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PROFESSOR: As you can probably tell from the volume of my voice, I'm not Mounji. I'm Bob Field, and I will be lecturing today as a special booby prize, because Bawendi is so wonderful.

Last time you heard about work and heat. So there's $p v$ work and it's given by the integral minus $p_{\text{external}} dv$ or just the integral from one to two of dw . And this little slash here means an inexact differential. The reason for inexact doesn't mean it's a crummy measurement, it means that it's path dependent, and so the value of this integral depends on how you get from one to two. w greater than zero means that work is done on the system, and it's really important to keep track of the signs of these things. For heat, heat is defined, or the energy unit for heat, calorie, is defined as the amount of heat needed to raise one gram of water from 14.5 degrees c to 15.5 degrees c. That great deal of specificity implies that heat is also path-dependent and again we have the convention that if heat is added to the system, the quantity is greater than zero.

OK, so that's a quick statement of what happened last time. Today we're going to talk about heat capacity. The first law, a process that takes a gas from p_1, V_1, T to p_2, V_2, T examined for various paths. And what you'll find is that the maximum work out is obtain for a reversible path. We'll then look at the quantity, internal energy, which we define through the first law, and we think of it as a function of two variables T and V . And whenever we say something like that, we'll be able to write a differential, the partial of u , with respect to T at constant V , dT , plus the partial of u with respect to V at constant T dV .

So, if we write something like this, it implies this kind of equation. And the main points of the latter part of the lecture is what are these quantities? How do we measure them? How do we understand them? This one turns out to be the heat capacity, and this one turns out to be something that we measure in the Joule-free expansion. So, that's the menu for today, at least that's what Mounji assigned me to cover, and I'll do the best I can.

So, let's talk about heat capacity. Heat capacity relates the amount of heat that you add to the system to the change in temperature, and this is the relationship. The heat-added, temperature, and this is a proportionality constant. Heat capacity depends on path. So, here are two kinds of experiments. Here we have a fixed volume, and we have a little candle, and we're adding heat, and when we add heat, the pressure does what?

STUDENT:

PROFESSOR: It increases and the temperature. OK, we're you know, this is MIT. You guys know something. You

should yell it out, not just whisper it. You have the confidence -- I mean maybe up the street we whisper, but here we know it. And, so here is a different kind of system where we have a constant external pressure. We add heat to the system. And so here the volume can change. The temperature can change. And so as we add heat here, the temperature goes up and the volume -- that was even quieter than last time. OK, but you know it. You understand it. Now, the coefficient that relates the amount of heat in to the temperature change is obviously going to be different for these two cases.

in this case, where we have a fixed volume, we say dq is equal that C_v , heat capacity dT , where the v specifies what's constant for the path. And so this is one path, constant volume. This has a particular value. Over here, we have $dq=C_p dT$, the heat, the proportionality between heat and temperature rise is given by this, the constant pressure heat capacity. They're different quantities. If we want to know the total heat added to the system, we can measure it, which is the straightforward thing, but sometimes you want to calculate in advance, or sometimes you want to calculate it on an exam. So, we do an integral over a path, for the heat capacity along that path, dT . So, for C_p and C_v , these are often quantities that are measured as a function of temperature, and one could, in fact, calculate this integral. For most problems on exams, those quantities are constant, independent of temperature. But there's no guarantee that they will be.

Now I get to tell a fun story. The relationship between heat and work was initially proposed in the 1840's by Joule. Now, there are two stories about Joule and how he came to this insight. One is that he observed when people were machining cannon barrels, a lot of heat was generated, and there was a lot of work done. And so maybe the work generated the heat. Or there was a relationship between work and heat. Well, this is ridiculous because people were making cannons long before 1840.

The other story, which is probably just as untrue, is that Joule, on his honeymoon, took his wife to a mountain resort, and they were sitting at the bottom of a waterfall, and he had this wonderful idea. And that was the water at the bottom of the waterfall is probably going to be hotter than the water at the top of the waterfall. So he grabbed his thermometer, and went and made a couple of measurements and discovered the first law of thermodynamics. In fact, the water at the bottom of the waterfall is hotter than the water at the top of the waterfall. And the idea was that gravity did work on the water and falling, and that work led to the generation of heat. If you think about this, you probably can come up with several other ideas for how the water at the bottom might be warmer than at the top. I mean it's flowing fast at the top, and it's sort of pooled at the bottom, and there is sunlight and all sorts of things that could make this coincidental as opposed to an insightful observation. But it's a good story,

Joule decided that there must be a direct relationship between work and heat. They are the same quantity. They are both forms of energy. And so, we have this cartoon. Again, we have an open beaker and a candle, and we're putting only heat into this beaker, and the temperature goes from T_1 to T_2 . And ΔT is given by the heat, which

has to do with how much of the candle burnt, divided by the constant pressure heat capacity.

Now you could do a similar sort of thing, but instead of having a candle, you have a paddle wheel, and the paddle wheel is spun by a weight that's dropping from here to here. So, this weight is being spun-- now I'm really fantastic at drawing this mechanical device, but you can imagine that dropping a weight can cause a paddle wheel to turn.

And we know about gravity, and we know about work. So, if you're doing physics, work is the integral of force, dx , x_1 to x_2 . Right, that's work. Now, gravity, well force, is equal to mass times acceleration, and the acceleration due to gravity is g . The force, as this weight drops is constant, and so the work is just going to be $m g h$, where this is h . So, it's a trivial matter, by looking at what is the weight, and how far does it drop, to say OK, how much work is done by the paddle wheel. And this is in an isolated, in an adiabatic container. All the energy that is inserted into this, which might be turbulence initially, becomes heat, or becomes -- it raises the temperature.

And so, again, we see a temperature increase, and we know the work, and the temperature increase, it's a constant pressure thing. And so we now have two observations. The same temperature increase, work and heat, and we have a relationship between heat and work. The first law of thermodynamics is -- I'm fine. I don't -- I'm all set, I only use this chalk. I brought it with me. The first law of thermodynamics, written concisely is dw plus dq , two inexact differentials, integrated over any closed path, is zero.

This is an abstract and powerful mathematical statement of the first law of thermodynamics. There are much better or more appealing expressions. One is, du , u is called the internal energy or just the energy, is equal to dq plus dw . OK, notice we have two inexact differentials and exact differentials. This is a condition. If you have a quantity which is constant over any closed path, that quantity is a thermodynamics state function. So, this observation is equivalent to saying that there must be something that is path independent. Therefore, we don't have a cross through the d . And the first law says, well heat and work are different forms of energy, and we can add them, and the path dependence of these two things is somehow cancelled in the fact that we have this internal energy.

So, we can also write Δu as integral from 1 to 2 of du . That's u_2 minus u_1 , and it's q plus w . So, these two quantities, again, are path dependent. This is not. That's the first law of thermodynamics. It seems trivial, but it's really important. It's almost as important as the second law of thermodynamics, which you'll see in a week or so.

There is a corollary to this. If we say we have a system, and it's in its surroundings. We can talk about du for the system well, that's q plus w . And we can say du for the surroundings. Well the system got its work from the surroundings. It either had work, got its heat from the surroundings, or it got worked on by the surroundings. And so, we can immediately write this and then we can write du for the universe, which is system plus surroundings is

equal to zero. This is the corollary. It's due to Clausius and it says the energy in the universe is conserved. Fairly powerful statement, and that's another form of the first law of thermodynamics.

OK, enough for really great discoveries. Now let's talk about some simple observations on isothermal gas expansions. The purpose here is to look at a series of processes in which temperature is held constant, and we're going to calculate how much work we get from allowing a gas to expand under various conditions. And what we'll discover is that when we allow the gas to expand reversibly, we get the most work. This is neat. This is important.

OK, so we have constant temperature, because it's isothermal. And let's do a series of experiments. First let's set the external pressure equal to zero. So we have an experiment that looks like this. We have a piston. We have a pair of stops. We have another pair of stops. We start at p_1, V_1 . and p_{external} is equal to zero. In other words, this is vacuum. And so what happens when we remove these stops is that the piston slams up against the next pair of stops. It goes very fast. You could calculate the time.

You could do all sorts of stuff, but what is important is that this piston in moving from here to here did no work on the surroundings because work is the integral of pressure dv , and the pressure external is zero. It doesn't matter what the pressure internal is. This is a point that is often confusing, because you can think, well maybe I could calculate what the internal pressure is even for this very rapid process. It doesn't matter. Thermodynamics is asking you, what work does this thing do on the surroundings or the surroundings do on the system? And there is no work done on the surroundings because pressure is zero. So, the work for this process is the integral, or minus the integral, $V_1, V_2, p dV$. And it's p_{external} and p_{external} is zero, so there's no work.

OK, the next example is, well, when this piston slams up against these stops, the gas has expanded -- we're doing this isothermally, so this is in contact with the heat bath. The gas has expanded. It has a particular pressure and a particular volume. Every time you do the experiment in equilibrium with the heat bath at T , you'll get the same p_2 and V_2 . One can know them. And so we can then say, OK, let's do this second expansion. and let's set p_{external} equal to p_2 . And we do the same sort of thing. We have stops here. We have p_1, V_1 . And we don't really need stops up here. We have a weight on the piston, and that weight is chosen so that it acts as though p_{external} is equal to p_2 . We know the pressure is equal to force per area. And so we know the force for a particular mass, and we know the area of the piston. so we know how to do this, and we know this thing when it hit these stops, the pressure with p_2 , and the volume was V_2 . Now we could put stops here at V_2 , but this piston would just kiss the stops. It would stop there because we've chosen p_2 . The work for that process is going to be minus V_1, V_2, p_2 , because that's what we chose p_{external} to be, dV , and that's going to be minus p_2, V_2 minus V_1 . That's the work. V_2 is larger than V_1 , and so this quantity here is positive, and we have a negative sign because the system did work.

OK, so now we can take the result from this and put it onto a p v diagram. p_1 , p_2 , V_1 , V_2 -- so here is the initial situation, and here is the final situation. And the equation of state, pressure versus volume at constant temperature, is going to have some form, let's just draw it in there like that. So that's an equation of state. It's like the ideal gas law, and one could know that in principle. OK, so we did work -- oh, I should mention p times V has units of energy or units of work. Remember that, because you're going to find lots of thermodynamics quantities, and you're often going to be writing on exams, deriving things on exams, and you're going to almost always want the combinations of quantities to have units of energy. So, dimensional analysis is extremely valuable in thermodynamics, and here is an example of it.

Anyway, the work associated with process number two is described by this box. Because we did work at constant pressure, and so it's just volume difference times pressure. OK, now we can do the process in two steps. So we start out with our piston. We have two weights on it. So we have p_1 , V_1 . We have stops. We've chosen two weights, so that this is p_3 . External pressure is p_3 . It's higher than p_2 . So we remove the stops, and the piston moves up, and now we remove one of these weights. and when we remove one of the weights, this gives an external pressure p_2 . So, the piston moves up again, one weight. So here is p_2 , p external. Here is p_3 . And so we have the work coming from two steps. And it's trivial to calculate what that will be, and when you do that, if we put p_3 in on this diagram, what you end up finding is that you get an initial little bit of work corresponding to V_3 . So we break up our work into three pieces, and we get more work out.

So the final process involves do it reversibly, or almost reversibly. We want p equal to p external for the entire expansion, and p external is decreased steadily from p_1 to p_2 . How do we do this? Well, we start out with our usual system, and we have a bunch of little pebbles on it. Each weighing, say, one 100th of the weight needed to establish p external is equal to p_1 . We remove a pebble, system expands. We remove another one, system expands. That's equivalent to doing the integral, and so, what we end up getting is that the reversible work is equal to minus integral V_1 , V_2 , p dV . Because what we've done is we forced p , pressure here, to be equal to the external pressure. We've changed the external pressure slowly, and again this is isothermal. There is a heat bath here that keeps the temperature constant.

So, the system does work on the surroundings, hence the minus sign. Now, if this is an ideal gas, we know that pressure is equal to nRT over volume. So we can put that in here and do this integral. We have minus V_1 , V_2 , nRT over V dV . These are all constant. It's isothermal. We can take them out. It's a closed system, so the number moles doesn't change. The ideal gas constant doesn't change, temperature doesn't change, and so we just have minus nRT integral V_1 , V_2 , dV over V . Now, we are very gentle in this course with respect to knowing integrals, but this is one you have to know. The integral of one over a quantity is the natural log. And so we can write this, minus nRT log V_2 over V_1 . That should not take a breath. You know that much about integrals.

OK, now we actually would like to simplify this or to write this in terms of not the volume change, but the pressure change. So, we have V_2 over V_1 . Well, what we can write that using the ideal gas law twice, V_2 is equal -- $pV = nRT$. So $V_2 = (nRT)/p_2$, and $V_1 = (nRT)/p_1$. So, the nRT 's cancel, and we have p_1 over p_2 . And so, we can rewrite this as the work is equal to minus $nRT \log p_1$ over p_2 , or $nRT \log p_2$ over p_1 . Now, p_2 is less than p_1 , so this is a negative quantity. The system has done work.

So the reversible process, we had this curve, and for the irreversible processes, we got this, and then this, whoops, and now we get the whole thing. So for the reversible process, the work done is the integral under the pressure volume state function, the function of state.

OK, what time is it? I'm going to actually get caught up, make up for but Bawendi's slow lecturing. That doesn't mean it's better, it just means that I'm making up for a problem that he created. OK, so what do we know so far? Maximum work out is by reversible path. Δu is q plus w . So the maximum work out required the maximum heat in. So a reversible process leads to requiring certain quantities to be maximized.

Now, we have u , q and w . We have a relationship between them. Often, for a particular state change, it is easy to calculate two of these, but not the third. And because there is an explicit relationship between u , Δu , q and w , you can always find the easy way to derive the change in internal energy or the heat or the work. Even if the thing that you really want is an integral that would be difficult to evaluate.

OK, now, we're going to look at the internal energy, and we're going to pretend that it is explicitly a function of temperature and volume. We could choose any two quantities, and, in fact, it turns out that these are going to prove, after we have the second law, not to be the best choice. But it's allowed to say the internal energy is a function of temperature and volume. When you say that, it implies that the differential is given by this pair of partial derivatives. $V dT$, partial of u with respect to the volume holding temperature constant, dV . So if you say this, it requires you to say this. Now, the purpose of this exercise is to give you a little bit of practice in figuring out what these quantities are. And do a little practice in manipulating these differentials.

So, we have, we're interested in the change in internal energy for various experimental constraints. And so, one constraint is the process be done reversibly. Well then, du is equal to dq reversible plus dw reversible, which is minus $p dV$, because p is equal to p external for a reversible process, and we can write that. We could have isolated. Suppose we're looking at the system isolated from the outside world. Well, dq is equal to zero and dw is equal to zero because it's isolated. So that implies du is equal to zero.

We could do an adiabatic process. Adiabatic means there's no heat transferred in or out of the system. We don't say anything about whether the system does work or has worked on -- implicitly here, we're talking about a closed system, so there's no mass leaving the system. But if it's adiabatic, then dq is equal zero, and for an adiabatic

process, then du is equal to dw .

OK, now this is a point we want to be careful. Be careful. Suppose we are doing an adiabatic process. We can do it reversibly, or we can do it irreversibly. So suppose we do it irreversibly. Suppose we just remove stops, and the system slams up against the other stops. Did no work. Does that mean du is zero? You bet it does not. So, it's important to write this little thing on here, du is equal to the reversible work, not just the work.

You can have a process where you can measure an irreversible process, where you could calculate the work done. It could be zero. It could be something else. But if it's not reversible, it's not du . And you will be invited to make that mistake on an exam, I'm sure.

OK, so, the thing about a state function is that the function has a value for initial conditions and at final conditions. And the difference between those is what you could measure. If you measure something else, you won't get du . Be careful, and this is going to be especially complicated and confusing when we get to quantities that have a more obscure meaning like entropy. I mean we can, we can sort of understand why OK, the total energy, if we measure it, we measure a process which is not reversible. Well it might not give the energy change for that process, but when we have a quantity which is more obscure, which the definition of that quantity requires a very specific prescription for calculating, you're going to get into trouble. So exam this and be sure you understand that.

OK, constant volume. Well for constant volume, dw is equal to zero. Why? How does it do, what is work? Well it's $p dv$ work if the volume doesn't change. There is no work. So in this case du is equal to dq , and we put a little v on it to imply the work, the change in internal energy is equal to the heat added at constant volume. Nothing reversible about it. It's now, all we have to do is say we're going to have heat at constant volume.

OK, and now we return to this differential. We want to ask the question, what are these two quantities? How do we know what they are? This should be particularly bothersome to you because, as you've already experienced in 5.60, there are a lot of partial derivatives. there are a lot of variables. There are a lot of things held constant. It's easy to get lost in this sea of quantities, none of which have obvious meaning. So now what we're going to do is start to extract what these things mean.

OK, so for a constant volume process, we can write du , partial derivative of u with respect to T at constant V , dT , plus partial derivative of u at constant V , dV . OK, for constant volume, this is zero. So this term is gone, and we rewrite this du , V is equal to du/dT , at constant V , dT v . So we, have a change in temperature done at constant volume, and we have a change in internal energy done at constant volume, and we rearrange this. And we discover that du/dT at constant V is equal to du/dT at constant V . What, have I done something silly? Oh well, yes

I have. dq_v , so du_v is equal to dq_v and so what I should have written here, this is true, we can get a partial derivative by taking two total derivatives at the same pressure, at the same quantity, but what I really wanted to do is to write dq_v is equal to the partial derivative of T , constant v dT_v . OK, and now, we know the relationship between heat and a temperature change is given by a quantity, a heat capacity for a particular path, and here it is. So what we've discovered from this relationship that du at constant volume is equal to dq_v . We have discovered that this partial derivative that appears in the definition, the abstract definition of the differential for internal energy, is just equal to the constant volume heat capacity. So, in this definition now, we have one term which we know. It's something that we can measure. We can measure the heat capacity at constant volume, and now we have another term, and if we can figure out how to measure it, we'll have a complete form for this differential which will enable us to calculate du for any process.

So let me write where I am now, or we are now. du is equal to $C_v dT$, plus partial of u with respect to volume at constant temperature dV . So, we've simplified the expression by replacing one of the partial derivatives by a quantity that we can measure. And we like to know what about this. So we need an experiment that will enable us to measure this quantity.

And that's where we get Joule, and I like to say it Joule's free expansion -- it's usually referred to as the Joule free expansion, which sort of implies that no energy flows, which actually is true, but it's an experiment proposed by Joule, and the experiment involves an adiabatic box. So we have system insulated from the outside world, and we have two bulbs. There's a valve between them. And so we have gas and we have vacuum. So the Joule free expansion involves opening this valve and asking what happens when this gas moves into the other bulb or distributes between the two. Well since the gas is expanding into vacuum no work is done. Since it's isolated, no heat is added. So du is equal to zero because dq and dw are both zero. So we can now take this expression and rewrite it under the condition of du is equal to zero. So we have du equal to zero, just a zero here. $C_v dT$ constant u plus the derivative du/dV at constant T , dV at constant u . This is just a number. We don't have to specify that it's measured at constant u . It's just a number. So now we rearrange this expression, and so we get du/dV at constant T is equal to minus C_v times dT_u over dV_u or minus C_v partial derivative of temperature with respect for volume a constant, free energy, a constant internal energy.

So, this is the quantity we want. It's related to the heat capacity, the constant volume of heat capacity and something you could measure. What happens as you expand into volume? Does the temperature go up? Does it not change? Joule actually did this experiment, and he observed that for the gas expansions that he could do, that the temperature did not increase measurably. So he made an incorrect conclusion.

Because something was small and unmeasurable, he said, well the best of my knowledge dT/dV at constant u is equal to zero. And that implies that since the quantity we want is given by this quantity, which is zero times a

constant, the quantity we want is also zero. So it would imply that du was equal to only the first term $C_v dT$.

Now, this is an important lesson in what you do in science. You make an observation. You make an observation doing an experiment that is as accurate as you can do. And so an experiment said the gas didn't increase its temperature when it expanded the vacuum. And so the next thing you do is you call up a journal and say I've discovered a fundamental law of nature. And, so you propose that there is no, that this derivative is zero, and that the internal energy is given simply by this quantity. It turns out that this quantity here, which is called η of J the Joule free expansion parameter, is not quite zero. When you expand a real gas into vacuum, the temperature goes down. So this is a very small number and for ideal gases, η J is equal to zero. This quantity is exactly zero for an ideal gas and we'll discover why eventually it has to do with what we mean by an ideal gas it turns out.

And so for many, many problems, especially on exams, especially on this first exam, you will be able to say that this is the relationship between internal energy and temperature. That u is a function of temperature only. It doesn't matter what other things change. The value of the internal energy is only determined by temperature. But this is only true for an ideal gas and it's approximately true for other things.

So, Δu is equal to zero for all isothermal ideal gas processes. And it's approximately equal to zero for all real gas processes. And so that means that Δu is always calculable from $C_v(T) dT$ for any ideal gas change. So even if work is done, it doesn't matter. All you care about is what was the temperature change? And this is always the easy way to calculate du , and it's often the easy way to calculate either q or w , using the first law. So, since du is equal to q plus w , and for an isothermal process this is equal to zero, $q = -w$. For an ideal gas, for an isothermal process. It simplifies your life enormously. You don't have to calculate much.

OK, so it's time to stop, I did, in fact, get caught up. I hope you didn't mind the enhanced velocity. Now Bawendi can do the beautiful stuff on lecture number four. Thank you.