Chemical Principles II
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Tutorial Problem-14

Okay, so, let us continue with some more problems on thermodynamic relations and more of that you practice, you will be better off actually doing that and you will see that different times you need different types of tricks, sometimes you need Maxwell's relations, sometimes you have to use Jacobean techniques, sometimes you have to go just the definition of the thermodynamic potentials like dU, dA, dG and dH. So, once you have these ammunitions with you, then you know it should be better off converting one form to the another form and then getting the desired answer that you want.

So, today we are going to practice some thermodynamic relation problems, few of them, so that we will see that what kind of tricks we need along the way. So, I myself do not know about the problems right now, I have not done that before, so we will make, we may get stuck at some point, then we will see how to solve them and things like that. Okay, so let us continue with that.

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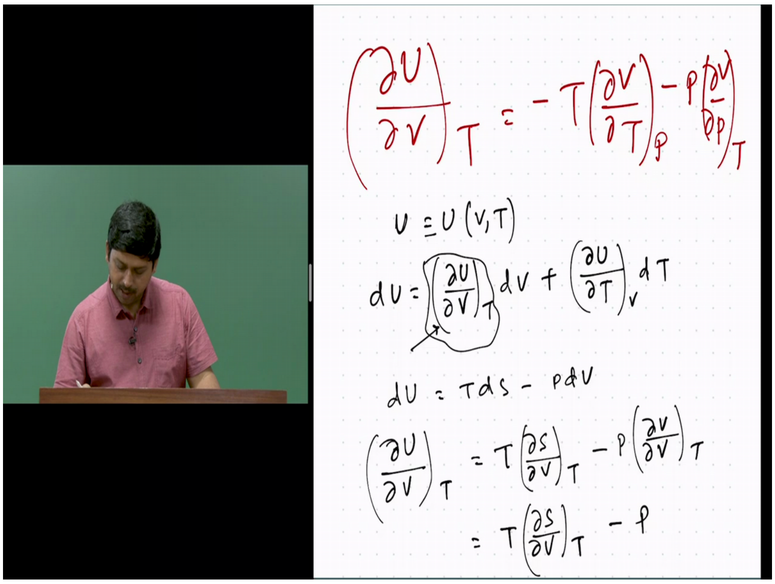

So the 1st problem that we have to do is, we have to show that del U by del V T equal to - d del V del T P - P del V del P T. This is almost similar to the Joule's expansion problem, right. So, we can start U as, or we can start U as a function of V and T. And we can express U in terms of P and T. So, dU is equal to del U by del V T dV + del U by del T V dT. Now, will that help us? No, because we only need this particular quantity, del U by del V T.

So that will not help because we want, we want only this thing. So, let us use our knowledge about dU. So, dU as you know is T ds - P dV, this we know, right. And once you know that we have to get dU by dV at a constant T, so we can differentiate both sides with dV, so we get dU, so this u is small and there is this, this U is capital, so we will just use capital thing. So, del U by del VT, so what we did is, we took the differentiation with respect to V at a constant T, whatever is asked for.

So, as I told you that right-hand side T will not be differentiated because only the differential will be the you know will be affected. So, del S by del V T - P del V by del V T. So, which means T del S by del V T - P because del V by del V is 1. Okay, so what they have asked for is del V by del T - del V by del P T. So, we do not see yet anything that is close to that, so we will have to expand a little bit more and see what we can get out of that.

So, we know that from Maxwell's relation that SPTV, del S by del V is del P by del T at a constant V and that is also not there. What we have here is an expression of P. But we can actually, you know, we can do a little bit of trick here. And we know that when you write SPTV, then del V by del T at a constant P is nothing but del S by del V at a constant T - of that. So, somehow we need del S by del V and then del V by del P of course will not come but you see we need to derivative with respect to P, not with respect to V.

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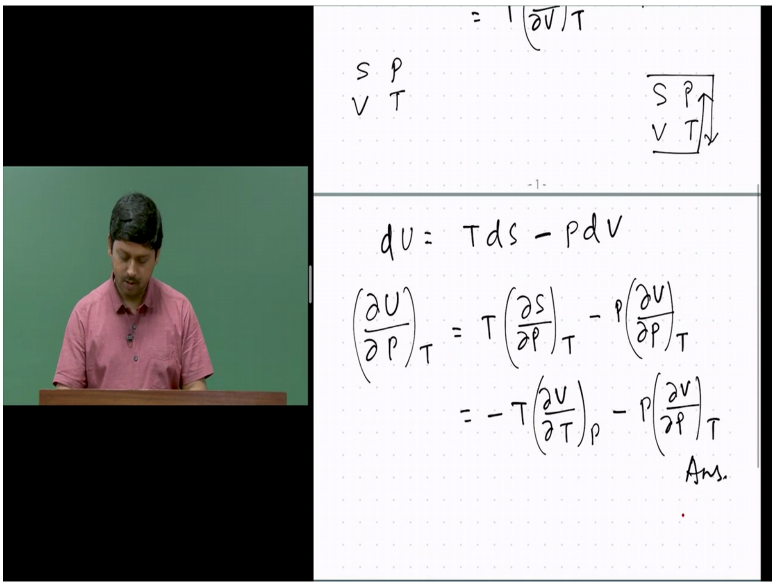

We need with respect to P in order to get that. So, I think the question may be wrong, we will just check. So, let us start with U again. dU is T dS - P dV and let us take a derivative with respect to P. I think the question is wrong. So dU by dP at a constant T is T del S by del P at a constant T - P del V by del P at a constant T. Okay. Now, if I do SPTV, then we know del S by del P at a constant T is del V by del T at a constant P, negative of that, so - P del V by del T at a constant P - P del V by del P at a constant T.

And what is asked for, - P del V by del P at a constant P - P del V by del P at a constant T, okay, so that is what we get. So, our question was wrong, it should have been del V by del P at a constant P, sorry del U by del P at a constant T and not V.

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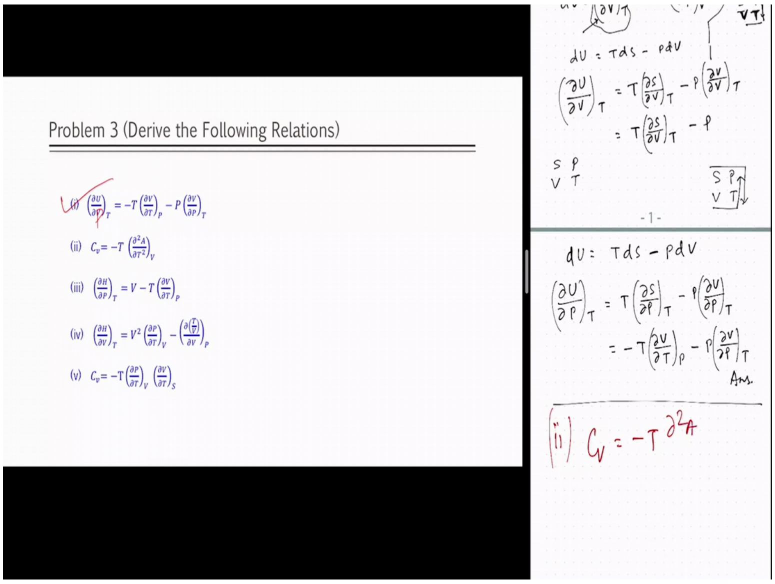

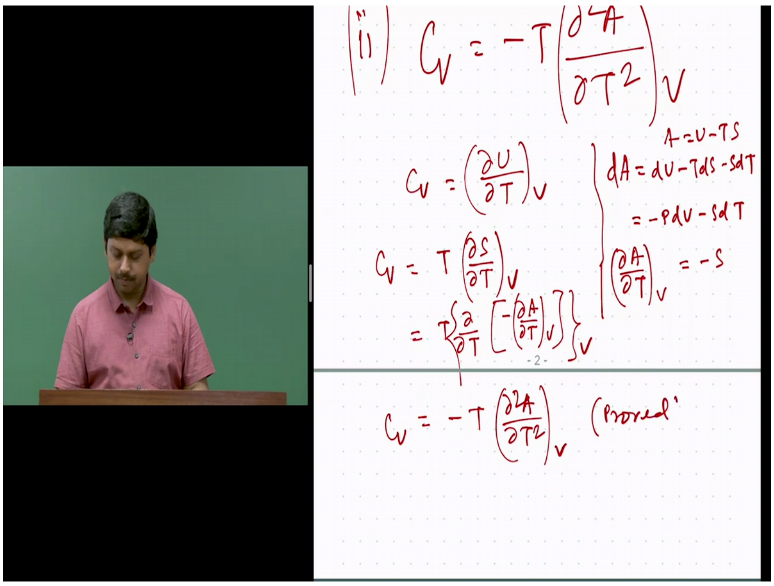

Okay, so let us go to the next problem. Second problem. Show that CV equal to - P del 2 A by del T2 V. Okay, so what is the definition of CV? We know that CV is del U by del T at a constant V, that is the definition of CV, right. So, how can we actually connect to something like a 2nd derivative of A. So, we have to understand in that is that whenever we write CV as dell, so that means we have to get 1st del A by del T, then only we can get the 2nd derivative with respect to V, right.

So, del A by del T. So, what is A? So, we have to know that what is A. So, as you know R a is U - TS, so d a is dU - T ds - S dT. So, we can even break it up and say that dV is TdS - P dV. So, it is - P dV - S dT. So, that is our A. Now if we take the derivative with respect to T at a constant V, at a constant V, this term will be 0 and that will be - S. So, del U by del T is - S, okay. So, then we know how to solve the problem.

So, this is the definition of CV and we know that this definition also can be written as del S by del V T del S by del V at a constant V. Okay, so that solves our problem because we know that S equal to - del A by del T V, that is our S and this derivative we have to do with respect to V again. Which means that CV now becomes - T del 2A by del T 2 at a constant V. And that is proved. Now we will go to the 3rd problem.

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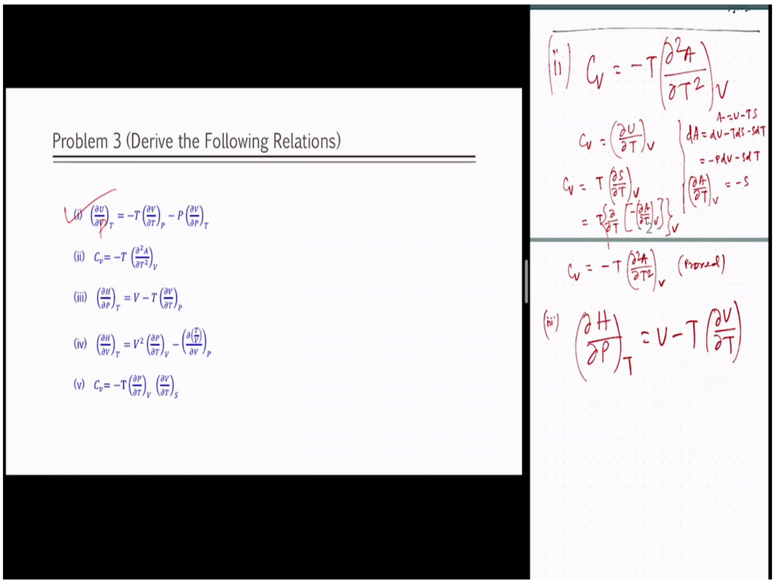

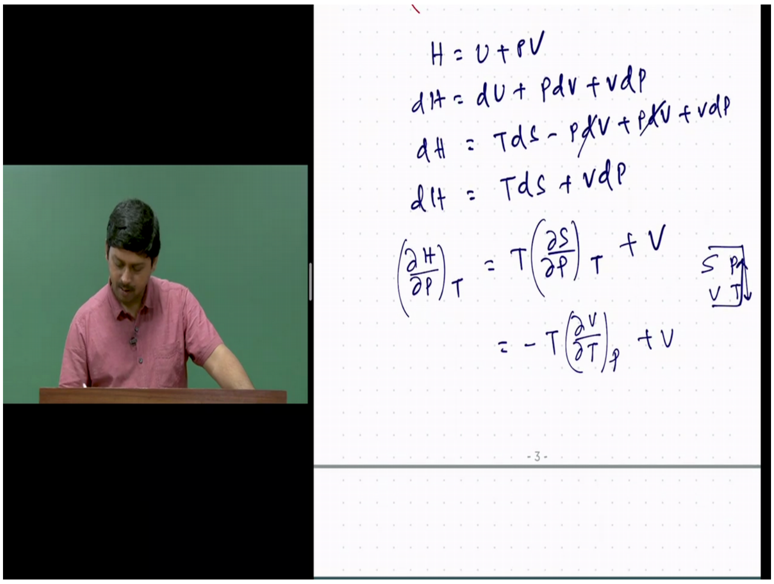

del H by del P at a constant P is equal to V - T del V by del T at a constant P. So, this is what we have to shown. Okay, here also we can write fast formula of H. You know H equal to U + PV, we will just start from the beginning. Then dH is dU + P dV + V dP and you know dU is T ds - P dV + P dV + V dP. So, dH is nothing but T ds + V dP, so you see we are just using the definition, nothing else. Now, we can always take a derivative with respect to P at a constant T. So del H by del P at a constant T is T del S by del V at a constant T + V.

And now this is very simple, so we are going to use Maxwell's relations SPTV, so del S by del V at a constant T is - del V by del P at a constant P. Okay, + V and that is del V by del P, yes, that proves it. Let us start the 4th problem.

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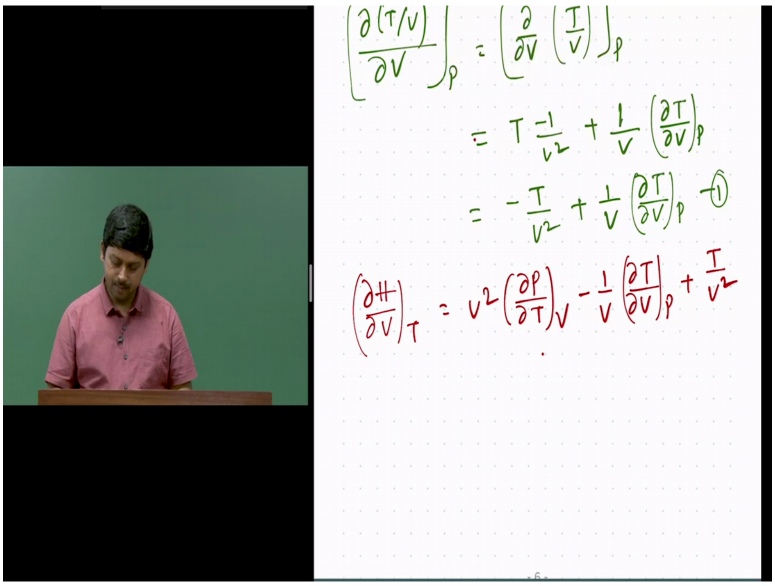

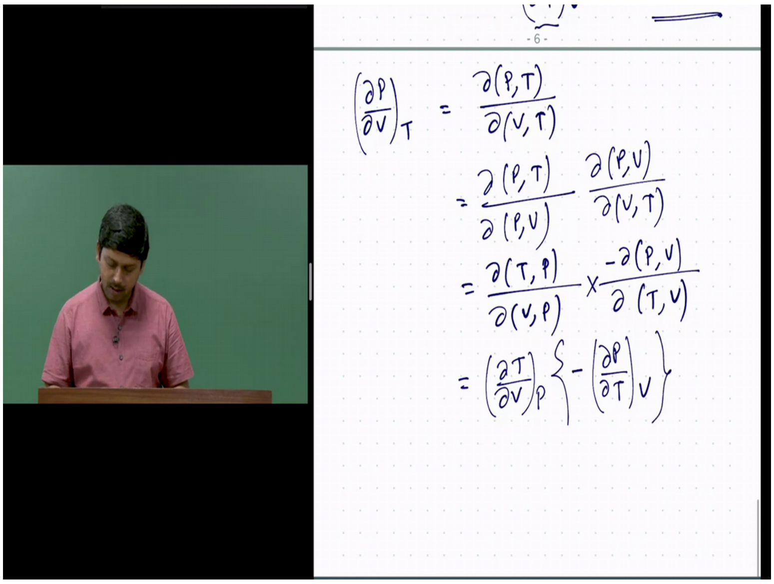

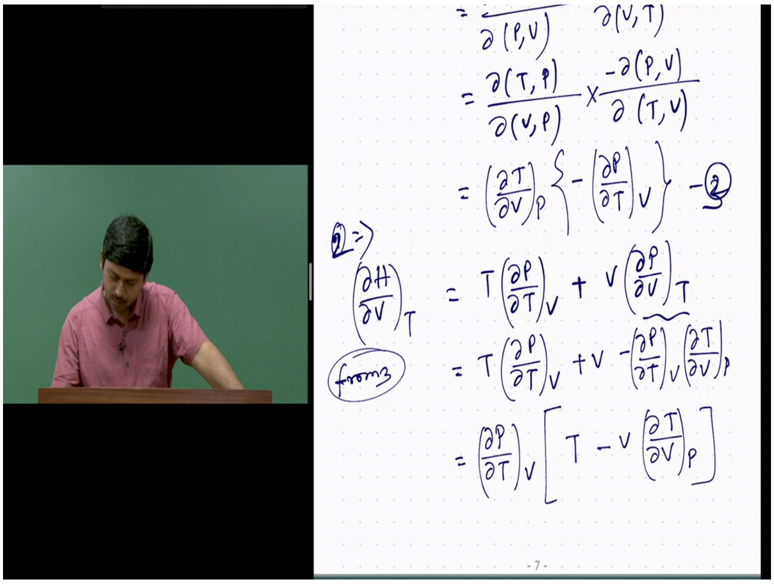

It says that del H by del V at a constant T is equal to V square del P del T V - del T by V by del V constant P, okay. So, you see the right-hand side is little bit complicated. So, let us 1st that the right-hand side right. So, what is del T by V by del V? What is this one 1st, let us see. So, that is del del V by T by V at a constant P which is product of 2 functions, so it is T del del V by 1 by V which is -1 by V square +1 by V into del T del V at a constant P.

Which is - T by V square +1 by V del T by del V at a constant P. Now, let us keep that is the question 1. So, because that is what we have to bring, so we have to show then del H by del V at a constant T is equal to V square del P by del T V and - this quantity, so -1 by V del T by del V P + P by V square. So, this is what we need to show. As you can see there are 3 terms here, that is okay, so let us see how we can do that. We can start with the definition of dH, which is T ds + V dP.

Let us take a derivative with respect to V at a constant T. So, del H by del V at a constant T is what we want, that is T del S by del V at a constant T + V del P by del V at a constant T. Now we know from Maxwell's relations, we will discreetly write SPTV, we know that del S by del V at a constant T is nothing but del P by del T at a constant V. So, you see we got, we got del P by del T but we got T and not V, we need V square. So, that also is not there. And del T by del V is also not coming from this.

So what we are going to do is that, we are going to now break down this del T del V and see what we get from there. Alternately we can break down this one, whichever is fine with us, we can we can do this one, del P del V T. So, del P tell V T is nothing but del P, T by del V, T. We need del T del V, which is we need TP by VP, TP is already there, TP, so I write PV. So, then I write PV and VT, okay. So, now we can write, explain these both numerator and denominator positions and we can get the same thing two negatives, so this is fine.

And now in this case here, we just change only one , let us keep it as P, V and let us change as T, V, so then we get dP dT V, again back from there. So, you see this one is nothing but del T by del V at a constant P, which we actually wanted here. But in addition what we get is - del P del T at a constant V. So, this is nothing but a product, so therefore del H by del V at a constant T equal to, from equation 1 we can say T del P by del T V + V del P by del V T, which is from equation 2 will be into - del P by del T V, del T by del V P.

Now I can take del P by del T V common, I am going to get T - V into del T by del V P. Remember I need to be here. So, let us see. We need, in order to get this particular thing T by V, we need to we need to be here. So, okay, so we can, that was equation 1 already, so I can just make it as equation number 2, this one and as 3. So, this from 2 we get and 3 we will we will, from 3 we will get this one, this particular thing from 3. So, now T - del T by del V, let us see here.

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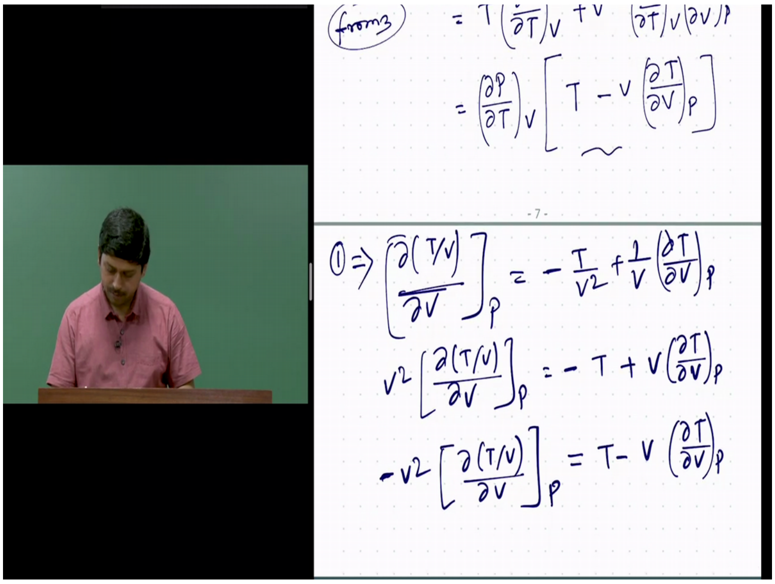

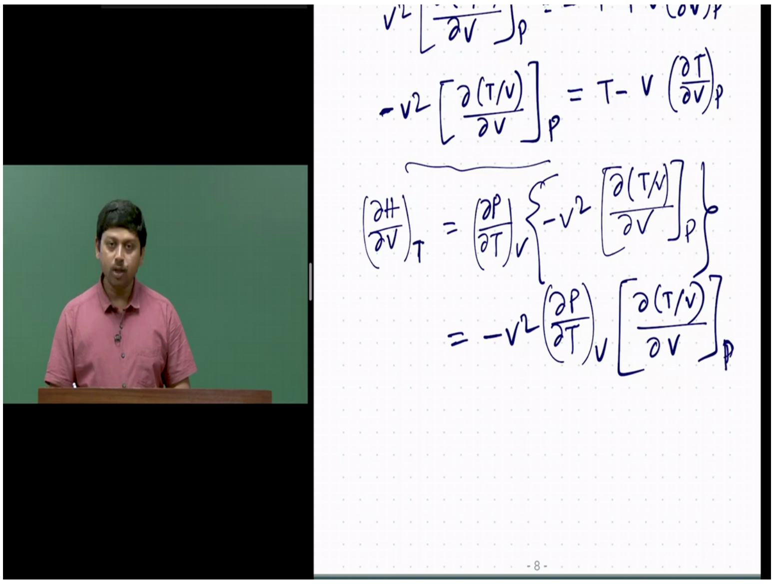

T -, if I take - of that, if I multiply by V square, then it will be, it will be T - B into, yes. So, from equation 1 now, so, I will just write equation 1 once more. What we got is del T by V, we need to see it once more, by del V at a constant P, at a constant P, is equal to - T by V square +1 by V del T by del V at a constant P. Just check once more, yes. So, that was from equation 1, now multiply by V square both sides, so we get V square into del T by V by del V at a constant P is - T + V into del T by del V at a constant P.

Takes the - on this side, so - V square del T by V by del V P is T - V del T by del V at a constant P. And that is what here, that is here. So, we can say that del H by del V at a constant T is equal to del P by del T V into - V square del T by V by del V P. However, that was not the one to be proven. I think it is a multiplication rather than a minus sign. So, if, so we found another mistake. But we know that it is just a mistake in the way it is written.

If we wrote this in the beginning, this part here, then there is absolutely no problem, otherwise this looks like a minus sign. Okay. So, basically, so yes, that is the same problem that is appearing here also, so there should be a bracket, so it is - V square del P del TV and del T by V by del V P. So, if we can do that and you can even find out the mistakes from the derivation, that is even better, right.

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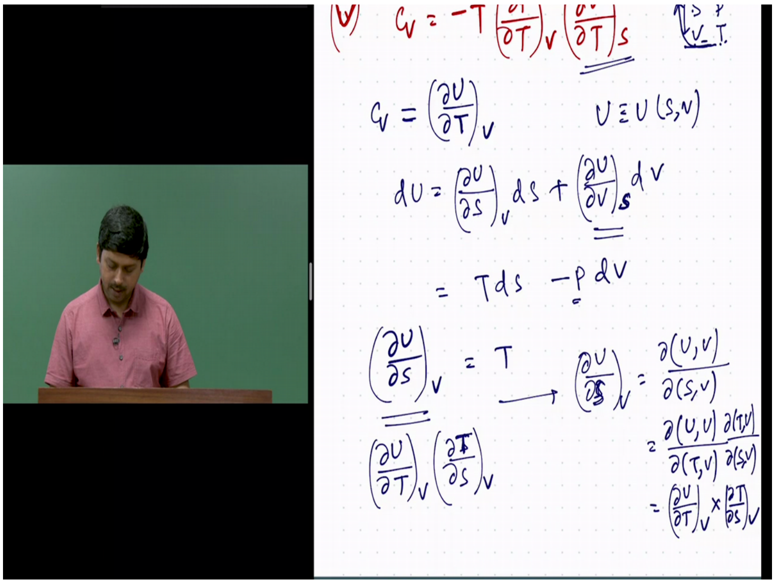

Now we go to the next problem, where we write, or it is V problem V, right. CV as - T del P by del T V del V del T S, just to make things complicated, you know CV is very simple, del U by del T at a constant V. Why was should write in such a complicated form, however this is just an exercise, so that when you can do that, we can do many other problems when you need. So, let us let us try to do that. So, start with the definition of CV, del U by del T at a constant V and that for CV is.

Now you see we can always write U as product of you know, expand in terms of V and T or, yah, we can expand that in terms of V and T. Or you know, U is a natural function of S and V, so do that in terms of S and V. So, del U by del S and it will give with the same thing by the way. del U by del S at a constant V dS class del U by del V at a constant S TV. So, we did not constant S because, see, this constant S is coming. So, as you know this is nothing but T dS - P dV.

You see that P then again is constant of like you know P is like del U by del V at a constant S, that is the P. So, I can always take derivative with spectra T, it will give me del V del T but it will not give me the S. So SPTV if I do, let us see, del V del T at a constant P I get, I of course get del S, del T del V at a constant S, which is just the inverse of this, we can use that. That way we will get that. If that is the case, I del T del V at a constant S is nothing but del P del S, - del P del S at a constant V.

If we only need with respect to S, then what else they can think of is we can I find U in terms of V and T and see what we get from there. We can do many many different ways. I am just thinking what will be the best choice, otherwise I will use the Jacobian anyway and do that. We can do the Jacobian and we can bring the S in the numerator anyway. So, that is not a problem, I am just showing you that S can appear in this particular form. So, if you take a derivative with respect to V, then you can have S.

For example del U by del T, I can have del U by del T V, then del V by del T S. Yes, that is possible, that is possible. So, okay. If I let us say try del U by del S at a constant V is just nothing but T, okay. Now this means I can write del U by del T, del U by del T at a constant V, then del S by, del T by del S at a constant V. Okay. So, can I write that? Let us see, you Jacobian and show you. So, this constitutional U by del S at a constant V is nothing but del U, V by del S, V.

So, I wrote del U, V by del T, V and then del T, V and then del S, V. Now, that becomes del U by del T at a constant V and this becomes del T by del S at a constant V. So, I can write that, that is also nothing but T. del U by del T at a constant V is by definition C, V, okay. And this is nothing but a inverse of del S by del T at a constant V inverse. So, CV is del S by del V V T.

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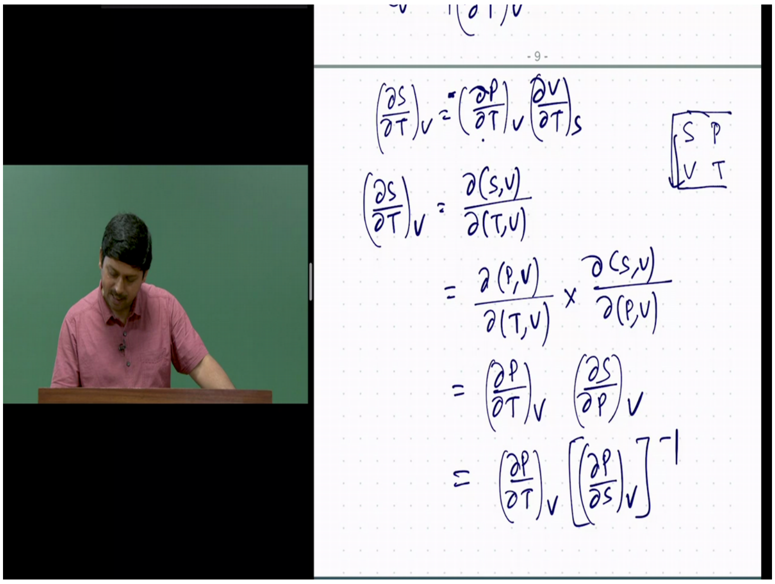

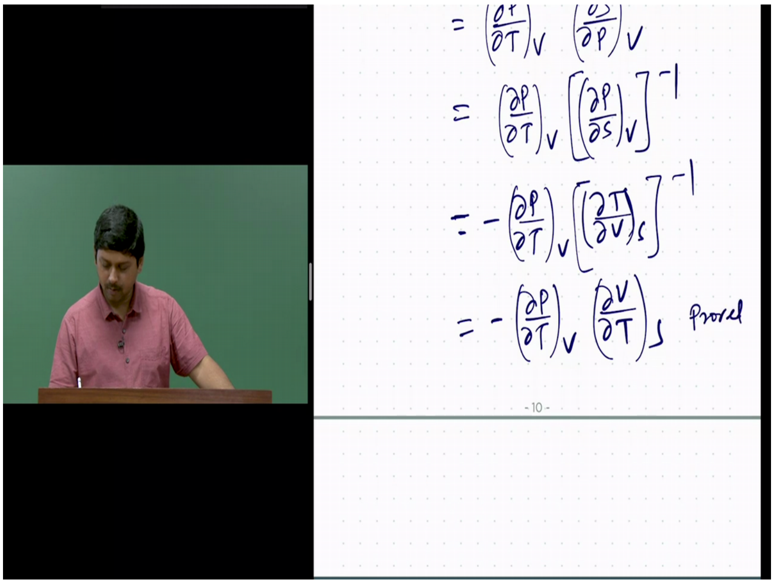

Okay, so we got T del S by del T V and that is not a big deal because we already know the formula, right. But C then we have to prove, we got, since we got T already, we have to prove that del S by del T is nothing but this thing. So, we have to prove del S by del T V is nothing but del P del T V then del V del TS and actually - sign of that. That is what you have to prove and that is easy by Jacobian. For example we can write del S by del TV is del S, V by del T, V is now, we want PTV, right, so we can have del P, V by del T, V, then del S, V is still there and we provide P, V here because then P, V will cancel and SV and TV will remain.

And that is del P by del T V and this is del S by del PV. Now we are going to use Maxwell's relation SPTV and we know del S by del P, okay, here it is, so now we are going to use, okay one more step. del P by del T V, then it is del P by del S at a constant V but inverse of that.

Now, we know that del P del S V is del T del V S, - of that. So, that is - of del T del V at a constant S, wait, inverse of that, which is - del P del TV is del V del T at constant S and that proves it.

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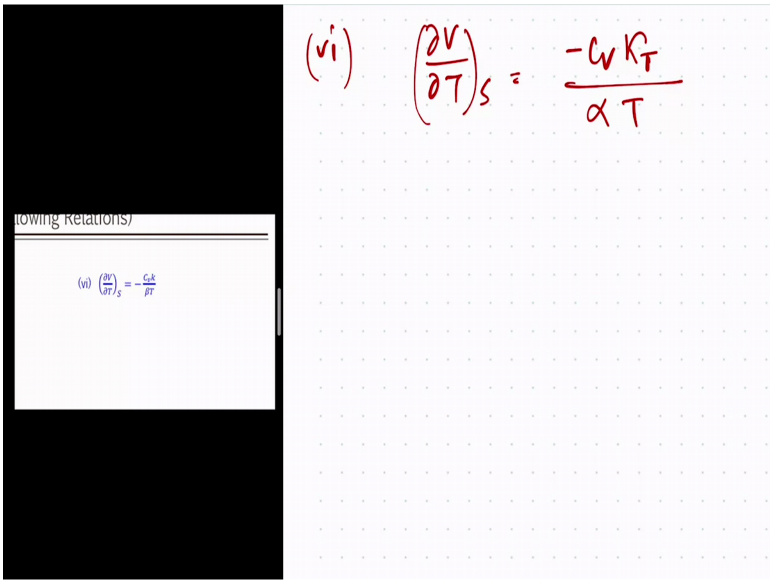

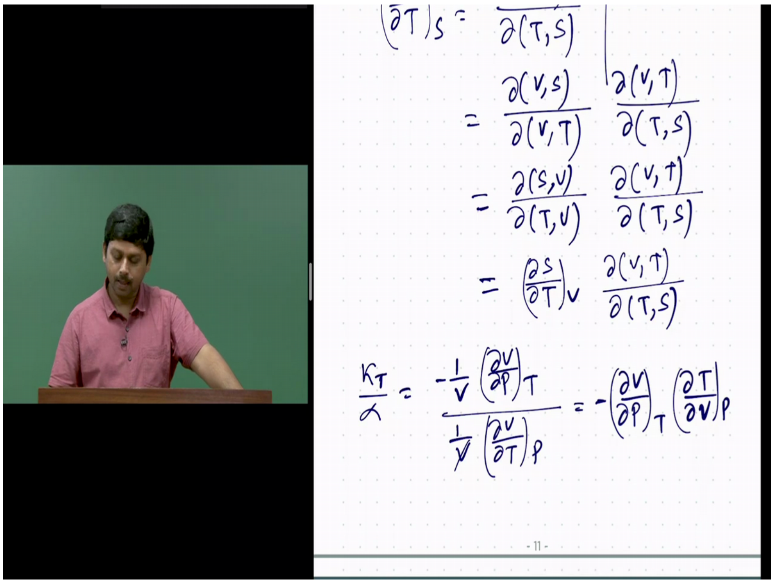

So now let us go to the 6th problem. del V by del T S, we have to show that it is - CV, I think Kappa denotes Kappa T according to the notation and beta is nothing but Alpha. So, we have to show this. Now, once you have, once you see that we have to we have to you know derive or break the thermodynamic relations into the heat capacities finally, like Alpha, Kappa T, CV and all that, then we know that we have to use Jacobian, we have to break down all possible ways.

So we will just straightaway do that, because that becomes extremely straightforward using Jacobian. So, we write del V del T at constant S as del V, S del T, S. Okay and of course we can use a trick and do that, we should do that anyway because we need CV and CV means del S by del T, we need that and we need Kappa T. So, we need PT term, so we will add a PT damn, so V, S and T is definitely required and V is also definitely required. So, we will use a VT term here, we will see. Okay.

And we get straightaway the CV, right away and then we get VT and T, S. We will see how helpful that is. Now, this means that we can write as S, V T, V and this side we can write using a minus sign as del V, T and del T, S, okay, we do not write the minus sign right now. So, we get here del S by del T at a constant V, which is CV by T, we know that. And that is del V, T by del T, S, we did not do anything with that, yes.

Was it helpful, I do not think it is so helpful. Okay, of course we get CV by T here, we need, okay, I think it is helpful. We know that while it is helpful because we have already done that before, that is why. So, for example we know that Kappa T is by definition, Kappa T is isothermal compressibility, so it will be -1 by V, we have to compress, red, so del V by del P at a constant temperature. And alpha we know as coefficient of thermal expansion, which is del V by del T at a constant pressure. So, now Kappa T by alpha, we have shown that before and I will show it here again, Kappa T by alpha is -1 by V del V by del P at a constant temperature by 1 by V del P by del T at a constant pressure.

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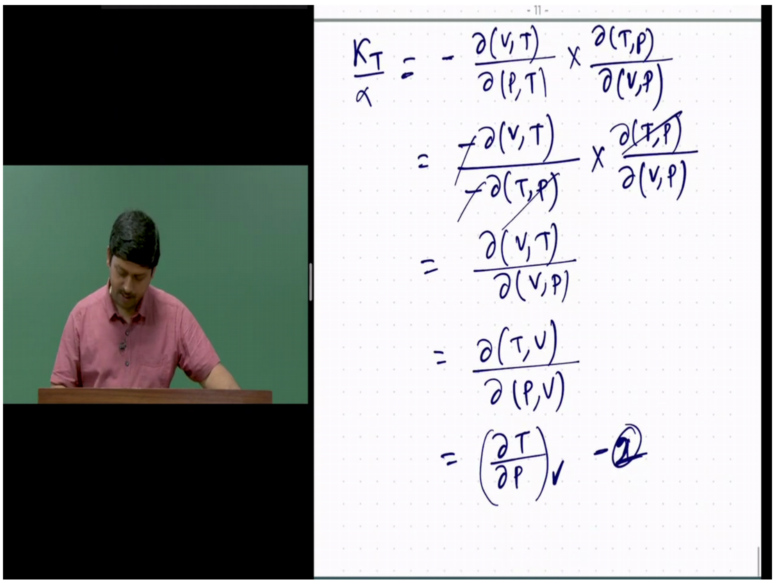

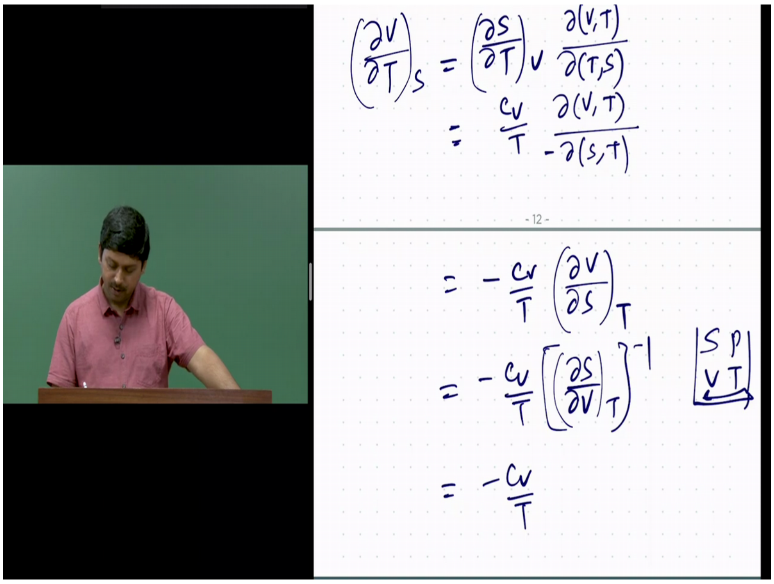

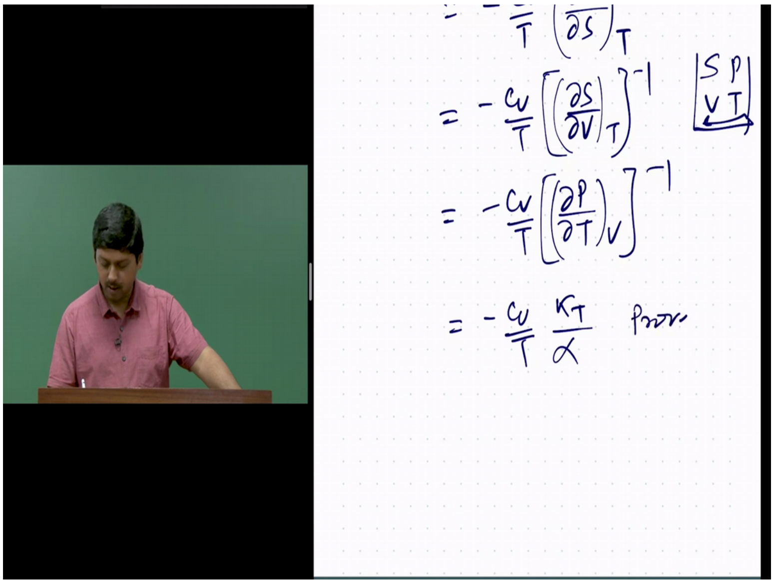

V and V cancels, giving this - del V by del P at a constant T and we can always write the inverse way, del V by del P at a constant T. And we can always write the inverse way, del T by del P at a constant P. So, Kappa T by Alpha is then - del VT by del PT, from the left-hand side, this one, right-hand side will be del T, P by del V, P. We can simplify it further, so this is - V, T and we can take a minus sign and write as T, P into T, P by V, P, so TP, TP cancels, minus minus cancels, giving me del VT by del VP.

We can switch both the variables and write del TV by del PV, giving me del T by del P at a constant volume. Now, that is now, now you see here, that is, that is fine, so now children we come back here, what we see is that we have, we are, so, now coming back to our original one, del V by del T at a constant S. So, let us write that equation has equation 1. And, okay, let us call that is equation 1 and that as equation 2 and then write the original one. del V by del T at a constant S del S by del V, from equation number-one del S by del T at a constant V and del VT by del TS.

Okay. Which is nothing but CV by T, we know that and this one we can write as del del T, we, - of that of course by del T, S or opposite, so let us do just the opposite of that, do not switch the numerator, switch the denominator and what does that give us - CV by T del V by del S at a constant T, that is what we get, which means we can write that as - CV by T del S by del V at a constant T and inverse of that. Now we are going to use Maxwell's relation because whenever this SPTV comes, we should use Maxwell's relation. So, del S by del V at a constant T is same as del P by del T at a constant V.

Inverse of that and what did we learn from equation number 2, that Kappa T by alpha is, okay, equation 2 can be written one more step as del P by del T V inverse. So, del P by del T V inverse is come for T by far. So, this is nothing but Kappa T by alpha, so that is also proved.