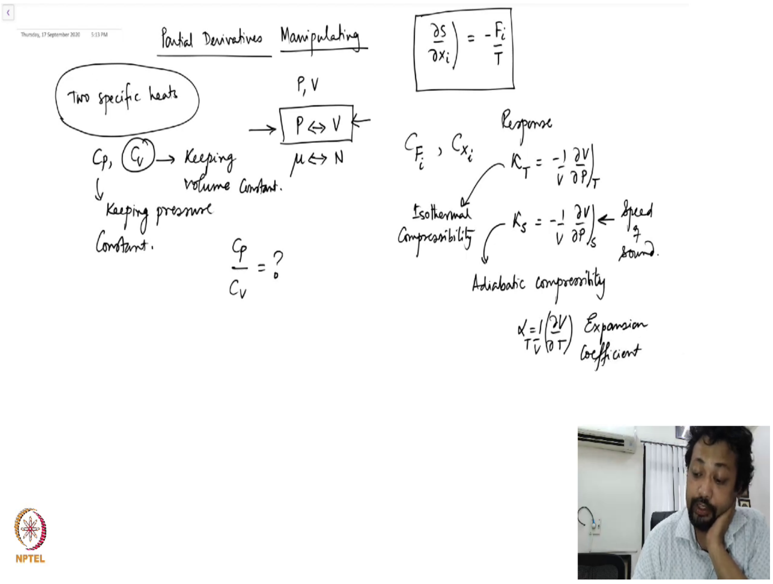
Statistical Mechanics
Prof. Dipanjan Chakraborty
Department of Physical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 11
Response Functions and Manipulating Partial Derivatives

(Refer Slide Time: 00:17)


Thursday, 17 September 2020 5:13 PM

Partial Derivatives Manipulating

$\left.\frac{\partial S}{\partial x_i}\right) = -\frac{F_i}{T}$

Two specific heats

P, V

$\rightarrow \boxed{P \Leftrightarrow V} \leftarrow$

$\mu \Leftrightarrow N$

C_P, C_V → Keeping volume Constant.

↓ Keeping pressure Constant.

$\frac{C_P}{C_V} = ?$

C_{F_i}, C_{x_i}

Response

$K_T = -\frac{1}{V} \left.\frac{\partial V}{\partial P}\right)_T$ Isothermal Compressibility

$K_S = -\frac{1}{V} \left.\frac{\partial V}{\partial P}\right)_S$ ← Speed of sound.

Adiabatic compressibility

$\alpha_T = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)$ Expansion Coefficient

Now, in the earlier class we had seen that the, how to use Jacobians to identify independent Maxwell’s relations for a thermodynamic systems. So, in this current we were now, what we are going to do is we are going to look at how we can manipulate partial derivatives in thermodynamic systems.

And we have seen quite a lot of them. Starting from the first from the first law we have derived equations. So, for the generalized equations of state as minus F i over T, where X i is a generalized coordinate. And the corresponding F i is the conjugate force. For a hydrostatic system for example, P is conjugate the pressure is conjugate to the volume, the particle number is conjugate to the chemical potential.

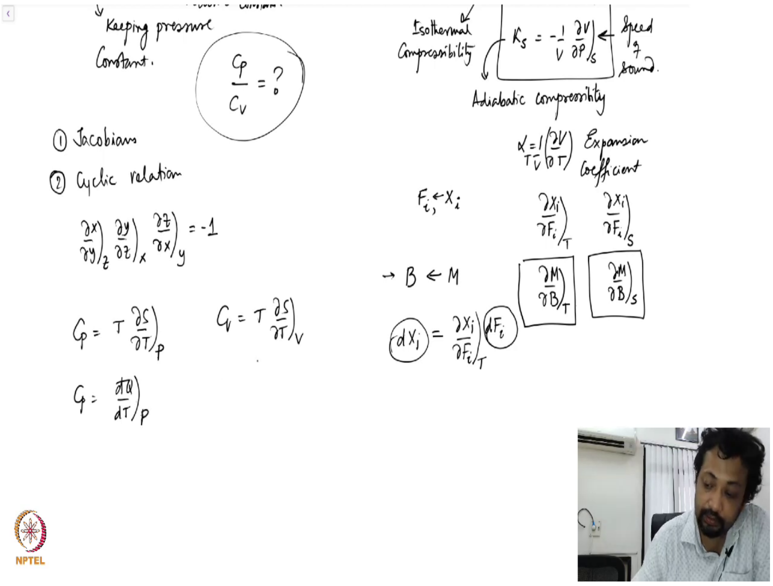
So, normally for a hydrostatic system this is the one pressure volume, which plays a very very significant role and therefore, one defines specific heats as C P and C V. So, essentially this is a specific heat that is defined for keeping pressure constant. And this is the specific heat that is defined by keeping volume constant. For any arbitrary thermodynamic system one can have C F i and correspondingly C X i. For a hydrostatic system this is very easily experimentally accessible and therefore, one defines this.

So, now first let us see I want to define find out what this ratio is number 1. On top of this equation of state that we had defined for a thermodynamic system, it also follows that there are various response functions that we have seen. One of them are of course, specific heat for a hydrostatic system.

You also have the compressibility kappa T which is minus 1 by V del V del P, temperature constant. One can also define a same compressibility in which case entropy is held constant. This quantity is called adiabatic compressibility and this is called isothermal compressibility.

Now, you should know that it is this compressibility that appears in speed of sound in a fluid. Other than that of course, you have alpha T which is del V del T 1 by V this is the expansion coefficient the volume expansion coefficient that you defined.

(Refer Slide Time: 03:40)



Keeping pressure Constant.

$\boxed{\frac{C_p}{C_v} = ?}$

① Jacobians

② Cyclic relation

$\left.\frac{\partial x}{\partial y}\right)_z \left.\frac{\partial y}{\partial z}\right)_x \left.\frac{\partial z}{\partial x}\right)_y = -1$

$C_p = T\left.\frac{\partial S}{\partial T}\right)_P$ $\quad C_v = T\left.\frac{\partial S}{\partial T}\right)_V$

$C_p = \left.\frac{dQ}{dT}\right)_P$

Isothermal Compressibility

$\boxed{K_S = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_S} \leftarrow$ Speed of Sound.

Adiabatic compressibility

$\alpha_T = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)$ Expansion Coefficient

$F_i, \leftarrow X_i$ $\quad \left.\frac{\partial X_i}{\partial F_i}\right)_T$ $\quad \left.\frac{\partial X_i}{\partial F_i}\right)_S$

$\rightarrow B \leftarrow M$ $\quad \boxed{\left.\frac{\partial M}{\partial B}\right)_T}$ $\quad \boxed{\left.\frac{\partial M}{\partial B}\right)_S}$

$\textcircled{dX_i} = \left.\frac{\partial X_i}{\partial F_i}\right)_T \textcircled{dF_i}$

If you change your thermodynamic system these definitions will change. For example, for any arbitrary thermodynamic system if you have F i as the generalized force, and the conjugate generalized coordinate is this well one should say the other way around.

The generalized coordinate is X i and the corresponding generalized force is F I, then one can of course, ask del X i del F i and this experiment one can do either keeping the temperature fixed for an isothermal process or one can define it as del X i del F i by keeping the entropy fixed right.

For if you look for other example for example, for a magnetic system you have magnetization as the, coordinate thermodynamic coordinate and magnetic field as the force in which case you essentially have del M del B temperature constant and del M del B this quantity is called the magnetic susceptibility.

This is adiabatic susceptibility this is isothermal susceptibility, typically in experiments it is always this quantity the isothermal compressible susceptibility which is which essentially plays a role right. So, for hydrostatic system these are essentially susceptibilities.

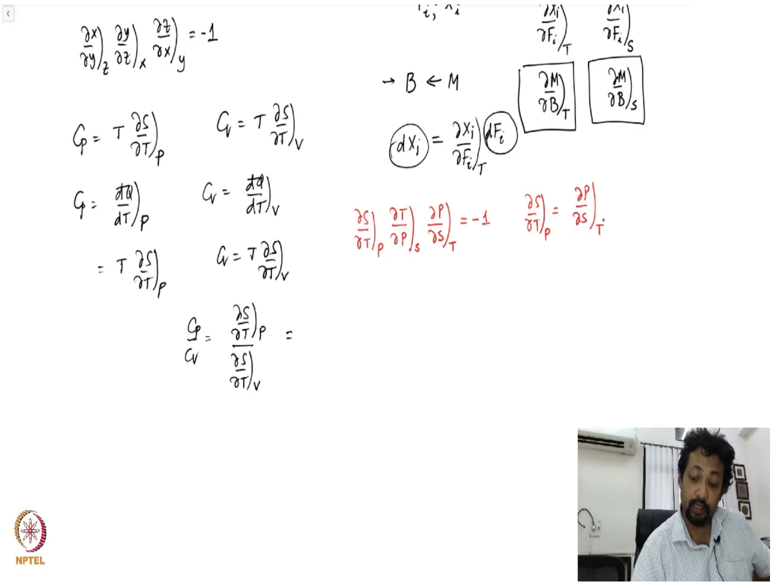
How does your generalized coordinate behave if you change your generalized force right? So, if you want to write down for any isothermal process in an any isothermal process, for such a system or for any arbitrary. Let us say for any arbitrary system if you want to write down d X i how your generalized coordinate has changed, then essentially you write it down as del F i temperature fixed d F i.

So, this is how your thermodynamic coordinate should change if you change your thermodynamic forces. So, you see partial derivatives are all around in thermodynamics and one needs to know how to manipulate such derivatives, Jacobians are of course, a very good way of doing that on top of the Jacobians.

So, number 1 is you can use the Jacobians, the second quantity that you frequently use is the cyclic relation, do not forget that. What does a cyclic relation say? Del x del y z constant del y del z x constant. And then you have del z del x y constant must be minus 1.

So, one frequently replaces x, y, z according to the quant relations one wants to find out. So, now, coming back to this, I want to find out the ratio of C P over C V. C P is defined as T del S del T pressure constant and C V is defined as T del S del T volume constant. If you want to know how do they come, well C P is d cut Q over d T pressure constant.

(Refer Slide Time: 06:50)



$$\left.\frac{\partial x}{\partial y}\right)_z \left.\frac{\partial y}{\partial z}\right)_x \left.\frac{\partial z}{\partial x}\right)_y = -1$$

$$\left.\frac{\partial x_i}{\partial F_i}\right)_T \qquad \left.\frac{\partial x_i}{\partial F_i}\right)_S$$

$$\rightarrow B \leftarrow M \qquad \boxed{\left.\frac{\partial M}{\partial B}\right)_T} \qquad \boxed{\left.\frac{\partial M}{\partial B}\right)_S}$$

$$dx_i = \left.\frac{\partial x_i}{\partial F_i}\right)_T dF_i$$

$$C_P = T \left.\frac{\partial S}{\partial T}\right)_P \qquad C_V = T \left.\frac{\partial S}{\partial T}\right)_V$$

$$C_P = \left.\frac{dQ}{dT}\right)_P \qquad C_V = \left.\frac{dQ}{dT}\right)_V$$

$$= T \left.\frac{\partial S}{\partial T}\right)_P \qquad C_V = T \left.\frac{\partial S}{\partial T}\right)_V$$

$$\frac{C_P}{C_V} = \frac{\left.\frac{\partial S}{\partial T}\right)_P}{\left.\frac{\partial S}{\partial T}\right)_V} =$$

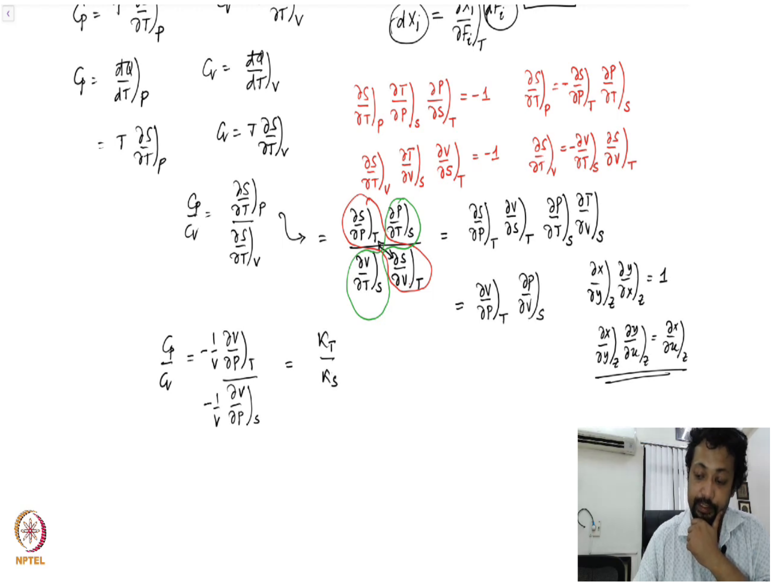
$$\left.\frac{\partial S}{\partial T}\right)_P \left.\frac{\partial T}{\partial P}\right)_S \left.\frac{\partial P}{\partial S}\right)_T = -1 \qquad \left.\frac{\partial S}{\partial T}\right)_P = \left.\frac{\partial P}{\partial S}\right)_T$$

And C V is d cut Q over d T volume constant and d cut Q from second law of thermodynamics is T d S and therefore, you have del S del T pressure constant. And this one you have T del S del T volume constant. So, clearly the ratio of C P over C V is del S del T pressure constant divided by del S del T volume constant.

There are several ways of finding it out I want to illustrate the cyclic use of the cyclic relations here I have S, derivative of S entropy with respect to temperature pressure mean health constant. So, I want to use x as S, I want to replace in the periodic in the cyclic relation, I want to replace x by S, y by T and z by pressure; that means, this gives me let me just use the color here.

Del S del T pressure constant, then you have del T del P entropy constant and then you have del P del S temperature constant is equal to minus 1. So, therefore, you get del S del T pressure constant is equal to del P del S temperature constant, divided by let us see.

(Refer Slide Time: 08:33)



$$C_p = \frac{dQ}{dT}\Big)_P \qquad C_v = \frac{dQ}{dT}\Big)_V$$

$$= T\frac{\partial S}{\partial T}\Big)_P \qquad C_v = T\frac{\partial S}{\partial T}\Big)_V$$

$$(dX_i) = \frac{\partial X_i}{\partial F_i}\Big)_T (dF_i)$$

$$\frac{\partial S}{\partial T}\Big)_P \frac{\partial T}{\partial P}\Big)_S \frac{\partial P}{\partial S}\Big)_T = -1 \qquad \frac{\partial S}{\partial T}\Big)_P = -\frac{\partial S}{\partial P}\Big)_T \frac{\partial P}{\partial T}\Big)_S$$

$$\frac{\partial S}{\partial T}\Big)_V \frac{\partial T}{\partial V}\Big)_S \frac{\partial V}{\partial S}\Big)_T = -1 \qquad \frac{\partial S}{\partial T}\Big)_V = -\frac{\partial V}{\partial T}\Big)_S \frac{\partial S}{\partial V}\Big)_T$$

$$\frac{C_p}{C_v} = \frac{\frac{\partial S}{\partial T}\big)_P}{\frac{\partial S}{\partial T}\big)_V} = \frac{\frac{\partial S}{\partial P}\big)_T \frac{\partial P}{\partial T}\big)_S}{\frac{\partial V}{\partial T}\big)_S \frac{\partial S}{\partial V}\big)_T} = \frac{\partial S}{\partial P}\Big)_T \frac{\partial V}{\partial S}\Big)_T \frac{\partial P}{\partial T}\Big)_S \frac{\partial T}{\partial V}\Big)_S$$

$$= \frac{\partial V}{\partial P}\Big)_T \frac{\partial P}{\partial V}\Big)_S$$

$$\frac{\partial x}{\partial y}\Big)_z \frac{\partial y}{\partial x}\Big)_z = 1$$

$$\frac{\partial x}{\partial y}\Big)_z \frac{\partial y}{\partial u}\Big)_z = \frac{\partial x}{\partial u}\Big)_z$$

$$\frac{C_p}{C_v} = \frac{-\frac{1}{V}\frac{\partial V}{\partial P}\big)_T}{-\frac{1}{V}\frac{\partial V}{\partial P}\big)_S} = \frac{K_T}{K_S}$$

We want to write down temperature. So, del S del P temperature constant times, del P del T entropy constant with a minus sign. Similarly, for this I want to again use the cyclic relation volume. So, del T del V entropy constant and then you have del V del T, sorry I have already used that del V.

So, T has come once, V has come, sorry T has come twice, V has come twice this has to be del V del S temperature constant is equal to minus 1, which means del S del T volume constant is del V del T entropy constant, del S del V temperature constant with a minus sign.

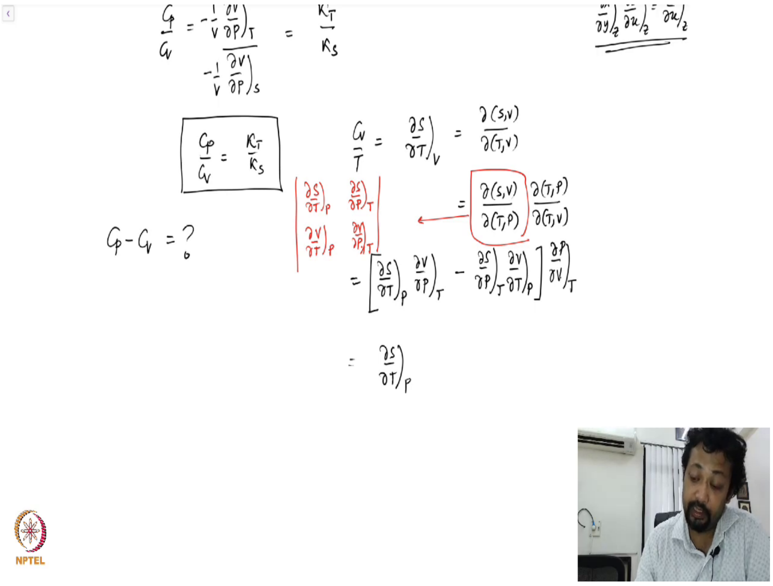
Therefore, this ratio is now, this ratio is now del S del P temperature constant, del P del T entropy constant divided by del V del T entropy constant del S del V temperature constant. Now, the minus sign has cancelled out. So, let us collect terms with the fixed quantities, del S del P temperature constant and then I have del V del S temperature constant, these two terms can be grouped together.

This can be grouped together because they have the temperature fixed in both the cases. And similarly these two can be grouped together because they have the entropy fixed. So, therefore I have del P del T entropy constant times del T del V entropy constant. This I know del S del P del V del S is del V del P temperature constant. And this is if you are careful to see entropy is held constant, this is del P del V entropy constant.

Remember what we are using now is del x del y z constant, this is the reciprocal relation del y del x z constant is equal to 1, right. Therefore, C p and C v is equal to [FL]. So, you can also say that del x del y z constant, del y del u z constant is actually, del x del u z constant.

This is also what we are using over here. Now, it follows therefore, that the first term is del V del P temperature constant divided by I have del V del P entropy constant. Let us rearrange and put bring in a minus 1 by V and you will see that this is kappa T over kappa S.

(Refer Slide Time: 12:35)



So, the ratio of the two specific heats C P over C V irrespective of the system is equal to kappa T over kappa S right. So, this is how you keep manipulate partial derivatives. What about this quantity C P minus C V, the celebrated relation that you found out and start, I want to derive the general expression for this. So, for this let us start off with C V over T.

Now C V over T is del S del T volume constant, which I write as del S comma V, del T comma V right there is no problem in writing that I will arrange this, rearrange this Jacobian to introduce del T del P del T comma P del T comma V right. It is the first one, the second one I know what it is.

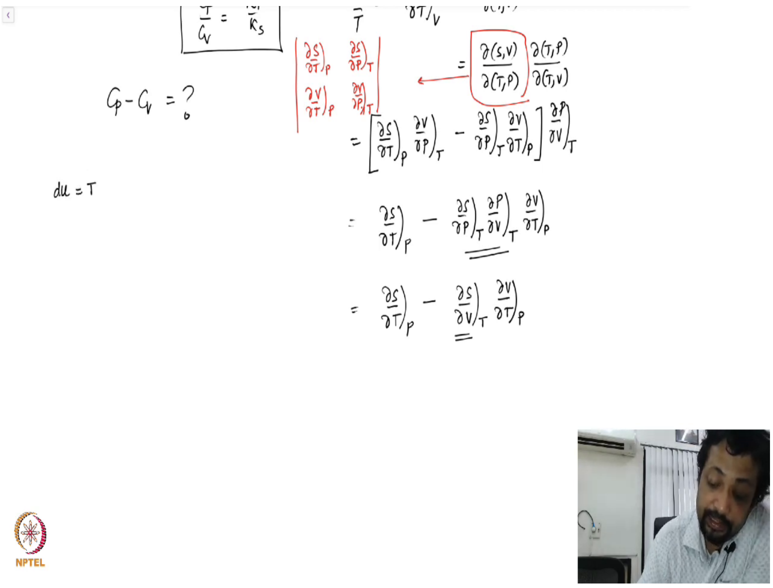
So, first one is del S del T pressure constant. See I am little bit carefully introducing the pressure because I want to relate C P and C V what I have got in the left hand side is C V by

T, I want the right hand side to be C P by T, which is del S del T pressure constant. Therefore, I have brought in T and P that is how the original thought process was.

So, del S del T pressure constant this is if you want to evaluate this Jacobian then, if you want to evaluate this Jacobian, then this Jacobian has a very simple form del S del T pressure constant del S del P temperature constant. Then I have del V del T pressure constant, del V del P temperature constant the determinant of this.

So, then if I evaluate this determinant I write down del S del P pressure constant, del V del P temperature constant minus del S del P temperature constant, del V del T pressure constant and this one I have del P del V temperature constant. So, life is very very simple now. What I have in the left hand side is del S del T, if I open the bracket this multiplies with this and if you use this relation over here.

(Refer Slide Time: 15:27)



$$C_p - C_v = ?$$

$$du = T$$

$$\begin{vmatrix} \left.\frac{\partial S}{\partial T}\right)_P & \left.\frac{\partial S}{\partial P}\right)_T \\ \left.\frac{\partial V}{\partial T}\right)_P & \left.\frac{\partial V}{\partial P}\right)_T \end{vmatrix} \leftarrow \boxed{\frac{\partial(S,V)}{\partial(T,P)}} \frac{\partial(T,P)}{\partial(T,V)}$$

$$= \left[\left.\frac{\partial S}{\partial T}\right)_P \left.\frac{\partial V}{\partial P}\right)_T - \left.\frac{\partial S}{\partial P}\right)_T \left.\frac{\partial V}{\partial T}\right)_P\right] \left.\frac{\partial P}{\partial V}\right)_T$$

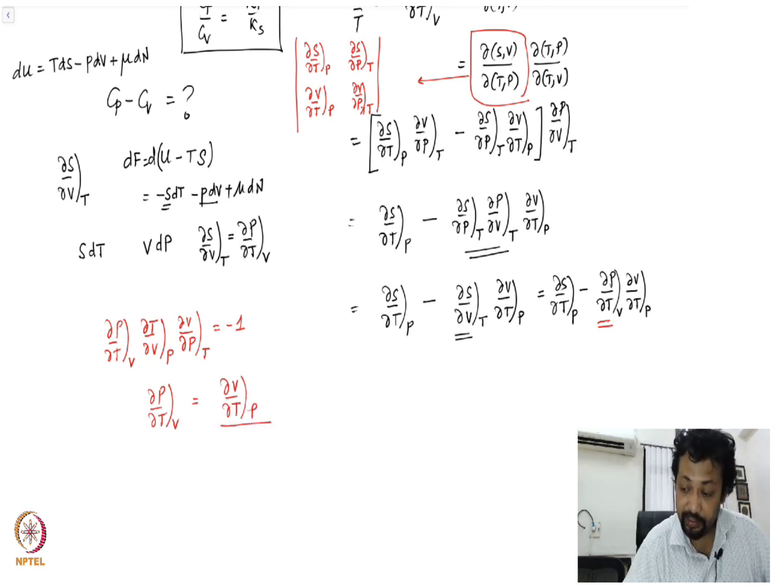
$$= \left.\frac{\partial S}{\partial T}\right)_P - \underline{\underline{\left.\frac{\partial S}{\partial P}\right)_T \left.\frac{\partial P}{\partial V}\right)_T}} \left.\frac{\partial V}{\partial T}\right)_P$$

$$= \left.\frac{\partial S}{\partial T}\right)_P - \underline{\underline{\left.\frac{\partial S}{\partial V}\right)_T}} \left.\frac{\partial V}{\partial T}\right)_P$$

Then essentially I have del S del T pressure constant minus del S del P temperature constant del P del V temperature constant. Del V del T pressure constant right, this is del S del V temperature constant del V del T pressure constant. So, let us see do I have anywhere del S del V, which I can use.

All I have to figure out is what is this derivative right. So, for this I have S, V. I want to now see here comes the utility of the Maxwell's relation. I want to figure out if there is a Maxwell relation that relates this derivative with something else.

(Refer Slide Time: 16:52)



$du = TdS - PdV + \mu dN$

$C_P - C_V = ?$

$\left.\frac{\partial S}{\partial V}\right)_T$

$dF = d(U - TS)$

$= -SdT - PdV + \mu dN$

SdT VdP $\left.\frac{\partial S}{\partial V}\right)_T = \left.\frac{\partial P}{\partial T}\right)_V$

$\left.\frac{\partial P}{\partial T}\right)_V \left.\frac{\partial T}{\partial V}\right)_P \left.\frac{\partial V}{\partial P}\right)_T = -1$

$\left.\frac{\partial P}{\partial T}\right)_V = \left.\frac{\partial V}{\partial T}\right)_P$

$$\begin{vmatrix} \left.\frac{\partial S}{\partial T}\right)_P & \left.\frac{\partial S}{\partial P}\right)_T \\ \left.\frac{\partial V}{\partial T}\right)_P & \left.\frac{\partial V}{\partial P}\right)_T \end{vmatrix} \leftarrow = \boxed{\frac{\partial(S,V)}{\partial(T,P)}} \frac{\partial(T,P)}{\partial(T,V)}$$

$$= \left[\left.\frac{\partial S}{\partial T}\right)_P \left.\frac{\partial V}{\partial P}\right)_T - \left.\frac{\partial S}{\partial P}\right)_T \left.\frac{\partial V}{\partial T}\right)_P\right] \left.\frac{\partial P}{\partial V}\right)_T$$

$$= \left.\frac{\partial S}{\partial T}\right)_P - \left.\frac{\partial S}{\partial P}\right)_T \left.\frac{\partial P}{\partial V}\right)_T \left.\frac{\partial V}{\partial T}\right)_P$$

$$= \left.\frac{\partial S}{\partial T}\right)_P - \left.\frac{\partial S}{\partial V}\right)_T \left.\frac{\partial V}{\partial T}\right)_P = \left.\frac{\partial S}{\partial T}\right)_P - \left.\frac{\partial P}{\partial T}\right)_V \left.\frac{\partial V}{\partial T}\right)_P$$

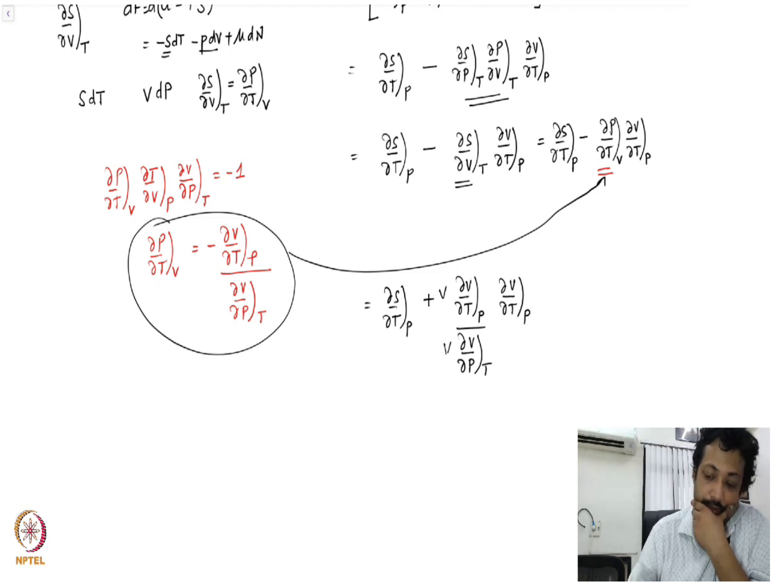
But this structure of this derivative. So, if you just look at the structure del S del V temperature constant, this immediately tells you that I have S d T correct, then I have V dP. So, what is then I have to figure out which one I can use. So, if I just look at d F, which is U minus T S is d of U minus T S is minus S d T, recall your first law again d U is equal to T d S minus P d V plus mu d N.

So, d U minus T d S, if you bring it in this side it is minus P d V plus mu d N. So, now, you see if I want to write down the Maxwell's relation for this two, I have del S del V temperature held constant is equal to del P del T volume held constant. So, this is how we go back and forth from the derivative what you have structure of your partial derivative, you have to figure out whether there exist a Maxwell relation.

So, I can clearly see my Maxwell relation tells me that the del S del V temperature constant is del P del T. So, I will do I will simply replace this by del P del T volume constant, del V del T pressure constant right. What is del P del T volume constant? This is still a quantity which I have to figure out, but then let us apply the cyclic rule.

del P del T volume constant, del T del V pressure constant, del V del P temperature constant is a minus 1. So, del P del T volume constant is del V del T pressure constant divided by del V del P temperature constant with a minus sign in front. So, then I use this relation over here.

(Refer Slide Time: 19:14)



$$\left.\frac{\partial S}{\partial V}\right)_T \qquad dF = d(U - TS)$$

$$= -SdT - pdV + \mu dN$$

$$SdT \qquad VdP \qquad \left.\frac{\partial S}{\partial V}\right)_T = \left.\frac{\partial P}{\partial T}\right)_V$$

$$= \left.\frac{\partial S}{\partial T}\right)_P - \left.\frac{\partial S}{\partial P}\right)_T \left.\frac{\partial P}{\partial V}\right)_T \left.\frac{\partial V}{\partial T}\right)_P$$

$$= \left.\frac{\partial S}{\partial T}\right)_P - \left.\frac{\partial S}{\partial V}\right)_T \left.\frac{\partial V}{\partial T}\right)_P = \left.\frac{\partial S}{\partial T}\right)_P - \left.\frac{\partial P}{\partial T}\right)_V \left.\frac{\partial V}{\partial T}\right)_P$$

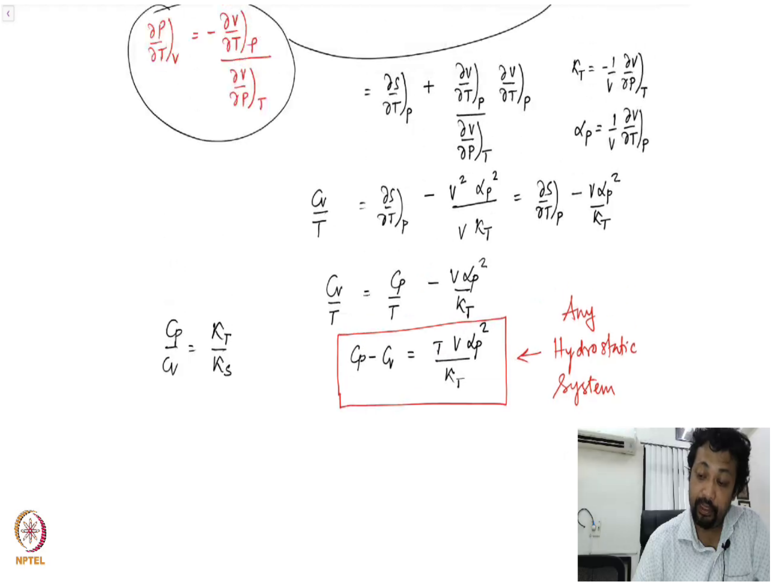
$$\left.\frac{\partial P}{\partial T}\right)_V \left.\frac{\partial T}{\partial V}\right)_P \left.\frac{\partial V}{\partial P}\right)_T = -1$$

$$\left.\frac{\partial P}{\partial T}\right)_V = -\frac{\left.\frac{\partial V}{\partial T}\right)_P}{\left.\frac{\partial V}{\partial P}\right)_T}$$

$$= \left.\frac{\partial S}{\partial T}\right)_P + \frac{V\left.\frac{\partial V}{\partial T}\right)_P}{V\left.\frac{\partial V}{\partial P}\right)_T} \left.\frac{\partial V}{\partial T}\right)_P$$

So, this means, this is del S del T pressure constant minus del V del T pressure constant divided by del V del P temperature constant times del V del T pressure constant, this becomes a plus. It is here that I have to figure out something. So, what I do here is, I multiply this by volume divide this by volume right. So, now, if I have to multiply by V square here.

(Refer Slide Time: 20:25)



$$\left.\frac{\partial P}{\partial T}\right)_V = -\frac{\left.\frac{\partial V}{\partial T}\right)_P}{\left.\frac{\partial V}{\partial P}\right)_T}$$

$$= \left.\frac{\partial S}{\partial T}\right)_P + \frac{\left.\frac{\partial V}{\partial T}\right)_P}{\left.\frac{\partial V}{\partial P}\right)_T}\left.\frac{\partial V}{\partial T}\right)_P$$

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_T$$

$$\alpha_P = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right)_P$$

$$\frac{C_V}{T} = \left.\frac{\partial S}{\partial T}\right)_P - \frac{V^2\alpha_P^2}{V\kappa_T} = \left.\frac{\partial S}{\partial T}\right)_P - \frac{V\alpha_P^2}{\kappa_T}$$

$$\frac{C_V}{T} = \frac{C_P}{T} - \frac{V\alpha_P^2}{\kappa_T}$$

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}$$

$$\boxed{C_P - C_V = \frac{T V \alpha_P^2}{\kappa_T}} \leftarrow$$

Any Hydrostatic System

Now, you see kappa T is minus 1 by V, del V del P temperature constant and alpha P, what did I define the response function here. Let us see yeah sorry this has to be alpha P because you are taking a derivative with respect to temperature. So, this has to be alpha P. Please be careful because you are taking a derivative with respect to temperature.

So, temperature cannot be held constant there. So, del V del T pressure constant right. So, this is del S del T pressure constant minus V square alpha P square divided by V kappa T right which is equal to del S del T pressure constant minus V alpha P square over kappa T.

The left hand side was C V by T. If you look at this structure of this the first term is actually C P by T. So, C P by T is minus V alpha P square over kappa T. It follows therefore; C P minus C V is T, V alpha P square over kappa T. This is the general relation for any hydrostatic system whether it is an ideal gas or a non-ideal gas, you should always have this relation.

So, there are two essential relation, what one is C P over C V, which I saw, we saw was kappa T over kappa S, the other one is C P minus C V. So, if you know these response functions you also know the specific heats correct.