PROFESSOR NELSON: So last time we just about finished up the discussion of thermochemisty, and we went through a description of calorimetry, how we actually make measurements of thermodynamic a quantities.

I should mention, which I didn't last time, that you know a calorimeter, apart from measuring heats of formation also is used to measure standard thermodynamic quantities like heat capacities. You know how much heat does it take to raise the temperature of something by a degree? Well, you put the material inside the calorimeter, and you have a heater and it's connected up to current source, and you can accurately measure how much heat you're putting in, because you can measure how much current is going into it, and you separately are measuring the temperature of the material, so it's a straightforward way of measuring the heat capacities, thermodynamic data of this sort.

So work on phase transitions, just ordinary properties of material. Chemical reactions, all the thermochemistry involved is done using constant pressure or constant volume calorimetry in a pretty routine way. So we talked about how to use the results of measurements like that to calculate reaction energetics, enthalpies of reaction.

And I just want to end the unit on thermochemistry with a real brief discussion of an approximate way of formulating heats of reaction, and that is in terms of bond energies. Now you know you're probably never going to sit down and do a series of thermodynamic calculations using bond energies.

You could always look up heats of formation of compounds and from those determine very accurately heats of reaction, by looking at the heats of formation of products and the heats of formation of the reactants and subtracting them. And since that data is available for a really wide range of materials, that's sort of the simplest approach and the most accurate one to determine reaction energetics.

On the other hand, if you just want to think about molecules, you know, you think about bonds. You know if you say I've got methane or ethane, I'm going to use a fuel and burn it and capture the energy. How much energy do we have in there?

Well the way you want to be thinking about that is all right, I'm going to take the starting material, the fuel, I'm going to break bonds, and I'm going to form some final product with new bonds. Roughly what kinds of energetics are we talking about?

In biological systems, it's also super important. You know you think about ordinary biochemical energetics, what's used is fuel in biology and what are the products that are formed? And again, it's just super important to be able to think sort of semi-quantitatively in terms of bond energies, because you don't want to always be going and looking up everything in tables.

If you need to do an extensive series of calculations, it's very useful to have the tables. But if you just want to think about how something is working, you know biological or system or an engine or another application, it's very useful to just be able to think in terms of bond energies.

So let's just go over bond energies. And you've seen this in 5.111 and 2, so I'm not going to belabor it but they're just a little bit of examples that I want to go through, just so it's fresh on your mind.

So the idea, of course, is to be able to have an idea of how much energy is involved in forming or breaking a single bond. So, if we just do this by example, we can take methane so it's a real simple case because we know it's just got four identical carbon hydrogen bonds, and we could say OK, let's just break them.

So we'll start with methane gas and go to one atom of carbon in the gas phase, plus four atoms of hydrogen in the gas phase. The energetics in this case aren't given by the usual heats of formation. You'd just say, if I want to know about methane, I can look up its heat of formation from the elements in their standards states. but the difference here is these elements aren't in their standard states.

Carbon in its standard state at room temperature and pressure is graphite, a solid, it's not carbon atoms in the gas phase, and hydrogen in the standard state is hydrogen molecules H_2, not individual atoms. All right, so we'd like to have this bond energy for these things. So let's just to make a cycle that will allow us to determine this. So this'll be our first step in that cycle, or one way of getting there. And this delta H of reaction is going to be by definition four times our bond energy for a carbon hydrogen bond. Now let's go to be elements that are in their standards states at room temperature and pressure.

So let's go to carbon as graphite. And let's go to two molecules of hydrogen gas, so this will be step two and this will be step three. And this will allow us to work because now we're starting in standard states, so we can just use regular heats of formation. And that's the key.

So if we look at step one delta H1 there as we've defined it, four times our bond energy. Two, this is just negative heat of formation of methane, which we can look up. And three, is similar. Essentially it's the heat of formation of carbon in the gas phase and hydrogen atoms in the gas phase, commonly called heats of atomization, but these are also tabulated just like heats of formation of ordinary compounds. In fact, in the appendix to your book that has thermodynamic data, you can find carbon gas phase atoms including heat of formation, and same with

individual hydrogen atom as opposed to hydrogen molecules in the gas phase.

So those data are available. So we can write delta Hc from atomization, and two times delta H of H2. This is the way this is tabulated and this is molar. And of course now we've written a cycle. So we know that to get from here to here is the same as to go through these two steps.

In other words delta H1 is the sum of delta H2 and delta H3. And so this says that our four times the carbon hydrogen bond energy is just given by minus the heat of formation of methane plus the heat of atomization of carbon, plus the two times the heat of atomization for hydrogen molecules.

And if we look up the numbers that are tabulated, what we discover is that our carbon hydrogen bond energy is 416.2 kilojoules per mole. Very useful to have numbers like that stored in your head. To have some basic idea of just ordinary chemical energetics in terms of bond energies. Hydrogen bonds, you know roughly 20 kilojoules per mole, and so forth.

Just having those kinds of energetic enables you to think in a qualitative way about what's likely to happen in an ordinary chemical or biochemical situation. OK, so this is in a sense the simplest case, because we've talked about the dissociation of a molecule that consists of all identical bonds. But it's straightforward to go from there to additional bond energies. So from this we've got a value for a sort of typical carbon hydrogen bond, right. We can do the same thing now for ethane, and that's got a single carbon carbon bond, as well as a bunch of carbon hydrogen bonds, but now the we know the carbon hydrogen bond energy, we can use that number plus the relevant heats of formation to determine the carbon carbon bond energy.

And we can keep going and extend this to essentially tabulate bond energies for a very large number of different sorts of bonds. So just as an example, ethane, so now we're going to have -- this I'll write it all out just some we can keep proper track of all the bonds that we're going to be breaking.

So C2H6 goes to two carbon gas phase atoms, and six hydrogen atoms. So in this case, our, I can write this again as one delta H1 is six times the carbon hydrogen bond energy plus the carbon carbon bond energy that we'd like to determine.

And again we can go through now a similar cycle. So again this now can be equilibrated with carbon graphite plus three molecules of hydrogen in the gas phase, just like before. And so from that we can see that we'll end up with an equality between these, and negative delta H naught formation for C2H6 or ethane, plus two delta H of carbon atomization, plus three delta H for atomization hydrogen molecule.

So we've already seen we could look up these numbers and this, and we've already determined a carbon hydrogen bond energy. So again, if we find all the relevant values, we can determine that our carbon carbon bond

energy is 342 kilojoules. And so on. So we can keep going and again build up a bigger and bigger inventory of bond energies just to provide us with the kind of intuition that we'd like to have to be able to think about ordinary molecular energetics.

Any questions about bond energies? All right. Of course, if we know bond energies, we also could make estimates of heats of formation. So if we have some new compound, we don't know its heat of formation, we know its structure. We know what bonds are involved. We could get an estimate for what we might expect for its heat of formation if we know those, and I think I'll just write this out on the board by example, but not work through the numbers explicitly.

You know, let's say we were going to make, you know, n pentane C_5H_{12}. And of course again keeping proper track of all the carbon carbon and carbon hydrogen bonds. But now in principle we know the carbon carbon bond energies and the carbon hydrogen bond energies. So we should be able to figure out the heat of formation of a compound like this, even if we don't know it from a table. And it's again through a similar sort of cycle so if we start with the atoms in the gas phase, and go to n pentane.

So this is now the bond energies which we basically know. And again make our cycle of involving the elements in their stable form at standard temperature and pressure. Then again, here's our one, two, three. Here's our minus delta H of atomization, and here's our heat of formation. And that's the point, is that now we can use what we've already elaborated for the bond energies and the known enthalpies of atomization, and we could determine the heat of formation.

If we do that, we wind up with a value of minus 152.6 kilojoules. If we measure it. If we look up in a table what the actual value is, we discover it's minus 146.4 kilojoules. So it's a few percent off. Why is it off? Why isn't it right?

STUDENT: [UNINTELLIGIBLE]

PROFESSOR NELSON: Yes, exactly. You know you can't use the C-H bonds from methane for every C-H bond, or the C-C bond in ethane for every carbon carbon single bond. There'll be variations, usually of modest magnitude, in the values. So this isn't going to be an exact calculation, but certainly this is close enough for allowing us to think qualitatively and semi-quantitatively about ordinary energetics. Another illustration of it is if we look at neopentane -- so same chemical formula. Same number of carbon carbon and carbon hydrogen bonds.

So according to the way we've done this calculation, we should get exactly the same number, because all we're doing is adding up the total number of bonds, and it's the same. But what we discover is that for neopentane, delta H of formation, neopentane is minus 166.1 kilojoules. So again it's different in this case in the other direction. But certainly close enough that allows us to think reasonably about what might happen in ordinary situations.

Any questions about bond energies? OK, now we're going to go to a new topic, and let me say, the topic we're going to start now, the second law, is really in a sense, this is the start of the whole rest of the term. So far, what we've covered essentially is conservation of energy, how you think about energetics and what contributes to them. That is heat and work. How to account for them all properly. What happens under constant volume or constant pressure conditions that led us to the definition of enthalpy right and so forth.

And once you get your arms around these ideas, and it takes some work to do that, but once you do, the actual execution of things can be pretty straightforward, and some of this can seem like just you know a lot of accounting. It's not. It takes some effort to become accustomed to it and familiar with how to properly think about heat and work and how they contribute to energy and so forth. But given that amount of effort, a lot of this can be reduced to fairly straightforward calculational stuff.

What we're about to start is a little different from that in some sense, and really in some ways more difficult because what we're going to try to understand starting with this next set of topics is what determines whether something happens spontaneously? We haven't really talked about that in any of this. We've talked about whether reactions are endothermic or exothermic. But as you're going to see that doesn't determine what happens spontaneously. It certainly is one of the factors, but by no means the only one.

What determines what happens just by itself? Or another way of saying that is, if I have some sort of system, it could be an engine. It could be a chemical reaction. It could be a biochemical system or some part of it. What determines where the equilibrium is and the direction that things would have to go in order to reach or approach the equilibrium? What is the equilibrium state of something? Actually, what we've discussed so far really doesn't allow us to determine that, and there are a few easy ways to sort of bring that out.

One is you can imagine constructing some kind of cyclic process that you know it could remove heat like a refrigerator does from a cool region and export the heat to a hotter region, like the room, or outside a window if it's an air conditioner or something like that. Just move the heat. That's it. Why not? I mean you could do that and not necessarily violate the first law. Or what about, here's a simpler case. What if I just have a chamber with a divider, and I pump out half of it, and I put gas in this half, so there's gas and there's vacuum, and then I remove the divider.

So I certainly expect that what happens is the gas fills the volume. Why? The first law didn't tell me that that needs to happen. Why doesn't it go back the other way, anyway, even without the barrier? Why doesn't the gas just by itself all wind up over here? Let's say it's a pretty dilute gas, so even if it does all end up in this half, you know the energy of any sort of unfavorable repulsions between molecules is negligible. Maybe they even have weak attractions?

Why doesn't that happened? It's a good thing for us that it doesn't happen. Why in this room doesn't the air all just sort of collect over there somewhere? Or just the oxygen molecules in the air and suffocate all of us.

The first law doesn't have anything to say about that actually. Whatever the reason it doesn't happen, we're not going to find the answer to that in the first law. So that's what the second law of thermodynamics and the development of entropy is all about. It's to help us understand what is the direction of spontaneous change? What governs that, and what's the equilibrium state that is reached when the spontaneous change occurs? OK?

So the second law is going to give us basically a principle that'll tell us the direction of spontaneous change. One way of thinking about that is it's going to allow it to sort of determine the direction of time. You know if we see initial or if we see one state and we see another state, we'll be able or know, time must have been going this way, right because the spontaneous change would happen in this direction.

So, I'm going to put up a couple of just statements of the second law of thermodynamics. I'll start with kind of an easy one. So maybe I'll start with that here.

Here's a statement by Clausius. The first law says that the energy of the universe is constant. We're always conserving in one way or another. And the second law is that the entropy of the universe is increasing. Now we're going to define entropy presently. But I'm writing this up just to give you some foreshadowing of how we're going to try to guide our thinking about spontaneous processes. This tells us about conservation of energy. This tells us about which direction things move in spontaneously, namely the direction that leads to an increase in this soon to be defined quantity entropy.

It's going to turn out to be a state function, and it'll help us understand the direction of spontaneous change. You know, like the first law the second law too was developed before there was a very well defined understanding of the molecular nature of matter. We're going to talk about the second law and entropy in macroscopic terms. Later on in the semester we'll also discuss them in microscopic terms. We'll do a little bit of what's called statistical mechanics, of microscopic, basically discussing the microscopic origins of entropy in terms of disorder of molecules.

But really, the thermodynamics of entropy and the second law evolved because people were trying to build things. It was the Industrial Revolution. people were trying to build engines, steam engines, and other kinds of devices, refrigerators other things. And they couldn't understand -- first of all, why couldn't you make it perfectly efficient?

You know, you'd have a steam engine. There'd be a source of heat. You could extract work. Never seemed like you could get it all and turn it all into work. Why not? And if not, what were the limitations on it? What was the best

efficiency you could achieve? So in a very practical way people were motivated to think very hard about these kinds of questions.

So let's just look at some of the things that brought out the need for this kind of consideration. So let me start by drawing one of the impossibilities. We could try to build a heat engine. Where we've got some temperature T1 which is hot, and some amount of heat, q1 goes into our system, and our system runs as a cycle. It goes around and around, because in any practical situation we're going to need to keep going and repeating the process. Some amount of work comes out. We'll call it minus w, because work is always defined as the work that's done by the environment on the system.

So if I'm drawing the arrow this way, then I want to write it as minus w. Now this would be just swell. This is it. That's the whole heat engine. This is running in a cycle. So we know that, delta u is zero. So that would mean that, you know, the amount of work out would just equal the heat in every time around. Never happens. Can't make it happen. The only way it works is if instead there's an additional part. Somewhere heat is also lost to a cold reservoir.

In other words, you know I burned some fuel. I consumed something to produce my hot source, and I'm going to then try to turn it into work, which I can, but only partly. There's going to be heat loss somewhere to a colder region, and I can't avoid it. And it was discovered that this was always the case. So this can be built where, just to be clear on these. q1 is a positive number, because again that's heat going from the environment to the system. This is our system running in a cycle. So q1 is positive, minus w is positive, that is work is being done on the environment by the engine. And minus q2 is positive. And T1 is greater than T2. That I can build.

Here's another thing we could try to do. It's sort of the opposite. We could try to produce a refrigerator but not have to do any work. So let's go the other way, in other words, let's go from T2 which is cold we're going to go in this direction now, which means q2 will be a positive number and here's our system running in a cycle. And now here's minus q1 now is going to be our positive number, and we're going to remove heat from q2 and move it, or from T2 a cold region and move it to some place that's hotter. Also a pretty nice idea. And also obviously impossible. It only works if I put work in there to make it happen, then yes I can take heat out of a cold body and move it up into a hotter reservoir of some sort.

So here's a refrigerator. Again T1 is greater than T2, and in this case q2 is greater than zero. I'm removing heat, minus q1 is greater than zero, that is heat is going up this way. Work is greater than zero. Has to be. Of course the thing is running in a cycle. delta u is zero. So that means that work must be minus q1 plus q2, right? And work is greater than zero, so that's saying minus q1 right that's a positive number, must be bigger than q2. In other words, I am taking some heat away from the cold region. The heat I'm dumping into the hotter region is bigger

than the amount that I taking away here, because it's also got this amount.

That's why, you know, if it's a humid or warm summer afternoon and you think oh what I a great idea, I've got this little fridge in my room. I'm going to open it up and cool the room off. Turns out not to work too well. Because of course what the fridge is doing, it's cold inside. So it's a machine that's removing heat from the inside and dumping it outside. There are coils in the back of the fridge, and if you touch them they're a little bit warm and so on. The heat is being lost to the room. How much heat?

Well, the work that goes in is also added. So the amount of heat that goes out into the room is bigger than the amount of heat that you're taking away from the space. That's bad. So if you try opening the refrigerator door to cool off your room at the same time as you're dumping heat into your room, all you discover is the net effect is to heat up your room. Because you know the amount of heat that the thing is removing from somewhere on the inside there and struggling to do that because you've left the door to the fridge open, right, is not as big as the amount out heat that's coming out in those coils on the back. It's not as big because that heat has not only the heat that you're removing from the inside, but also this amount of work. It's all conserved because delta u is zero. The thing is running in a cycle.

Try it sometime. You can verify this experimentally in a very simple way. It's not a very effective way to work, and it wastes a little bit of energy, but could be worth it in the interest of knowledge and discovery.

Let me write an alternate statement of the second law of Clausius. All spontaneous processes are irreversible. When I open that panel in the container, I've got gas on one side and vacuum in the other and it expands in there, it happens spontaneously, and it's irreversible. It's not just going to go back.

And now let me write a mathematical statement of the second law. And we'll celebrate it's importance by using this color. Going around in a cycle, if I integrate the quantity dq reversible over T, I get zero. Remember this, this is our special function.

Let me just keep going a little more though. Let me also write another version. If I write dq for an irreversible path over T, right, less than zero. It's not the same. This is a state function. This isn't. Remember of course that the heat that's exchange between the system and the environment depends on the path. If there is a reversible path, and you see how much heat was exchange with the environment, and you look at that divided by temperature integrate over the whole thing, you discover that as long as the path is reversible, it only depends on the states at the beginning and the end of the path.

In other words if you have various ways you can go from state one to two that are reversible, it's always the same. We saw that for just a couple of examples, a couple lectures back. Remember, we looked at these thermodynamic

cycles and just said, well let's just calculate those. And those were, those all involved reversible processes.

So, in effect, we looked at different paths to go from one state to another. We had a cycle, and one path went to here, and the other path went back. We discovered that, in fact, this one zero around the cycle or the way we expressed it at the time is the value of this was the same regardless of the way we got from one state to the other, whether we took a straightforward route or a more circuitous route, as long as they were reversible.

We're going to define dS as dq reversible over T, and since we're dealing with a state function delta S going from state one to two of dq reversible over T is S2 minus S1 state function. And S as state function is the entropy, and of course the us, it will always be special.

All right, now, the second law, you know it's difficult to understand and to get your arms around, because you know, do I really calculate this? I actually have to find a reversible path in order to do the calculation. Normally, you know, when you calculate delta u and delta h and so forth, you have various ways to calculate them that can be pretty straightforward. But here, you actually have to determine the heat exchanged between the system and the environment, and you know that does, in general, depend on the path. But it turns out that this quantity, you know, the differential of that heat over the temperature, also depends on path unless it's a reversible pass. Any reversible path will lead to the same results.

It doesn't depend on path among reversible paths. What that means in practice is if we say OK, start here and end here and calculate the entropy, you actually have to sort of figure out a reversible way of getting from here to here so that you can do that calculation.

So it's really very different from ordinary functions that you've been dealing with. A lot of people, you know, because the second law is difficult to understand, you know you can easily go online and see thousands of violations of the second law. It's still easy to look, to go find claims of perpetual motion machines. Some of them cost a lot of money. You can buy them, see how they work. But and also, all sorts of schemes for producing energy.

Go online and see, right. You're just, they're just crazy ideas about getting energy from nothing. Getting energy from the heat that's just already present in the air. I mean there's heat in the air, all this motion, it must have energy. We should be able to extract it and use it. Turns out we can't do that. It has to look something like this. OK. I want to look at some more statements of the second law. To do that I just want to indicate one definition which is just to be clear what these things mean.

These are what I've called heat reservoirs or hot or cold bodies. Here's what I mean to be more specific. A heat reservoir is basically a very large thermal mass at the same temperature. And the real idea is that you can bring

heat out of it as much as you want and the temperature won't change. It's an idealization. right If you have something that's big enough, and it's at a constant temperature, of course you can take heat away, but it's just so enormous that you won't measurably change it's temperature.

In practice you might be able or approach that limit. OK, now let's look at some more definitions or statements of the second law. This is from Kelvin of Kelvin temperature scale fame. It's impossible to convert heat into work with a system that operates in a cycle. I'm going to write this all out. I know you've got it in your notes too, but it's super important. To convert heat into work with a system that operates in a cycle, without at the same time transferring some heat to a colder reservoir.

OK, a couple of things to notice. One is, you know, in some sense the second law is kind of negative, right? Must not have been done in the new age. It tells us what we can't do. And that really is in a sense what it's all about. It's telling us what are our limitations of what can be accomplished. Very important part of this statement -- in a cycle. Of course any practical engine has to keep going, so there's going to be a cycle in some way or another, but it's important because, you know, there are some -- if I'm not operating in a cycle, I can convert heat into work just fine.

You know, I could have a heat source, got a candle, and I've got a piston, maybe I've got a weight on it. I've got something stopping it. And then I remove the stoppers and let it go, and because of the heat, there's expansion. It pushes up, right, and it'll be up higher somewhere. Worked! Heat turned into work. I don't have a cold body somewhere. But I only did this once. There was just one stroke of the piston. If I want to continue it and run in a cycle, somehow I've got to have a place where the heat goes.

So this sort of diagram describes effectively the way the Kelvin statement works. This works fine and like we illustrated before, it doesn't work fine if I don't have this part of it. I won't be able to just take all the heat and convert it to work, like I, in principle, could do, if I don't need to run it in a cycle.

Here is yet another statement by Clausius And we'll end with that one. Maybe I'll just read this one, so we can not go over the time. So, it's impossible for any system to operate in a cycle that takes heat from a colder reservoir, transfers it to a hotter reservoir, without at the same time converting some work into heat. In other words, it's a statement kind of similar to the Kelvin statement, but applying to the case of moving heat from a colder to a hotter region. Can't do it, unless some work is also converted to the heat that gets released into the hot region.

I think we'll stop there. Next time what we'll do is lay out a very well-defined kind of engine called Carnot cycle that allows us to very explicitly go through and say OK, let's just work out the steps of isothermal and adiabatic expansions and contractions. In other words, how does the engine really work? And just calculate it going around in a cycle and see exactly how all this is born out. And we'll see that next time.