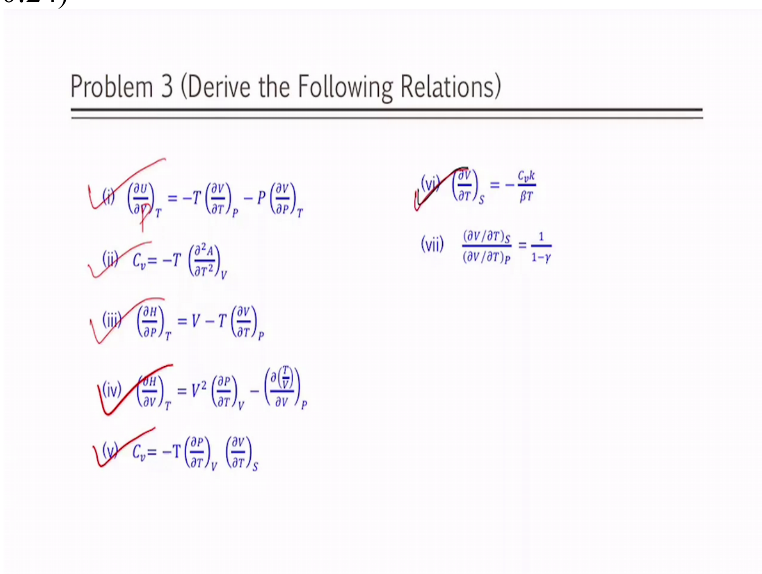
Chemical Principles II
Dr Arnab Mukherjee
Department of Chemistry
Indian Institute of Science Education and Research, Pune
Tutorial Problem-15

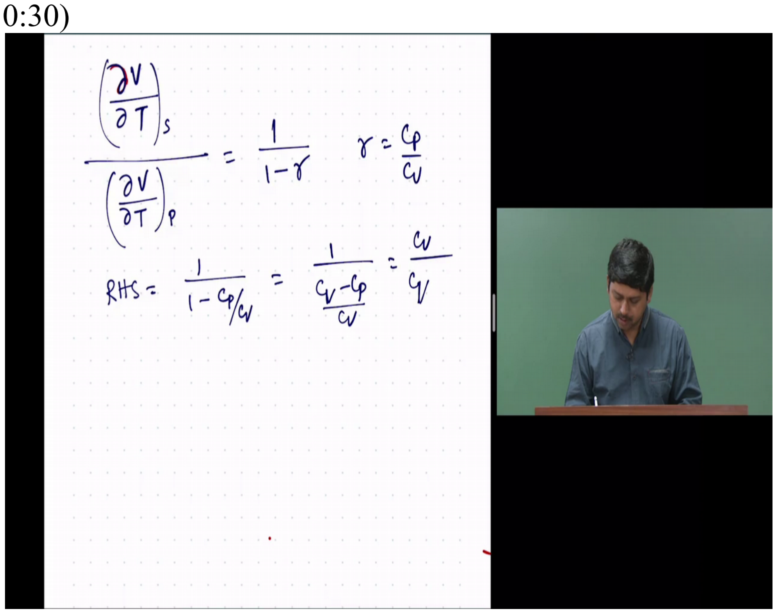
Okay. So we will continue solving the thermodynamic relations problem.

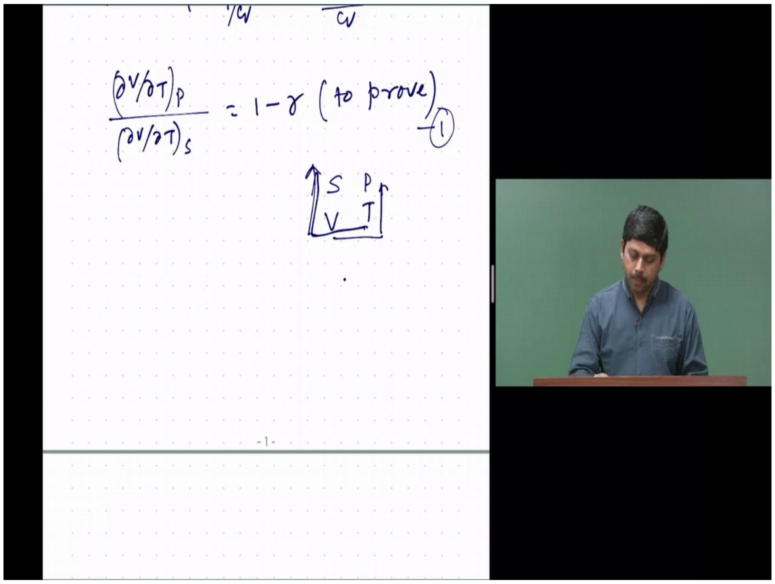
(Refer Slide Time 0:24)



And the next problem that we are going to do is this one. So let us let me write down.

(Refer Slide Time 0:30)



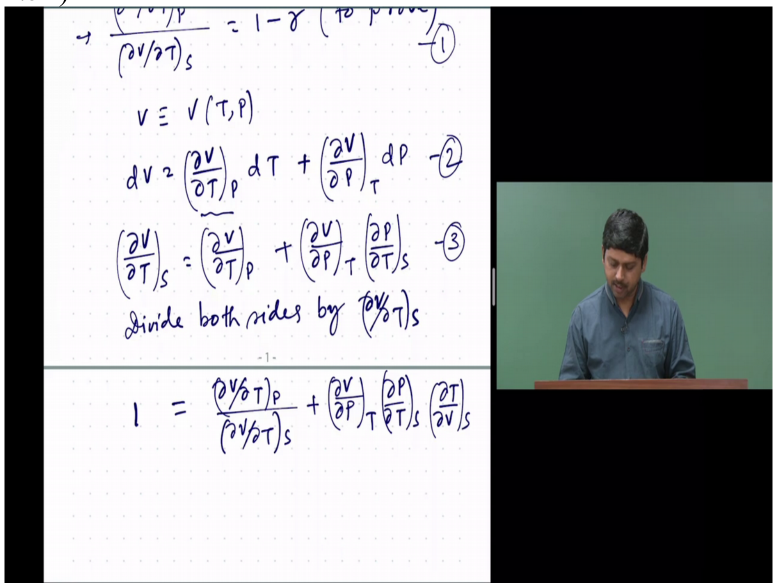


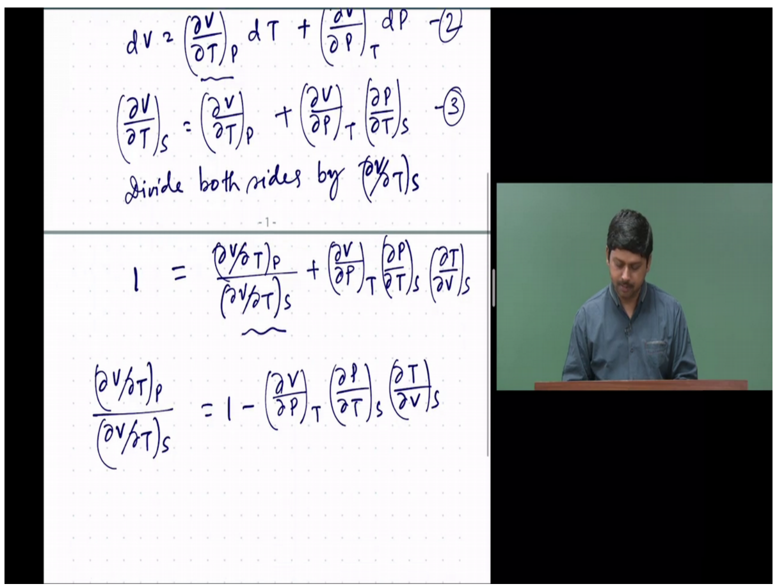
We have to show that Del V Del T at a constant S divided by Del V Del T at a constant P is 1 by 1 - gamma where we know that gamma is CP by CV. Now before I saw that, let us do the right-hand side a little bit. So right-hand side is 1 by 1 - CP by CV giving me 1 by CV - CP by CV which is CV by CV - CP. Now you see that I can make the equation a little bit simpler by solving the reciprocal of this which means that if you want to do this Del V Del T P by Del V by Del TS then I am expecting 1 - gamma and 1 - gamma is nothing but **CP** CV - CP by CV or 1 - CP by CV.

So that is a little bit easier. So we are going to go that way. So we are going to solve this one and then we will prove that the reciprocal of that is 1 by 1 -ma. So so let us start doing that. Okay. So we have to show that this is = 1 - gamma. This is to prove. We have to prove this. Okay. Let us call that equation 1. Okay. We can always use Jacobean techniques or many other methods that we discussed but there are also other tricks involved because you see that when you do Maxwell's relation, S, P, T, V, then we can always do DVDT at a P and then in order to do the S, we have to do DT DV at a constant S.

That is a tricks because the line will go like this only. So therefore we cannot go get easily DVDT at S but we can always taken was of DT DV at constant S as DVDT at a constant S. okay. So we can do that but let us **let us** do a different tricks.

(Refer Slide Time 2:52)



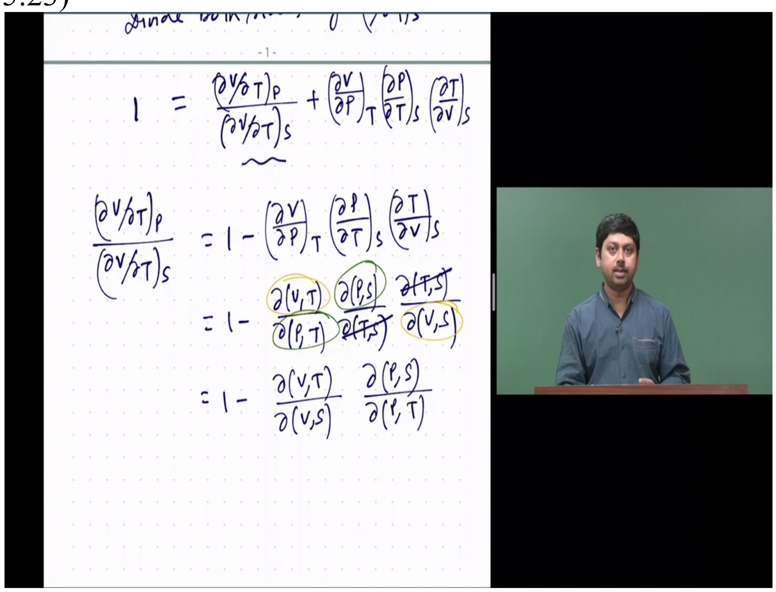


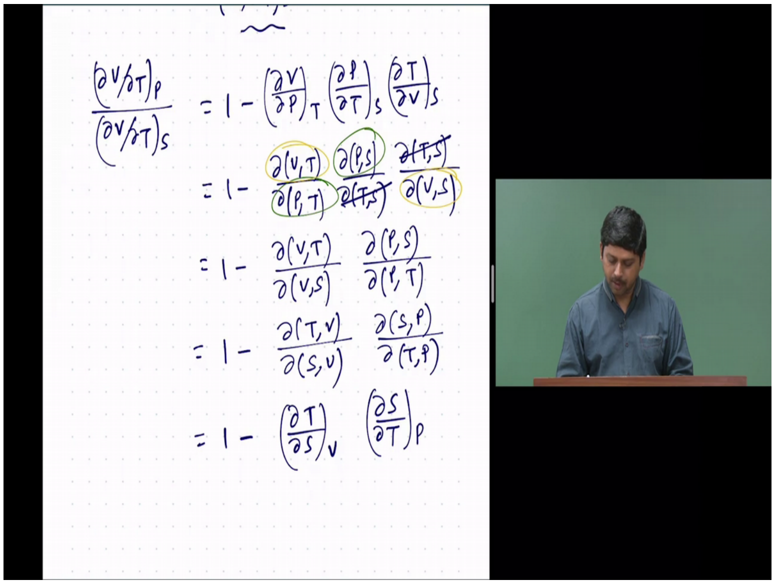
So you know that V is a function of T and P. So any one variable is function of other 2 variables. So that way, we can always express the total differential of a variable with respect to the changes in the other 2 variables. So DV we can write as Del V Del T at a constant P DT + Del V Del P at a constant T DP. We can write that. So we are writing the total change. Now you see, I am already having the term Del V Del T at a constant P. I need Del V Del T at a constant S.

So therefore we cannot differentiate equation 2 by with respect to T at a constant S and write that as Del V Del T at a constant S is Del V Del T at a constant P and DTD DT by DT will be just 1 + Del V Del T at a constant T and Del P Del T at a constant S. So we have done that. So now you see, this gives me equation 3. Now we need this quantity, Del V Del T, we need this quantity, Del V Del T at a constant P by Del V Del T at a constant S. So divide both sides by Del V Del T at a constant S. So what do we get? 1 + no sorry, we will get 1 = Del V Del T at a constant P by Del V Del T at a constant S because this is what we wanted to get, right?

And then decide we will get Del V Del P at a constant T Del P Del T at a constant S and we are dividing by this one, Del V Del T at a constant S. So we get inverse of that. Del T Del V at a constant S. okay. So which means that this quantity Del V Del T at a constant P by Del V Del T at a constant S is 1 - Del V Del P at a constant T Del P Del T at a constant S and Del T Del V at a constant S. okay. So now we need the help of Jacobean and we can write all that in Jacobean term.

(Refer Slide Time 5:23)



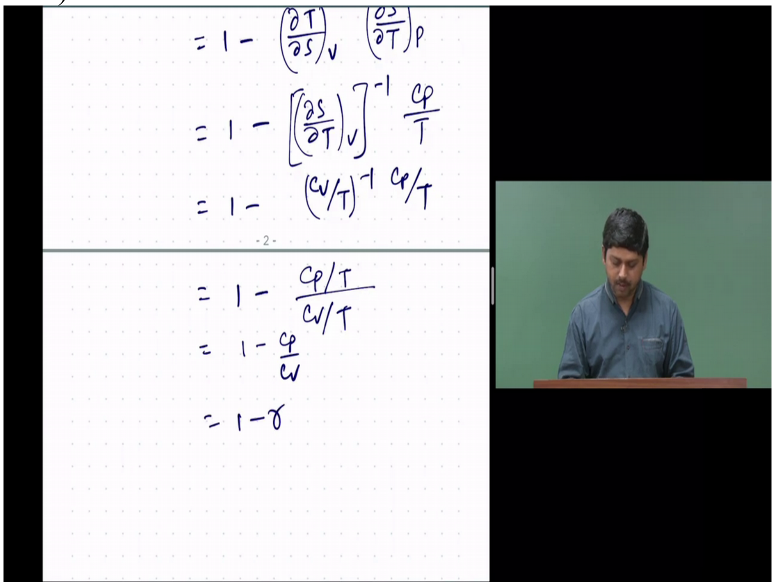


So this will give us VT by Del PT, this will give us, 2^{nd} one will give us Del PS by Del TS. 3^{rd} one will give us Del TS by Del VS. Now you see, this TS and this TS will cancel each other and we can write as 1 - and remember we have to get CP and CV. So CP and CVs are Del S by Del T at a constant P and Del S by Del P at a constant V. So you see, we are getting similar thing. When we use these 2, I will just circle them.

When we use these 2, we are going to get 1 and when we use these too, we are going to get the other one. So now let us write that. Del VT divided by Del VS and Del PS divided by Del PT. Because we know that we are going to get CP by CV, right? So that is why we chose this root. Now you see, I can interchange both the variables and write TV by SV and here I can write SP by Del TP. Since I changed both then it is positive only. So 1 -, so TV by SV is nothing but as you can see, it is inverse of CV.

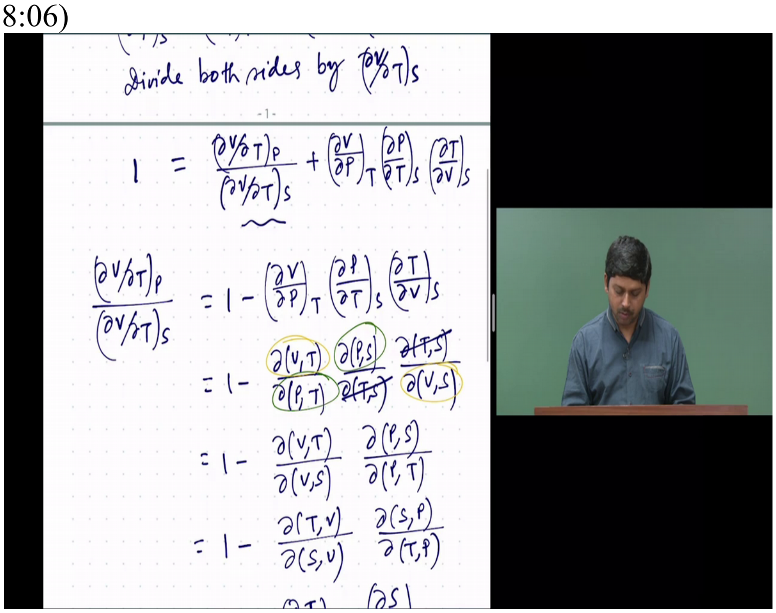
So if we want little bit you know one more step, then I can write 1 by Del S by Del T at a constant V. I hope you understand the step that I did. I just or I can or I can write it in a more this thing. So I will write Del T by Del S at a constant V and I write Del S by Del T at a constant P.

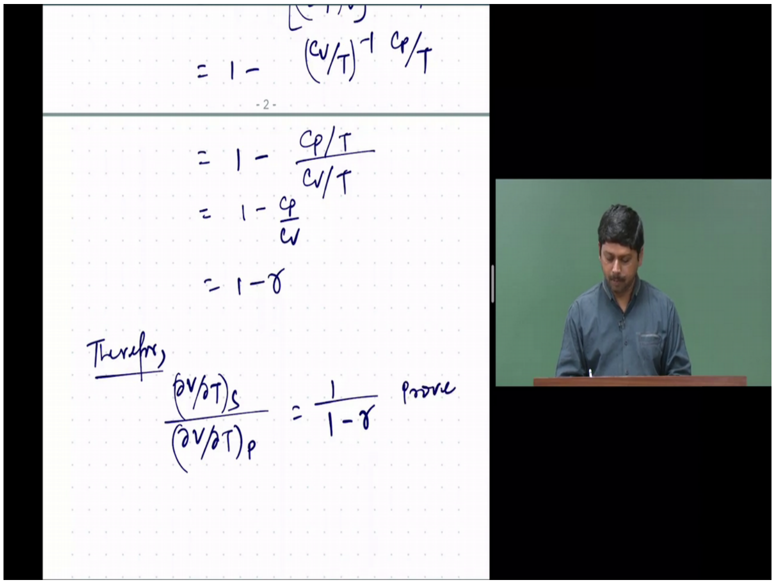
(Refer Slide Time 7:30)



So you know that this is inverse of Del S by Del T at a constant V inverse and Del S by Del T at a constant P is nothing but, we know it is CP by T. So 1 - and this was CV by T inverse and this is CP by T. So what we get here is 1 - CP by T divided by CV by T which is 1 - gamma.

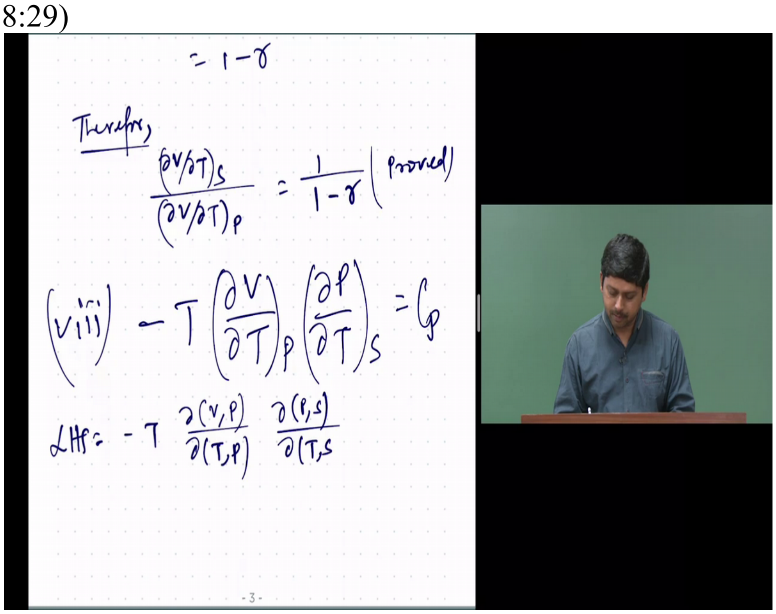
(Refer Slide Time 8:06)

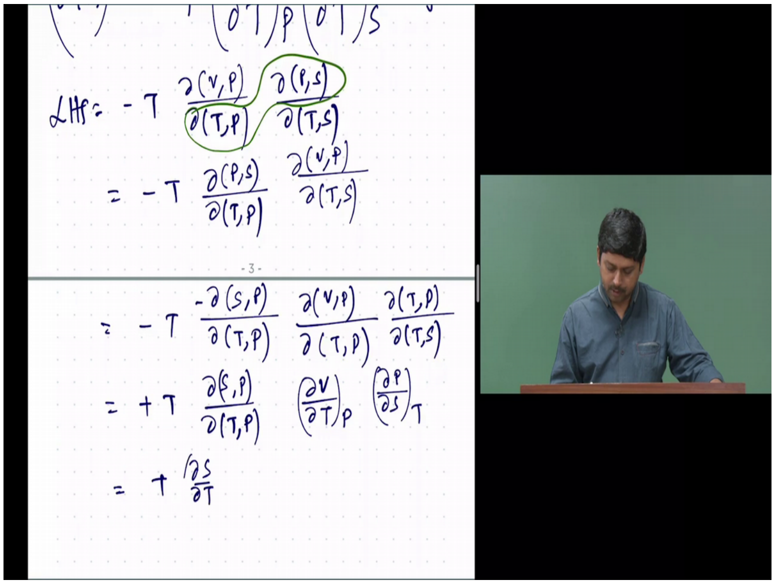




Now we started with this quantity but what we wanted is inverse of that. So Del V by Del T at a constant S therefore Del V by Del T at a constant S by Del V by Del T at a constant P is inverse of 1 - 1 by - gamma 1 by 1 - gamma. Okay. So let us go to the next problem.

(Refer Slide Time 8:29)





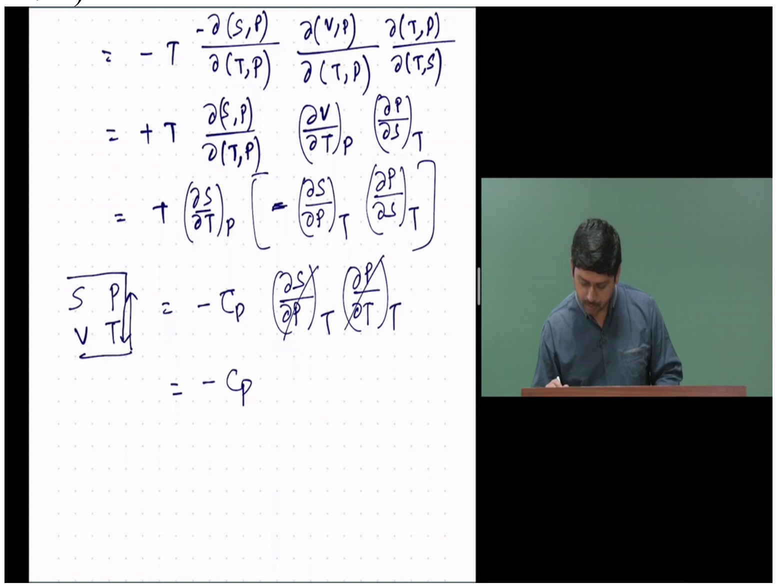
Next problem that we have to show is CP is = this quantity. It is easily start with the right-hand side. So we will start with the right-hand side. First we write that. So V iii, we have to show that - T Del V Del T P Del P Del T S is = CP. That is what we have to show. Okay. So this is straightforward. So we will start with the left-hand side and we will just expand it Jacobean form.

So we will write Del VP by Del TP and we will write Del PS by Del TS. So - T and as you can see that I can combine these 2 quantity, these 2 and write that as Del PS by Del TP. I can write Del PS by Del TP. And Del VP by Del TS. Let me see whether we are right right or not. So Del VP Del TP Del PS Del TS, fine. Now Del PS and TP, there is a reason because you know that we want to do Del S by Del T at a constant pressure and VP and that gives us TS. So that is fine.

Let us continue. - T now this one we can write as Del SP by Del TP but I need a - sign for that. And this quantity is, there is nothing common in that because we have VP and TS. So we will have to find out something for that. So we can say it is VP by Del what you can take? TP. Ya, we can take TP. Yup, we can take TP and then we can multiply that with TP and it will be PS. Okay. So now what we get? - - +, so + T Del SP by Del TP which is going to give us CP already.

And let us see what this quantity give us. This is Del V by Del T at a constant P and this is Del P by Del S at a constant T. So T into Del S by Del T at a constant P, this quantity is CP we know. So this should cancel each other.

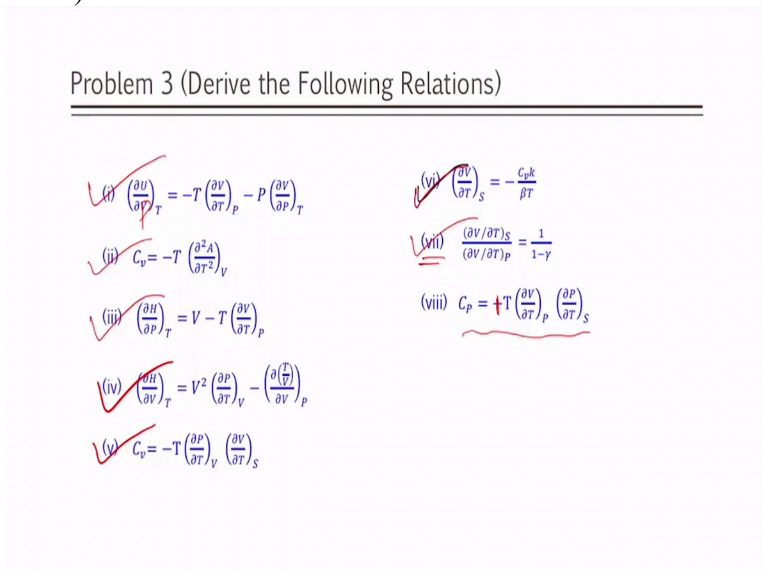
(Refer Slide Time 11:24)



So we can see that again we will write Maxwell's relation, S P T V. You see how helpful it is to write always SPTV because it gives quick quick thing. So Del V by Del T at a constant P means we have to go this way which means whenever we go this way, we just go the parallel way. So Del S by Del P at a constant T but it will be negative. So - Del S by Del P at a constant T and it is Del P by Del S at a constant T. So you can see that we are going to get, so this **is this** is going to cancel each other as you can see.

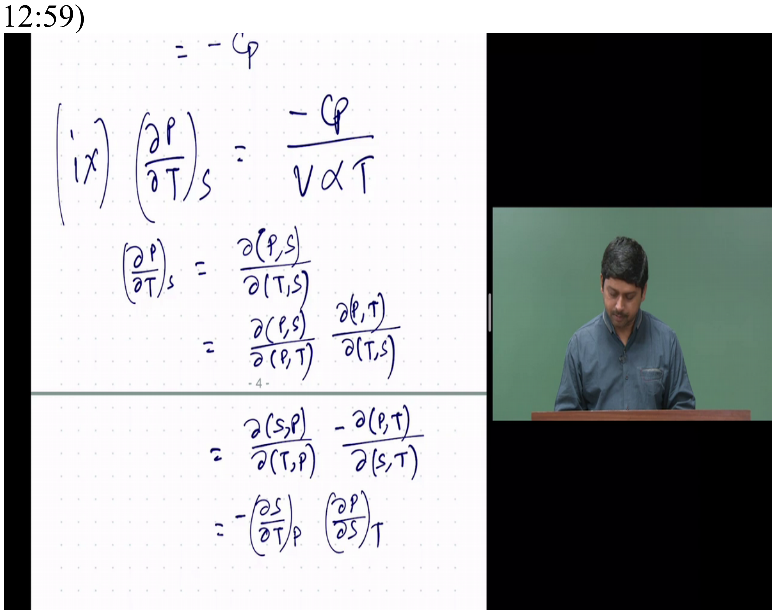
So first first of all we write - CP by taking the -, this -. And that leaves us with Del S by Del P at a constant T and Del P by Del S at a constant T which will cancel each other because they are just inverse of each other and we are going to get - CP. So - CP is the answer. So although although it is written + CP but it should be - CP.

(Refer Slide Time 12:34)



So that means it should be +. Okay. So now, we are going to go to the next problem. We have to show this one. Remember again the notational issues because Gemanski use beta as coefficient of thermal expansion, Alpha. So we have taken that from Gemanski. So actually what we have to show is next problem with is IX.

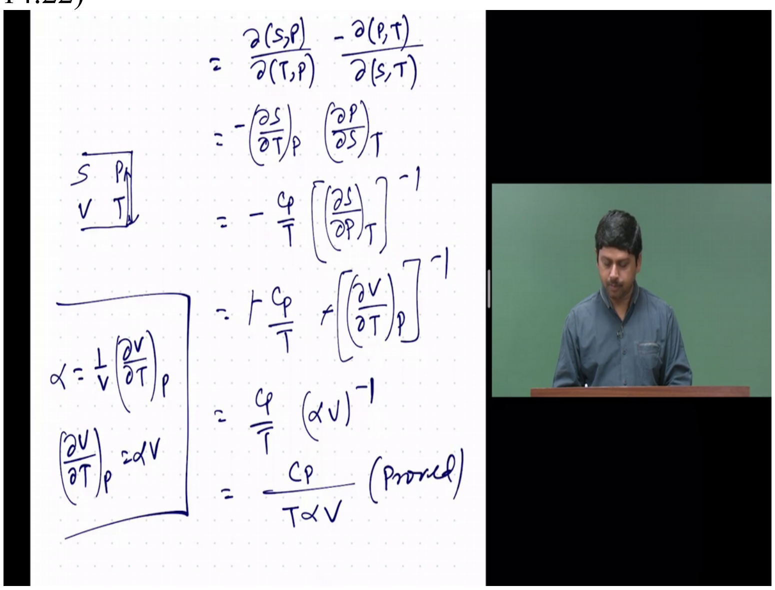
(Refer Slide Time 12:59)



We have to show that Del P by Del T at a constant S is - CP by V alpha T where alpha is coefficient of thermal expansion. So let us see that. Okay. So we will start with that and so again we are going to use Jacobean. So Del P by Del T at constant S is Del PS by Del TS. We need CP, remember. So that means, we are going to write that as Del PS by Del PT and then you have to multiply with Del PT and the Del TS. So that is going to give us Del SP and the Del TP because you know that I can interchange both of them.

And the right-hand side I can write with a - sign, I can write that as - Del PT by Del ST. okay. So this one is going to give us CP by T or I will just write one more step to show that it is CP by T, there is a - sign here and that is nothing but Del P by Del S at a constant T.

(Refer Slide Time 14:22)

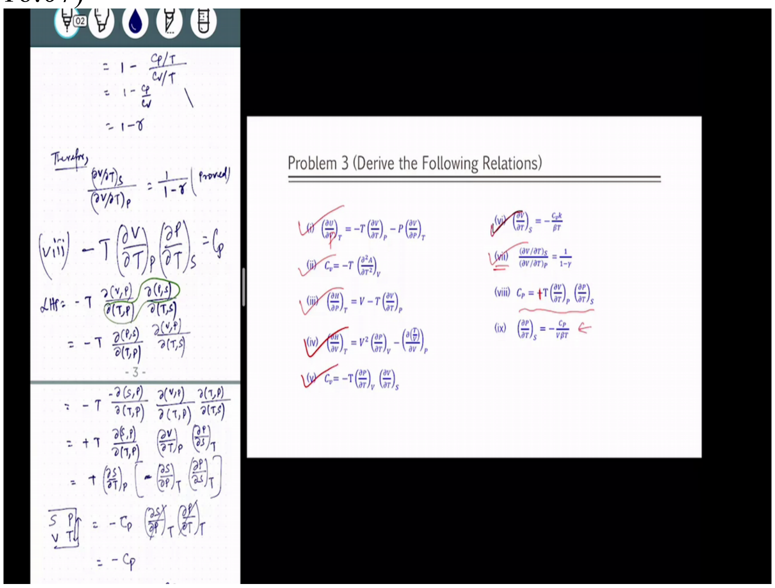


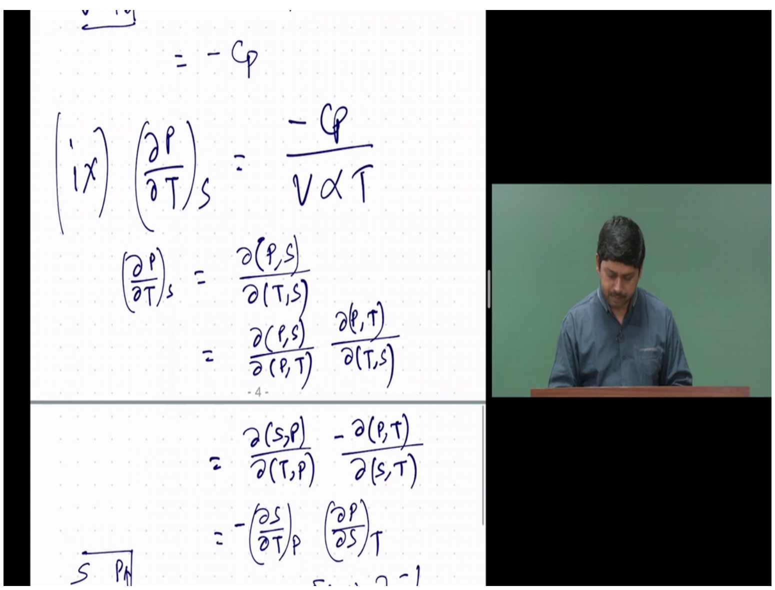
Okay. Now this is nothing but - CP by T. And what is this quantity? We need again Maxwell's relation for that, SPTV and we have to show that which direction it is going. So P, S okay. So you can see that I cannot write PS at a constant T like this because it is PS at a constant V. So whenever that kind of situation occurs to you, you see that you have to go this way, SP at a constant T only. You cannot do PS at a constant T.

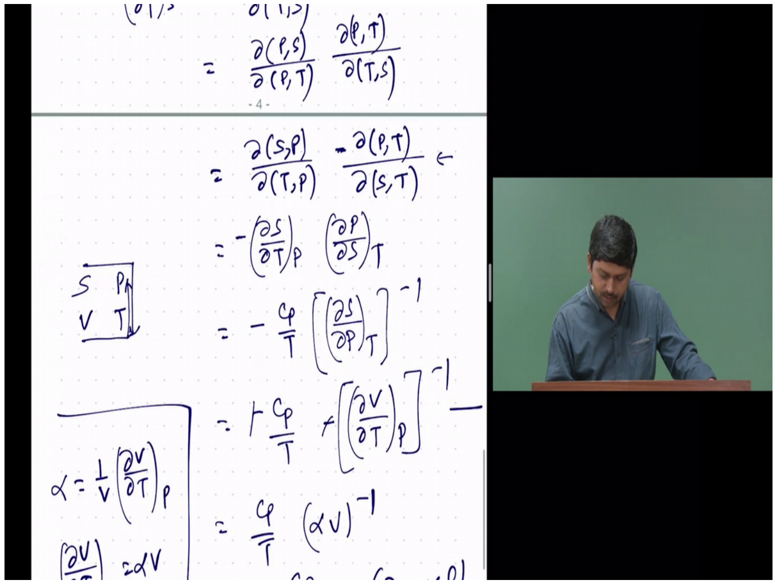
So it is SP at a constant T. So we can write Del S by Del P at a constant T inverse. Okay. So now what we see that SP at a constant T is nothing but VT at a constant P, negative of that. So - Del V by Del T at a constant P inverse of that, right. - - cancels here. So CP by T. And what is Del V by Del T at a constant P? By definition, it is nothing but alpha V. Alpha B in reverse. So we get CP by T alpha V because remember, Alpha is by definition is 1 by V Del V by Del T at a constant P. So therefore Del V by Del T at a constant P is nothing but alpha V. So that is also proved.

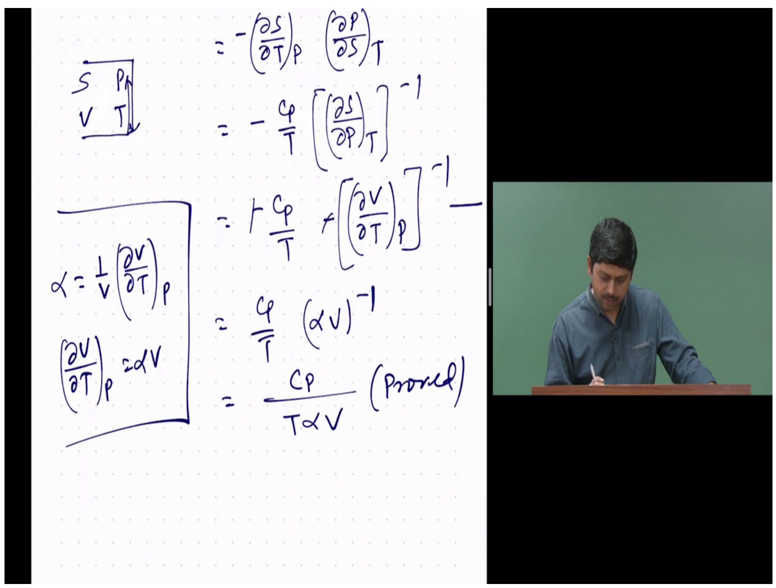
So I hope that during these exercises, you will see that what are the tricks and when and where things are done. When I am using inverse, when I am using Jacobean, when I am writing it in your different forms and adding things. So if you practice more of such problems, I think it will become easier. Okay. So now we will go to the next problem. Ya.

(Refer Slide Time 16:07)



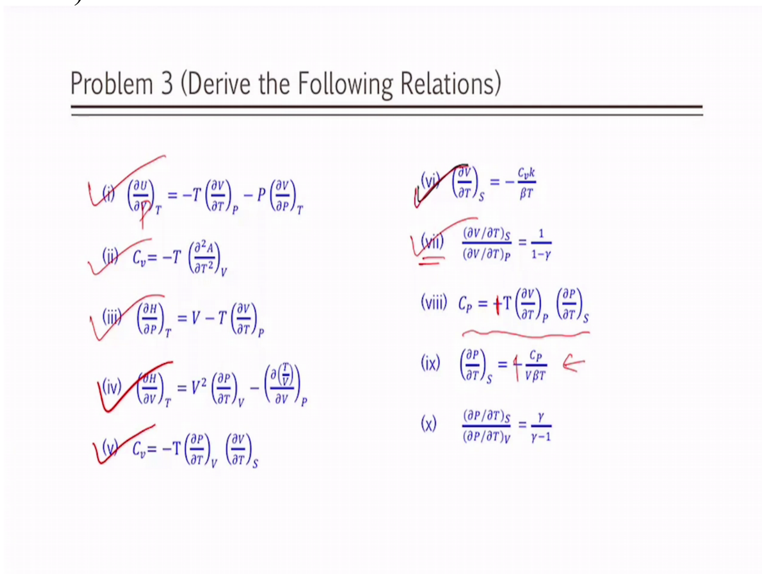






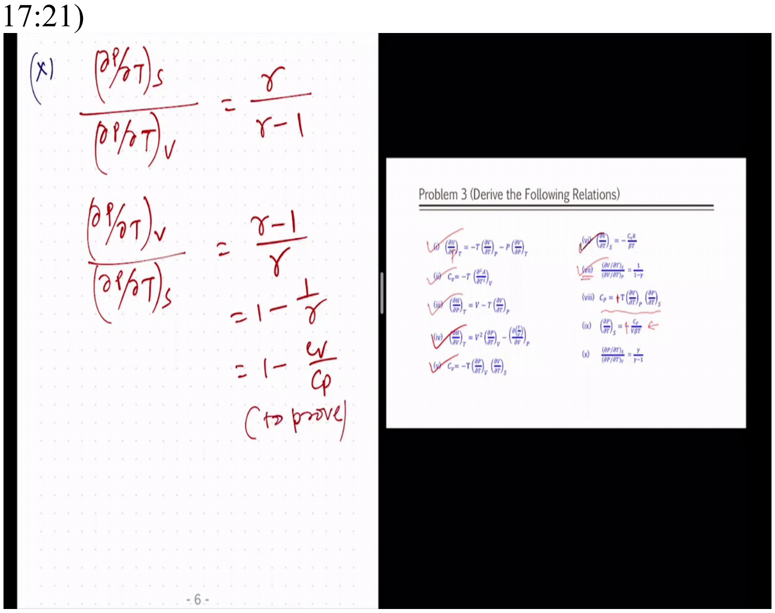
So you can see that there is a - sign here but we will first check that whether question is right or not because **let** let us see that if I have done any mistake or not. So I was supposed to prove that - sign but however we will just go through that once more and see whether it is correct or not. So Del P by Del S PS and PS, PS and PT, PT, then SP TS and then PT, ST. This - sign comes because of interchanging out that one. And then STP, that is fine. Then PST, that is also fine. Then that - sign is there, SPT. Inverse, that is also fine. Now when I am converting SP to T, S PT of course it is SP to T is going down and VT to P is going up, so there will be a - sign. - - becomes +. So this is +. So therefore the problem is not correct.

(Refer Slide Time 17:05)



So therefore the problem is not correct. It should be +. Now we will do the last problem of this thermodynamic relation because I think we have done enough so so that now these things become comfortable for you.

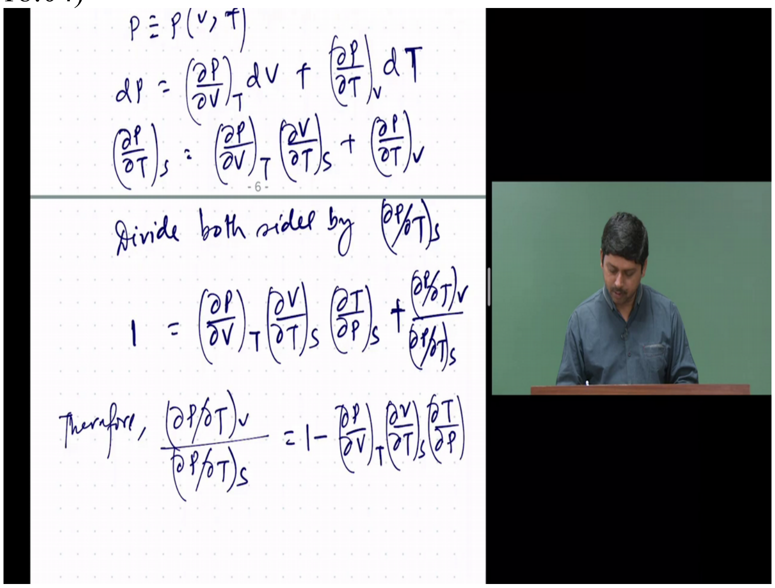
(Refer Slide Time 17:21)



So last problem says that Del P by Del T at a constant S divided by Del P by Del T at a constant V and you have to prove that to be gamma by gamma - 1. So again you see gamma by gamma - 1 is a Oxford but I would like to prove this one, the inverse of this. Del P by Del T at a constant V

Del P by Del T at a constant S is gamma - 1 by gamma which is 1 - 1 by gamma which is 1 - CP by CP. This is what we need to prove. To prove. Okay.

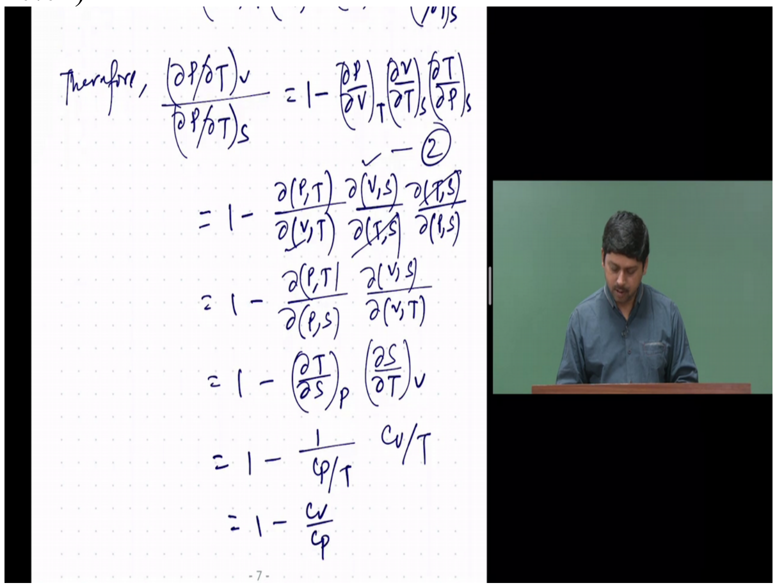
(Refer Slide Time 18:04)

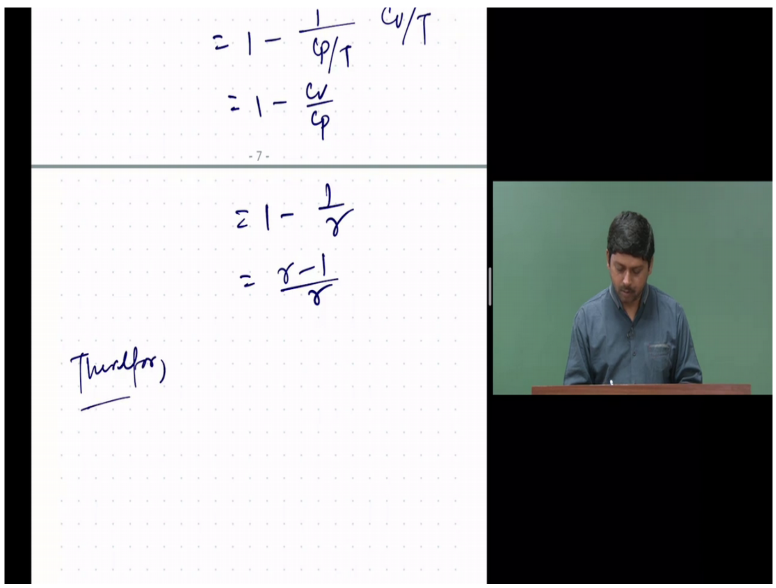


So we will use the same tricks that we used for the V problem. So we can write again P as a function of V and T. Just like we did V as a function of P and T, we can do P and the function of B and T and we can write DP as Del P by Del V at a constant T DV + Del P by Del T DT. Now we need Del V by Del T at a constant S. So divide both sides or integrate both sides. Sorry differentiate both sides by T and then at a constant S.

So what we get is that Del P by Del T at a constant S is Del P by Del V at a constant T DV by DT at a constant S + Del P by Del T at a constant V. DT by DT will not be there any more. So now divide both sides by Del P by Del T at a constant S. we will get 1 = Del P by Del V at a constant T, Del V by Del T at a constant S and we are dividing by Del P by Del T at a constant S. So which means it is Del S by Del P at a constant S + we are going to get what we are looking for Del P by Del T at a constant V by Del P by Del T at a constant S. Therefore Del P by Del T at a constant V Del P by Del T at a constant S which we are trying to prove in this is 1 - Del P by Del V at a constant T Del V by Del T at a constant S Del T by Del P at a constant S. So let us call it equation 2.

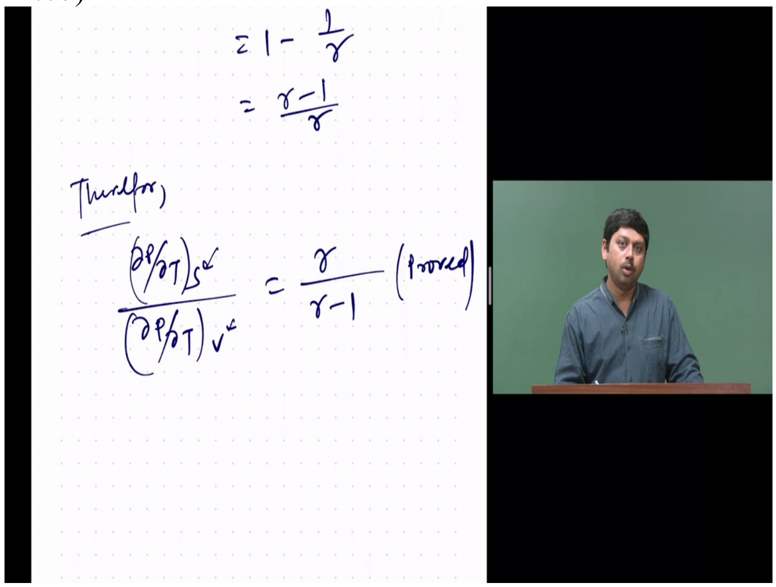
(Refer Slide Time 20:01)





Now okay so I can continue that, that is not a problem. That is = 1 - Del PT Del VT Del VS Del TS Del TS Del PS. You see how easy it becomes. TS TS cancel leaving us 1 - now we can combine PT and PS. So Del PT Del PS and we can combine VS VS and VT. So it becomes VS and VT. And we know that we can interchange P numerator and denominator, giving us Del T by Del S at a constant P and this will give us by interchanging Del S by Del T at a constant V which gives us 1 - this is 1 by CP by T and this is save by T which is 1 - CV by CP which is 1 - 1 by gamma or gamma - 1 by gamma.

(Refer Slide Time 21:07)



So therefore what we wanted is inverse of this Del P by Del T at a constant S by Del P by Del T at a constant V is gamma by gamma - 1 and that is proved. Also another interesting thing to note is that just by changing the constraint, the values are very different. So they are not able to 1 right? When you take S as a constraint and V is a constraint, that change in the pressure with respect to temperature is not same when you take the constraints different because the process itself is different.

When you fix the volume, you do not do any work and you hit the system and increase the pressure. When you take S as constant, then you are talking about an adiabatic system, a reversible adiabatic system. Therefore S is not changing and you are trying to you know do some work and then get that. So therefore the things are not the same and therefore you. okay. So now we are going to do some other kind of problems. Of course related to this but also we need different kinds of tricks and different kind of thinking involved. So.