Module #1: Units, Chemical Equations, and Stoichiometry Revisited

Introduction

There are probably no concepts more important in chemistry than the three listed in the title of this module. In your first-year chemistry course, I am sure that you learned quite a lot about each of these concepts. You certainly did not learn everything, however. Whether we are talking about units, chemicals equations, or stoichiometry, there is simply too much information to possibly learn in just one year. As a result, we will take another look at each of these concepts in this first module. This will help you "warm up" to the task of recalling all of the things you learned in your first year chemistry course, and it will help to learn each of these valuable concepts at a much deeper level.

Units Revisited

Almost regardless of the chemistry course, units are always covered first, because a great deal of chemistry is based on properly analyzing units. In your first year course, you were taught how to solve problems such as the one in the following example:

EXAMPLE 1.1

A sample of iron has a mass of 254.1 mg. How many kg is that?

In this problem, we are asked to convert from milligrams to kilograms. We cannot do this directly, because we have no relationship between mg and kg. However, we do know that a milligram is the same thing as 0.001 grams and that a kilogram is the same thing as 1,000 grams. Thus, we can convert mg into g, and then convert g into kilograms. To save space, we can do that all on one line:

$$\frac{254.1 \text{ mg}}{1} \times \frac{0.001 \text{ g}}{1 \text{ mg}} \times \frac{1 \text{ kg}}{1,000 \text{ g}} = 0.0002541 \text{ kg} = 2.541 \times 10^{-4} \text{ kg}$$

The sample of iron has a mass of 2.541 x 10^{-4} kg.

Did this example help dust the cobwebs out of your mind when it comes to units? This should all be review for you. I converted the units using the factor-label method. Because this is a conversion, I had to have the same number of significant figures as I had in the beginning, and even though it was not necessary, I reported the answer in scientific notation. If you are having trouble remembering these techniques, then go back to your first-year chemistry book and review them.

There are a couple of additional things I want you to learn about units now. I am not going to show you any new techniques; I am just going to show you new ways of applying the

techniques that you should already know. Do you remember the concept of molarity? Molarity is a concentration unit that you learned in first year chemistry. It is expressed in moles per liter. There are other ways of expressing concentration, however. For example, you can express concentration in grams per milliliter instead. Well, if you have concentration in one unit, you should be able to convert it to another unit, right? Study the next example.

EXAMPLE 1.2

The concentration of HCl in a solution of muriatic acid is about 0.35 g per mL. What is the molarity of the HCl in muriatic acid?

Now remember, molarity is a concentration unit, just like grams per milliliter, so all we need to do is make a conversion. Hopefully, you remember how to convert grams into moles. You find the mass of HCl from the periodic chart and realize that the mass tells you the number of grams it takes to make a mole of HCl. The mass of HCl is 36.5 amu, so this tells us that it takes 36.5 grams of HCl to make one mole. We also know that a mL is the same as 0.001 L. Now that we know both of the relationships between what we have and what we know, we can set up the conversion:

$$\frac{0.35 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mole}}{36.5 \text{ g}} \times \frac{\text{mL}}{0.001 \text{ L}} = 9.6 \frac{\text{mole}}{\text{L}} = 9.6 \text{ M}$$

Although there is nothing new here, you probably haven't seen a conversion done in this way. Despite the fact that the unit is a derived unit (g/mL), you can still do conversions on it. I could have just converted grams to moles and gotten the unit moles/mL. I could have just converted mL to L and gotten g/L. In this case I did both. When working with derived units, remember that you can convert any unit that makes up the derived unit. Thus, 0.35 g/mL is the same thing as 9.6 M.

Okay, we are almost done reviewing units. There is just one more thing that you need to remember. Sometimes, units have exponents in them. You were probably taught how to deal with this fact in your first year chemistry course, but we need to review it so that you *really* know how to deal with it.

EXAMPLE 1.3

One commonly-used unit for volume is the cubic meter. After all, length is measured in meters, and volume is length times width times height. The more familiar unit, however, is cubic centimeters (cc) which is often used in medicine. If a doctor administers 512 cc of medicine to a patient, how many cubic meters is that?

Once again, this is a simple conversion. If, however, you do not think as you go through it, you can mess yourself up. We need to convert cubic centimeters to cubic meters. Now remember, a cubic centimeter is just a cm^3 and a cubic meter is just a m^3. Now we have no relationship between these units, but we do know that 1cm = 0.01 m. That's all we need to know, as long as we think about it. Right now, I have the following relationship:

$$1 \text{ cm} = 0.01 \text{ m}$$

This is an equation. I am allowed to do something to one side of the equation as long as I do the exact same thing to the other side of the equation. Okay, then, let's cube both sides of the equation:

$$(1 \text{ cm})^3 = (0.01 \text{ m})^3$$

$$1 \text{ cm}^3 = 0.000001 \text{ m}^3$$

Now look what we have. We have a relationship between cm^3 and m^3, exactly what we need to convert between!

$$\frac{512 \ \cancel{cm^3}}{1} \times \frac{0.000001 \text{ m}^3}{1 \ \cancel{cm^3}} = 5.12 \times 10^{-4} \text{ m}^3$$

So 512 cc's is the same as <u>5.12×10^{-4} m^3</u>.

Now when most students do a conversion like the example without thinking, they simply use the relationship between cm and m to do the conversion. That, of course does not work, because the cm^3 unit does not cancel out, and you certainly don't get the m^3 unit in the end:

$$\frac{512 \text{ cm}^3}{1} \times \frac{0.01 \text{ m}}{1 \ \cancel{cm}} = 5.12 \text{ m} \cdot \text{cm}^2$$

Do you see what happened? The cm unit canceled one of the cm out of cm^3, but that still left cm^2. Also, since m is the unit that survives from the conversion relationship, you get the weird unit of $m \, cm^2$! When you are working with units that have exponents in them, you need to be very careful about how you convert them. Make sure you are using a conversion relationship that will definitely give you the unit you want in the end.

ON YOUR OWN

1.1 The speed limit on many highways in the United States is 65 miles per hour. What is the speed limit in meters per second? (There are 1609 meters in a mile.)

1.2 The instantaneous rate of disappearance of NaOH in a chemical reaction is $1.02 \frac{\text{moles}}{\text{L} \cdot \text{s}}$.

What is the rate in $\frac{\text{grams}}{\text{mL} \cdot \text{hr}}$?

1.3 The size of a house is 1600 square feet. What is the square yardage of the house?

1.4 In physics, acceleration is expressed in the unit m/s^2. If a car accelerates at $1.1 \ m/s^2$, what is the acceleration in km/hr^2?

A New Look at Chemical Equations

In your first year chemistry course, you learned how to balance chemical equations and use them in stoichiometry. When you were balancing equations, you probably learned that chemical equations can be treated, in many ways, the same as you treat algebraic equations. For example, as you learned to balance chemical equations, you were taught that you can multiply both sides of a chemical equation by any number, just as if it were an algebraic equation. If you have the following chemical equation:

$$N_2 \ (g) + 3H_2 \ (g) \qquad 2NH_3 \ (g) \tag{1}$$

You can multiply this equation by 3 to get:

$$3N_2 \ (g) + 9H_2 \ (g) \qquad 6NH_3 \ (g) \tag{2}$$
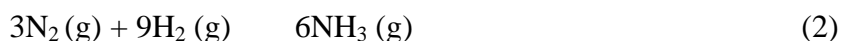
Both of these are legitimate, balanced chemical equations. Why in the world would you want to do such a thing? Well, you'll find out in a moment.
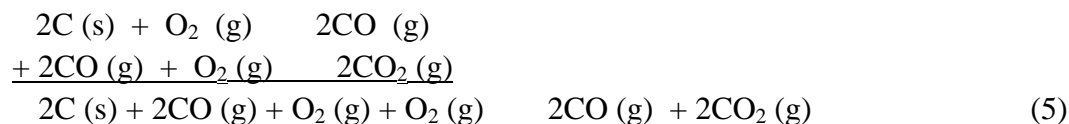
Before you find out about that, however, I need to point out something that you probably didn't realize when you learned how to multiply equations by numbers. You probably didn't realize that the same property which allows you to multiply chemical equations by numbers also allows you to *add chemical equations together*. For example, when you burn carbon in a limited amount of oxygen, the following chemical reaction occurs:

$$2C \ (s) \ + \ O_2 \ (g) \qquad 2CO \ (g) \tag{3}$$
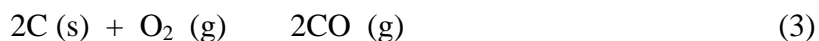
If, however, more oxygen becomes available, the carbon monoxide formed in Equation (3) can further be burned to make carbon dioxide, according to this chemical equation:

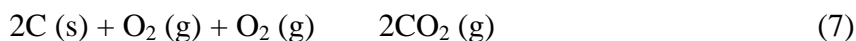$$2CO \text{ (g)} + O_2 \text{ (g)} \qquad 2CO_2 \text{ (g)} \tag{4}$$
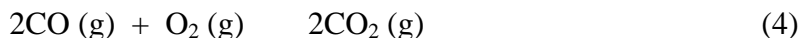
What is the overall chemical reaction, then? The carbon first burns to make carbon monoxide, but then the carbon monoxide burns to form carbon dioxide. What is the overall reaction? Well, we can *add Equations (3) and (4) to get that overall reaction*:

$$\begin{array}{l} 2C \text{ (s)} + O_2 \text{ (g)} \qquad 2CO \text{ (g)} \\ + \ 2CO \text{ (g)} + O_2 \text{ (g)} \qquad 2CO_2 \text{ (g)} \\ \hline 2C \text{ (s)} + 2CO \text{ (g)} + O_2 \text{ (g)} + O_2 \text{ (g)} \qquad 2CO \text{ (g)} + 2CO_2 \text{ (g)} \end{array} \tag{5}$$

Is Equation (5) the overall reaction, then? Not quite. Just like in algebraic equations, you can *cancel equivalent terms* from each side of the equation. Notice, for example, there is a "2CO (g)" on both sides of the equation. Thus, we can cancel them:

$$2C \text{ (s)} + \cancel{2CO \text{ (g)}} + O_2 \text{ (g)} + O_2 \text{ (g)} \qquad \cancel{2CO \text{ (g)}} + 2CO_2 \text{ (g)} \tag{6}$$

This leaves us with:

$$2C \text{ (s)} + O_2 \text{ (g)} + O_2 \text{ (g)} \qquad 2CO_2 \text{ (g)} \tag{7}$$

Is that the overall equation, then? Once again, not quite. Notice that there are 2 "O_2 (g)" terms on the left-hand side of the equation. Just like in algebraic equations, you can group like terms in chemical equations. This leaves us with:

$$2C \text{ (s)} + 2O_2 \text{ (g)} \qquad 2CO_2 \text{ (g)} \tag{8}$$
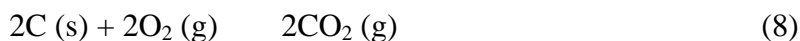
In principle, we are done, because there are no longer any equivalent terms to group or cancel. However, most chemists like to keep the stoichiometric coefficients as simple as possible. Since all of the coefficients in Equation (8) are divisible by two, we will also divide both sides of the equation by 2 to get:

$$C \text{ (s)} + O_2 \text{ (g)} \qquad CO_2 \text{ (g)} \tag{9}$$

Finally, we see that Equations (3) and (4) add up to this very simple equation.

You should see, then, that sometimes complicated chemical processes can be simplified by adding chemical equations. Study the following example which illustrates this process again.

EXAMPLE 1.4

The destruction of ozone by chlorine atoms from chlorofluorohydrocarbons (CFCs) proceeds as follows: First, a chlorine atom reacts with ozone:
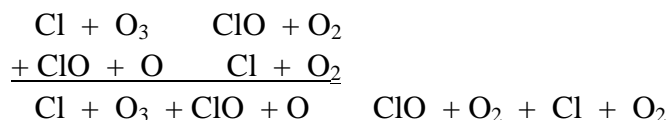
$$Cl + O_3 \qquad ClO + O_2$$

The compound ClO, however, is not stable, and it immediately reacts with free oxygen atoms in the air:

$$ClO + O \longrightarrow Cl + O_2$$
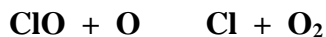
What is the overall chemical reaction for the destruction of ozone?

To find the overall reaction, we can add these two reactions up:

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$+ \underline{ClO + O \longrightarrow Cl + O_2}$$
$$Cl + O_3 + ClO + O \longrightarrow ClO + O_2 + Cl + O_2$$

Notice there are two ClO terms on each side of the equation. They can therefore be canceled. The same goes for the Cl terms on each side.

$$\cancel{Cl} + O_3 + \cancel{ClO} + O \longrightarrow \cancel{ClO} + O_2 + \cancel{Cl} + O_2$$

This gives us the following equation:

$$O_3 + O \longrightarrow O_2 + O_2$$

To finish up, we can group the two O_2 terms on the right side of the equation:

$$\underline{O_3 + O \longrightarrow 2O_2}$$

So once again, the final equation is much simpler than the previous equations which describe the process.

Now I want you to notice something about the example you just studied. Notice that while Cl is a reactant in the first equation, it is not a reactant in the overall equation. Why? Well, although Cl is used up in the first equation, it is produced in the second equation. As a result, the amount of Cl present never changes. Thus, when you look at the overall reaction, it looks like Cl just isn't a part of the reaction. Now you should remember from your first year course that we give a name to substances that take part in chemical reactions but do not get used up or produced. We call them **catalysts**. In this case, Cl is acting like a catalyst. When someone shows you the way ozone is destroyed on a step-by-step basis, you see Cl being both used and then later produced. However, when you view the overall reaction, you lose all information regarding Cl.

You should also remember from your first year chemistry course that when a chemical reaction is presented in a step-by-step manner, we call that a **reaction mechanism**. In chemical terminology, then, the first two equations I presented in the example are the reaction mechanism for the overall reaction that we determined by the end of the example. Which way is best to show the reaction? That depends on what you are looking for. The reaction mechanism is a

detailed description of the reaction process, but it is so detailed that you might miss the overall effect of the chemical reaction. The overall equation gives you a good view of what happens, but you lose detail. Make sure that you can add chemical equations together by performing the following "on your own" problem.

ON YOUR OWN

1.5 When nitrogen dioxide gas is mixed with carbon monoxide gas, two reactions occur. In the first reaction, two NO_2 molecules react as follows:

$$2NO_2 (g) \quad NO_3 (g) + NO (g)$$

The nitrogen trioxide formed in that reaction then reacts with the carbon monoxide present as follows:

$$NO_3 (g) + CO (g) \quad NO_2 (g) + CO_2 (g)$$

What is the overall chemical reaction that occurs?

A New Look At Hess's Law

Okay, so now we can add chemical equations together. What's the big deal? Well, do you remember Hess's Law? You learned it in your first year course as a way to calculate the **change in enthalpy** of a chemical reaction. Remember, the change in enthalpy (abbreviated as H) tells us how much energy is released into the surroundings (when H is negative) or absorbed by the reaction (when H is positive). You should have learned Hess's Law as:

$$H = \quad H_f \text{ (products) } - \quad H_f \text{ (reactants)} \tag{10}$$

Where H is the change of enthalpy of the reaction, and H_f is the enthalpy of formation of the reactants and the products. When using Equation (10), you take the H_f for each product (you look them up in a table), multiply by the stoichiometric coefficient of the product, and subtract from that the sum of the H_f's of each reactant times its stoichiometric coefficient. When you are done, you have the H of the chemical reaction.

Well, it turns out that this formulation of Hess's Law is really only a special application of Hess's Law. Remember, Hess's Law is stated as follows:

Hess's Law - Energy is a state function and is therefore independent of path.

In your first year course, you should have learned that Equation (10) is a consequence of this statement. However, the statement itself tells us something much more dramatic. Hess's Law

tells us that the Δ H of a chemical reaction is independent of *how* the reaction takes place. In other words, suppose I looked at the overall chemical equation for the destruction of ozone:

$$O_3 + O \rightarrow 2O_2 \tag{11}$$

Hess's Law states *regardless of how this reaction occurs, the Δ H is the same*.

What do I mean by this? Well, as you saw in the previous section, chlorine that comes from CFCs is a catalyst in the destruction of ozone. There are, however, many other catalysts from ozone destruction, including hydrogen atoms. Here's how a hydrogen atom catalyzes the decomposition of ozone:

$$H + O_3 \rightarrow OH + O_2 \tag{12}$$
$$OH + O \rightarrow H + O_2 \tag{13}$$

You can verify for yourself that the overall chemical reaction produced in these two steps is precisely the same as Equation (11), which is the overall chemical equation produced by the chlorine-catalyzed decomposition sequence shown in the previous section.
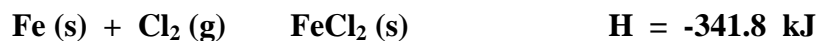
Hess's Law states that whether ozone is destroyed with a chlorine catalyst or a hydrogen catalyst, the overall change in enthalpy will be the same, because the overall chemical reaction is the same. Thus, it does not matter *how* the reaction occurs. The Δ H will always be the same, as long as the overall chemical reaction is the same.

How is this possible? Think about it. Each chemical equation has its own Δ H. Thus, Equation (12) and Equation (13) each have their own Δ H. Similarly, each step of the reaction mechanism presented in Example 1.4 also has its own Δ H. The energetics work out so that when you add the Δ H's of each individual step in a reaction mechanism (just like you added the equations), the total Δ H will always be the same as long as the final reaction is the same!

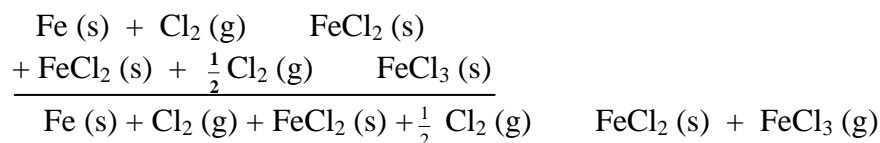If all of that is just a little over your head, study the next example to see how it works.

EXAMPLE 1.5

When solid iron and chlorine gas are reacted together, the product is solid $FeCl_3$. This reaction (most likely) proceeds in two steps:

$$Fe \ (s) + Cl_2 \ (g) \rightarrow FeCl_2 \ (s) \qquad \Delta H = -341.8 \ kJ$$
$$FeCl_2 \ (s) + \frac{1}{2}Cl_2 \ (g) \rightarrow FeCl_3 \ (s) \qquad \Delta H = -57.7 \ kJ$$

What is the overall reaction and its Δ H?

To get the overall reaction, we add these two reactions together:

$$Fe \text{ (s)} + Cl_2 \text{ (g)} \quad FeCl_2 \text{ (s)}$$
$$+ FeCl_2 \text{ (s)} + \tfrac{1}{2} Cl_2 \text{ (g)} \quad FeCl_3 \text{ (s)}$$
$$\overline{Fe \text{ (s)} + Cl_2 \text{ (g)} + FeCl_2 \text{ (s)} + \tfrac{1}{2} Cl_2 \text{ (g)} \quad FeCl_2 \text{ (s)} + FeCl_3 \text{ (g)}}$$

Once we cancel the $FeCl_2$ (s) on each side of the equation and group the Cl_2 (g) terms on the left-hand side of the equation together, we get the overall reaction:

$$\underline{Fe \text{ (s)} + \tfrac{3}{2} Cl_2 \text{ (g)} \quad FeCl_3 \text{ (s)}}$$
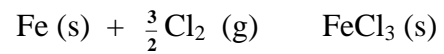
Now don't be concerned about the fraction in the equation. Although there is no such thing as 3/2 of a Cl_2 molecule, there is no real problem with the fraction in the equation. If we wanted to, we could multiply the equation by 2 to get rid of the fraction, but as we will see in a moment, that can lead to some complications with Hess's Law.

Well, now that we figured out the overall equation, how do we get the H? Since we just added the two equations together to get the overall equation, we can just add the two H's together to get the overall H.

$$H = -341.8 \text{ kJ} + -57.7 \text{ kJ} = -399.5 \text{ kJ}$$
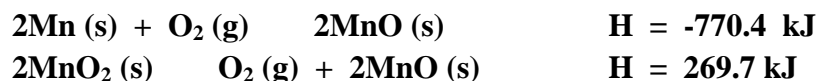
The overall H, then, is <u>-399.5 kJ</u>.

So Hess's Law states that if we can add two equations together to get an overall chemical equation, we can add the H's to get the overall H. Now notice in the example that I said the reaction mechanism presented is *probably* the way that iron and chlorine gas react. Well, if we're not correct and the reaction mechanism is different, does that mean that the overall H we just calculated is wrong? NO! That's the beauty of Hess's Law. Since enthalpy is a state function and is independent of path, it doesn't matter whether or not the reaction actually occurs that way! If it occurs that way, or if it occurs another way, the overall H will be the same!

Think, for a moment, about the implications here. Whether or not we know *how* a chemical reaction works, if we can add other equations together to get the overall equation, we can calculate the H! So, if we know the H of a few equations and we can add up those equations to get an overall chemical equation, we can add the individual H's to get the overall equation's H.
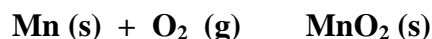
Okay, you might be thinking, that doesn't sound so bad. Well, in principle, it's not. However, things can get really tricky when you start realizing that since we can multiply equations by a number as well as add them together, we can find ways to construct *a lot* of overall chemical equations. Study the following example to see what I mean.

EXAMPLE 1.6

Given the following information:

$$2Mn \text{ (s) } + O_2 \text{ (g)} \longrightarrow 2MnO \text{ (s)} \qquad \Delta H = -770.4 \text{ kJ}$$
$$2MnO_2 \text{ (s)} \longrightarrow O_2 \text{ (g)} + 2MnO \text{ (s)} \qquad \Delta H = 269.7 \text{ kJ}$$

Calculate the ΔH for

$$Mn \text{ (s) } + O_2 \text{ (g)} \longrightarrow MnO_2 \text{ (s)}$$

Now that we know Hess's Law allows us to add up chemical equations and their corresponding ΔH's all we need to do is figure out how to get the first two equations to add up to the third. Now if you look at the first two equations, it is clear that we cannot just add them together. For example, our final equation has MnO_2 (s) as a product, but neither of the first two reactions have MnO_2 (s) as a product. If we just add the two equations together, then, there will not be an MnO_2 (s) on the products side. Are we out of luck? Not at all.

You should remember from your first year chemistry course that *any* chemical equation can be written backwards, with the products as reactants and reactants as products. The second equation written backwards is as follows:

$$O_2 \text{ (g)} + 2MnO \text{ (s)} \longrightarrow 2MnO_2 \text{ (s)}$$
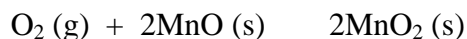
We now have MnO_2 (s) as a product. Wait a minute, though, if we write the equation backwards, what happens to ΔH? Well, the ΔH given above indicates that when the reaction runs as written, the reaction absorbs 269.7 kJ of energy. Well, if we write the equation backwards, then we are talking about the *reverse* of the reaction. If the reaction as written *absorbs* 269.7 kJ of energy, then the reverse reaction will *release* 269.7 kJ of energy. How do we denote that? When a reaction releases energy, its ΔH is negative. Thus, for the reaction as written above,
$\Delta H = -269.7$ kJ.

Okay, so now we have two reactions that we can add up to get the third, right? Not quite. After all, if we add this equation to the very first one we were given, then we would have $2MnO_2$ (s) as a product. What we are looking for is an equation that has MnO_2 (s) as a product *without* the 2. Are we out of luck, then? Not at all. Remember, we can multiply chemical equations by numbers, so let's multiply the equation above by one-half:

$$\tfrac{1}{2} O_2 \text{ (g)} + MnO \text{ (s)} \longrightarrow MnO_2 \text{ (s)}$$
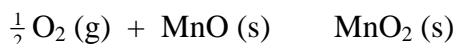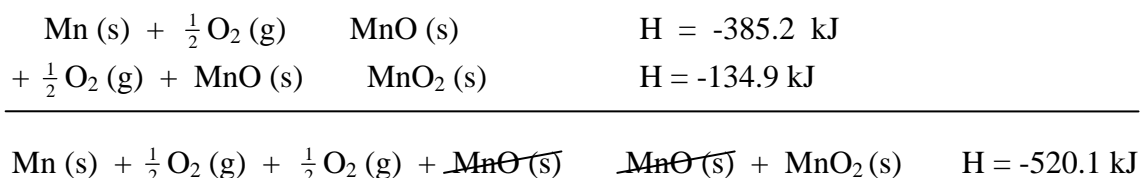
Now we have MnO_2 (s) as a product, just as it is in the equation we want to end up with. What about the ΔH, however? Is the ΔH the same? No. Remember, the ΔH tells us about how much

energy is released or absorbed in a reaction. If I multiply the equation by 1/2, then only half as much energy will be released. Thus, I need to multiply ΔH by 1/2 as well, making the new ΔH = -134.9 kJ.

Are we ready to add the equations, then? Not quite. Look at the first equation. It has 2Mn (s) as a reactant. The equation we want, however, has only one Mn (s) as a reactant. Thus, we need to multiply that equation (and its ΔH) by one half:

$$Mn \ (s) \ + \ \tfrac{1}{2} O_2 \ (g) \longrightarrow MnO \ (s) \qquad \Delta H \ = \ -385.2 \ kJ$$
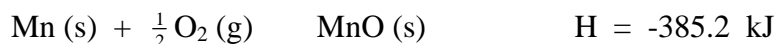
Now we can finally add the equations together, along with their ΔH's:

$$Mn \ (s) \ + \ \tfrac{1}{2} O_2 \ (g) \longrightarrow MnO \ (s) \qquad \Delta H \ = \ -385.2 \ kJ$$
$$+ \ \tfrac{1}{2} O_2 \ (g) \ + \ MnO \ (s) \longrightarrow MnO_2 \ (s) \qquad \Delta H = -134.9 \ kJ$$

$$Mn \ (s) \ + \ \tfrac{1}{2} O_2 \ (g) \ + \ \tfrac{1}{2} O_2 \ (g) \ + \ \cancel{MnO \ (s)} \longrightarrow \cancel{MnO \ (s)} \ + \ MnO_2 \ (s) \qquad \Delta H = -520.1 \ kJ$$

Once we cancel the MnO (s) on each side of the equation and group the O_2 (g) terms on the reactants side of the equation, we get:

$$Mn \ (s) \ + \ O_2 \ (g) \longrightarrow MnO_2 \ (s)$$
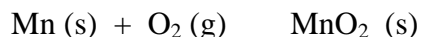
This is exactly the equation for which we wanted to calculate the ΔH. Thus, $\underline{\Delta H = -520.1 \ kJ}$.

Do you see what happened in the example? Hess's Law says that we can add *any* equations together and, when we do that, the ΔH of the overall reaction will be the sum of the ΔH's for the individual reactions that we added together. So, in order to calculate the ΔH of the reaction, I just kept manipulating the equations until they could add together to make the chemical equation for which I wanted to calculate the ΔH. If I reversed the chemical equation, I changed the sign on the ΔH. If I multiplied the equation by a number, then I multiplied the ΔH by the same number. In the end, when the equations could add up to the equation in which I was interested, the ΔH's would add to the ΔH of the reaction in which I was interested.

Let's see how that happens in another example. As you study the example, keep in mind the following statements:

When you reverse a chemical equation, the ΔH of the reaction changes sign.

When you multiply a chemical equation by a number, you must multiply the ΔH by that same number.

EXAMPLE 1.7

Calculate the ΔH of the following reaction:

$$Zn\ (s)\ +\ S\ (s)\ +\ 2O_2\ (g)\ \longrightarrow\ ZnSO_4\ (s)$$

from the following information:

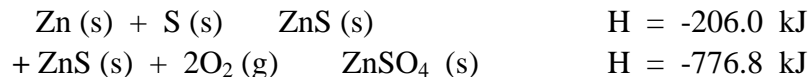|		
$ZnS\ (s)\ \longrightarrow\ Zn\ (s)\ +\ S\ (s)$		**$\Delta H = 206.0\ kJ$**
$\frac{1}{2}ZnS\ (s)\ +\ O_2\ (g)\ \longrightarrow\ \frac{1}{2}ZnSO_4\ (s)$		**$\Delta H = -388.4\ kJ$**

To solve this problem, we just need to manipulate these two equations until they add to the one in which we are interested. To start out, the equation that we are interested in has Zn (s) and S (s) as reactants. Of the two equations we are given, only the first one has these two elements in it. Unfortunately, they are on the wrong side of the equation. We need them as reactants, not products. So, we need to reverse the chemical equation. When we do that, we need to change the sign on the ΔH:

$$Zn\ (s)\ +\ S\ (s)\ \longrightarrow\ ZnS\ (s)\qquad\qquad \Delta H = -206.0\ kJ$$

In the second equation we are given, the $ZnSO_4$ (s) is on the products side, as it is in our equation of interest. In addition, the O_2 (g) is on the reactants side, as it is in our equation of interest. Thus, we need not reverse the reaction here. However, notice that we need one $ZnSO_4$ (s) as a product, but the equation has only 1/2 of that substance. Therefore, we need to multiply the second equation by 2. When we do that, we need to multiply the ΔH by 2 as well.

$$ZnS\ (s)\ +\ 2O_2\ (g)\ \longrightarrow\ ZnSO_4\ (s)\qquad\qquad \Delta H = -776.8\ kJ$$
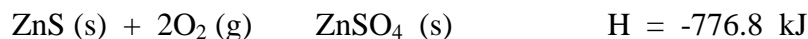
Now we have 2 equations that have everything we need all in the right places. Thus, we just need to add them up. If they add to the equation of interest, then the sum of their ΔH's will add to the ΔH of the equation of interest.

$$\begin{aligned}
&Zn\ (s)\ +\ S\ (s)\ \longrightarrow\ ZnS\ (s) &\Delta H = -206.0\ kJ\\
+\ &ZnS\ (s)\ +\ 2O_2\ (g)\ \longrightarrow\ ZnSO_4\ (s) &\Delta H = -776.8\ kJ
\end{aligned}$$

$$Zn\ (s) + S\ (s) + \cancel{ZnS\ (s)} + 2O_2\ (s)\ \longrightarrow\ \cancel{ZnS\ (s)}\ +\ ZnSO_4\ (s)\qquad \Delta H = -982.8\ kJ$$

Once we cancel the ZnS (s) from both sides of the equation, we have the chemical equation we originally wanted, so we also have the ΔH:
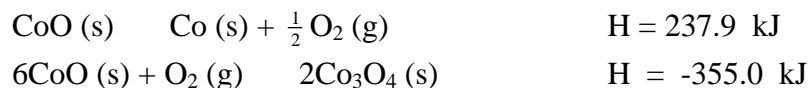
$$Zn\ (s) + S\ (s) + 2O_2\ (s)\ \longrightarrow\ ZnSO_4\ (s)$$
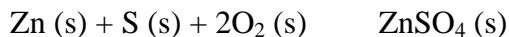
Which means $\underline{\Delta H = -982.8\ kJ}$.

So when we use Hess's Law, it sometimes works like a puzzle. If you have a few equations with known   H's, then you can manipulate them to get the equation in which your are interested. Once you do that, you can get the   H of that equation. If you noticed how I went about attacking the problem, you will see that I look at each equation individually and decide first whether or not it has the substances I want on the correct side of the equation. If not, I reversed the equation and changed the sign of the   H. Next, I looked at the stoichiometric coefficients. If the equation did not have the proper stoichiometric coefficient, then I multiplied the equation as well as the   H.
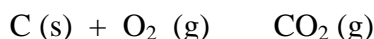
Now I want you to notice something about the example problem. Think back to the classifications that you learned for chemical reactions in your first year chemistry course. How would you classify the reaction whose   H you calculated? It's a formation reaction, because it forms $ZnSO_4$ from its constituent elements. Now if you remember, when you used Hess's Law in your first year chemistry course, the   H's you looked up in tables were   H's of formation. Did you ever wonder where those numbers came from? Well, some came directly from experiment, because it is possible to run some formation reactions in a calorimeter. Other formation reactions, however, do not lend themselves to measurements of the   H. To measure the   H of those formation reactions, chemists measure the   H's of related chemical reactions and then perform calculations like the ones in Examples 1.6 and 1.7.
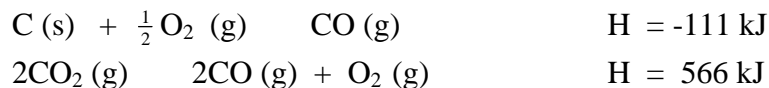

ON YOUR OWN

1.6 Calculate the   H of formation for Co_3O_4 (s) given the following information:

CoO (s) Co (s) + $\frac{1}{2}O_2$ (g)   H = 237.9 kJ

$6CoO$ (s) + O_2 (g) $2Co_3O_4$ (s)   H = -355.0 kJ

1.7 Calculate the   H for the combustion of carbon:

C (s) + O_2 (g) CO_2 (g)

Given that

C (s) + $\frac{1}{2}O_2$ (g) CO (g)   H = -111 kJ

$2CO_2$ (g) $2CO$ (g) + O_2 (g)   H = 566 kJ


Stoichiometry and Limiting Reagents

The subject of stoichiometry is probably the most fundamental aspect of chemistry. Although you might think you learned all there is to know about stoichiometry, there is still

plenty more to learn. Before we hit that, however, I want to go through one quick example of stoichiometry in an attempt to further dust the cobwebs from your mind.


EXAMPLE 1.8

When hydrogen and oxygen are ignited, a violent reaction occurs, releasing a huge amount of energy, usually in the form of an explosion. This reaction, which produces water, is responsible for the 1937 explosion that destroyed the famous dirigible known as the Hindenburg. If 10.0 grams of oxygen are ignited in an excess of hydrogen, how many grams of water will be formed?

In this problem, we are given the number of grams of oxygen and are also told that oxygen is the limiting reagent because there is an excess of hydrogen. Thus, the amount of products produced will be dependent only on the amount of oxygen in the reaction. Well, we are told (in words) what the reaction is, so we start there:

$$H_2 \text{ (g)} \; + \; O_2 \text{ (g)} \qquad H_2O \text{ (g)}$$
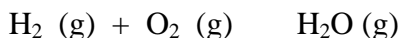
The equation is not balanced, so we have to do that first:

$$2H_2 \text{ (g)} \; + \; O_2 \text{ (g)} \qquad 2H_2O \text{ (g)}$$
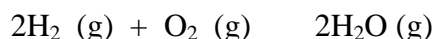
Now we know how oxygen relates to water in this reaction. For every one mole of oxygen gas, 2 moles of water are formed. Of course, we do not have the number of moles of oxygen, we have grams. Thus, to be able to use the chemical equation at all, we must first convert to moles:

$$\frac{10.0 \, \text{g} \, O_2}{1} \times \frac{1 \text{ mole } O_2}{32.0 \text{ g } O_2} = 0.313 \text{ moles } O_2$$

Now that we have moles of oxygen, we can use the information in the chemical equation's stoichiometric coefficients to convert from moles of oxygen to moles of water:

$$\frac{0.313 \text{ moles } O_2}{1} \times \frac{2 \text{ moles } H_2O}{1 \text{ mole } O_2} = 0.616 \text{ moles } H_2O$$

That tells us the answer in moles, but the nasty guy who wrote the problem wants the answer in grams, so we have one more conversion to go:

$$\frac{0.616 \text{ moles} \, H_2O}{1} \times \frac{18.0 \text{ g } H_2O}{1 \text{ mole } H_2O} = 11.3 \text{ g } H_2O$$

The reaction produces 11.3 g H₂O.

Does that example ring a few bells? It should! You did those kinds of exercises over and over again in your first year chemistry course. There were a couple of things you probably didn't cover, however. Notice that in the example, you were told what the limiting reagent was because you were told that the other reagent (hydrogen) was "in excess." Suppose you weren't told that. Suppose you were just told how much of each reagent was in the experiment. Is there any way that you can determine what the limiting reagent is on your own? Study the following example to find out.

EXAMPLE 1.9

PCl_5 is an important ingredient in the making of certain insecticides. It can be made by the following reaction:

$$P_4 \text{ (s)} + 10Cl_2 \text{ (g)} \quad 4PCl_5$$

How many grams of PCl_5 can be made from 10.0 g of P_4 and 30.0 g of Cl_2?

In this problem, we are not told what reagent is in excess and what one is the limiting reagent. We will have to determine that for ourselves. How can we do this? Well, the chemical equation says that for every 1 mole of P_4, there must be 10 moles of Cl_2. Let's convert to moles to see if that is really the relationship between moles of P_4 and moles of Cl_2.

$$\frac{10.0\,g\,P_4}{1} \times \frac{1 \text{ mole } P_4}{124 \text{ g}\,P_4} = 0.0806 \text{ moles } P_4$$

$$\frac{30.0\,g\,Cl_2}{1} \times \frac{1 \text{ mole } Cl_2}{71.0\,g\,Cl_2} = 0.423 \text{ moles } Cl_2$$

Looking at those two numbers, we see that there are many, many more moles of Cl_2 than of P_4. Does this mean that P_4 is the limiting reagent? No! We have to look at the chemical equation to do that. The chemical equation tells us that for every one mole of P_4, there must be 10 moles of Cl_2. Well, since we have 0.0806 moles of P_4, there need to be 0.806 moles of Cl_2. Are there that many moles of Cl_2? No, there are only 0.423 moles of Cl_2. What does that tell us? Well, it tells us that there isn't enough Cl_2 to take care of the P_4 that we have. This means that Cl_2 will run out before P_4 does, making Cl_2 the limiting reagent!

Now that we know Cl_2 is the limiting reagent, we know that all products are limited by the amount of Cl_2. Thus, the amount of P_4 is irrelevant, and we can continue on in our calculation using just the number of moles of Cl_2. We can use the information in the chemical equation's stoichiometric coefficients to convert from moles of Cl_2 to moles of PCl_5:

$$\frac{0.423 \text{ moles } Cl_2}{1} \times \frac{4 \text{ moles } PCl_5}{10 \text{ moles } Cl_2} = 0.169 \text{ moles}\,PCl_5$$

That tells us the answer in moles, but we need the answer in grams, so we have one more conversion to go:

$$\frac{0.169 \; \cancel{\text{moles} \, PCl_5}}{1} \times \frac{208.5 \; \text{g} \; PCl_2}{1 \; \cancel{\text{mole} \, PCl_5}} = 35.2 \; \text{g} \; PCl_2$$

The reaction produces <u>35.2 g PCl$_5$</u>.

Do you see what I did to determine what the limiting reagent was? I looked at the chemical equation and determined how many moles of one reactant it would take to completely use up the other reactant. I then calculated the number of moles of each reactant and looked for that relationship. In this case, there needed to be 10 times as many moles of Cl_2 as PCl_5. There weren't. This told me that Cl_2 would get used up first and was therefore the limiting reagent. What if there had been more than 10 times as many moles of Cl_2 as there were moles of P_4? Well, then I would know that after all of the P_4 was used up, there would still be Cl_2. Thus, P_4 would be used up first and would therefore be the limiting reagent.

Now before I go on to show you two more examples, I want to point out a couple of things. Notice first that even though there were 3 times as many grams of Cl_2 as there were of P_4, Cl_2 was still the limiting reagent. Why? Remember that grams *have nothing to do with a chemical equation*. The number of grams of a reactant doesn't tell you anything about how much product will be made. In order to know anything about how a reactant relates to another reactant or to a product, you must compare *moles*.

Okay, then, let's compare moles. There are many, many more moles of Cl_2 than there are of P_4 in the example. Why, then, was Cl_2 the limiting reagent. Well, even though we are talking moles now, we still need to look at the chemical equation to see *how many* moles of each reactant are needed. Looking at the chemical equation, 10 times as many moles of Cl_2 were needed as compared to P_4. Since there was not anything close to 10 times as many moles of Cl_2, then Cl_2 was the limiting reagent. It is *very* important for you to realize that you cannot use number of grams or even number of moles by itself to determine limiting reagent. You *must* take a look at the chemical equation to determine *how many moles* of each reactant is needed. Only then can you determine the limiting reagent. See how this happens in the next two examples.

EXAMPLE 1.10

Calcium acetate [Ca(CH$_3$CO$_2$)$_2$] is a chemical important in the process of dyeing fabrics. It is made with the following reaction:

Ca(OH)$_2$ + 2CH$_3$CO$_2$H   Ca(CH$_3$CO$_2$)$_2$ + 2H$_2$O

How many grams of calcium acetate can be made from 10.0 grams of each reactant?

We need to determine the limiting reagent before we can really answer the question. Looking at the chemical equation, there need to be 2 moles of CH_3CO_2H for every one mole of $Ca(OH)_2$. Let's convert to moles to see if that is really the relationship between the number of moles of each reactant.

$$\frac{10.0\ g\ \cancel{CH_3CO_2H}}{1} \times \frac{1\ mole\ CH_3CO_2H}{60.0 g\ \cancel{CH_3CO_2H}} = 0.167\ moles\ CH_3CO_2H$$

$$\frac{10.0 g\ \cancel{Ca(OH)_2}}{1} \times \frac{1\ mole\ Ca(OH)_2}{74.1 g\ \cancel{Ca(OH)_2}} = 0.135\ moles\ Ca(OH)_2$$

Are there 2 moles of CH_3CO_2H for every one mole of $Ca(OH)_2$? Well, since there are 0.135 moles of $Ca(OH)_2$, there would need to be 0.270 moles of CH_3CO_2H. There aren't quite that many, so CH_3CO_2H will run out first.

Now that we know CH_3CO_2H is the limiting reagent, we know that all products are limited by the amount of CH_3CO_2H. Thus, the amount of $Ca(OH)_2$ is irrelevant, and we can continue on in our calculation using just the number of moles of CH_3CO_2H.

$$\frac{0.167\ \cancel{moles\ CH_3CO_2H}}{1} \times \frac{1\ mole\ Ca(CH_3CO_2)_2}{2\ \cancel{moles\ CH_3CO_2H}} = 0.0835\ moles Ca(CH_3CO_2)_2$$

$$\frac{0.0835\ \cancel{moles Ca(CH_3CO_2)_2}}{1} \times \frac{158.1 g\ Ca(CH_3CO_2)_2}{1\ \cancel{mole Ca(CH_3CO_2)_2}} = 13.2\ g\ Ca(CH_3CO_2)_2$$

The reaction produces <u>13.2 g $Ca(CH_3CO_2)_2$</u>.

Rutile (TiO_2) is now used as a pigment in white paints. It replaces the toxic pigment known as white lead, whose chemical formula is $Pb_3(OH)_2(CO_3)_2$. Rutile is made from a natural ore ($FeTiO_3$) via the following reaction:

$$2FeTiO_3\ +\ 4HCl\ +\ Cl_2 \qquad 2FeCl_3\ +\ 2TiO_2\ +\ 2H_2O$$

How many grams of Rutile will be made from 50.0 g of $FeTiO_3$, 100.0 g HCl, and an excess of Cl_2?

We need to determine the limiting reagent before we go any further. We know that Cl_2 is not the limiting reagent because we are told there is an excess of Cl_2. Thus, the only real question is whether $FeTiO_3$ or HCl is the limiting reagent. Looking at the chemical equation, there need to be 2 moles of $FeTiO_3$ for every 4 moles of HCl. Let's convert to moles to see if that is really the relationship between the number of moles of each reactant.

$$\frac{50.0 \text{ g FeTiO}_3}{1} \times \frac{1 \text{ mole FeTiO}_3}{151.7 \text{ g FeTiO}_3} = 0.330 \text{ moles FeTiO}_3$$

$$\frac{100.0 \text{ g HCl}}{1} \times \frac{1 \text{ mole HCl}}{36.5 \text{ g HCl}} = 2.74 \text{ moles HCl}$$

Are there 2 moles of $FeTiO_3$ for every 4 moles of HCl? Well, since there are 0.334 moles of $FeTiO_3$, there would need to be twice as many moles of HCl, or 0.668 moles. There are a LOT more than that present, which means that after all of the $FeTiO_3$ is used up, there will still be a lot of HCl left over. Thus, $FeTiO_3$ is the limiting reagent.

Now that we know $FeTiO_3$ is the limiting reagent, we know that all products are limited by the amount of $FeTiO_3$. Thus, the amount of HCl (and Cl_2) is irrelevant, and we can continue on in our calculation using just the number of moles of $FeTiO_3$.

$$\frac{0.330 \text{ moles FeTiO}_3}{1} \times \frac{2 \text{ moles TiO}_2}{2 \text{ moles FeTiO}_3} = 0.330 \text{ moles TiO}_2$$

$$\frac{0.330 \text{ moles TiO}_2}{1} \times \frac{79.9 \text{ g TiO}_2}{1 \text{ mole TiO}_2} = 26.4 \text{ g TiO}_2$$

The reaction produces 26.4 g TiO_2.

In order to determine the limiting reagent, then, we convert all reactants to moles and try to determine which will run out first by comparing the amount of moles we have to the mole relationship in the chemical equation. Whichever reactant runs out first is the limiting reagent, and we use it to determine everything else. Try this on your own.

ON YOUR OWN

1.8 One of the ores which we mine for silver is $KAg(CN)_2$. In order to get silver from this, it must be processed in the following reaction:

$$2KAg(CN)_2 \text{ (aq)} + Zn \text{ (s)} \qquad 2Ag \text{ (s)} + Zn(CN)_2 \text{ (aq)} + 2KCN \text{ (aq)}$$
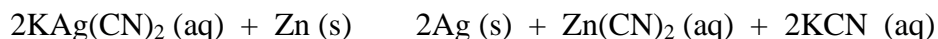
How many grams of silver will be produced when 100.0 g of $KAg(CN)_2$ is reacted with 75.0 g Zn?

1.9 Many of the barbecue grills that people have in their backyard use the combustion of propane (C_3H_8) for heat. How many grams of water would be produced by the combustion of 10.0 g of propane with 75.0 g of oxygen gas? You have to remember the definition of a combustion reaction in order to get the chemical equation you need to solve this problem!

Stoichiometry, Percent Yield, and Multiple Reactions

Now that you've dusted the cobwebs out of your mind when it comes to stoichiometry, there is one more skill I want you to learn in this module. Stoichiometry is a powerful tool in chemistry, and it is used over and over again, especially in situations where chemists are synthesizing compounds. Since you have the basic tools of stoichiometry in your mind now, it is important to make you aware of at least two things that complicate stoichiometry in the "real world." The first concept is **percent yield** and the second is the fact that most chemical processes in the real world use more than just one reaction to make the product of interest.

The first concept is the easiest of the two to learn, and it is really just a consequence of experimental error. When you use stoichiometry to calculate how much product will be produced in a chemical reaction, the number that you get is really an upper limit. In other words, no matter how careful an experimenter you are, when you actually perform the reaction in a lab, you will never, never get as much product as stoichiometry indicates that you should. This isn't because stoichiometry is wrong, but it is because experimental error will *always* result in lost product. Even the most talented experimenter in the world will not make as much product as he or she *should* make, because of unavoidable experimental errors.

Because you can never make as much product as stoichiometry indicates that you should, chemists use the concept **percent yield**.

Percent yield - The actual amount of product you make in a chemical reaction, divided by the amount stoichiometry indicates you should have made, times 100

If you look at the definition, you can see what percent yield tells us. Suppose stoichiometry says that I should make 10.0 grams of a substance in a chemical reaction. When I do the reaction and measure the mass of the product, I see that I actually made 9.0 grams. The percent yield would be:

$$\frac{9.0 \text{ g}}{10.0 \text{ g}} \times 100\% = 90\%$$
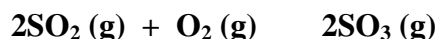
This means that I made 90% of what I should have made. Percent yield, therefore, is high when there are few experimental errors and is low when there are many. In a moment, you will see some problems with percent yield.

The second concept is a little harder to master. When chemists synthesize compounds, the process is usually quite long and complicated, involving several different reactions.

Chemists still have to employ stoichiometry to determine how much starting materials to use, but they must apply stoichiometry to several reactions. How can that be done? Study the following example to find out.


EXAMPLE 1.11

Sulfuric acid (H_2SO_4) is one of the Unites States' most important exported commodities. The following three equations illustrate one of the ways it is prepared commercially from iron sulfide:

$$4FeS_2 \text{ (s)} + 11O_2 \text{ (g)} \quad 2Fe_2O_3 \text{ (s)} + 8SO_2 \text{ (g)}$$

$$2SO_2 \text{ (g)} + O_2 \text{ (g)} \quad 2SO_3 \text{ (g)}$$

$$SO_3 \text{ (g)} + H_2O \text{ (l)} \quad H_2SO_4 \text{ (l)}$$

If a chemist starts with 1.13 kilograms of FeS_2 and an excess of oxygen and water, how much H_2SO_4 should be produced? If the chemist actually produces 1.51 kg of H_2SO_4, what is the chemist's percent yield?

How do we go about solving this? We know that FeS_2 is the limiting reagent, but how do we calculate the amount of H_2SO_4 made? Well, we could calculate how much SO_2 is made in the first reaction, and then use it to calculate how much SO_3 is made in the second reaction. Then we could use that result in the third reaction to finally find out what we want to know. Sounds like a lot of work, doesn't it? Well, it is a lot of work and, quite frankly, it is not necessary. After all, look at the product in which we are interested: H_2SO_4. It has hydrogen atoms, sulfur atoms, and oxygen atoms in it. Where do the hydrogen atoms come from? They come from the water that is a reactant in the third reaction. Where do the oxygen atoms come from? They come from the water and oxygen used as reactants in all three equations. Where do the sulfur atoms come from? They come from the FeS_2.

Now think about it a minute. The hydrogen and oxygen atoms come from reactants which we are told are in excess. The sulfur atoms come from the limiting reagent: FeS_2. So, the sulfur atoms in sulfuric acid all come from the limiting reagent FeS_2. What if I have one mole of FeS_2. Given an excess of water and oxygen, how much H_2SO4 can come from 1 mole of FeS_2? Well, 1 mole of FeS_2 will give us two moles of sulfur atoms, right? Given plenty of hydrogen and oxygen atoms (from water and oxygen), then 2 moles of sulfur atoms will give us 2 moles of sulfuric acid. In the end, then, these three chemical equations work together to tell us that when water and oxygen are in excess, each mole of FeS_2 will give us 2 moles of H_2SO_4. In other words:

$$1 \text{ mole } FeS_2 = 2 \text{ moles } H_2SO_4$$
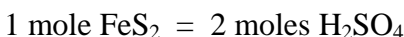
This relationship is all we need to do the stoichiometry:

$$\frac{1.13\times 10^{3} \text{ g FeS}_2}{1} \times \frac{1 \text{ mole FeS}_2}{120.0 \text{ g FeS}_2} = 9.42 \text{ moles FeS}_2$$

$$\frac{9.42 \text{ moles FeS}_2}{1} \times \frac{2 \text{ moles H}_2\text{SO}_4}{1 \text{ moles FeS}_2} = 18.8 \text{ moles H}_2\text{SO}_4$$

$$\frac{18.8 \text{ moles H}_2\text{SO}_4}{1} \times \frac{98.1 \text{ g H}_2\text{SO}_4}{1 \text{ mole H}_2\text{SO}_4} = 1.84 \times 10^{3} \text{ g H}_2\text{SO}_4$$

So these three reactions should produce 1.84 kg H$_2$SO$_4$. Since the chemist produced only 1.51 kg of sulfuric acid, the percent yield is:

$$\frac{1.51 \text{ kg}}{1.84 \text{ kg}} \times 100\% = 82.1\%$$

The percent yield, then, is 82.1%.

Do you see what I did in the example? I tried to determine the source of each element in the product of interest. Once I did that, I saw what element came from the limiting reagent. Then I used the number of that element present in the limiting reagent and in the final product to develop a mole relationship between the limiting reagent and the product. After that, the stoichiometry was a breeze. Notice that I did not do anything with the stoichiometric coefficients that were in the chemical reactions. I was relating two chemicals *solely* by their elements. As a result, I did not need to worry about the coefficients. Remember, the coefficients in chemical equations relate the moles of one substance to the moles of another substance *within that chemical equation*. Since I was working across three chemical equations, the stoichiometric coefficients really held no meaning for this technique.

Now it's important to realize that this method will only work when the element you use comes *only* from one source, and that source is the limiting reagent. Notice that the first equation produces SO$_2$, and that SO$_2$ is then used in the next equation. Suppose if, in addition to the SO$_2$ from the first equation, another sulfur-containing compound (like Na$_2$S) was used as a reactant in the second equation. At that point, FeS$_2$ would not be the only source of sulfur in the production process, and we would not be able to use the technique we used.   Also, if FeS$_2$ had not been the limiting reagent, we could not have done what we did. This technique, therefore, is quite powerful, but you need to know when you can and cannot use it. Try this technique yourself by solving the following "on your own" problem.

ON YOUR OWN

1.10 The following three equations represent a process by which iron (Fe) is extracted from iron ore (Fe_2O_3) in a blast furnace:

$$3Fe_2O_3 \ + \ CO \qquad 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 \ + \ CO \qquad 3FeO \ + \ CO_2$$

$$FeO \ + \ CO \qquad Fe \ + \ CO_2$$
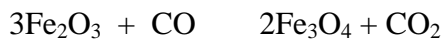
If a blast furnace starts with 1.00 kg of iron ore and ends up making 293 g of iron, what is the percent yield? Assume that CO is in excess.

Did you struggle a little bit through this module? It's okay if you did. Part of the problem is due to the fact that it had been a while since you did stoichiometry and chemical equations. As time goes on, you will remember more and things will get easier. For right now, don't worry if you have to go back to your first-year chemistry book in order to bring all of the concepts back to mind.

ANSWERS TO THE ON YOUR OWN PROBLEMS

1.1 To solve this problem, we simply have to convert miles to meters and hours to seconds. It doesn't matter that they are both a part of our original unit. As long as we use the factor-label method, everything will work out:

$$\frac{65 \text{ miles}}{1 \text{ hour}} \times \frac{1609 \text{ m}}{1 \text{ mile}} \times \frac{1 \text{ hour}}{3600 \text{ s}} = 29 \frac{\text{m}}{\text{s}}$$

Sixty-five miles per hour doesn't sound as fast when you say it as <u>29 m/s</u>.

1.2   To get the unit of interest, we need to convert moles to grams using the mass of NaOH; we need to convert L to mL; and we need to convert seconds to hours. The mass of NaOH from the periodic chart is 39.0 amu, which means there are 39.0 grams in a mole of NaOH. The conversion from mL to L and seconds to hours you should know.

$$\frac{1.02 \text{ moles}}{1 \text{ L} \cdot \text{s}} \times \frac{39.0 \text{ g}}{1 \text{ mole}} \times \frac{3600 \text{ s}}{1 \text{ hour}} \times \frac{0.001 \text{ L}}{1 \text{ mL}} = 143 \frac{\text{grams}}{\text{mL} \cdot \text{hr}}$$

The rate is <u>143 g/(mL hr)</u>.

1.3 We can't use the conversion of 3 feet in 1 yard right away, because we want to convert from square feet into square yards. Thus, we need a relationship between those quantities. We can get such a relationship by squaring both sides of the relationship that we do have:

$$3 \text{ ft } = \text{ 1 yd}$$

$$9 \text{ ft}^2 = \text{ 1 yd}^2$$

Now we can do the conversion:

$$\frac{1600 \text{ ft}^2}{1} \times \frac{1 \text{ yd}^2}{9 \text{ ft}^2} = 180 \text{ yd}^2$$

The house has an area of <u>180 square yards</u>. If your answer was 177.8, go back and review significant figures from your first year course.

1.4 This problem requires us to convert between m and km as well as s^2 and hr^2. The first is easy; the second requires us to square the relationship between hours and seconds:
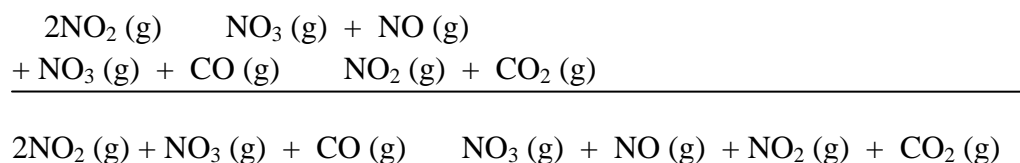
$$1 \text{ hr } = \text{ 3600 s}$$

$$1 \text{ hr}^2 = \text{ 12960000 s}^2$$

Notice that I did not round significant figures here. This is because the relationship between hours and seconds is exact, so the precision is infinite. As a result, I keep all figures. Now we can do the conversion:
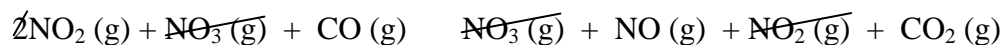
$$\frac{1.1 \; \cancel{m}}{s^2} \times \frac{1 \; km}{1,000 \; \cancel{m}} \times \frac{12960000 \; s^2}{1 \, hr^2} = 1.4 \times 10^4 \; \frac{km}{hr^2}$$

An acceleration of 1.1 m/s^2 is the same as <u>1.4 x 10^4 km/hr^2</u>.

1.5 To get an overall reaction, we just add up the two reactions given:

$$2NO_2 \; (g) \quad\quad NO_3 \; (g) \; + \; NO \; (g)$$
$$\underline{+ \; NO_3 \; (g) \; + \; CO \; (g) \quad\quad NO_2 \; (g) \; + \; CO_2 \; (g)}$$

$$2NO_2 \; (g) + NO_3 \; (g) \; + \; CO \; (g) \quad\quad NO_3 \; (g) \; + \; NO \; (g) \; + NO_2 \; (g) \; + \; CO_2 \; (g)$$

Now we can cancel terms that appear on both sides of the equation:

$$\cancel{2}NO_2 \; (g) + \cancel{NO_3 \; (g)} \; + \; CO \; (g) \quad\quad \cancel{NO_3 \; (g)} \; + \; NO \; (g) \; + \cancel{NO_2 \; (g)} \; + \; CO_2 \; (g)$$

Notice that there are two NO$_2$ (g) molecules on the reactants side and only one on the products side. Thus, I can use the one on the products side to cancel one of the NO$_2$ (g) on the reactants side, but I cannot cancel the other. That's why I marked out the "2" next to the NO$_2$ (g) on the reactants side and not the entire molecule. Since there are no like terms to group together, we are done:

$$\underline{NO_2 \; (g) \; + \; CO \; (g) \quad\quad NO \; (g) \; + \; CO_2 \; (g)}$$

1.6 Before we begin, we need to know what equation we are trying to calculate the   H of. A formation equation takes the elements in a molecule and reacts them together to form that molecule. We must use the elements in their natural form, however. Since oxygen is a homonuclear diatomic, its natural form is O$_2$. The formation reaction is:

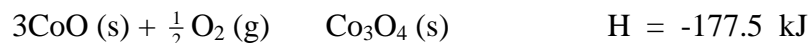$$3Co \; (s) \; + \; 2O_2 \; (g) \quad\quad Co_3O_4 \; (s)$$
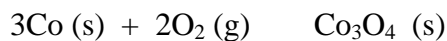
Now we need to get the two equations above to add to this one. In order to get that to happen, the first equation will have to be reversed, because currently Co (s) and O$_2$ (g) are products, but we need them as reactants:

$$Co \; (s) + \tfrac{1}{2} O_2 \; (g) \quad\quad CoO \; (s) \quad\quad\quad\quad H = \text{-237.9 \; kJ}$$
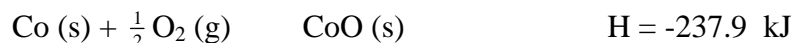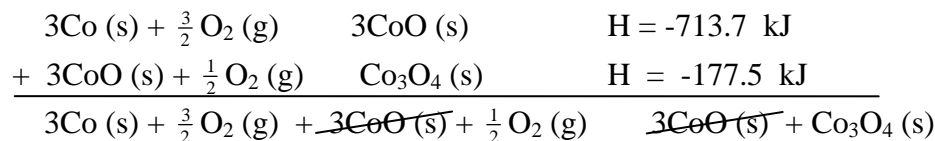
This is the only equation from which we get Co (s). Thus, the stoichiometric coefficient must be 3, because we need a 3Co (s) term in our final equation. Thus, I need to multiply both the equation and the ΔH by 3:

$$3Co \text{ (s)} + \tfrac{3}{2} O_2 \text{ (g)} \longrightarrow 3CoO \text{ (s)} \qquad \Delta H = -713.7 \text{ kJ}$$
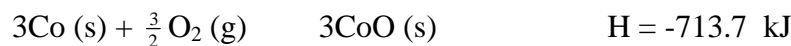
Notice that this does not give us the right coefficient with the oxygen. That's okay, though, because we get oxygen from the next equation as well. That equation has Co_3O_4 (s) as a product, so it need not be reversed. However, it has two of them, and we only want one in our equation. Thus, we need to multiply the equation and the ΔH by one-half:

$$3CoO \text{ (s)} + \tfrac{1}{2} O_2 \text{ (g)} \longrightarrow Co_3O_4 \text{ (s)} \qquad \Delta H = -177.5 \text{ kJ}$$

Now we can add the equations and the ΔH's:

$$3Co \text{ (s)} + \tfrac{3}{2} O_2 \text{ (g)} \longrightarrow 3CoO \text{ (s)} \qquad \Delta H = -713.7 \text{ kJ}$$
$$+ \ 3CoO \text{ (s)} + \tfrac{1}{2} O_2 \text{ (g)} \longrightarrow Co_3O_4 \text{ (s)} \qquad \Delta H = -177.5 \text{ kJ}$$
$$\overline{3Co \text{ (s)} + \tfrac{3}{2} O_2 \text{ (g)} + \cancel{3CoO \text{ (s)}} + \tfrac{1}{2} O_2 \text{ (g)} \longrightarrow \cancel{3CoO \text{ (s)}} + Co_3O_4 \text{ (s)}}$$

Once we combine like terms, we get our original equation:

$$3Co \text{ (s)} + 2O_2 \text{ (g)} \longrightarrow Co_3O_4 \text{ (s)}$$
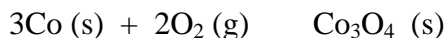
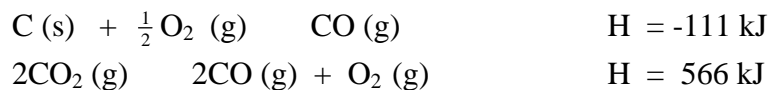The ΔH is then just the sum of the two ΔH's listed with those reactions, or <u>-891.2 kJ</u>.

1.7 Calculate the ΔH for the combustion of carbon :

$$C \text{ (s)} + O_2 \text{ (g)} \longrightarrow CO_2 \text{ (g)}$$

Given that

$$C \text{ (s)} + \tfrac{1}{2} O_2 \text{ (g)} \longrightarrow CO \text{ (g)} \qquad \Delta H = -111 \text{ kJ}$$
$$2CO_2 \text{ (g)} \longrightarrow 2CO \text{ (g)} + O_2 \text{ (g)} \qquad \Delta H = 566 \text{ kJ}$$
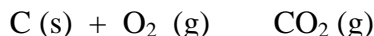
The first reaction is fine. It has C (s) and O_2 (g) as reactants, which is what we need. The coefficient with the C (s) is correct, but the coefficient with the O_2 (g) is not. That's okay, however, because we will get more O_2 from the next reaction. In that reaction, we must reverse it because that's the only way to get CO_2 (g) as a product. Also, we will have to divide the equation (and its ΔH) by 2 in order to get the correct coefficient next to the CO_2.

$$CO \text{ (g)} + \tfrac{1}{2} O_2 \text{ (g)} \longrightarrow CO_2 \text{ (g)} \qquad \Delta H = -283 \text{ kJ}$$

Now we can add the equations:

$$CO \ (g) \ + \ \tfrac{1}{2} O_2 \ (g) \qquad CO_2 \ (g) \qquad\qquad \Delta H \ = \ -283 \ kJ$$
$$+ \ C \ (s) \ + \ \tfrac{1}{2} O_2 \ (g) \qquad CO \ (g) \qquad\qquad \Delta H \ = \ -111 \ kJ$$

$$\cancel{CO \ (g)} \ + \ \tfrac{1}{2} O_2 \ (g) + \ C \ (s) \ + \ \tfrac{1}{2} O_2 \ (g) \qquad CO_2 \ (g) \ + \ \cancel{CO \ (g)}$$
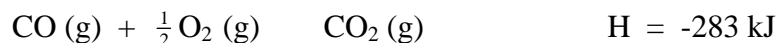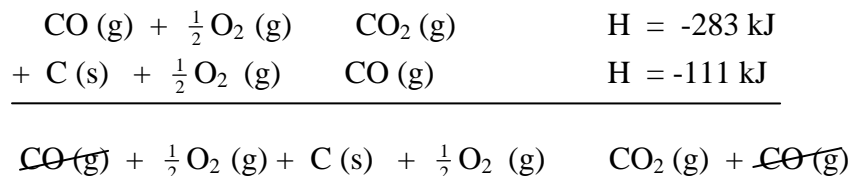
After canceling the CO (g) on both sides of the equation and combining the O_2 (g) terms on the reactants side of the equation, we are left with the equation of interest:

$$C \ (s) \ + \ O_2 \ (g) \qquad CO_2 \ (g)$$
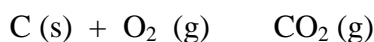
So the ΔH is simply the sum of the ΔH's listed for the two equations after we manipulated them, or <u>-394 kJ.</u>

1.8 We need to determine the limiting reagent before we can really answer the question. Looking at the chemical equation, there need to be 2 moles of $KAg(CN)_2$ for every one mole of Zn. Let's convert to moles to see if that is really the relationship between the number of moles of each reactant.

$$\frac{100.0 \ g \ \cancel{KAg(CN)_2}}{1} \times \frac{1 \ mole \ KAg(CN)_2}{199.0 \ g \ \cancel{KAg(CN)_2}} = 0.5025 \ moles \ KAg(CN)_2$$

$$\frac{75.0 \ g \ \cancel{Zn}}{1} \times \frac{1 \ mole \ Zn}{65.4 \ g \ \cancel{Zn}} = 1.15 \ moles \ Zn$$

Are there 2 moles of $KAg(CN)_2$ for every one mole of Zn? Well, since there are 1.15 moles of Zn, there would need to be 2.30 moles of $KAg(CN)_2$. There aren't nearly that many, so $KAg(CN)_2$ will run out first.

Now that we know $KAg(CN)_2$ is the limiting reagent, we know that all products are limited by the amount of $KAg(CN)_2$. Thus, the amount of Zn is irrelevant, and we can continue on in our calculation using just the number of moles of $KAg(CN)_2$.

$$\frac{0.5025 \ \cancel{moles \ KAg(CN)_2}}{1} \times \frac{2 \ moles \ Ag}{2 \ \cancel{moles \ KAg(CN)_2}} = 0.5025 \ moles \ Ag$$

$$\frac{0.5025 \ \cancel{moles \ Ag}}{1} \times \frac{107.9 \ g \ Ag}{1 \ \cancel{mol \ Ag}} = 54.22 \ g \ Ag$$

The reaction produces <u>54.22 g of silver</u>.

1.9 Before we can do anything, we need to know what equation we are working with. Combustion is defined as a reaction that adds oxygen and produces carbon dioxide and water. The combustion of propane, then, would be:

$$C_3H_8 \ + \ O_2 \qquad CO_2 \ + \ H_2O$$

This reaction is not balanced, so we need to do that next:

$$C_3H_8 \ + \ 5O_2 \qquad 3CO_2 \ + \ 4H_2O$$

Now that we have the equation, we can determine the limiting reagent. Looking at the chemical equation, there need to be 5 moles of O_2 for every one mole of C_3H_8. Let's convert to moles to see if that is really the relationship between the number of moles of each reactant.

$$\frac{10.0 \ \cancel{g \ C_3H_8}}{1} \times \frac{1 \ \text{mole} \ C_3H_8}{44.1 \ \cancel{g \ C_3H_8}} = 0.227 \ \text{moles} \ C_3H_8$$

$$\frac{75.0 \ \cancel{g \ O_2}}{1} \times \frac{1 \ \text{mole} \ O_2}{32.0 \ \cancel{g \ O_2}} = 2.34 \ \text{moles} \ O_2$$

Are there 5 moles of O_2 for every one mole of C_3H_8? Well, since there are 0.227 moles of C_3H_8, there would need to be 1.14 moles of O_2. There are more than that, so after all of the C_3H_8 molecules are used up, there will still be O_2. Thus, C_3H_8 will run out first.

Now that we know C_3H_8 is the limiting reagent, we know that all products are limited by the amount of C_3H_8. Thus, the amount of O_2 is irrelevant, and we can continue on in our calculation using just the number of moles of C_3H_8.

$$\frac{0.227 \ \cancel{\text{moles} \ C_3H_8}}{1} \times \frac{4 \ \text{moles} \ H_2O}{1 \ \cancel{\text{mole} \ C_3H_8}} = 0.908 \ \text{moles} \ H_2O$$

$$\frac{0.908 \ \cancel{\text{moles} \ H_2O}}{1} \times \frac{18.0 \ g \ H_2O}{1 \ \cancel{\text{mol} \ H_2O}} = 16.3 \ g \ H_2O$$

The reaction produces <u>16.3 g of water</u>.

1.10 To do this problem, we look for an element that is in the product and also in a reactant of the first equation. In this case, it's easy. After all, the product is Fe. Thus, the element we need to look for must also be Fe. It is in the Fe_2O_3 which is a reactant in the first reaction. This is the only source of Fe, because the Fe-containing compounds that are reactants in the next two equation come from the previous equation. Thus, Fe_2O_3 is the only source of Fe. There are 2 Fe's in each Fe_2O_3 molecule, so one mole of Fe_2O_3 will make 2 moles of Fe.

$$1 \text{ mole } Fe_2O_3 = 2 \text{ moles Fe}$$
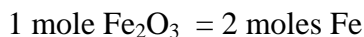
With that relationship, we can do stoichiometry.

$$\frac{1.00 \times 10^3 \text{ g } Fe_2O_3}{1} \times \frac{1 \text{ mole } Fe_2O_3}{159.6 \text{ g } Fe_2O_3} = 6.27 \text{ moles } Fe_2O_3$$

$$\frac{6.27 \text{ moles } Fe_2O_3}{1} \times \frac{2 \text{ moles Fe}}{1 \text{ mole } Fe_2O_3} = 12.5 \text{ moles Fe}$$

$$\frac{12.5 \text{ moles Fe}}{1} \times \frac{55.8 \text{ g Fe}}{1 \text{ mole Fe}} = 698 \text{ g Fe}$$

So these three reactions should produce 698 g Fe. Since the furnace produced only 293 g of sulfuric acid, the percent yield is:

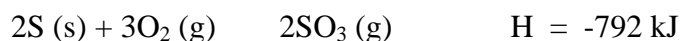$$\frac{293 \text{ g}}{698 \text{ g}} \times 100\% = 42.0\%$$

The percent yield, then, is 42.0%.

REVIEW QUESTIONS

1. A chemist presents a possible reaction mechanism for a chemical reaction she has been studying. If she adds up every equation in the reaction mechanism, what should she get in the end?

2. State Hess's Law.

3. When you reverse a chemical equation, what must you do to its H?

4. When you multiply a chemical equation by a number, what must you do to its H?

5. Suppose you had a chemical equation with H_2O (l) on one side and H_2O (g) on the other, could you cancel those terms?

6. Suppose you had a chemical equation with $2H_2O$ (l) on one side and H_2O (l) on the other, could you cancel those terms?

7. Why is the limiting reagent such an important thing to know in stoichiometry?

8. Other chemistry books teach another way to determine the limiting reagent. In those books, you are told to do the stoichiometry assuming one reactant is the limiting reagent and then go back and do the stoichiometry *again*, assuming the other reactant is the limiting reagent. I think that's too much work. However, suppose you did a problem that way. You will get two answers for the amount of product. One answer will be bigger than the other. Which is the correct answer?

9. Suppose you did a limiting reagent problem as described above and got two answers that were equal. What would that tell you?

10. Two students do the same experiment. One gets a percent yield of 45% and the other a percent yield of 65%. Which student is the more careful experimenter?

PRACTICE PROBLEMS

1. The volume of a box is 0.034 m^3. What is the volume in cm^3?

2. Electrical fields are measured in Volts per meter. If an electrical field has a strength of 45 V/m, what is the strength in milliVolts per cm? (MilliVolt has the same relationship to Volt as milliliter does to liter.)

3. The density of a substance is 1.2 g/cm^3. What is the density in kg/m^3?

4. Given the following reaction:

$$2S \text{ (s)} + 3O_2 \text{ (g)} \quad 2SO_3 \text{ (g)} \qquad \Delta H = -792 \text{ kJ}$$

What is the ΔH of this reaction?

$$4SO_3 \text{ (g)} \quad 4S \text{ (s)} + 6O_2 \text{ (g)}$$

5. The following series of equations is a possible reaction mechanism for a certain reaction. What is the reaction?

$$2NO \quad N_2O_2$$

$$N_2O_2 + H_2 \quad N_2O + H_2O$$

$$N_2O + H_2 \quad N_2 + H_2O$$

6. Calculate the ΔH for the following reaction:

$$2NO \text{ (g)} + O_2 \text{ (g)} \quad 2NO_2 \text{ (g)}$$

given the following data:

$$N_2 \text{ (g)} + O_2 \text{ (g)} \quad 2NO \text{ (g)} \qquad \Delta H = 180.6 \text{ kJ}$$

$$N_2 \text{ (g)} + 2O_2 \text{ (g)} \quad 2NO_2 \text{ (g)} \qquad \Delta H = 66.4 \text{ kJ}$$
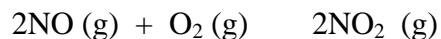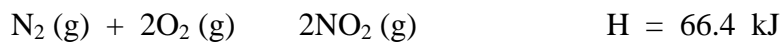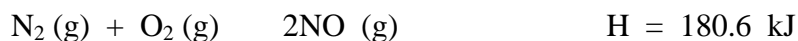
7. Calculate the enthalpy of formation of acetic acid, CH_3CO_2H (l), given the following data:

$$CH_3CO_2H \text{ (l)} + 2O_2 \text{ (g)} \quad 2CO_2 \text{ (g)} + 2H_2O \text{ (l)} \qquad H = \text{-871 kJ}$$

$$C \text{ (s)} + O_2 \text{ (g)} \quad CO_2 \text{ (g)} \qquad H = \text{-394 kJ}$$

$$H_2 \text{ (g)} + \tfrac{1}{2}O_2 \text{ (g)} \quad H_2O \text{ (l)} \qquad H = \text{-286 kJ}$$
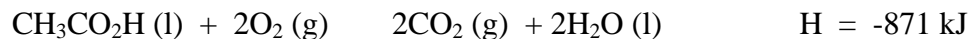
8. Ethylene glycol is a popular component of automobile antifreeze. In order to make ethylene glycol, chemists must first make ethylene oxide (C_2H_4O) from the following reaction:

$$2C_2H_4 + O_2 \quad 2C_2H_4O$$
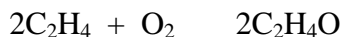
If a chemist starts with 11.0 g of C_2H_4 and 11.0 g of O_2, how much ethylene oxide should the chemist make?

9. In order to make acetylene (C_2H_2) for acetylene torches, chemists must first make calcium carbide (CaC_2) according to this reaction:

$$CaO + 3C \quad CaC_2 + CO$$

A chemist reacts 1.00 kg of CaO with 1.00 kg of carbon. If the chemist ends up with 1.00 kg of calcium carbide, what is the percent yield?

10. Nitric acid, HNO_3, is manufactured industrially with the following sequence of reactions:

$$4NH_3 + 5O_2 \quad 4NO + 6H_2O$$

$$2NO + O_2 \quad 2NO_2$$

$$3NO_2 + H_2O \quad 2HNO_3 + NO$$
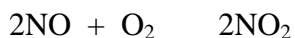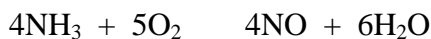
In this process, the NO made in the last reaction is recycled back into the second reaction and used as a reactant. In the end, *all* of the NO produced is recycled back so that when the manufacturing process is complete, no NO remains. If a chemist starts with 35.0 grams of NH_3 and an excess of water and oxygen, how much nitric acid can be made?

THE PERIODIC CHART OF ELEMENTS

1A																	8A
1 **H** 1.01	2A											3A	4A	5A	6A	7A	**2** **He** 4.0
3 **Li** 6.94	**4** **Be** 9.00											**5** **B** 10.8	**6** **C** 12.0	**7** **N** 14.0	**8** **O** 16.0	**9** **F** 19.0	**10** **Ne** 20.2
11 **Na** 22.0	**12** **Mg** 24.3	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B	**13** **Al** 27.0	**14** **Si** 28.1	**15** **P** 31.0	**16** **S** 32.1	**17** **Cl** 35.5	**18** **Ar** 39.9
19 **K** 39.1	**20** **Ca** 40.1	**21** **Sc** 45.0	**22** **Ti** 47.9	**23** **V** 50.9	**24** **Cr** 52.0	**25** **Mn** 54.9	**26** **Fe** 55.8	**27** **Co** 58.9	**28** **Ni** 58.7	**29** **Cu** 63.5	**30** **Zn** 65.4	**31** **Ga** 69.7	**32** **Ge** 72.6	**33** **As** 74.9	**34** **Se** 79.0	**35** **Br** 79.9	**36** **Kr** 83.8
37 **Rb** 85.5	**38** **Sr** 87.6	**39** **Y** 88.9	**40** **Zr** 91.2	**41** **Nb** 92.9	**42** **Mo** 95.9	**43** **Tc** 97.0	**44** **Ru** 101.1	**45** **Rh** 102.9	**46** **Pd** 106.4	**47** **Ag** 107.9	**48** **Cd** 112.4	**49** **In** 114.8	**50** **Sn** 118.7	**51** **Sb** 121.8	**52** **Te** 127.6	**53** **I** 126.9	**54** **Xe** 131.3
55 **Cs** 132.9	**56** **Ba** 137.3	**57** **La** 138.9	**72** **Hf** 178.5	**73** **Ta** 180.9	**74** **W** 183.9	**75** **Re** 186.2	**76** **Os** 190.2	**77** **Ir** 192.2	**78** **Pt** 195.1	**79** **Au** 197.0	**80** **Hg** 200.6	**81** **Tl** 204.4	**82** **Pb** 207.2	**83** **Bi** 209.0	**84** **Po** (209)	**85** **At** (210)	**86** **Rn** (222)
87 **Fr** 223.0	**88** **Ra** 226.0	**89** **Ac** 227.0	**104** (261)	**105** (262)	**106** (263)	**107** (264)	**108** (265)	**109** (266)									

58 **Ce** 140.1	**59** **Pr** 140.9	**60** **Nd** 144.2	**61** **Pm** 145.0	**62** **Sm** 150.4	**63** **Eu** 152.0	**64** **Gd** 157.3	**65** **Tb** 158.9	**66** **Dy** 162.5	**67** **Ho** 164.9	**68** **Er** 167.3	**69** **Tm** 168.9	**70** **Yb** 173.0	**71** **Lu** 175.0
90 **Th** 232.0	**91** **Pa** 234.0	**92** **U** 238.0	**93** **Np** 237.0	**94** **Pu** (244)	**95** **Am** (243)	**96** **Cm** (247)	**97** **Bk** (247)	**98** **Cf** (251)	**99** **Es** (252)	**100** **Fm** (257)	**101** **Md** (258)	**102** **No** (259)	**103** **Lr** (260)