# Chapter 8 STOICHIOMETRY, Part 2



We continue with more stoichiometry topics. Our fundamentals are in place. The four basic steps which we covered in the last Chapter remain our primary method for attacking problems of this type, at least within the context of dimensional analysis. As food for thought, we open this Chapter with a question many people often ask in their daily lives.

## 8.1 What do we do with the leftovers???

What leftovers? Well, we didn't have any yet, but you can end up with some, depending on how you actually run a reaction. I will begin this part by referring to our $H_2/Cl_2$ reaction from Chapter 7 and the examples which we worked at that time. Recall the balanced equation.

$$H_2 + Cl_2 \rightarrow 2\ HCl$$

Let me summarize those results.

- ✓ The problem started with 24.77 g $H_2$ as given information.
- ✓ We first calculated that this 24.77 g $H_2$ would react evenly (no more, no less) with 871.1 g $Cl_2$.
- ✓ Secondly, we calculated that 895.9 g HCl could be made from the 24.77 g $H_2$.
- ✓ For a third example, we used the 871.1 g $Cl_2$ to calculate the amount of product, which gave us the same answer of 895.9 g HCl.

If we actually do the reaction beginning with 24.77 g $H_2$ (given info) and 871.1 g $Cl_2$ (calculated by stoichiometry), then we say we are running the reaction at "stoichiometric amounts" or "stoichiometric conditions". The two phrases are equal and you can use either one. The terms mean that <u>all reactants are present in amounts as calculated by stoichiometry for each other</u>. When our reaction of 24.77 g $H_2$ and 871.1 g $Cl_2$ is done, you should have 895.9 g HCl, as calculated. There would only be HCl molecules afterwards; all $H_2$ molecules and all $Cl_2$ molecules reacted. There would be no more molecules of $H_2$ left and there would be no more molecules of $Cl_2$ left.

Frequently we don't do reactions at stoichiometric conditions. Let's say we load the pot with 24.77 g $H_2$ and 914.3 g $Cl_2$. Notice that this is more $Cl_2$ than we can use. When the reaction finishes, you would still have 895.9 g HCl, but you also have leftover chlorine. The 24.77 g of hydrogen molecules still reacted with just 871.1 g of chlorine molecules, as required by the stoichiometry and the balanced equation. That part doesn't change. But you put more than enough chlorine molecules into the pot to start. How much more?

| | |
|---|---|
| You started with: | 914.3 g of chlorine molecules |
| and the reaction used: | 871.1 g of chlorine molecules |
| which means there are: | 43.2 g of chlorine molecules leftover |

What happens to the leftovers? Nothing. They're still there at the end. When the reaction is over, you have your product of 895.9 g of HCl molecules and you have 43.2 g of chlorine molecules left over. There are no $H_2$ molecules since all of these reacted.

Why would you want to put too much of one reactant into the pot? Isn't that wasteful? Well, maybe, but not necessarily. There are many reasons for doing this and it's a very common practice in the laboratory and in industry. Having extras of one reactant often helps to make the whole process go better and faster. How? Well, I can't go into that right now because we haven't covered enough other turf. Much of this ties into "equilibrium" which will get a bit of mention in Chapter 12 and much more extensive coverage in much later chapters. Some of the reasons tie into the speed of reactions which will be discussed beginning in Chapter 48. Some of this ties into still other aspects. We're not really in a spot where I can go into details. That means you'll have to take my word for it. There are some things, however, which we can take care of right now, and that is why I even brought this up. We will see how this is handled by stoichiometry calculations.

In this present example starting with 914.3 g chlorine molecules, we knew there was going to be leftover chlorine because we had done all the calculations in Chapter 7 for stoichiometric conditions. We knew that 24.77 g $H_2$ and 871.1 g $Cl_2$ were the stoichiometric amounts for each other because we calculated one from the other. However, a typical problem of this type does not start there. I'll show you how these typical problems start, but first we need some terminology.

## 8.2 Excess and limiting

We don't call leftovers "leftovers". We call them excesses. The leftover amount is called the "excess amount". In the illustration above starting with 24.77 g $H_2$ and 914.3 g $Cl_2$, we had 43.2 g leftover $Cl_2$. We say 43.2 g $Cl_2$ is the excess amount. We also say $Cl_2$ is the "excess reagent" (or "excess reactant") for the reaction. The excess reagent is the one whose initial amount is greater than needed based on the amounts of other reactants. On the other hand, $H_2$ is the reactant which runs out completely. When all 24.77 g of hydrogen molecules reacted, that was the end of it. No more $H_2$ molecules, no more reaction. We call $H_2$ the "limiting reagent" (or "limiting reactant"). The limiting reagent is the one in shortest stoichiometric supply at the start of the reaction. When it's gone, it's gone. The reaction is done. Since the limiting reagent runs out and ends the reaction, the limiting reagent determines how much product can be made. It doesn't matter if other reactants are still floating around ready for action. ONCE ANY REACTANT IS USED UP, YOU'RE FINISHED. Done. Completed. Over. That's all the product you can get. The limiting reagent limits the amount of product possible.

CAUTION!!! It is important for you to be aware of the difference between this scenario and a reaction conducted under stoichiometric conditions. Under stoichiometric conditions, all reactants are put into the pot in stoichiometric amounts. They all run out and are used up at the same time. Nobody is in excess. Since they all run out evenly and at the same time, the amount of product can be calculated from any of the reactants. We actually did this in the last Chapter with the $H_2/Cl_2$ reaction. For the HCl product, we calculated that 895.9 g HCl could be made from the 24.77 g $H_2$ and we also calculated that the same 895.9 g HCl could be made from the 871.1 g $Cl_2$. Let me repeat: under stoichiometric conditions, the amount of product can be calculated from any of the reactants. On the contrary, if any reactant is limiting, then the amount of product must be calculated from that amount of that reactant.

OK, let's turn now to a typical problem with limiting reagent. By the way, this kind of problem is actually called a "limiting reagent problem". I'm getting tired of $H_2$ and $Cl_2$. Let's do something different. We'll do a reaction to make silver bromide. We'll start with silver nitrate and sodium bromide as the reactants. Sodium nitrate will also be produced by this process.

$$AgNO_3 + NaBr \rightarrow AgBr + NaNO_3$$

Ever use or been treated with silver nitrate? Silver nitrate has been used as an antiseptic agent in a variety of medical applications. The second reactant, sodium bromide (and also potassium bromide) has had medical roles in sedatives, anti-epilepsy drugs, etc. (It was even in the movies, as a spellbound Alfred could tell you.) This use has decreased due to side effects, but these bromide compounds are still used in select medical applications, including veterinary use. What about the product, silver bromide? Ever use it? It's rare nowadays but it was the norm not too long ago: silver bromide was the leading light-sensitive compound used in photographic films. It's the stuff that actually reacts with light.

Here's the setup for the problem. An aqueous solution of 14.01 g silver nitrate and an aqueous solution of 10.91 g sodium bromide are prepared in separate beakers. Both compounds are ionic compounds. They are colorless by themselves and when they dissolve in water their solutions are also colorless. When the two solutions are mixed, a reaction occurs which causes a cloudy, yellowish-white appearance. The cloudiness is due to tiny particles of solid silver bromide which eventually settle to the bottom of the container. The sodium nitrate product is colorless and stays dissolved in the water. By the way, I mentioned the use of phases in chemical equations in Chapter 6. This would be a nice illustration to show you how "aqueous" phase is used.

$$AgNO_3(aq) + NaBr(aq) \rightarrow AgBr(s) + NaNO_3(aq)$$

Don't forget: aqueous means *dissolved* in water. Since the AgBr isn't dissolved, it can't be called aqueous.

OK, that's the setup. Now the question: for this process with the given amounts of reactants, how many grams of silver bromide can be made?

First, a bit of background. Whenever the amounts of two or more reactants are given to you in a problem, then the very first thing you need to know is whether these are stoichiometric conditions or not. Sometimes the problem will say so. Sometimes, like right now, it won't. If it doesn't say so, you should assume it is NOT stoichiometric conditions. Why is this necessary? If the reactant amounts are stoichiometric amounts, then you can calculate the amount of product from any one of the reactant amounts. On the other hand, if the reactant amounts are not stoichiometric amounts, then you must calculate the amount of product based on the limiting reagent.

We started with 14.01 g silver nitrate and 10.91 g sodium bromide. We assume these are not stoichiometric amounts. We assume that one reactant is the limiting reagent and the other reactant is the excess reagent. Which is limiting and which is excess? That's not obvious. You can't just look at the number of grams because the answer also involves moles. There are several ways to do these kinds of problems and I will illustrate one which is fairly common. This method applies to those problems which ask for the amount of a product as part of the problem. There are other ways which your instructor may cover and prefer. Again, these are multiple methods. Use the one that works best for you.

The present approach is based on a sentence from upstairs: the limiting reagent limits the amount of product possible. We can calculate the amount of product which would be possible from the given amount of each reactant. That means we do a separate stoichiometry calculation starting from each reactant amount. Then we compare those results. The reactant which will make the least amount of product is the limiting reagent and that determines the amount of product.

Let's get started.

The problem specifically asks for the amount of silver bromide which can be prepared; sodium nitrate will also be made, but the problem does not request that. We ignore sodium nitrate and we focus only on the silver bromide product. We will do two calculations: we will calculate how much silver bromide can be made from 14.01 g silver nitrate and we will calculate how much silver bromide can be made from 10.91 g sodium bromide.

$$\begin{array}{ccccccc} AgNO_3 & + & NaBr & \rightarrow & AgBr & + & NaNO_3 \\ 14.01\text{ g} & & 10.91\text{ g} & & ???\text{ g} & & \end{array}$$

Our problem begins with these two basic stoichiometry calculations. Step 1, as always, needs a balanced equation and this has been provided. You can check this yourself. (Don't always assume that equations are balanced when given to you. Sometimes instructors want you to balance the equation first.)

First calculation: how many g AgBr can be made using 14.01 g $AgNO_3$?

This is standard stoichiometry. Plot your path: start with the amount of $AgNO_3$ provided.

g $AgNO_3$

• Step 2. Remember the molar mass connection to get to moles. The molar mass for $AgNO_3$ is 169.9 g.

g $AgNO_3$ → mol $AgNO_3$

Of the two possible molar mass conversion factors, you need: $\dfrac{\text{mol } AgNO_3}{169.9\text{ g } AgNO_3}$

• Step 3. Rxn ratio. The coefficients in the balanced equation for $AgNO_3$ and AgBr are 1:1.

g $AgNO_3$ → mol $AgNO_3$ → mol AgBr

Of the two possible rxn ratios, you need: $\dfrac{1\text{ mol AgBr}}{1\text{ mol } AgNO_3}$

• Step 4. Now molar mass for AgBr. It's 187.8 g.

g $AgNO_3$ → mol $AgNO_3$ → mol AgBr → g AgBr

Of the two possible molar mass conversion factors, you need: $\dfrac{187.8\text{ g AgBr}}{\text{mol AgBr}}$

• Now string it all together.

path: g $AgNO_3$ → mol $AgNO_3$ → mol AgBr → g AgBr

$$14.01\text{ g } AgNO_3 \times \frac{\text{mol } AgNO_3}{169.9\text{ g } AgNO_3} \times \frac{1\text{ mol AgBr}}{1\text{ mol } AgNO_3} \times \frac{187.8\text{ g AgBr}}{\text{mol AgBr}} = 15.49\text{ g AgBr}$$

This ends our first calculation. We have determined that 15.49 g AgBr product can be made from the 14.01 g $AgNO_3$ which were provided.

Now we need to do the second calculation, basing it on the given amount of NaBr. Plot your path. It's basically the same. You'll need the molar mass of sodium bromide (102.89 g), along with other numbers from above. You have to do more of the details here, since I'm not giving all of them for every problem. I'll give you the full path. You fill in what's needed.

path: g NaBr → mol NaBr → mol AgBr → g AgBr

10.91 g NaBr × ———— × ———— × ———— = 19.91 g AgBr

I gave you the answer so you can be sure you put all the conversion factors in correctly. You need to fill this in. Plug in your numbers, punch them out, round them off, and be sure you get 19.91. If not, find and fix your mistake.

Alright let's summarize what we have from the calculations and we can make our conclusions.

✓ First calculation: We have enough $AgNO_3$ to make 15.49 g of formula units of AgBr.
✓ Second calculation: We have enough NaBr to make 19.91 g of formula units of AgBr.

Remember. The limiting reagent limits the amount of product. The calculations show that a smaller amount of product is obtainable from the $AgNO_3$. We see that we can make 15.49 g AgBr, after which all $AgNO_3$ has reacted. At that point, there are no more formula units of $AgNO_3$ available in order to continue. The reaction is over. Done. Although the second calculation says we have enough NaBr to make 19.91 g AgBr, the reaction still stops at 15.49 g AgBr due to the limit imposed by the amount of $AgNO_3$. Thus, we have too much NaBr and there will be leftovers of NaBr. We conclude $AgNO_3$ is the limiting reagent. NaBr is the excess reagent. The answer to the original question is that 15.49 g AgBr can be made under these conditions. You're done with the problem.

Now let's change the problem and carry it out a bit further to illustrate several aspects. We've just concluded that you end up with 15.49 g AgBr in the pot. You also end up with some $NaNO_3$ as the other product. How much $NaNO_3$ do you get? The original problem did not ask for this, but you can calculate the amount of this product, too. Fortunately, you don't have to do two calculations again. That's because the limiting reagent applies to the WHOLE reaction. As soon as the limiting reagent is gone, everything stops. Once the limiting reagent is identified, all stoichiometric outcomes for all other reagents are determined from that. Since we already know that $AgNO_3$ is the limiting reagent, we can calculate the amount of $NaNO_3$ just from 14.01 g $AgNO_3$. As above, I'll give the full path and I'll give you the answer. You can go back in and insert the conversion factors and make sure you're doing it right. You'll need the molar mass for sodium nitrate (85.00 g), along with some earlier numbers.

path: g $AgNO_3$ → mol $AgNO_3$ → mol $NaNO_3$ → g $NaNO_3$

14.01 g $AgNO_3$ × ———— × ———— × ———— = 7.009 g $NaNO_3$

Be sure you get this answer. Otherwise, find and fix the error.

Here's another aspect. Sodium bromide is the excess reagent, which means that some of it will be left over. How much NaBr is actually left over? In order to answer that, we must first calculate how much of the NaBr actually reacted. Since the limiting reagent determines the stoichiometric outcome for everybody else, that's what you start with: your first job is to calculate the amount of NaBr which reacted with the 14.01 g $AgNO_3$. I'll outline it and you can fill it in.

path: g $AgNO_3$ → mol $AgNO_3$ → mol NaBr → g NaBr

14.01 g $AgNO_3$ × ———— × ———— × ———— = 8.484 g NaBr

This result says that, out of the 10.91 g sodium bromide which were provided initially, 8.484 g actually reacted with the 14.01 g silver nitrate. To find the amount of NaBr left over, we just do a subtraction the same way as we did for the $H_2/Cl_2$ example earlier in this Chapter.

| | |
|---|---|
| You started with: | 10.91 g of formula units of NaBr |
| and the reaction used: | 8.484 g of formula units of NaBr |
| which means there are: | 2.43 g of formula units of NaBr leftover |

There you have it: 2.43 g NaBr is the excess amount.

Let me summarize everything we did.

| | | |
|---|---|---|
| ‣ We started with: | 14.01 g $AgNO_3$ | 10.91 g NaBr |
| ‣ We calculated the amount of AgBr product possible from each: | 15.49 g AgBr | 19.91 g AgBr |

‣ The reaction is limited to the lesser amount of AgBr; here, the lesser amount derives from the $AgNO_3$, so $AgNO_3$ is the limiting reagent. 15.49 g of AgBr product were possible, and this ended the problem as originally stated.

‣ We took the problem further and we calculated that 7.009 g $NaNO_3$ would also be made, based on $AgNO_3$ as limiting reagent.

‣ Also based on $AgNO_3$, we calculated that 8.484 g of the original NaBr would actually react in the process.

‣ Finally, we showed that 2.43 g NaBr would be left over as the excess amount.

The grand tally in the pot after the reaction is done would be:

15.49 g of formula units of silver bromide product
7.009 g of formula units of sodium nitrate product
2.43 g of formula units of sodium bromide leftover
no formula units of silver nitrate at all

That's everything from the reaction.

These types of problems can get very long and drawn out, but keep in mind that most of the grunt work is the basic stoichiometry string.

As always, be able to think through the given information and figure out where you have to go. The bottom line comes down to the usual thing: practice, practice, practice.

### 8.3 The real world versus the ideal world

I want to go into something different at this point. You could say that it's a different aspect of stoichiometry but it's really a dose of reality. I mentioned reality checks as Catch #3 in Chapter 1. I said we would run into them. This is our first, good reality check.

As described in Chapter 1, reality checks occur when things don't go by plan. In the real world of doing chemical reactions and making compounds, there are numerous problems which can arise along the way. Some reactions require heating and sometimes you might not heat it hot enough or you might not heat it long enough. Some reactions require cooling and then similar considerations can apply as to whether you got it cold enough or cooled it long enough. Many things can also happen even after the reaction is done. The primary goal after many reactions are done is to get the product you want separated from everything else. I can illustrate this with the $AgNO_3$/NaBr reaction which we just finished. I said we wanted to make silver bromide. Our starting point was a solution of silver nitrate and a solution of excess sodium bromide. We mix the two solutions and we make a slurry. There's the solid AgBr which you want, there's dissolved $NaNO_3$ which was the other product, there's the excess amount of NaBr reactant (still dissolved), and there's the water in which you did the reaction. OK, now you made the silver bromide and now you have to get it out of the pot. Since the AgBr formed as a solid and everything else stays dissolved in solution, then we can filter the mixture to collect the AgBr. Then we rinse it with clean water and then we dry it out. These steps are easy. Things can be much worse. What if two solids are formed and they're mixed together? What if the product you want is a liquid? What if the product you want is a gas? For some reactions there could be 5 - 10 or more steps involved. By the way, all of these steps after a reaction is done are called the "work-up".

Spills and other losses can occur anywhere along the road. If you've ever done lab experiments you may know about some of this. One thing students dread about lab class is winding up with Mr./Ms. Klutzo as their lab partner. They drop things, spill things, make a mess everywhere, etc. Each step in the process is an invitation for something to go wrong. Actually, anybody can have an accidental drop or spill. Some people are more likely than others. And anybody can have just a plain old, bad day. This stuff happens. I've been there.

Notice the parallels to cooking. Baking needs to be done at the right temperature for the right amount of time or the cake is flat. Setting a gelatin in a mold needs chilling for a certain amount of time or you wind up with slop. Spills can happen. Maybe you just cranked that old mixer up to warp speed and half of your cake batter is plastered on the wall. How about cookies? Probably one of the best series of kitchen chemistry reactions, in my opinion, is based on the Original Nestlé Toll House Chocolate Chip Cookies recipe. It says you should get 5 dozen. I've done this recipe on several occasions (years ago). I never got 60 cookies. Of course, there are special rules which apply for cookies, since cookies require multiple trays in and out of the oven in order to do the whole batch. There's a separate Law of Nature that applies to multi-tray baking operations; that Law of Nature states that, in any multi-tray baking operation, one tray must burn. You can't get around this. It doesn't matter if you preheat the oven for thirty minutes or thirty days. One tray (or more) will burn. Some of the outcome will not be the product it's supposed to be. It won't be edible. At least not by humans.

All of these things illustrate a fundamental outcome in cooking and in chemistry in general. There's the theoretical amount of product which you should get and then there's the actual amount of product which you really end up with after all reaction and work-up steps are done. This is a simple case of ideal versus real. This is the reality check.

There are several new terms to introduce. The theoretical or ideal amount of the product which you should get is called the "theoretical yield". In baking, the recipe tells you what it should be. In chemistry, the theoretical yield is the amount of product as calculated by stoichiometry. In the chocolate chip cookie recipe, the theoretical yield is 60 cookies based on using the recipe amounts. In the reaction to make silver bromide, the theoretical yield is 15.49 g AgBr based on the limiting reagent of 14.01 g $AgNO_3$.

The actual or real amount of the product which you finally end up with is called the "actual yield". This is something that happens; this is not something you can predict. For example, if you happen to wind up with 45 cookies, then that is your actual yield. If you happen to wind up with 13 g AgBr, then that is your actual yield.

A third term is "percent yield". This is just the ratio of real versus ideal written as a percentage.

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

For an actual yield of 45 cookies, your percent yield is calculated as follows.

$$\text{percent yield} = \frac{45 \text{ cookies}}{60 \text{ cookies}} \times 100\% = 75\%$$

For an actual yield of 13 g AgBr, your percent yield is calculated as follows.

$$\text{percent yield} = \frac{13 \text{ g AgBr}}{15.49 \text{ g AgBr}} \times 100\% = 84\%$$

Percent yield is a very useful measure of the overall success of the entire operation as a whole. That includes the reaction itself and all the work-up steps associated with getting the actual product out. We want a percent yield as close as possible to 100%, but sometimes you're stuck with lower and sometimes you're stuck with much lower; it depends on how hard the reaction and the work-up are to do. In research, each time someone publishes a new compound, they report how it was made, which includes the reaction and the work-up steps. In my own research group over the years, we had reported percent yields for different procedures from ~10% up to ~90%. Why the range? It just depends. And there's no sure way of predicting it in advance.

So keep these terms in mind. Theoretical yield, actual yield and percent yield. Remember that theoretical yield is ALWAYS the amount calculated by stoichiometry. And that means based on limiting reagent, too. Whenever a stoichiometry problem asks you to calculate the amount of product possible from some amount of such-and-such, then it's asking for the theoretical yield.

## Problems

1. True or false.
   a. A limiting reagent is used up completely during a reaction.
   b. Some amount of an excess reagent will be present at the end of a reaction.
   c. If a reaction is done at stoichiometric amounts of all reactants, then no reactant is in excess.
   d. A 70% yield means the theoretical yield is less than the actual yield.

2. The following equation is balanced.

$$S_4N_4 + 4\ Ag_2O \rightarrow 4\ Ag_2S + 4\ NO$$

The reaction is conducted beginning with 26.37 g $S_4N_4$ and 69.23 g $Ag_2O$. How many grams of NO can be made?

3. The following equation is balanced.

$$PCl_3 + 3\ HF \rightarrow PF_3 + 3\ HCl$$

The reaction starts with 29.6 g $PCl_3$ and 23.4 g HF.

a. How many grams of $PF_3$ can be made?

b. How many grams of HCl can be made?

c. How many grams of the excess reagent are left over at the end?

4. The reaction of hydrogen sulfide, water and elemental bromine produces sulfur dioxide and hydrogen bromide.

a. Write the balanced equation.

b 8.14 g hydrogen sulfide, 7.76 g water and 112 g bromine are combined. How many grams of sulfur dioxide can be made?

5. The following equation is balanced.

$$2\ KOH + H_2SO_4 \rightarrow K_2SO_4 + 2\ H_2O$$

The reaction is conducted using 6.21 g KOH and excess $H_2SO_4$. The actual yield of $K_2SO_4$ is 9.22 g. What is the percent yield?

6. The following equation is balanced.

$$B_2H_6 + 3\ K_2O \rightarrow 2\ K_3BO_3 + 3\ H_2$$

The reaction is conducted beginning with 60.0 g $B_2H_6$ and excess $K_2O$. The actual yield of $H_2$ is 9.66 g. What is the percent yield?