Lecture 5:

When we began our study of chemistry, I said that we would examine the nature

of the transformations of chemicals. Such transformations are called chemical reactions.

It is important that we have a way of representing these reactions which is both

unambiguous and predictive. Verbal descriptions of reactions are valuable, but are often

cumbersome. In addition, verbal descriptions make quantitative study of the reactions

and quantitative predictions regarding the reactions difficult. For this reason, we

represent chemical reactions symbolically in the form of a chemical equation.

An example of this is the reaction:

$$KBr(aq) + AgNO_3(aq) \rightleftharpoons KNO_3(aq) + AgBr(s)$$
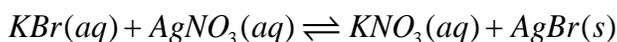
This equation is the same as saying that potassium bromide in an aqueous solution reacts

with silver nitrate in an aqueous solution to form an aqueous solution of potassium nitrate

and solid silver bromide. Another example of a chemical equation is for the reaction:

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l).$$
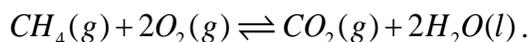
Note that a complete equation includes not only the identity and relative amounts of

products and reactants, but also their phases. The most common phases are solid (s),

liquid (l), gas (g) and an aqueous solution (aq), i.e. a solution in which water is the

solvent. Some times when a gas is a product of the reaction, we indicate that with an

upward arrow, ($\uparrow$), and when a solid is a product of the reaction we indicate that with a

downward arrow, ($\downarrow$). Being able to convert between an equation and a description of a

reaction in words is an essential skill of chemistry.

Notice that in both of our examples, the product side of the equation had the same

number of each element that the reactant side did. In our first example, the reactant side

has one potassium, one bromine, one silver, one nitrogen and three oxygen atoms. The product side also has one potassium, one bromine, one silver, one nitrogen and three oxygen atoms. In our second example, there is one carbon, four hydrogens and four oxygens on the reactant side, and one carbon, four hydrogens and four oxygens on the product side. When the number of atoms of each element is the same on both sides of the equation, we say that the reaction is **balanced**. The requirement that reactions be balanced is a consequence of the **law of conservation of matter**. It states, simply enough, that matter is neither created nor destroyed during a chemical reaction. What this means is that in chemical reactions, elements are only rearranged, not created or destroyed. Since they are only rearranged, the number of each at the beginning of the reaction and the number at the end of the reaction must be the same.

Balancing is a powerful tool. When an equation is properly balanced it allows our equations to become predictive. For example, in a few minutes we will learn how to predict how much product can be formed from a given mass of reactant. We can also figure out more esoteric things like how much heat is released when a given mass of reactant is consumed, or how much the pressure changes. These latter two may be critical to making sure that a reaction is safe to run.
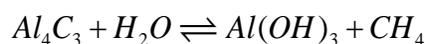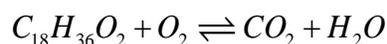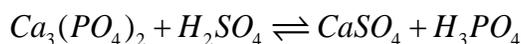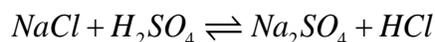
Let's try to balance the reaction

$$N_2(g) + H_2(g) \rightleftharpoons NH_3(g).$$
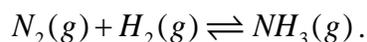
Unfortunately there is no simple set of rules that makes it easy to balance a reaction every time (the exception is balancing reactions involving transfer of electrons from one molecule to another, so-called redox reactions, but you will deal with them in Chem 317.) The only advice I can give you is to start by balancing the elements that are present in the

smallest numbers in the reactants. That approach usually ends in a successful solution after a relatively small number of tries.
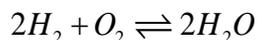
Let's practice a few more times:

$$NaCl + H_2SO_4 \rightleftharpoons Na_2SO_4 + HCl$$

$$Ca_3(PO_4)_2 + H_2SO_4 \rightleftharpoons CaSO_4 + H_3PO_4$$

$$C_{18}H_{36}O_2 + O_2 \rightleftharpoons CO_2 + H_2O$$

$$Al_4C_3 + H_2O \rightleftharpoons Al(OH)_3 + CH_4$$

Note again that after balancing equations the coefficients need to be the smallest possible whole numbers. As an example,

$$4H_2 + 2O_2 \rightleftharpoons 4H_2O$$
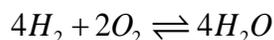
is incorrect since it doesn't use the smallest possible whole numbers.

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

is correct. However, there are times when fractional coefficients are acceptable. Later we will define a quantity called enthalpy of formation, which is the heat change when one mole of a product is formed. This means that in calculations involving enthalpy of formation, the balanced equation will need to result in one mole of product, in this case

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O \ .$$
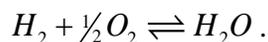
In general, though, it is preferable to balance equations using only whole numbers.

A new concept that is important in describing chemical reactions is the percent yield. Not all reactions go to completion. In fact, some new organic reactions, before they are perfected, convert only 5% of the reactants to products. Understanding reaction yield is particularly important for chemical engineering or for considerations of the

environmental impact of a chemical process. The lower the percent yield is the more

wasteful a process is. For industry, that means it's costlier, and for the environment it

means that the waste generated is much higher.

But what is a **percent yield**? It is simply the ratio of the mass of product formed,

divided by the maximum mass of product that can be formed from the reactants,

multiplied by 100%. We call the maximum amount of product that can be formed from

the reactants the **theoretical yield**. Therefore, the formula for percent yield is

$$\% \ Yield = \frac{actual \ yield(g)}{theoretical \ yield(g)} x100\% \ .$$

For example, consider the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
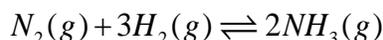
Suppose that we begin with 28.0 g of N_2 and 6.06 g of H_2. Then the theoretical yield of

NH_3 will be 34.1g. (I will show you how to determine this shortly.) Now suppose that

after running the reaction we weigh the NH_3 produced and find that we have made only

25.6 g of NH_3. In this case our percent yield is:

$$\% \ Yield = \frac{actual \ yield(g)}{theoretical \ yield(g)} x100\% = \frac{25.6g}{34.1g} x100\% = 75.0\%$$

Now we need to know **how to calculate theoretical yields**. Suppose for the

reaction we've just looked at,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g),$$
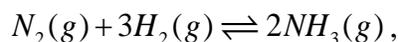
we begin with 5.00 g of N_2. What is the maximum amount of ammonia that can be

formed, I.E., the theoretical yield? There are two cases to consider here. The first is

where there is enough H_2 present so that all of the N_2 can react. Clearly, if we run out of

hydrogen before the nitrogen is used up, less ammonia will form than if we were able to use all of the nitrogen. The second is where the amount of hydrogen is insufficient.

How do we figure how much hydrogen we need to react with all of the nitrogen? We use moles and the coefficients we obtained by balancing our reaction. These coefficients are called stoichiometric coefficients.

Our approach is as follows:

First we convert grams of N_2 to moles of N_2. Then we use our coefficients to determine how many moles of H_2 we need. Then we convert back to grams of H_2. Broken down it looks like this – note the use of units in the calculations.

$$5.00 g \; N_2 \; x \frac{1 mol \; N_2}{28.013 \; g \; N_2} = .1784 \, mol \; N_2$$

Now we need to convert from moles of N_2 to moles of H_2. Our balanced reaction tells us that we need 3 moles of H_2 for every mole of N_2, so

$$.1784 \, mol \; N_2 \; x \frac{3 mol \; H_2}{1 mol \; N_2} = .5352 \, mol \; H_2$$

Finally, we convert moles of H_2 to grams of H_2:

$$.5352 \, mol \; H_2 \; x \frac{2.0159 g \; H_2}{mol \; H_2} = 1.08 g \; H_2$$

Note that while I've broken this down into three calculations for the sake of clarity, it can be done in a single calculation, involving all three steps:

$$5.00 g \; N_2 \; x \frac{1 mol \; N_2}{28.013 \; g \; N_2} \; x \frac{3 mol \; H_2}{1 mol \; N_2} \; x \frac{2.0159 g \; H_2}{1 mol \; H_2} = 1.08 \; g \; H_2$$

So we've learned that as long as we have at least 1.08 g of H_2, all 5.00 g of N_2 will be reacted, and we can therefore use the 5.00 g of N_2 to figure out how much ammonia is formed. We use the same approach we used to see how much hydrogen was needed:

First we convert grams of N_2 to moles of N_2. Then we use the coefficients from our balanced reaction to determine how many moles of ammonia are formed for each mole of N_2, and finally convert moles of ammonia to grams of ammonia.

Since the approach is basically the same as the one we just used, I'll combine the three steps in a single calculation:

$$5.00g \; N_2 \; x \frac{1 \, mol \; N_2}{28.013g \; N_2} \, x \frac{2 \, mol \; NH_3}{1 \, mol \; N_2} \, x \frac{17.031g \; NH_3}{1 \, mol \; NH_3} = 6.08g \; NH_3$$

Notice that it would not have been possible to do any of these calculations correctly without first having balanced the reaction.

We're making progress. We know how to calculate the theoretical yield when there is just enough of each reactant that none of them run out before the reaction is complete. But what if one of the reactants runs out before all of the reactants can be consumed? The answer is that **the amount of product is determined by the amount of the reactant which runs out first**. When we have a situation where one reactant runs out first, we call that reactant a **limiting reagent**. If we are given a reaction, and the masses of each of the reactants, before we can calculate our theoretical yield, it is necessary to determine which of the reagents (another name for reactants) is limiting, so that we base our calculation on the correct reactant.

To determine the limiting reagent, calculate the number of moles of each reactant, and then divide by its stoichiometric coefficient. The reagent with the smallest resulting number will be limiting.

For example, for our ammonia reaction, suppose that we have 7.50 g of N_2 and 2.50 g of H_2? Which is limiting?

$$(7.50g\ N_2\ x\frac{1\,mol\ N_2}{28.013g\ N_2})/1=.2677$$

$$(2.50g\ H_2\ x\frac{1\,mol\ H_2}{2.016g\ H_2})/3=.4133$$

Since the number resulting from our calculation is smaller for N_2, N_2 is limiting. Thus for this amount of each reactant, we would calculate the theoretical yield from the N_2.

A second approach, which works but is labor intensive, would simply be to calculate the theoretical yield from the amount of each of the reactants. The one which results in the smallest theoretical yield is limiting. The smallest theoretical yield will be the correct one.

Lecture 6

We need to extend our study of the quantities involved in chemical reactions by considering how to describe and manipulate the amounts of material when our reactions occur in solution. You are probably more familiar with reactions in solution than with reactions in other phases, because of the relative simplicity in carrying out solution phase chemistry.

When we describe amounts of material in solution phase chemistry, the critical quantity is still the mole, but unlike in the case of solid or gas phase chemistry, mass is no longer the easiest way to measure the amount of material. The reason is that every solution consists of a combination of at least two substances, the solvent and the solute. We define the solvent as the larger component in a solution, and the solute as the smaller component. So for example, in a solution containing 5.00 g of NaCl and 1000 mL of water, water would be the solvent, and NaCl the solute. You can see what the problem is with using sample mass to characterize such systems. The bulk of the mass is typically the solvent, yet the chemically interesting part, the part that reacts, is the solute. The solution is to use volumes to characterize the size of a solution, and use concentrations to quantify the amount of solute in the sample.

We will define two types of concentrations. The first is the mass concentration. Mass concentration is defined as the mass of the solute divided by the volume of the solution, i.e.,

$$mass\ conc. = \frac{g\ solute}{L\ solution}$$

with units of grams/L. This unit is both useful and common, but even more common and more useful is the molarity, or moles of solute per liter of solution. The molarity is symbolized by a capital M, and is defined as

$$M \equiv \frac{n_{solute}}{V_{solution}(L)}.$$

Notice a couple of things about both of these concentration units. First, typically the unit of volume we use is liters. This means that if we use some other unit of volume in making our measurement we need to convert to liters. This suggests that this would be a good time to look at common units of volume you may run into. We've already mentioned the liter. The liter in SI units is one dm^3. You may see either of these units, but liter is more common. Often you will measure volumes in smaller units, most commonly mL. 1L = 1000 mL. Frequently, instead of mL, you'll see small volumes expressed as cm^3. This is the same as mL. Thus $1L = 1\ dm^3 = 1000\ mL = 1000\ cm^3$.

The other thing to notice is that we are dividing by volume of solution, not volume of solvent. The reason for this is that when the vast majority of solutions are made, the volume of the solvent changes. Sometimes the solvent shrinks a bit, and sometimes it expands. So the volume of the solvent in a solution is not well defined. This is the reason that we need to divide by the total volume of solution.

But if the volume of the solvent changes, how do we accurately determine the volume when we make a solution? The answer is that we use a device called a volumetric flask. You've either already used them in lab or will use them shortly.

The first thing you'll notice about a volumetric flask, is that it only has a single volume indicated. It is indicated by a line somewhere in the neck of the flask. When you make a solution, you first add your solute, and then carefully add your solvent, so that the solute is dissolved, and for an aqueous solution, the bottom of the meniscus is just touching the line. This means that you've made a solution that's exactly the volume written on the flask.

Let's do some quick examples using molarity:

Example 1: How many moles of $AgNO_3$ are there in a 35 mL of a 0.78 M aqueous solution?

Approach: We have two pieces of information to work with, the volume of our sample and the concentration. We simply multiply the volume by the concentration to obtain moles. We can tell that this is the correct approach by writing down the definition of

molarity, $M \equiv \dfrac{n_{solute}}{V_{solution}(L)}$. We can use this to solve for n, to get

$$n_{solute} = M * V_{solution}$$

The only challenge here is to make sure that we use the correct units.

$$35\,mL\,AgNO_3(aq) x \frac{1.00L\,AgNO_3(aq)}{1000\,mL\,AgNO_3(aq)} x \frac{0.78\,mol\,AgNO_3}{L\,AgNO_3(aq)} = 2.7 x 10^{-2}\,mol\,AgNO_3$$

Example 2: How many moles of Na^+ are there in 75.0 mL of 0.200 M $Na_3PO_4(aq)$

Approach: The approach is the same as the previous example, with one exception. The number of mols of Na_3PO_4 is not the same as the number of mols of Na^+, since the formula of the compound tells us that each molecule contains three sodium atoms.

Therefore, we need one additional step to convert from moles of Na3PO4 to moles of Na$^+$.

$$75.0\, mL\, Na_3PO_4(aq) \times \frac{1.00 L\, Na_3PO_4(aq)}{1000\, mL\, Na_3PO_4(aq)} \times \frac{0.200\, mol\, Na_3PO_4}{L\, Na_3PO_4(aq)}$$

$$x \frac{3\, mol\, Na^+}{1\, mol\, Na_3PO_4} = 4.5x10^{-3}\, mol\, Na^+$$

Example 3: How many moles of NaCl are necessary to make 100 mL of a 1.00 M solution.

Approach: We start with the definition of molarity, $M \equiv \dfrac{n_{solute}}{V_{solution}(L)}$. This definition contains all three quantities that are involved in this question, the volume and concentration that we are given, and the number of moles that we want to know. To solve the problem, we simply take the definition and solve it for the quantity we want:

$$n_{solute} \equiv M\ xV_{solution}(L).$$

The only remaining issue is to take our usual care to make sure all units match.

$$100\, mL\, NaCl(aq) x \frac{1 L\, NaCl(aq)}{1000\, mL\, NaCl(aq)} \times \frac{1.00\, mol\, NaCl}{L\, NaCl(aq)} = .100\, mol\, NaCl$$

Example 4: How many grams of NaOH are necessary to make 250 mL of a 1.50 M solution?

Approach: The approach here is the same as in the previous example, except that we need one additional step, to convert from moles of NaOH to grams, using the molar mass.

$$250\, mL\, NaOH(aq) x \frac{1 L\, NaOH(aq)}{1000\, mL\, NaOH(aq)} \times \frac{1.50\, mol\, NaOH}{1 L\, NaOH(aq)} \times \frac{40.00 g\, NaOH}{mol\, NaOH} = 15.0 g\, NaOH$$

In addition to preparing solutions by dissolving solutes in solvents, another common way that we prepare a solution of a given concentration is by diluting a

previously made solution. Thus it is important to understand how to calculate the new concentration after a dilution.

The most important thing to remember in any dilution calculation is that the number of moles of solute in the sample being diluted does not change during the dilution. Only the solution volume changes.

So for example, suppose we have 200 mL of a 1.000 M solution of ethanol in water. How many moles of ethanol do we have in this solution?

$$n_{ethanol} = \frac{1.000\, mol\, ethanol}{L\, ethanol\,(aq)} x\, 200 mL ethanol(aq) x \frac{1L\, ethanol(aq)}{1000\, ml\, ethanol(aq)} = 0.200\, mol\, ethanol$$

Now we place this 200 mL of the ethanol solution into a 1.000 L volumetric flask, without adding any more water. Now how many mols of ethanol do we have in the solution? Still 0.200 mol, because we haven't changed the amount of solute. Now we add enough water to bring the volume to 1.000 L exactly. How many moles of ethanol are in the solution now? Still 0.200, because we still haven't done anything to change the amount of solute. BUT, the concentration has now changed, because

$$M_{ethanol} = \frac{n_{ethanol}}{V_{solution}}$$

and we've changed the total volume of the solution. The new concentration of the ethanol is

$$M_{ethanol} = \frac{0.200\, mol\, ethanol}{1.000 L\, solution} = \frac{0.200\, mol\, ethanol}{L} .$$

Again, during a dilution, the number of moles in the solution doesn't change, just the total volume of the solution.

This is summarized in a simple form by the lever rule. The lever rule is

$$M_1V_1 = M_2V_2.$$

In this equation, V_1 is volume of the sample that you are diluting. Note that if you take

50 mL out of a 1000 mL bottle and dilute it, V_1 is 50 mL, the actual amount you're

diluting, not the amount in the bottle you took it from. M_1 is the molarity of this initial

sample. V_2 is the volume to which you are diluting the sample, and M_2 is the final

molarity. Note that this rule is completely consistent with our statement that the number

of moles of solute stays the same during a dilution, because molarity times volume is the

number of moles, and M_1V_1, the initial number of moles, is equal to M_2V_2, the final

number of moles.

As an example, suppose that you take 50 mL of a 0.982 M solution of NaOH, and

dilute it to 250.0 mL. The final concentration will be given by our lever rule:

$$M_2 = M_1 * \frac{V_1}{V_2} = 0.982M \ NaOH(aq) * \frac{0.050 \, L \, NaOH(aq)}{0.250 \, L \, NaOH(aq)} = 0.196M \ NaOH(aq).$$

Since multiplying volumes and molarities gives us moles, we can use this to

determine the yield of a reaction in which the reactants are in the form of aqueous

solutions. Suppose we are studying the reaction:

$$2AgNO_3(aq) + Na_2CrO_4(aq) \rightleftharpoons Ag_2CrO_4(s) + 2NaNO_3(aq).$$
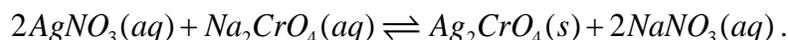
How many grams of silver chromate will be formed if we begin with 45.0 mL of 1.70M

AgNO$_3$(aq), and the silver nitrate is the limiting reagent?

Approach: We convert concentration and volume to moles, then convert moles of silver

nitrate to moles of product using the coefficients from our balanced reaction, and then

convert moles of product to grams of product.

$$45 \, mL \, AgNO_3(aq) \times \frac{1L \, AgNO3(aq)}{1000 \, mL \, AgNO3(aq)} \times \frac{1.70 \, mol \, AgNO_3}{L \, AgNO3(aq)} \times \frac{1 \, mol \, Ag_2CrO_4}{2 \, mol \, AgNO_3} \times \frac{331.73g \, Ag_2CrO_4}{mol \, Ag_2CrO_4} = 12.7g \, Ag_2CrO_4$$

We can also use volumes and molarities to find out exactly how many moles of one reactant it takes to react completely with another, or, if the second reactant is also in the form of a solution, what volume of the solution it takes to react completely with another. Suppose we are studying the reaction:

$$HCl(aq) + NaOH(aq) \rightleftharpoons NaCl(aq) + H_2O(l)$$
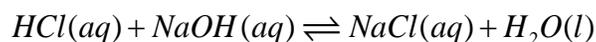
If we start with 50.0 mL of 0.950 M NaOH(aq), a) how many moles of HCl are needed to react completely with it, and b) how many mL of a 0.750 M HCl(aq) solution are needed to react completely with it.

$$50.0\,mL\,NaOH(aq) \times \frac{1L\,NaOH(aq)}{1000\,mL\,NaOH(aq)} \times \frac{0.950\,mol\,NaOH}{L\,NaOH(aq)} \times \frac{1mol\,HCl}{1mol\,NaOH} = 0.0475\,mol\,HCl$$

To use this to determine the number of mL of 0.750 M HCl(aq) we need, we use our definition of molarity, but place the volume on top so that the units properly cancel
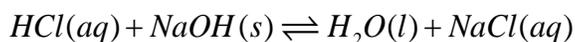
$$0.0475\,mol\,HCl \times \frac{1.00L\,HCl(aq)}{0.750\,mol\,HCl} = .0633L\,HCl(aq)$$

which of course is the same as 63.3 mL of the aqueous HCl.

We can also ask how many ml of the 0.750 M HCl it would take to react with 2.90g of NaOH.

Approach: After balancing the reaction, the critical step is to convert the amount of our starting material, NaOH, to mols, and then find out how many mols of HCl are required to react with it. We then use the definition of molarity to convert from moles of HCl to ml of HCl(aq).

The balanced reaction is:

$$HCl(aq) + NaOH(s) \rightleftharpoons H_2O(l) + NaCl(aq)$$

$$2.90 \, g \, NaOH(s) \, x \, \frac{1 \, mol \, NaOH(s)}{40.00 \, g \, NaOH(s)} \, x \, \frac{1 \, mol \, HCl}{1 \, mol \, NaOH} \, x \, \frac{1.00L \, HCl(aq)}{0.750 \, mol \, HCl} \, x \, \frac{1000 \, mL \, HCl(aq)}{1.00L \, HCl(aq)} = 96.6 \, mL \, HCl \, (aq)$$

These last examples are particularly important because of a common and important

analytical technique called titration. In titration we determine the concentration of an

unknown substance by reacting it completely with a solution of known concentration.

For example, we might determine the concentration of a solution of NaOH(aq) by

reacting it completely with a known concentration of HCl(aq). As we can see from the

balanced equation above, the reaction will be complete when we've added a number of

mols of HCl(aq) that is equal to the number of the mols of NaOH(aq) that we began with.

The point at which the reaction is complete is called the endpoint of the titration. Once

the volume of titrant (the substance you are adding) necessary to reach the endpoint is

measured, we can calculate the moles of the unknown substance, and then by using the

volume we began with, calculate its concentration.

How can we tell experimentally that we have reached the endpoint of the

titration? One way that we will learn toward the end of the semester is to measure pH as a

function of titrant added to the flask, and analyze the resulting graph. However, before

we use this approach we have a lot to learn about acids and bases and about chemical

equilibria.

A simpler, albeit somewhat less precise, method for determining the endpoint is to

use a chemical indicator. An indicator is a chemical that changes color when the

chemical in the unknown is completely consumed. In our upcoming lab, we will use the

indicator phenolphthalein, which turns from clear to pink when all the HCl is consumed,

and our solution has an excess of even a fraction of a drop of NaOH, i.e. when our

solution is basic. So if you are titrating a sample of HCl with an unknown concentration

with a sample of NaOH with known concentration, the moment the solution turns even

the faintest pink, you've added a number of moles of NaOH that are equal to the number

of moles of HCl that you started out with, and you can calculate the concentration of the

unknown.

Let's do an example of using a titration to determine the concentration of an

unknown sample of HCl. Example: a 20 mL sample of HCl(aq) with an unknown

concentration is placed in a flask, and three drops of phenolphthalein are added. The

solution is titrated with a 1.056 M solution of NaOH. The solution turns the palest pink

after 35.5 mL of the NaOH have been added to the solution. What is the concentration of

the unknown HCl(aq) solution?

Approach: We need to begin by balancing our reaction. We can figure out the number of

moles of NaOH we used by using the definition of molarity. Then we figure out the

number of moles of our unknown by recognizing that it is completely consumed at the

endpoint, and therefore the stoichiometry tells us how many moles were present. Finally,

we divide the number of moles of the unknown by the volume of its solution, and this

tells us the concentration.

The balanced reaction is:

$$HCl(aq) + NaOH(aq) \rightleftharpoons H_2O + NaCl(aq)$$
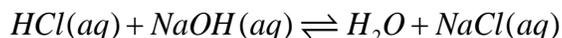
The number of moles of HCl is given by

$$35.5\,mL\,NaOH(aq)\,x\,\frac{1.056\,mol\,NaOH}{1000\,mL\,NaOH(aq)}\,x\,\frac{1\,mol\,HCl}{1\,mol\,NaOH} = 3.749x10^{-2}\,mol\,HCl$$

Now we calculate the concentration of the HCl, remembering that the volume of the

sample that we titrated was 20 mL.

$$M(HCl(aq)) = \frac{n_{HCl}}{V_{Solution}} = \frac{3.749x10^{-2} \, mol \, HCl}{20.0 \, mL \, solution} \, x \frac{1000 \, mL \, solution}{1.000 \, L \, solution} = 1.87M \, HCl(aq)$$

Lecture 7

Part of our understanding of the different ways that chemicals can change involves classifying both materials and reactions. We've already begun with this type of classification of substances in several ways. Now we are going to add an additional classification for solutes. We typically divide all solutes into electrolytes and non-electrolytes.

The classification comes from the history of chemistry in this country, in which electrochemistry, the use of electricity to drive chemical reactions, and conversely, the use of chemical reactions to generate electricity, was the dominant form of early chemical endeavor. As such early chemists were interested in whether solutes conduct electricity.

An electrolyte is a solute that conducts electricity when in solution. In the case of aqueous solutions, electrolytes are compounds that dissociate into cations and anions when dissolved. The most familiar example of this would be common table salt, $NaCl(s)$, when $NaCl(s)$ dissolves in water it separates into a $Na^+(aq)$ and a $Cl^-(aq)$. Each ion is completely surrounded by water molecules.

Molecular compounds can also be electrolytes. The classic example of this is the acid hydrochloric acid. In the gas phase it is molecular, with the formula $HCl(g)$. However, when it dissolves in water it dissociates into a proton, H^+, and a chloride ion, Cl^-.

Not all electrolytes dissociate completely when in solution. For example, in contrast to $HCl(aq)$, which dissociates completely to protons and chloride ions when dissolved in water, $HF(aq)$, stays mostly in the form of HF, with only one in 20 HF molecules breaking up to form protons and fluoride ions. When a molecule that has

dissolved is only partially dissociated, we say that that substance is a weak electrolyte. A substance that completely dissociates when dissolved is called a strong electrolyte. Another example of a weak electrolyte is acetic acid, CH_3COOH, which mostly stays in this form, with only about 1 in 10 molecules dissociating to form protons, H^+, and the acetate ion, CH_3COO^-. NaCl and HCl are strong electrolytes.

Note that a substance like AgCl(s), which dissolves only to a very small extent, is still a strong electrolyte, because all of the AgCl which does dissolve to form AgCl(aq) dissociates to form silver cations and chloride anions.

Some substances are not electrolytes at all. When dissolved in water they do not dissociate at all, but retain their identity as molecules completely. Examples of this are ethanol, C_2H_5OH, which stays as a whole molecule once dissolved, and sugar, $C_6H_{12}O_6$, which also stays as a discrete molecule after dissolution. One piece of experimental evidence that distinguishes electrolytes from non-electrolytes is to measure how well a solution conducts electricity. A solution of electrolytes will conduct electricity well, while a solution of non-electrolytes will have a high resistance.

We can classify reactions as well. There are several different types, each of which has some unique characteristics. The main types are double exchange reactions, single exchange reactions, combination reactions and decomposition reactions. We will discuss each of these today. As you move on in your study of chemistry, you'll learn about other classifications of reactions.

The reaction between NaCl(aq) and $AgNO_3$(aq) is one example of a **double replacement reaction**, also called a metathesis reaction. The reaction is:

$$NaCl(aq) + AgNO_3(aq) \rightleftharpoons AgCl(s) + NaNO_3(aq).$$
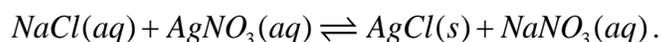
You can see from this example why this is called a double replacement reaction, since both the Na^+ and the Ag^+ replace their partner ions. Note that in this example, two solutions are mixed and the result is the formation of a solid and a solution. Since a solid formed by the reaction of two aqueous solutions is called a precipitate, this kind of double exchange reaction is called a precipitation reaction.

The biggest challenge in recognizing a precipitation reaction is deciding whether a precipitate will form when two aqueous solutions are combined. One approach is to turn to a reference work such as the CRC Handbook of Chemistry and Physics, which compiles information about the solubilities of a massive number of compounds (among other data). However, there are a small number of solubility rules which can be used to determine the qualitative solubilities of quite a large number of compounds. Unfortunately the only way to learn these rules is to memorize them. The rules are:

1. All common compounds of Group 1A ions (Li^+, Na^+, K^+, etc) and ammonium ion (NH_4^+) are soluble.

2. All nitrates (NO_3^-), acetates (CH_3COO^- or $CH_3CO_2^-$), and most perchlorates (ClO_4^-) are soluble.

3. All common chlorides (Cl^-), bromides (Br^-), and iodides (I^-) are soluble except those of Ag^+, Pb^{+2}, Cu^+, and Hg_2^{2+}. All common fluorides (F^-) are soluble, except those of Pb^{+2} and group 2A.

4. All common sulfates (SO_4^{-2}) are soluble except those of Ca^{+2}, Sr^{+2}, Ba^{+2}, Ag^+ and Pb^{+2}.

5. All common metal hydroxides are insoluble, except those of group 1A, and the heavier members of group 2A beginning with Ca^{+2}.

6. All common carbonates (CO_3^{-2}) and phosphates (PO_4^{-3}) are insoluble, except those of group 1A and of NH_4^+.

7. All common sulfides are insoluble except those of group 1A, group 2A, and NH_4^+.

So for example if we look at the reaction

$$2NaBr(aq) + Pb(NO_3)_2(aq) \rightleftharpoons PbBr_2 + 2NaNO_3$$
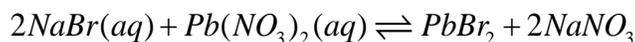
by consulting our solubility rules we see that $NaNO_3$ is soluble (because it contains both a group 1A metal and a nitrate group), but the $PbBr_2$ is insoluble, therefore it forms a solid, and this is a precipitation reaction. In contrast,

$$Mg(NO_3)_2(aq) + Ca(ClO_4)_2(aq) \rightleftharpoons Mg(ClO_4)_2 + Ca(NO_3)_2$$
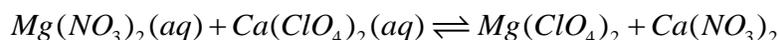
forms no precipitate since both $Mg(ClO_4)_2$ (containing perchlorate) and $Ca(NO_3)_2$ (containing nitrate) are soluble.

Another example of a double replacement reaction is the reaction between hydrochloric acid and sodium hydroxide:

$$HCl(aq) + NaOH(aq) \rightleftharpoons H_2O(l) + NaCl(aq)$$
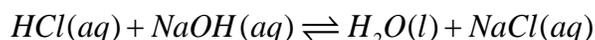
You can see that in this reaction both the H^+ and the Na^+ change partner ions. This type of reaction is called an acid-base neutralization, and is another important subset of double replacement reactions.

We will deal in detail with acid-base reactions later in the semester, but this type of reaction is so ubiquitous that it is important to introduce some of the basic concepts now. First we need to define acids and bases. The most useful definition for our current purpose is the Brønsted-Lowry definition. According to this definition an acid is a proton (H^+) donor, and a base is a proton acceptor. Your book has a list of common Brønsted-

Lowry acids. The most common bases are metal hydroxide compounds, such as NaOH

or Ca(OH)$_2$, metal oxide compounds (Li$_2$O), and both ammonia (NH$_3$) and amines

(compounds that include NH$_2$).

The most common reaction of acids with bases is a type of double replacement

reaction called a neutralization reaction, in which an acid and a base react to form water

and a salt, where a salt is an ionic compound formed by the reaction of acids and bases.

Here are some examples:

$$2NaOH + H_2SO_4 \rightleftharpoons 2H_2O + Na_2SO_4$$
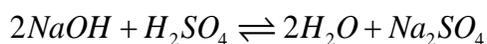
Note that the effect of the reaction is to take two nasty substances, the acid and base, and

to replace them with two innocuous substances, water, and a salt. Here is another

example.

$$3Mg(OH)_2 + 2H_3PO_4 \rightleftharpoons Mg_3(PO_4)_2 + 6H_2O$$
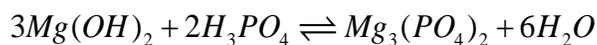
You can see that here too, the acid and base are both destroyed and replaced by milder

substances, hence the name neutralization.

A logical question to ask is what DOES happen if we have a double exchange

reaction that does not result in either an acid-base neutralization or formation of a

precipitate. The easiest way to show this is to introduce a new tool called a **net ionic**

equation. The basic idea of a net ionic equation is to show only those parts of the

reaction that actually undergo change during the reaction. There are three steps that we

take in generating a net ionic equation from a molecular equation. **First we write down**

and balance the molecular equation. As an example

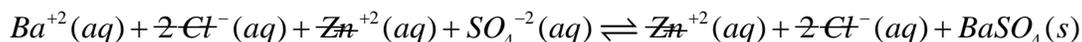$$BaCl_2(aq) + ZnSO_4(aq) \rightleftharpoons ZnCl_2(aq) + BaSO_4(s)$$
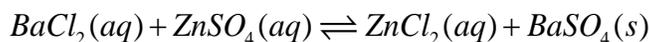
The next step is to write a **complete ionic equation**. In this equation, we write the species which are dissociated as separate ions. All those ionic species which are written as aq, will be dissociated. The solid is not, so our complete ionic equation is

$$Ba^{+2}(aq) + 2Cl^-(aq) + Zn^{+2}(aq) + SO_4^{-2}(aq) \rightleftharpoons Zn^{+2}(aq) + 2Cl^-(aq) + BaSO_4(s)$$
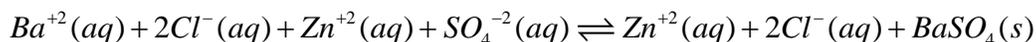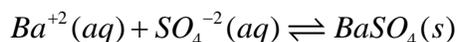
Note that when the reaction is written this way that the barium and sulfate ions combine to form barium sulfate, but the zinc and chloride ions are in the same form on both sides of the reaction and are therefore unchanged. We call ions in a complete ionic equation that are unchanged **spectator ions**.
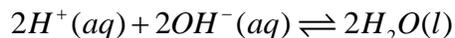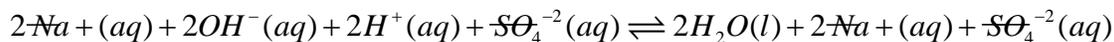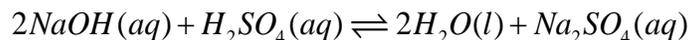
The final step in generating our net ionic equation is to eliminate the spectator ions from both sides of the equation:

$$Ba^{+2}(aq) + \cancel{2Cl^-}(aq) + \cancel{Zn^{+2}}(aq) + SO_4^{-2}(aq) \rightleftharpoons \cancel{Zn^{+2}}(aq) + \cancel{2Cl^-}(aq) + BaSO_4(s)$$

yielding our net ionic equation:

$$Ba^{+2}(aq) + SO_4^{-2}(aq) \rightleftharpoons BaSO_4(s)$$

Let's see what happens when we generate a net ionic equation for one of our acid-base reactions:

$$2NaOH(aq) + H_2SO_4(aq) \rightleftharpoons 2H_2O(l) + Na_2SO_4(aq)$$

$$2\cancel{Na}+(aq) + 2OH^-(aq) + 2H^+(aq) + \cancel{SO_4^{-2}}(aq) \rightleftharpoons 2H_2O(l) + 2\cancel{Na}+(aq) + \cancel{SO_4^{-2}}(aq)$$

$$2H^+(aq) + 2OH^-(aq) \rightleftharpoons 2H_2O(l)$$

or more properly

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$
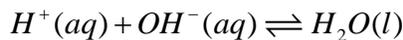
So now, we can return to our original motivation for looking at net ionic equations, to figure out what happens if we have a double replacement reaction that is not a neutralization and does not result in formation of a precipitate. An example would be

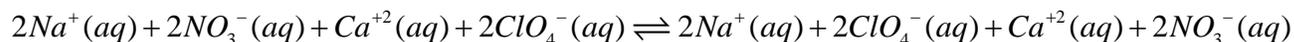$$2NaNO_3(aq) + Ca(ClO_4)_2(aq) \rightleftharpoons 2NaClO_4(aq) + Ca(NO_3)_2(aq)$$
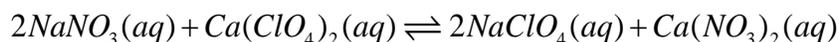
We write our full ionic equation:

$$2Na^+(aq) + 2NO_3^-(aq) + Ca^{+2}(aq) + 2ClO_4^-(aq) \rightleftharpoons 2Na^+(aq) + 2ClO_4^-(aq) + Ca^{+2}(aq) + 2NO_3^-(aq)$$

This time when we eliminate the unchanged species, everything is eliminated. All that's left is our double arrow. In other words, when a double replacement occurs that doesn't result in formation of a solid, a neutralization, or formation of a gas, no net reaction has occurred. This is sometimes abbreviated as NR.

A new type of reaction is called a single replacement reaction, which is also a type of oxidation-reduction reaction, commonly abbreviated by the term redox reaction. Single replacement reactions are typically reactions of either soluble ionic compounds or acids with metals. In such reactions electrons are transferred from one species to another. An example of this type of reaction is

$$CuSO_4(aq) + Zn(s) \rightleftharpoons ZnSO_4(aq) + Cu(s)$$
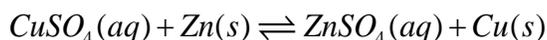
Note that the reason we call this single replacement is that the sulfate moves from copper to Zn, but nothing moves back.

Another example of a single replacement reaction is

$$2HBr(aq) + Zn(s) \rightleftharpoons ZnBr_2(aq) + H_2(g).$$
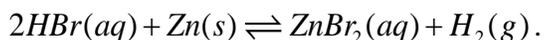
In this case the bromide ions transfer from the hydrogen bromide to the Zn.

When the reaction is written in molecular form it is not easy to see that electrons are transferred in these types of reactions, but if we write the net ionic equations, it

becomes much easier to see. So for example in the case of our first reaction, our net ionic equation is:

$$Cu^{+2}(aq) + Zn(s) \rightleftharpoons Cu(s) + Zn^{+2}(aq).$$
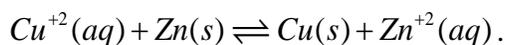
We see in this form that the copper goes from a charge of +2 to a charge of 0, and therefore must be gaining two electrons from the zinc. The zinc goes from a charge of zero to a charge of +2, so it must be losing two electrons to the copper. This can be formalized by dividing the reaction into two so-called half reactions, one in which electrons are gained, and one in which electrons are lost, i.e.

$$Cu^{+2}(aq) + 2e^- \rightleftharpoons Cu(s)$$
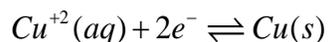
in which we explicitly see the gain of electrons by copper and

$$Zn(s) \rightleftharpoons Zn^{+2}(aq) + 2e^-$$

in which we explicitly see the loss of electrons by zinc. Reactions in which electrons are lost are called oxidation reactions, and reactions in which electrons are gained are called reduction reactions. Oxidation and reduction reactions must occur at the same time since all electrons that are lost by one substance must be absorbed by another, hence the name oxidation-reduction reactions.

Therefore, a substance which is reduced oxidizes its partner, and therefore is called an oxidizing agent. Conversely, a substance which is oxidized reduces its partner and therefore is called a reducing agent.

There is another way to tell that an oxidation or reduction is occurring. It is to assign oxidation numbers, which are effective charges of atoms in molecules, to each of the atoms in each of the species in a reaction. Oxidation of a species occurs if the

oxidation number of one of the atoms increases. Reduction of a species occurs if the oxidation number of one of the atoms decreases.

We assign oxidation numbers using the following rules:

1. Atoms in the form of pure elements have an oxidation number of 0

2. For atomic ions the charge is the same as the oxidation number

3. Group 1a has an oxidation number of 1, group 2a has an oxidation number of 2, group 7a has an oxidation number of -1.

4. Oxygen in compounds usually has an oxidation number of -2. However, in peroxide compounds (XOOY) it has an oxidation number of -1.

5. Hydrogen is usually +1, but occasionally may be -1.

6. The oxidation numbers of other elements can usually be inferred from these rules.

7. As a check at the end of assigning oxidation numbers, in charged species the oxidation numbers of all the atoms must add up to the charge on the species, and in neutral species, the oxidation numbers of all the atoms must add up to zero.

So in the case of $ZnSO_4$, we proceed as follows. We know that SO_4^{-2} has a charge of -2, so the Zn must have a charge of +2, and an oxidation number of 2. In SO_4^{-2}, the oxygens each have oxidation numbers of -2, for a total of -8, In order for SO_4 to have a charge of -2, the S must have an oxidation number of 6. So we've assigned the oxidation numbers

There are a few more reaction types. In a combustion reaction, each of the elements in a compound combines with oxygen to form its stablest oxide. So for example

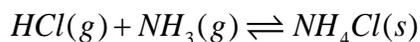$$2C_4H_{10}(g)+13O_2(g)\rightleftharpoons 8CO_2(g)+10H_2O(l),$$
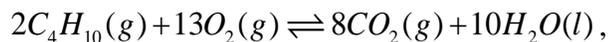
where $CO_2(g)$ and $H_2O(l)$ are the stablest oxides of carbon and hydrogen respectively.

In a combination reaction two molecules combine to yield one, as in

$$H_2O(l)+CO_2(aq)\rightleftharpoons H_2CO_3(aq)$$

or

$$HCl(g)+NH_3(g)\rightleftharpoons NH_4Cl(s)$$
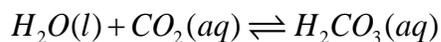
A decomposition reaction reverses the association reaction, usually as a result of heating. Sometimes they are spontaneous, i.e.,

$$H_2CO_3(aq)\rightleftharpoons H_2O(l)+CO_2(g)$$
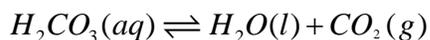
This last example is a common one. It is the source of bubbles in carbonated beverages, and frequently occurs following the natural neutralization of acid rain by carbonate in healthy bodies of water.

Lecture 8

At this point we are going to turn a bit toward the theoretical end of chemistry and have our first taste of a subject called **thermodynamics**. Thermodynamics deals with the **flow of energy** in physical processes. Thermodynamics is an extremely powerful subject. It is powerful because it is **predictive**. In fact, there are two types of predictions which thermodynamics can make which are of intense interest to chemists. First it can tell us **which processes are possible** and which are impossible. Obviously knowing this can prevent the waste of a tremendous amount of time. Secondly, it can tell us **which processes will occur spontaneously**, i.e. without doing work on the system, and which will not. As a corollary to this latter type of prediction, when thermodynamics tells us that a process will not occur spontaneously, we can use thermodynamics to determine the conditions, if any, under which a process will occur spontaneously.

All of thermodynamics has to do with changes of **energy**. There are **three laws** on which thermodynamics is based. In this section we'll be dealing with the consequences of the first law only. The **first law** of thermodynamics states that energy is neither created nor destroyed, but simply converted from one form to another. This law is also called the **law of conservation of energy**. The second law states that the entropy of the universe increases for any spontaneous process, again, a process that will occur without us doing work. Finally, the third law of thermodynamics states simply that the entropy of a perfect crystal of a pure substance at the absolute zero of temperature is 0. We'll come back to these latter two laws of thermodynamics at the end of the semester.

Let's look at some consequences of the first law, especially where it is concerned with the transfer of heat when the pressure is constant. Chemists are particularly concerned

with what happens when pressure is constant, because many reactions are done in open vessels, like beakers or Erlenmeyer flasks, where the pressure is just the pressure exerted by the atmosphere. Since we often nudge a process along by heating our sample, we are also interested in how much heat is transferred. Heating reactions at constant pressure is so common that we give a special name to the amount of heat given off or absorbed under these conditions. We call the amount of heat absorbed under conditions of constant pressure the change in enthalpy, ΔH. In fact, ΔH is often defined by $\Delta H = q_p$, where q is the symbol for heat and the subscript p indicates that the pressure is constant.

Notice that I've been talking about the transfer of heat or the transfer of energy. If we are talking about transferring energy from one place to another what places are we talking about? It turns out to be convenient to divide the universe (remember that this is the subject of the first law of thermodynamics) into **system** and **surroundings**. The system is simply defined as "what we are interested in" while the surroundings are even more simply defined as "everything else". For example, I could call a flask of acid my system, in which case everything else is the surroundings. If I heat this flask, this means that I am taking energy from outside the flask (the surroundings) and putting it into the flask (the system). If on the other hand, I cool the flask, I would be taking heat from inside the flask (the system) and putting it outside the flask (the surroundings).

It's very common for heat to be either released or absorbed in the course of a chemical reaction. Let's consider a couple of quick examples. First consider the case in which acid and base are mixed, for example, HCl and NaOH. This reaction results in the neutralization of the acid and the base. Does anyone remember from the reactions lab what happens when you mix HCl and NaOH? [Test tube gets hot] So the reaction $H^+(aq) + OH^-$

$(aq) \rightarrow H_2O(l)$ gives off heat. We say that this reaction is **exothermic**. There are various ways of expressing this concept of exothermicity:

1) We could write the equation for the reaction as

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) + \text{heat},$$
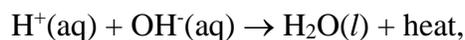
which is the same as saying that **heat is a product of the reaction**.

2) We can say that **heat is given off by the reaction**

3) We can say that **heat is transferred from the system to the surroundings**.

4) We can say that **the reaction or process is exothermic**.

5) We can say that **ΔH is negative.**

6) We can say that **the reactants have higher energy than the products.** Why does this make ΔH negative for exothermic reactions? $\Delta H_{rxn} = H_{product} - H_{react}$. If $H_{product} < H_{react}$ then ΔH is negative, and heat is given off.

It is important for you to realize that all of these statements mean the same thing, since at one time or another you'll be seeing all of them.

Now let's look at another reaction. Suppose I were to mix some ammonium chloride and some water. This was the basis of your cold packs in the second part of the thermo lab. The result of dissolving the NH_4Cl in water was to make the water colder. The water bag felt cold because the reaction

$$H_2O(l) + NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$$
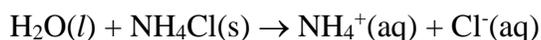
was absorbing energy in the form of heat from the water. When a reaction like this one, or some other process, like boiling water, requires heat, we call it an **endothermic** process. Let's run through several ways of describing an endothermic process or reaction

.   1) We can **write the reaction with heat as a reactant**, for example,

$$H_2O(l) + NH_4Cl(s) + heat \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$$

2) We can say that **heat is absorbed**.

3) We can say that **heat is transferred from the surroundings to the system**.

4) We can say **the process is endothermic.**

5) We can say **ΔH is positive**.

6) We can say **the products have more energy than the reactants**. We can see that this last will be the same as saying ΔH is positive. Since $\Delta H_{rxn} = H_{product} - H_{react}$, if $H_{product} > H_{react}$ then ΔH is positive, and heat is absorbed. Again, all of these statements are equivalent.

For some reason people seem to have a harder time understanding endothermic processes than exothermic processes. Just remember that they are complementary: **An exothermic process gives off heat at constant pressure while an endothermic process absorbs heat at constant pressure**.

Now consider the acid-base reaction again. WAS IT DONE AT CONSTANT PRESSURE? [Yes] HOW DID WE KNOW THAT HEAT WAS GIVEN OFF? [Felt the flask] WHAT WAS THE SYSTEM FOR THIS EXPERIMENT? [Flask and liquid] WHAT WERE THE SURROUNDINGS?

[Hand, lab bench, air, everything else] So heat was transferred from the liquid reagents to your hand. The amount of heat is ΔH, the change in the enthalpy as the reaction proceeds from reactants to products.

Why do we care what ΔH is? It tells us whether we need to heat a reaction to make it go, or cool it to keep it from going out of control. If we find that a reaction is endothermic, then we know we have to add heat for it to occur. If it is very endothermic, then we know we have to add a lot of heat. If a reaction is exothermic then we don't need to add heat. If it is very exothermic, then we have to be careful to avoid fires or explosions.

Let's look at a couple of examples. For the combustion of methane, the reaction can be written

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + heat\ (802\ kJ) \quad \Delta H°_{rxn} = -802kJ.$$
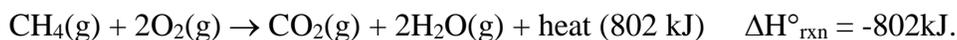
Q: IS THIS REACTION EXOTHERMIC OR ENDOTHERMIC? [exothermic] **The superscript ° means that all of the reactants and products were in the standard state, a pressure of one atmosphere**. Just about every enthalpy that you look up in a book will be for this one atmosphere standard state.

Note that the units we used for ΔH can be joules or calories. A Joule is an SI unit of energy, and the calorie is the old English unit. The Joule is $1\ kg\ m^2\ s^{-2}$, and is the amount of energy that a 2kg block has if it is moving 1 m/s. A calorie is defined as the amount of energy it takes to heat 1 g of water by 1°C. 1 cal is 4.184J. There is another unit called the Calorie (capitalized). The Calorie is 1 kcal. Guess which one the energy content of your food is measured in!

Heat is not the only means of changing the energy of a system. For systems in which the amount of the chemical components doesn't change, the other main means of

changing the energy of a system is work. Work is defined as force times distance, where the force is any force opposing the motion. What this means is that neither motion nor an opposing force is sufficient for work to take place – both must be present. The quantitative definition of work for motion along the x-axis is:

$$w = -F_x * \Delta x ,$$

where F_x .is the force in the x direction, and Δx is the displacement along the x-axis. If the force is in units of Newtons (N), and the displacement is in meters, then the units of work will be Joules.

For a system in which the chemical composition remains unchanged, only work and heat can change the internal energy of the system, and this is expressed as the equation

$$\Delta U = q + w ,$$

where q is the symbol for heat, w for work and ΔU is short for the change in internal energy. This is the first law of thermodynamics expressed as an equation.