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PROFESSOR BAWENDI: Last time you talked about the first law of thermodynamics. And you talked about isothermal expansion, the Joule expansion. You saw a very important result. which is that for an ideal gas, the energy content is only dependent on the temperature, nothing else. Not the volume, not the pressure, it just cares about the temperature. So, if you have an isothermal process for an ideal gas, the energy doesn't change.  $q$  plus  $w$  is equal to zero for any isothermal process. And you also saw that  $du$  then could be written as  $C_v dT$  for an ideal gas always. This is not generally true. If you have a real gas and you write  $du$  is  $C_v dT$ , and your path is not a constant volume path, then you are making a mistake. But for an ideal gas, you can always write this. And this turns out to be very useful to remember.

OK, now most processes that we deal with are not constant volume processes. So energy, which has this wonderful property here,  $du$  is  $C_v dt$  for constant volume process, which happens to be equal to  $dq$ , constant volume, because there's no change. there's no work if you've got a constant volume process. So  $du$  here is a very interesting quantity, because it's related to the heat that's going in or out of the system under constant volume process. But as I said, we're not operating usually in a constant volume environment. When I flail my arms around I generate work and heat. This is not a constant volume process. If I'm the system, what's constant when I do this? Anybody have an idea? What's the one function of state? I'm the system, the rest are the surrounding. What's the one function of state that's constant when I'm doing all my chemical reactions to move my arms around? Temperature?

STUDENT: Pressure?

PROFESSOR BAWENDI: Pressure, right. Pressure is constant. What is the pressure at? One atmosphere, one bar. So the most interesting processes are the processes where pressure is constant. When I had have a vial on bench top, and I do a chemical reaction in the vial, and it's open to the atmosphere, the pressure is constant at one atmosphere. When you've got your cells growing in your petri dish, the pressure is constant at one atmosphere, even if they're evolving gas, pressure is constant.

So we'd really like to be able to find some sort of equation of state, or some sort of rather function of state that's going to relate the heat going in or out of the system with that function of state, because this isn't going to do it.  $du$  only relates to the heat under constant volume. And the heat is a really important thing to know. How much heat do you need to put into a system, or how much heat is going to come out of a system when something is

happening in the system? All right, this is a really important quantity to know. Your boiling water or whatever, you want to know how much heat do you need to boil that amount of water under constant pressure?

And this is where enthalpy comes in. You've all heard of enthalpy.  $H$  we're going to write it as the function of temperature and pressure. And the reason enthalpy was invented was exactly for that reason, because we need some way to figure out how to relate the heat coming in or out of a system under a constant pressure process. Because it's so important. And I should add and also under reversible work, where the external pressure is equal to the internal pressure.

OK, so we're going to define enthalpy as  $u + pV$ , these are all functions of state here, So  $H$  is a function of state, and we're going to see now how this is, indeed, related to the heat flow in and out of the system. If you have a constant pressure, reversible work process. Let's take a system. Under constant pressure  $T_1, V_1$ , going to a second -- this is the system, so let me write the system here. And it's more dramatic if the system is a gas,  $p, T_2, V_2$ , And let's look at what happens to these functions of state, to  $H$  to  $u$  under this transformation.

OK, so let's look at  $\Delta u$ .  $\Delta u$  is  $q$  plus  $w$ . That's the first law. And this is a constant pressure path, so now I can write, this  $q$  is actually  $q$  under constant pressure. Little  $p$  means the path is a constant pressure path. And I'm doing reversible work. So that  $w$  is minus  $p, dV$  where  $p$  is the pressure inside the system, minus  $p \Delta V$ . Rearrange that,  $\Delta u$  is plus  $p \Delta V$  is equal to  $q_p$ .

All right, so this is the heat flowing in or out of the system, and these are all functions of state. This depends on the path. It tells you right here, the path is constant pressure. These don't depend on the path, right.  $V$  doesn't care how you get there.  $u$  doesn't care how you get there. In this case,  $p$  is a constant because the path is constant. So we can bring the  $p$  inside,  $\Delta u$  plus  $\Delta p V$  it's  $q_p$ . Take this  $\Delta$  outside again,  $\Delta$  of  $u$  plus  $p V$  is equal to  $q_p$ . And there you have it. There is the  $H$  right there. The  $u$  plus  $p V$ .  $\Delta H$  is equal to  $q_p$ .

And this is the reason why enthalpy was invented, and why it's so important. Because we want to know this. So this for a finite change. If you want to have an infinitesimally small change, you end up writing  $dh$  is  $dq_{sub p}$ . It's not always equal to the heat. It's only equal to the heat if your process is constant pressure reversible work.

OK, so this is the kind of, this is the kind of concept that needs to be branded into your brain, so that if I come into your bedroom in the middle of the night and I whisper to you  $\Delta H$ , you know, you should wake up and say  $q_p$ , right? Heat under constant pressure reversible work. This should become second nature. This is where the intuition comes from. This is why people right tables and tables of  $\Delta H$ 's. Why you have  $\Delta H$ 's from all these reactions, because this is basically the heat, and the heat is something we can measure, we can control. We can figure out how much heat is going in and out of something. This is what we're interested in.

OK, so last time you looked at -- any questions on this first? Yes.

STUDENT: [INAUDIBLE] from the  $T \Delta V$  to the  $\Delta p$  here? What was the reasoning behind that?

PROFESSOR BAWENDI:  $p$  is constant here. It's constant pressure. OK, so now, last time you looked at the Joule expansion to teach you how to relate derivatives like  $du/dV$ .  $du/dV$  under constant temperature.  $du/dT$  under constant volume. You use the Joule expansion to find these quantities. Now these quantities were useful because you could relate them. The slope of changes, with respect to volume or temperature of the energy with respect to quantities that you understood, that you could measure. We're going to do the same thing here.

So if we take as our natural variables for enthalpy to be temperature and pressure, and we have some sort of change in enthalpy,  $dH$ , and it's going to be related to changes in temperature and pressure through the derivatives  $dH$  through the slope of the enthalpy in the  $T$  direction, keeping pressure constant,  $dT$  plus the slope of enthalpy in the pressure direction, keeping the temperature constant,  $dp$ , and these are knobs that we can turn.

We can change of temperature. We can change the pressure. These are physical knobs that are available to us as experimentalists. And so when we turn these knobs on our system, we want to know how the enthalpy is changing for that system. Because eventually they will tell us maybe things about how heat is changing further on. OK, but in order to relate turning these physical knob to this quantity here, which we don't have a very good feel for, we've got to have a feel for the slopes. If I keep the pressure constant. I change the temperature, what does that mean? What is  $dh/dT$ ? If I keep the temperature constant, and just change the pressure,  $dH$  is going to change, but how is it going to change? What does this mean in terms of something I can physically understand?

That's the program now for the next few minutes. What are these quantities? What is  $dH/dT$  as a function, keeping pressure constant, what is  $dH/dp$ , keeping temperature constant? All right, let's start with the first one,  $dH/dT$ , keeping the pressure constant. And we're going to look at a reversible process to help us out, but the result is going to be independent of whether or not we have a reversible process or irreversible process. Constant pressure, that means  $dp$  is equal to zero.

So for reversible process, constant pressure, what do we know? This is already branded in your brain, right? Reversible process, constant pressure  $dH=dq$ . So we can write that down,  $dH=dq$ , constant pressure. That's by definition of enthalpy. That's why we created enthalpy. What else do we know? Well we can go look up here, looking at the differential, there are no approximations here. This is just an equality. I have a constant pressure process. This term here is equal to zero. That means that  $dH$  is also equal to  $dH/dT$ , constant pressure  $dT$ . All right, so now I've got more  $dH/dT$  under constant pressure.  $dH$  is equal to this, and it's also equal to this. All right, these two are equal to each other. Now, I know how to relate the heat flow to temperature change, through the heat capacity.  $dq$  constant pressure is that heat capacity, and I have to tell you the path for the heat capacity. So

it's  $C_{p}$ , the heat capacity under a constant pressure path,  $dT$ , all right? So these two are equal to each other. So, these two are equal to each other as well, which tells me that this derivative,  $dH/dT$  constant pressure is  $C_p$ .

So now I have my first of my two slopes, in terms of something that's related to my system, the heat capacity of the system. Something I can measure and I can tabulate, and when I turn my  $dT$  knob here I know what's going to happen to the enthalpy. So this is the first, this is the one. So it's very similar to what we saw with the volume and the energy, where  $du/dV$  under constant temperature was equal to  $C_v$  in this case here, right. and you're going to find that there's a lot of these analogies between energy and enthalpy.

You just change volume to pressure and basically you're looking at enthalpy under a constant -- anything that's done at a constant volume path with energy, there's the same thing happening under constant pressure path for enthalpy. So you can guess the answer usually that way.

OK, so now we have the other one,  $dH/dp$  constant temperature. How do we relate this to something physical? Well, it's going to be an experiment, very much like the Joule experiment. The Joule experiment was a constant energy experiment, right. Here we're going to have to find a constant enthalpy experiment, and that is going to be the Joule-Thomson experiment. That's going to extract out a physical meaning to this derivative here.

OK, the Joule-Thomson experiment. This is going to get us  $dH/dp$  constant temperature. What is this experiment? You take a throttle valve, which consists of some sort of porous plug between two cylinders that is insulated. There is insulation here. Insulation on the bottom. It's like a, think about a tube, a large tube, insulated tube, with a bunch of -- a frit inside here, which prevents flow of gas, which slows down the flow of gas from one side to the other. It's a blockage in this tube here.

Then you put two pistons, one on that side here, and one on this side here, and the external pressure here, we're going to call that  $p_1$ . The external pressure here, we're going to call that  $p_2$ , and we're going to do it slowly enough that the pressure on this side of the cylinder is in equilibrium with the external pressure, and the pressure on this side of the cylinder is in equilibrium with this pressure. But not so slowly that these two are in equilibrium with each other. So this is restricting the flow, so there's some sweet spot here. When I'm pushing slowly enough here that the pressure here is equal to that one, but not so slowly that the air flow from here to here is fast, compared to how fast I'm pushing. You got the picture here? Any questions on that?

All right, then as I push through, I'm going to start with all of my gas on this side, and at the end, I'm going to have all the gas on the other side. Let me first ask you this, is this a reversible or in irreversible process? Right, let me add one more piece of data here which I said in words, but which is actually important to write down before doing the problem. Is this a reverse -- any guesses?

How many people vote for that this is a reversible process? I've got one vote back there, two votes, three votes, four votes. Anybody else? How many people think this is irreversible? It's about a tie, and everybody else doesn't now. All right, I'm going to give you ten seconds, fifteen seconds to make up your mind. You're not allowed to be on the fence here. You've got to decide, all right? This is, you can talk to your neighbors, you know, do a little bit of thinking. And I'm going to give you ten seconds to figure this out, what your vote is for that.

All right, let's try again. How many people vote that this is reversible? That looks like a majority to me. Irreversible? Let's look at the show of hands? All right, so this is the majority here. Good thing physics doesn't work on the rule of the majority, otherwise we'd be in big trouble. Wow, let's walk through that.

I'm sorry to say that this is the wrong answer. OK, why is that the wrong answer? Well, just think, you know, think about it. You're pushing through here.  $p_1$  is greater than  $p_2$ . What does it mean for a process to be in equilibrium or reversible? It means at any point you can reverse the direction of time, and it will look fine, right. So now I'm pushing on this plug here, with  $p_1$  greater than  $p_2$ . I'm pushing, I'm pushing, I'm pushing.  $p_1$  is greater than  $p_2$ . Then I want to reverse direction of time. I want the arrow of time to go so that the gas goes from  $p_2$  to  $p_1$ .  $p_2$  is less than  $p_1$ . Is that going to work out? If  $p_2$ , the pressure in  $p_2$ , is less than the pressure in  $p_1$ , is the gas going to want to go from  $p_2$  to  $p_1$  and the whole thing reverse back?

You've got to put more pressure on one side than the other if you want to push that gas through the throttle, right? So this is where the time scale issue comes into play. I said let's do this slowly enough that this  $p_1$  is in equilibrium with this  $p_1$ , but not so slowly that this pressure is equivalent to that pressure. If I do it really, really slowly, so that everything is reversible, well I won't be able to do it, because  $p_1$  and  $p_2$  are different. But suppose that I fix my pistons here, with  $p_1$  greater than  $p_2$ , and I don't touch it, eventually  $p_1$  will be equal to  $p_2$ . I'll come to some sort of equilibrium. So this is a system which is out of equilibrium. If I stop, if I move slowly, if I move more slowly, then these two will want equilibrium. So this is an irreversible process. The Joule-Thomson experiment is irreversible.

OK, important -- if you are part of this group here, think about it and make sure you understand that. All right, so this is the experiment. Now what are we doing with that? The initial state, let's look at what we are doing.

So initially, we're going to have our piston, there's the plug sitting here. Our piston on the right side here fully out, and the piston on my right side, your left side, fully inside. There's no gas on that side here. So there's  $p_2$  sitting here. There is  $p_1$  sitting here, and all of the gas is sitting on that side of the plug. Then after we're done with the experiment, we'll have transferred all of the gas from one side to the other.  $p_1$  here.  $p_2$  sitting here. And there's going to be some volume  $V_2$  and some volume  $V_1$ , but are not necessarily the same. Especially since the pressures are different. we don't know yet about temperature so I don't know what to say about these volumes because I don't know what the temperatures' are going to do.

OK, so let's go through this and see what we would do which is to calculate the heat and the work. This is well insulated. So, what is the -- let's do the first one here. What's  $q$  for this process here? Anybody?

STUDENT Zero.

PROFESSOR BAWENDI: Zero, right. This is an adiabatic process. It's well insulated. Heat is not going in or out, adiabatic.  $q$  is equal to zero. So all we need to find out is the work now. Let's divide it up into the two sides, the work going on on the left hand side, my left hand side or your left hand side, and the work going on on the right hand side. So let's first look at the left hand side.

OK, so  $w$ , first of all, work is being done to the system on the left hand side here. I'm pressing on the gas. So I expect that to be a positive number. The pressure is constant,  $p$ . The  $V$  goes from  $V_1$  to zero. So we write down  $p_1$ ,  $V_1$ . On the right hand side, the work, let's call this left hand side, let's call this right hand side.

Here there's an expansion going on, so the system is doing work to the external world. This piston is being brought out, so we expect the work to be negative, negative. And we start out with zero volume. We end up with a volume of  $V_2$ , and the external pressure is constant to  $p_2$ . Minus  $p_2$ ,  $V_2$ . Minus  $p$  delta  $V$ . So the total work is the work from the left hand side plus the work on the right hand side, which is  $p_1 V_1$  minus  $p_2 V_2$ . Which I can rewrite as minus delta  $pV$ . Delta  $pV$  is  $p_2 V_2$  minus  $p_1 V_1$ . It's the pressure volume multiplied together at the final state, minus pressure volume from the initial state, with the minus sign here because it's the negative of that.

All right, what is delta  $u$ ? delta  $u$  is  $q$  plus  $w$ .  $q$  is zero. delta  $u$  is just  $w$ . So this is also just delta  $u$ . delta  $u$  is minus delta  $pV$ , for the process. OK, delta  $H$  is delta of  $u$  plus  $pV$ . By definition, that's how we define enthalpy up here.  $H$  is  $u$  plus  $pV$ . Delta  $H$  is delta of  $u$  plus  $pV$ , which is equal to delta  $u$ , plus delta  $pV$ .

Now delta  $u$  is minus delta  $pV$ . So I have minus delta  $pV$  plus delta  $pV$ . This is equal to zero. So this irreversible process, this Joule-Thomson process, is a constant enthalpy process. Delta  $h$  for this process is equal to zero. Adiabatic  $q$  equal to zero. It's also delta  $H$  which is zero. The two didn't necessarily follow, because remember, delta  $H$  is  $dq$  so  $p$  is only true for a reversible constant pressure process. This is an irreversible process.

So a priori, this was not necessarily true. It turns out after you do all the math, it turns out to be delta  $H$  equals zero. All right, so this is the experiment. How do we go from that experiment to the terms that we're trying to get, these slopes. Remember, we're trying to get delta  $H$ , we're trying to get  $dH/dT$  constant pressure and  $dH/dp$  constant temperature. OK, these are the two things were trying to get here.

OK, so let's write down, what we know here. I'm missing something. Oh, we already know one thing. We already know this guy here. We already did that. OK,  $dH/dT$  constant pressure is  $C_p$ . That was easy one. So we already

know that. So now we can write our differential  $dH$  as  $C_p dT$  plus  $dH/dp$ , constant temperature,  $dp$ .

Now we want to find out what this guy is here. Now for this experiment, this is a constant enthalpy experiment for the Joule-Thomson experiment, this is equal to zero. So I can rearrange this to get this  $dH/dp$  in terms of things that I can either measure, like the heat capacity, or that I have control of, like  $dT$  and  $dp$ . So in this case,  $dH/dp$  constant temperature is minus  $C_p dT/dp$ , and this is under constant temperature, no, not constant temperature. Whatever the experi -- for that the experiment is.

For that experiment, the constraint, so we need a constraint here, right, we need a constraint here. Right? We need a constraint here. The constraint isn't constant temperature because the temperature is going to be changing. It's not constant pressure, because we have a  $\Delta p$  going on. It's not constant volume either. The constraint is the constraint of the experiment, and the constraint of the experiment is that the enthalpy is constant. So the constraints we have here, is the constant enthalpy. It's the constant enthalpy process that we're looking at. This we can do experiments on. It's tabulated in books, and this we can measure in the experiment.  $\Delta p$  here is the change in pressure from the left side to the right side, and we can put a thermometer, measure the temperature before the experiment, and measure the temperature after the experiment.

So this is something we can measure. So now we have this derivative, in terms of physical quantities, things that we can measure. Things that we can relate to the properties of the substance that we're doing the experiment on.

So this is basically  $\Delta T$  and  $\Delta p$  and the Joule-Thomson experiment. And so Joule and Thomson did these experiments, and they measured lots of gases, and they found that, in fact, this was something that they could measure. Sometimes it was positive, sometimes it was negative, and it was an interesting number. And so they defined them, after many experiments, the limit of this,  $\Delta T / \Delta p$  and the limit of  $\Delta p$  goes to zero as the Joule-Thomson coefficient. So, basically  $dT/dp$ , constant enthalpy is equal to  $\mu$ , by definition, Joule-Thomson, where  $\mu$  Joule-Thomson is the Joule-Thomson coefficient, just like you saw last time  $\eta_{sub j}$  was the Joule coefficient for  $dT/dV$  under constant energy.

So there's, again, total analogy here between what we're doing with enthalpy to what you did last time with energy, replace  $p$  with  $T$  and  $H$  with  $u$ . Flip those two and you get the same thing. OK, so now we have  $dH/dT$  is equal to  $C_p$ , and we can also write, then,  $dH/dp$  under constant temperature is equal to minus  $C_p \mu$  Joule-Thomson. We have our two derivatives in terms of physical quantities, which is going to allow us, then, whenever we have a change to go back and, when we have a change where we adjust the temperature and the pressure, we'll be able to know what the enthalpy change is.

OK, now let's take two cases. Let's first start talking about ideal gases. The last time you saw that for an ideal gas, the energy only cared about the temperature. It didn't care what the volume was doing.  $du/dV$  under constant

temperature was equal to zero for an ideal gas. And by analogy, we expect the same thing to be true here, because enthalpy and energy have all this analogy going on here. So let's look at an ideal gas. So for an ideal gas, we saw that  $u$  was only a function of temperature.

We also have the equation of state for an ideal gas,  $pV = nRT$ . We can write our definition of enthalpy,  $h$  is  $u$  plus  $pV$ . This only depends on the temperature.  $pV = nRT$ . So we have  $u$  only depends on temperature plus  $nRT$ . The only valuable now on this side is temperature. Pressure and volume have dropped out. So enthalpy, for an ideal gas, only cares about temperature. Pressure has dropped out of the picture completely here. So there is no  $p$  dependence here.  $H$  for an ideal gas is only a function of temperature. This is not true for a real gas, fortunately, but it's true for an ideal gas.

So for an ideal gas then,  $dH/dp$  under constant temperature, that has to be equal to zero. Because temperature is constant  $H$  only cares about temperature. and that's equal to zero. And if that's equal to zero, that means that the Joule-Thomson coefficient for an ideal gas is also equal to zero.

We're going to actually prove this later in the course. Right now, you're taking it for granted. Right now we told you Joule did all these experiments and he found out that for an ideal gas, that the limit in an ideal gas case was that the  $\eta_J$  was equal to zero. Therefore, from experiments,  $u$  is only a function of temperature for an ideal gas, and therefore from these experiments, we come out with  $\Delta H$   $dH/dp$  is equal to zero. The Joule-Thomson coefficient is equal to zero.

Later we are going to prove it exactly. but right now you're going to have to take it for granted. So, if the Joule-Thomson coefficient is equal to zero, just like we wrote,  $du = C_v dT$  for an ideal gas, we're going to have  $dH = C_p dT$  for an ideal gas as well.  $dH$  is  $C_p dT$ . This term goes away.  $dH = C_p dT$ . That's the only thing that's left behind.

So if you know the heat capacity, you know the change in temperature, you know what enthalpy is doing for an ideal gas. This needs to be stressed that this is the ideal gas case. Now regular gases, real gases, fortunately as I said, don't obey this. This is important because we use this all the time for when, when we do technology.

One example of Joule-Thomson coefficient being not equal to zero for a real gas that you've like experienced is if you take a bicycle pump, take a bicycle pump, and you're pumping up your tire, you're working pretty hard, so you're getting hot. But if you touch the valve going into your tire, which basically measures the temperature of the air going into your tire, that is getting hot, right.

So if you've got to pump that tire really a lot, then you're going to you're going to really feel a lot of heat there. The compression of the, basically it's an adiabatic compression. You're taking the air inside of the pump and you're compressing it. You're doing it so fast that there's not enough time for heat to come out of the gas that's inside the



pump towards the walls of the pump.

So your time scale it just fast enough that this is basically an adiabatic compression. You're compressing it really fast, all right, so you're changing the pressure. You're changing the pressure, and the temperature is going up.  $dT/dp$  is positive.  $dT/dp$  is positive.  $dT/dp$  is positive, well that's  $\mu_{JT}$ .  $dT/dp$  is  $\mu_{JT}$ . So for a real gas like air, this is a positive number. It's not zero. Air is not an ideal gas. It's one simple example of -- The fact that  $\mu_{JT}$  is not zero for real gases is how we are able to liquify things like hydrogen and helium, by compressing them and pushing them through a nozzle, and the expansion through the nozzle cools the gas. Right, in this case here it wouldn't happen if it was an ideal gas.

Or in many kinds of gas refrigerators where you push a gas through a nozzle close to room temperature, what you find is that the gas coming out on the other side under lower pressure is cooler than the gas that went through on the other side. Real refrigerators actually work with liquids that go into gases so use the latent heat of the liquid, so it doesn't really work like the Joule-Thomson expansion. So this is real. This is real, unlike the Joule coefficient which is very small so that most gases have tiny Joule coefficients. So if you do a Joule experiment, you hardly measure a temperature change. With real gases, here you do actually measure it. You can feel it with your finger on your bicycle tire.

OK, so we're going to see this using a Van der Waal's gas. Let's look at a Van der Waal's gas and see what happens in the Van der Waal's gas. Any questions, first? What we've been talking about, the Joule-Thomson experiment, constant enthalpy process?

OK, so let's take our Van der Waal's gas. Remember the equation of state for Van der Waal's gas is not  $pV$  is equal to  $nRT$ , but  $p$  plus the attraction term. And then  $V$  minus the excluded volume term is equal to  $RT$ . Two parameters, this is the attraction between two atoms or molecules in the gas phase. This is the repulsion, not the repulsion. This is the fact that we occupy a finite volume in space, because they're little hard spheres in this molecule.

OK, in a few weeks, you're going to find out that we can calculate  $dH/dp$  from this equation of state, and you're going to find out that  $dH/dp$  from that equation of state is proportional to  $b$  minus  $a$  over  $RT$ . This is going to be probably a homework at some point to do this. For now, let's take it for granted. Let's take it for granted that we know how to calculate this derivative from an equation of state like this. But now we're going to use that. OK. So since  $dH/dp$  under constant temperature is proportional to minus  $\mu_{JT}$ , then we have that  $dT/dp$  under constant enthalpy than it is related to the negative of this,  $a$  over  $RT$  minus  $b$

All right, this is how the temperature changes when you change, when you have pressure changing. So when you do an expansion or compression, my adiabatic compression of my bicycle pump is  $dT/dp$ . All right. Or when I do

an expansion of hydrogen or helium at low temperature, through a Joule-Thomson experiment, when I want to liquify hydrogen or helium. I want to cool a gas with a Joule-Thomson experiment, what temperature do I have to be at?

So this tells you that you have to be careful what temperature you're at, because depending on how high, how big this temperature here is, you could either be, have a negative  $dT/dp$ , if this first term is small enough, meaning if temperature is very high, then you end up with a negative term. If the temperature is very small, then one over the temperature is large, and the first term wins and you have a positive number.

So there's some special temperature which is going to depend on the gas where the first term is going to be equal to the second term, where Joule-Thomson is zero, or it's going to behave like an ideal gas. So when that is the case, we're going to call that temperature the inversion temperature or  $T_{inv}$ . We call that inversion because on one side you end up cooling if you compress. And on the other side of that temperature you end up heating if you compress.

OK, so there's some temperature,  $T_{inv}$  minus  $b$  where the gas behaves like an ideal gas. The Joule-Thomson coefficient is zero and that inversion temperature, you can solve for it. Inversion temperature is equal to  $a$  over  $R$  times  $b$ . OK, so when you are at that temperature, everything looks like an ideal gas, as far as the enthalpy changes are concerned. Now if you're at the temperature which is higher than the inversion temperature, in that case here,  $a$  over  $RT$  is small compared to  $b$ , and this is going to turn out to be negative. So if you had a high temperature, this  $a$  is small compared to  $b$ . If you're negative, which means that  $dT/dp$  at constant  $H$  is less than zero.

So that means that if you compress something it's going to cool. The temperature rises when the pressure drops, right? Or in this case here, if I do my Joule experiment  $\Delta p$  is negative,  $p_2$  is less than  $p_1$ , that means that  $\Delta T$  is positive, right? So in this experiment here, this side is going to heat up. So for materials where  $T_{inv}$  is low, lower than room temperature, then you would end up heating up in this expansion. You're basically expanding the gas from one side to the other and the expansion causes the temperature to rise.

If  $T$  is less than  $T_{inv}$ , you have the opposite case, and  $dT/dp$  is greater than zero. So in this experiment here,  $\Delta p$  is less than zero. You need to have this whole thing greater than zero. So  $\Delta T$  is less than zero as well. So if you're below the inversion temperature and you do the Joule-Thomson experiment, you're going to end up with something that's colder on this side than that side. Ideal gas would be the same temperature.

But now, so this is where the refrigeration comes in. So if you take a gas, and you're below the inversion temperature and you make it go through this irreversible process, the gas comes out colder from that side than that side. So the work that you're doing to expand, to go through this experiment, ends up cooling the gas.

OK, for most gases, T inversion is much greater than 300 degrees Kelvin. Much greater than room temperature. For most gases, if you do this experiment at room temperature, you end up cooling the gas, and you can cool it measurably, which is why also, your bicycle pump, you know, you push down, you compress, this is an expansion here. You're expanding from this side to that side. Bicycle pump you are compressing the gas, which is the opposite, you end up heating up the air in the bicycle pump in your compression.

There are two exceptions to this rule that most gases have a T inversion which is greater than 300 degrees Kelvin, and that's hydrogen. The T inversion for hydrogen turns out to be 193 degrees Kelvin, and the T inversion for helium turns out to be 53 degrees Kelvin.

And so when, there's a lot of liquid helium that's being used on campus. We use a liquid helium. And so in order to make a liquid helium, you can't take helium at room temperature and do this, because if you did, you would just heat it up, because the room temperature is above the inversion temperature, so Joule-Thomson would heat up the helium. So you need first to take the liquid helium and cool it below 53 degrees Kelvin before you can do the Joule-Thomson to cool it even further to make liquid helium.

So you have to do it in stages. You take your room temperature liquid helium, and you cool it with liquid nitrogen to 77 degrees Kelvin, the new, you're not quite there yet, unfortunately right? Then you take hydrogen you cool it would liquid nitrogen to 77, then you can use your hydrogen gas. Do a Joule-Thomson hydrogen gas which you first cool with liquid nitrogen. Liquid nitrogen, 77, that's below 193, so you can do Joule-Thomson on hydrogen, cool the hydrogen to below 53, then use your cold hydrogen to cool the helium, and then you can do the Joule-Thomson on the helium to cool it further until it liquifies.

So that's what you do when you make liquid helium. All right, any questions on this lecture or any of the concepts that we talked about? The last thing that we're going to do today then is to look at a relationship which is going to turn out to be very useful. It's a relationship for ideal gases which relates the heat capacities at constant pressure and constant volume.

$C_p = C_v + R$ . This is very useful because often you just have lots of tables of  $C_p$ 's but sometimes you want to know what the energy change is going to be for the ideal gas, and you know that  $du$  is  $C_v dT$  not  $C_p dT$ . So, you need to know what  $C_v$  is, and if this is true always, then there's a very easy way to go from one to the other.

We're going to do it two ways. Today we'll do the first way, and then next time we'll do the second way. The first way is just to turn the crank on the math, and the second way is to do a little bit more imaginative about the process.

OK, let's just turn the crank on the maths. What do we know about the  $C_p$  and  $C_v$ ? Well  $C_p$ , we already know how to relate it to  $dH/dT$  through the slope of the enthalpy, and we also related  $C_v$  to the slope of the energy with respect to temperature under constant volume. And we also know that  $H$  is  $u$  plus  $pV$ . Right,  $H$  is  $u$  plus  $pV$ . So we're going to take the derivatives of both sides of this equation here, by, with respect to temperature, keeping pressure constant. So we have  $dH/dT$  keeping pressure constant, is  $du/dT$  keeping pressure constant.

Got to keep track of what's being constant, kept constant, plus  $d(pV)/dT$ , keeping pressure constant.  $dH/dT$  keeping pressure constant, that's just  $C_p$ , and then we have  $du/dT$  keeping pressure constant. The  $p$  is constant here, comes out of the equation, so we have  $p$  and then we have  $dV/dT$  well it's an ideal gas, an ideal gas for  $dV/dT$  for an ideal gas is equal to  $R$  over  $p$  because  $pV$  is equal to  $RT$ , right. So  $dV/dT$  is  $R/p$ . So  $dV/dT$  is times  $R$  over  $p$ , the  $p$ 's are going to cancel out here.

OK, so now it's very tempting at this state to say, oh there's the answer right here.  $du/dT$  is  $C_v$ . There I have it  $C_p$  is equal to  $C_v$  plus  $R$ , right? But even though it looks like that's the right way to do it, it's actually not right because it turns out to be right by sort of by accident. But here you've got pressure constant.  $du$ , this is  $du$ , not  $H$  here.  $du/dT$  is only equal to  $C_v$  when the volume is constant, not when the pressure is constant.

So if you're going to turn the crank on the math correctly, you're going to have to change this  $p$  into a  $V$  somehow. Because this isn't  $C_v$  mathematically speaking. We don't know what it is yet. In order to change this from a  $p$  to a  $V$ , you have to use the chain rule. So let's use the chain rule. And then we'll be done. OK, so  $u$  is actually a function of temperature and volume, which in this case here could be a function of pressure and temperature. So if we want  $du/dT$  under constant pressure, you have to use the chain rule. There's the pressure sitting right here. It's going to be  $du/dT$  under constant volume, plus  $du/dV dV/dT$  under constant pressure. All right, chain rule.  $du/dT$  constant pressure is the direct derivative with respect to temperature here, which is sitting by itself under constant volume, keeping this constant but there is temperature sitting right here too. That's where that term comes from,  $du/dV dV/dT$ .

Now, for an ideal gas,  $du/dV$  under constant temperature is equal to zero. It doesn't care what the volume is doing. It only cares what temperature is. If temperature is constant, there's no change in energy. For an ideal gas, this is zero. It's not zero for a real gas. Right, so this whole term disappears and for an ideal gas, it turns out that  $du/dT$  constant pressure is equal to  $du/dT$  constant volume, but this is equal to  $C_v$  for an ideal gas. It wouldn't be true for a real gas, and this is a common mistake that people make for real gases to equate this. This is only true for an ideal gas. Since it's true for an ideal gas, then we can go ahead and replace this with  $C_v$ , and then we have  $C_p$  with  $C_v$  plus  $R$ , which is what we were after. OK, next time we'll do the other way of getting to the same answer.