

A conceptual presentation of gravimetric analysis: A limiting reagent problem

Supplement to Lecture 7

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Scenario: You are presented with a test tube with 10.00 g of white powder in it. You are told the white powder is a mixture of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, f.w. $244.2 \text{ g} \cdot \text{mol}^{-1}$) and sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, f.w. $322.3 \text{ g} \cdot \text{mol}^{-1}$). You do not know what portion of the white powder is which compound. In other words, your goal is to determine the composition of the white powder.

Secret knowledge: When I originally prepared the white powder, I used 5.00 g of each compound. Let's see if we can get this result.

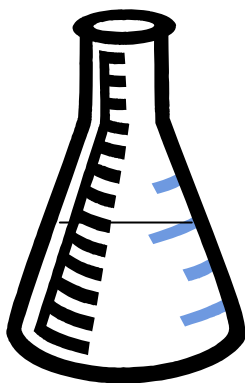
Solving the problem

1. How can we get a reaction to occur?
2. What reaction would occur?
3. What would you need to measure?
4. How would you measure it?
5. What information could you calculate by knowing that?
6. What additional information might you need?

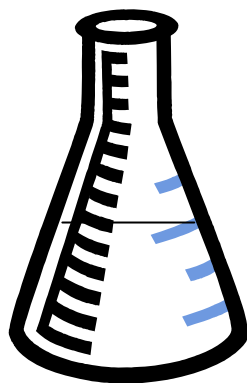
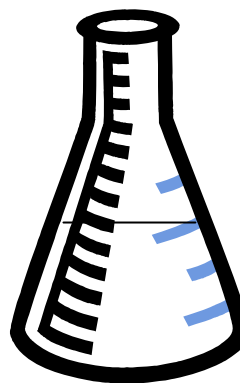
1. Getting a reaction to occur

One way to separate the white powders is to painstakingly separate every individual crystal under a microscope (since the crystal structures of the two compounds are probably different and would result in differently shaped crystals). This would be very time consuming. Doing a chemical reaction would be faster.

To get a chemical reaction to occur, we need a medium in which the chemical reaction can take place, because the two solids won't react with each other while in the solid form in the test tube. But first, we need to know if the two individual compounds dissolve in water.

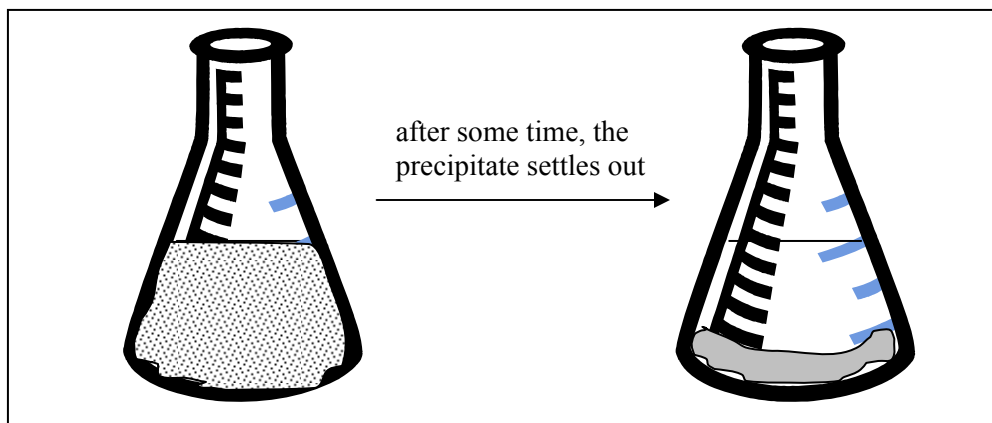


Pure water

Water with some
 $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
added to itWater with some
 $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
added to it

All three flasks look like water. In other words, the two compounds do dissolve in water.

So, let's add the white powder from the test tube to some water. Watch what happens.



(Note: I have shown the precipitate as gray so that you can see it in the picture on paper, but in reality it is a white precipitate.)

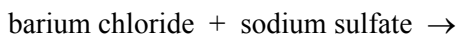
2. What reaction did occur?

When the two compounds were mixed into water, the ions in the compounds became solvated in the water, so that water became the medium in which the reaction took place. So, here is the start of the chemical reaction:

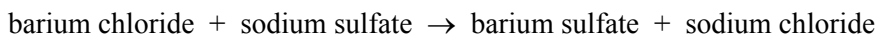


First of all, where did the waters of hydration go? When the crystals dissolved, the waters of hydration became part of the liquid water in which the crystals dissolved.

To figure out what reaction occurred, think of this as a dance to which two couples enter, and then choose each other's partners at the dance and leave in different configurations. It's easier to figure out these kind of reactions if you use words:



When the couples switch places, the cations (metal ions) and anions (nonmetal ions or polyatomic ions) have to continue to be the kinds of ions they are.



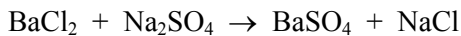
One (or more) of these products must be the chemical that precipitated. It turns out that it is the barium sulfate, as you'll learn about later in the course. But you could also have figured this out because you know that sodium chloride is just table salt, and you know that table salt dissolves readily in water, so it must not be the precipitate.

But before we go on to the next question, let's finish writing the chemical reaction, and then let's balance it also, since we'll need that too. First, all the chemicals must be written as compounds that are neutral, so you need to use the charges on each ion to figure out how to make neutral compounds:

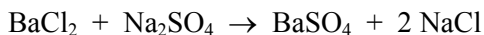
- ▶ barium sulfate is made of Ba^{2+} ions and SO_4^{2-} ions, so the neutral barium sulfate compound must be in a 1:1 ratio of ions: BaSO_4

- ▶ sodium chloride is made of Na^+ ions and Cl^- ions, so the neutral sodium chloride compound must be in a 1:1 ratio of ions: NaCl

Now, the unbalanced chemical reaction is:



Then, to balance it, first determine the species that need to be balanced. They are the four individual ions: the barium ion (1 in, 1 out), the chloride ion (2 in, 1 out), the sodium ion (2 in, 1 out) and the sulfate ion (1 in, 1 out). The correctly balanced chemical equation is:

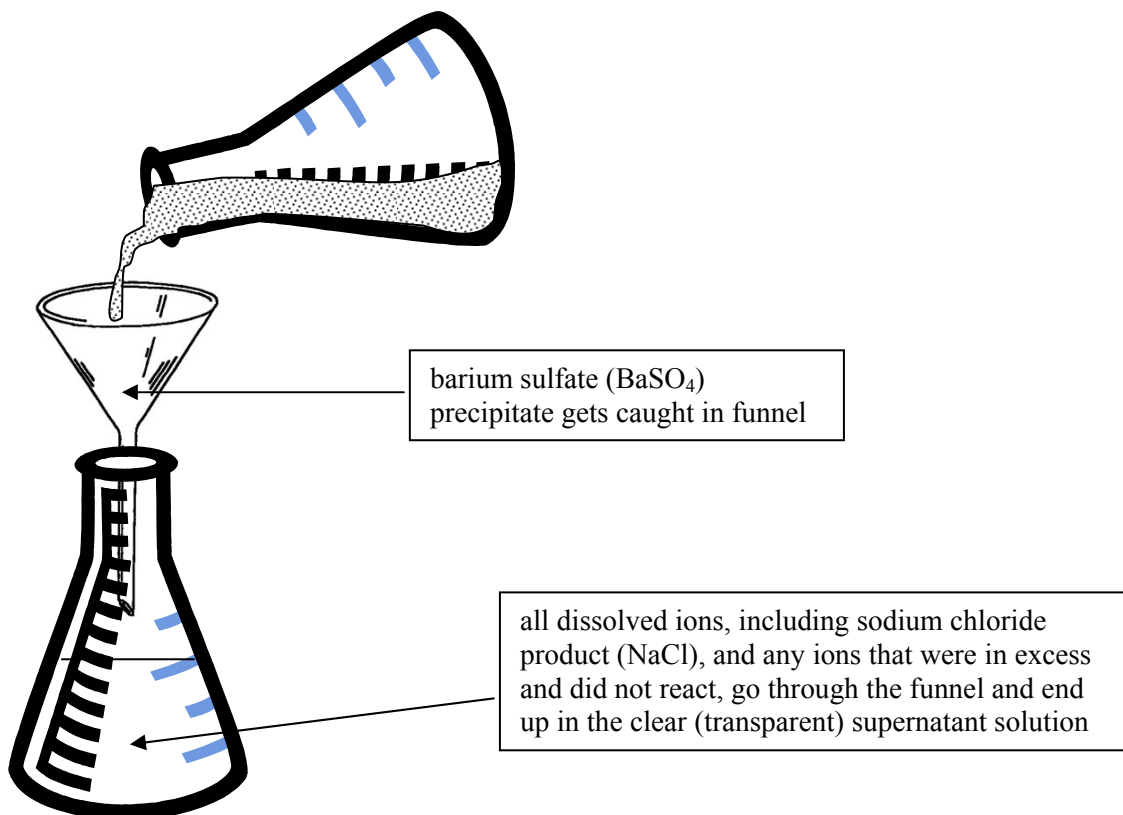


3. What do you need to measure?

Getting back to our original problem, what we need to measure to figure out the composition of the white powder is the amount of barium sulfate (BaSO_4) that precipitated.

4. How do we measure it?

To measure it, filter the whole result (in the box on the previous page). The barium sulfate precipitate will remain in the filter paper, and the solution will go through to the bottom (this is called the supernatant solution). Make sure you have measured the mass of the empty filter paper first.



After all of the BaSO_4 has been captured on the filter paper, dry the filter paper with the BaSO_4 on it. Then measure the mass of the dried BaSO_4 and filter paper. Subtract the mass of the filter paper, and you will have the mass of the BaSO_4 that was produced in the reaction.

The mass of BaSO_4 produced was 3.62 grams.

5. What information could you calculate by knowing that?

If you know the mass of BaSO₄ produced, then you can use stoichiometry to calculate the amounts of the two reactants that reacted.

$$3.62 \text{ g BaSO}_4 \times \frac{1 \text{ mol BaSO}_4}{233.4 \text{ g BaSO}_4} \times \frac{1 \text{ mol BaCl}_2}{1 \text{ mol BaSO}_4} = 0.0155 \text{ mol BaCl}_2$$

$$3.62 \text{ g BaSO}_4 \times \frac{1 \text{ mol BaSO}_4}{233.4 \text{ g BaSO}_4} \times \frac{1 \text{ mol Na}_2\text{SO}_4}{1 \text{ mol BaSO}_4} = 0.0155 \text{ mol Na}_2\text{SO}_4$$

However, if one of the two reactants (barium chloride or sodium sulfate) was present in excess, then only one of these can be correct, and there is more than that of the excess one.

So far we have:

The reaction is: $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2 \text{NaCl}$

	BaCl ₂	Na ₂ SO ₄	BaSO ₄	NaCl
before	some	some	0	
change			+0.0155 mol	
after	one of these was limiting and the other was present in excess		$3.62 \text{ g} \times \frac{1 \text{ mol BaSO}_4}{233.4 \text{ g BaSO}_4}$ = 0.0155 mol	

6. What additional information is needed?

To figure out which reactant was present in excess, we have to test the supernatant solution (the solution that went through the filter paper). There are two possibilities:

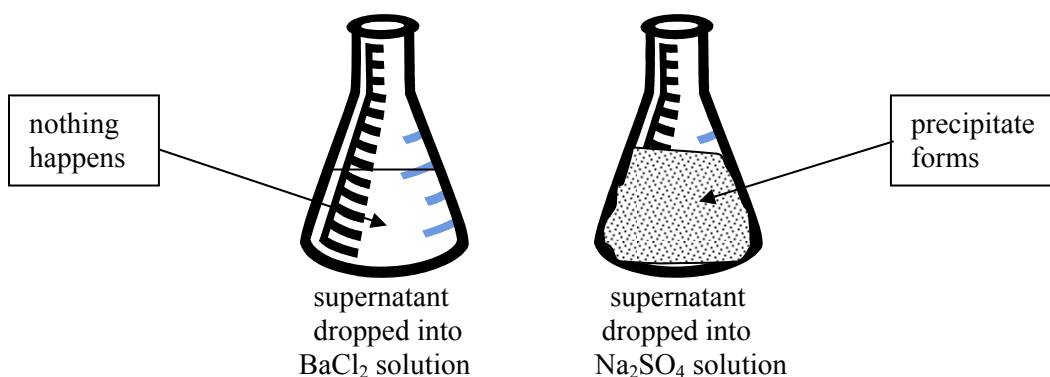
Possibility #1: BaCl₂ is limiting

If there was excess Na₂SO₄, then all the Ba²⁺ and Cl⁻ ions reacted, but some Na⁺ and SO₄²⁻ ions that were dissolved in the original solution were not used up. So if some excess Na⁺ and SO₄²⁻ ions were present, then they showed up in the supernatant solution. If they are in the supernatant solution, then if we place a few drops of supernatant into solutions of BaCl₂ and Na₂SO₄, we should see a reaction happen in the BaCl₂ solution and no reaction should happen in the Na₂SO₄ solution.

Possibility #2: Na₂SO₄ is limiting

If there was excess BaCl₂, then all the Na⁺ and SO₄²⁻ ions reacted, but some Ba²⁺ and Cl⁻ ions that were dissolved in the original solution were not used up. So if some excess Ba²⁺ and Cl⁻ ions were present, then they showed up in the supernatant solution. If they are in the supernatant solution, then if we place a few drops of supernatant into solutions of BaCl₂ and Na₂SO₄, we should see no reaction happen in the BaCl₂ solution and a reaction should happen in the Na₂SO₄ solution.

What actually happens is:



Therefore, the supernatant must contain some BaCl_2 that was in excess in the original mixture of solids. If BaCl_2 was in excess, then Na_2SO_4 was the limiting reagent (possibility #2).

Now we have: The reaction is: $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2 \text{NaCl}$

	BaCl_2	Na_2SO_4	BaSO_4	NaCl
before	excess	limiting	0	
change	used up some of it	used up all of it	+0.0155 mol	
after	some left	none left	$3.62 \text{ g} \times \frac{1 \text{ mol BaSO}_4}{233.4 \text{ g BaSO}_4}$ = 0.0155 mol	

When 0.0155 mol of BaSO_4 was formed, how much Na_2SO_4 was used?

$$0.0155 \text{ mol BaSO}_4 \times \frac{1 \text{ mol Na}_2\text{SO}_4}{1 \text{ mol BaSO}_4} = 0.0155 \text{ mol Na}_2\text{SO}_4$$

So now we have:

	BaCl_2	Na_2SO_4	BaSO_4	NaCl
before	excess	there must have been 0.0155 mol of this to start	0	
change	used up some of it	- 0.0155 mol	+0.0155 mol	
after	some left	none left	0.0155 mol	

Therefore, the amount of hydrated $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ that must have reacted to form BaSO_4 is

$$0.0155 \text{ mol Na}_2\text{SO}_4 \times \frac{1 \text{ mol Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}{1 \text{ mol Na}_2\text{SO}_4} \times \frac{322.3 \text{ g Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}{1 \text{ mol Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}} = 5.00 \text{ g Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$$

So, now we know that the original mixture (which was 10.00 g total) contained 5.00 g of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Therefore the rest of it (10.00 - 5.00 g = 5.00 g) was $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

This matches with the secret knowledge we have from the very beginning.