Chemical Principles II.
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Module 3
Lecture 16
Joule-Thomson effect (For Ideal Gases).

So, welcome to the next module. So we have learned till now how to calculate work in constant temperature. And today we are going to understand that how an expansion, free expansion, whether it will lead to decrease in temperature or not. Because remember we discuss that in the free expansion case, the work that is 0. But whether the temperature will decrease or not, that is what we are going to see today. And there was a famous experiment by Joule, who devised an experiment in to understand whether the free expansion will lead to a change in temperature or not and followed by another one called Joule Thomson effect.

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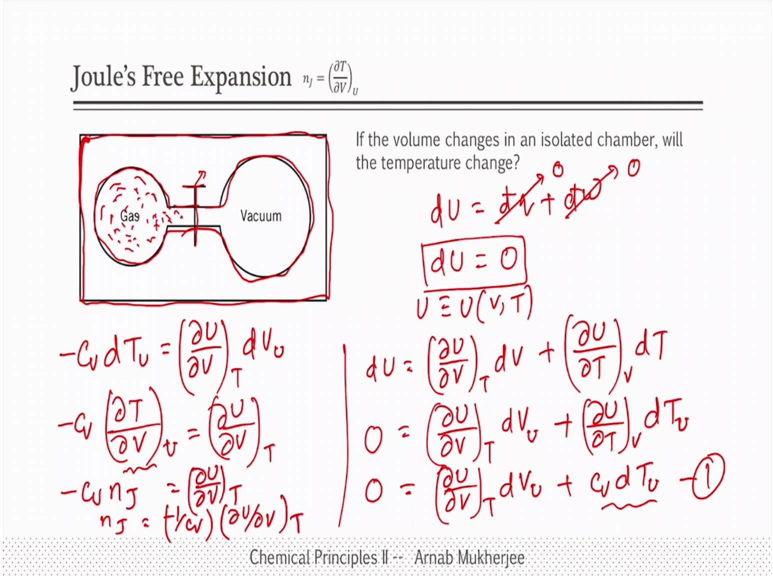

Joule's Free Expansion $n_J = \left(\frac{\partial T}{\partial V}\right)_U$

If the volume changes in an isolated chamber, will the temperature change?

$$dU = \cancelto{0}{đq} + \cancelto{0}{đw}$$

$$\boxed{dU = 0}$$

$$U \equiv U(V,T)$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$0 = \left(\frac{\partial U}{\partial V}\right)_T dV_U + \left(\frac{\partial U}{\partial T}\right)_V dT_U$$

$$0 = \left(\frac{\partial U}{\partial V}\right)_T dV_U + C_v\, dT_U \quad ①$$

$$-C_v\, dT_U = \left(\frac{\partial U}{\partial V}\right)_T dV_U$$

$$-C_v \left(\frac{\partial T}{\partial V}\right)_U = \left(\frac{\partial U}{\partial V}\right)_T$$

$$-C_v n_J = \left(\frac{\partial U}{\partial V}\right)_T$$

$$n_J = (-1/C_v)(\partial U/\partial V)_T$$

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So first today we are going to talk about Joule's free expansion process. So, the free expansion process is designed in such a way that in, there are 2 chambers in isolated system, so this is an isolated system, which means that total energy will be conserved or an isolated system will not allow any heat exchange to go in or out. So there will be no exchange of heat and initially the gas molecules are confined to one side of the chamber. Right, so this is what is preventing it and then at some point this stopper will be removed and the gas will expand to the full volume.

Now in that particular case, what you think will happen to the temperature? Will it decrease? Okay. So why do you think it will decrease? Okay. So let us see now. Let us say we know from the 1st law of thermodynamics that dU equal to dQ + dW, right. Now I said that the system is not isolated system, so basically this whole chamber is isolated, okay, this is an isolated chamber. Which means our dQ is going to be 0, there is no exchange of heat going in or coming out and we know that a free expansion process dW is also 0, right.

So dU is going to be 0, now if dU is going to be 0, then do you think that temperature is going to decrease? So this is what we are going to understand today, what is going to happen in this particular process. So, let us now expand the dU, so again I will remind you that U we can expand as a function of volume and temperature, so therefore you can write total differential dU in terms of both V and T, dU by dV T dV + dell U by dell T V dT.

Now since in this particular case, our total change in U is 0, we are going to put that on the left-hand side. So 0 equal to dell U by dell V T dV. Now when I write dV, I have already used a condition, that condition is dU is 0. dU is 0, right, we have used that condition. In order to denote that we are using that condition, we are going to use this subscript U, that indicates that dV at a constant U, okay, + dell U by dell T V dT U, okay. Now we are going to rearrange this equation, now you know that dU by, now you know the, one of the quantities you know, so dell U by dell V T dV U + dU by dT V you know as CV, right, CV, dT U.

So, no other assumption, nothing has been used till now in this derivation. Now we are going to rewrite this equation on the left-hand side by taking this particular quantity on the left-hand side. So it will be - CV dTU is equal to dell U by dell V T dV U. Okay. So we are trying to understand that how much change in the temperature is going to happen if the volume expands in the condition that U remains constant. Okay, that is what we are going to observe.

Now we rewrite this equation by dividing both sides by dV, we divide both sides. So - CV, when I divide both sides, I can write that as dT by dV at a constant U is equal to dU by dV at a constant T. Now this quantity dell T by dell V at constant U is called Joule's coefficient, that I have mentioned here on the top you see. Joule's free expansion gives us this quantity. So, remember the right-hand side quality, dell U by dell V at a constant T is not possible to be obtained in experiment, because there is no way to measure internal energy.

We can see a change in enthalpy and things like that, but one cannot measure it directly. Rather it is much more easier to revise a system in which there is no exchange of heat and therefore U can become the, we can measure the temperature before and after expansion and thereby you can calculate the quantity in J. And once we have J, we know the CV, we will be able to calculate the right-hand side quantity. You will see often in thermodynamics that we will use this kind of partial derivatives.

And often it looks like that they are there to give us pain, you know, I used to think that way. However, the reason is that these are there to really to relieve us from the pain. Because if you want to observe or measure certain quantities, we can always relate it to something else and thereby we can get the same thing. Which means that in order to see that, if I change the volume, keeping the temperature constant in an isothermal condition, how much change of U will happen, I can get that by knowing 2 things, CV and dell T by dell V at a constant U. That is the sole purpose of having this relation.

So, I can write now I n J, CV nJ is dell U by dell V at a constant T or nJ is -1 by CV dell U by dell V at a constant T. So this is the, this is the quantity, if we calculate that by knowing nJ we will know, I will remove this right-hand side, whether there will be change in temperature or not.

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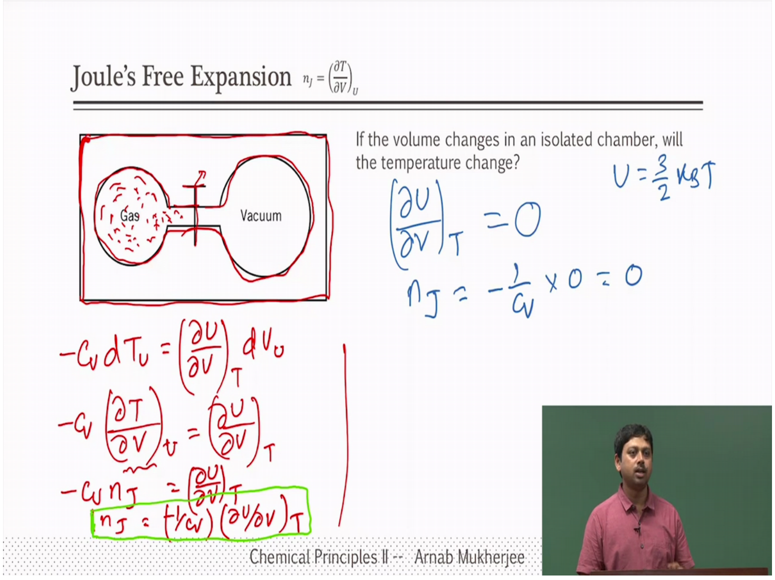

Joule's Free Expansion $n_J = \left(\frac{\partial T}{\partial V}\right)_U$

If the volume changes in an isolated chamber, will the temperature change?

$U = \frac{3}{2} k_B T$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$n_J = -\frac{1}{C_V} \times 0 = 0$$

$$-C_V dT_U = \left(\frac{\partial U}{\partial V}\right)_T dV_U$$

$$-C_V \left(\frac{\partial T}{\partial V}\right)_U = \left(\frac{\partial U}{\partial V}\right)_T$$

$$-C_V n_J = \left(\frac{\partial U}{\partial V}\right)_T$$

$$\boxed{n_J = (-1/C_V)(\partial U/\partial V)_T}$$

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What this is this quantity, dell U by dell V at a constant T for ideal gas. So, ideal gas we know that U equal to 3 by2 KBT, right. So, dell U by dell V at a constant T is going to be 0, because U does not depend on volume. So when I change the volume, if temperature is fixed, the U is not going to change. Right, that is what this particular quantity tells us, right. That is the temperature is same, U is going to be always same, whether you change the volume or not. If U will be a function of volume, then only U will change, when volume is changed.

But if U is not a function of volume, then how is it going to change? So, for ideal gas, therefore nJ is -1 by CV into 0 is equal to 0. So Joule's coefficient is 0 for ideal gas. Which indicates that when we will lift the stopcock, stopper, then the gas will expand, however for ideal gas there will be no change in temperature. So free expansion of an ideal gas does not change the temperature. So, you understand from this, right. Now question is that will that happen for, you know actual real gas also or not, right. And we have to understand that, right.

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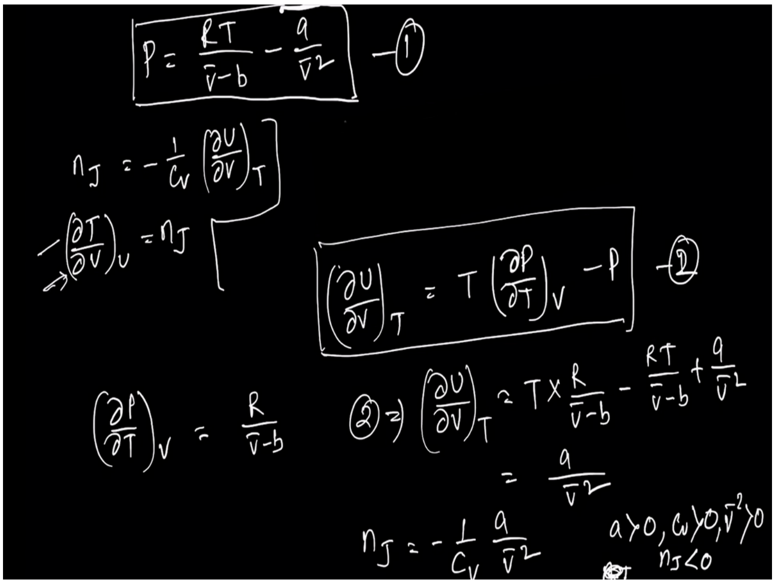

$$\boxed{P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}} \quad -①$$

$$n_J = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$$

$$\left(\frac{\partial T}{\partial V}\right)_U = n_J$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P} \quad -②$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V}-b}$$

$$② \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T \times \frac{R}{\bar{V}-b} - \frac{RT}{\bar{V}-b} + \frac{a}{\bar{V}^2} = \frac{a}{\bar{V}^2}$$

$$n_J = -\frac{1}{C_V}\frac{a}{\bar{V}^2} \qquad a>0, C_V>0, \bar{V}^2>0 \qquad n_J<0$$

So before, okay, so if you want to understand that, let us go here. Let us try to take an easier example which the Van Der Waal's gas. P equal to RT by V - b - a by V square, we know that. So let us keep this equation of state in mind and try to calculate the quantity that is required to calculate the Joule's coefficient. We derived Joule's coefficient nJ as -1 by CV dell U by dell V at a constant T, so this is what we are going to calculate, right. How we are going to do that? Because this above equation does not give us any information about U, right, so how we are going to do that? Any idea?

Because if I have to use this, remember what is the left-hand side, left-hand side is dell T by dell V at a constant U, that is equal to our nJ. So, that this left-hand side is also not possible to calculate. Because how do I get, how do we guarantee that U is going to be constant. And here also it is difficult because we do not have a nice vision of U, we only have an equation of state. You will learn later that this equation of state is actually derivative of a fundamentally question, that means derivative of U already. So how do we get that?

So, in order to get that, we will use some tricks. In order to do that, I am going to do some derivations, which you will not going to understand right now, because I am skipping some steps here. So once we learn those things, again we will do the same thing. So, let me do that quickly. What I am going to tell you for the time being is that dell U by dell V T can be expressed in terms of this relation. How we are arriving at this relation, you will only come to know after we cover the 2nd law of thermodynamics, when we introduce some quantity called entropy and Maxwells relations.

However it is important to show that how this is going to affect and therefore I am going to just show you the relation. So for the time being, you just accept this formula as is. You are going to learn that very easily, did not problem. So now we know that dell U by dell V T can be expressed in terms of this relation, T dell P by dell T V - P. And we know from equation 1 how to calculate dell P by dell T. Let us calculate that, dell P by dell T V is the derivative of the equation 1 which is R by V - b.

So therefore from equation to 2 we get dell U by dell V T is equal to T into R by V - b - P. And P is RT by V - b + y by V square. Which is a by V square. So, therefore nJ is going to be -1 by CV a by V square. Now you remember a was positive or negative? We have discussed about a for helium, it was then and a lot of values, a was a positive quantity. Since a is greater than 0, CV is greater than 0 and it V bar is obviously greater than 0 because it is a square, your nJ is going to be less than 0.

If nJ is less than 0, what does it mean, that if V increases, T decreases. I already told you that A denotes the strength of interaction between the particles, high are the values of a, lower the temperature decreases, or higher the decrease in temperature will happen. Because what happens is that, physically speaking when the articles are close together, when you increase the volume, the particles will have to move apart from each other against the strength of interaction. And that, the work that they will do will actually reduce the temperature of the system, okay.

So, we can see that even for a very simple system like Van Der Waal's gas, when we put interaction, we see that an expansion will cause decrease in temperature. And remember our big bang theory? So, our universe is an isolated system and it expanded, so while expansion 2 things happened, one is the conversion of energy to matter, which will of course reduce the amount of energy of the system. And a volume expansion, in which things will go far apart from each other, which will reduce the temperature of the system.

So it is not like an adiabatic process, it is an expansion, because for an adiabatic process, you will come to know that, we are going to talk about adiabatic process, you will come to know that it has to push against some external pressures. But our universe is some system where nothing is there beyond, so you can think of that as an expansion that is happening which pulls down the temperature, just like Joule expansion process. Okay, so we see that that is what is happening, now we are going to talk about, so this is a process that happens at constant internal energy.

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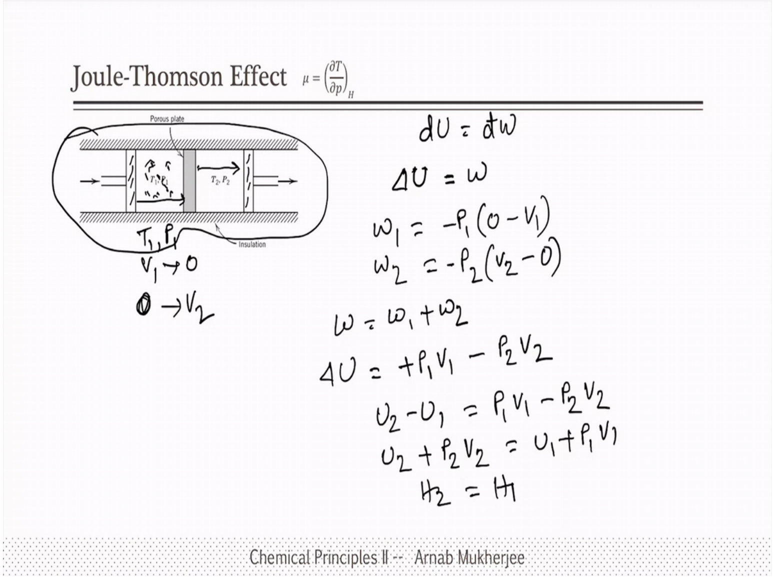

Joule-Thomson Effect $\mu = \left(\frac{\partial T}{\partial p}\right)_H$

$$dU = dw$$

$$\Delta U = w$$

$$w_1 = -P_1(0 - V_1)$$

$$w_2 = -P_2(V_2 - 0)$$

$$w = w_1 + w_2$$

$$\Delta U = +P_1V_1 - P_2V_2$$

$$U_2 - U_1 = P_1V_1 - P_2V_2$$

$$U_2 + P_2V_2 = U_1 + P_1V_1$$

$$H_2 = H_1$$

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Now, similar to that, there is Joule Thomson effect, which talks about constant enthalpy process, okay. So we talked about constant energy process, now we will talk about constant enthalpy process. So, in order to do for observe the change in temperature due to change in pressure, so earlier there were changing in temperature due to increase in volume, or change in value. Now we are going to talk about change in temperature due to change in pressure. And you see that it has to be done in such a way that overall enthalpy remains constant. Just like in earlier case, the overall energy was remaining constant.

So that is the difference between Jules expansion or Jules coefficient and Jules Thompson coefficient. In one case U was constant, another case, H is constant. Now this device that you see here, in fact makes the enthalpy constant. How, we are going to talk about. So let us say our initial system is such that there are some gas particles here, there are gas particles here at temperature T1 and pressure P1. And this is a piston that is going to be pushed and this is a this place is a porous region, this is the porous region.

When you push the system up to this much point, all the classes will go on the other side. And initially this piston was here and then it has gone up to this much. Is it clear now? So, initially the gas was on the left chamber at temperature T1 and pressure P1, you push the gas through the porous membrane to the other side, creating different temperature T2 and different pressure P2. In the process the volume became, from the one it went to 0 and in the right-hand side the volume from 0 it went to let us say V2, Correct.

Now let us see what happens in this particular situation. Okay. Again the overall system, the whole system is kind of isolated. So again we will use the 1st law dU is equal to dQ + dW, but since dQ equal to 0, it is just dW. Now we have to calculate what is the work done in the whole process. So let us say in the whole process the change in the internal energy is U and we have to calculate the amount of work done W. So W in the 1st step, when it goes from V1 to 0, in how much, what is external pressure it is dealing with, P1, right.

So - V1, it goes from V1 to 0, so 0 - V1, okay, because final volume - initial volume. And in the next step the external pressure is P2, because that is the final pressure that is going to be there, so - P2 and it goes from 0 to V2. So the total work done if W1 + W2 and we can write that as P1 + P1 V1 - P2 V2, right. And that is our delta U. Now delta U let us write that as U2 - U1 is equal to P1 V1 - P2 V2. Now they are the equation, U2 + P2 V2 is equal to U1 + P1 V1. Now is it familiar? It is enthalpy, so U2 + P2 V2 is H2 and right-hand side is H1.

So that means that enthalpy in this particular whole setup is constant. So, now once the setup is there, such that the whole process enthalpy is going to be constant, but pressure is changing, we want to understand how much change in the temperature will take place, right. So, for that what we are going to do is that we are going to write it here, H as a function of P and T.

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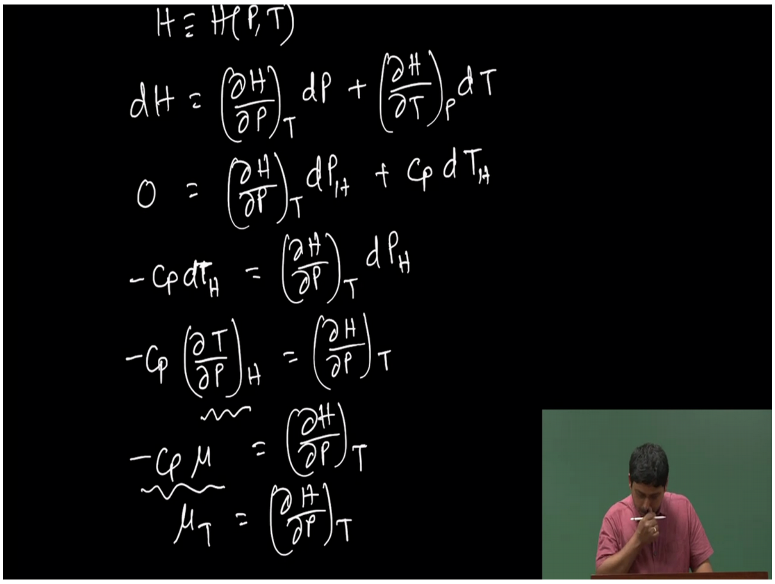

$$H \equiv H(P,T)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$0 = \left(\frac{\partial H}{\partial P}\right)_T dP_H + C_p\, dT_H$$

$$-C_p\, dT_H = \left(\frac{\partial H}{\partial P}\right)_T dP_H$$

$$-C_p \underset{\sim}{\left(\frac{\partial T}{\partial P}\right)_H} = \left(\frac{\partial H}{\partial P}\right)_T$$

$$\underset{\sim}{-C_p\, \mu} = \left(\frac{\partial H}{\partial P}\right)_T$$

$$\mu_T = \left(\frac{\partial H}{\partial P}\right)_T$$

Remember that I will just remind you again, that we can write in whichever variable we want to, however naturally P and T are going to be important for H. So let us write the overall thing, dell H, we are going to do the same way you can see that. dell H by dell PT dP + dell H by dell TP dT. Now since our enthalpy is constant, so it is going to be 0 and now we are going to indicate the P with H, in order to denote. And you know what is the dell H by dell T P, right. What is that, dell H by dell T P, CP. So just it away right CP dTH.

Rearrange the equation, - CP dTH equal to dell H by dell PT dPH, divide both sides by dPH, it is going to give you, okay. So what we are seeing here on the left-hand side, that how much change in the temperature happens due to change in the pressure, when the overall process is done at a constant enthalpy. And this is the quantity that is called Joule Thomson coefficient. So, - CP mu is dell H by dell PT.

And - CP mu is called isothermal Jules Thomson coefficient, sometimes that is also measured and in that case it is nothing but dell H by dell PT. That means change in the enthalpy for a change in pressure at a constant pressure. Okay. So you can measure either U, sorry, you can measure either mu or you can measure mu T, they are not same. Because there is CP sitting here and CP may or may not be temperature dependent. So, you do not have to worry about CP if you are calculating only the mu T, because then it is already taken into account. Okay.

So what you are going to calculate basically, you going to calculate the change in temperature due to change in pressure. So often what happens is that in you know laser experiments, when you want to have a jet cooled spectroscopy technique, where high-pressure gas comes and suddenly it goes to a larger space, where the pressure is very low and the temperature goes down very much. And in that very low temperature there will be formation of dimor and Trimor. So in our Institute, Professor Alok das works on spectroscopic techniques using this Jules Thomson effect.

So now that we know this one, we will just go back. Just remember that then mu T is dell T, I will just compare that with our Joule coefficient here itself. Joule coefficient was nJ and nJ was -1 by CV, instead of CP it was CV, dell instead of H, it was U, instead of P, it was V, that is it. So U, you can see U and V are going together, H and P are going together, okay. Okay, so the question is that in both cases, in Jules case and Joule Thomson case, both president volume are changing, so what is the difference?

The difference is as you can see mainly is in that 1st process in Jules case, total internal energy is constant, whereas in Jules Thomson case, total enthalpy is constant, so that is the main difference. And the main variable that you are looking at is pressure in the case of Joule Thomson, because you want to see as a change in pressure how it is happening. So if the pressure remains same, even if the volume changes, you are not going to see any change. So it is basically what you want to measure.

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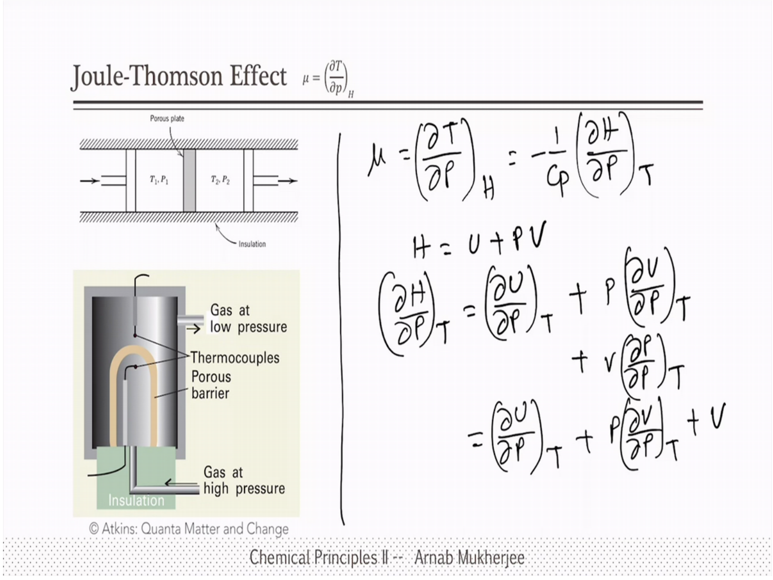

Joule-Thomson Effect $\mu = \left(\frac{\partial T}{\partial p}\right)_H$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

$$H = U + PV$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T$$

$$= \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V$$

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And you see this is the setup in which the gas comes at a high pressure and then goes through this particular porous region, this yellow colour and then it goes to a larger volume at a low-pressure. Now I would like to ask you, okay, so before I ask you that one, let us write down once more that mu is dell T by dell P H which is -1 by CP dell H by dell P at a constant T, right. I remember that by correlating what was for Jules. If you by chance forget the formula, you can correlate with one of them and then remember.

Now, what is the value of mu in case of ideal gas? How do you calculate that for an ideal gas? Can you tell me how to do that? Because CP is certainly not going to be 0, to the positive value for ideal gas and you already know that CP value for ideal gas, CP is CV + R, CV is C by2 R, so CP is 5 by2 R. So, we have to calculate dell H by dell PT, right. So we know that H is equal to U + PV. So dell H by dell P at a constant temperature is dell U by dell P at a constant temperature + P into dell V by dell P T.

Why did not I do dell P dell P, because that will be, is it correct, oh I am doing that, so + V dell P by dell P at T. Now dell P by dell P is basically 1, so I can write that as V, so dell U by dell P T + P dell V by dell P T + V. Now what will be the value for that at an ideal gas? So, we have to calculate this quantity, we have to calculate this quantity and this quantity, okay, in order to do that. So I will need a larger space, so I will go back and do that once more.

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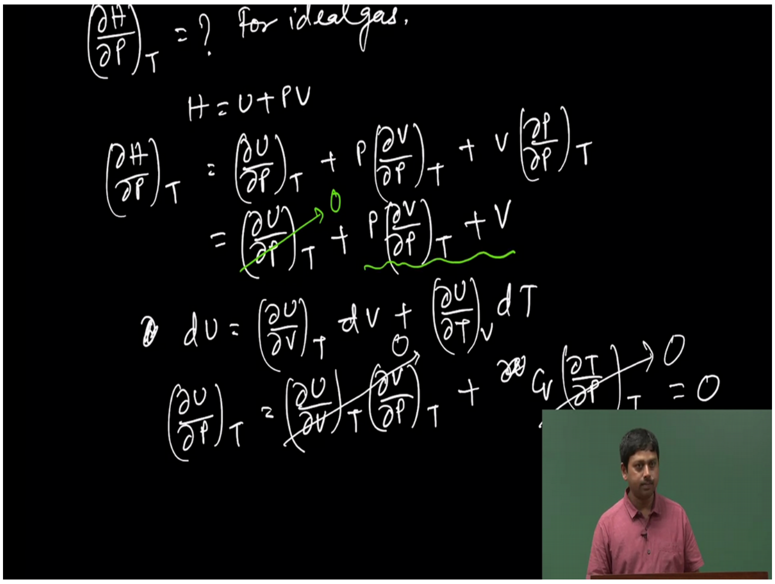

$\left(\frac{\partial H}{\partial P}\right)_T = ?$ For ideal gas.

$H = U + PV$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T$$

$$= \cancel{\left(\frac{\partial U}{\partial P}\right)_T} \xrightarrow{} 0 + \underbrace{P\left(\frac{\partial V}{\partial P}\right)_T + V}$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$\left(\frac{\partial U}{\partial P}\right)_T = \cancel{\left(\frac{\partial U}{\partial V}\right)_T}\overset{0}{} \left(\frac{\partial V}{\partial P}\right)_T + C_V \cancel{\left(\frac{\partial T}{\partial P}\right)_T} \xrightarrow{} 0 = 0$$

dell H by dell P at a constant temperature for ideal gas. So, we know that H is equal to U + PV. See, we are not remembering anything, we will be start from the scratch and do that. So dell H by dell PT, dell U by dell P T + P dell V by dell PT + V dell P by dell P T. dell U by dell P T + P dell V by dell PT + V. Now we have to see what is dell U by dell P T, correct. So remember what we are doing,, like last time, dell U or rather dU can be written as, is the function of both V and T as dell U by dell V T dV + dell U by dell T V dT.

Now I can take the derivative with respect to pressure at a constant temperature on both sides. So dell U by dell P T is dell U by dell V T dell V by dell P T + dell U by dell P which is CV, dell T by dell P at a constant temperature. Okay, so here is the interesting thing that comes when I do the derivation, you see, what happens. You see that dell U by dell V T we already know to be 0, right. So because, so therefore the whole term is going to be 0. And dell P by dell T at a constant T is what, 0, right. Because we are trying to take a derivative of temperature at a constant temperature.

So that means the whole term is going to be 0. So therefore just to use a different colour, this is going to be 0. Now what I am remaining with is these 2 quantities okay. So, therefore I am going to erase this part and then calculate that quantity.

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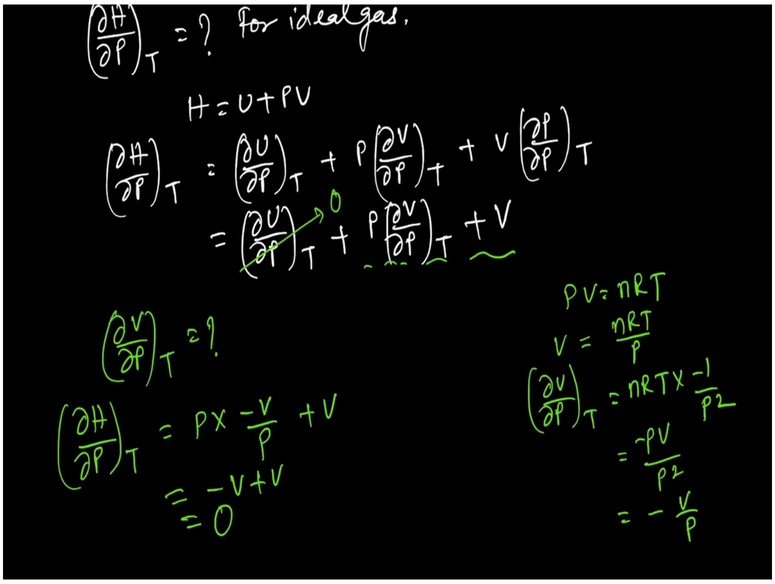

$\left(\frac{\partial H}{\partial P}\right)_T = ?$ For ideal gas.

$H = U + PV$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T$$

$$= \cancel{\left(\frac{\partial U}{\partial P}\right)_T} \rightarrow 0 + P\left(\frac{\partial V}{\partial P}\right)_T + V$$

$\left(\frac{\partial V}{\partial P}\right)_T = ?$

$PV = nRT$

$V = \frac{nRT}{P}$

$$\left(\frac{\partial V}{\partial P}\right)_T = nRT \times \frac{-1}{P^2} = \frac{-PV}{P^2} = -\frac{V}{P}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = P \times \frac{-V}{P} + V = -V + V = 0$$

Now what is dell P, dell V, dell V by dell P at a constant temperature, what is that, remember? PV equals to nRT, so therefore V equal to nRT by P, so dell V by dell P, that means I am taking the derivative with respect to pressure at a constant temperature, nRT is fixed, into -1 by P square, correct. And what is nRT? NRT is again PV, right. So PV by P square, so - V by P. So I am going to put that, so dell H by dell P T is equal to P into - V by P + V, which is giving me - V + V is 0.

So which means that for an ideal gas the dual function coefficient is also going to be 0. Now do you think that for a real gas the temperature is going to decrease or increase when you go from high pressure to go pressure? Because you saw that when you go from low-volume to high-volume for Van Der Wal gas, temperature decreases. What happens from high pressure to low-pressure, will it decrease or not? Or will it increase or will it remain constant? For ideal gas of course both will remain constant, I am talking about a real gas. And since real gas is difficult, we can take Van Der Wal's gas as an example and try to understand what is going to happen, right.