Statistical Mechanics
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Lecture – 12
Working with Thermodynamics

So, we have seen the utility of Maxwell's relations, we have seen the utility of Jacobians and we have seen how to manipulate partial derivatives. We want to carry forward that same discussion now in and explicitly or rather illustrate how to tackle Thermodynamic systems or the thermodynamic processes.

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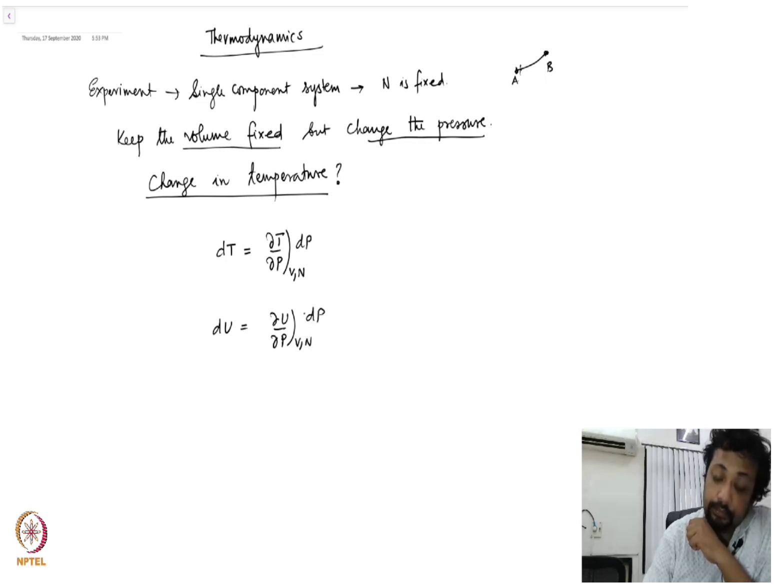

So, typically in thermodynamics one as we have seen that one deals with processes and one often will encounter partial derivatives this is inevitable in thermodynamics. For example, in an experiment let us say you have a single component system. You will say hydrostatic system only that is the easiest or that is the best example that we can have. Here, N the particle number is fixed ok.

Now, suppose you keep the volume fixed, but change the pressure and you want to find out how much change in the temperature there can be, right. So, what I am required to find out is change in temperature. See all of these quantities are experimentally measurable quantities and which means accessible experimentally.

So, I want to find out d T. So, one can imagine that I have taken the system from A to B let us say in a quasi static way where I have kept the volume fixed, but I have changed the pressure. So, I want to figure out how much change in the temperature there is.

For this I will imagine first an infinitesimal step I have taken on this path from going from A to B and I want to change this incremental change infinitesimal change d T and that for me is going to be del T del P; because I am changing the pressure, but keeping the volume and particle number fixed times d P. One can asks how much internal energy is going to change.

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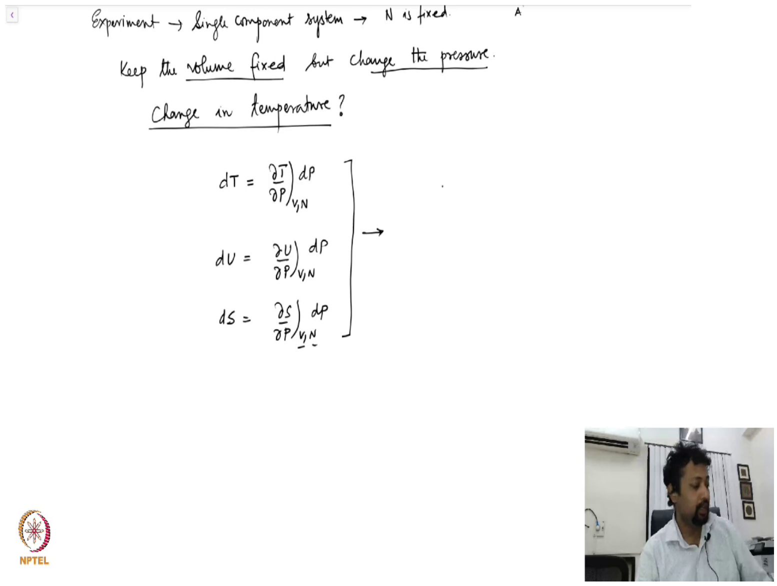

What would be the entropy change in such a case so on and so forth? A volume and particle number is having fixed. So, you see all of these you can very easily understand if you have a grip over manipulating partial derivatives say inevitable in thermodynamics absolutely inevitable, right. So, what we want to do here is, we want to give you some examples some illustrative examples. Always remember I mean where one can see how to do these things.

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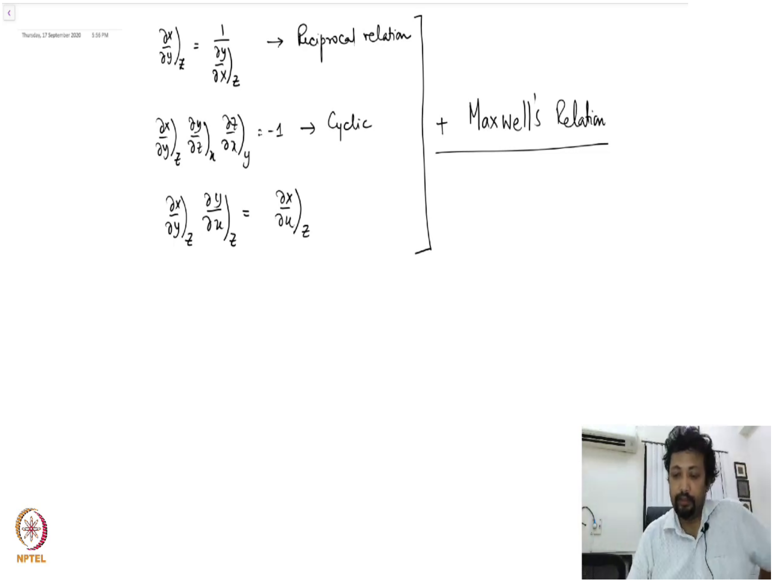

Always remember the relations that we typically use if z is held constant is 1 over del y del x z this is your reciprocal relation and then you have del x del y z constant, del y del z x constant, del z del x y constant is minus 1. This is what is called cyclic relation.

And finally, if you have del x del y z constant and then you have del y del u z constant by chain of this is z constant. This is chain rule of differentiation applied to partial derivatives; plus what is going to come to a rescue is called Maxwell's relation right.

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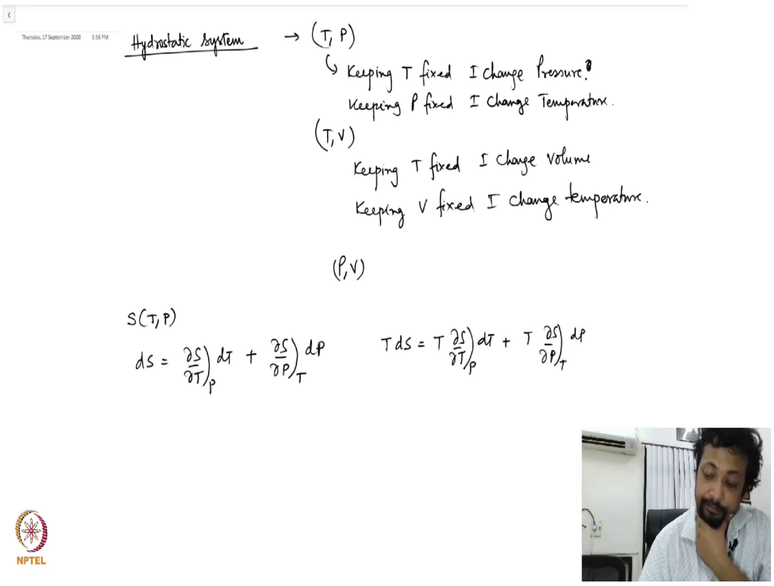

Now, first so, let us start. So, for example, if I am given for a hydrostatic system, I know the information about T and P. So, for example, it can be keeping T fixed I change pressure. It can be T and V once again keeping T fixed I change volume and here also keeping P fixed I change volume sorry, I change temperature keeping V fixed I change temperature.

So, several of these situations it can also be a function of P and V right. Let us take one of this see I can write down the entropy now as a function of T and P because this is the information that is given to me. So, it follows d S is del S del T pressure constant dT plus del S del P temperature constant d P, correct? And, therefore, T d S is equal to T del S del T pressure constant dT plus T del S del P temperature constant d P.

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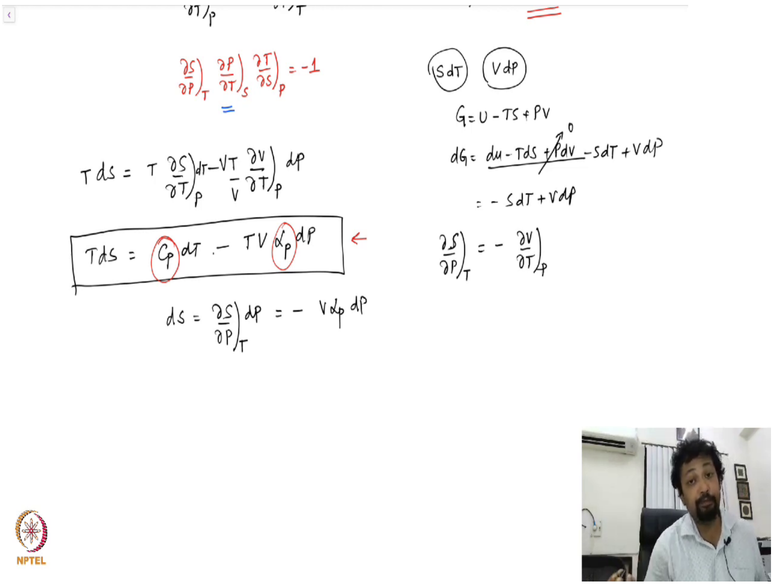

Now, I have to figure out how to evaluate this. So, one possible way of clearly evaluating this would be to write down del S del P temperature constant, del P del T entropy constant and then I have del T del S pressure constant as minus 1, correct? I can also try to figure out and then once again here I have to figure out what is del P del T entropy constant.

I can also try to see if there is a Maxwell relation corresponding to this. So, if I look at the structure of this derivative then I have del S del P temperature constant. So, I have S d T and the derivative is with respect to a pressure. So, therefore, I have d P V d P. So, I have to figure out a combination free energy which has whose differential has this combination.

If you look at U minus TS plus PV then d G is du minus T d S plus P d V n is held fixed. So, will not worry about n minus S d T plus V d P this by first law is 0. So, minus S d T plus V d

P therefore, del S del P temperature constant del S del P temperature is constant is minus del V del T pressure constant.

So, your T d S is T del S del T pressure constant minus T del V del T pressure constant d P, correct. So, one can divide by volume here and bring a volume on top to give you C P sorry, there is a dT here T del S delta is C P dT minus TV alpha P d P. So, your first law completely written down in terms of material parameters if you know the temperature dependence of specific heat with and the pressure dependence of compressive expansion coefficient then you know the answer.

Now, I am asking you that if you want to measure for example, for this particular case when S is a function of T d S change in entropy is del S del P. Let us say if d T is fixed isothermal process it is just del S del P temperature constant d P which is minus T V alpha P d P, simple T. Sorry, the T is going to go away because T T cancels on both sides.

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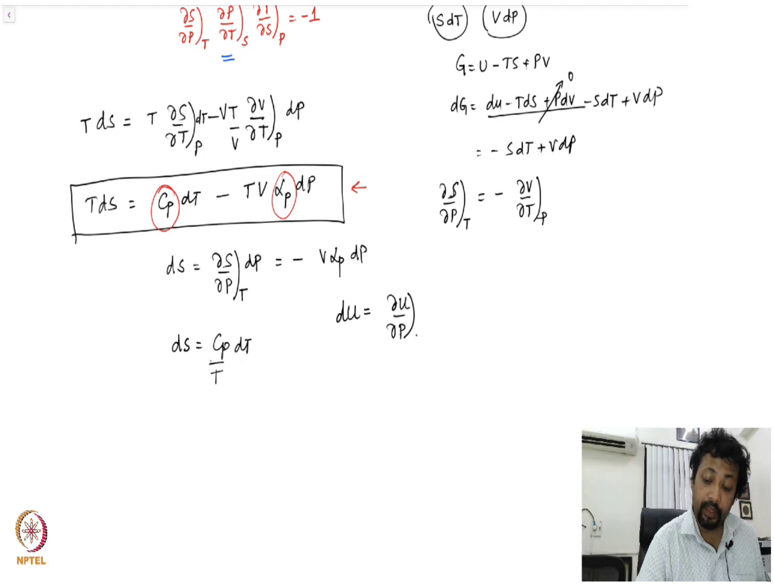

If you want to say that look I have kept my pressure fixed I want to measure the change in entropy if my temperature doubles as it goes from state a to state b then answer is C P by T d T that is it because you have set d P equal to 0, correct.

The more general, if you allow for both pressure and temperature this is going to be the case. u if I want to measure du, then it is going to be del u del P. So, du is T d S plus P d V, but there is no volume here.

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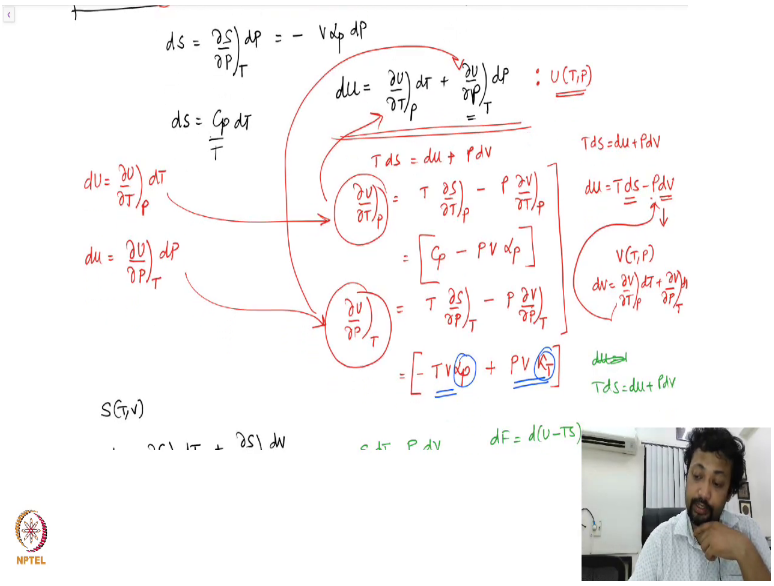

So, we will simply write down del u del T pressure constant d T plus del u del V sorry, del u del P temperature constant d P and again here one has to figure out what is going to be del u del P temperature constant.

So, let us see. I have T d S is equal to du plus P d V, correct? So, I want to figure out del U del T pressure constant. del U del T pressure constant is T del S del T pressure constant plus P del V del T pressure constant. Sorry, it is minus this goes over here minus, but T del S del T is pressure constant is C P minus P V alpha P.

Similarly, del U del P temperature constant is T del S del P temperature constant minus P del V del P temperature constant. Again, I know what del S del P temperature constant is this is just going to be minus T V alpha P minus plus P V kappa T.

So, once you know both of these, you can clearly replenish them over here to figure out the change in temperature, right. So, if you say look I want to keep the pressure fixed then d U is del U del T and I have changed the temperature d T which here is the this relation will be used.

If you want to say look I have kept the temperature fixed I want to measure the change in the energy as the pressure is doubled you are going to use this. This relations are only with respect to your response functions been kappa T alpha P, they are not specific for any system right. What about the second case? In the second case that we discussed or that we started of discussing was T and V.

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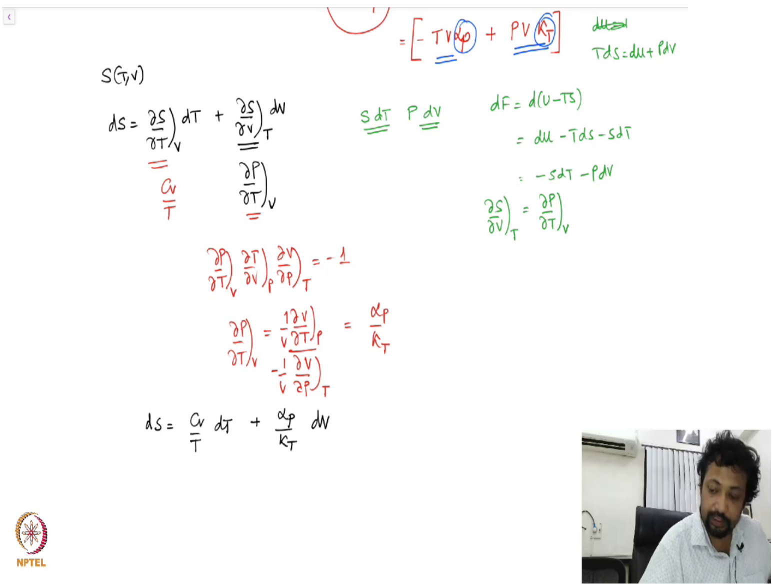

Here again you can write down S as a function of T and V and d S is del S del T volume constant dT plus del S del V temperature constant d V this part is very easy. This is the part which is very easy; this is C V by T at this part that we have to figure out.

So, now, again I look at the structure of this relation and you see S and V let us see if I can figure out a Maxwell's relation. So, this means I have S d T and P d V, correct. So, S dT and P d V the combination appears for Helmholtz free energy. d F is d of U minus TS. Again, n is always held fixed here.

So, we will not worry about that d u minus T d S minus S d T which is minus S d T and du minus T d S is essentially minus P d V; because your first law is du is T d S is du plus d V nu dn vn is 0 therefore, we do not worry about it and therefore, it follows that del S del V temperature constant is del P del T volume constant variance. So, this from now I have del P del T volume constant.

It is still not yet finished, but I know how tomanipulate this derivative there is yet another step that is involved here I use the cyclic identity del P del T volume constant, del T del V pressure constant, del V del P temperature constant is minus 1. So, always remember del P del T volume constant is equal to del V del T pressure constant del V del P temperature constant.

In both cases I divide by V there is a minus sign in front sorry, we will not put the minus sign there, but rather we will put the minus sign here because that is how we define the compressibility. So, this is alpha P by kappa T. So, therefore, your entropy equation now becomes d S is C V by T dT plus alpha P by kappa T sorry d V.

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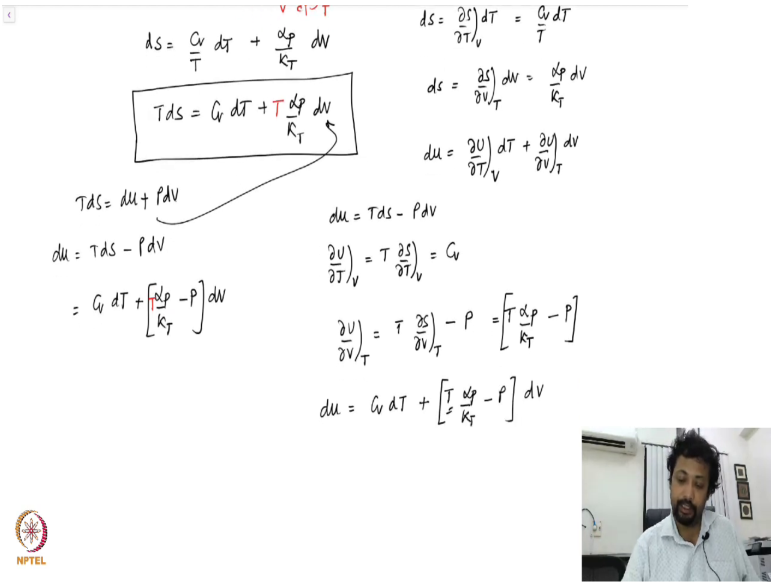

So, T d S is C V d T plus alpha P over kappa T; clearly if I want to find out the change in entropy. If V is held constant, but the temperature changes then my change in entropy is del S del T volume constant V is being held constant d T, correct? And the temperature doubles which is essentially C V by T d T.

If I hold the temperature fixed and the volume the information that is given to me that the volume doubles I want to find out the change in entropy this is going to be del S del V temperature constant d V which is alpha P over kappa T times d V right.

du again here is del U del T. I am looking at T and V volume what did we do here ok? So, del U del T volume held constant d T plus del U del V temperature held constant d V, correct? So, du is T d S minus P d V. So, del U del T volume held constant is T del S del T volume held constant is the specific heater constant volume and del U del V temperature held constant is equal to T del S del V temperature held constant minus P.

But, we just now calculated del S del V right, we calculated del S del V temperature held constant is equal to del P del T volume held constant and therefore, this is equal to alpha P over kappa T, T times this minus P, right. So, if you put it over here. In fact, you can get these relations always from the first law also.

So, if you put it over here du is C V d T plus del U del V temperature constant is T alpha P over kappa T minus P d V because you know the T d S is du minus P plus P d V. So, this becomes here it becomes just adds to this, but I should have a somewhere plus sign because this is du is T d S minus P d V which is equal to C V d T plus alpha P over kappa T minus P d V. This T factor should not come anywhere. So, one has to check right.

So, there has to be a T factor here the T factor comes in when you are multiplying throughout by T. So, this is correct T alpha P kappa T minus P. So, it is consistent. Just a remark, the way we have done this part where we have calculated this and I shown that U as a function here it assumes that U as a function of T and P in the earlier.

So, this is the example where we assume that S is a function of T and P and then we went on to calculate U as a function of T and P, I just want to say that here I have essentially I can do the same calculation, I can arrive at the same result from the first law which is T d S is equal to d U plus P d V and d u is T d S minus P d V. I have the expression for T d S which I have derived over here, but I do not have d V; this is d V whereas, what I am interested in here is d P.

So, here then you do an additional step where you write down V as a function of T and P and then you write down d V is del V del T pressure constant d T plus del V del P temperature constant d P and you replace it over here and combine all of these expressions together, you are going to come up with the same expression that perhaps would be one of the exercises right. The final one I want to discuss and I want to discuss them very briefly where I am concerned about P and V S as a function of P and V.

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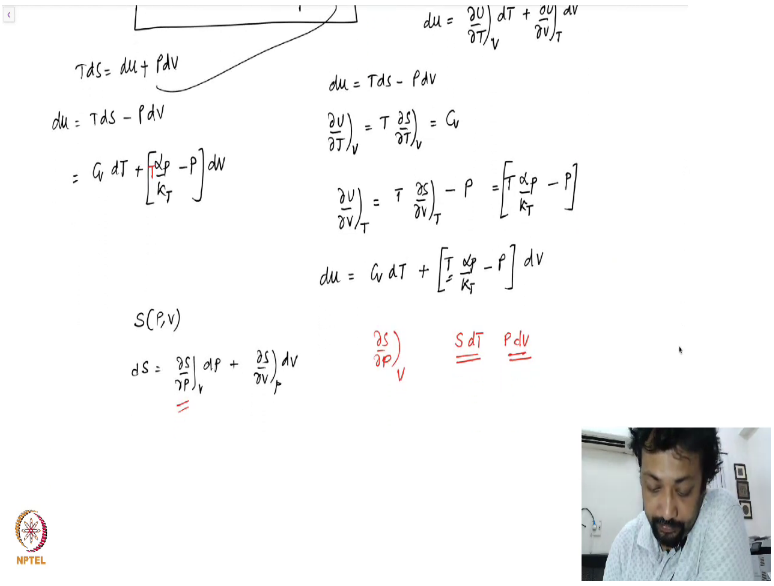

Here so, again d S is del S del P volume constant d P plus del S del V pressure constant d V. So, I have to now look at the structure of this relations del S del P volume constant. So, then I am looking for S and I am looking for P d V and d T.

See S always conjugates with T therefore, you should always have S d T and P d V and dimension of energy remember that because your first law is the crucial thing here. S d T P d V of course, the thing that comes to your mind is your free energy.

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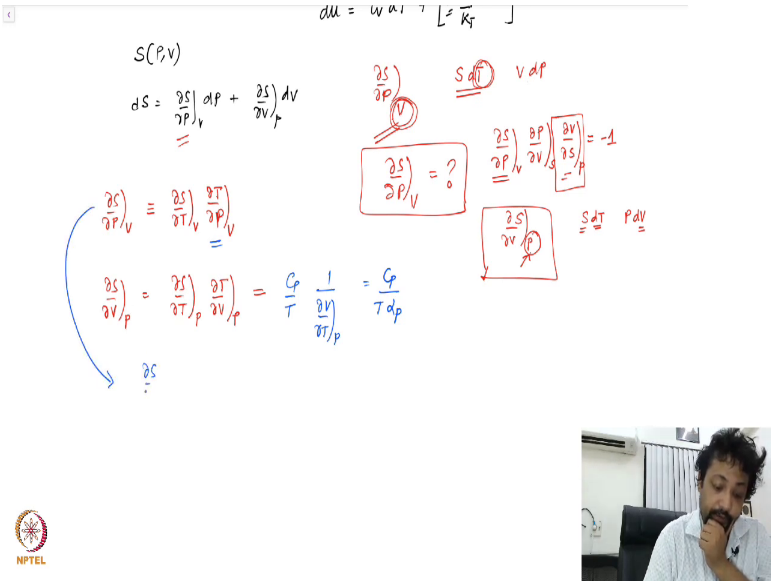

Here you cannot have I am sorry. This cannot be P d V then the derivative is with respect to volume this has to be V d P, but we have seen that right where did we see we when we looked at the Gibbs free energy? So, del S del P temperature constant is del V del T pressure constant. Do I have? I cannot do this.

So, del S del P now there is a volume which is constant here. So, this is kind of a very very strange derivative for which I cannot use any Maxwell's relation. So, then I have del S del P volume constant and I have to figure out how to do this. One possible way of trying it out is to del S del P volume constant del P del V entropy constant del V del S pressure constant is equal to minus 1.

So, you can relate del S del P with respect to del V del S, but here also you land up in trouble because this derivative is slightly strange why? Because you have del S del P for a derivative which is del S del V pressure constant. So, you cannot apply a Maxwell relation because you know your Maxwell relation must have I mean free corresponding free energy for which you want to derive such relation mass will always have P d V.

So, S derivative with respect to volume is usually the variable which is conjugate to S that is held fixed, but it is something else which is held fixed it is a pressure which is held fixed. So, there has is no easy way out for doing these things. So, how to proceed with these two quantities? It might look very very complicated things for at first, but you see del S del P volume constant this is equivalent to saying that I have del S del T volume constant del T del V sorry, del T del P volume constant.

Similarly, del S del V pressure constant is actually del S del T pressure constant del T del V pressure constant, correct? This part is straight forward del S del T pressure constant is just C P over T del T del V is 1 over we can write down this as del V del T pressure constant which is C P over T alpha P one of the response functions, but del P del T.

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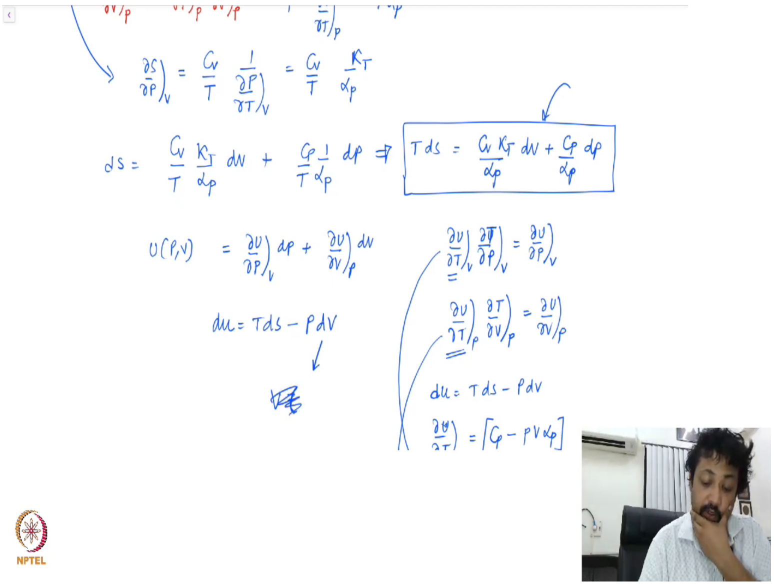

So, this one I can write down is del S del T volume constant is C V over T and this is del P del T volume constant, but look I have I know what del P del T volume constant is it is alpha P by kappa T; I can use this now. This is del P del T is alpha P over kappa T. So, this is C V over T 1 over alpha P kappa T.

So, d S is C V over T kappa T over alpha P d V plus C P over T alpha P d P or this implies T d S is equal to C V kappa T over alpha P d V plus C P over alpha P d P right. U as a function of P and V one can still do the exercise. Here I have del U del P volume constant d P plus del U del V pressure constant d V and here I want to use again del U del T volume constant del T del P volume constant is del U del P volume constant.

So, this one you know, this is C V. The other one is going to be del U del T pressure constant and then you have del T del V pressure constant is equal to del U del V pressure constant.

This is the one which is slightly more complicated, but we have already done that. We have done what if sorry this is del u del T pressure constant.

So, del U del T pressure constant is if you write down du as T d S minus P d V, then del U del T the pressure constant I think we did this before, right? Yeah, del U del T pressure constant is right over here it is C P minus P V alpha P.

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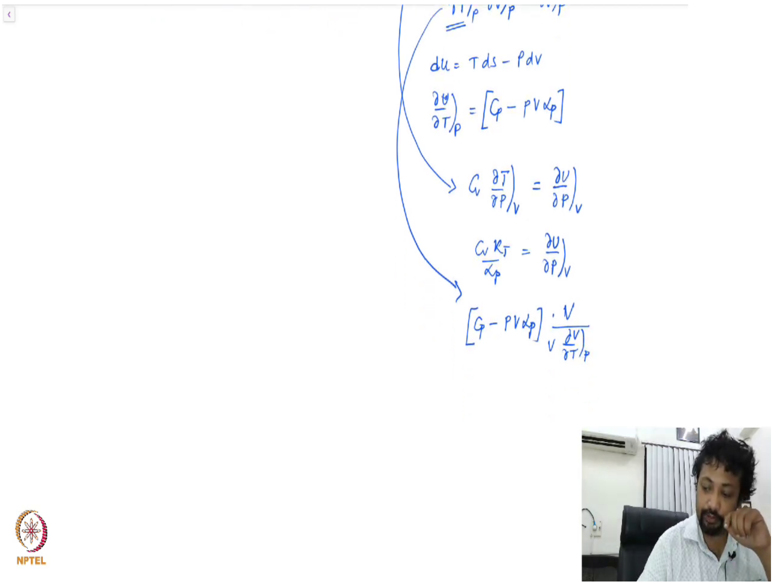

So, we can. So, this is C P minus P V and C P and this one straight forward I know this is going to be this is going to be C V del T del P volume constant is equal to del U del P volume constant, but del P del T we have again calculated here. We have again calculated del P del T volume constant as this alpha P over kappa T.

So, C V kappa T over alpha P is del U del P volume constant and here this becomes this relation now becomes del U del T pressure constant is C P minus P V alpha P times there has to be a volume is here. So, volume, volume del V del T pressure constant.

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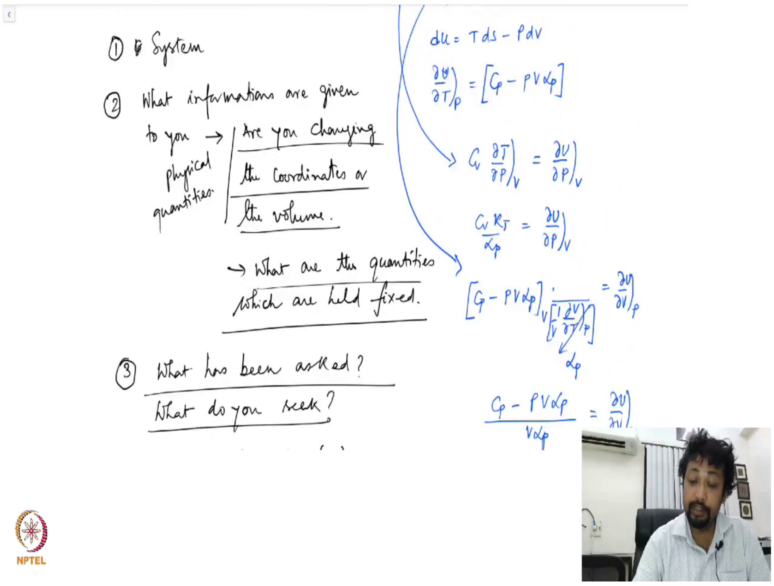

So, let us recast this slightly so, that it is more easy to manipulate is V 1 by V is equal to del U del V pressure constant this you know is alpha P. So, this is C P minus P V alpha P divided by V alpha P is del U del V pressure constant.

You can also calculate this relation from your first law because you know T d S, you know this equation and you also know du is T d S minus P d V and then here you simply write V is equal to a function of I want that is fine. I do not have to write anything here because it is already a function of volume. So, you will get the answers that you are looking for good.

So, now, you know how to manipulate partial derivatives in to calculating all these quantities, right. So, please understand that in dealing with thermodynamic processes pay attention to, number 1 - what is the system; number 2 – what information are given to you; which means are you changing the coordinates or the volume and what are the coordinates or let us say quantities which are held fixed?

So, read the question or whatever information must carry this are you changing the coordinate or the volume which means what are the physical quantities that are being changed? Are you changing the temperature? Are you changing the pressure? Are you changing your volume and then again what are the quantities which are held fixed?

Is it an adiabatic process? Is the entropy is being kept fixed? Is it an isothermal process? Is the temper; that means, the temperature is get fixed? Is it an isobaric process; that means, the pressure is kept fixed is it a isochoric process; that means, it is a; it is a volume which is get fixed? So, these information you must clearly find out.

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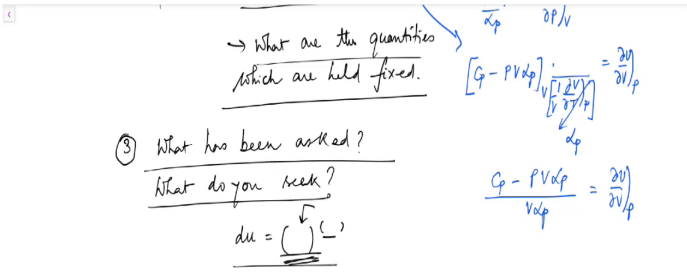

And, the last point is what has been asked? What do you seek? For example, do you seek the change in internal energy? Then you find out du is equal to with respect to what? A derivative with respect to the quantity that is being changed; in the sense that you seek to find out the how much the internal energy has changed if your temperature has doubled keeping the volume fixed or your pressure has halved keeping the temperature fixed.

So, all these things so, you have to figure out what do you see what has been asked. When you combine all these information's, then essentially everything now boils down to manipulating these partial derivatives this the ones that is going to come over here.

And there of course, you are going to use the three relations that we did. You are going to use this we did not have it here we are going to use the cyclic relation, you are going to use the reciprocity relation and you are going to use the chain rule of derivative and on top of it you are going to use the Maxwell’s relations and finally, the first law. All of this combined is going to give you the answer.