Lecture 9

ΔH for a process depends on how much material is involved. This should make sense to you. If I burn 5 grams of charcoal and heat is given off, you'd expect that burning 10 g of charcoal would give off twice as much heat. So now suppose that combustion of 1 g of sugar (MW 180) causes 5J to be given off, i.e. $\Delta H = -5.00$ J. How much heat would be given off for 1 mol of sugar? Let's use dimensional analysis to get the answer.

$$1\ mol\ sugar\ x\ \frac{180\ g\ sugar}{1\ mol\ sugar}\ x\ \frac{-5J}{1\ g\ sugar} = -900J\ mol^{-1}$$

For another example, when 0.32 g of C reacts with S_8 to give carbon disulfide, 2.38 kJ is absorbed. Calculate the heat in kJ when 1 mol of carbon disulfide is formed from carbon and sulfur. We start by writing down a balanced reaction -

$$4\ C(gr) + S_8(s) \rightarrow 4\ CS_2(l)$$

At this point we know how much energy is absorbed when 0.32 g of C reacts. We want to use dimensional analysis to find out how much heat is required to form 1 mol of CS_2. Our starting point is 2.38 kJ / .32 g C and our ending point is kJ/ mol CS_2.

$$\frac{2.38\ kJ}{0.32\ g\ C}\ x\ \frac{12\ g\ C}{1\ mol\ C}\ x\ \frac{1\ mol\ C}{1\ mol\ CS_2} = 89.25kJ\ /\ mol\ CS_2$$

Let's do one final example, this time for the process of condensation. When an inch of rain falls on New York City, it results in a rainfall of 1.98×10^{10} L. Using the following data determine how much energy is released to the atmosphere when this much rain is formed from water vapor. For $H_2O(l) \rightarrow H_2O(g)$ $\Delta H_{vap} = 44$ kJ/mol. Since our process is the opposite of vaporization, ΔH for our process = -44kJ/mol.

Now we can write

$$1.98 \ x \ 10^{10} \ L \ x \frac{1000ml}{1L} x \frac{1g}{1ml} x \frac{1mol \ H_2O}{18 \ g \ H_2O} x \frac{-44kJ}{1mol} = -4.84x10^{13} \ kJ$$

The enthalpy, H, is one of a special class of functions called **state functions**, which also includes energy, entropy, and temperature. The special feature of state functions is that the change of a state function is **dependent only on its initial and final values** and **not the way you change it**.

To illustrate this idea, imagine that you are **climbing a mountain**. There are many different routes that you can take to get to the top, and you will have to walk a different distance for each. Therefore, the distance you walk when you go from the bottom to the top depends on how you choose to go and is not a state function. This means that if you want to know the distance you walk you must specify every step of the path you choose, which is extremely inconvenient. In contrast, the change in altitude when you walk from the bottom of the mountain to the top of the mountain is always the same, no matter what path you choose. This means that altitude is a state function, and also that all you need to know to calculate a change in altitude is the height you end at and the height you begin at. This is clearly a much simpler calculation.

Functions, such as the distance you walk, which depend on the path you choose, are known as **path functions**. Another example of a path function is life itself, since the poet Robert Frost has written: “And I, I took the road less traveled by, and that has made all the difference.” If life was a state function, taking the road less traveled would not have made any difference.

The big advantage of enthalpy being a state function is that it means that **we can determine**

enthalpy changes for processes that we have not measured directly. We do this by finding two or more processes which if done in sequence are the same as the process we are interested in. We then measure the enthalpy for these processes and add them. The sum of these enthalpies is the same as the enthalpy for the overall process.

Suppose for example we are interested in the reaction A + D → B + E, but we can't run the reaction to measure the enthalpy. Now suppose we have two reactions where we've measured the enthalpies and whose sum is the reaction we are interested in:

$$A \rightarrow B + C \quad \Delta H = 10\ kJ$$

$$\underline{D + C \rightarrow E \quad \Delta H = 20\ kJ}$$

$$A + D \rightarrow B + E \quad \Delta H = 30 kJ$$

Not only can we add them to get the reaction we are interested in, but the sum of their enthalpy changes will be the enthalpy change for the reaction we are interested in. This ΔH is the same we would have gotten if we had measured the enthalpy for the reaction A + D → B + E directly. It doesn't matter how we got from A and D to B and E, the enthalpy change is the same.

For example, suppose we want to know ΔH for the reaction

$$H_2O(g) \rightarrow H_2(g) + 1/2O_2(g).$$

It would be hard to measure ΔH for this because of a property of water called hydrogen bonding that makes it hard to measure the properties of single water molecules. However, we can still figure out ΔH for this reaction by measuring ΔH for two other processes. If we know the enthalpies of the following two reactions:

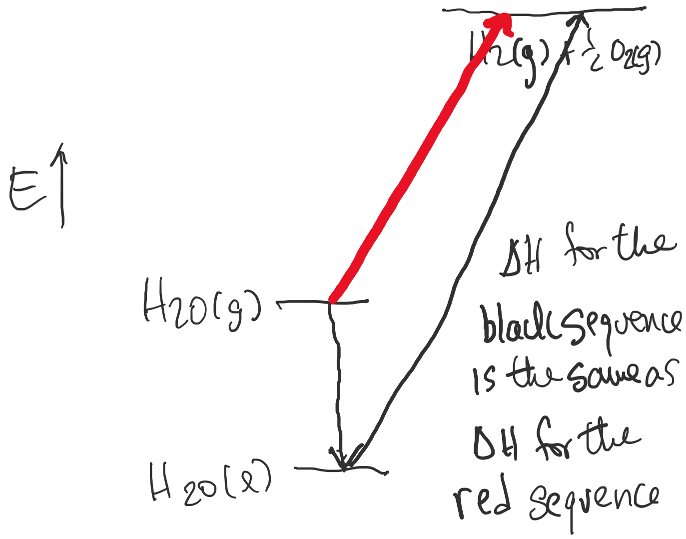
$$H_2O(g) \rightarrow H_2O(l) \qquad \Delta H = -41 \text{ kJ/mol } H_2O$$

$$\underline{H_2O(l) \rightarrow H_2(g) + 1/2O_2(g) \quad \Delta H = 283 \text{ kJ/mol } H_2O,}$$

we can add them up to get

$$H_2O(g) \rightarrow H_2(g) + 1/2O_2(g) \quad \Delta H = 243 \text{ kJ/mol } H_2O.$$

We could represent this in a diagram:[Start with $H_2O(g)$, then go to $H_2O(l)$ then up to H_2 + O_2. Net enthalpy is the same as if we went straight up.]



Let’s do another example. Suppose you want to find out how much heat it takes to make acetylene, C_2H_2, from its elements. The reaction is $2C(gr) + H_2(g) \rightarrow C_2H_2(g)$. We are given the following data:

$$C_2H_2(g) + 5/2\ O_2 \rightarrow 2\ CO_2(g) + H_2O(l) \quad \Delta H = -1300 \text{ kJ/mol}$$

$$C(gr) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ/mol}$$

$$H_2(g) + 1/20_2(g) \rightarrow H_2O(l) \quad \Delta H = -285.9 \text{ kJ/mol}$$

The goal is to add these three reactions in such a way that their sum will be the reaction for the formation of acetylene. The reaction we want has two carbon atoms on the left side of the equation. We'll use our second reaction to get these carbon atoms, but we have to multiply it by two:

$$2\ \mathrm{x}[C(gr) + O_2(g) \rightarrow CO_2(g)]\quad \Delta H = 2\mathrm{x}{-393.5}\ \mathrm{kJ/mol.}$$

Remember that when we multiply the reaction by two we also have to multiply the ΔH by 2, since ΔH depends on the amount of chemical we react. Now we need a hydrogen molecule on the left side of the equation, and we use the third equation for this:

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)\quad \Delta H = -285.9\ \mathrm{kJ/mol}$$

Finally, we need an acetylene on the right. We can use our first reaction for this, although we need to flip it around to get the acetylene on the correct side:

$$2\ CO_2(g) + H_2O(l) \rightarrow C_2H_2(g) + 5/2\ O_2\quad \Delta H = 1300\ \mathrm{kJ/mol}$$

Notice that **when we write the reaction backwards we have to change the sign of the ΔH** from negative to positive.

If we add the three reactions, we find that everything we don't want cancels out to give

$$2C(gr) + H_2(g) \rightarrow C_2H_2(g).$$

Now we just add up all of our ΔH's to give $\Delta H = 227.1$ kJ/mol.

What we just did in each of these examples is to use **Hess's Law**. Hess's law says "If two or more chemical equations are added together, the ΔH for the resulting equation is equal to the sum of the ΔH's for the separate equations."

One of the consequences of Hess's law, which we've just seen, is that if we have a reaction and we know ΔH, that $\Delta H_{\mathrm{backward}} = -\Delta H_{\mathrm{forward}}$. Similarly, we can say $\Delta H_{\mathrm{forward}} = -\Delta H_{\mathrm{backward}}$.

I'd like to introduce a subclass of enthalpies called the enthalpy of formation. The

enthalpy of formation is a special and very useful type of heat of reaction. The enthalpy of formation, which used to be called heat of formation, is **the amount of heat it takes to make one mole of a compound from its elements in their stablest form under conditions of constant pressure**. When you look up heats of formation in a book, the symbol you'll see is ΔH_f^0, which is the symbol for standard heat of formation. Once again, the standard condition is a pressure of one atmosphere. Even though standard enthalpies of formation are commonly reported at 298K, they can be measured and calculated at any temperature.

By definition:

ΔH_f^0 **of any element in its reference state at the given temperature is zero.**

ΔH_f^0 **= amount of heat to form 1 mol of a substance under 1 atm pressure.**

Note that the reference state of an element is the stablest form at a given temperature and pressure. If we want to form gaseous water from its elements at 298 K, the reaction would be

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g) \quad \Delta H_f^0\,(H_2O(g)) = -243\ \text{kJ/mol}$$

Notice that the stablest forms of hydrogen and oxygen at 298K and 1 atm pressure are $H_2(g)$ and $O_2(g)$.

If we want to form liquid water from its elements, the reaction would be

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l) \quad \Delta H_f^0\,(H_2O(l)) = -283\ \text{kJ/mol}$$

Notice from these examples that **the enthalpy of formation depends on the phase of the product**. For the case of methane, the reaction would be

$$C(gr) + 2H_2(g) \rightarrow CH_4(g) \quad \Delta H_f^0(CH_4(g)) = -74.81 \text{ kJ/mol}$$

where C(gr), carbon in the form of graphite, is the reference state of carbon at 298 K and 1 atm. When we did our first example of Hess's law, one of the reactions we used was for the heat of formation of liquid water.

Enthalpies of formation are useful because if we want to find ΔH_{rxn}^0 for some reaction we can just say

$$\Delta H_{rxn}^0 = \text{Sum of } \Delta H_f^0(\text{products}) - \text{Sum of } \Delta H_f^0(\text{reactants}).$$

For example, for the combustion of methane, the overall reaction is

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

To get ΔH_{rxn}^0 we subtract the enthalpies of formation of the reactants from the enthalpies of formation of the products:

$$\Delta H_{rxn}^0 = \Delta H_f^0(CO_2) + 2\,\Delta H_f^0(H_2O) - \Delta H_f^0(CH_4) - 2\,\Delta H_f^0(O_2)$$

Now the question is, where do we get the heats of formation to use in this calculation? The answer is from a book. An excellent source of heats of formation is the CRC "Handbook of Chemistry and Physics" of which we have several copies in the library. Your book also has a moderate sized table in Appendix B on pages A-8 to A-12. If we look these up we find

$$\Delta H_f^0(CO_2(g)) = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^0(H_2O(l)) = -283 \text{ kJ/mol}$$

$$\Delta H_f^0(CH_4(g)) = -74.86 \text{ kJ/mol}$$

We don't find a value for $\Delta H_f^0(O_2(g))$. This is because, as we've already said, it is defined as zero. Remember, the ΔH_f^0 of any element in its reference state at a given temperature is zero. So now

$$\Delta H_{rxn}^0 = -393.5 \text{ kJ/mol} + 2(-283 \text{ kJ/mol}) - (-74.86 \text{ kJ/ mol}) - 2 \text{ x } 0 = -884 \text{ kJ/mol.}$$

This is a particularly useful version of Hess's law, because it allows us to calculate ΔH for just about any reaction just by using ΔH_f^0.

Lecture 10

Just a quick additional note about ΔH's. If we simply write ΔH^0_{rxn}, the ΔH could refer to any kind of reaction. It could be for formation of water or combustion of octane or anything. In order for people to know what we're talking about we usually have to write out the specific reaction we're referring to. So for example, if our reaction involved a physical change like the dissolution of ammonium chloride we'd write out the reaction for the dissolution of ammonium chloride. If it involved a chemical change like the reaction between NaOH and HCl, we write out the neutralization reaction. Sometimes however, a reaction is so common that rather than write out the reaction we identify it by a subscript on ΔH. The one of these common reactions that we have already seen is formation of a compound from its elements, where the fact that a formation reaction is involved is indicated by the subscript f in ΔH^0_f. Another common reaction is combustion, a reaction in which a substance is reacted with oxygen to form the stables oxides of each element, indicated by the subscript c, as in ΔH_c. In both of these cases, the subscript replaces the full reaction equation.

Another special enthalpy is called the **bond enthalpy**, the heat required to break a bond. Bonds are held together with fairly large amounts of energy. If we take a water molecule and break all its bonds, the reaction is $H_2O(g) \rightarrow 2\ H(g) + O(g)$ and we have broken two OH bonds. The enthalpy is ΔH = 925 kJ/mol. Since we've broken two bonds, to get the enthalpy per bond, symbolized as ΔH_{BE}, we divide the overall enthalpy by two to get ΔH_{BE} = 463 kJ/mol.

Why are bond dissociation enthalpies of interest? There are two primary reasons: First, if we compare ΔH_{BE} for two different bonds we can get an idea about which bonds are strongest. For example, a typical bond between C and H takes 414 kJ/mol to break, while a typical SiH bond takes only 293 kJ/mol to break. So by comparing the bond enthalpies, we can learn that CH bonds are stronger than SiH bonds. We can then use this information to direct our research, to try to develop theories and experiments to understand why the CH bond is so much stronger. Second, we can use bond dissociation enthalpies to estimate heats of reaction when we don't have more accurate information at hand. We can do this because ΔH^0_{rxn} = the energy it takes to break all the bonds - the energy released when we combine the atoms into new bonds in the molecules we want. Equivalently, this can be thought of as

$$\Delta H^0_{rxn} = \text{Sum (bond energies of all the bonds in the reactants)}$$

$$- \text{Sum (bond energies of all of the bonds in the products).}$$

There are a couple of reasons that the answers we get using ΔH_{BE} are only estimates. When you read a bond dissociation enthalpy in a table the number reported is an average number. They get it by measuring the heat when that kind of bond is broken for many different compounds and averaging them. And this works fairly well, because, for example, most C-H bonds will be about the same strength. However, the strength of CH bonds in different molecules is a bit different, so our results won't be completely accurate. The second is that these dissociation enthalpies are typically for gas phase dissociation, and the actual dissociation energy depends on whether the molecule is in the form of a gas or in a liquid or solid or in an aqueous solution. Nonetheless using bond dissociation enthalpies this way is a useful tool if enthalpies of formation are not available.

For example, let's estimate $\Delta H^0_c(CH_4(g))$, where the c indicates a combustion reaction, from the CH, O=O, C=O, and OH bond dissociation energies. The balanced equation is

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$$

To use bond dissociation energies, we break this reaction into four steps

$$CH_4(g) \rightarrow C(g) + 4\ H(g) \quad \Delta H_{BE} = 4 \times 410\ kJ = 1640\ kJ$$

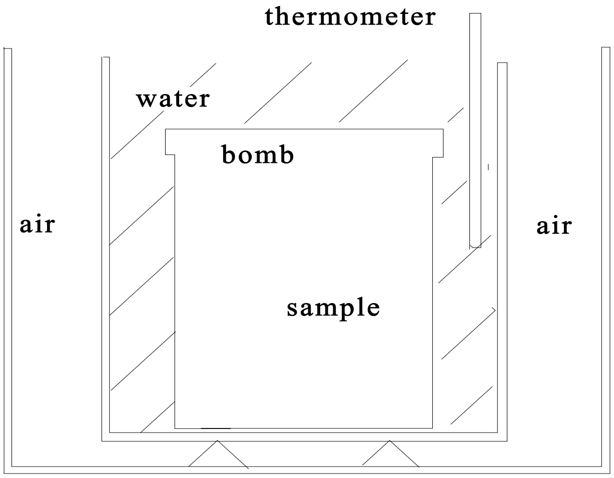
$$2 \times (O_2(g) \rightarrow 2O(g)) \quad \Delta H_{BE} = 2 \times 498\ kJ = 996\ kJ$$

$$C(g) + 2O(g) \rightarrow CO_2(g) \quad \Delta H = -2 \times \Delta H_{BE}(C{=}O) = -\ 2 \times 732\ kJ = -1464\ kJ$$

$$2 \times (2H(g) + O(g) \rightarrow H_2O(g)) = -4 \times \Delta H_{BE}(O\text{-}H) = -4 \times 460\ kJ = -1840\ kJ$$

(Notice that this last reaction is for $H_2O(g)$, since bond energy calculations assume that everything is a gas. This makes our solution approximate since combustion reactions yield liquid water.) Adding up the ΔH's for the four steps gives $\Delta H^0_{rxn} \rightarrow$ 1640 kJ + 996 kJ - 1464 kJ -1840 kJ = -668 kJ. If we look up the actual $\Delta H^0_c(CH_4(g))$ = -890.3, we see that bond enthalpy calculations do get us in the ballpark of the actual number, but are also clearly approximate. In this case one cause of the inaccuracy is the average nature of bond enthalpies, and the other is the use of gas phase numbers to estimate the energy of a reaction with a liquid product.

You may be wondering how ΔH's are determined. The answer is a technique called **calorimetry**. Typically, what is measured is an enthalpy of combustion. We put a sample of known weight in a device called a bomb calorimeter, add a whole bunch of oxygen, and ignite the substance with a spark. When the sample is finished burning, the heat from the reaction causes the temperature of the calorimeter to rise. Now at this point we know the number of moles of our sample, and the change in



temperature, i.e. we know ΔT/mole. We want kJ/mol so this means that we need a conversion factor with units kJ/T.

This conversion factor is called the **heat capacity, C_p**. The heat capacity is **the amount of heat necessary to raise the temperature of a sample by 1K**. This means that $C_p = \Delta H/\Delta T$. The heat capacity depends on how much material we have. For example, to raise the temperature of 1 gram of water takes 4.18J, while to raise the temperature of 100 g of water takes 418 J.

We use heat capacity to calculate the heat added to the calorimeter when we know a temperature change ΔT. The equation we use is $\Delta H = C_p\Delta T$. So suppose we know that C_p for a sample is 75.2 J/K, and the temperature goes up 2K. ΔH = 2K x 75.2 J/K = 150.4 J. Again it is important to remember that the size of your sample matters - the bigger the sample, the bigger the heat capacity.

There are two different kinds of heat capacity in books. One is $\overline{C}_p$**, the molar heat capacity**, = C_p per mole of substance. The other is **C_{sp} = specific heat** = C_p per gram of substance.

So for example for water $\overline{C}_p$ = 75.24 J/mol K, while

$$C_{sp} = 75.24 \text{ J/mol K} \times (1 \text{ mol } H_2O/\ 18.0 \text{ g } H_2O) = 4.184 \text{ J/g K}.$$

Note that you can tell immediately whether you have been given a specific heat or a molar heat capacity simply by looking at the units. It is also important to understand that when using heat capacities to calculate heat, the equation

$$\Delta H = C_p \Delta T$$

refers neither to the specific heat or the molar heat capacity but the overall heat capacity. If you are given a molar heat capacity, it must be converted to heat capacity by

$$C_p = n\overline{C}_p$$

where *n* is the number of moles of the substance, before being used to calculate ΔH. and if you are given a specific heat capacity it must be converted to heat capacity by

$$C_p = mC_{sp}$$

where *m* is the mass of the substance in grams, before being used to calculate ΔH.

Let's do an example of using heat capacities. When 4 kg of water were used to cool an engine the temperature rose from 298K to 323K. C_{sp} for water is 4.18 J / g K. How much heat did the engine give off?

$$\text{Heat} = \Delta H = C_p\Delta T.$$

$$\Delta T = 323\text{K} - 298\text{K} = 25\text{K}.$$

$$C_p = 4000 \text{ g } H_2O \text{ x } 4.18 \text{ J/g K} = 1.67 \text{ x } 10^4 \text{ J/K}.$$

Therefore

$$\text{heat} = 1.67 \text{ x } 10^4 \text{ J/K x } 25\text{K} = 4.18 \text{ x } 10^5 \text{ J} = 4.18 \text{ x } 10^2 \text{ kJ}.$$

Now let's do an example of a calorimetry problem. NH_4NO_3 combusts according to the reaction

$$NH_4NO_3 \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g).$$

2.00 g of NH_4NO_3 are exploded in a bomb calorimeter, with a heat capacity of 4.92 kJ/K. The temperature of the calorimeter increases by 3.06 K. What is ΔH_c for one mole of NH_4NO_3? C_p x ΔT = ΔH for 2 g = 4.92 kJ/K x 3.06 K = 15.05 kJ/2.00 g NH_4NO_3. Now we just use dimensional analysis to get kJ/mol.

$$\frac{15.06\ kJ}{2.00\ g\ NH_4NO_3} x \frac{80.0\ g\ NH_4NO_3}{1mol\ NH_4NO_3} = 602.4\ kJ / mol\ NH_4NO_3$$

Now this is really important. This heat we just calculated is the increase in heat of the calorimeter. In order for the calorimeter to get all that heat, it had to be given up by the exploding NH_4NO_3. So the NH_4NO_3 lost this energy, and therefore ΔH for the reaction is -602.4 kJ/mol. The reason for the sign change, is that ΔH for the universe is zero. $\Delta H_{UNIV} = \Delta H_{water} + \Delta H_{rxn} = 0$, since energy is conserved. Therefore, $\Delta H_{rxn} = -\Delta H_{water}$.

Lecture 11

Our topic for the next few lectures is a return to the structure of the atom, and a discussion of the ways in which atoms combine to form molecules. This will include a discussion on several levels of the nature of chemical bonds.

In High School most of you learned the model for the atom developed by Neils Bøhr. Bøhr developed his model in response to the failure of classical physics to explain important experimental results from the beginning of the 20th Century. In order to discuss the results that led Bøhr to come up with his model, and ultimately resulted in the replacement of the Bøhr model by **quantum mechanics**, we need to talk about two topics from physics, light or electromagnetic radiation, and standing waves.

For a long time, there has been a running argument about what **light** is. One of the early 19th century theories, due to Hamilton, said that light consisted of a stream of **particles**. This was supplanted in the late 19th century by a series of experiments demonstrating that light had **wave** characteristics. Since the nature of light is important to our understanding of the structure of atoms and molecules, we need to talk a bit about light and waves.

In order to do this, we'll have to do some quick nomenclature on **waves**. A simple wave looks like a **sine** function. Let me draw two for you. (longer and shorter wavelengths). These two waves are clearly not the same, so we need words that help us describe the difference between them. The words we use most frequently to distinguish these two different waves are frequency, wavelength, and amplitude. The **wavelength** is the distance from the crest of one wave to the crest of the next, and has the symbol λ. Like ocean waves and sound waves, all waves move. The **frequency**, ν, is the number of peaks which will pass by a point in one second. Frequency and wavelength are not independent, but are related by the equation $\lambda\nu = c$, where c is the speed of light, 3.00 x 10^8 m/s. The **amplitude** is the height of the peak.

Let's do a quick example with wavelength and frequency. When I was a postdoctoral fellow, I built a laser which gave off beautiful red light, at a wavelength $\lambda = 620$ nm. What was the frequency of the light? We have $\lambda\nu = c$, so

$$\nu = \frac{c}{\lambda} = \frac{3.00x10^8 m/s}{620nm} x \frac{10^9 nm}{1m} = 4.83x10^{14} s^{-1}$$

Notice that the **units of frequency** are inverse seconds. This unit is now called the Hertz, abbreviated Hz. Notice also that in order to do our frequency calculation correctly we had to make sure we were working in units of meters, the SI unit.

We have said that light has the characteristics of waves. In particular, light is composed of electromagnetic **waves**, waves in which electric and magnetic fields rapidly oscillate. The wavelengths of our electromagnetic waves vary over a huge range. The longest that you are probably familiar with are radio waves, which have wavelengths in the range from 10 cm to a km. On the short end of the spectrum are gamma rays, which have wavelengths of about 10^{-14} m, and are the kind of light emitted when radioactive elements like uranium and plutonium decay. In between, and going from long wavelengths to short, we have microwaves, about 1 cm; infrared light, which is the light which carries heat, at about 10^{-3} cm; visible light which is centered at 500 nm; ultraviolet light, at about 100nm; and X-rays, at about 1 nm. All of these are electromagnetic radiation. The only difference between them is their wavelengths.

The **visible part** of the spectrum is broken into various colors, each of which corresponds to a range of wavelengths. You can see this most dramatically in a rainbow, where the light of the sun is split into its component colors. You can reproduce this rainbow effect by shining light through a prism. The colors of visible light are violet at about 400 nm, blue at about 450 nm, green at about 510 nm, yellow at 550 nm, orange at 590 nm, and red at 640 nm. Notice as you go from violet to red the wavelengths get longer and longer. An old mnemonic that can help you to remember the orders of the colors from long wavelength to short wavelength is Roy G. BIV for red, orange, yellow, green, blue, indigo, violet. If you haven't heard of indigo before, it's the deep blue color of new Levis blue jeans.

Now we know something about light and waves. Let's examine some of the experiments that told physicists at the beginning of this century that they needed a new theory for atoms and light. The first has to do with something called **black body radiation**. Black body radiation is simply another name for the fact that **hot objects give off light**. Many of you see examples of this nearly every day at home, when the burner on your electric stove glows a reddish orange when it's on high. The light that is given off by a black body changes with temperature. Two things happen. First more light is given off at high temperatures. Second, the light shifts to shorter and shorter wavelengths as the temperature gets higher. You may have heard indirectly of this when people say that a red star is a cool one and a blue star is a hot one or when people talk of red hot as very hot and white hot as even hotter. If we plot the amount of light vs. wavelength at two different temperatures, we can see both these trends. Notice that for both temperatures, the curve is roughly bell shaped.

The problem that 19th century physicists had was that no matter how hard they tried, they couldn't come up with a theory which matched experiment. None of their theoretical curves were bell shaped. All of their curves kept increasing and increasing as they moved toward the ultraviolet. This inability of theory to match experiment was called "the **ultraviolet catastrophe**."

At this point **Max Planck** stepped in with a new idea. The theories that the classical physicists had used said that black body radiation came from the way atoms moved in a solid. Up to this point, everyone had thought that an atom could have any amount of energy it wanted, a basically sensible idea. Planck said that there was some minimum energy that an atom could give off, and that any energy given off by the atom had to be some integral multiple of this minimum. This implies in turn that atoms have to have energies which are also integral multiples of this minimum. Since atoms can't have energies that are in between these integer multiples, it means that the energies of atoms are discontinuous, a radical concept for the time. **We call this discontinuity of energy quantization, and say that the energy is quantized.**

The energy is given by the equation $\Delta E = nh\nu$, where ν is the frequency of the atom's motion, h is a constant called Planck's constant and equal to 6.6262×10^{-34} Js, and n is any integer. So for example, if an atom is moving in a solid at 2.5×10^{13} Hz, it can only have energies which are multiples of $h\nu = 6.6262 \times 10^{-34}$ Js * 2.5×10^{13} Hz = 1.65×10^{-20} J.

Planck's model, as unintuitive as it was, was a success, because he used it to come up with an equation that matched the experiments on black body radiation. Despite this success, most physicists at the time thought that his model worked just because of a fluke and not because it established a new physical principle.

The second event in the development of the new physics was **Einstein's** explanation of a phenomenon called the **photoelectric effect.** In the photoelectric effect, light strikes a metal surface, and an electron shoots out from the surface. If the frequency of the light is smaller than a certain minimum frequency no electrons shoot out, no matter how intense the light is. If the light is above this threshold frequency, increasing the intensity of the light increases the number of electrons ejected, while increasing the frequency increases the energy of the electrons. This is inconsistent with the understanding of classical physics. The predictions of classical physics were that increasing the intensity would increase the kinetic energy, and that no threshold frequency should exist.

Einstein concluded that this effect could be explained if light came in little particles, which we now call photons, and if the energy of these particles of light was given by the formula

$$E_{\text{photon}} = h\nu,$$

where in this case, ν is the frequency of the light. We say that the energy of light is **quantized**, i.e., it cannot take on any value it wants, but only certain fixed values. Before this it was thought that light of any frequency could have any energy. Notice that **Planck** said that **the energy of atoms moving had to come in small packets**, while **Einstein said the same thing about the energy of light**.

The threshold frequency can be explained if you assume that the electron is held into the metal by attractive forces, and that the threshold frequency represents the frequency of a photon that exactly matches the energy required to remove an electron from the metal. This energy is called the work function, Φ. The observation of increasing kinetic energy with increasing frequency is now explained simply by calling upon conservation of energy. Each photon has a well-characterized energy given by $E = h\nu$. This energy increases as frequency increases. If the energy of the photon exactly matches the work function, electrons are ejected with zero kinetic energy. When the energy of the photon increases above this threshold value, there is energy left over after overcoming the work function, and this energy is expressed as kinetic energy of the ejected electron. This is all summarized in the following equation:

$$h\nu = \Phi + \tfrac{1}{2} m v^2 ,$$

where h is Planck’s constant, ν is the frequency of the photon, Φ is the work function of the metal, which is different for each metal, and the final term is the kinetic energy of the electron.

Let’s do an example where we calculate the energy in a photon. Let’s calculate the energy in a photon from the laser I built, with a wavelength of 620 nm. Remember that E = hν. ν and λ are related by ν = c/λ, so this becomes E = hc/λ = (6.6262 x 10^{-34} Js)(3.00 x 10^{8} m/s)/(620 x 10^{-9} m) = 3.20 x 10^{-19} J. This may seem like a tiny amount of energy until we realize this is for one photon. For a mole of photons this is (3.20 x 10^{-19} J/photon)x(6.023 x 10^{23} photons/mol) = 193 kJ/mol.

The next phenomenon I'd like to talk about is the **spectrum of atoms**. By spectrum I mean the wavelengths of light which are emitted when an atom is highly energized, or which are absorbed when light shines on an atom. All atomic emission spectra consist of a series of lines at different wavelengths, λ, separated by regions in which no light is given off (illustrate). In the case of hydrogen atoms, these lines have a very regular arrangement, starting out far apart, but getting closer and closer together. There are three important series, the **Lyman series** in the ultraviolet which starts at 122 nm and runs to 91.2 nm, the **Balmer series** in the visible which starts at 656 nm and runs to 365 nm, and the **Paschen series** in the infrared which starts at 1,876 nm and runs to 821 nm. It turns out that the frequencies for all three of these series follow a single very simple formula, called the **Rydberg formula**,

$$\nu = \frac{c}{\lambda} = 3.29034x10^{15}\, s^{-1}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where n_1 and n_2 are integers and $n_2 > n_1$. Let's calculate the wavelength of the first of these lines. The simplest case is when $n_2 = 2$ and $n_1 = 1$. In this case light is given off at a frequency of $\nu = 3.29034 \times 10^{15} \times (1 - 1/4) = 2.46 \times 10^{15}$ Hz. We convert this to wavelength by using $\lambda = c/\nu$, and find that $\lambda = 121.9$ nm, the first line in the Lyman series. By choosing different values of n_1 and n_2, we can get other lines in the Lyman series or lines in the other series. For example, if $n_1 = 2$ and $n_2 = 3$, $\nu = 3.29034 \times 10^{15} \times (1/4 - 1/9) = 4.57 \times 10^{14}\ s^{-1}$ or 656 nm, the first line in the Balmer series. The rest of the lines in the series are obtained by using higher and higher values of n_2.

Both the line nature of the spectrum and the Rydberg formula were a serious challenge to classical physics. First of all, according to classical physics, the light emitted by atoms should be some kind of continuous spectrum, not a line spectrum with major gaps in it. Second of all, there was nothing in all of classical physics that could explain why there were integers in the Rydberg formula. (The integers are the mathematical representation of the discontinuity). In short, the spectrum of hydrogen in particular and of atoms in general, suggested that the energies of electrons in atoms were restricted to certain values, and using the language that we just introduced, were quantized.

The final experiment I want to talk about was done here in the United States, and showed that electrons, which everyone knew were particles, behaved like waves. The phenomenon they observed was called **diffraction**, in which a light wave passing through a group of closely spaced slits appears as alternating bright and dark strips. Diffraction is a characteristic limited to waves. When **Davison and Germer** at Bell Labs in NJ passed fast moving electrons through a crystal, they found these same diffraction patterns. In fact, the diffraction patterns were the ones which would have been expected for x-rays. The only conclusion that could be drawn is that **particles**

behave like waves. In fact, this confirmed an earlier theory by **DeBroglie**, which said that the **wavelength of a particle is given by $\lambda = h/mv$**, where h is Planck's constant, m is the mass of the particle and v is its velocity. Let's calculate the wavelength of a particle using the DeBroglie equation. What is the wavelength of an electron moving at 5.6×10^{6} m/s (about 1/50 the speed of light)? We use $\lambda = h/mv = 6.6262 \times 10^{-34}$ Js/(5.6×10^{6} m/s*9.11×10^{-31}kg) = 1.29×10^{-10} m. Notice that this is about the same wavelength as an X-ray.

In short, these experiments showed 1) the energy of a photon is quantized, 2) the energies that an atom can take on are limited to restricted values, and 3) particles behave like waves and waves behave like particles.

Lecture 12

Last time we discussed several experiments that led scientists at the beginning of the last century to reconsider the physical descriptions of microscopic matter, matter on the scale of size and mass of atoms and molecules. In short, these experiments showed 1) the energy of a photon is quantized, 2) the energies that an atom can take on are limited to restricted values, and 3) particles behave like waves, and waves behave like particles.

In the early part of the 20th century a number of different models of the atom were proposed which were able to account for experimental observations with increasing success. The earliest of these 20th century models was the so called Plum Pudding Model of J.J. Thomson. In the plum pudding model, the electrons were distributed in a positively charged solid sphere, much as blueberries are distributed in a blueberry muffin (or would be if the muffin was spherical, and had the number of blueberries that a good muffin should have).

However, shortly after the Plum Pudding Model was proposed, Ernest Rutherford with his famous gold foil experiment showed that there is a lot more empty space in the atom than Thomson's model claimed. He shot helium nuclei into a gold foil. Most of the particles went straight through, without bending their paths. Some were slightly deflected, and others bounced straight back. The ones that went through showed that the atom is mostly empty space. The ones that bounced back showed that the bulk of the mass of the atom was concentrated in a very small volume. Therefore, in 1911, Rutherford postulated that the atom consisted of a tiny positively charged nucleus in which most of the mass was concentrated, surrounded at a significant distance by much lighter electrons.

There were still problems with Rutherford's model. According to classical physics, negative particles orbiting a positive center should gradually have their orbits decay (i.e. gradually spiral in towards the nucleus) – in other words, classical physics predicted that the atom would be unstable, despite the fact that stable isotopes of hydrogen or carbon or iron or copper can exist for biiiillllions of years. In addition, his model did not take into account the wave-particle duality demonstrated by Einstein, DeBroglie, Davisson and Germer.

Bohr's contribution was to say, hey, if particles behave like waves, maybe I can use this to explain the spectrum of hydrogen! By using just one property of waves, the wavelength, Bohr reasoned that the electron in a hydrogen atom could only take on certain energies or states. Each of these states was given a number, called a quantum number, the lowest being one, the next being two and so on. In each of these states the electrons move around an orbit of fixed radius. The **energy of an electron** in one of these states was given by the equation

$$ENERGY = E_n = \frac{-Rhc}{n^2}$$

In this equation, h is Planck's constant, c is the speed of light, and R is Rydberg's constant, equal to 1.0974 x 10^7 m^{-1} in units of inverse meters. Again, the state of the hydrogen atom was defined by the value of n. The larger the value of n, the higher the energy of the electron and the larger the radius of the orbit.

When Bohr used this equation to calculate the energies of two different states and then took their difference he found that they were equal to the energy of one of the lines in the hydrogen spectrum. In fact, **every line in the spectrum of hydrogen could be calculated by taking the difference in energy between two different states.** Let's do an example.

An electron in the state labeled by **n = 1, called the ground state**, has an energy given by E_1 = -Rhc/n^2 = (-1.0974 x 10^7 m^{-1})(6.62 x 10^{-34} Js)(3.00 x 10^8 m/s) = -2.18 x 10^{-18} J. This is called the ground state because it is the lowest possible energy for a hydrogen atom. An electron in the state labeled by **n = 2, called the first excited state**, has energy given by E_2 = (-1.0974 x 10^7 m^{-1})

(6.62 x 10^{-34} Js)(3.00 x 10^8 m/s)/4 = -5.45 x 10^{-19}J. Notice that the energies are all negative. This is just a convention to remind us that when the electron and the nucleus in hydrogen are close together they are more stable than when they are far apart, since opposites attract. If we take the difference, we get $E_2 - E_1$ = 1.634 x 10^{-18} J. Remember that the energy of a photon is given by E = hν = hc/λ. This means that the wavelength that this energy corresponds to is λ = hc/E = 122 nm. This is exactly the wavelength of the first line of the hydrogen spectrum.

Bohr then explained the line nature of the hydrogen spectrum by saying that light was given off when an electron dropped from a state with a high energy to a state with a low energy. For example, an electron could drop from n= 5 to n = 3, or in the case we just looked at n = 2 to n = 1. When the electron drops from the high state to the low, the energy of the photon is equal to the difference in energy between the two states. Conversely, when light is absorbed by a hydrogen atom, an electron jumps from a lower energy state to a higher energy state, and the energy difference between these two states must equal the energy of the photon. Amazingly, this simple idea of Bohr's reproduced the both the absorption and the emission spectrum of hydrogen to a remarkable degree. Unfortunately, it didn't work for the spectra of any atoms with two or more electrons, like helium and the rest of the atoms in the periodic table.

One hint as to the nature of the problem with the Bohr model came from **Werner Heisenberg**. He developed something called the **uncertainty principle**, which states that you can't know exactly where a particle is and exactly where it is going at the same time. He expressed this in an equation, $\delta x \delta(mv) \geq \frac{\hbar}{2}$, where δx is the uncertainty in the position of the particle and δ(mv) is the uncertainty in the momentum of the particle. $\hbar = \frac{h}{2\pi}$ = 1.055 x 10^{-34} Js. Let's use this to calculate the uncertainty in the position of an electron traveling at 1.7 x 10^8 m/s, when the uncertainty in the velocity is 1%. This means that the uncertainty in this momentum is also 1% and is equal to 1.7 x 10^{6} m/s x 9.11 x 10^{-31} kg. The equation tells us that

$$\delta x \geq \frac{\hbar}{2\delta(mv)} = \frac{1.055x10^{-34}Js}{2*9.11x10^{-31}kg*1.7x10^{6}m/s} = 3.4x10^{-11}m.$$

This uncertainty is similar to the radius of one of the Bohr orbits.

What problem does the uncertainty principle point out with the Bohr model? Remember that the Bohr model says that electrons move in orbits. This is the same as saying that we know where the electron is and where it is going at all times. Heisenberg said that we couldn't know both of these things. Therefore, there is a fundamental problem with the Bohr model.

The ultimate solution to this problem came from **Erwin Schrödinger**. He looked at the wave nature of particles, and suggested that **electrons in matter behave like standing waves**. You all should be aware that waves travel. You can see this yourselves when you are standing on the beach and you see one wave after another come toward you. You can tell the waves are moving because you can see the motion of the crests. However, sometimes if the conditions are right, you can create a wave where the crests appear to stand still. Some of you may have done this by holding a rope at one end and rapidly whipping the other end up and down. Now mind, the wave is moving, but only up and down, and not backwards or forwards. A wave like this is called a standing wave. A special characteristic of standing waves is that there is always some place on a standing wave that doesn't move at all. This position is called a **node**. The distance between nodes is exactly 1/2 of a wavelength, or $\lambda/2$.

The neat thing about this is that **standing waves always are divided into whole numbers of pieces**. You never get 1.33 peaks or 2.7 nodes. Another way to say this is that their length is always a multiple of $\lambda/2$. Let’s show this by drawing the first few standing waves on a string. The first is only one half of a full wave. The second is a full wave, and is exactly one wavelength or 2 x $\lambda/2$ long. This wave has a node in its center. The third is one and a half waves, and is 3 x $\lambda/2$ long. This wave has two nodes.

Now remember that the general message we've been getting is that for atoms and photons and electrons, energy comes in little packets called quanta. The smallest energy is one quantum. A lot of energy means a large whole number of quanta. Since standing waves come in whole numbers of half waves, and energy comes in whole numbers of quanta, Schrödinger drew a connection between half waves and quanta and suggested that electrons in atoms behaved like standing waves.

Waves follow mathematical formulas called wave equations. Therefore, Schrödinger postulated that electrons must have wave equations which describe their behavior. Using everything that was known at the time about the wave behavior of electrons, Schrödinger constructed a wave equation for electrons. When he solved it, he discovered that the positions of electrons in atoms were described by a small number of integers or quantum numbers.

The solutions of Schrödinger's wave equation are called wave functions or **orbitals**. **There are only certain allowed wave functions. Each wave function, symbolized by ψ_n, corresponds to an allowed energy.** When we take these two points together, it is the same as saying that **the energy of the electron is quantized**. Another important point about Schrödinger’s solution is that we can no longer talk about the orbits of electrons. Instead of having electrons moving in fixed orbits, all we can know about an electron is the portion of space where it might be found. It is the wave functions or orbitals that tell us where these portions of space are. The orbitals can therefore be thought to yield the average position of the electrons. **Each orbital yields a different average position for the electron.**