PROFESSOR NELSON: Well, last time we started in on a discussion of entropy, a new topic, and I started out by writing out some somewhat verbose written descriptions that had been formulated that indicate certain limitations about things like the efficiency of a heat engine, and what can be done reversibly and so forth. And these verbal descriptions lead to some pictures that I put up and I'll put up again about how you might try to accomplish something like run an engine or move heat from a colder to a warmer body. And what some of the limitations are on things like that.

I'll show those again, but what I want to do mostly today is try to put a mathematical statement of the second law in place that corresponds to the verbal statements that we saw last time.

So, just to review what we saw before, we looked at a heat engine where there is some hot reservoir at some temperature, T1, and it's connected to an engine running in a cycle. We could, write the work that we generate that comes out as negative w. And then there's a cold reservoir at some lower temperature T2. So the way I've got things written here, q1 is positive. Heat's flowing from the hot reservoir to the engine that runs in a cycle. Work is coming out. A positive amount of work is being generated and is coming out, so minus w is positive, and this minus q2 is positive, that is heat is also flowing into a cold reservoir.

And what we saw last time is that this was necessary to make things work, this part of it in particular. You couldn't just run something successfully in a cycle and get work out of it, using the heat from the hot reservoir, without also converting some of the heat that came in to heat that would flow into a cold reservoir. All the heat couldn't get successfully converted into work.

That would be desirable, but it's not possible. And, similarly, if we try to run things backward and build a refrigerator, so now we have our cold reservoir, and we're going to remove heat from it, and pump it up into a hot reservoir. And to do this, we saw that you have to put work in, right, you can't just remove heat from a cold reservoir, move it up to a hot reservoir, without doing some work to accomplish that.

So here, q2 is greater than zero. The work is greater than zero, and minus q1 is greater than zero, that is heat is flowing this way. So these are just the pictures that we saw last time. And then we had some statements of the second law of thermodynamics that I won't re-write up here, but, for example, Clausius gave us the statement that it's impossible for a system to operate in a cycle the takes heat from a cold reservoir, transfers it to a hot reservoir,

that is acts like a refrigerator, without at some, at the same time, converting some work into heat. Work has to come in to make that happen. And we had the similar statement by Kelvin about the heat engine that required that some heat gets dumped into a cold reservoir in the process of converting the heat from the hot reservoir into work.

Fine. Now what I want to do is put up a specific example of the cycle that can be undertaken inside here in an engine, and we can just calculate from what you've already seen of thermodynamics. What happens to the thermodynamics parameters, and see the results in terms of the parameters including entropy.

So let's try that. So, the engine that I'm going to illustrate is called a Carnot engine. And the cycle it's going to undertake is called a Carnot cycle, and it works the following way: we're going to do pressure volume work. So this is something that, by now, you're pretty familiar with. So we're going to start at one, go to two and this is going to be in isotherm at temperature T1, and all the paths here are going to be reversible.

So that's our first step. Then we're going to have an adiabatic expansion. So this is an isothermal expansion. Here comes an adiabatic expansion, to point three. So at this point the temperature will change. Then we're going to have another isothermal step, a compression to some point four. So this is an isotherm at some different temperature T2, a cooler temperature, because this was an expansion. We know in an adiabatic expansion the system's going to cool. And now we're going to have another adiabatic step, an adiabatic compression. And that's it. That's going to take us back to our starting point. So that's our cycle. Of course there are lots of ways we can execute the cycle, but this is a simple one, and these are steps that we're all familiar with at this point.

So this is the picture, and this is a cycle that undertakes it. So let's just look step by step at what happens. So going from one to two, it's an isothermal expansion a T1, so delta u is q1, we'll call it, plus w1, for the first step. Going from two to three, that's an adiabatic expansion, so q is equal to zero in that step. And delta u is equal to what we'll call w1 prime. So we'll use w1 and w1 prime to describe the work involved. The work input during the expansion steps. Step three to four isothermal compression, delta u is going to be q2 plus w2.

And finally, we're going to go back to one. We're going to close the cycle with another adiabatic step. q is zero. Delta u is w2 prime. Now, the total amount of the work that we can get out is just given by the area inside this curve.

We'll call it capital W. It's just minus the sum of all these things, because of course these are just defined as the work done by the environment to the system. So it's minus w1 plus w1 prime plus w2 plus w2 prime. The heat input is just q1, and we'll define that as capital Q. And I just want to write those because what I really want to get at is what's the efficiency of the whole thing? And in practical terms, we can define the efficiency as the ratio of the heat in to the work out. We would like that to be as high as possible.

So it's just capital W over capital Q, which is to say it's minus all that stuff over q1. Now the first law is going to hold in all of these steps, and we're going around in a cycle. So what does that tell us about a state function like u? What's delta u going around the whole thing? I want a chorus in the answer here. What's delta u?

STUDENT: Zero.

PROFESSOR NELSON: Excellent. MIT students, yes! OK, so the first law, we know that the, going around the cycle the integral of delta u is zero. And that has to equal q plus w, summed up for all the steps. Which is to say q1 plus q2 is equal to minus w1 plus w1 prime plus w2 plus w2 prime.

So that means we can rewrite this efficiency. We can replace this sum by just the some of q1 plus q2. So sufficiency is q1 plus q2 over q1. Or we can write it as one plus q2 over q1.

Now that already tells us what we know, which is that the efficiency is going to be something less than zero, right? Because we've got one and then we're adding q2 over q1 to it, but we've got negative q2 is a positive number. Heat is flowing this way. So q2, the heat in this way is negative. q2 over q1 is negative. q2 of course is positive. That is heat flowing from the hot reservoir to the engine.

So that efficiency is something less than one, and we'd like to figure out what that is. So let's just state that. Well, now let's go back to each of our individual steps and look, based on what we know about how to evaluate the thermodynamic changes that take place here, let's look at each one of the steps and see what happens.

So from one to two it's isothermal. And now we're going to specify, we're going to do a Carnot cycle for an ideal gas. It's an ideal gas. It's an isothermal change. What's delta u? You know, it's like lots of courses and all sorts of things that you're seeing, they're always the same. What delta u?

STUDENT: Zero.

PROFESSOR NELSON? Right. Delta u is zero, and it's also equal to this. So that says the q1 is the opposite of w1. It's an isothermal expansion, so dw is just negative p dV. So it's, this is just the integral from one to two of p dV. And it's an ideal gas, isothermal, right. RT over V. Were going to make it for a mole of gas, so it's R times T1, and then we'll have dV over V. So that's just the log of V2 over V1. Let's have one mole, n equals one. Okay two going to three that's this, it's adiabatic, right. So delta u is just equal to the work but we also know what happens because the temperature is changing from T1 to T2.

So delta you is just Cv times T2 minus T1. du is Cv dT. It's an ideal gas, and that's equal to w1 prime. Now, this is a reversible adiabatic path, so there's a relationship that I'm sure you'll remember. Namely, T2 over T1 is equal to

V2 over V3. Don't be confused by the subscripts. We're talking about quantities both starting at two and going to three. So it's V2 and V3. They're different volumes. The temperature though at two is the same as it was at one, so it's still a temp at T1, and this temperatures is at T2.

Anyway T2 over T1 is equal to V2 over V3 to the power gamma minus one. So we're going to kind of store that for the moment. Now going from three to four right, so we have another isothermal process for an ideal gas, so I won't try to make you sing again so soon. Delta u is zero. And so just like here, now q2 is minus w2, that's integral going from three to four p dV. So it's R T2, right, now we're at a lower temperature times the log of V4 over V3. So that's our work in this path and heat.

And finally going from four back to one. So we've already seen that q is zero. So we know that delta u is just Cv times T1 minus T2. Now we're going from T2 up to T1. And this is equal to w2 prime. And now, just like we had before, again we've got a reversible adiabatic path, so T1 over T2 has to equal V4 over V1, to the gamma minus one, okay.

All right, now, if this is the case, of course, this is just the inverse of this. So this just must be the inverse of this. We can combine these two to see that V4 over V1 must equal V3 over V2. So now we have a relationship between the ratios of these volumes that are reached during these adiabatic paths.

Now, let's just look at our efficiency. So we saw that efficiency is one plus q2 over q1. Let's just use our expressions that we've found for q2 and q1. We're going to have q2 over q1. R is going to cancel. We're going to have the ratio of temperatures and the ratio of these logs.

So it's T2 over T1 times the log of V4 over V3, over the log of V2 over V1, but we just arrived at this relationship between these volumes. And this of course tells us that V4 over V3 is V1 over V2. Right. I'm just inverting these. So here it is. Here's the V4 over V3, oops, sorry. V2 over V1, this is equal to the inverse of this. So the ratio of the logs is just minus one. So this is just, sorry, I forgot about the one here. One plus this, but this is the same as one minus T2 over T1. That's our expression for the efficiency.

All right, isn't that terrific? Now, we have an expression. We can figure out the efficiency. All we need to know is the temperatures. What's the temperature of the hot reservoir? What's the temperature of the cold reservoir? We're done. That's the efficiency. As we expected, it's less than one, and of course if we build an engine, we want it to be as high as possible, as close to one as possible. What that means is we want to run the hot reservoir as hot as possible and the cold reservoir as cold as possible.

In principle, this value, this efficiency, can approach 1 as the low temperature approaches absolute zero. If this were to be an absolute zero Kelvin, then we could we can have something, wait a minute. Sorry, it's T2. As T2

goes to zero, the cold reservoir, then this goes to zero and our efficiency approaches one.

So that would be the best we can do. And that basically make sense, right? The whole thing is being powered by sending heat from the hot to the cold reservoir. The colder that cold reservoir is, the hotter that hot reservoir is, the better off we are. The more work we can get out of it. The closer the efficiency will get to one.

So in some sense, the first law would suggest you can sort of break even. That is, it gives us the relationship between energy and work and heat. It might suggest that you could convert all the work to heat. The second law says that really, you can't do that. The only way you could possibly contemplate it is to be working at absolute zero Kelvin. Guess what the third law is going to tell us? You can't get to zero Kelvin. We'll see that shortly. But this is those closest you could come at least by trying to do that to having your efficiency approach one.

Now, we've seen that q2 over q1 is equal to negative T2 over T1. So let me just rewrite that as q1 over T1 is minus q2 over T2. Or in other words, q1 over T1 plus q2 over T2 is zero. But q1 and q2, each one of those is just the integrated amount of heat that was transferred going along a reversible constant temperature path. Which means that q1 over T1, that's this delta S thing that we saw before.

And what we can say about this is it's saying that if we go around in a cycle and look at dq reversible over T it's zero, because that's what these quantities are. Now, of course, we can run the engine backward and build a refrigerator, and if you've got your lecture notes from last period, your 8-9, well, they're labeled 8-9 lecture notes, I made an attempt to define something which was a little bit misguided. And so instead of defining efficiency the way you've got it written there, I'm going to define what's called something different for a refrigerator which is called the coefficient of performance.

So it's the following: so we can define the coefficient of performance written as eta as q2 over minus w. In other words, you know, it's how much heat can we pull out of the cold reservoir, for whatever amount of work that we're going to put in in order to do that? Well of course, we'd like that to be as big as possible. But of course, this is just q2 over minus q1 plus q2. Just to be clear, so it's heat extracted over the work in. So let me just rewrite that as, I just want to divide by q1 everywhere. So I'm going to write this as q2 over q1 over minus one plus q2 over q1. I want to do that because we know that q2 over q1 is negative T2 over T1. So this is negative T2 over T1 over negative one minus T2 over T1.

I can cancel those, and then I'm going to multiply through by T1. So this is just going to be T2 over T1 minus T2, that's our coefficient of performance. So it's a measure of how well we can do to run the refrigerator. So you know, what the second law is doing, in words, it's putting these restrictions on how well or how effectively we can convert heat into work in the case of the engine, or work into heat extracted in the case of a refrigerator. And it follows qualitatively from just your ordinary observations about the direction in which things go spontaneously, right.

You know the heat isn't going to flow from a cold body to a hot body without putting some work in to make that happen. And so, we'll be able of follow that further and see really how to determine the direction of spontaneity for a whole set of processes, really in principle for any processes, went analyzed properly.

So the first step to doing that is I want to just generalize our results so far for a Carnot cycle. You might think well okay, but this is a pretty specialized case. We've formulated one particular kind of engine, and seen how we can analyze what it does, come up with relations that seem of value for efficiency and other quantities. How general is it? Well, let's take a look.

So, what I want to do is make a new engine which really just consists of two engines, side by side. One is our Carnot engine as we've seen it, and the other is just any other reversible engine. So generalize our Carnot engine results.

So let's take our hot reservoir and draw it bigger. We know it has to big anyway, since we can extract heat from it without changing the temperature. And on this side, we're going to write out an engine, and we're going to say this is a Carnot engine. so on the side of it we have q1 prime. We're going to have w prime. And we're going to have q2 prime, and we're going to draw the arrows in the positive direction in these cases. Or in the defined directions I should say.

Here is our colder reservoir. OK, so here is just an engine like what we've already seen, and I'm going to specify that this is a Carnot engine which is to say all the results that we just derived hold for this case. And side by side, we're going to run another engine. So it's got q2, and it's got a cycle w. And it's got q1.

So this is some other engine that runs using reversible processes. So I can define the efficiency of each one of them. The efficiency for the one on the left is minus w over q1, The efficiency prime for the one on the right is minus w prime over q1 prime.

Now I want to just assume that in some way they're different. So let's assume that epsilon prime is greater than epsilon. So in other words, this engine is running less efficiently than my Carnot engine. It's also reversible. And now since it's reversible, we can run it forward or backward. So we can run this one backward and we can use the work that comes out as the input, well sorry, use this work that comes out of the one of the right to run this one backward, which is to say we'll move heat from cold to hot. So use work out of right-hand side to run left-hand backward. Why not? We need work to come in, we might as well get it from here.

So, the total work that we can get out must be zero, out of the whole sum of them. After all, we're taking the output work that we get from the right, and using it all to drive the left. So that means that minus w prime must equal w.

And w is greater than zero. that is in this one we have the environment doing work on the system.

OK, now we've assumed that epsilon prime is greater than epsilon. So we can just write out what those are, minus w prime over q1 prime is greater than minus w over q1. But we know that minus w prime is the same thing as w. So w over q1 prime is greater than minus w over q1. Which is the same thing just to be a little bit maybe pedantic because w over minus q1, and the only reason I'm writing that is to illustrate that this says that q1 must be less than q1 prime. So q1 is less than zero.

Remember this one's running backward, we're pumping heat up. q1 prime is greater than zero, it's running as an engine. It's taking heat from the hot reservoir. Well, that's interesting. That says that minus q1 prime plus q1 is greater than zero. Well, it's a pretty interesting result. There's no work being done on, out of the whole thing. This is providing work that's being used in here, but if you take the whole outside of the surroundings and this whole thing is the system, no net work, these things cancel each other, and yet heat's going up. How did that happen?

Well it happened because we clearly must have a faulty assumption underlying what we've just done. This can't possibly be true. This is impossible. So what this says is the efficiency of any reversible engine has to be one minus T2 over T1. It's not a result that's specific to the one cycle that we put up. And you know, you could have a reversible engine with lots and lots of steps, but you could always break them down into some sequence of adiabatic and isothermal steps. So you know your cycle, you know, you could have a whole complicated sequence on a p v diagram of steps going back.

As long as it's reversible, you know what the efficiency has to be, and in principle, you could break it down into a bunch of steps that you could formulate as isothermal and adiabatic. They might have to be formulated as very small steps, in order to do that, but you could. What this says too, is this result that we found, right, now of course that's our integral dS is zero. It's general. Entropy S is a state function, generally.

Now remember, we went through before how it's a state function but to calculate it, you'd need to find a reversible path, along which you can figure this out. But the fact is it's a state function, in a general way.

Now, if we go back to our Carnot cycle which is a set of reversible paths, it's useful to compare this to what happens in an irreversible case. In a real engine, of course, you can approach the reversible limit. Every step won't be perfectly reversible. And of course it's not hard to see what happens. Let's just take our reversible engine and modify it a little bit. Let's imagine that instead of all the steps being reversible, let's just put in one irreversible step. Let's do this. Instead of this reversible isothermal step, Let's make it an irreversible isothermal step. We can have a different isothermal step. Of course in the reversible case, you're always pushing against an external pressure, which is essentially equal to the internal pressure. Let's not do that. Let's imagine maybe instead we just immediately dropped the pressure and let the system expand against the lower pressure.

Now we know we're going to get less work out of it in that case. You've seen that before. And the work in this case is the area inside here. The work in this step is just the area under this curve. So in some way we're going to have a difference here between the irreversible case and the reversible one.

So if we do that, then what I want to do is just see what happens to dq over T, so in our irreversible engine, one to two, what we know for sure is that minus w in the irreversible step, that's the work out, extracted in that step, is going to be smaller than minus w in the reversible case. So w irreversible is bigger than w reversible. And of course, in either case, delta u is q plus w, so it's q irreversible plus w irreversible, but of course, u being a state function it's the same in either case. So it's the same as q reversible plus w reversible. And we've just seen that this is bigger than this, but the sums are equal. So this has to be less than this.

q irreversible is less than q reversible. In other words, and irreversible isothermal expansion takes less heat from the hot reservoir than a reversible one does. It makes sense, right, because you know we got less work out and delta u is the same right, so it must be that less heat got transferred. So the expansion against lower pressure draws less heat from the hot reservoir right. So now let's look at the efficiency of our irreversible engine. So it's one plus q2. Now q2 was in this step, and we're going to leave that reversible, right, but q1 is irreversible. And this has got to be less than one plus q2 reversible over q1 reversible, which is to say it's less than our efficiency in the reversible case. Why?

This is smaller than this, but it's a negative number. So this negative number has a bigger magnitude than this negative number. We're subtracting them from one and they're less than one, so this is bigger than this. And all we know about this is that it's really for some irreversible reversible step.

All we really needed to know about it is that this is smaller right. So it's going to be the case for any irreversible engine. And that's the point. So it's that the irreversible efficiency is lower than the reversible one. But, of course, since we saw that this is smaller than it was in the reversible case, we can also write that dq irreversible over T is less than dq reversible over T.

Which is to say if we go around a cycle for dq irreversible over T, that's less than zero. It's only in the reversible case that dq over T around a cycle is equal to zero. So to write that in a general way, it's actually formulated by Clausius. Going around in a cycle the integral of dq over T is less than or equal to zero. Never greater.

OK, what we'll see shortly is that this will allow us to see that for an isolated system the entropy never decreases. It only can go up. And in fact any spontaneous process will make it go up. Only in the case of reversible processes. Of course, then you can see that this will be zero. Anything else, which is to say any spontaneous process, it'll be less than zero. We'll see that next time, and then we'll generalize in a broader sense to look at the

direction in which spontaneous processes go.