Statistical Mechanics
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Lecture – 10
Maxwell's Relation – Part III

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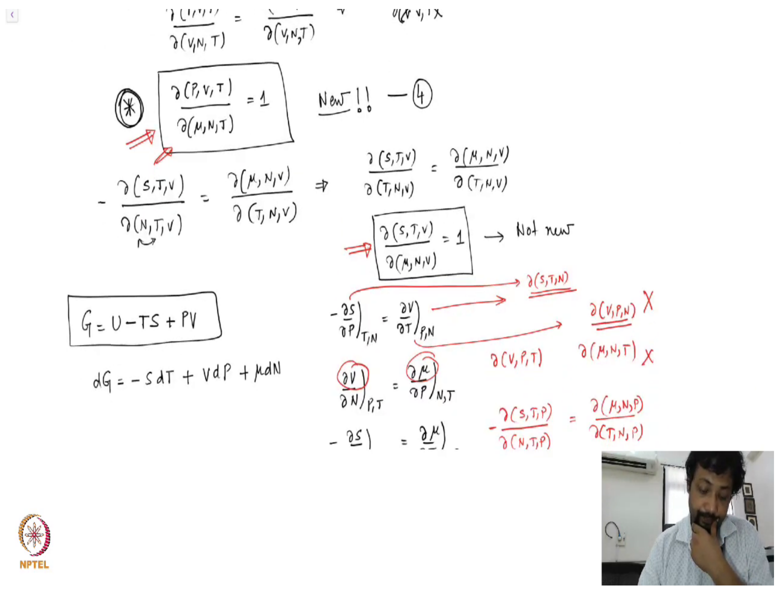

What about the Gibbs free energy? If you have forgotten, you can always start from scratch that tells you G is equal to U minus TS plus PV. So, G, and if I do dG, dG is going to be minus S dT. So, dU minus TdS plus PdV, I will be left out with minus dT SdT plus VdP.

And this is going to be this is going to be minus dN. So, let us dN is going to be plus mu dN. You can mentally do the differential here. The first term is going to be dU, then minus T dS. And then if you take a differential of one is a dV here, it should be PV.

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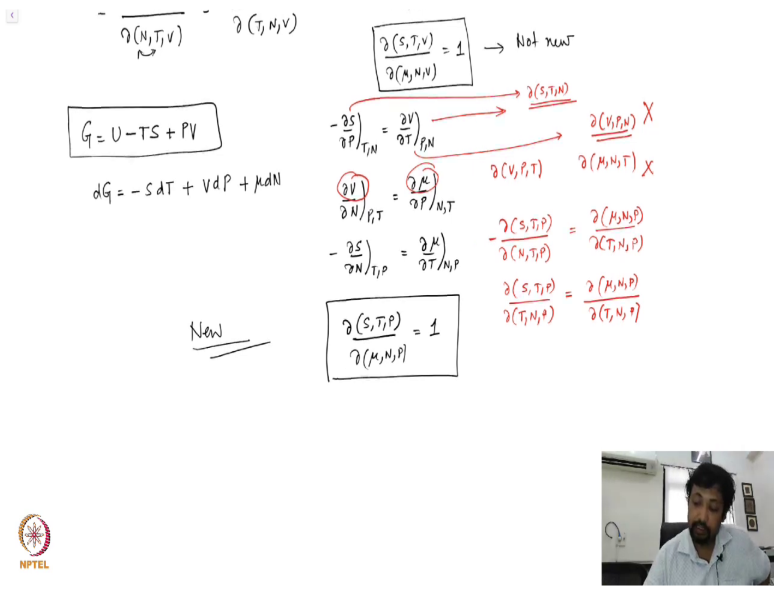

Then this becomes plus PdV. But dU plus P dV minus T dS is mu dN that is the first law. And what are the differentials you are left out with minus S d d T plus VdP that is all you have over here. So, this gives you three Maxwell's relation once again minus del S del P, your T and N constant is del V del T del V del T, P and N constant.

Then you have del V del N del V del N, P and T are held constant. And you see you have del mu del P, N and T are held constant. Finally, it is minus del S del N, T and P are held constant. This is del mu del T, N and P are held constant. Now, if you have followed the way we have derived all of this, then you can very easily check. If these three Maxwell's relations are giving any new of these three, the you have a new Maxwell's relation.

Look over here. Here for example, in the numerator the combination is del S, T, and N. And here so if you carefully look at this, this in the form of the Jacobean the numerator becomes here. And in the right hand side, you are going to have del of V, P and N. So, you are looking at a combination of a Maxwell's relation which will have del of S, T, N; and del of V, P, N. Have we derived that? Here.

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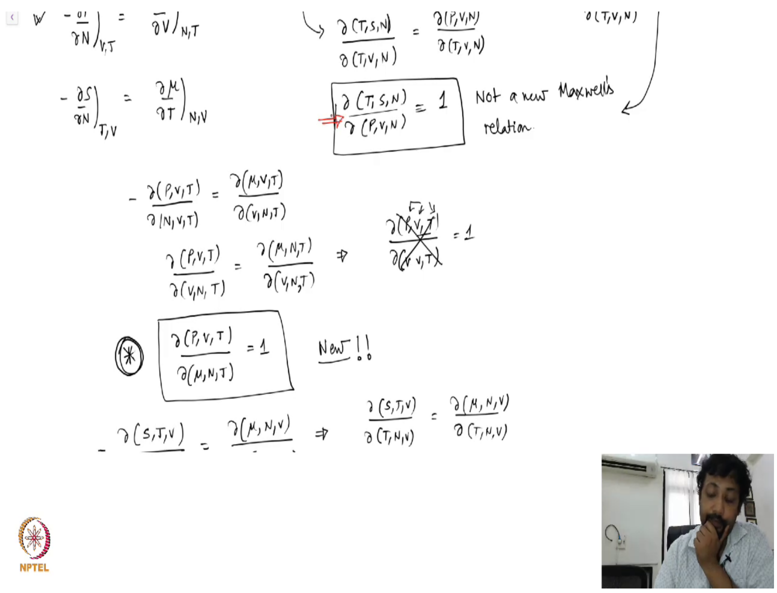

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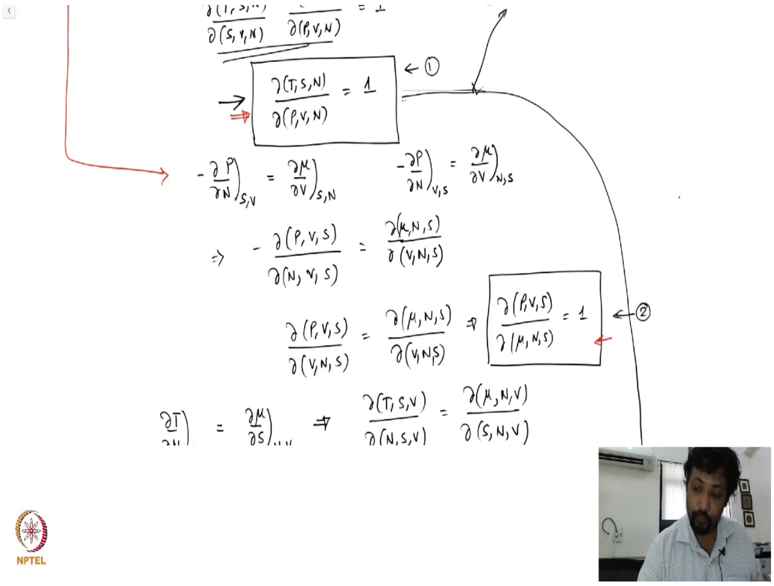

And again over here. So, clearly, however, where you write it down in the form of whenever you write it down in the form of a Jacobean, this will not give you a new Maxwell relation. What about this? This is again V, P and T – this part; and the right hand side will be mu, N and T, this part in the form of a Jacobean.

Do I have V, P and T? Over here. So, this one again does not give you a new Maxwell relation. What about this? This is S, T and P; and the left hand side is mu, N and P. Do I have S, T, P combination? I probably do not have this, but one should still check. No, so I do not have this.

So, let us then del of N, T comma P is equal to del of T comma N comma P with the minus sign here, the minus sign I am going to observe in the denominator to give you del of S, T comma P del of T, N, P is equal to del of mu, N, P and del of T, N, P. So, you come up with the new Maxwell’s relation which is del of S, T, P del of mu, N, P is equal to 1. This is a brand new Maxwell’s relation which was not derived earlier.

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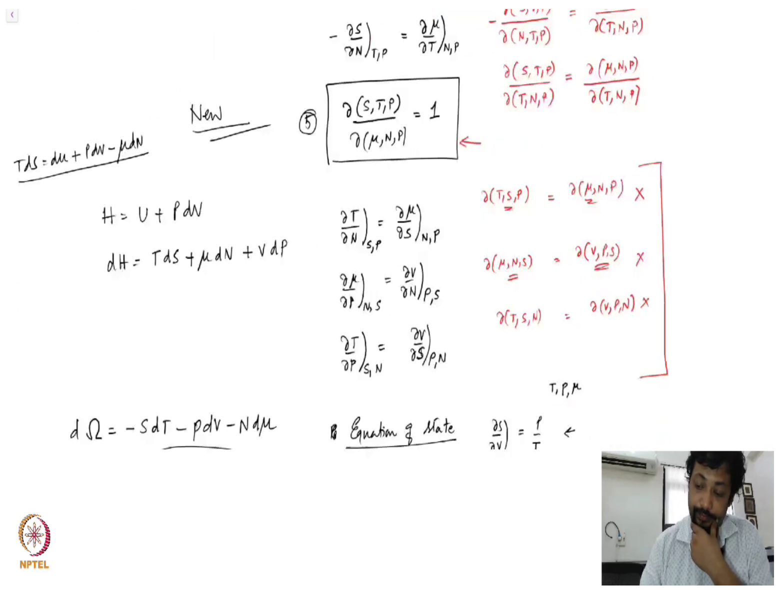

Look at H. H is U plus PV. So, you do a differential in dH which is dU plus P dV. Now dU plus P dV is T dS minus mu dN. So, dU plus P dV is TdS minus mu dN. So, you have T dS minus mu dN. Is that correct? Or it is plus mu dN, because your first law is T dS is equal to dU plus P dV minus mu dN.

Never forget your first law. And therefore, this is, and then again you have plus of V dP. Once again you can write down the Maxwell’s relations, it is a little bit of a laborious job or rather boring in T dS, but it is a good exercise that one should do at least once. So, del T del N is equal to del mu del S P is definitely held constant.

Here S, here S and P are held constant; here N and P are held constant. Then del mu del P is equal to del V del N. Now, del mu del P entropy is definitely held constant on both sides. This is N comma S; this is P comma S. And finally, you have del T, del P is equal to del V, del S.

What are the quantities that are held constant? N is definitely held constant over here; and then S and N, and here P and N. Look at the combinations here now. In this you have del of T, S, P; and the right hand side is del of mu, N, P. I am not writing the denominator, it should be obvious to you now, but you have this combination right over here. So, this does not give you anything.

Then you have del of mu, N, S is equal to del of V, P, and S. So, one has to go back and look whether we have this. I am looking for a combination mu, N and S. Do I have a mu N and S? So, del of P, V, S, del of mu, N, S, and exactly what I have over here is P, V, S, and mu, N, S.

So, this does not again give me a new Maxwell's relation. And finally, here I have del of T, S, N; and the right hand side is delta V, P, N. This one I am now already sure that we have it, and we can look up. And this is the one which was also derived from the internal energy U, T, S, N, and P, V, N.

So, I have this combination here, so this three. So, therefore, you do not get any new Maxwell's relations from this. You can very well write down, but they are not independent. They are the ones which we have derived already before it is not a new Maxwell's relation that we have done.

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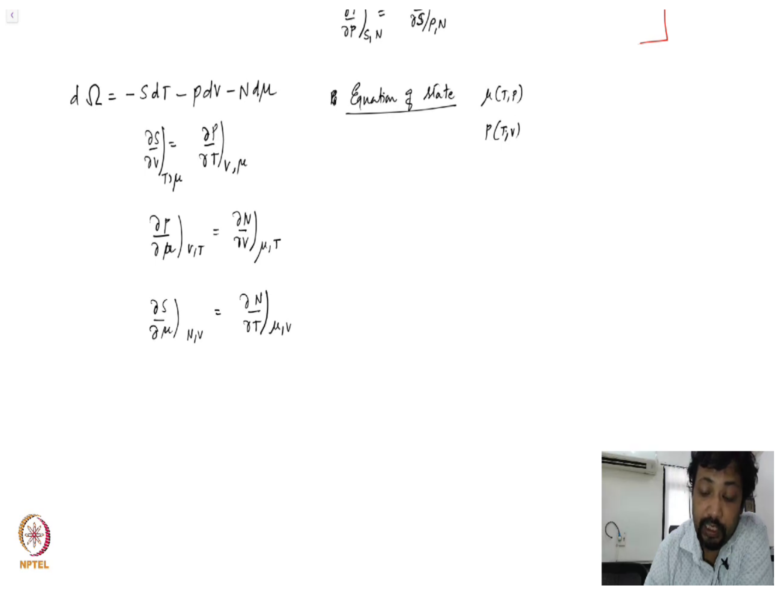

What else are we left with? We are left with omega. Omega if I write down is minus S dT minus P dV minus N d mu. So, del S del V is equal to del P del T. mu is definitely held constant when you do take the derivative with respect to T, V is held constant, here your T and mu are held constant.

Then you have del P, del mu, del P, del mu, V and T are held constant; del N, del V, mu and T are held constant. And finally, del S del mu, del S del mu, N and V are held constant, you have del N del T mu and V are held constant. Now, what I want to emphasize is that besides the whole idea of using Jacobean is to find out whether there are any independent Maxwell's relations. Jacobeans in thermodynamics also has broad applications.

We shall see later on. But Maxwell's relations also have the advantage that you can relate thermodynamic derivatives. For example, if you do not know what is del S del V, T, N chemical potential is held constant, that is actually del P del T, volume and chemical potential is held constant.

Now, recall your equation of state you had P as a function of equation of you have for this particular system. You have equation of state, one is mu as a function of T P right, and pressure as a function of T, V. So, one can eliminate the temperature or the volume. So, let us write down this. So, in hydrostatic system, I know that del S del V is equal to P by T; and del S del N is equal to minus mu by T. You can easily figure out the quantities which held constants.

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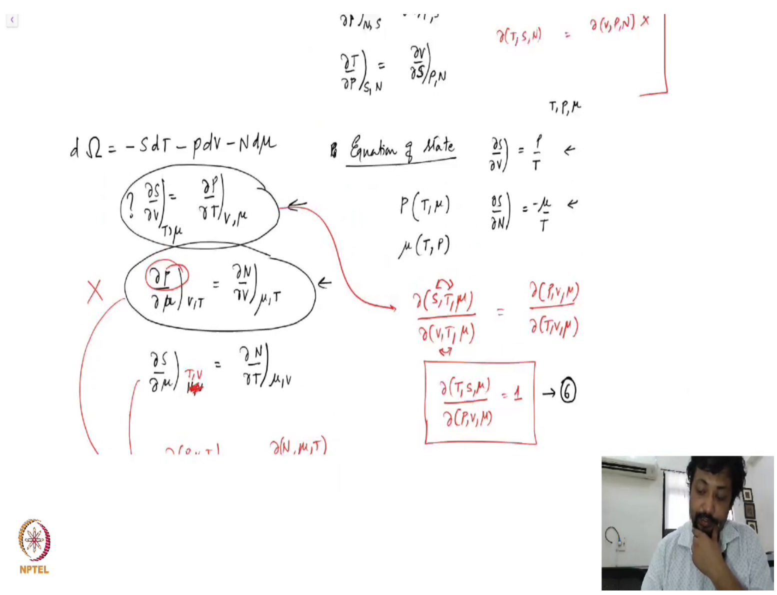

So, therefore, this is one equation of state, this is another equation of state. So, here of course, P is a function. So, you have three generalized forces T, P and mu, not all of them are independent. So, you can write down P as a function of T comma mu or T comma yeah. So, this is one of the relations.

You can also write down mu as a function of T comma P. So, these derivatives essentially are very, very useful in relating. So, this might be a very complex derivative which is not straight forward accessible to you, but you can easily relate this. So, this is one of the uses of Maxwell's relation.

Anyway coming back to the original discussion that we are having that, here if you see then the first let us look at this one, the this one is S, T, mu, and the right hand side is P, V, and mu right. So, do I have S, T, mu, and P, V, mu anywhere? I do not have. If I do not have, then I want to calculate this.

This means S T mu del of V, T and mu is equal to P, V, mu, del of T, V, mu. So, one can just interchange V and T here, and T and S here to give you T S mu del of P, V, mu is equal to 1. So, this is one Maxwell's relations which we did not have.

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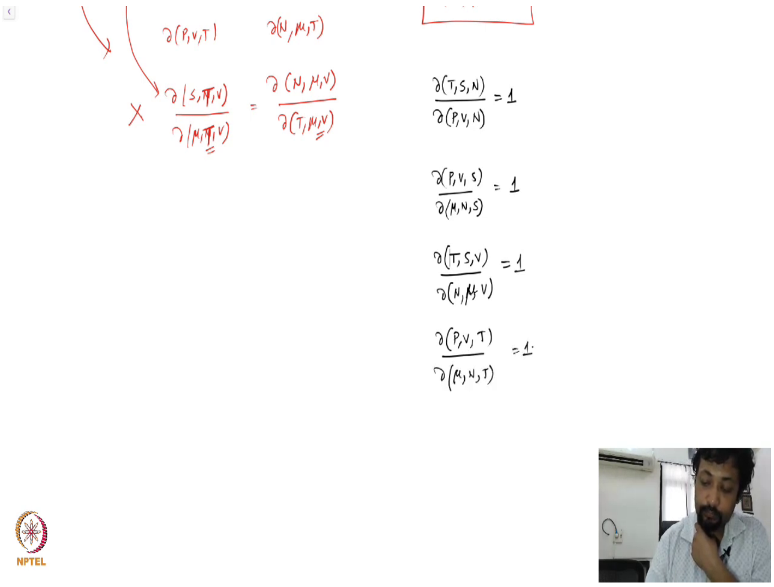

What about this one? This one is del of P, V, T. This part and del of N, mu, T. Do I have this combination somewhere? Let us check. Here, so nothing, this one cannot give me a new Maxwell's relation for its, then again I have del of S, N, V; for this part, I have del of S, N, V is equal to del of N, mu, V not equal to so.

On the right hand side, I have del of N, mu, V. I am not writing the denominator that I said earlier S, N, V. Let us see. Do I have S and the combination would be S, N, V, and N, mu, V. I am sorry, this is S, N, V this is N, mu v, but that means, my Maxwell. So, if I work out the Maxwell's relation here, then this is mu, N, V is equal to del of T, mu, V. But this and this do not match.

So, one has to see whether we written it down carefully. So, del S, del mu, T and V held constant is del N, del T, mu and V held constant. So, this is the correct form. Therefore, I have S of T, V; and I have N of mu, V; and the bottom I have mu, T, V, and T, mu, V. This,

this is fine. So, I have a I have to look for a combination of S, T, V, and N, mu, V. Do I have a combination of S, T, V, anywhere? Look?

Here. Therefore, this is no longer new. So, finally, there are 6 independent Maxwell's relation, and we shall list them together. The first three follow from the Maxwell's relation from the internal energy 1, 2 and then I have 3.

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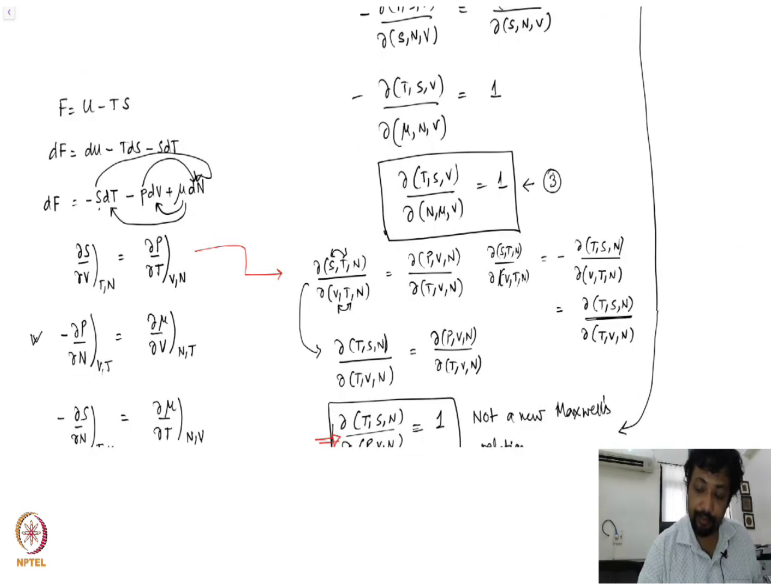

Then as we see this is 4, this is 5, and finally, this is 6. So, if we collect everything together, del of T, S, N, del of P, V, N is equal to 1, you should always check whether you written it down. Yes, then the second one is P, V, S, and mu, N, S. So, del of P, V, S, del of mu, N, and S is equal to 1. The third one is T, S, V, and N, mu, V, del of T, S, V, and del of N, mu, V is equal to 1. The fourth one is P, V, T, and mu, N, T is 1.

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$$\frac{\partial(T,S,V)}{\partial(N,\mu,V)} = 1$$

$$\frac{\partial(P,V,T)}{\partial(\mu,N,T)} = 1$$

$$\frac{\partial(S,T,P)}{\partial(\mu,N,P)} = 1$$

$$\frac{\partial(T,S,\mu)}{\partial(P,V,\mu)} = 1$$

The fifth one is del of S, T, P, and mu, N, and P is equal to 1. And the sixth one is del of T, S, mu, and del of del of T, S, mu, del of P, V, mu is equal to 1. So, these are the six independent Maxwell's relations that you have for the hydrostatic system right. We were to end our lecture here, and continue it later on.