] \ \times \ (2.0 \times 10^{-3})^2$$

Solving for $[Cu^{2+}]$:
$$[Cu^{2+}] \ = \ \frac{1.6 \times 10^{-19}}{(2.0 \times 10^{-3})^2}$$

$$[Cu^{2+}] = \frac{1.6 \times 10^{-19}}{4.0 \times 10^{-6}}$$

$$[Cu^{2+}] = 4.0 \times 10^{-14} \ M$$

This shows that the amount of Cu^{2+} ions left in the solution after this procedure is indeed very small. This would be a lot less harmful to the environment than the original $[Cu^{2+}]$ which was 0.050 M. The precipitate of $Cu(OH)_2$ which was formed in this process would undergo some process to recover the copper.

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Sometimes problems are given which require a couple more steps. Here's an example:

Example:

5.0 Litres of tap water has a $[Ca^{2+}]$ of 0.0060 M. Calculate the maximum mass of sodium carbonate (Na_2CO_3) which can be added without forming a precipitate of $CaCO_3$.
Solution:

The Ca^{2+} ions are going to precipitate with the CO_3^{2-} ions in the sodium carbonate which is added. The Na^+ ions are spectators.

Even though there is a <u>precipitation</u> here, we write the equilibrium equation for the <u>dissolving</u> of $CaCO_3$ (*Remember the K_{sp} refers to the dissolving equilibrium.*) :

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)}$$
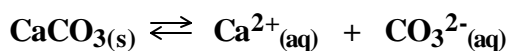
Then, as you might guess, we write out the K_{sp} expression:

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

We look up and substitute in the K_{sp} and the $[Ca^{2+}]$:

$$5.0 \times 10^{-9} = (0.0060) \ [CO_3^{2-}]$$

Then we solve for $[CO_3^{2-}]$:

$$[CO_3^{2-}] = \frac{5.0 \times 10^{-9}}{(0.0060)}$$

$$[CO_3^{2-}] = 8.33 \times 10^{-7} \ M$$

We now have the <u>Molar Concentration </u>of CO_3^{2-} ions and we need to find the **mass** of Na_2CO_3. Remember the <u>volume</u> of the sample is 5.0 Litres.

First, we convert Molar Concentration (M) of CO_3^{2-} into **moles**, using the equation:

$$\textbf{moles} \;=\; \textbf{M} \;\;\textbf{x}\;\; \textbf{Litres}$$

$$\textbf{moles} \;=\; \textbf{8.33 x } 10^{-7} \textbf{ moles/L x } \textbf{5.0 L}$$

$$\textbf{moles} \;=\; \textbf{4.167 x } 10^{-6} \textbf{ moles of } CO_3^{2-}$$

Since <u>one</u> Na_2CO_3 forms <u>one</u> CO_3^{2-}, the moles of Na_2CO_3 will be <u>the same as</u> the moles of CO_3^{2-} ions.

$$\textbf{moles of } Na_2CO_3 = \textbf{4.167 x } 10^{-6} \textbf{ moles}$$

In order to convert <u>moles</u> to <u>grams</u> (mass), we must first calculate the <u>Molar Mass </u>of Na_2CO_3:

$$\textbf{Na}_2\,\textbf{CO}_3$$

Molar Mass =   2(23.0) + 12.0 + 3(16.0) = 106.0 g/mol

Now, we can calculate the <u>grams</u> (mass) of Na_2CO_3 :

$$\textbf{Mass} = \textbf{ 4.167 x } 10^{-6} \textbf{ moles x } \frac{\textbf{106.0 grams}}{\textbf{1   mole}}$$

$$\textbf{Mass } = \textbf{ 4.417 x } 10^{-4} \textbf{ grams}$$

So the maximum mass of Na_2CO_3 which can be added without causing a precipitate would be 4.4 x 10^{-4} grams. (Rounded to 2 SD's)

Time for you to try one like this:

5.   Calculate the mass of NaI which must be added to 500.0 mL of a 2.0×10^{-4} M solution of $Pb(NO_3)_2$ in order to form a saturated solution of PbI_2 .

<u>**Check your in</u>Tutorial 11 Solutions.**

Finding Which Precipitate Will Form First

Sometimes a solution is added to another solution with a mixture of ions. You may be asked to determine which precipitate will form first.

Again, that extremely useful K_{sp} will help you with this.

Let's look at an example first:

0.010 M NaI is added dropwise to a solution containing 1.0 M Ag^+ and 1.0 M Cu^+. Which precipitate will form first?
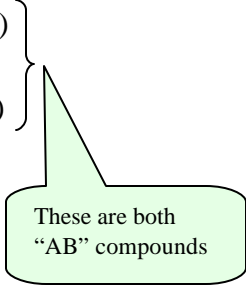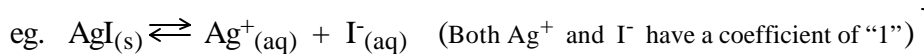Solution:

First recognize that the Na^+ ions in the NaI does not form any precipitates (it is soluble in everything.) and it is a spectator ion. The I^- ion forms a precipitate with Ag^+ and with Cu^+. Look up the Ksp's of AgI and CuI.

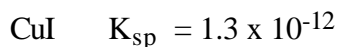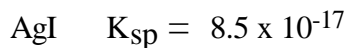Short-Cut Method for Multiple Choice Only!

Although we don't encourage short-cuts, one is possible here if you understand K_{sp} and what it means.

This method only works if **_both ions in the dissociation equation have the same coefficient. (ie. They are both the same type of compound (Both "AB" or both "AB₂")_**

eg. $AgI_{(s)} \rightleftharpoons Ag^+_{(aq)} + I^-_{(aq)}$ (Both Ag^+ and I^- have a coefficient of "1")

     $CuI_{(s)} \rightleftharpoons Cu^+_{(aq)} + I^-_{(aq)}$ (Both Cu^+ and I^- have a coefficient of "1")

We look up the Ksp's on the Ksp table:

These are both "AB" compounds

AgI $K_{sp} = 8.5 \times 10^{-17}$

CuI $K_{sp} = 1.3 \times 10^{-12}$

Since the AgI has a <u>lower</u> K_{sp}, you can reason that it must also have a <u>lower</u> solubility.

So this means that if you add I^- ions to a solution containing both Ag^+ and Cu^+ ions, the one with LOWER solubility will precipitate first.

This is because it's K_{sp} will be reached first because it is lower.

So the precipitate AgI will be formed first.

A Better Method!

This method is better because it is easier to understand and it can be used for <u>any</u> two precipitates, <u>whatever</u> the coefficients in their dissociation equations are! This would be the only method if one precipitate is an "AB" compound and the other is an " AB_2" compound. It is also the required method for written response type questions or problems.

First, have a look at this diagram to help you understand what's going on. Only the ions involved in forming precipitates are shown. The spectators are left out to make it simpler.:
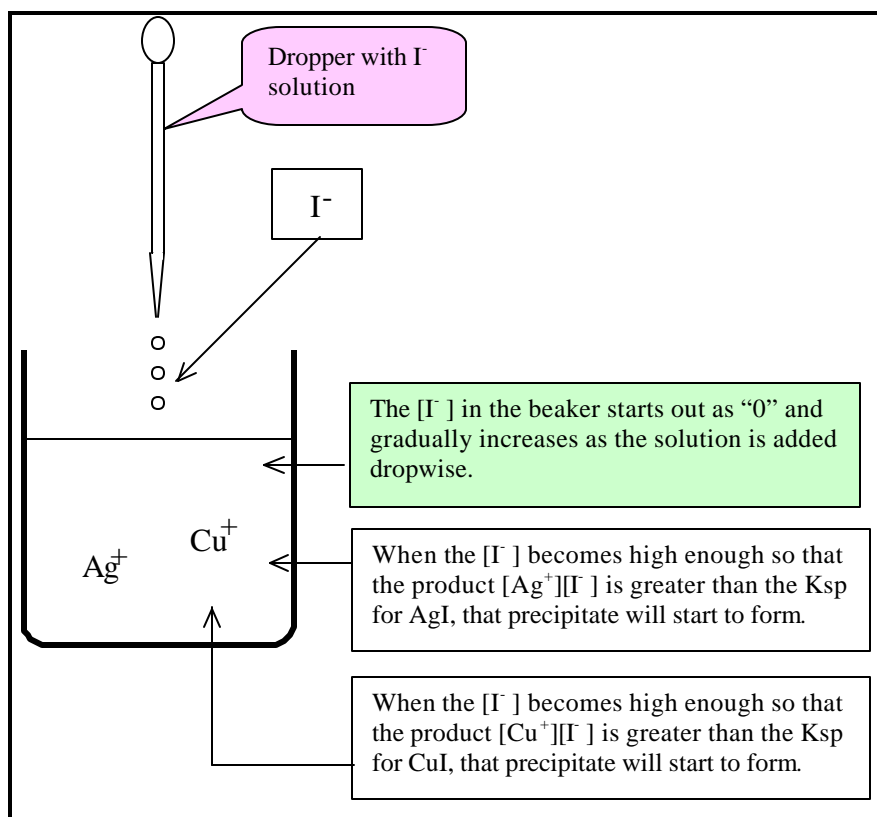
Here is the question again:

0.010 M NaI is added dropwise to a solution containing 1.0 M Ag^+ and 1.0 M Cu^+.
Which precipitate will form first?

Look up Ksp's: (AgI $\rightarrow$ K_{sp} = 8.5×10^{-17} CuI $\rightarrow$ K_{sp} = 1.3×10^{-12})

Knowing the K_{sp}'s we can calculate the [I⁻] needed to just start the formation of the precipitate AgI. We do it like the following:

$$AgI_{(s)} \rightleftharpoons Ag^+_{(aq)} + I^-_{(aq)}$$

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

$$8.5 \times 10^{-17} = (1.0) \times [I^-] \, (\textit{[Ag}^+\textit{] was given in the problem.})$$

$$[I^-] = \frac{8.5 \times 10^{-17}}{1.0} = 8.5 \times 10^{-17} \ M$$

So the $[I^-]$ needed to just start precipitation with Ag^+ is **8.5×10^{-17} M**.

In a similar way, we can calculate the $[I^-]$ needed to start precipitation of CuI:

$$CuI_{(s)} \rightleftharpoons Cu^+_{(aq)} + I^-_{(aq)}$$

$$K_{sp} = [Cu^+] \, [I^-]$$

$$1.3 \times 10^{-12} = (1.0) \times [I^-] \, (\textit{[Cu}^+\textit{] was given in the problem.})$$

$$1.3 \times 10^{-12} = (1.0) \times [I^-]$$

$$[I^-] = \frac{1.3 \times 10^{-12}}{1.0} = 1.3 \times 10^{-12} \ M$$

So the $[I^-]$ needed to just start precipitation with Cu^+ is **1.3×10^{-12} M**.

As the I^- ions are slowly added dropwise, their concentration in the beaker starts out as "0" and gradually increases.

The value 8.5×10^{-17} needed for formation of AgI is less than 1.3×10^{-12} which is needed for the formation of CuI.
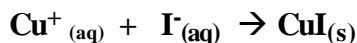
The underline value, 8.5×10^{-17}, will be reached **first**, (*as it starts out as "0" and gradually increases.*) Therefore:

The precipitate AgI will form first:

$$Ag^+_{(aq)} + I^-_{(aq)} \rightarrow AgI_{(s)}$$
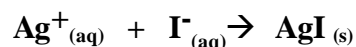
When the Ag^+ is all used up by the I^-, the $[I^-]$ can start building up again.

Once the $[I^-]$ reaches the higher value of 1.3×10^{-12}, the precipitate CuI will start forming:

$$Cu^+_{(aq)} + I^-_{(aq)} \rightarrow CuI_{(s)}$$

Here's a question for you to try. This one cannot be done with the short-cut method.

6. If 0.1 M KCl is added dropwise to a beaker containing 0.10 M Ag^+ and 0.10 M Pb^{2+}, which precipitate would form first? Show all equations and calculations.

Check your answer in Tutorial 11 Solutions.

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Self-Test on Tutorial 11

1. 500.0 mL of 2.0 x 10^{-4} M $Pb(NO_3)_2$ solution is mixed with 800.0 mL of
    3.0 x 10^{-3} M NaI solution. Do the necessary calculations to see if a precipitate will form or not.

Check your in Tutorial 11 Solutions.

2.   If 5.5 grams of $AgNO_3$ solid is added to 50.0 mL of 2.0 x 10^{-3} M KIO_3 solution, will a
      precipitate of $AgIO_3$ form?

Check your answer in Tutorial 11 Solutions.

3.   Find the maximum possible $[IO_3^-]$ in a solution in which $[Pb^{2+}]$ = 3.0 x 10^{-4} M.

Check your answer in Tutorial 11 Solutions.

4.   If 0.20 M Na_2CO_3 solution is added slowly to a mixture of 0.010 M $Ba(NO_3)_2$ and
      0.010 M $AgNO_3$, which precipitate would form first. Show all calculations in a logical way.

Check your answer in Tutorial 11 Solutions.