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PROFESSOR NELSON: Well, today we're going to continue with the lecture that was started last time that had the scintillating and descriptive title "some thermodynamic processes". And we're going to continue along those lines, and really there a couple of things that I want to do to follow up what you saw last time. One is that you've got introduced and led through a couple of elementary thermodynamic cycles.

And I want to do a little bit more of that today. And one of the -- there are really two reasons. One is that as you saw last time doing a thermodynamic cycle can be extremely useful, because if you have one path along which some change occurs, but along which it's not necessarily easy to calculate all of the thermodynamic changes along such a path, it may be irreversible, lots of variables may change. It can be easier instead of looking at the complicated path to devise a cycle that involves several easier steps, each one of which is facile for the calculation of what happens to the thermodynamic properties. So in that case, it's much easier to go through several elementary step, and then the one complicated path you know because going around the entire cycle state functions, you know that they won't have any change. So in that sense, going through a thermodynamic cycle can be useful because it helps you calculate thermodynamic qualities.

But the other reason to go through the thermodynamic cycles and really to develop great facility with them is because there are just an awful lot of things in nature and things that we build that run in cycles, where we want to calculate the thermodynamics, right. If we build an engine for a car or anything else, it almost always is going to have some key element that's operating in a cycle, otherwise it won't keep going, right. But it's not just engines that we might build. It's biological engines, right. Things that either produce or consume biological fuel to do different sorts of processes. Also, of course of key importance to understand what the, in that case, biological thermodynamics are. And again, there'll be key elements that run in cycles and understanding those can be extremely important in understanding how cellular function works.

OK, so what I'd like to do is go through one cycle, and then I'll suggest another for you to work through on your own. So consistent with the title of the lecture, we've got a section from your last lecture notes entitled "some thermodynamic cycles". And what we're going to do is go through a cycle, please note these office hours and locations, which I think wasn't specified before. So we're going to go through a thermodynamic cycle, and here's what I want to calculate when we do this.

Delta u , delta H , familiar state functions, changes in their values, q , w , heat and work. And I also want to introduce

one new function. I won't give it a name yet, but it's going to have the unusual form dq over T . OK, we'll call it special function. It's so special that we'll call this quantity dS . OK, we'll just go through this on a whim, and this is going to be foreshadowing something that'll take on tremendous importance in subsequent lectures, but I'm going to use the opportunity now to just introduce the behavior of it in going around a cycle.

If that's for me, tell them I'm busy please.

OK, so let's look at the cycle we'll go through. We're going to look at pressure volume changes, similar to what you saw before. This time, we're going to have initial and final volumes, V_1 and V_2 and different pressures where we might end up. And we're going to look at two ways to go to a final volume V_2 . One of them is going to end up at pressure p_2 and the other is going to end up at pressure p_3 . One of them is going to be a reversible isothermal path. This is going to be our path we'll label A, reversible isothermal which is to say constant T , right? And we're going to start at temperature T_1 , so since it's constant temperature, this is going to end up at temperature T_1 . And then we're also going to consider a reversible adiabatic path. This'll be our path B, reversible adiabatic. And then we'll close this circle, this cycle. This is going to end up at a different temperature by the way. You saw this last time in a slightly different way. Last time what you saw is we compared isothermal and adiabatic paths that ended up at the same final pressure, and what you saw is that therefore, they ended up in different final volumes. So this is just a little bit different from that. So this is going to end up at a different temperature, we'll call it T_2 . And then we're going to close the cycle.

And so this is a constant volume path then. This is path C, constant volume. OK? So now let's go around the cycle and just compare notes on what happens to the thermodynamic quantities as we do that. So here's path A, it's isothermal. And I didn't specify, but let's make sure to do so, we've got a, it's going to be an ideal gas. OK, so A is constant temperature. What does that mean for Δu in path A? Zero right? Ideal gas, no temperature change, right has to be zero because du is $C_v dT$ for an ideal gas. dT is zero, there's no temperature change. OK, how about ΔH , zero $C_p dT$ for an ideal gas. dT is zero.

All right, now, it's reversible. So that means we can immediately write down an expression for the work. Since it's reversible, it's negative $p dV$ right? And since it's an ideal gas then we can replace p , right, with RT over V , right? We want to do that because we have too many variables here. We've already got dV we'll get rid of p as an additional variable and replace it with V which is already in here.

So it's minus $R T_1 dV$ over V , right? I can put in T_1 because we're a constant temperature. so now we can just integrate straight away and find that the work in path A it's just the integral of that quantity minus integral of $R T_1$ going from V_1 to $V_2 dV$ over V . so it's minus $R T_1 \log V_2$ over V_1 .

All right, so let's just do a reality check here. The way I've got this drawn, the volume is going up in the process.

It's an expansion. So is this system doing work on the surroundings, or are the surroundings doing work on the system? Somebody say it real loud. Yes, the system is working on the surroundings, right? It's pushing out against them.

Work is defined as the work that the surroundings do on the system. So this is the negative number, right? V_2 is bigger than V_1 . This is positive. This whole thing is negative.

All right, q has to be just the opposite of this because we've already figured out that there's no change in u . This is just q plus w . There's w , q has to be $R T_1 \log$ of V_2 over V_1 . OK, so that means heat is being imparted to the system, right, from the surroundings in a manner that compensates exactly the amount of work done. OK, All right, so these are the thermodynamic quantities that you're familiar with already. Let's just quickly look at our special function. It's not going to be hard to calculate because it's a constant temperature path, so that T in the bottom is just T_1 , right. You've already looked at q , right. So dq A over T_1 it's just $R \log V_2$ over V_1 right. So there's our special function for this particular path.

OK, so that's path A. Now let's compare to path B. So if path B is an adibat, what's zero? q , it's adiabatic, that means there's no heat exchanged between the system and the surroundings. So what happens, q B is zero. There is a change in temperature, right?

We've got, if we say it's a mole of gas, it's going from p_1 , V_1 , and T_1 to one mole of our gas at p_3 , V_2 , and T_2 . So unlike before now temperature is going to change. So that means that Δu isn't zero this time. du , it's an ideal gas. So this is $C_v dT$ and of course we can just integrate this straight away. So Δu B is C_v times T_2 minus T_1 , right. and similarly dH is $C_p dT$ right. So ΔH in pathway B is just $C_p T_2$ minus T_1 okay?

All right, what we've already got that q is zero. Δu is q plus w . Δu isn't zero. So this must be equal to work, right? And now we can look at our special function, but since this is zero right dq B is zero, along path B, so our special function, dS , so we're going to go, dq B over T is equal to zero. OK?

OK, finally let's look at our third path, this constant volume path, that's going to connect T_1 and T_2 , right? Constant volume, what's zero?

STUDENT: [INAUDIBLE]

PROFESSOR NELSON: A little more noise here. What's zero?

STUDENT: Work.

PROFESSOR NELSON: Work, great. So, path C constant volume means our work in path C is zero, right? Now,

our temperature is going to change from T_2 to T_1 , and we just saw what happens to u and H when that happens going from T_1 to T_2 , and it's no different. It's an ideal gas going along these path. So we can immediately write $\Delta u = C_v (T_1 - T_2)$. $\Delta H = C_p (T_1 - T_2)$, right?

Work is zero. $\Delta u = w + q$, work plus heat. This is zero, this isn't. This must be heat q_B , right. So again, there are our familiar thermodynamic quantities, but now let's also look at our special function. It's not going to be zero this time because we have non zero heat exchange between the system and the environment, right.

So are integral of dq_C over T , right, which is our heat, but in this case we can do this calculation easily because since work is zero, we can equate dq with du , right. So we can write this as our integral from T_1 to T_2 , du over T . du is just $C_v dT$, right. So this is just $C_v \log T_2$ over T_1 . OK?

So now we've completed the cycle. So let's just compare. Let's compare what happened in path A to what happened in paths B and C. Yes?

STUDENT: [INAUDIBLE]

PROFESSOR NELSON: Ah sorry, yes of course. Thank you. Yes, oh yes, so.

STUDENT: [INAUDIBLE]

PROFESSOR NELSON: And it's right because, thank you again, it's because we're going from T_1 to T_2 . So I'm getting confused by the oh sorry, we're going from T_2 to T_1 . So it's in reverse of the order of the subscripts and I let this confuse me. There it is. There it is. There. Thank you, any other details which should be pointed out? All right, then let's proceed.

So what we're going to do is our comparison of what happened on pathway A to what happened in combined pathways B and C, right? So here are results for pathway A, right, for $\Delta u = 0$ $\Delta H = 0$. I didn't actually explicitly write it or did I? Let's just write it again. Here's our work in path A, and here's our heat exchange in path A. Now let's look at the sum of B and C. So B plus C, here is $\Delta u_B = C_v (T_2 - T_1)$. $\Delta u_C = C_v (T_1 - T_2)$, the sum is zero right. That's the sum of Δu in these two paths, and if we look at Δu in just path A, it's zero.

And it's going to be the same without ΔH . The only difference is it'll be C_p instead of C_v , but there it is for pathway B. There it is for a pathway C. So the state functions that we're familiar with are doing what we expect they ought to be doing, right? If you go around in a cycle, starting and ending at the same place, the state functions have to stay the same. They only depend on the state the system is in. They don't depend on the path, and that's what we've shown, right. Similarly if we go from this point to this point through path A or if we do it

through the combination of these two paths, and the change in u and H in any state function, those have to be the same. It turns out they're zero in both cases, and that's what we've seen, right?

Now let's compare what happens to work and heat. So here are expressions for work and heat. They're opposites for the pathway A. Here's pathway B and C. In C the work is zero. In B it isn't, it's C_v times T_2 minus T_1 , right. The work isn't equal to the work in pathway A, right, because you know work is not a state function it depends on the path right, and there are different amounts of work done on the system, or done by the system on the surroundings in these two different processes. They're both expansions. They'll both have net work done on the surroundings, but not the same amount, right.

And of course it's going to be the same with heat. We've already seen that Δu is zero. So we know that in each case the heat is going to be the opposite of the work, but the work isn't the same in these two different ways of getting from here to here, right. So let's just see it explicitly. Here's our q_A . Here's heat exchanged in pathway A and in pathway B heat is zero, and in pathway C, here is q_C it's $C_v T_1$ minus T_2 .

So again, for both heat and work we don't get the same result. Now let's look at our special function, right. So here's path A. We found that it's $R \log V_2$ over V_1 . Pathway B is zero. Pathway C it's $C_v \log T_1$ over T_2 . All right, let's just look at that a little more carefully. $R \log V_2$ over V_1 . B plus C, $C_v \log T_1$ over T_2 , right. Just some weird combination of functions, right? But, of course, it's not quite like that. Why? Because this path is an adiabatic path. And you already saw last time there was this relationship between the temperature and volume changes along an adiabatic path. So let me just write that down. Adiabatic reversible path.

What you saw is that T_1 over T_2 was V_2 over V_1 to the power R over C_v . Isn't that something? So what does that mean? We take this C_v and put in the exponent here, right. And we put this R up in the exponent here. What are we going to discover? Those two things are equal right, T_1 over T_2 to the power C_v is V_2 over V_1 to the power R , so dS over path A equals dS over paths B plus C, okay?

So what this suggests is that whatever this funny special function is, at least for this one cycle that we've, tried it's behaving like a state function, right. It seems like its change is independent of path. Start here, end up here, do it through two different pathways, end up in the same place, right. OK, now that's all the foreshadowing I'm going to give it for right now. We will certainly come back to this very special function shortly.

Before I move on, I'm just going to put on the board another cycle, and I'm going to urge you to work through that on your own. It's worked through already, let's see, I believe it's worked through in the notes, yes. So if you need the help of the notes it's in there, but I would urge you to work through it on your own, and it's the following: let's start with the same path A, all right?

So we've got our reversible adiabatic path right. And now, try working through what happens if we close the cycle in a different way, right, like this. So here's a path that's constant pressure, and here is a path that's constant volume, similar to the constant volume path that we did before, but not between the same pressures, right. So we can label this one D and this one E, and I urge you to just try going through that and verifying for yourself that again the state functions will behave the way state functions should, and you can see whether this special function once again behaves like a state function, right. And of course you should expect to see that the work and the heat again won't behave like state functions which they are, then you'll see you have different results for those, depending on the path, OK?

Any questions about going through these cycles and using expressions like this and so forth? Expressions like this you know turn up in various places, like in the equations sheet that appears at the end of exams, right? Which means that you may not need to be committing it to memory. On the other hand it means that you should, it's the sort of thing that you should be familiar with so that the need to use it is something that you'll conjure when you're working on a problem and there's a reversible adiabat, and you have temperatures and volumes that change that you might like to relate to each other.

Cycles that are suggested that you go through and aren't gone through in class also sometimes turn up on exams too, by the way. So that said, let's move on to the next topic, which is thermochemistry. So, so far what you've seen in most of the examples in the class are essentially mechanical kinds of changes, pressure volume sorts of changes, where the system is doing essentially a kind of mechanical work, pressure volume work on the surroundings or vice versa and heat is being exchanged, and you're calculating the basic thermodynamics just like we went through, of processes of that sort.

Now I'd like to start introducing something that's really central to chemical thermodynamics, mainly chemistry, right. Let's start looking at chemical reactions, right, and understanding what the changes in thermodynamic properties are that occur when chemical reactions occur, and the immediate application is to calculate the change in enthalpy, which, as you've seen it, at constant pressure which is the condition under which an awful lot of chemistry is done, that's just the heat. Which means we're going to calculate heats of reaction, right.

You're running some reaction. It's in the atmosphere. It's at constant pressure. You know, you mix acid and base together and the thing heats up like crazy, right. Or other things might react spontaneously. You can feel something cooling off right. I mean simple examples of these happen when you, you know, if you buy cold or hot packs. You break the seal between them and feel the thing get cold, for example, right. What's happening there? Well, the selection of reactants has been done judiciously to provide either heat or to provide something that's cool.

And all of that is coming out of the heat of reaction, whether it's positive or negative. Of course the biggest practical application is burning of fuel. You might use the heat to, and convert it into pressure volume work, right? So if it's an internal combustion engine, you'll do a reaction. There will be the heat of reaction. There'll be a volume change, depending on the conditions under which it occurs, and you can extract work through the reaction and so forth.

So let's just to see how you run through some of those calculations. Now let me just ask who here took 5.111? And who here took 5.112? OK, now you've seen some thermal chemistry in 5.111 and 5.112. So I'm going to do some review of that, but I'm also going to call on the thermochemistry that I'm pretty sure you're familiar with. So I won't go painstakingly over every element of the notes here. Subsequently we'll go on into additional topics that you haven't seen, and I'll treat them in full detail.

OK, so let's do some thermochemistry. What we want to do is we'd like to be able to predict for any reaction what's the heat of reaction. And so what we're going to calculate is ΔH . So for any kind of reaction we should be able to do that, right? And we're going to treat constant pressure situations certainly at first and most of the time, right? Constant pressure, right, reversible ΔH is going to give us our heat of reaction, OK.

And then if we can also determine Δu , then we know this, we know Δu is q plus w , then we can determine work as well, right? And typically, we'll be treating at least some cases where we're dealing with ideal gases in which case we can easily get Δu . And then we'll be able to in a very straightforward way get w . So it's a really powerful and simple formalism, once we set up what is needed to go through it, right?

So let's just consider any reaction. The one that I've got written down for you is it's the reverse of the rusting of iron, right? So iron left to own devices in the atmosphere in the presence of a little bit of water, and the atmosphere will start combining with the water to form iron oxide.

There's an equilibrium between the two. So we'll have an iron oxide species. It's a solid. It's combining with hydrogen which is a gas to give iron, also a solid and water, right? So the way I've written this we're imagining the iron, the solid iron immersed in the water as a liquid, could be calculated otherwise as well, but in this case we're imagining the water as liquid and going in this direction then it's forming iron oxide and evolving hydrogen gas, okay?

And our heat of reaction or enthalpy of reaction is defined as the enthalpy at constant pressure. Isothermal conditions, temperature won't change and reversible work. For Isothermal reaction constant pressure reversible, right?

Of course, they're all sorts of conditions under which a reaction could be wrong in the lab or outdoors or however,

right. But this is the way we're going to define ΔH of reaction. We want to have that definition clear because in fact we're going to, we might want tabulate heats of reaction, right, and of course want to know what the conditions are for the tabulated values apply. And we're going to want to calculate them from other quantities, and again, we're going to need to know each case what are the relevant conditions?

OK, so what happens? Well, we should be able to get this. We should be able to calculate ΔH . It's a state function. If we know the enthalpy of the products minus the enthalpy of the reactants, right. It's a state function. And we can do this in principle except for one important detail, which is that enthalpy, just like energy u isn't measured on an absolute scale but on a relative scale, right?

You know, if you want to measure the potential energy of something in a gravitational field, you have to define the zero somewhere, right, because it's arbitrary. You can set it anywhere you want. It's the same with enthalpy. Enthalpy is just u plus pV . So there is an arbitrary set point that needs to be defined, right? Because what you actually measure in the lab are changes in enthalpy, just like what you measure when you look at energy change of some sort, you measure the change in energy, right.

The absolute number that you assign to it is something that's arbitrary. You have to set what the zero is. And so there's a well-understood convention for what the zero is. What we define as zero is the enthalpy of every element in its natural state at room temperature and ambient pressure.

In other words, we choose a convention for the zero of enthalpy, so that then we can write enthalpies of products and reactants always referring to the same standard state. And then we calculate changes, the convention is understood with respect to what is the zero, right.

And so our tabulated values, they'll all work. They'll all refer to the same standard state. And we'll be able to use the formalism that we set up. So our reference point for H , it's 298.15 Kelvin, one bar and in that standard state our molar enthalpy is defined as zero for every element in its stable form. OK, very important.

OK, now, given that reference point, all we need to do to get the value of enthalpy that we're going to use for each reactant and each product is calculate how much does the enthalpy change to form it from the elements in their stable form at room temperature and pressure, right.

So we're going to replace the H or we're going to put in for the H what we'll call our heat of formation or ΔH of formation starting from the elements in their stable states at room temperature and pressure, for each of these things. And we can do that because now we're going to have instead of just sort of H , it's going to be ΔH of formation for each of these things, is going to appear in our calculation of H , but that's OK.

ΔH of formation means the enthalpy of this compound minus the enthalpy of its constituent elements in their

most stable state at room temperature and pressure. But we've defined the enthalpy of those elements in their stable state at room temperature and pressure as zero, right? So we're just subtracting, in effect, zero, right, from the enthalpy of the product, but of course it's important have that established because the heat of formation is something you could measure, right?

You could run the reaction, take solid iron, gaseous oxygen, form iron oxide, measure the heat of formation of it, tabulate it. We know it. We know it forever, right. And for any of the other compounds. So in other words, by defining that reference state, we can then figure out or measure heats of formation of a vast number of compounds. We can tabulate them. We can know them, and then when we have reactions that inter-convert different compounds, we can calculate the heat of reaction is just the difference between the heat of formation of the reactants, and the heat of formation of the products, right.

So let's just write that out. So first of all, for example, right, molar enthalpy of hydrogen gas at 298.15 K is zero. Hydrogen gas it's in its most stable state, right at room temperature and pressure. That little zero, that little superscript means one bar always. OK.

A molar enthalpy of or whatever, iron, as a solid at 298.15 Kelvin is zero. Iron as an element is a solid. That's its most stable state at room temperature and pressure, right, and so on. And then we can figure out heats of formation. Now in this particular reaction, I've got hydrogen gas, iron solid. Those already are elements in their most stable forms at room temperature and pressure.

But this is a compound, right, it has some non-zero heat of formation from the elements. So is water, right? So I need to find out the heats of formation of the iron oxide and the water. And if I do that then I can find out the change in enthalpy of this reaction. It's just going to be the heat of formation of these three moles of water, minus the heat of formation of the iron oxide. OK.

So how am I going to do that? Well, I need to write the reaction that forms that compound from its elements, right? And I want to tabulate that for an enormous number of materials, right? So for example, if I want to look at HBr, there's a simple case, right, hydrogen bromine.

What's my heat of formation? ΔH_f . It's going to have our little zero, right? How do I calculate it? Well, I need to write the reaction that forms this from its constituent elements. What is it? Well, $\frac{1}{2} \text{H}_2$ as a gas, temperature, at one bar, plus $\frac{1}{2}$ bromine, no actually bromine is a liquid at room temperature and one atmosphere. They form HBr which is a gas at room temperature and one bar, right.

I can measure that. And the heat of reaction for this, ΔH of reaction is equal to ΔH of formation, of HBr as a gas at our temperature and one bar, okay? So that's how we determine our heats of formation. We measure

them for all these compounds. And then we go back to reactions like this, and we can just very simply determine the heat of reaction because all we're doing is the following cycle.

We go from reactants to products and there's some heat of reaction, and here's the cycle that we have. We go to the elements in their standard states, in both cases. So we're really just doing our ΔH is the negative sum of ΔH of formation for the reactants, all right? Because here what we're doing is we're going to take apart our reactants and form the elements from them, right?

So written this way, for example, I'm going to pull these things apart, and I'm going to have solid iron, and I'm going to have gaseous oxygen, and I know the enthalpy of that reaction. That's just given by the heat of formation, the enthalpy of formation of iron oxide. Here, now I'm going to take those same elements, and I'm going to make the products, right. I know it's going to work because I already had this reaction, so all the, you know, I'm going to conserve atoms in the right way.

So here, I'm going to have ΔH , is just the sum for all the products of ΔH of formation, right? Here I'm going to put together all the products. So this is a positive heat of formation. This is the negative heat of formation, right?

In other words, I've got reactants, and I've got products. What's ΔH of reaction? It's ΔH of formation of the products minus ΔH of formation of the reactants. That's the important message, ΔH of formation of the products, minus ΔH of formation of the reactants.

Any questions? All right, tomorrow I'll go through the remaining details. The truth is after this, it's all arithmetic, right? We're just going to go through it and execute it a little bit. And then we'll move on and talk about how we'd actually make some of these measurements of ΔH and compare them to what we calculate. See you tomorrow.