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PROFESSOR: So last time we talked about the zeroth law, which is the common-sense law, which says that if you take a hot object next to a cold object, heat will flow from the hot to the cold in a way that is well defined, and it allows you to define temperature. It allows you to define the concept of a thermometer. You have three objects, one of them could be a thermometer. You have two of them separated at a distance. You take the third one, and you go from one to the other, and you see whether heat flows, when you touch one object, the middle object, between those two objects.

Let me talk to you about temperature scales. We talked about the Celsius scale then the Fahrenheit scale. The late 1800's were a booming time for temperature scales. People didn't really realize how important it was to properly define the reference points: Fahrenheit's warm-blooded or 96 degrees, and Romer's 7.5 degrees. Romer because he didn't want to go below zero degrees measuring temperature outside in Denmark Those are kind of silly. But they're the legacy that we have today, and that's what we use.

In science, we use somewhat better temperature scales. And the temperature scale that turns out to be well-defined and ends up giving us the concept of an absolute zero is the ideal gas thermometer. So, let's talk about that briefly today first.

The ideal gas thermometer. It's based on Boyle's law. Boyle's law was an empirical law that Mr. Boyle discovered by doing lots of experiments, and Boyle's law says that the limit of the quantity pressure times the molar volume, so this quantity here, pressure times the molar volume, as you let pressure go to zero. So, you do this measurement, you measure with the gas, you measure the pressure and the molar volume. Then you change the pressure again, and you measure the pressure in the volume, and you multiply these two together, and you keep doing this experiment, getting the pressure smaller and smaller, you find that this limit turns out to be a constant, independent of the gas. It doesn't care where the gas is. You always get to the same constant. And that constant turns out to be a function of the temperature. The only function it is -- it doesn't care where the gas is. It only cares where the temperature is.

All right, so now we have the makings of a good thermometer and a good temperature scale. We have a substance. The substance could be any gas. That's pretty straightforward. So now we have a substance, which is a gas, with a property. So now the volume of mercury, or the color of something which changes with temperature, or the resistivity. In this case here, our property is the value of the pressure times the volume, times the molar

volume. That's the property. The property is the limit as  $p$  goes to zero of pressure times molar volume. It's a number. Measure it. It's a number. It's going to come out. That's the property that's going to give us the change in temperature.

Then we need some reference points. And Celsius first used the boiling point of water, and called that 100 degrees Celsius, and the freezing point of water and called that zero degrees Celsius. And then we need an interpolation scale. How to go from one reference point to the other with this property. This property, which we're going to call  $f(t)$ .

There are many ways you can connect those two dots. If I draw a graph, and on one axis I have this temperature. The idea of temperature with two reference points, zero for the freezing point of water, 100 degrees for the boiling point of water. And on the y-axis I've got the property  $f(t)$ . It has some value corresponding to  $t$  equals zero. So let's get some value right here. There's another value connected to this property here, when  $t$  is equal to 100, a reference point here.

Now there many ways I can connect these two points together. The simplest way is to draw a straight line. It's called the linear interpolation. My line is not so straight, right here. You could do a different kind of line. You could do a quadratic, let's say. Something like this. That would be perfectly fine interpolation. All right, we choose to have a linear interpolation. That's a choice, and that choice turns out to be very interesting and really important, because if you connect these two points together, you get a straight line that has to intercept the x-axis at some point.

Now what does it mean to intercept the x-axis here? It means that the value of  $f(t)$  for this temperature is zero. That means that at this point right here,  $f(t)=0$ . That means the pressure times the volume equals zero, for that gas. And if you're below this temperature here, this quantity,  $p$  times  $v$  it would be negative. Is that possible? Can we have  $p v$  negative? Yes? No, it can't be. Negative pressure doesn't make any sense, right? Negative volume doesn't make any sense. That means that this part here, can't happen. That means that this temperature right here is the absolute lowest temperature you can go to that physically makes any sense. That's the absolute zero. So the concept of an absolute zero, a temperature below which you just can't go, that's directly out of the scheme here, this linear interpolation scheme with these two reference points. If I had taken as my interpolation scheme, my white curve here, I could go to infinity and have the equivalent of absolute zero being at infinity, minus infinity.

So, this temperature, this absolute zero here, which is absolute zero on the Kelvin scale. The lowest possible temperature in the Celsius scale is minus 273.15 degrees Celsius. So that begs the notion of re-referencing our reference point, of changing our reference points. To change a reference point from this point here being zero, instead of this point here being zero. And so redefining then the temperature scale to the Kelvin scale, where  $t$  in

degrees Kelvin is equal to  $t$  in degree Celsius, plus 273.15. And then you would get the Kelvin scale.

All right, it turned out that this thermometer here wasn't quite perfect either. Just like Fahrenheit measuring 96 degrees being a warm-blooded, healthy man, right, that's not very accurate. Our temperature probably fluctuates during the day a little bit anyways, it's not very accurate. And similarly, the boiling point, defining that at a 100 degrees Celsius, well that depends on the pressure. It depends whether you're in Denver or you're in Boston. Water boils at different temperatures, depending on what the atmospheric pressure is; same thing for the freezing point.

So that means, then, you've got to define the pressure pretty well. You've got to know where the pressure is. It would be much better if you had a reference point that didn't care where the pressure was. Just like our substance doesn't care where the gas is. It's kind of universal. And so now, instead of using these reference points for the Kelvin scale, we use the absolute zero, which isn't going to care what the pressure is. It's the lowest number you can go to. And our other reference point is the triple point of water -- reference points become zero Kelvin, absolute zero, and the triple point. The triple point of water is going to be defined as 273.16 degrees Kelvin. And the triple point of water is that temperature and pressure -- there's a unique temperature and pressure where water exists in equilibrium between the liquid phase, the vapor phase, and the solid phase. So the triple point is liquid, solid, gas, all in equilibrium.

Now you may think, well I've seen that before. You take a glass of ice water and set it down. There's the water phase, there's the ice cube is the solid phase, and there's some water, gas, vapor, and that's one bar. Where am I going wrong here? The partial pressure of the water, of gaseous water, above that equilibrium of ice and water is not one bar, it's much less.

So the partial pressure or the pressure by which you have this triple point, happens to be  $6.1 \times 10^{-3}$  bar. There's hardly any vapor pressure above your ice water glass. So this unique temperature and unique pressure defines a triple point everywhere, and that's a great reference point.

Any questions? Great. So now we have this ideal gas thermometer, and out of this ideal gas thermometer, also comes out the ideal gas law. Because we can take our interpolation here, our linear interpolation, the slope of this line. Let's draw it in degrees Kelvin, instead of in degrees Celsius. So we have now temperature in degrees Kelvin. We have the quantity  $f(t)$  here. We have an interpolation scheme between zero and 273.16 with two values for this quantity, and we have a linear interpolation that defines our temperature scale, our Kelvin temperature scale.

And so the slope of this thing is  $f(t)$  at the triple point, which is this point here, this is the temperature of the triple point of water, divided by 273.16. That's the slope of that line. The quantity here, which is  $f(t)$  of the triple point, divided by the value of the x-axis here. So that's the slope, and the intercept is zero, so the function  $f(t)$ , you just

multiply by  $t$  here. This is the slope.  $f(t)$  is just the limit. As  $p$  goes to zero of  $p$  times  $v$  bar. And so now we have this quantity,  $p$  times  $v$  bar, and the limit of  $p$  goes to zero is equal to a constant times the temperature.

That's a universal statement. It's true of every gas. I didn't say this is only true of hydrogen or nitrogen, This is any gas because I'm taking this limit  $p$  equals to zero. Now this constant is just a constant. I'm going to call it  $r$ . I'm going to call it  $r$ . It's going to be the gas constant, and now I have  $r$  times  $t$  is equal to the limit,  $p$  goes to zero of  $p$  times  $v$  bar. It's true for any gas, and if I remove this limit here,  $r$  times  $t$  is equal to  $p$  times  $v$  bar, I'm going to call that an ideal gas.

See, this is the property of an ideal gas. What does it mean, ideal gas? It means that the molecules or the atoms and the gas don't know about each other.

They effectively have no volume. They have no interactions with each other. They occupy the same volume in space. They don't care that there are other atoms and molecules around. So that's basically what you do when you take  $p$  goes to zero. You make the volume infinitely large, the density of the gas infinitely small. The atoms or molecules in the gas don't know that there are other atoms and molecules in the gas, and then you end up with this universal property. All right, so gases that have this universal property, even when the pressure is not zero, those are the ideal gases. And for the sake of this class, we're going to consider most gases to be ideal gases. Questions?

So now, this equation here relates three state functions together: the pressure, the volume, and the temperature. Now, if you remember, we said that if you had a substance, if you knew the number of moles and two properties, you knew everything about the gas. Which means that you can re-write this in the form, volume, for instance, is equal to the function of  $n$ ,  $p$ ,  $t$ . In this case,  $V = (nRT)/P$ . Have two quantities and the number of moles gives you another property. You don't need to know the volume. All you need to know is the pressure and temperature and the number of moles to get the volume. This is called an equation of state. It relate state properties to each other. In this case it relates the volume to the pressure and the temperature.

Now, if you're an engineer, and you use the ideal gas law to design a chemical plant or a boiler or an electrical plant, you know, a steam plant, you're going to be in big trouble. Your plant is going to blow up, because the ideal gas law works only in very small range of pressures and temperatures for most gases.

So, we have other equations of states for real gases. This is an equation of state for an ideal gases. For real gases, there's a whole bunch of equation the states that you can find in textbooks, and I'm just going to go through a few of them.

The first one uses something called a compressibility factor,  $z$ . Compressibility factor,  $z$ . And instead of writing  $PV = RT$ , which would be the ideal gas law, we put a fudge factor in there. And the fudge factor is called  $z$ . Now we

can put real instead of ideal for our volume.  $z$  is the compressibility factor, and  $z$  is the ratio of the volume of the real gas divided by what it would be were it an ideal gas. So, if  $z$  is less than 1, then the real gas is more compact than the ideal gas. It's a smaller volume. If  $z$  is greater than 1, then the real gas means that the atoms and molecules in the real gas are repelling each other and wants to have a bigger volume.

And you can find these compressibility factors in tables. If you want to know the compressibility factors for water, for steam, at a certain pressure and temperature, you go to a table and you find it. So that's one example of a real equation of state. Not a very useful one for our purposes in this class here. Another one is the virial expansion. It's a little bit more useful. What you do is you take that fudge factor, and you expand it out into a Taylor series. So, we have the  $p v_{\text{real}} / r t$  is equal to  $z$ . Now, we're going to take  $z$  and say all right, under most conditions, it's pretty close to 1, when it's an ideal gas. And then we have to add corrections to that, and the corrections are going to be more important, the larger the volume is. Remember, it's the limit of  $p$  times  $v$  goes to zero, so if you have a large volume with a large pressure, then you're out of the ideal gas regime.

So let's take Taylor series in one over the volume, it's going to be one over the volume squared, etcetera. And these factors on top, which are going to depend on the temperature, are the virial coefficients, and those depend on the substance. So you have this  $p B(t)$  here. This is called a second virial coefficient. And then, so you can get, you can actually find a graph of this  $B(t)$ . It's going to look something like this. It's the function of temperature, as  $B(t)$ . There's going to be some temperature where  $B(t)$  is equal to zero. In that case, your gas is going to look awfully like an ideal gas. Above some temperature is going to be positive, below some temperature is going to be negative.

Generally, we ignore the high order terms here. So again, if you do a calculation where you're close enough to the ideal gas, and you need to design your, if you have an engineer designing something that's got a bunch of gases around, this is a useful thing to use. Now, the most interesting one for our class, the equation of state that's the most interesting, is the Van der Waals equation of state, developed by Mr. Van der Waals in 1873. And the beauty of that equation of state is that it only relies on two parameters.

So let's build it up. Let's see where it comes from. Let me just first write it down, the Van der Waals equation of state.  $p + a / v^2$  times  $v - b$  equals  $r t$ . All right, if you take  $a$  equal to zero, these are the two parameters,  $a$  and  $b$ . If you take those two equal to zero, you have  $p v$  is equal to  $r t$ . That's the ideal gas law.

Let's build this up. Let's see where this comes from, where these parameters  $a$  and  $b$  comes from. So, the first thing we're going to do is we're going to take our gas in our box, let's build a box full of gases here. We've got a bunch of gas molecules or atoms. OK, there's the volume of a box here. While these gas molecules or atoms

through first approximation, are like hard spheres. They occupy a certain volume. Each atom or molecule occupies a particular volume. And so, we can call  $b$  is the volume per mole of the hard spheres, volume per mole that is the little sphere that the molecules are. So that the volume that is available to any one of those spheres is actually smaller than  $v$ . Because you've got all these other little spheres around, so the actual volume seen by any one of those spheres is smaller than  $v$ . So when we take our ideal gas law,  $p \bar{v}$  is equal to  $r t$  we have to replace  $\bar{v}$  by the actual volume available to this hard sphere. So instead of  $\bar{v}$ , we write  $\bar{v} - b$ , equal  $r t$ .

OK, that's the hard sphere volume of the spheres. Now, those molecules or atoms that are in here, also feel each other. There are a whole bunch of forces that you learn in 5.112, 5.111 like with Van der Waals' attractions and things like this. So there are attractive forces, or repulsive forces that these molecules feel, and that's going to change the pressure that the molecules feel.

For instance, if I have, what is pressure? Pressure is when you have one of these hard spheres colliding against the wall. There's the hard sphere. It wants to collide against the wall to create a force on the wall, and I have a couple of the hard spheres that are nearby, right, and in the absence of any interactions, I get a certain pressure. This thing would but careen into the wall, kaboom! You'd have this little force, but in the presence of these interactions, you've got these other molecules here that are watching this, you know, their partner sort of wants to do damage to themselves, like hitting that wall, and they say, no! Come back, come back, right?

There is an attractive force. There are no other molecules on that side of the wall. So there's an attractive force that makes the velocity within not quite as fast. The force is not quite as strong as it was without this attractive force. So the real pressure is not quite the same because of this attractive force as it was, as it would be without the attractive forces. The pressure is a little bit less in this case here.

So instead of this  $p$  here. Now if I re-write this equation here as  $p$  is equal to  $r t$  divided by  $\bar{v} - b$ , just re-writing this equation as it is. So the pressure is going to depend on how strong this attractive force is. So the pressure is going to be less if there's a strong attractive force. And the  $1/\bar{v}^2$  is a statistical, is basically a probability of having another molecule, a second molecule in the volume of space.

So, if the molar volume is small, then  $1/\bar{v}$  is large, there's a large probability of having two spheres together in the same volume. If the molar volume is large, that means that there's a lot of room for the molecules, and they're now going to be close to each other, and so this isn't going to be as important.

So,  $a$  is the strength of the interaction,  $\bar{v}$  is how likely they are to be close to each other. And that's going to affect the actual pressure seen by the gas. And  $a$  is greater than zero when you have the attraction. And that gives use the Van der Waals' equation of state, with two parameters, the hard sphere volume and the attraction.

You don't have to go look up in tables or books. You don't have to have all the values of the second virial coefficient, or the fudge factor, just two variables that make physical sense, and you get an equation of state which is a reasonable equation of state, and that's the power of the Van der Waals' equation of state, and that's the one we're going to be using later on this class to describe real gases. Question?

OK, so we've done the zeroth law. We've done temperature, equations of state. We're ready for the first law. We're just going to go through these laws pretty quickly here. Remember, the first law is the upbeat law. It's the one that says, hey, you know, life is all rosy here. We can take energy from fossil fuels and burn it up and make it heat, and change that energy into work. And it's the same energy, and we probably can do that with 100% efficiency. We can take heat from the air surrounding us and run our car on it with 100% efficiency.

Is this possible? That's what the first law says, it's possible; work is heat, and heat is work, and they're the same thing. You can break even, maybe. So let's go back and see what work is. Let's go back to our freshman physics. Work, work is if you take a force, and you push something a certain distance, you do work on it. So if I take my chalk here and I push on it, I'm doing work to push that chalk. Force times distance is work. The applied force times the distance. There are many kinds of work. There's electrical work, take the motor, you plug it into the wall, electricity makes the fan go around, that's electrical work. There's magnetic work. There is work due to gravity.

In this class here, we're going to stick to one kind of work which is expansion work. So expansion work, for instance, or compression work, is if you have a piston with a gas in it. All right, you put a pressure on this piston here, and you compress the gas down. This is compression work. Now the volume gets smaller.  $p$  external here. Pressure, the piston goes down by some volume  $\Delta V$ . The piston has a cross-sectional area,  $A$ , and the force -- pressure is force per volume area. So the force that you're pushing down on here is the external pressure times the area. Pressure is force per volume area. That's the force you're using to push down.

Now the work that's it is calculated when you push down with the pressure on this piston here, that work is force times distance,  $f \times \Delta V$ .  $f$  is  $p$  external times  $A$ , times the distance  $\Delta V$ . So that's  $p$  external times the change in the volume. The area times this distance is a volume, and that is the change in volume from going to the initial state to the final state. Now we need to have a convention. We've got force. Work is force times distance, it's  $p$  external times  $\Delta V$ , and I'm going to be stressing a lot that this is the external pressure. This is the pressure that you're applying against the piston, not the pressure of the gas. It's the pressure the external world is applying on this poor system here.

OK, but we need a convention here. The convention, and then we need to stick to it. And this convention, unfortunately, has changed over the ages. But we're going to pick one, and we're going to stick to it, which is that if the environment does work on the system, if we push down on this thing and do work on it, to compress it, then

we call that work negative work. No, we call that work positive work. All right, so that means we need to put a negative sign right here, by convention. So if  $\Delta v$  is negative, in this case  $\Delta v$  is negative, OK,  $\Delta v$  is negative, pressure is a positive number, negative times negative is positive, work is greater than zero. We're doing work on the system, to the system. In this case here, work is positive.

If you have expansion on the other side, if the system is expanding in the other direction, if you're going this way, right, you're going to do work to the environment. There might be a mass here. This could be a car. Pistons in the car, right, so the piston goes up. That's going to drive the wheels. The car is going to go forward. You're doing work on the environment.  $\Delta v$  is going to be negative.  $w$  is going to be negative. Sorry, I got it backwards again.  $\Delta v$  is positive in this direction here, the work is negative. So work on the system is positive. Work done by the system is negative. Convention, OK, this negative sign is just a pure convention. You just got to use it all the time. If you use an old textbook, written when I was taking thermodynamics, they have the opposite convention, and it's very confusing. But now we've all agreed on this convention, and work is going to be with the negative sign here. OK, any questions?

This is an example where the external pressure here is kept fixed as the volume changes, but it doesn't have to be kept fixed. I could change my external pressure through the whole process, and that's the path. We talked about the path last time being very important. Defining the path. So if I have a path where my pressure is changing, then I can't go directly from this large volume to this small volume. I have to go in little steps, infinitely small steps. So, instead of writing work is the negative of  $p_{\text{external}}$  times  $\Delta v$ , I'm going to write a differential.  $dw$  is minus  $p_{\text{external}}$   $dv$ , where this depends on the path, it depends on path and is changing as  $v$  and  $p$  change.

Now I'm going to add a little thing here. I'm going to put a little bar right here. And the little bar here means that this  $dw$  that I'm putting here is not an exact differential. What do I mean by that? I mean that if I take the integral of this to find out how much work I've done on the system, I need to know the path. That's what this means here. It's not enough to know the initial state and the final state to find what  $w$  is.

You also need to know how you got there. This is very different from the functions of state, like pressure and temperature. There's a volume, there's a temperature, than the pressure here. There's other volume, temperature and pressure here, corresponding to this system here. And this volume, temperature and pressure doesn't care how you got there. It is what it is. It defines the state of the system. The amount of work you've put in to get here depends on the path. It's not a function of state. It's not an exact differential. So the  $\Delta v$  here is an exact differential, but this  $dw$  is not. That's going to be really important. So if you want to find out how much work you've done, you take the integral from the initial state to the final state of  $dw$  minus from one to two  $p_{\text{external}}$   $dv$ , and you've got to know what the path is. So let's look at this path dependence briefly here.



We're going to do two different paths, and see how they're different in terms of the work that comes out. So we're going to take an ideal gas, we can assume that it's ideal. Let's take argon, for instance, a nice, non-interacting gas. We're going to do a compression. We're going to take argon, with a certain gas, certain pressure  $p_1$ , volume  $V_1$ , and we're going to a final state argon, gas,  $p_2$ ,  $V_2$ . Where  $V_1$  is greater than  $V_2$ , and  $p_1$  is less than  $p_2$ . So if I draw this on a  $p$   $v$  diagram, so there is volume on this axis. There's pressure on this axis. There is  $V_1$  here. There's  $V_2$  here. There's  $p_1$  here, and  $p_2$  here. So I'm starting at  $p_1$ ,  $V_1$ . I'm starting right here. And I'm going to end right here. Initial find -- there are many ways I can get from one state to the other. Draw any sort of line to go here, right? There are a couple obvious ones, which we're going to -- we can calculate, which we're going to do.

So, the first obvious one is to take  $V_1$  to  $V_2$  first with  $p$  constant. So take this path here. I take  $V_1$  to  $V_2$  first, keeping the pressure constant at  $p_1$ , then I take  $p_1$  to  $p_2$  keeping the volume constant at  $V_2$ . Let's call this path 1. Then you take  $p_1$  to  $p_2$  with  $V$  constant. An isobaric process followed by a constant volume process.

You could also do a different path. You could do, let me draw  $p$   $v$ , there's my initial state. My final state here, I could take, first, I could change the pressure, and then change the volume. So the second process, if you take  $p_1$  to  $p_2$ ,  $V$  constant, and then you take  $V_1$  to  $V_2$  with  $p$  constant. This is path number two. Both are perfectly fine paths, and I'm going to assume that these paths are also reversible. Let's assume that both are reversible, meaning that I'm doing this pretty slowly, so as I change, let's say I'm changing my volumes here,  $V_1$  to  $V_2$ , it's happening, I'm compressing it slowly, slowly, slowly so that at any point I could reverse the process without losing energy, right? It's always an equilibrium.

All right, let's calculate the work that's involved with these two processes. Remember it's the external pressure that's important. In this case, because it's a reversible process, the external pressure turns out to be always the same as the internal pressure. It's reversible, that means that  $p_{\text{external}}$ , equals  $p$ . I'm doing it very slowly so that I'm always in equilibrium between the external pressure and the internal pressure so I can go back and forth.

So, let's calculate  $w_1$ . The work for path one. First thing is I change the volume from  $V_1$  to  $V_2$  The external pressure is kept constant,  $p_1$ , so it's minus the integral from 1,  $V_1$  to  $V_2$ ,  $p_1$ ,  $dv$ . And then the next step here is I'm going from -- the pressure is changing. I'm going from  $V_2$  to  $V_2$   $dv$  -- what do you think this integral is? Right, so this is easy part, zero here. This one is also pretty easy. That's minus  $p_1$  times  $V_2$  minus  $V_1$ .  $p_1$  times  $V_2$  minus  $V_1$ . What that turns out to be, this area right here. It's  $V_1$  minus  $V_2$  times  $p_1$ . This is  $w_1$  here. OK, I can re-write this as  $p_1$  time  $V_1$  minus  $V_2$  and get rid of this negative sign here. Now  $V_1$  is bigger than  $V_2$ , so this is positive. So I am compressing, I'm doing work to the system, positive work everything follows our convention.

Number two here, OK, the first thing I do is I change the pressure under constant volume,  $V_1$ ,  $V_1$  minus  $p$   $dv$ , and then I change the volume from  $V_1$  to  $V_2$  and then this is  $p_2$ ,  $dv$ . This first integral is zero  $V_1$  to  $V_1$ , then I get minus

$p_2$  times  $V_2$  minus  $V_1$  or  $p_2$  times  $V_1$  minus  $V_2$ . Again, a positive number.

I'm doing work to the system to go from the initial state to the final state. But it's not the same as  $w_1$ . In this case, I have  $p_1$  times  $\Delta V$ . In this case here, I have  $p_2$  times  $\Delta V$ . And  $p_2$  is bigger than  $p_1$ .  $w_2$  is bigger than  $w_1$ . The amount of work that you're doing on the system depends on the path that you take.

All right, how do I, practically speaking, how do I do this? Anybody have an idea? How do I keep  $p_1$  constant while I'm lowering the volume?

STUDENT: Change the temperature?

PROFESSOR: Change the temperature, right. So what I'm doing here is I'm cooling, and then when I'm sitting at a fixed volume and I'm increasing the pressure, what am I doing? I'm heating, right? So I'm doing cooling and heating cycles. So in this case here, I cool and then I heat. In this case here, I heat and then I cool. All right, so I'm burning some energy, I'm burning some fuel to do this somehow, to get that work to happen.

All right, now suppose that I took these two paths, and coupled them together. So in this case, it's the amount of work is the area under that curve. And in this case here, the amount of work is bigger,  $w_2$  is bigger, and it's the area under this curve.

Now, suppose I took this two paths, and I took -- couple them together with one the reverse of the other. So I have my initial state, my final state, my initial state, my final state here. And I start by taking my first path here. I cool, I heat. So there's  $w_1$ . So the  $w$  total that I'm going to get, is  $w_1$ , and then instead of the path from  $V_1$  to, from 1 to 2 going like this as we had before, I'm going to take it backwards. If I go backwards, to work -- everything is symmetric, the work becomes the negative from what I had calculated before, so this becomes minus what I calculated before for  $w_2$ .

The total work, in this case here, is  $p_1$  times  $V_1$  minus  $p_2$  times  $V_1$  minus  $V_2$ , it's  $p_1$  minus  $p_2$  times  $V_1$  minus  $V_2$ . This is a positive number,  $p_1$  is smaller than  $p_2$ . This is a negative number. The total work is less than zero. That's the work that the system is doing to the environment. I'm doing work to the environment. The work is negative, which means that work is being done to the environment. And that work is the area inside the rectangle.

What you've built is an engine. You cool, you heat, you heat, you cool, you get back to the same place, but you've just done work to the environment. You've just built a heat engine. You take fuel, rather you take something that's warm, and you put it in contact with the atmosphere, it cools down. You take your fuel, you heat it up again. It expands. You change your constraints on your system, you heat it up some more, then you take the heat source away, and you put it back in contact with the atmosphere. And you cool it a little bit, change the constraints, cool it

a little bit more, and heat, and you've got a closed cycle engine. We're going to work with some more complicated engines before.

But the important part here is that the work is not zero. You're starting at one point. You're going around a cycle and you're going back to the same point. The pressure, temperature, and volume are exactly the same here as when you started out. But the  $w$  is not zero. The  $w$ , for the closed path, and when I put a circle there on my integral that means a closed path, when you start and end at the same point, right, this is not zero. If you had an exact differential, the exact differential around a closed path, you would get zero. It wouldn't care where the path is. Here this cares where the path is. So, work is not a function of state. Any questions on work before we move on to heat, briefly?

So heat is a quantity that flows into a substance, something that flows into a substance that changes its temperature, very broadly defined. And, again, we have a sign convention for heat. So heat, we're going to call that  $q$ . And our sign convention is that if we change our temperature from  $T_1$  to  $T_2$ , where  $T_2$  is greater than  $T_1$  then heat is going to be positive. Heat needs to go into the system to change the temperature and make it go up. If the temperature of the system goes down, heat flows out of the system, and we call that negative  $q$ . Same convention is for  $w$ , basically.

Now, you can have a change of temperature without any heat being involved. I can take an insulated box, and I can have a chemical reaction in that insulated box. I can take a heat pack, like the kind you buy at a pharmacy. Break it up. It gets hot. There's no heat flowing from the environment to the system. I have to define my terms. My system is whatever's inside the box. It's insulated. It's a closed system. In fact, it's an isolated system. There's no energy or matter that can go through that boundary. Yet, the temperature goes up. So, I can have a temperature change which is an adiabatic temperature change. Adiabatic means without heat. Or I could have a non-adiabatic, I could take the same temperature change, by taking a flame, or a heat source and heating up my substance. So, clearly  $q$  is going to depend on the path. I'm going from  $T_1$  to  $T_2$ , and I have two ways to go here. One is non-adiabatic. One is adiabatic. All right, now what we're going to learn next time, and Bob Field is going to teach the lecture next time, is how heat and work are related, and how they're really the same thing, and how they're related through the first law, through energy conservation. OK, I'll see you on Wednesday then.