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

Introduction

There are probably no concepts in chemistry more important than the three listed in the title of this module. In your first-year chemistry course, I am sure you learned quite a bit about each of them. 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. This will help you "warm up" to the task of recalling all the things you learned in your first-year chemistry course, and it will help you to learn each of these valuable concepts at a much deeper level.

Units Revisited

Units are generally covered first in a chemistry course, because a great deal of chemistry is based on properly analyzing them. 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. What is the mass in kg?

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:

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

The sample of iron has a mass of $\underline{2.541 \times 10^{-4} \text{ kg}}$.

Did this example help blow the cobwebs in your mind away when it comes to units? It should all be review for you. I converted the units using the factor-label method. Because the conversion factors are exact, I have the same number of significant figures in the answer 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, 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. 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 (like molarity), you should be able to convert it to another unit (like grams per milliliter), right? Study the next example to see how that is done.

EXAMPLE 1.2

The concentration of HCl in a solution of muriatic acid is about 0.35 g/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 to 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 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 want to determine, we can set up the conversion:

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

Although there is nothing new here, you probably haven't seen a conversion done in this way. Despite the fact that the initial unit was a derived unit (g/mL), we can still do conversions on it. With the first conversion factor, we canceled the unit of grams and replaced it with moles. That gave us a unit of moles/mL. Then we had to convert mL into liters, which is what the second conversation factor did. Now, of course, we could have done this in two steps. We could have gotten the answer in moles/mL, written it down, and then converted it into moles/L. However, we just chose to combine both steps into one. Also, we could have started by converting mL to liters and then converting grams to moles. Either way, the result would have been the same. The main thing was that we realized we had to get rid of both grams and mL and replace them with moles and liters. Since there is a direct relationship between moles and grams (through the periodic chart), we had to convert grams into moles. Since there is a direct relationship between mL and liters, we had to convert mL into liters. Thus, a concentration of 0.35 g/mL is the same thing as 9.6 M.

Muriatic acid is 9-10 M HCl commonly sold in hardware stores for use in cleaning and etching stone, concrete, etc. It is very caustic and must be handled with extreme care.

The key in trying to figure out how to do these more complex conversions is to think about what you are given and what you need to know. For example, to get molarity, you need to get moles per liter. Since you start out with grams per mL, grams should be converted to moles so that the numerator of the final unit ends up as moles. In the same way, since you start with mL in the denominator of the first unit, it must be converted to liters so that liters ends up in the denominator of the final unit.

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 you do not think as you go through it, however, 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. We have no relationship between these units, but we do know that 1 cm = 0.01 m. That's all we need to know, as long as we think about it. Right now, we have the following relationship:

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

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

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

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

Now look what we have. We have a relationship between cm^3 and m^3 – exactly what we need to do the conversion!

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

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

When most students do a conversion like this 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:

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

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 1,609 meters in a mile.)

1.2 The instantaneous rate of disappearance of NaOH in a chemical reaction is 1.02 $\frac{moles}{L \cdot sec}$. What is the rate in $\frac{grams}{mL \cdot hour}$?

1.3 The size of a house is 1,600 square feet. What is the square yardage of the house?

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

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 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:

$$N_2 (g) + 3H_2 (g) \rightarrow 2NH_3 (g) \tag{1.1}$$

You can multiply this equation by 3 to get:

$$3N_2 (g) + 9H_2 (g) \rightarrow 6NH_3 (g) \tag{1.2}$$
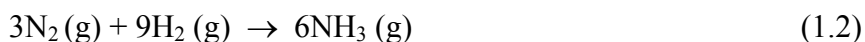
Both of these are legitimate, balanced chemical equations. Why in the world would you want to do such a thing? Well, you'll find out in a moment.

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 that 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 can occur:

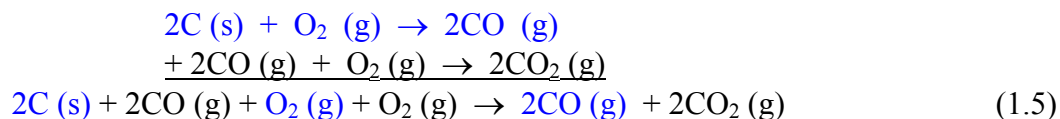$$2C (s) + O_2 (g) \rightarrow 2CO (g) \tag{1.3}$$

If, however, more oxygen becomes available, the carbon monoxide formed in Equation (1.3) can further be burned to make carbon dioxide, according to this chemical equation:

$$2CO (g) + O_2 (g) \rightarrow 2CO_2 (g) \tag{1.4}$$
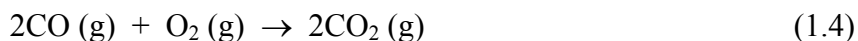
Suppose you first burned carbon in limited oxygen so that only the reaction given by Equation (1.3) occurred. Then, afterward, suppose you added more oxygen so that the reaction given by Equation (1.4) occurred. What would be the end result? In the end, all the carbon would be turned into carbon dioxide. The *overall* process, then, is that carbon is added to oxygen to make carbon dioxide. The fact that it happened in two steps might not be all that important, so it would be nice to be able to have a chemical equation that represents the overall process.
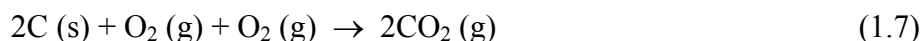
How can we get the overall chemical equation? We can *add Equations (1.3) and (1.4) together*! I will make Equation (1.3) blue so that you can see where the reactants and products from that equation go when the two equations are added together:

$$2C \text{ (s)} + O_2 \text{ (g)} \rightarrow 2CO \text{ (g)}$$
$$+ 2CO \text{ (g)} + O_2 \text{ (g)} \rightarrow 2CO_2 \text{ (g)}$$
$$2C \text{ (s)} + 2CO \text{ (g)} + O_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow 2CO \text{ (g)} + 2CO_2 \text{ (g)} \tag{1.5}$$

Is Equation (1.5) the overall equation, 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. Therefore, we can cancel them:

$$2C \text{ (s)} + \cancel{2CO \text{ (g)}} + O_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow \cancel{2CO \text{ (g)}} + 2CO_2 \text{ (g)} \tag{1.6}$$

This leaves us with:
$$2C \text{ (s)} + O_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow 2CO_2 \text{ (g)} \tag{1.7}$$

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

$$2C \text{ (s)} + 2O_2 \text{ (g)} \rightarrow 2CO_2 \text{ (g)} \tag{1.8}$$

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 (1.8) are divisible by two, we will also divide both sides of the equation by two to get:
$$C \text{ (s)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} \tag{1.9}$$

So, after all that work, we see that Equations (1.3) and (1.4) add up to the very simple equation given in Equation (1.9).

In the end, then, complicated chemical processes can often be simplified by adding chemical equations together. You need to realize that this is not just some abstract procedure. It represents something that happens in the real world. For example, consider burning coal in a fireplace. Often, the supply of air to the burning coal gets low, resulting in the kind of incomplete combustion that is given by Equation (1.3). However, if the ventilation around the coal fireplace is good, as the CO (g) rises, it will be exposed to more O_2 (g) in the air around the fireplace. If this happens in areas where it is hot, the reaction given by Equation (1.4) will occur. As a result, the overall reaction occurring in the fireplace is given by Equation (1.9). This is important, since CO (g) is toxic even at relatively low

concentrations, while CO_2 (g) is not. So as long as there is enough ventilation to supply the fireplace with adequate air, it doesn't matter that incomplete combustion occurs *at first*. As long as the CO (g) is eventually turned into CO_2 (g), the overall reaction is given by Equation (1.9), and the fireplace does not produce much toxic gas. Example 1.4 shows you how this is done for another common reaction.

EXAMPLE 1.4

The destruction of ozone by chlorine atoms from chlorofluorohydrocarbons (CFCs) proceeds as follows: First, a CFC is hit by ultraviolet light, causing a chlorine atom to split off from the rest of the molecule. That atom then reacts with ozone according to the following equation:

$$Cl + O_3 \rightarrow ClO + O_2$$

The compound ClO, however, is not stable, and it quickly reacts with free oxygen atoms in the air to form Cl and O_2:

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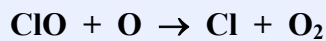
What is the overall chemical equation for the destruction of ozone?

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

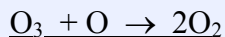$$Cl + O_3 \rightarrow ClO + O_2$$
$$+ \; ClO + O \rightarrow Cl + O_2$$
$$Cl + O_3 + ClO + O \rightarrow ClO + O_2 + Cl + O_2$$
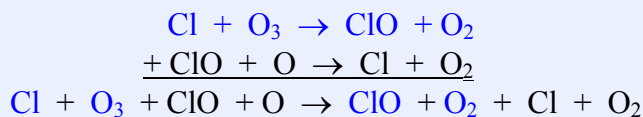
Notice there are two ClO terms on each side of the equation. They can be canceled. The same goes for the Cl terms on each side.

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

This gives us the following equation:

$$O_3 + O \rightarrow O_2 + O_2$$

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

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

So once again, the final equation is much simpler than the previous equations that describe the process, and it clearly shows that ozone is being destroyed in 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 reaction, it is produced in the second reaction. As a result, the amount of Cl present never changes. Thus, when you look at the overall equation, 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? It depends on what you want to know. 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:

$$2NO_2 \text{ (g)} \rightarrow NO_3 \text{ (g)} + NO \text{ (g)}$$

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

$$NO_3 \text{ (g)} + CO \text{ (g)} \rightarrow NO_2 \text{ (g)} + CO_2 \text{ (g)}$$
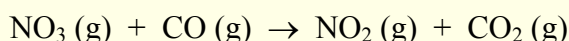
What is the overall chemical reaction that occurs?

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 ΔH) tells us how much energy is released into the surroundings (when ΔH is negative) or absorbed by the chemicals in the reaction (when ΔH is positive). You should have learned Hess's Law as:

$$\Delta H = \sum \Delta H_f \text{ (products)} - \sum \Delta H_f \text{ (reactants)} \qquad (1.10)$$

In this equation, ΔH is the change of enthalpy of the reaction, and ΔH_f is the enthalpy of formation of the reactants and the products. When using Equation (1.10), you take the ΔH_f for each product (you look each up in a table), multiply by the stoichiometric coefficient of the product, and subtract from that the sum of the ΔH_f's of each reactant times its stoichiometric coefficient. When you are done, you have the ΔH 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:
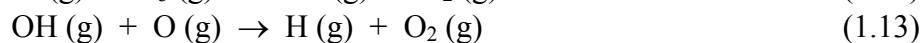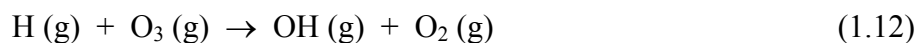
<u>Hess's Law</u> - Enthalpy is a state function and is therefore independent of path.

In your first-year course, you should have learned that Equation (1.10) is a consequence of this statement. However, the statement itself tells us something much more dramatic. Hess's Law tells us that the ΔH 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:

$$O_3 \, (g) \; + \; O \, (g) \; \rightarrow \; 2O_2 \, (g) \qquad\qquad (1.11)$$

Hess's Law states that *regardless of how this reaction occurs, the ΔH 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 for ozone destruction, including hydrogen atoms. Here's how a hydrogen atom catalyzes the decomposition of ozone:

$$H \, (g) \; + \; O_3 \, (g) \; \rightarrow \; OH \, (g) \; + \; O_2 \, (g) \qquad\qquad (1.12)$$
$$OH \, (g) \; + \; O \, (g) \; \rightarrow \; H \, (g) \; + \; O_2 \, (g) \qquad\qquad (1.13)$$

You can verify for yourself that the overall chemical reaction produced in these two steps is precisely the same as Equation (1.11), which is the overall chemical equation produced by the chlorine-catalyzed decomposition sequence shown in the previous section.
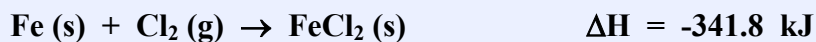
Hess's Law states that whether ozone is destroyed with a chlorine catalyst or a hydrogen catalyst, the overall change in enthalpy will be the same, because the overall chemical reaction is the same. Thus, it does not matter *how* the reaction occurs. The ΔH will always be the same, as long as the overall chemical reaction is the same.

How is this possible? Think about it. Each chemical equation has its own ΔH. Thus, Equation (1.12) and Equation (1.13) each has its own ΔH. Similarly, each step of the reaction mechanism presented in Example 1.4 also has its own ΔH. The energetics work out so that when you add the ΔH's of each individual chemical reaction (just like you added the equations), the total ΔH 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.
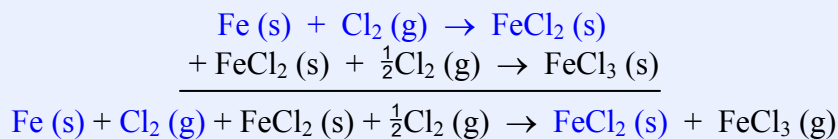
EXAMPLE 1.5

When solid iron and chlorine gas react together, the product is solid $FeCl_3$. This reaction (most likely) proceeds in two steps:
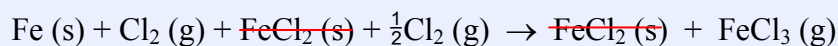
$$Fe \, (s) \; + \; Cl_2 \, (g) \; \rightarrow \; FeCl_2 \, (s) \qquad\qquad \Delta H \; = \; \text{-341.8 kJ}$$

$$FeCl_2 \, (s) \; + \; \tfrac{1}{2}Cl_2 \, (g) \; \rightarrow \; FeCl_3 \, (s) \qquad\qquad \Delta H \; = \; \text{-57.7 kJ}$$

What is the overall reaction and its ΔH?

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

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

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

We need to cancel the $FeCl_2$ (s) on each side of the equation:

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

Now we can group the Cl_2 (g) terms on the left-hand side of the equation together to get the overall equation:

$$Fe \text{ (s)} + \tfrac{3}{2}Cl_2 \text{ (g)} \rightarrow FeCl_3 \text{ (s)}$$
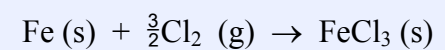
Don't be concerned about the fraction in the equation. Although there is no such thing as $\tfrac{3}{2}$ of a Cl_2 molecule, there is no real problem with the fraction in the equation. If we wanted to, we could multiply the equation by 2 to get rid of the fraction, but as we will see in a moment, we would have to do something to the ΔH as well.

So now that we've figured out the overall equation, how do we get the ΔH? Since we just added the two equations together to get the overall equation, we can just add the two ΔH's together to get the overall ΔH:

$$\Delta H = \text{-341.8 kJ} + \text{-57.7 kJ} = \text{-399.5 kJ}$$

The overall ΔH, then, is -399.5 kJ.

So Hess's Law states that if we can add two or more equations together to get an overall chemical equation, we can add the ΔH's to get the overall ΔH. 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 ΔH 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 ΔH 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 ΔH! So if we know the ΔH of a few equations and we can add up those equations to get an overall chemical equation, we can add the individual ΔH's to get the overall equation's ΔH.
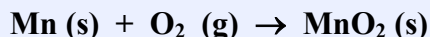
"Okay," you might be thinking, "that doesn't sound so bad." Well, in principle, it's not. However, things can get really tricky when you start realizing that since we can multiply equations by a number as well as add them together, we can find ways to construct *a lot* of overall chemical equations. Study the following example to see what I mean.

**EXAMPLE 1.6**

Given the following information:

$$2Mn \text{ (s)} + O_2 \text{ (g)} \rightarrow 2MnO \text{ (s)} \qquad \Delta H = \text{-770.4 kJ}$$
$$2MnO_2 \text{ (s)} \rightarrow O_2 \text{ (g)} + 2MnO \text{ (s)} \qquad \Delta H = 269.7 \text{ kJ}$$
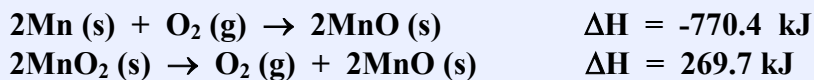
**Calculate the ΔH for**
$$Mn \text{ (s)} + O_2 \text{ (g)} \rightarrow MnO_2 \text{ (s)}$$

     Now that we know Hess's Law allows us to add 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, 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, then, can be written backwards as:

$$O_2 \text{ (g)} + 2MnO \text{ (s)} \rightarrow 2MnO_2 \text{ (s)}$$
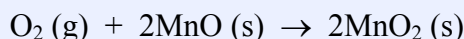
We now have MnO_2 (s) as a product. Wait a minute. If we write the equation backwards, what happens to ΔH? Well, the ΔH given above indicates that when the reaction runs as written, the reaction absorbs 269.7 kJ of energy. If we write the equation backwards, we are talking about the *reverse* of the reaction. If the reaction as written *absorbs* 269.7 kJ of energy, 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, ΔH = -269.7 kJ.

     So now we have two reactions that we can add to get the third, right? Not quite. After all, if we add this equation to the very first one we were given, we would have $2MnO_2$ (s) as a product. What we are looking for is an equation that has *a single* MnO_2 (s) as a product. Are we out of luck? Not at all. Remember, we can multiply chemical equations by numbers, so let's multiply the equation above by one-half:
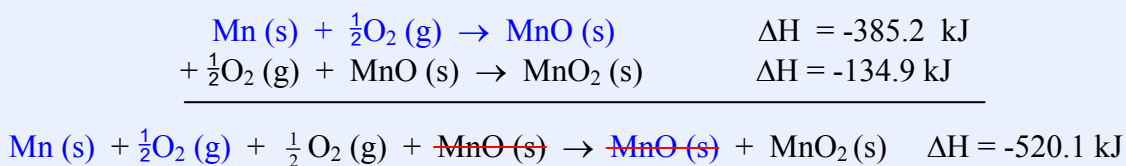
$$\tfrac{1}{2}O_2 \text{ (g)} + MnO \text{ (s)} \rightarrow MnO_2 \text{ (s)}$$
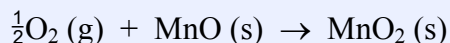
Now we have just one MnO_2 (s) as a product, which is what we want in the end. What about the ΔH, however? Is the ΔH the same? No. Remember, the ΔH tells us about how much energy is released or absorbed in a reaction. If we multiply the equation by $\frac{1}{2}$, then only half as much energy will be released. Thus, we need to multiply ΔH by $\frac{1}{2}$ 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:

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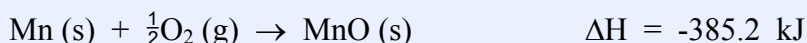
Now we can finally add the equations together, along with their ΔH's:

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

$$Mn\ (s)\ +\tfrac{1}{2}O_2\ (g)\ +\ \tfrac{1}{2}O_2\ (g)\ +\ \text{\sout{MnO (s)}}\ \rightarrow\ \text{\sout{MnO (s)}}\ +\ MnO_2\ (s) \quad \Delta H = -520.1\ kJ$$

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:

$$Mn\ (s)\ +\ O_2\ (g)\ \rightarrow\ MnO_2\ (s)$$
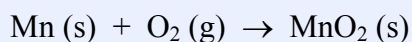
This is exactly the equation for which we wanted to calculate the ΔH. Thus, <u>ΔH = -520.1 kJ</u>.

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 equation will be the sum of the ΔH's for the individual equations that we added together. So, in order to calculate the ΔH of a reaction, I just keep manipulating equations until they add together to make the chemical equation for which I want to calculate the ΔH. If I reverse the chemical equation, I change the sign on the ΔH. If I multiply the equation by a number, I multiply the ΔH by the same number. In the end, when the equations add up to the equation in which I am interested, the ΔH's add to the ΔH of the reaction in which I am interested.

Before moving on to another example that uses this technique, I thought I would spend just a moment telling you something interesting about the product of the overall reaction in Example 1.6. MnO_2 is a black solid that is found in the naturally-occurring mineral pyrolusite (pye' roh loo' syte). It was used by ancient cave painters to produce a deep black for their paintings. Today, it is commonly used as a catalyst in reactions such as the decomposition of hydrogen peroxide (H_2O_2) and the decomposition of potassium chlorate ($KClO_3$).

FIGURE 1.1
Cave Paintings That Contain MnO_2

These cave paintings were found on the walls of a famous cave near Lascaux, France and are thought to be thousands of years old. The black comes mostly from MnO_2.

Let's get back to the process outlined in Example 1.6. In order to master this technique, you must keep the following points in mind:

1. **When you reverse a chemical equation, you must change the sign of the equation's ΔH.**

2. **When you multiply a chemical equation by a number, you must also multiply the ΔH of the equation by that same number.**
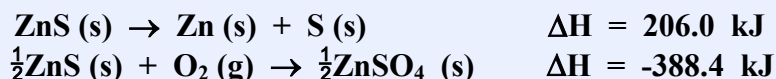
Let's do another example so you can get the hang of this.
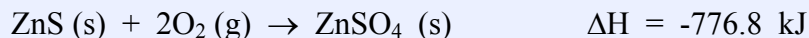

EXAMPLE 1.7

Calculate the ΔH of the following reaction:

$$Zn \text{ (s)} + S \text{ (s)} + 2O_2 \text{ (g)} \rightarrow ZnSO_4 \text{ (s)}$$

from the following information:

$$ZnS \text{ (s)} \rightarrow Zn \text{ (s)} + S \text{ (s)} \qquad\qquad \Delta H = 206.0 \text{ kJ}$$
$$\tfrac{1}{2}ZnS \text{ (s)} + O_2 \text{ (g)} \rightarrow \tfrac{1}{2}ZnSO_4 \text{ (s)} \qquad \Delta H = -388.4 \text{ kJ}$$

To solve this problem, we just need to manipulate these two equations until they add to the one for which we want the ΔH. Well, that equation has Zn (s) and S (s) as reactants. Of the two equations with known ΔH's, 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 of the ΔH:

$$Zn \text{ (s)} + S \text{ (s)} \rightarrow ZnS \text{ (s)} \qquad\qquad \Delta H = -206.0 \text{ kJ}$$

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 with the known ΔH has only $\tfrac{1}{2}$ $ZnSO_4$. Therefore, we need to multiply that equation by two. When we do that, we need to multiply the ΔH by two as well (2 x -388.4 kJ = -776.8 kJ).

$$ZnS \text{ (s)} + 2O_2 \text{ (g)} \rightarrow ZnSO_4 \text{ (s)} \qquad\qquad \Delta H = -776.8 \text{ kJ}$$

Now we have 2 equations that have everything we need in all the right places, so we just need to add them up. If they add to the equation of interest, the sum of their ΔH's will add to the ΔH of the equation of interest.

$$Zn \text{ (s)} + S \text{ (s)} \rightarrow ZnS \text{ (s)} \qquad\qquad \Delta H = -206.0 \text{ kJ}$$
$$+ ZnS \text{ (s)} + 2O_2 \text{ (g)} \rightarrow ZnSO_4 \text{ (s)} \qquad\qquad \Delta H = -776.8 \text{ kJ}$$

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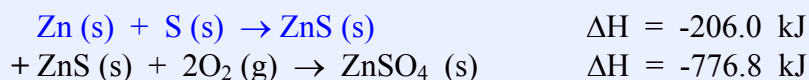
Once we cancel the ZnS (s) from both sides of the equation, we have the chemical equation we originally wanted, so we also have the ΔH:
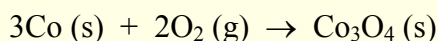
$$Zn \ (s) + S \ (s) + 2O_2 \ (s) \ \rightarrow \ ZnSO_4 \ (s)$$
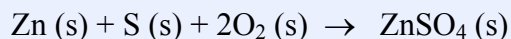
Which means <u>ΔH = -982.8 kJ</u>.

So when you use Hess's Law, it sometimes works like a puzzle. If you have a few equations with known ΔH's, you can manipulate them to get the equation in which you are interested. Once you do that, you can get the ΔH of that equation. When you attack these kinds of problems, you should look at each equation individually and decide first whether or not it has the substances you want on the correct side of the equation. If not, reverse the equation and change the sign of the ΔH. Next, look at the stoichiometric coefficients. If the equation doesn't have the proper stoichiometric coefficients, multiply the equation to get the proper coefficients, and then multiply the ΔH by that same number.

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 overall reaction in the example? It's a formation reaction, because it forms $ZnSO_4$ from its constituent elements. Think about when you used Hess's Law in your first-year chemistry course. The ΔH's you looked up in tables were ΔH's of formation ($ΔH_f$). 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 easily lend themselves to direct measurements of the ΔH. To measure the ΔH of those formation reactions, chemists measure the ΔH's of related chemical reactions and then perform calculations like the ones in Examples 1.6 and 1.7.

ON YOUR OWN

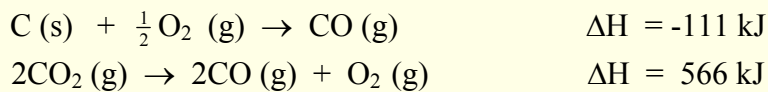1.6 Calculate the ΔH for the formation of Co_3O_4 (s) from its elements:

$$3Co \ (s) \ + \ 2O_2 \ (g) \ \rightarrow \ Co_3O_4 \ (s)$$

given the following information:

$$CoO \ (s) \ \rightarrow Co \ (s) + \tfrac{1}{2}O_2 \ (g) \qquad\qquad ΔH = 237.9 \ kJ$$
$$6CoO \ (s) + O_2 \ (g) \rightarrow \ 2Co_3O_4 \ (s) \qquad\qquad ΔH = -355.0 \ kJ$$
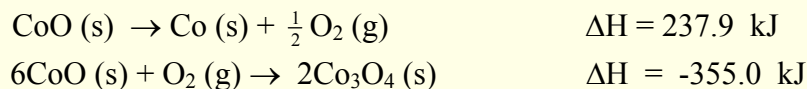
1.7 Calculate the ΔH for the complete combustion of carbon given the following information:

$$C \ (s) \ + \ \tfrac{1}{2}O_2 \ (g) \ \rightarrow \ CO \ (g) \qquad\qquad ΔH = -111 \ kJ$$
$$2CO_2 \ (g) \ \rightarrow \ 2CO \ (g) \ + \ O_2 \ (g) \qquad\qquad ΔH = \ 566 \ kJ$$

<u>Stoichiometry and Limiting Reactants</u>

Stoichiometry is probably one of the most fundamental concepts in chemistry. Although you might think you learned all there is to know about stoichiometry, there is still plenty more to learn. Before we start with the new material, however, I want to go through one quick example of stoichiometry in an attempt to further dust the chemistry cobwebs from your mind.

EXAMPLE 1.8

When hydrogen and oxygen are ignited, a violent reaction occurs, releasing a lot of energy, often in the form of an explosion. This reaction, which produces water, is mostly responsible for the 1937 explosion that destroyed the German zepplin 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?
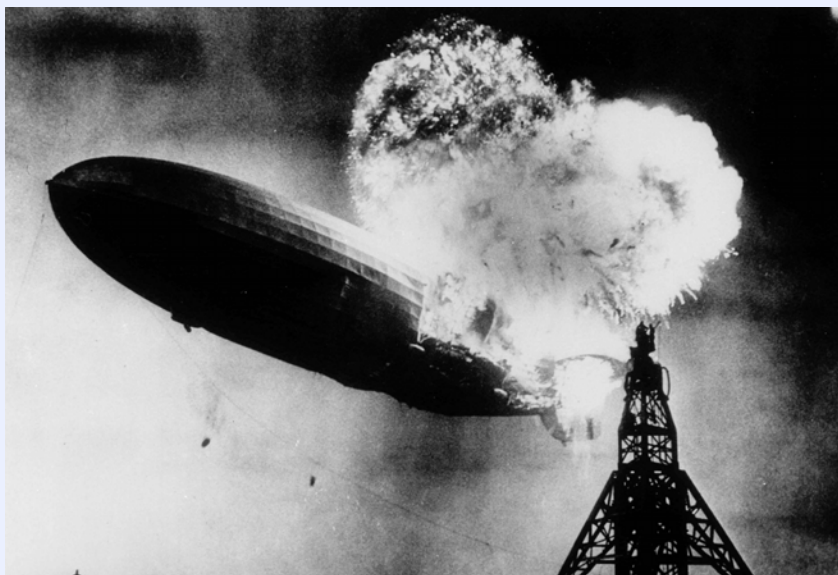
The flames you see in this photo of the *Hindenburg* disaster are mostly the result of the combustion of hydrogen.   *Image in the public domain*

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

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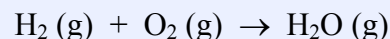
The equation is not balanced, so we have to do that first:

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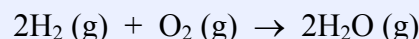
Now we know how oxygen relates to water in this reaction. For every one mole of oxygen gas, two moles of water are formed. Of course, we do not have the number of moles of oxygen; we have grams. Thus, to be able to use the chemical equation at all, we must first convert to moles:

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

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:

$$\frac{0.313 \text{ moles } O_2}{1} \times \frac{2 \text{ moles } H_2O}{1 \text{ mole } O_2} = 0.6126 \text{ moles } H_2O$$

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:

$$\frac{0.626 \; \cancel{\text{moles } H_2O}}{1} \times \frac{18.0 \text{ g } H_2O}{1 \; \cancel{\text{mole } H_2O}} = 11.3 \text{ g } H_2O$$

The reaction produces 11.3 g H_2O.

Does that example ring a few bells? It should! You did that kind of problem over and over again in your first-year chemistry course. Now that your memory has been jogged, let's cover a couple of things you probably didn't learn in your first-year chemistry course. In the example, you knew the limiting reactant because you were told that the other reactant (hydrogen) was "in excess." Suppose you weren't told that. Suppose you were just told how much of each reactant was used in the reaction. Is there any way that you can determine what the limiting reactant 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:

$$P_4 \text{ (s)} + 10Cl_2 \text{ (g)} \rightarrow 4PCl_5$$
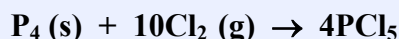
How many grams of PCl_5 can be made from 10.0 g of P_4 and 30.0 g of Cl_2?

In this problem, we are not told which reactant is in excess and which one is the limiting reactant. We will have to determine that for ourselves. How can we do this? Well, the chemical equation says that for every one mole of P_4, there must be ten 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.

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

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

Looking at those two numbers, we see that there are many, many more moles of Cl_2 than there are of P_4. Does this mean that P_4 is the limiting reactant? No! We have to look at the chemical equation to determine that. The chemical equation tells us that for every one mole of P_4, there must be *ten* 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? 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 reactant!

Now that we know Cl_2 is the limiting reactant, we know that the amount of 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:

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

The reaction produces 35.2 g PCl_5.

Do you see what I did to determine the limiting reactant? 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 wasn't. This told me that Cl_2 would get used up first and was therefore the limiting reactant. 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 left over. Thus, P_4 would be used up first and would therefore be the limiting reactant.

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 reactant. 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 reactant? 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 wasn't anything close to 10 times as many moles of Cl_2, then Cl_2 was the limiting reactant. It is *very* important for you to realize that you cannot use number of grams or even number of moles by itself to determine the limiting reactant. 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 reactant.

If you are having a hard time understanding how to determine which reactant is the limiting reactant, I want to show you one other method that is taught in many chemistry books. I don't particularly like this method, as it reduces the amount of *reasoning* you must do. However, determining the limiting reactant is so important that I am willing to let you do it via *any* method, as long as you can get the right answer.

The alternate method for determining the limiting reactant is to simply carry the calculation a bit further with *every* reactant. If we go back to the example problem, we started off by calculating the number of moles of each reactant. We learned that we had 0.0806 moles of P_4 and 0.423 moles of Cl_2. Suppose I couldn't reason my way through which was the limiting reactant. In that case, then, I could just continue to the next step, using *both* reactants. Thus, I could use the chemical equation to convert from moles of P_4 to moles of PCl_5. The chemical equation tells me that for every mole of P_4 I get four moles of PCl_5:

$$\frac{0.0806 \text{ moles } P_4}{1} \times \frac{4 \text{ moles } PCl_5}{1 \text{ mole } P_4} = 0.322 \text{ moles } PCl_5$$

Also, as was done in the example, I can convert moles of Cl_2 to moles of PCl_5, using the fact that there are 10 moles of Cl_2 for every 4 moles of PCl_5:

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

So now I have two different answers for the number of moles of PCl_5 made. It is either 0.322 moles or 0.169 moles. Which is correct? We already know which is correct, because we just did the example, but assume you didn't know yet. How could you tell which is correct? Think about it. The limiting reactant is the one that *runs out first*. As a result, it will produce *the least amount of product*. Thus, if you use this method, you convert to moles using all reactants, and then you choose the *lowest number of moles* as the answer. That will ensure you are always using the limiting reactant.

Study the following example in which I use *both* methods to determine the limiting reactant.

EXAMPLE 1.10

Calcium acetate [Ca(CH₃COO)₂] is a chemical used to set dyes that color fabrics. It can be made with the following reaction:

$$Ca(OH)_2 \ + \ 2CH_3COOH \ \rightarrow \ Ca(CH_3COO)_2 \ + \ 2H_2O$$
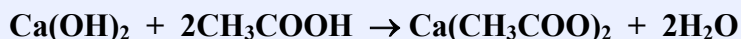
How many grams of calcium acetate can be made from 10.0 grams of each reactant?

We need to determine the limiting reactant before we can answer the question. Looking at the chemical equation, there need to be two moles of CH_3COOH 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.

$$\frac{10.0 \text{ g } CH_3COOH}{1} \times \frac{1 \text{ mole } CH_3COOH}{60.0 \text{ g } CH_3COOH} = 0.167 \text{ moles } CH_3COOH$$

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

Are there two moles of CH_3COOH 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_3COOH. There aren't quite that many, so CH_3COOH will run out first.

If you want to use the other method for determining the limiting reactant, you would look at the chemical equation and convert *both* reactants to products. For every two moles of CH_3COOH, one mole of $Ca(CH_3COO)_2$ is made. Thus:

$$\frac{0.167 \text{ moles } CH_3COOH}{1} \times \frac{1 \text{ mole } Ca(CH_3COO)_2}{2 \text{ moles } CH_3COOH} = 0.0835 \text{ moles } Ca(CH_3COO)_2$$

For every one mole of $Ca(OH)_2$, one mole of $Ca(CH_3COO)_2$ is made. Thus:

$$\frac{0.135 \text{ moles } Ca(OH)_2}{1} \times \frac{1 \text{ mole } Ca(CH_3COO)_2}{1 \text{ mole } Ca(OH)_2} = 0.135 \text{ moles } Ca(CH_3COO)_2$$

Using this method, we also see that CH_3COOH is the limiting reactant, since it produces the lower amount of product. Either way, then, CH_3COOH is the limiting reactant, so it determines how much product is made. We just learned that it makes 0.0835 moles $Ca(CH_3COO)_2$, so we can use that information to determine the grams of $Ca(CH_3COO)_2$:

$$\frac{0.0835 \text{ moles } Ca(CH_3COO)_2}{1} \times \frac{158.1 \text{g } Ca(CH_3COO)_2}{1 \text{ mole } Ca(CH_3COO)_2} = 13.2 \text{ g } Ca(CH_3COO)_2$$

The reaction produces 13.2 g Ca(CH$_3$COO)$_2$.

TiO_2 (found in the naturally-occurring mineral Rutile) is used as a pigment in white paints. It replaces the toxic pigment known as white lead, whose chemical formula is $Pb_3(OH)_2(CO_3)_2$. TiO_2 can also be made from another natural ore ($FeTiO_3$) via the following reaction:

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

How many grams of TiO_2 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 reactant before we go any further. We know that Cl_2 is not the limiting reactant 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 reactant. Looking at the chemical equation, there need to be two moles of $FeTiO_3$ for every four 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 0.330 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 be a lot of HCl left over. Thus, $FeTiO_3$ is the limiting reactant.

If you want to use the other method, you would look at the chemical equation and convert *both* reactants to products. For every two moles of $FeTiO_3$, two moles of TiO_2 are made. Thus:

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

For every four moles of HCl, two moles of TiO_2 are made:

$$\frac{2.74 \text{ moles HCl}}{1} \times \frac{2 \text{ moles TiO}_2}{4 \text{ moles HCl}} = 1.37 \text{ moles TiO}_2$$

Using this method, we also see that $FeTiO_3$ is the limiting reactant, since it produces the least amount of product.

Now that we know $FeTiO_3$ is the limiting reactant, and we know how many moles of TiO_2 it makes, we can convert moles of TiO_2 to grams:

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

The reaction produces <u>26.4 g TiO$_2$</u>.

In order to determine the limiting reactant, 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 reactant, and we use it to determine everything else. Alternately, we just convert *all* reactants to moles of product and use the answer that gives us the *least* amount of product. Try this on your own.

ON YOUR OWN

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

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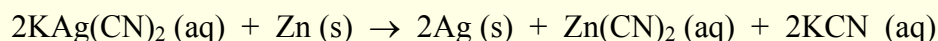
How many grams of silver will be produced when 100.0 g of $KAg(CN)_2$ is reacted with 75.0 g Zn?

1.9 Many of the barbecue grills that people have in their backyards 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!

Before we move on to the final section of this module, I want you to do an experiment that utilizes some of what you have learned in this module.

EXPERIMENT 1.1
The Strength of Household Ammonia

Note: Sample calculations for this experiment can be found at the end of the solutions to the Module #1 practice problems.

Supplies:
From the laboratory equipment set:
- Test tube rack
- Three test tubes
- Four medicine droppers
- Phenolphthalein
- Safety goggles

From your home:
- White vinegar
- Clear household ammonia (For best results, this should have been purchased fairly recently. It can be found with the household cleaners at most supermarkets.)
- Five white Styrofoam cups (The smaller they are, the better.)
- Rubbing alcohol (This is used only for cleanup, and it might not be necessary at all.)

Introduction – Vinegar is a solution of acetic acid in water. Most brands use a 5% mass to volume solution, which means there are 5 grams of acetic acid (CH_3COOH) in every 100 mL of vinegar. Most household ammonia is also a 5% solution of ammonia (NH_3) in water. However, as you will see, the strength of household ammonia varies dramatically, due to the nature of ammonia.

1. Pour ammonia into one of the Styrofoam cups until it is about ¼ full and set it aside. You will not use it for a while. **Caution: Ammonia smells pretty bad. Work in a well-ventilated room, and put this cup of ammonia some place that is not frequented by people**.
2. Rinse out the medicine droppers and test tubes thoroughly with water. Give them plenty of time to dry before you get started. If that means stopping chemistry today and picking it up tomorrow, that's fine.
3. Pour ammonia in a second Styrofoam cup until it is ¼ full.
4. Pour vinegar into a third Styrofoam cup until it is ¼ full.
5. Use one medicine dropper to take ammonia out of the second cup and put it into a test tube until the ammonia reaches the 5 mL mark on the test tube. Be sure to hold the test tube up straight as you fill it so the ammonia level can be read accurately. From now on, use this medicine dropper and test tube *only* for ammonia.
6. Pour the ammonia from that test tube into a fourth Styrofoam cup. Make sure you get as much of the ammonia out of the test tube as possible.

7. Use a second medicine dropper to add two drops of phenolphthalein to the ammonia in the cup. It will turn pink or red. From now on, use only this medicine dropper for phenolphthalein. Swirl the cup so the phenolphthalein mixes well with the ammonia.

8. Use a third medicine dropper to take vinegar out of the third cup and put it into a second test tube until the vinegar reaches the 14 mL mark on the test tube. Be sure to hold the test tube up straight as you fill it so the vinegar level is accurate. From now on, use only this medicine dropper for vinegar.

9. Empty the medicine dropper back into the third cup if there is any vinegar left in it.

10. Use that same (empty) medicine dropper to take vinegar out of the test tube and add it *slowly* to the Styrofoam cup that has the ammonia and phenolphthalein in it. Swirl the cup as you add the vinegar. You should see the pink/red color get lighter and lighter. Eventually, you want to get to the point where you are adding vinegar a drop at a time. You should reach a point where a single drop of vinegar removes the last vestige of pink color from the solution in the Styrofoam cup. If you recall what you learned in first-year chemistry, this is an **acid/base** titration.

11. This shouldn't happen, but if you add all 14 mL of vinegar from the test tube and there is still pink in the cup, that is fine. Just make sure you have completely emptied the vinegar from the test tube into the cup and then once again add vinegar to the test tube until it reaches the 14 mL point. After that, you can continue.

12. Once you have gotten the pink/red color out of the solution in the cup, return any unused vinegar that is in the medicine dropper to the *test tube* that has the vinegar in it.

13. Read how much vinegar is left in the test tube. Subtract that reading from 14 mL to determine how many mL of vinegar you had to add to the cup to get rid of the pink/red color. If you ended up refilling the test tube, add 14 mL to the answer to account for the fact that you completely emptied the test tube once.

14. Remember how an acid/base titration works. Phenolphthalein is an **indicator**. It is pink/red in the presence of a base and clear in the presence of an acid. As you added vinegar, the following reaction occurred:

$$NH_3 \text{ (aq)} + CH_3COOH \text{ (aq)} \rightarrow NH_4^+ \text{ (aq)} + CH_3COO^- \text{ (aq)}$$
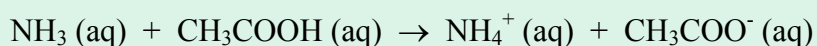
As long as there was excess NH_3, the phenolphthalein stayed pink. Thus, when you first started adding vinegar, CH_3COOH was the limiting reactant. As long as the solution had some pink/red in it, CH_3COOH was still the limiting reactant, because there was excess NH_3. As soon as the solution turned clear, however, the NH_3 was used up, making it the limiting reactant. Thus, if you stopped the experiment right when the solution turned clear, you added just enough CH_3COOH to use up all the NH_3. That's how an acid/base titration works.

15. Given the fact that the concentration of CH_3COOH in vinegar is 5 g per 100 mL, convert that to moles per liter.

16. Convert the number of mL of vinegar added (you determined it in #13) into liters.

17. Multiply the concentration you got in #15 by the number of liters you got in #16 to determine how many moles of CH_3COOH you added.

18. Given the chemical equation above, the number of moles of CH_3COOH is equal to the number of moles of NH_3. Thus, your answer for #17 is also the number of moles of ammonia in 5 mL of the household ammonia you used.

19. Since you used 5 mL (0.005 L) of ammonia solution, if you divide the number of moles of NH_3 by 0.005 L, you have the concentration of the ammonia solution in moles per liter.

20. Convert the moles per liter you got in #19 to grams per 100 mL. That's the percent of ammonia in the ammonia solution you used. Was it equal to 5%? It probably was not. Why? Finish the experiment to find out.
21. The rest of this experiment needs to be completed after the first Styrofoam cup with ammonia has been sitting out for at least 12 hours. It can sit out longer, but 12 hours is the minimum.
22. Repeat the entire experiment, but this time, use the ammonia from the first Styrofoam cup instead of ammonia from the bottle. Use a new medicine dropper and test tube for this new ammonia solution, and use a new Styrofoam cup for the titration.
23. Compare the percent of the ammonia you got the first time (using ammonia from the bottle) to the percent you got the second time (using the ammonia that had been sitting out).
24. Clean up your mess. This includes thoroughly rinsing the test tubes and medicine droppers. If the medicine dropper you used for phenolphthalein has a white residue, rinse it a few times with rubbing alcohol.

How do the percents of the two ammonia solutions compare? The percent of ammonia in the solution that set out for at least 12 hours should have been *significantly* lower than that of the ammonia solution that came straight from the bottle. Why? Because ammonia is a gas. The household ammonia that you buy is actually a solution in which ammonia gas has been *dissolved* in water. When the solution is exposed to air, some of the gas escapes solution and goes into the surrounding air. In fact, that's why household ammonia stinks. If you are unfortunate enough to get a whiff of household ammonia, you are actually smelling the NH_3 gas that has escaped from solution. This is also why the concentration of household ammonia varies widely from brand to brand and even bottle to bottle. The different manufacturing processes of different brands cause different levels of exposure to the air, which causes different amounts of ammonia to escape. In addition, the longer a bottle sits on a shelf, the more ammonia escapes from solution, because most bottles are not completely airtight. As a result, the older the bottle, the weaker the concentration of ammonia.

Stoichiometry, Percent Yield, and Multiple Reactions

Now that you've dusted the cobwebs out of your mind when it comes to stoichiometry, there are two more skills 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 that produce useful materials involve more than just one chemical reaction.

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, ever get as much product as stoichiometry indicates that you should. This isn't because stoichiometry is wrong; 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 of **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 experiment and measure the mass of the product, however, I find that I actually made only 9.0 grams. The percent yield would be:

$$\frac{\text{actual mass}}{\text{mass that should have been made}} \times 100\% = \frac{9.0\ \cancel{g}}{10.0\ \cancel{g}} \times 100\% = 90\%$$

This means that I made 90% of what I should have made. Percent yield, therefore, is high when there are few experimental errors and low when there are many. In a moment, you will see some problems with percent yield.

The second concept I want you to learn is a little harder to master. When chemists synthesize compounds, the process is usually long and complicated, involving many different reactions. Chemists still have to use 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:

$$4FeS_2\ (s)\ + 11O_2\ (g)\ \rightarrow\ 2Fe_2O_3\ (s)\ +\ 8SO_2\ (g)$$

$$2SO_2\ (g)\ +\ O_2\ (g)\ \rightarrow\ 2SO_3\ (g)$$

$$SO_3\ (g)\ +\ H_2O\ (l)\ \rightarrow\ H_2SO_4\ (l)$$
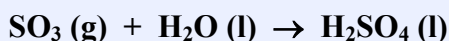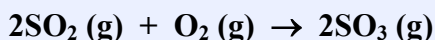
If a chemist starts with 1.13 kilograms of FeS_2 and an excess of oxygen and water, how much H_2SO_4 should be produced? If the chemist actually produces 1.51 kg of H_2SO_4, what is the chemist's percent yield?

How do we go about solving this? We know that FeS_2 is the limiting reactant, 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 find out what we want to know. Sounds like a lot of work, doesn't it? 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 equation. 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 and *only* the FeS_2.

How can I say that the sulfur atoms in H_2SO_4 come only from FeS_2? Look at the three chemical equations. FeS_2 and O_2 are reactants in the first one. That means the chemist must have FeS_2 and O_2. In the second equation, SO_2 and O_2 are reactants. However, notice that SO_2 is a *product* in the first reaction. Thus, the chemist doesn't need SO_2. It is made in the first reaction. So once the first reaction is done, the second reaction needs only more O_2, and it will run. The third reaction has SO_3 and H_2O as reactants. Once again, however, SO_3 is a product of the second reaction, so the chemist doesn't need to add that. It will be there once the second reaction is done. Thus, the only thing the chemist needs to add to get the third reaction going is H_2O. If you review, then, the only thing the chemist adds is FeS_2, O_2, and H_2O. FeS_2 is the only source of S, so all S in H_2SO_4 comes from FeS_2.

Now think about this for a minute. The hydrogen and oxygen atoms come from reactants which we are told are in excess. The sulfur atoms come from the limiting reactant: FeS_2. So the sulfur atoms in sulfuric acid all come from the limiting reactant FeS_2. What if we have one mole of FeS_2. Given an excess of water and oxygen, how much H_2SO_4 can come from one mole of FeS_2? Well, one mole of FeS_2 will give us two moles of sulfur atoms, right? Given plenty of hydrogen and oxygen atoms (from water and oxygen), two moles of sulfur atoms will give us two moles of H_2SO_4, because each mole of H_2SO_4 needs only one mole of S. 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 two moles of H_2SO_4. In other words:

$$1 \text{ mole FeS}_2 = 2 \text{ moles H}_2\text{SO}_4$$
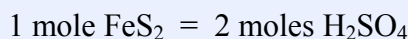
This relationship is all we need to do the stoichiometry:

$$\frac{1.13\times10^3 \ \cancel{\text{g FeS}_2}}{1} \times \frac{1 \text{ mole FeS}_2}{120.0 \ \cancel{\text{g FeS}_2}} = 9.42 \text{ moles FeS}_2$$

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

$$\frac{18.8 \ \cancel{\text{moles H}_2\text{SO}_4}}{1} \times \frac{98.1 \text{ g H}_2\text{SO}_4}{1 \ \cancel{\text{mole H}_2\text{SO}_4}} = 1.84\times10^3 \text{ g H}_2\text{SO}_4$$

So these three reactions should produce 1.84 kg H_2SO_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 reactant. Then I used the number of that element present in the limiting reactant and in the final product to develop a mole relationship between the limiting reactant 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
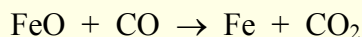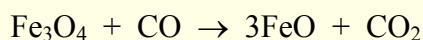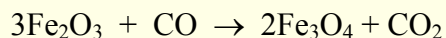
equations. I was relating two chemicals *solely* by their elements. As a result, I did not need to worry about the coefficients. Remember, the coefficients in chemical equations relate the moles of one substance to the moles of another substance *within that chemical equation*. Since I was working across three chemical equations, the stoichiometric coefficients really held no meaning for this technique.

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 reactant. 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_2S) 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 reactant, we could not have done what we did. This technique, therefore, is quite powerful, but you can only use it when the limiting reactant is the *sole* source of one element in the chemical of interest. 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:

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

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

$$FeO \ + \ CO \ \rightarrow \ Fe \ + \ CO_2$$

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 has been a while since you did stoichiometry and worked with 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:

$$\frac{65 \text{ miles}}{1 \text{ hour}} \times \frac{1,609 \text{ m}}{1 \text{ mile}} \times \frac{1 \text{ hour}}{3,600 \text{ sec}} = 29 \frac{\text{m}}{\text{sec}}$$

Sixty-five miles per hour doesn't sound as fast when you say it as <u>29 m/sec</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 40.0 amu, which means there are 40.0 grams in a mole of NaOH. The conversion from mL to L and seconds to hours you should know.

$$\frac{1.02 \text{ moles}}{1 \text{ L} \cdot \text{sec}} \times \frac{40.0 \text{ g}}{1 \text{ mole}} \times \frac{3,600 \text{ sec}}{1 \text{ hour}} \times \frac{0.001 \text{ L}}{1 \text{ mL}} = 147 \frac{\text{grams}}{\text{mL} \cdot \text{hour}}$$

The rate is <u>147 g/(mL·hour)</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:

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

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

Now we can do the conversion:

$$\frac{1,600 \text{ ft}^2}{1} \times \frac{1 \text{ yd}^2}{9 \text{ ft}^2} = 180 \text{ yd}^2$$

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 sec^2 and hour^2. The first is easy; the second requires us to square the relationship between hours and seconds:
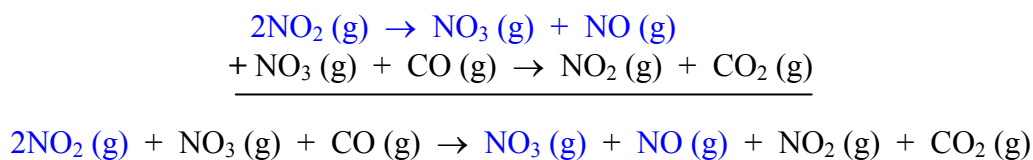
$$1 \text{ hr} = 3,600 \text{ sec}$$

$$1 \text{ hr}^2 = 12,960,000 \text{ sec}^2$$

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:
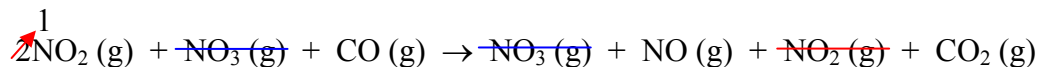
$$\frac{1.1 \; \cancel{m}}{1 \; \cancel{sec^2}} \times \frac{1 \; km}{1,000 \; \cancel{m}} \times \frac{12,960,000 \; \cancel{sec^2}}{1 \; hour^2} = 1.4 \times 10^4 \; \frac{km}{hour^2}$$

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

1.5 To get an overall equation, we just add up the two equations given:

$$2NO_2 \; (g) \rightarrow NO_3 \; (g) + NO \; (g)$$
$$+ \; NO_3 \; (g) + CO \; (g) \rightarrow NO_2 \; (g) + CO_2 \; (g)$$
$$\overline{}$$
$$2NO_2 \; (g) + NO_3 \; (g) + CO \; (g) \rightarrow NO_3 \; (g) + NO \; (g) + NO_2 \; (g) + CO_2 \; (g)$$

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

$$\overset{1}{\cancel{2}}NO_2 \; (g) + \cancel{NO_3 \; (g)} + CO \; (g) \rightarrow \cancel{NO_3 \; (g)} + NO \; (g) + \cancel{NO_2 \; (g)} + CO_2 \; (g)$$

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:

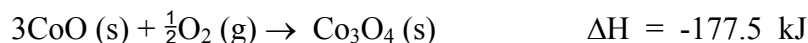$$\underline{NO_2 \; (g) + CO \; (g) \rightarrow NO \; (g) + CO_2 \; (g)}$$
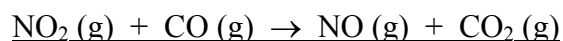
1.6   We need to get the two equations with known ΔH's to add to the one in which we are interested. In order to get that to happen, the first equation will have to be reversed, because currently Co (s) and O$_2$ (g) are products, but we need them as reactants:

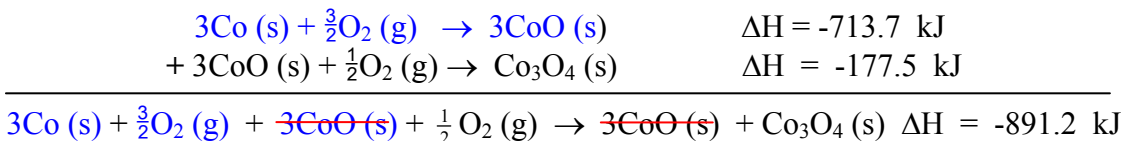$$Co \; (s) + \tfrac{1}{2}O_2 \; (g) \rightarrow CoO \; (s) \qquad\qquad \Delta H = -237.9 \; kJ$$
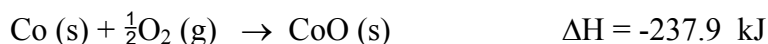
This is the only equation from which we get Co (s). Thus, the stoichiometric coefficient must be 3, because we need 3Co (s) in our final equation. As a result, I need to multiply both the equation and the ΔH by 3:

$$3Co \; (s) + \tfrac{3}{2}O_2 \; (g) \rightarrow 3CoO \; (s) \qquad\qquad \Delta H = -713.7 \; kJ$$
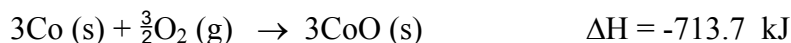
Notice that this does not give us the right coefficient with the oxygen. That's okay, though, because we get oxygen from the next equation as well. That equation has Co$_3$O$_4$ (s) as a product, so it need not be reversed. However, it has two of them, and we only want one in our equation. Thus, we need to multiply the equation and the ΔH by one-half to get:

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

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

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

$$3Co\ (s) + \tfrac{3}{2}O_2\ (g)\ +\ \cancel{3CoO\ (s)} + \tfrac{1}{2}O_2\ (g)\ \rightarrow\ \cancel{3CoO\ (s)}\ +\ Co_3O_4\ (s)\ \ \Delta H\ =\ \text{-}891.2\ kJ$$

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

$$3Co\ (s)\ +\ 2O_2\ (g)\ \rightarrow\ Co_3O_4\ (s)$$
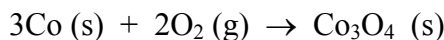
The ΔH is just the sum of the two ΔH's listed with those reactions, or -891.2 kJ.

1.7 In this problem, the chemical equation for which you must calculate the ΔH is not given. However, you should remember from your first-year chemistry course that the complete combustion of carbon is given by the equation:

$$C\ (s)\ +\ O_2\ (g)\ \rightarrow\ CO_2\ (g)$$
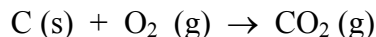
Thus, that's the equation for which we need to find the ΔH.

The first reaction we were given is fine as it is written. 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.

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

Now we can add the equations:

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

$$\cancel{CO\ (g)}\ +\ \tfrac{1}{2}O_2\ (g)\ +\ C\ (s)\ +\ \tfrac{1}{2}O_2\ (g)\ \rightarrow\ CO_2\ (g)\ +\ \cancel{CO\ (g)} \qquad \Delta H\ =\text{-}394\ kJ$$
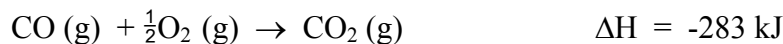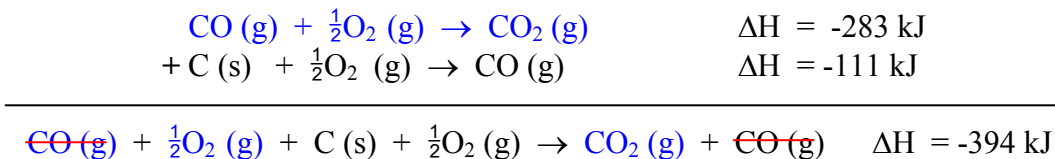
After canceling the CO (g) on both sides of the equation and combining the O_2 (g) terms on the reactants side of the equation, we are left with the equation of interest:

$$C\ (s)\ +\ O_2\ (g)\ \rightarrow\ CO_2\ (g)$$
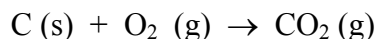
So the ΔH is simply the sum of the ΔH's listed for the two equations after we manipulated them, so $\Delta H\ =\text{-}394\ kJ$.

1.8 We need to determine the limiting reactant 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.

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

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

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.

Using the alternate method, we convert both to product to see which produces the least amount of product. Two moles of KAg(CN)₂ make two moles of Ag, so:

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

For every one mole of Zn, two moles of Ag are made:

$$\frac{1.15 \ \cancel{\text{moles Zn}}}{1} \times \frac{2 \text{ moles Ag}}{1 \ \cancel{\text{mole Zn}}} = 2.30 \text{ moles Ag}$$

So once again we see that KAg(CN)₂ is the limiting reactant, because it produces the least amount of product.

Now that we know KAg(CN)₂ is the limiting reactant, and we know the number of moles of product it makes, we can convert to grams:

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

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

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

$$C_3H_8 \text{ (g)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + H_2O \text{ (g)}$$
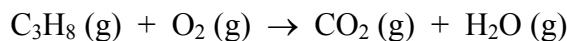
This reaction is not balanced, so we need to do that next:

$$C_3H_8 \text{ (g)} + 5O_2 \text{ (g)} \rightarrow 3CO_2 \text{ (g)} + 4H_2O \text{ (g)}$$
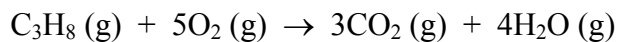
Now that we have the equation, we can determine the limiting reactant. Looking at the chemical equation, there need to be 5 moles of O_2 for every one mole of C_3H_8. Let's convert to moles to see if that is really the relationship between the number of moles of each reactant.

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

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

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.

Using the alternate method, we convert both reactants to products to see which one produces the least amount:

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

$$\frac{2.34 \text{ moles } O_2}{1} \times \frac{4 \text{ moles } H_2O}{5 \text{ moles } O_2} = 1.87 \text{ moles } H_2O$$

Either way, then, we see that C_3H_8 is the limiting reactant. Since we already know how many moles of product it will make, we can just convert to grams to finish the problem:

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

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 equations come from the previous equations. Thus, Fe_2O_3 is the only source of Fe. There are 2 Fe atoms in each Fe_2O_3 molecule, so one mole of Fe_2O_3 will make two moles of Fe.

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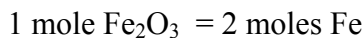
With that relationship, we can do stoichiometry.

$$\frac{1.00\times10^3 \text{ g Fe}_2\text{O}_3}{1} \times \frac{1 \text{ mole Fe}_2\text{O}_3}{159.6 \text{ g Fe}_2\text{O}_3} = 6.27 \text{ moles Fe}_2\text{O}_3$$

$$\frac{6.27 \text{ moles Fe}_2\text{O}_3}{1} \times \frac{2 \text{ moles Fe}}{1 \text{ mole Fe}_2\text{O}_3} = 12.5 \text{ moles Fe}$$

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

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

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

The percent yield, then, is 42.0%.

Cartoon by Speartoons

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 ΔH?

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

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 reactant such an important thing to know in stoichiometry?

8. A chemist makes two solutions at room temperature. Solution "a" is made by dissolving 0.3 grams of KNO_3 (s) in a 100 mL of water. Solution "b" is made by dissolving 0.3 grams of H_2S (g) in water. The chemist leaves the solutions sitting on the shelf, but the stoppers on the bottles are loose, so the seal is not airtight. Which solution will most likely be significantly weaker in solute concentration the next morning?

9. Suppose you did a limiting reactant problem using the alternate method discussed in the book. Thus, you convert both reactants to products, and they each end up producing exactly the *same number of moles* of product. What does 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?
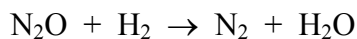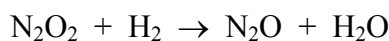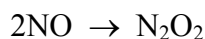
PRACTICE PROBLEMS

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? (The unit milliVolt has the same relationship to Volt as the unit milliliter does to liter.)

3. The density of a substance is 1.2 g/cm^3. What is the density in kg/m^3?
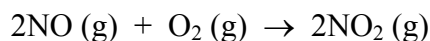
4. Given the following reaction:

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

What is the ΔH of this reaction?
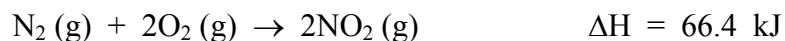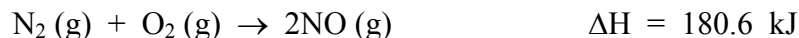
$$4SO_3 \text{ (g)} \rightarrow 4S \text{ (s)} + 6O_2 \text{ (g)}$$
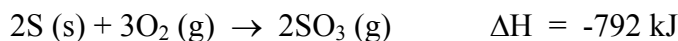
5. The following series of equations is a possible reaction mechanism for a certain reaction. What is the reaction?

$$2NO \rightarrow N_2O_2$$

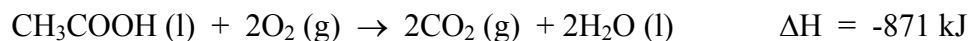$$N_2O_2 + H_2 \rightarrow N_2O + H_2O$$

$$N_2O + H_2 \rightarrow N_2 + H_2O$$

6. Calculate the ΔH for the following reaction:

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

given the following data:

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

$$N_2 \text{ (g)} + 2O_2 \text{ (g)} \rightarrow 2NO_2 \text{ (g)} \qquad \Delta H = 66.4 \text{ kJ}$$

7. Calculate the enthalpy of formation (ΔH_f) of acetic acid, CH_3COOH (l), given the following data:

$$CH_3COOH \text{ (l)} + 2O_2 \text{ (g)} \rightarrow 2CO_2 \text{ (g)} + 2H_2O \text{ (l)} \qquad \Delta H = \text{-871 kJ}$$

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

$$H_2 \text{ (g)} + \tfrac{1}{2}O_2 \text{ (g)} \rightarrow H_2O \text{ (l)} \qquad \Delta H = \text{-286 kJ}$$

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:

$$2C_2H_4 + O_2 \rightarrow 2C_2H_4O$$
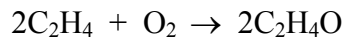
If a chemist starts with 11.0 g of C_2H_4 and 11.0 g of O_2, what mass of ethylene oxide should the chemist be able to make?

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

$$CaO + 3C \rightarrow CaC_2 + CO$$
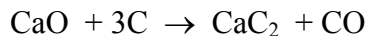
A chemist reacts 1.00 kg of CaO with 1.00 kg of carbon. If the chemist ends up with 1.00 kg of calcium carbide, what is the percent yield?

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

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

$$2NO + O_2 \rightarrow 2NO_2$$

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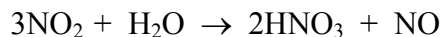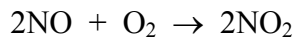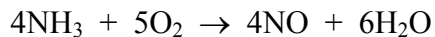
In this process, the NO made in the last reaction is recycled back into the second reaction and used as a reactant. In the end, *all* of the NO produced is recycled back so that when the manufacturing process is complete, essentially no NO remains. If a chemist starts with 35.0 grams of NH_3 and an excess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