PROFESSOR NELSON: Well, so last time we did a little bit more work on thermodynamic cycles, and basically went around a cycle and looked at some state functions, delta u and delta H. Saw that around a closed cycle those zero because they're state functions. So if you start and end at the same place, they've got end at the same place that they started. There's no change in them, and then we also looked at some at non-state functions, work and heat, and saw that those aren't zero going around a cycle. Of course you can do work in a cyclic process, and heat can be exchanged with the environment at the same time.

So we calculated those values too. And we also looked at this other funny function that's our special function. We looked at this integral dq over T. It's so special that we called this derivative dS, and saw that at least for the cycle we looked at, it also behaved as a state function behaves. That is, going around the cycle, it had no net change, and we'll see this come back later on.

Then we went on to look at thermochemistry, and that's what I want to continue today. So really, the main result that we saw last time is that we can describe the enthalpy of reaction, so if we have reactants going to products, and we'd like to know our heat of reaction or enthalpy of reaction, remember it's a constant pressure as we're considering it, so it's equivalent to heat of reaction, than the way we can do this is construct a cycle where we're going to express these in terms of their constituent elements.

We're going to all the way back to the atoms. Right, so if we have the elements in their standard states, that is their most stable forms at room temperature and pressure, then what we're really doing is we're saying let's take the reactants and let's pull them all apart into their separate elements, they're separate atoms. And then put them back together this way, and we'll calculate the enthalpy of this process, the enthalpy of this process. It's a cycle, so that'll give us the enthalpy of reaction, all right?

So this delta H is our sum for delta H of formation for the reactants, right. And this is our sum of the quantity for the products, right. And in this way, then we can express our delta H of reaction is just going to be given a sum of the heats of formation or the difference between the heats of formation of the products and the reactants, right? Now, of course, we have to weight this by the number of moles of each reactant to each product involved in the reaction.

So to write this a little more carefully, it's, you want to write the sum over i of nu i delta H naught of formation of i

summed over the products. This is per mole minus sum over i, nu i here over the reactants in the same quantity. Delta H per mole f i, right? So in other words, were taking each of the products and we're going to weight them by their stoichiomeric coefficients, and we're going to have in this delta H of reaction their heats of formation, and then we're going to have the negative heats of formation of the reactants, because that's being subtracted, okay?

So, just to go through a basic example, let's just look at the burning of methane. So we've got methane gas, combining with oxygen gas, so you have carbon dioxide gas and liquid water, and we'll consider the whole thing at room temperature and pressure, right. So let's just undertake this set of processes. Let's decompose these to the elements. So in other words, our methane gas, we're going to write the chemical equilibrium between this and the solid carbon. That is to say let's specify graphite, it's not diamond, right, graphite is the stable form of carbon at room temperature and pressure. And then, hydrogen gas two moles of hydrogen gas and we're going to have a delta H of formation. This is for CH4 in the gas phase, right?

And then over here, we have our oxygen but 2 O2 gas going to, well 2 O2 gas -- the point is oxygen already is in it's stable form at room temperature and pressure, right? That is the elemental form of oxygen, of course, is as oxygen molecules in the gas so there's no delta H formation for oxygen. The gas is zero, right.

And then second phase of this, now we're going to take the elements that we've produced, and we're going to put them back to make products, right? So there we've got carbon as graphite, and a solid plus an oxygen gas goes to make CO2 gas, right. And we've got our positive delta H of formation associated with that. And finally we've got hydrogen gas plus oxygen gas giving us two water molecules and this is in the liquid phase, and there's some delta heat of formation associated with that, okay.

So there is our set of individual processes that's going to constitute our cycle, right. If we take the combination of all those, which is to say we just take both steps in this cycle, then we'll have our net reaction, which is to say we'll have this, right. So what that says is our heat of reaction is our heat of formation per mole of CO2 gas, right. Plus 2 times the heat of reaction or heat of formation per mole of liquid water minus heat of formation per mole of methane, right.

And things we can easily look up. So in a simple way, we can determine, we can calculate what the heat of reaction is for something like this, right. And you'll see in the back of your book, you'll see moderately extensive tables of heats of formation, and if you go online you'll see, you can find extremely extensive tabulated values of heats of formation, that have been measured for an enormous number of compounds. And from that, then you can look at enthalpies of reaction for countless numbers of reactions, right.

So by using the tabulated data, we can really determined heats of formation for most reactions that you might contemplate, OK? Of course, the cyclic steps that we've taken to do this apply not just for breaking down reactants

and product into the elements in their standards states, but of course we could also look at whole sets of reactions and write cycles as well, right.

So for example, if we wanted to look at the reaction of something like carbon graphite plus oxygen gas to make carbon monoxide gas, well normally this isn't the way the reaction would work. Normally if you just tried to make this happen what you would wind up with the CO2, not CO, right. But one way to approach this is you could look at the individual reactions of going, you could go to CO2 and then you can go with CO2 and oxygen and combine, or combine CO and oxygen to get CO2, right? So normally, CO2 is formed, but you could calculate the heat of reaction. Of course you could go back to the elements, but you can also say well, let's just take a known heat of reaction for, or heat of formation for CO2, and then also combine that with the heat of reaction for CO plus oxygen forming CO2 and determine this that way, all right, OK, so once you have done this, once we've got the heat of reaction then there are a few simple results that are useful. One is we know immediately whether when we run a reaction heat is going to be released in the process out to the environment, or whether heat is going to be taken in, right. So, and of course if you ever used a hot pack or a chemical hot pack or cold pack, you've seen examples of the two of those, where the constituents are selected to give you either heat released or heat taken up, right.

So in particular delta H of reaction less than zero, that means a negative amount of heat, which means that heat is released, right. Yes, that is it's exothermic. Positive enthalpy of reaction, which is to say a heat of reaction is positive. Remember the way we define heat is positive it means that there is heat that is coming from the environment into the system, right. In other words heat is absorbed or taken up by the reacting system. That's endothermic, okay.

All right, one more important aspect of this that we need to be able to deal with, and that is the heats of formation that you'll find tabulated typically are going to be given for room temperature and pressure. And it's very common that you might want to know the thermodynamic condition for reactions, especially at other temperatures, very common, of course. And it's not hard to see how the heat of reaction at room temperature can be related to they heat of reaction at other temperatures.

So let's just look at that. So remember your fundamental relation, dH, if you write that as a function of temperature and pressure, partial of H with respect to T, constant pressure, dT, plus partial of H with respect to p at constant temperature, dp. But if we're working at constant pressure then dp is zero. So we just got the derivative with respect to temperature. That's our heat capacity, right, Cp. And we may have tabulated values of Cp for an enormous number of materials. So now, if we look at the temperature dependence of delta H for reaction, really what we're going to need to do is look at how that heat capacity changes going from reactants to products, right? So in other words, d delta H of reaction, with respect to temperature. That's what we want to find out, right? So how does delta H change if we change the temperature?

Well, it's just given by Cp dT for the reactants and the products, right? For the products minus the reaction, that is it's delta Cp, we need the sum over the products. Nu i, Cp i minus same sum over reactants, i, nu i Cp i, right. Similar to what we saw before. Now we need to integrate, right. So if we integrate between some pair of temperatures, T1 and T2, we do this and we have this quantity, d delta H of reaction with respect to temperature, dT, all this is at constant pressure, right. Let's just be careful to specify that. Well, so of course, this is then just delta H of reaction at T2 minus delta H of reaction at T1. This is looking good. This is what we want to get, is our heat of reaction at some new temperature T2. If we already know it at some initial temperature, usually room temperature, T1.

And it's just given by the integral from T1 to T2 of delta Cp dT. Now in general, this is as far as we can go, but at least if the temperature change isn't too big, for most materials that heat capacities doesn't depend very strongly on temperature, right. If you take some material, and you measure its heat capacity, right, how much heat do I have to put into it in order to change its temperature by a degree, right. And I make that measurement at room temperature. And then maybe I raise the temperature to whatever, room temperature, maybe 20 degrees hotter than room temperature. And I again say OK, now how much heat do I need to raise this thing's temperature by 1 degree?

The amount of heat I need to put in to do that is not very different from what it was at room temperature right. In other words the heat capacity didn't change very much. So, the result of that is that at least for modest temperature excursions, it may be the case that we can simplify this and simply say it's just the difference in heat capacities times the temperature change. Again, we can't always be assured of that, but it's often the case. Any questions on any of this so far?

OK, now what I want to do is just describe a little bit of how do you measure all this stuff, right? So what we've done so far is just lay out in principle how we should describe heats of reaction, and of course assuming that we've got everything in tables we can always look them up, but sometimes you want to make new compounds, right. Sometimes you'd like to know what the energetics are involved there, right, and so it's useful to be able to actually measure something.

So how do we do It? This is what's called calorimetry. So we're going to make measurements to determine heat of reaction values. Actually, calorimetry is used for all sorts of things. It can be used to determine, for example, the energetics of phase transitions. Maybe you're not looking at a reaction, but you've got some new compound, and you're looking at it go from liquid to solid or to gas. And you can see what the heat involved in a process like that is as well.

So what happens? Well, the objective in the case of a reaction, we have reactants at some temperature going to products at that temperature, and that is our heat of reaction at that temperature. That's how it's defined, right, at constant temperature. OK? What do we actually measure? Well, what we can really do is we can put the reactants in some container, put the whole thing in an insulated place, you know, hold things in a big insulated box. Run the reaction. Maybe it produces heat. If it does, then the whole thing will heat up, right? The stuff that's inside the reacting volume, and whatever's right around it there inside the big box, it's all going to heat up.

So I'll start at some initial temperature, T1. I won't end up at the same temperature. It'll be hotter. How much hotter? Well, that depends on how much heat was produced. So in principle, if I measure how much hotter, I can determine how much heat was produced, and from that, I should be able to calculate delta H at T1.

So let's think about how that's really working. I've really got reactants at T1, plus a calorimeter at T1, and I'm going to end up with products -- well let's let me just write that's over. In fact, let's start by just putting a little sketch of the whole thing up.

So here's my reacting stuff, maybe it's a liquid. It's going to take place in there. It's going to be a constant pressure, it might be open to the air, or even if it isn't, there might be plenty of room, and it's a liquid anyway, so the pressure isn't going to change significantly. I want to measure the temperature. And the whole thing is insulated right. I don't want to have to deal with heat escaping to the outside environment in a way that might be difficult or complicated to measure or calculate. OK, so this, what I've sketched here would be a constant pressure calorimeter. There's a reaction. Normally this is used for a reaction in the condensed phases and liquid usually. So this is a constant pressure calorimeter. It's set up to be well-insulated so it's adiabatic. That's the set up. We're going to run the reactants, the reaction. The reactants are going to turn into products.

Let's look at what happens. So what happens is my reactants at T1 plus calorimeter at T1 turn into products at T2 plus my calorimeter at T2, right. That's my process. That's what really happens. Now that, the enthalpy of that process isn't what I want, right, because the temperature has changed, also the calorimeter is heated up.

So I need to relate this to what I do want. Let's label this one. It is adiabatic. It is taking place inside this thing, and it's a constant pressure, and we'll do it reversibly, right. So that's what we've got. Now, we can always take these things the products and the calorimeter at temperature T2 and cool them or warm them to get to products plus calorimeter at T1, right.

Let's label that two. It's still at constant pressure. It's reversible. It's a temperature change. Now to make that happen, it's not adiabatic, right. If I wanted to do that, I'd need a heating element or something to cool, so I could make that temperature change happen, right.

Well, so now I can complete the cycle. I've got reactants and calorimeter at T1. Fewer products and calorimeter at T1, right. Calorimeter doesn't change in this process. So here I've got some delta H associated with changing the temperature. This delta H though, this is what I want. This is delta H of reaction at T1, right? It's isothermal, constant pressure, reversible. Just what I want. That's how I've defined delta H of reaction. This is what I'm after.

All right, so now let's see how we execute it, and do the calculations that allow us to calculate this. So, one, what's delta H in step one? Yes, exactly, it's adiabatic, right constant pressure. it's zero. Delta H1 is zero, right. What we're really going to do in practice is we're going to measure, we're going to use our thermometer and say great, how much did the temperature change, right.

So now, then we're going to use what we're going to learn from step two in order to calculate this part, what we could call step three. OK, so two, that's the crucial part. It's constant pressure. It's just given by the corresponding heat, and it's just a temperature change, right. So we know how to do this, integral from well it's T1 to T2, depending on which way we go of Cp for the whole system dT. OK?

It's just how much heat is involved when we change the temperature. Now, the products have some heat capacity associated with them right, it takes a certain amount of heat if we make their temperature change, to either put it in or take it away, depending on which direction the temperature is changing. Same with the calorimeter, OK.

In actual practice though, the calorimeter, is going to be this big hunk of metal, and really what's going to, there's going to be some stuff in here, right, they'll be a fluid, it will usually be some sort of oil. There's a pretty big thermal mass. Now we run the reaction and it produces heat. Most of the heat is going to warm up or cool off all that oil and stuff. There's a moderate amount of material in the actual reaction. You want to design the calorimeter to fulfill that condition,

Of course, you can't make it so enormous that even for, that for any ordinary reaction there's not even a measurable temperature change, right, because if you have your enough oil to fill up this room, it would take a huge amount of heat to change it by even a tiny, it's temperature but even a tiny amount. So the calorimeter is designed sort of to scale to match the maybe the ordinary volume of reactants that you'll put in there, such that, pretty much all the heat's just going to heat up the calorimeter, and there's only a small amount that's going toward heating up the products, right. So in general, or at least usually it'll be the case, that this is approximately equal to integral from T1 to T2 Cp of just the calorimeter dT.

And that generally is just given by the heat capacity the calorimeter times delta T, right.. Because the heat capacity of the calorimeter just like this thing is not strongly temperature dependent, OK.

So the point is we can calculate delta H associated with this process pretty readily, OK. That leaves three, right.

But delta H for step three must just be the opposite of this delta H because this was zero and we know that were going around a cycle, right.

And that's our heat of reaction. So we're going to be able to do this, right? OK, now this is one way to do calorimetry, and it's practical as long as all the materials are in condensed phases, solids and liquids. If gases are involved it can work, but it can be tricky to keep the pressure constant, right, because that means that now the moles of gas might be changing, and that means in some way the volume has to be adjustable. You'd need some sort of balloon or membrane that will allow that to happen.

Could be done, but easier is to just do the whole thing at constant volume, right, and just run the reaction that way and redo the calculation to be a constant volume rather than constant pressure calorimeter, right. And it's not hard to do that.

So let's just look at what happens in that case. It's almost the same. So let's see, just to finish the job here though, all this says is delta H of reaction is just negative Cp for the calorimeter times delta T, all right. so that's what we think we know in constant pressure calorimetry.

Yes, and if we have gases involved, it's pretty similar, but now what will have is something like this. We'll have a reaction vessel that's sealed, it's constant volume. That'll be inside our calorimeter. It's insulated, and there's still a thermometer, so we can measure the temperature.

So this is still adiabatic. It's insulated, but now it's constant volume, OK. Now, you know with constant volume, now it's not going to be delta H that's straightforward to measure, it's going to be dealt u, all right. But it's going to be almost the same, right? So let's just think about what happens here. Now it's the cycle that we've got will still basically look the same. That is its reactants at T1 plus calorimeter at T1, going to products at T2 plus calorimeter at T2, right? And it's still adiabatic, but now it's constant volume. And it's also reversal right.

So this is our process one. Now, process two, we're going to end up here with our products, again at T1 plus our calorimeter at T1, right. So now we have a constant volume reversible temperature change.

And so this part now isn't exactly what we want to determine delta H, because it's a isothermal constant volume, reversible products or reversible process that takes a reactant to T1 to a product of T1. What these are going to give us are delta u values. This'll give us delta u of reaction, right, T1, right. It's a constant volume.

All right, so in the end, we're going to determine delta u here, and then in the end, we're going to have to relate that to delta H, but that's straight forward enough to do. So let's look at how we'll analyze what happens. So one adiabatic, constant volume process, right. What's zero in that case? In this case delta H was zero in the constant pressure example. Now we've got a constant volume process. What's zero? It's u, because u is to q plus w right,

heat and work, but it's adiabatic. So there's no heat, exchange with the environment, and it's constant volume, so there's no p dV work, right.

So q is zero adiabatic. Work is zero. Delta u1 is zero. And again just in the constant pressure case, what happens that we're going to measure in step one, which is to say in actually running the reaction is the temperature's going to change. Right? The whole thing's going to come to some new equilibrium temperature between the products and the oil or whatever's around it, and we're going to measure that.

OK, two, now it's a temperature change, right? We know how to calculate delta u for a temperature change. It's very similar here, but what's going to be different from the case with constant pressure? There's a real important detail that's different if you want to calculate what happens at constant pressure when you change the temperature? What happens at constant volume? Looking at this expression, what's got to be different? Cv, right. We're not going to have the constant pressure heat capacity, we're going to have the constant volume heat capacity, right.

So delta u for step two, that's our q under constant volume conditions, integral from T1 to T2 Cv for our whole system dT. Integral from T2 to T2, and now I can separate again the calorimeter from the product, and at least approximately, again, it'll be Cv for the calorimeter dT, which is to say then it's Cv of the calorimeter times delta T. Great.

Three, well delta u1 was zero. Delta u2 was there Cv delta T, so now all we need since the whole thing is going around in a cycle, Since we know delta u3 must be negative delta u2, and that is our delta u of reaction, right?

So delta u of reaction is approximately equal to negative Cv for the calorimeter times delta T. So, this is what we're going to measure, and this is what we're going to determine. And now we're almost done, except what we really want is delta H and not delta V, right. So now we're going to use the fact that H is u plus pV. Delta H is delta u plus delta pV, and now this is all at constant temperature in the end, right? We've determined delta u for some temperature T1, right.

So what happens then we're going to use the ideal gas law. So it's approximately delta u plus delta nRT. That's a constant. That's a constant. So it's delta u plus RT, we can say T1 is the temperature we've used here, delta n of the gas.

In other words, what matters here in changing the pressure volume product? What matters is we turned some reactants into some products. How many moles of gas are there in each case, in reactants and products? If that changes, of course you know that the pressure in there is going to change at constant volume if the amount of gas in there is changing. And nothing else is going to make a significant contribution to it, OK?

So finally, then delta H of reaction for our temperature T1 is approximately minus Cv of the calorimeter times delta T plus R T1 delta n of gas. Change of the number of moles of gas, right. We're going to measure that, and now we're going to determine this. In practice, we'll already know the heat capacity of our calorimeter, when we buy it, right?

So we don't really need to put in a certain amount of heat and change the temperature of the products and the calorimeter and so on. What we need to do is just measure how much the temperature changed, OK. It's worth getting just sort of roughly calibrated how big is this compared to the rest of this stuff. That is, how different is delta u from delta H, all right. And of course it's straightforward to do this, and I've written this out in the notes, so I won't re-write the numbers here. But I gave an example looking at combining HCl and oxygen right.

So 4 HCl plus oxygen gas. This two in the gas going to water and the liquid, plus chlorine gas at room temperature. Well, what you find out is delta u of reaction is minus 195 kilojoules for the reaction as written. And it turns out, as written, if you say OK, how much, what changed for the pV product? Well here we've got four moles of gas, five moles of gas. Here just two, so we changed the number of moles of gas by three. All right, how much did it matter, right? Well it matters. It's measurable.

So now delta H of reaction turns out to be minus 202 kilojoules. So, you know, seven out of a couple of a hundred, right, a few percent, kind of typical. In other words, if you look at energetics of ordinary reactions where you're, you know, you're making and breaking covalent bonds, there's a fair amount of energy stored in those, right? The additional change due to changing pressure volume is certainly measurable. You don't want to just ignore it, but in cases like that, it's usually a small fraction of the total. A few percent is typical, okay.

All right, let me just go through one numerical example of a calorimetry calculation, OK. I won't put all the numbers up on the board because our time is running short, but I just want to outline it. All I really want to do is calibrate you a little bit for what happens with ordinary calorimeter heat capacities that makes the calculation turn out to be relatively easy, right.

So let's just write it out. Let's take iron sulfide as a solid, plus 11 halves oxygen gas to make iron oxide, also a solid, plus sulphur dioxide gas. All right. We'll start at T1 is 298 Kelvin. T2, maybe we don't know it yet, right. OK, so we know how to calculate what's going to happen, delta H and delta u, because we can look up the heats of formation and so forth of all the compounds, right.

So if we do that, what we discover is that delta H of formation whoops, something's wrong here. This is sulphur -- what am I doing, boy, S and it's a two, sorry, and the heat of formation is minus 180 kilojoules per mole, that's oxygen, it's zero. Boy, I'm, I don't know what is about this reaction that's vexing me but it's not that complicated.

Here it's minus 824 kilojoules per mole minus 297 kilojoules per mole, right.

So that's our input thermodynamic data. So first of all, let's just do a heat of reaction calculation, right. Taking the product minus the reaction, right. So it's minus 824 plus 4 times minus 297 minus 2 times minus 180. Right? In other words I've got the stoichiometric coefficients in there and the values, and I'm subtracting the reactants from products wind up with minus 1652 kilojoules per mole.

Well, it depends on what we write, what we consider mole, right, maybe I should just write kilojoules as written. OK, I'm going to skip the delta and get the change in moles of gas calculation. It's straightforward to do. What I really want to do is just give an example of what happens when you throw the thing, the material into a calorimeter and see how much the temperature changes.

So let's imagine we start with 0.1 moles of our iron sulfide, and then we have a stoichiometric amount of oxygen, and the whole thing is done in a constant volume calorimeter, and we see what happens. Now the crucial element is what is the heat capacity of the calorimeter, right? And it's, again it's a macroscopic pretty big thing, so typical might be 10 kilojoules per Kelvin, and that's pretty big, right? Noticed that's not per mole, right. I mean the calorimeter is a big thing filled the little oil or whatever is inside it, right?

And it's for that whole unit that you've got some heat capacity. How much heat does it take the warm the entire thing up or the insides of the thing up by a degree? It's that number right. Ordinary heat capacities are in Joule's per Kelvin mole, not kilojoules, right.

And what that's telling you is probably your reactants and products, so the amount of heat that's involved in changing the air temperature is going to be negligible compared to what happens to the whole calorimeter. OK? So now if we say, OK, we we've done this calculation starting with 2 moles of this, but now we're going to be at 0.1 mole, so we're going to need to divide by 20, right.

So instead of minus 1652, it's going to turn out delta u is minus 1648 kilojoules, so, and then divide by twenty, we end up with minus 82.4 kilojoules, that is, that's the delta u of reaction for what happens if you'd put in not two moles of this, but 0.1 mole of this, right. Practical amounts is the reason I'm using numbers like this, right.

So now, what's delta T? Well here's Cv, right, so delta T is just our minus 10 kilojoules per degree oh sorry, it's our minus 82.4 kilojoules. That's the heat released, divided by minus 10 or 10 kilojoules per Kelvin, right. It's 8.2 Kelvin. In other words, how much does the temperature of the whole thing change when you put an ordinary amount of material in there and run a reaction, right. Well, what do you do? You calculate how much heat is released in the reaction. And then what's going to matter is what's the heat capacity of the whole, of the calorimeter?

I didn't even need to know that heat capacity of the product, right. Because it's effect the thermal mass of the product is negligible compared to the thermal mass of the calorimeter.

Now in real practice, I'll do the calculation in reverse. I'll measure how much the temperature changed in the calorimeter, right. I'll know the heat capacity, and what I'll really be calculating is OK, how much heat must have been released in the reaction to make that temperature change happen?

And that in the case of constant volume, in this case that's my delta u, and then I'll add my little delta n term to get delta H.

Any questions on calorimetry? OK. See you Friday. We'll finish on calorimetry and thermochemistry and then we'll start in on one of the really most difficult topics that we'll deal with all semester, which is a second law and our special function that we've seen just a little bit so far.