Chemical Principles II.
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Module 3
Lecture 15
Heat is a Path Function.

Now let us talk about heat and we showed you what is a path function by taking different paths and just now you have seen that depending on a number of steps, you are getting different amount of work. Right, so it also indicates that, each process, when you are taking one step, is one path. If you are taking 2 steps, is another path, 3 steps, another path, infinite step, another path. So, path meaning how you are going from P1 V1 to P2 V2, that is called path. Each path is giving you different value. So, work is the path function, you know and hate is a Path function also, now we are going to establish that why heat is a Path function.

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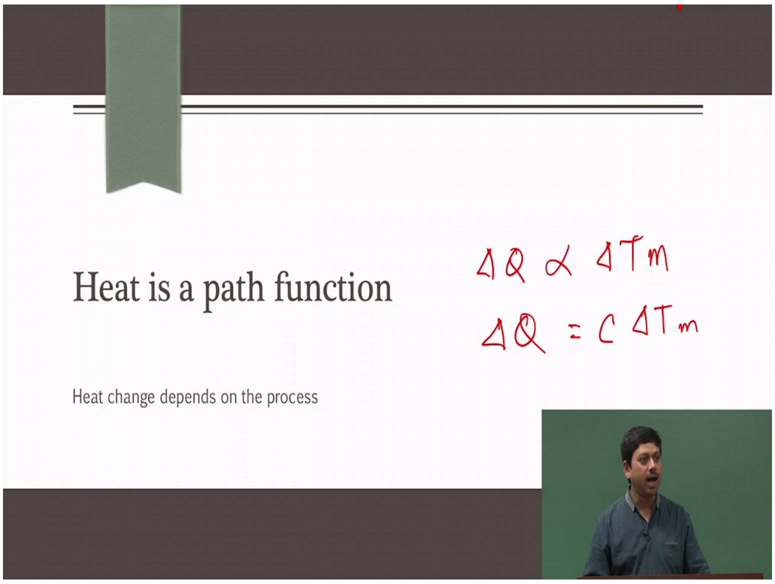
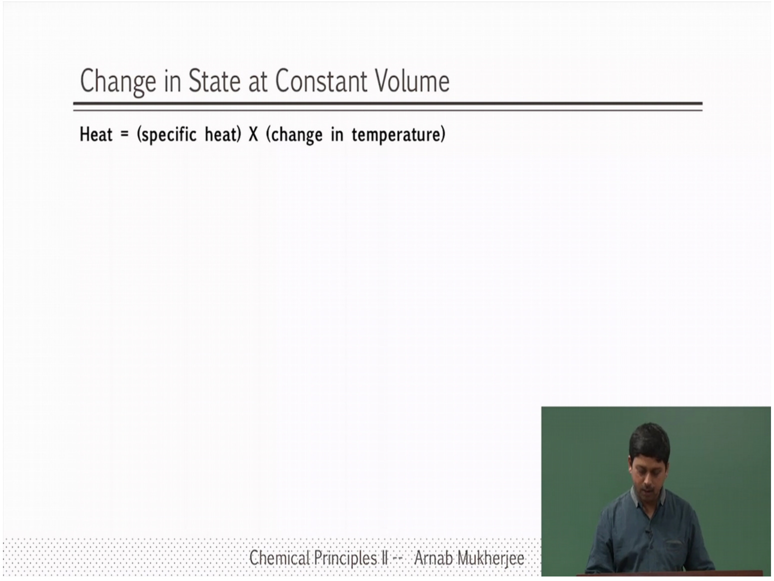


Heat is a path function

$\Delta Q \propto \Delta T_m$

$\Delta Q = C \Delta T_m$

Heat change depends on the process



Change in State at Constant Volume

Heat = (specific heat) X (change in temperature)

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Now what is our standing about heat? Our understanding about heat is that heat is something which is proportional to temperature. Now how it can be a Path function? It is proportional to temperature, right. And also we have seen that it is proportional to mass, right. But there is another quantity that heat depends on, which is a specific heat, right. Specific heat of a system, that for unit mass system for changing a unit amount of temperature, how much it is required. And that specific heat varies from system to system, for water we take it to be 1.

Now it turns out, for gases there is no single specifically possible, it depends on how the process is carried out. Is it carried out by as a constant worry process or a constant pressure process. On that the specific heat will depend on. And first we are going to talk about the changes in as a constant volume process. So, again, as I said, heaters, specific heat constant temperature, so let us do that calculation.

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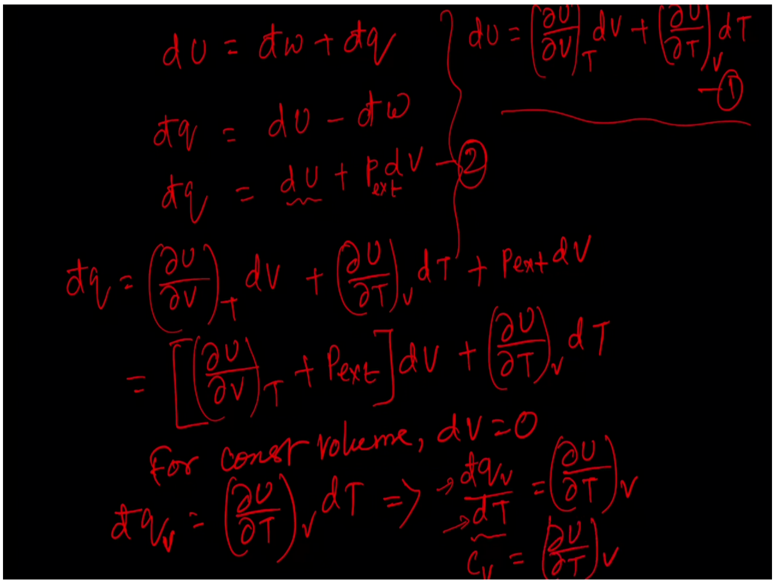

$$dU = \text{đ}w + \text{đ}q$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \quad \text{—} ①$$

$$\text{đ}q = dU - \text{đ}w$$

$$\text{đ}q = dU + P_{ext}\, dV \quad \text{—} ②$$

$$\text{đ}q = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + P_{ext}\, dV$$

$$= \left[\left(\frac{\partial U}{\partial V}\right)_T + P_{ext}\right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

For const volume, $dV = 0$

$$\text{đ}q_V = \left(\frac{\partial U}{\partial T}\right)_V dT \Rightarrow \frac{\text{đ}q_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

We know that dU is equal to dQ + dW, you start from you know extremely basic things. Fundamental first law of thermodynamics, we always start from first law of thermodynamics in these kind of cases, right. So that we do not have to remember anything, always start from the beginning and then you can rearrange everything on your way. We are looking for heat, so dQ is equal to dU - dW. By definition we can write that dU + P External dV, although I write just P, we take it to be P External, so dQ is P External dV.

Now what is dU? dU, you will see that what is the importance of exact differential. dU is an exact differential and U depends on both V and T, so let us write that in terms of exact differential. del U by del V at a constant T dV + del U by del T, constant V dT, okay. Now, this equation, let us replace in equation 1 and equation 2. So we write dQ is equal to del U by del V T dV, it is better to write P External here, so you know you can understand that. I am just replacing this dU part by this thing, dU by dT V dT + P External dV.

Now put the 2 dvs together, dU by dV T + P External dV + dU by dT V dT. So, we got the expression of Q. Right now there is no assumption has been taken, we have expressed Q in terms of this thing. Remember we have taken this as a function of VT, but we could have taken it as a function of P and T or P and V as well, that does not matter. You will see that for the ease of our calculations, we adopt the variables that we require, okay. So, now we are going to do an assumption, not assumption but we are going to take a condition or a constraint.

We say that the process is done at constant volume. Constant volume means what? That V has not changed. If V has not changed, then what does that mean? dV is going to be zero. So for constant volume, dV is equal to 0. So, therefore we get dQ is equal to del U by del T V dT. Which gives us and we write V here, just to denote that it is a constant volume change in the heat. So now dQ V by dT is equal to dU by dT V. Now what is this dU by dT dQ by dT term? Can you tell me what is that?

What it says, it says that what is the temperature, if I change the temperature, much will be the change in the heat at a constant volume. You remember heat is a function of 3 things like temperature, mass and specific heat. So if you divide heat by temperature, what you are going to get? Mass and specific heat, for a fixed mass you will get specific heat. So specific heat is defined by the fact that for a unit mass, how much change in the heat will happen given this much change in the temperature.

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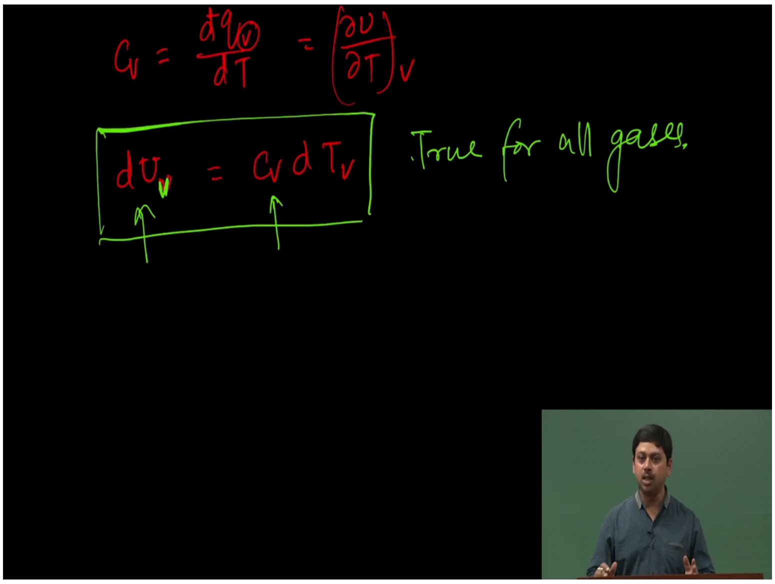

$$C_V = \frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\boxed{dU_V = C_V\, dT_V}$$

True for all gases.

And since this quantity is done at a fixed volume, we call that specific heat at a fixed volume CV. So, CV is now defined to be dU by dT at a constant volume. What we write, that CV, which is specific rate at constant volume is dQ by V by dT, this V is very important, this V denotes that we are talking about constant volume process, never neglect those things, is equal to del U by del T at a constant V, that is our CV.

Which means that, if I now try to write it in a different way, then we can write, I can take that dT on this side and write that dU at a constant V is CV dT at a constant V. And this is true for all gases. Not just ideal gas, it is true for all gases and it is a very interesting important result, which means that if we know the specific heat of the system, we will be able to know the change in the internal energy is the process is done at a constant volume, because internal energy is not something that can be measurable.

We have to understand what is measurable and what is not measurable. And remember again that all those definitions of heat, work, everything, have stemmed from somewhere. So, we first understood what is temperature by associating that to physically measurable quantity of gas Systems, PV. That gives us a sense of temperature or definition of temperature. From temperature we got the definition of heat, right. And now from heat we are getting a definition of internal energy or changes the internal energy, right. Though we have started from somewhere and we are going to get all the relevant quantities.

We will not be able to measure this dU directly, we will do that in computation but not experimentally. But a measurement of this, measurement of heat at a constant volume will help us to calculate the CV and therefore will help us also to calculate the internal energy of the system. And that is what is so important about this particular equation, okay. Now let us go back and see what I have here.

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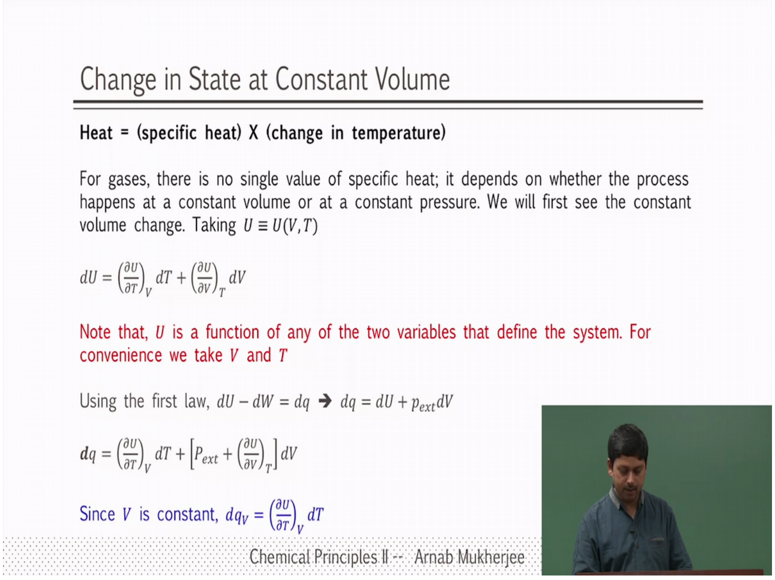

Change in State at Constant Volume

Heat = (specific heat) X (change in temperature)

For gases, there is no single value of specific heat; it depends on whether the process happens at a constant volume or at a constant pressure. We will first see the constant volume change. Taking $U \equiv U(V,T)$

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

Note that, U is a function of any of the two variables that define the system. For convenience we take V and T

Using the first law, $dU - dW = dq \rightarrow dq = dU + p_{ext}dV$

$$dq = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P_{ext} + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

Since V is constant, $dq_V = \left(\frac{\partial U}{\partial T}\right)_V dT$

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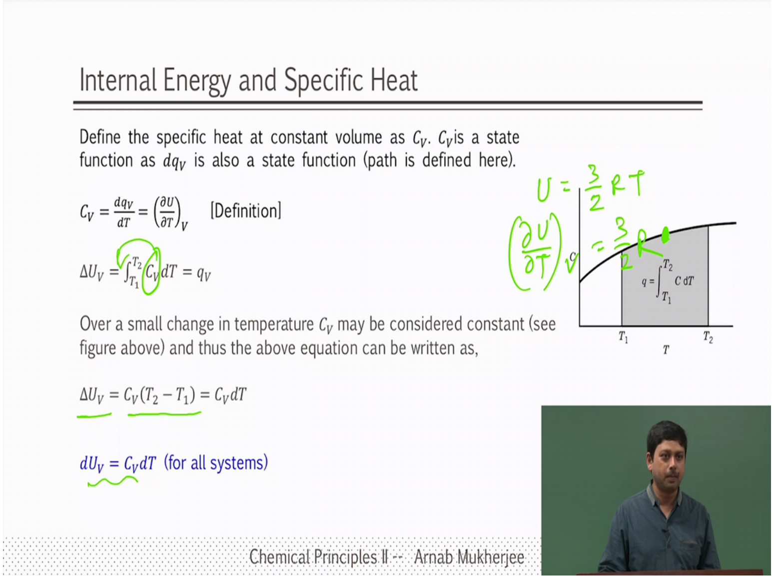

Internal Energy and Specific Heat

Define the specific heat at constant volume as C_V. $C_V$is a state function as dq_V is also a state function (path is defined here).

$$C_V = \frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{[Definition]}$$

$$\Delta U_V = \int_{T_1}^{T_2} C_V dT = q_V$$

Over a small change in temperature C_V may be considered constant (see figure above) and thus the above equation can be written as,

$$\Delta U_V = C_V(T_2 - T_1) = C_V dT$$

$dU_V = C_V dT$ (for all systems)

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I have that, I have discussed this and I have discussed this one, okay. Now I have discussed also this particular quantity here, CV, and this particular quantity also I have talked about, that you can get the change in the internal energy by integrating the CV dT. Now when I do that, when I do this particular integration, the CV may or may not be dependent on temperature, right. Because C, it is within the integration, this particular CV is inside the integration, it may or may not be dependent on temperature.

But it turns out that for a region of our interest, when you are changing the temperature from T1 to T2, in that region CV may not vary much with the temperature. And in that case we can always take out the CV outside the integration and we will get change in the interval energy as CV T2 - T1. The ideal gas system that we are going to talk about does not depend on temperature, okay. And that we can very easily see. So for example we know that U equal to 3 by2 RT, so dU by dT, the constant volume, is going to be 3 by2 R for ideal mono atomic particle, not for any other thing, mono atomic particle.

One particle ideal gas has 3 by2 RT energy, one molar gas and CV is therefore 3 by 2, R does not depend on temperature, in that case our internal energy we can write like this. And I have already discussed about this particular thing. This is a typical graph showing how CV varies with temperature. So essentially we are saying that, we are taking some midpoints, some these values in the midpoint somewhere for our CV. Of course it will not be exactly accurate but it all depends on how much accuracy you want in our calculation.

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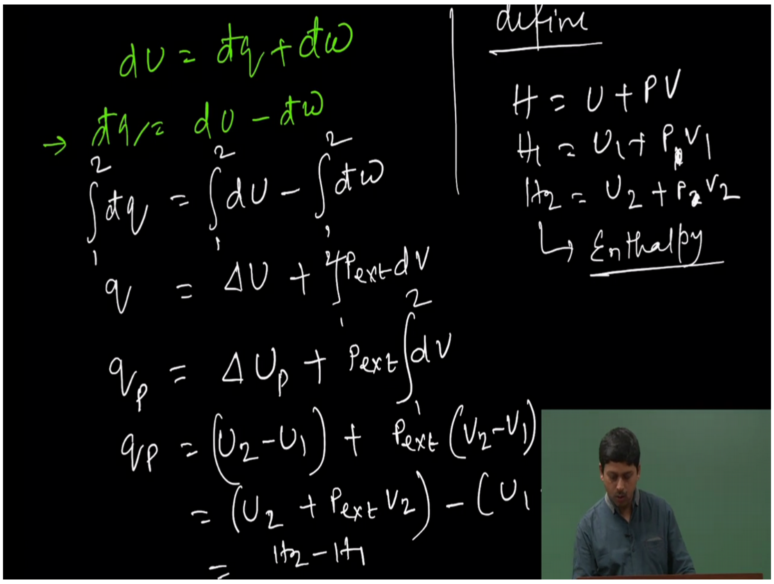

$$dU = \text{đ}q + \text{đ}w$$

$$\rightarrow \text{đ}q = dU - \text{đ}w$$

$$\int_1^2 \text{đ}q = \int_1^2 dU - \int_1^2 \text{đ}w$$

$$q = \Delta U + \int_1^2 P_{ext}\, dV$$

$$q_p = \Delta U_p + P_{ext}\int_1^2 dV$$

$$q_P = (U_2 - U_1) + P_{ext}(V_2 - V_1)$$

$$= (U_2 + P_{ext}V_2) - (U_1$$

$$= H_2 - H_1$$

$$=$$

define

$$H = U + PV$$

$$H_1 = U_1 + P_1V_1$$

$$H_2 = U_2 + P_2V_2$$

↳ Enthalpy

And that is where the error bars and everything comes in, the picture, nothing is accurate. Like it depends on how many decimal places you want the result to be correct. Now we are going to talk about the change in the constant pressure. dU is equal to dQ + dW and write dQ is equal to and write dQ is equal to dU - dW. And then we can say that there is a change in the internal energy, right, so let us say that changes happening in 2 states, 1 and 2, we are going to want to do.

And internal energy at the position 1 is U1 and the internal energy at the position to is U2. So do you, so we can say, so this is infinitesimal change, so let us say we talk about different amount of change. So, there is a difference between when we write d versus del. So, when we write del, it signifies we are talking between final and initial 1. For example, del U is U2 - U1, however dU when we write, we are talking about an arbitrary infinitesimal change, that is the rotation we are going to use in thermodynamics.

So when it is Q, let us say Q equal to delta U - dW makes Place P external delta V. You see, can I write like that? I can write like that only when, yes, why you are not, so we are taking Q to be a change in heat. Q is the amount of heat that is required to be input or output. So that is the change. This is a change but is this part correct? What was the definition of work? Integration P external dV, so this part is not correct. Actually what I should have done is that I will tell you. I should have written this way.

Going from step that step to next step, I should have done this. Integration of dQ equal to integration of dU - integration of dW, correct. That would have been the case from 1 to 2, now I am saying that 1 to 2 is just Q. This one is delta you that I have defined to be U2 - U1, now in this case I should write P external TV integration 1 to 2, up to that it is fine. But then in the next step when I write Q to be delta you + P external dV, I am assuming the external to be constant. So, therefore I have to put P here, and then I can write that.

You see it is a very small difference, but the earlier one was not correct, now it is correct because we are assuming the process is done all along at a constant pressure. For example if you do PV diagram, let us this is PV, you are doing a PV diagram, you are going exactly that way, then it is correct. So, now integration of V from 1 to 2 is nothing but V2 - V1, so it is U2 - U1 + P External V2 - V1 equal to QP. Now I will simplify it again. U to + P external V 2 - U1 + P external V1, is it okay.

I have has put U and PV together, okay. Is this last line fine? Now, I define a new quantity H to be U + PV. Such that my H1 is equal to U1 + PV 1 and H2 is U 2 + P2 V2. Now, P remaining constant, I can write is P. Okay. Once I do that, I can write QP as H2 - H1, okay. Now what did I get, that heat at a constant pressure is changed in quantity, which we call as Enthalpy. So, change in heat at a constant pressure is nothing but change in enthalpy. Enthalpy is our own definition and we define that to be U + PV.

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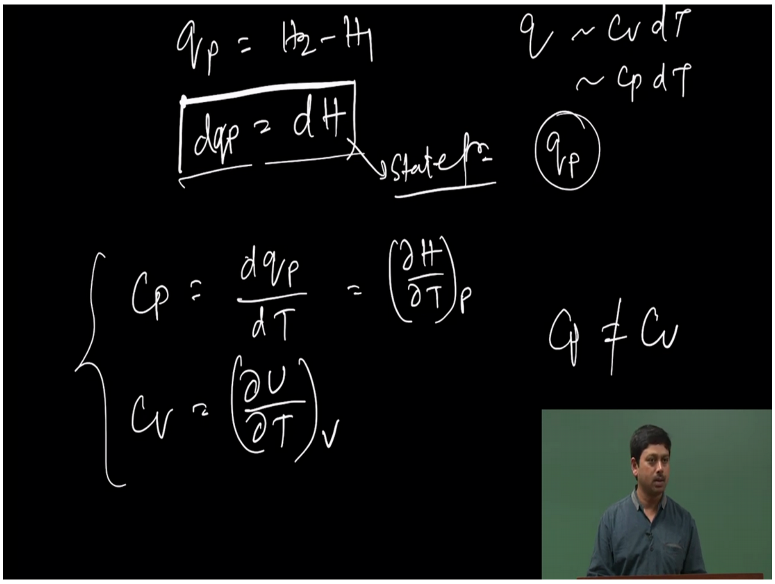

So I will clear it and write once more. So QP we got to be H2 - H1, so in that case d QP is nothing but dH. And you will see later on that it is a quantity that has natural variable of P and T. It is easy to express this quantity in terms of PT, just like it is easy to express U in terms of V and T. Okay. So this is our new quantity, now specific heat at a constant pressure will be the same thing, dQ, by the way I should not, should not cut the d. So by notation the d is cut to denote that it is a path function. But once I have specified whether the process is done at a constant pressure or constant volume, is no longer path function.

So you see Q is a part function, because Q can be changed by either constant pressure process or constant volume process. But if I already specify the pressure is done at a constant pressure and say QP, then it is no longer a part function. I have 2 different ways to go somewhere and each are different of different lengths. However if I say okay, I have to go only that way, then it is no longer different. So, therefore QP is no longer a path function, QP is a State function and so does H, H is also a State function.

So now coming back to that same thing, I will just write it below. CP is d QP, so therefore I should not cut it, that is why it comes from, should not cut d. So CP is dQ by dT, which is nothing but del H by del T at constant pressure, it is clear. So what we got, CV we got as del U by delta T at a constant V and CPV got as del H by del T at a constant P. You know, do not write del U by del T at a constant P for CV because it will be different and not the other way round. And do not think that, del U by del T at constant P will give you CP, that also not going to give you.

You have seen that by derivation that it is like this. One is del H by delta at a constant P, another is del U by del T at a constant V. And these 2 quantities are different and therefore CP is not equal to CV. And since they are not equal, then QP and KUV, they are also different and therefore heat is a path function, okay. So, I think I have done all that here, I am just going over because after that. I have done that, you, so we have said that heat observed in a process at a constant pressure is equal to the change in enthalpy.

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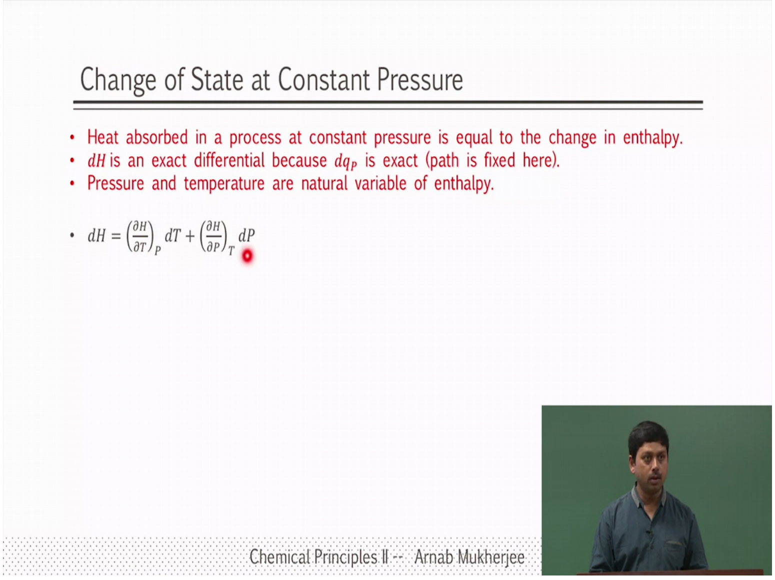

Change of State at Constant Pressure

- Heat absorbed in a process at constant pressure is equal to the change in enthalpy.
- dH is an exact differential because dq_P is exact (path is fixed here).
- Pressure and temperature are natural variable of enthalpy.
- $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$

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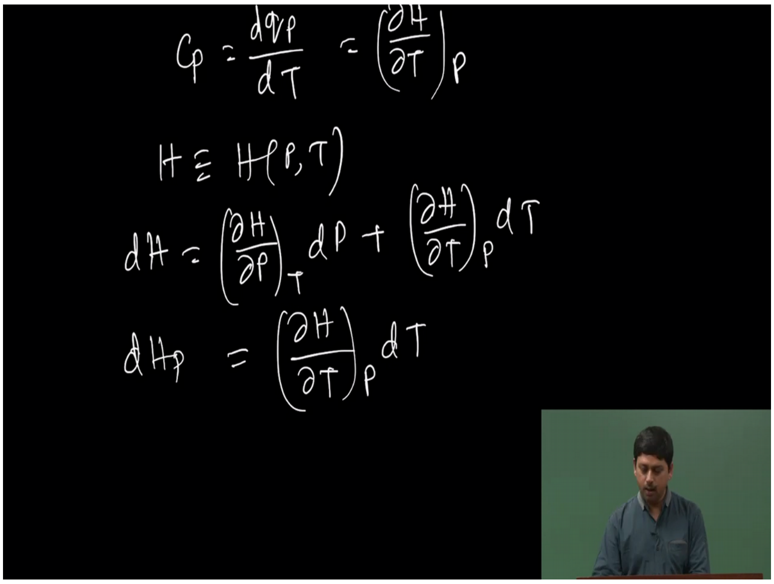

$$C_p = \frac{dq_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

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

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

$$dH_P = \left(\frac{\partial H}{\partial T}\right)_P dT$$

dH is an exact differential because d QP is exact, we have discussed that, pressure and temperature are natural variables of enthalpy, just to tell you that, we are going to use that later on. And so now we can see that this part, I can just for you, so since pressure and temperature are natural variables, we can expect the differential amount of H in terms of these 2 quantities, okay. So we have seen that CP is d QP by dT which is del H by del T at a constant pressure, that we know.

And I said that H, natural variable of H is PT. Whenever that happens, you can always write that in terms of these 2 variables. You will write it so many times, that will become extremely easy, okay. Now we know that the, we want to talk about the constant pressure process, so therefore this quantity is going to go to 0. So del HP will be del H by del T at constant pressure, dt. I do not know what we are going to get from that, just one seconds. Yes, I understand my argument, I will do that once more.

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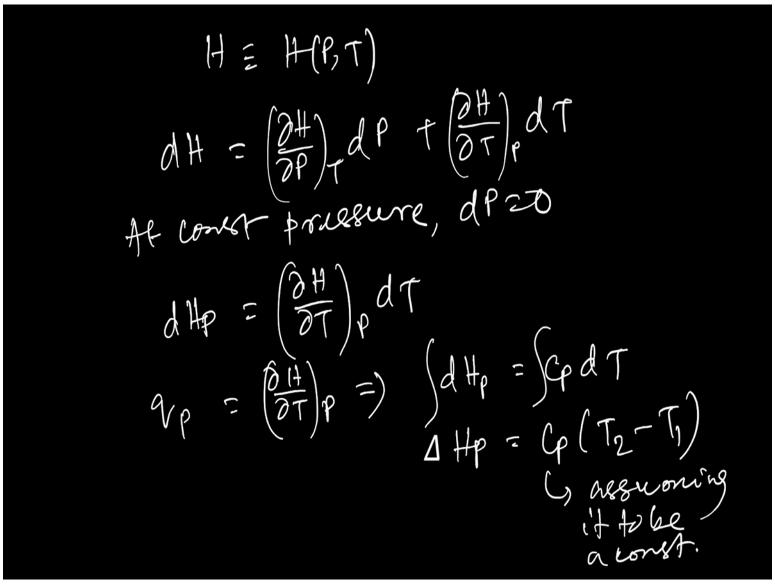


$H \equiv H(P,T)$

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

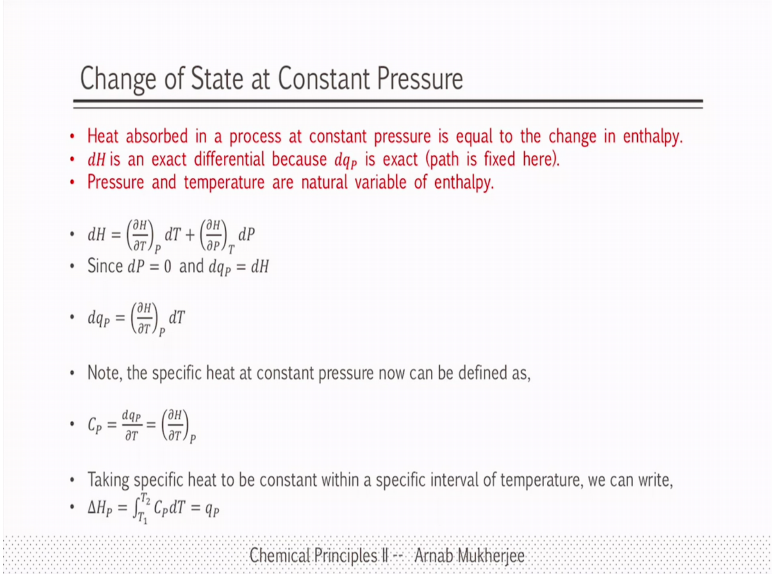
At const pressure, $dP = 0$

$$dH_p = \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$q_p = \left(\frac{\partial H}{\partial T}\right)_P \Rightarrow \int dH_p = \int C_p\, dT$$

$$\Delta H_p = C_p(T_2 - T_1)$$

↳ assuming it to be a const.



Change of State at Constant Pressure

- Heat absorbed in a process at constant pressure is equal to the change in enthalpy.
- dH is an exact differential because dq_P is exact (path is fixed here).
- Pressure and temperature are natural variable of enthalpy.

- $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$
- Since $dP = 0$ and $dq_P = dH$
- $dq_P = \left(\frac{\partial H}{\partial T}\right)_P dT$
- Note, the specific heat at constant pressure now can be defined as,
- $C_P = \frac{dq_P}{\partial T} = \left(\frac{\partial H}{\partial T}\right)_P$
- Taking specific heat to be constant within a specific interval of temperature, we can write,
- $\Delta H_P = \int_{T_1}^{T_2} C_P dT = q_P$

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So, H has a natural variable of CT, so therefore you can write dH as del H by del P T dP + del H by del T P dT. Now at a constant pressure, dP equal to 0, and therefore dHP is nothing but del H by del T P dT. Now we know that QP, specific heat is del H by del T P, right. So, therefore we can write that del HP is CP dT. So, if you have to calculate the change in enthalpy for a constant pressure process, we can calculate that, right. Or we can also calculate the change in enthalpy by assuming CP to be independent of temperature, they can express that change in the enthalpy as CP T2 - T1.

What we have done, we have just integrated on both sides. And assuming CP is constant, assuming it to be a constant, okay. I think that is what is done here, yes and we can get also the, by integrating we can get the heat. Now this is the last part of today's lecture. That we can show that CP is always greater than CV. Now how do we do that? So that is the question.

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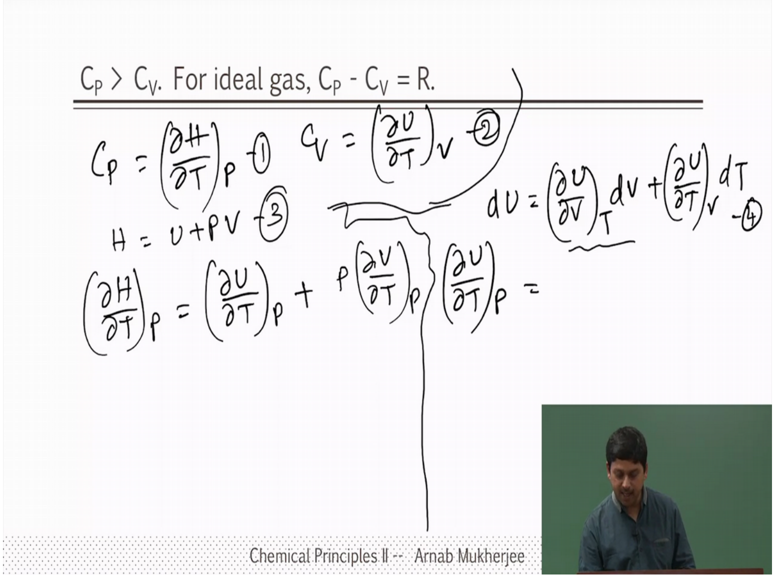

$C_P > C_V$. For ideal gas, $C_P - C_V = R$.

$C_P = \left(\frac{\partial H}{\partial T}\right)_P$ ① $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ ②

$H = U + PV$ ③

$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$ ④

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

$\left(\frac{\partial U}{\partial T}\right)_P =$

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So that is a very nice derivation that we are going to do. So CP by definition is del H by del T at a constant pressure and what is CV? del U by del T at a constant volume. Now let us start with CP, now we know that H is U + PV, right, so let us call it a question 1, equation to an equation 3. So then integrating both sides of equation 3 with T, we are going to get del H by del T at constant pressure is equal to del U by del T at a constant pressure + since P is a constant, because you are doing at constant pressure, we do not have to do that product differentiation, we can just take P, now tell we are going to get del V by del T at a constant pressure. Okay, this is fine, this step?

Now you see, we have del U by del T at a constant pressure, we know that we cannot write that as CV because CV is del U by del T at constant volume. But here we get constant pressure, so we cannot just substitute that. So what we are going to do is that we are going to, that is a little bit lengthy process, we have to again express U in terms of P and T. So del U by del V T dV + del U by del T V dT. And this next up is very important. And listen carefully, this I had several times problems, when I studying myself.

See, I have this quantity del U by del V T and at a constant volume. I want to get to del U by del T at a constant pressure, I have this, I have this, I want to get to this. Now do I get? That is what we are trying to do right now. I have this, but I want to get to this. If I have to get to this, I have to take a derivative of U with T at a constant pressure, have to do that. Right now I would have that, right now what I have is this one. So what we have done is we have expressed the total differential of U, which I can always write like that.

Now I can take a derivative of this particular thing with respect to T at a constant pressure. So doing that I am going to get del U by del T at constant pressure, right. I am doing the derivative now, of this particular equation, equation number 4, I am doing the derivative on both sides of equation number 4 with respect to temperature, keeping pressure constant. What will be the right-hand side? Now the most problematic at is the right-hand side. Should we take a product or should we not take a product?

Like should we do as a product of these 2 things or not? Now, in order for you to understand, I would like to tell you that this is where the problem sometimes M. This d is a differential amount, so when I say I am taking the derivative with respect to a particular quantity, what essentially am doing is that I am dividing by dT at constant pressure at taking the limit to come at limit of temperature to 0. So essentially am dividing by delta T. So if I divide this particular country by delta T, my this quantity is not going to change, because that is dT is going to come.

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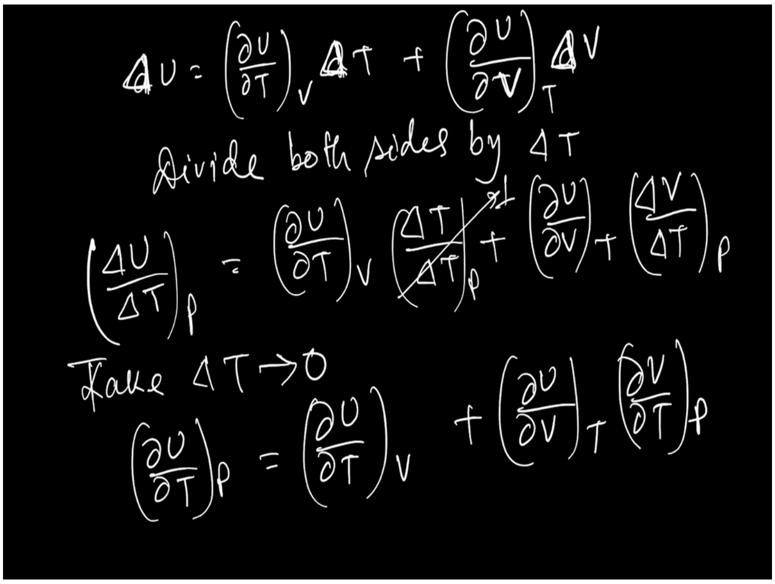


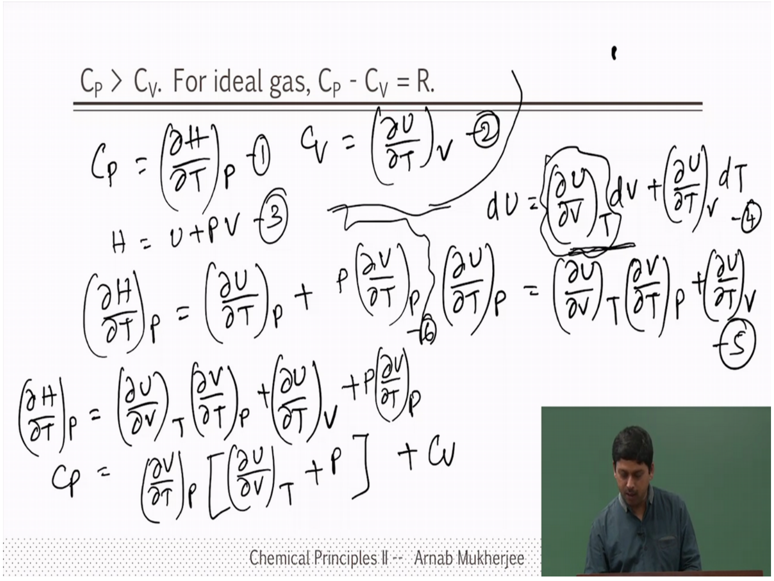
$$\Delta U = \left(\frac{\partial U}{\partial T}\right)_V \Delta T + \left(\frac{\partial U}{\partial V}\right)_T \Delta V$$

Divide both sides by ΔT

$$\left(\frac{\Delta U}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \overset{1}{\cancel{\left(\frac{\Delta T}{\Delta T}\right)_P}} + \left(\frac{\partial U}{\partial V}\right) + \left(\frac{\Delta V}{\Delta T}\right)_P$$

Take $\Delta T \to 0$

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



$C_P > C_V$. For ideal gas, $C_P - C_V = R$.

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \quad ① \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad ②$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \quad ④$$

$$H = U + PV \quad ③$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \quad ⑥$$

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V \quad ⑤$$

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

$$C_P = \left(\frac{\partial V}{\partial T}\right)_P\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] + C_V$$

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If you want I can do it in one more step, okay, let me write it here. dU is dU by dT constant volume + del U by del V dV, okay, this is what we have. What we are doing is that divide both sides by, in fact imagine that it is not dU, imagine that it is del U. 1st principle, both sides by del T. What we are going to get, del U by del T but at a constant pressure, so since I am dividing this quantity is not going to change, del T by del T + del U by del T, okay.

But the change is such a way that, I am doing that at constant pressure. Take delta T tends to 0, what I am going to get now, is it clear? So, you see this quantity, not taking this particular quantity, I am not taking the derivative again, not taking the derivative of this quantity is this quantity. Essentially when I am saying I am taking a derivative, it essentially means that I am changing the, already a differential amount of the numerator is already there, I am dividing by a differential amount of the denominator, which is delta T.

And that gives me a derivative of this quantity. This goes to 1 and this is giving me a derivative del V by del T at P. Okay, is it clear? If this is clear, then you will have no problem in future of taking this partial derivative so success you have difficulty, always go back to the 1st principles and that is what when we talked about partial derivative last class, we talked about how we are getting that partial derivative. Remember we did it from 1st principles by changing the differential amounts and we discussed about what partial derivative means, that pressure remains constant, volume changes, when you are talking about at constant pressure partial derivative.

So essentially when you are talking about partial derivative is, we are going to the 1st principle of changing some amount, infinitesimal amount of a particular quantity and looking at how the other quantity this changes. And that is what we are doing it here. So, now I will write it here again, del U by del T at P is del U by del V T, del U by del T P + del U by del T V because dT by dT will cancel, meaning that it will give 1, even if it is a constant pressure because it is going to be 1.

So now I am going to, I have to replace this equation number 5 in my equation number 6, means I have to replace this dU by dT P by this whole quantity. And the space is little bit less, so I will just try to write once here. del H by del T at a constant pressure is therefore del U by del V at a constant temperature, del U by del T at a constant pressure + del U by del T at a constant volume. You see interestingly when I change this variable, just P, then it is so different compared to when it was del U by del T V. del U by del T at a constant V is very different from del U by del T at a constant P.

So I am taking the temperature and looking at how the internal energy changes. If that is done at constant volume versus at constant pressure, is entirely different process. That is what it is denoted by these subscripts. So that is why its substitutes are essentially, they are extremely important, do not neglect that. So, now, so this is now I have substituted that del U by del T P I have substituted, then I am going to write this particular terms that is left out, del V by del T at a constant pressure.

I am going to erase this part. Now what is this particular quantity? del U by del V T, is it familiar, del U by del V T? No, del U by del T P, no, but is it something is, there, yes, del V by del T P is common thing from these 2 equations, so I am going to take that. del U by del T, P is common, which is giving me del U by del V T + P + dU by dT V, what is this quantity, CV. And del H by del TP, what is that quantity? CP. So, I have got, now I am going to erase the top part.

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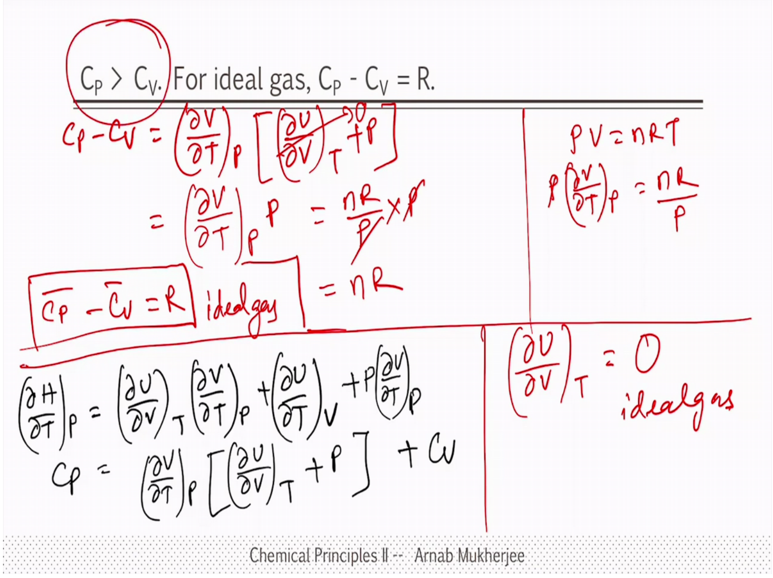

$C_P > C_V$. For ideal gas, $C_P - C_V = R$.

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[\cancel{\left(\frac{\partial U}{\partial V}\right)_T}^{\,0} + P\right]$$

$$= \left(\frac{\partial V}{\partial T}\right)_P P = \frac{nR}{\cancel{P}} \times \cancel{P}$$

$$= nR$$

$$\boxed{\bar{C}_P - \bar{C}_V = R} \text{ ideal gas}$$

$$PV = nRT$$

$$\cancel{P}\left(\frac{\partial V}{\partial T}\right)_P = nR$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

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

$$C_P = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] + C_V$$

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

ideal gas

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Okay so, we got that CP - CV therefore is this particular big quantity, which is del V by del T P del U by del V T + P, that is it, yes. Now we have to see what each of these quantities is. What is del U by del V T, what does it say? del U by del V T, del U by del V T says that if I change my volume at a constant temperature, whether internal energy is going to change or not? Now, can you tell me whether it is going to change or not for ideal gas? For ideal gas it is not going to change, why, because U does not depend on V.

Whether V is a small or big, does not matter, it is always dependent on temperature only. If temperature is constant, that is not going to change, even if you change the volume. However, it is not true for real gases. Remember, because real gas has attraction, so when you change the V, the particles get separated from each other and energy is going to increase actually if they are coming from stable states, it depends on where you start. So, this quantity is going to be 0 for ideal gas.

So than we land up with del V by del T P into P because this quantity is 0. And what is del U by del T P? So, we have to go back to PV equals to nRT. So let us, PV equal to nRT and it is a constant pressure differentiation. So P is a constant. So let us differentiate with respect to T on both sides, so P del B by del T at a constant P is equal to nR, so del U by del T is nR by P, so let us write that nR by P into P is equal to nR. So CP bar which is heat capacity at a constant pressure for one mole - CV bar, the same thing at a constant volume is equal to R for ideal gas alone.

By the end of the class of we are going to do it in general, that means irrespective of whether it is ideal gas or not, and you will see this quantity is going to be much more complicated, it will be T V Alpha square by Cuppa T. We have not defined any of these, so right now you do not worry about it but you are going to have a very general expression of CP - CV. But for ideal gas, CP - CV is R and since let R is a positive quantity, we can say that CP is greater than CV. Now mathematically it is easily understand that it is greater than CV but physically can you explain why CP is greater than CV?

It is a very important question in thermodynamics that why CP greater than CV? Is CP is, when you change your, when you give heat at a constant pressure and CV is when you give heat at a constant volume. So when you do at a constant volume, what happens is that there is no work done. So whatever heat was getting, you are putting an, is going there, swast to change the internal energy. So, however for CP, in order to, when you heat at constant pressure, what is happening, your wall is also changing.

So the amount of heat is going in 2 ways, to change the volume, that needs to do the work and then whatever the rest is there, that is going to change the heat. So you have to put more heat in to change the same amount of temperature. So CP is that, you need more heat to change the same amount of temperature in case when there is a constant pressure, because some amount of heat is going into work. But in the CV case, since the volume is same, nothing is going to work, so everything is going to change the heat, and that is the reason CP is greater than CV, always, irrespective of whether it is a real gas or ideal gas. But the amount will depend on what system we are considering. So we will end today.