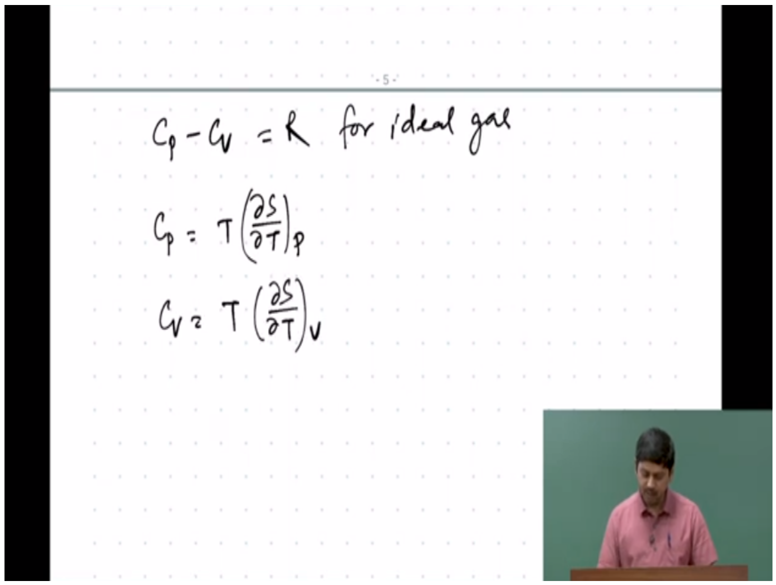
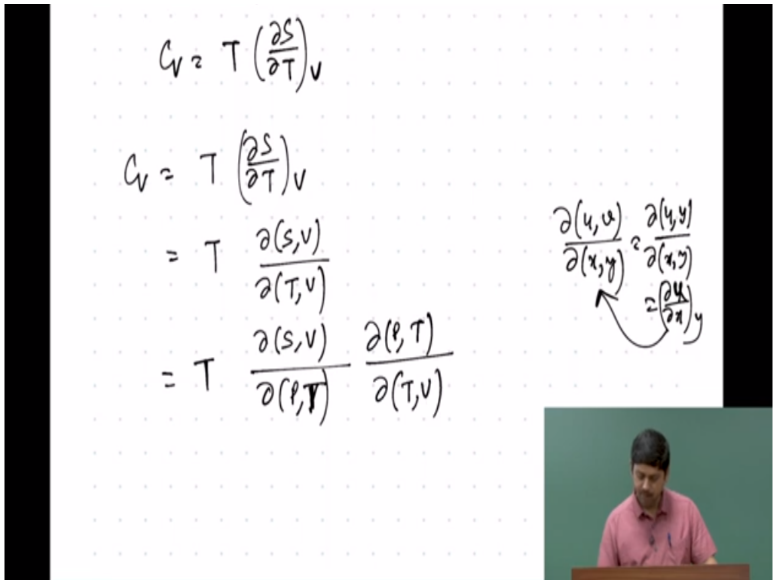
Chemical Principles 2
Professor Dr. Arnab Mukherjee
Department of Chemistry
Indian Institute of Science Education Research, Pune
Thermodynamic Relations: Jacobian Method Part 02

(Refer Slide Time: 00:16)



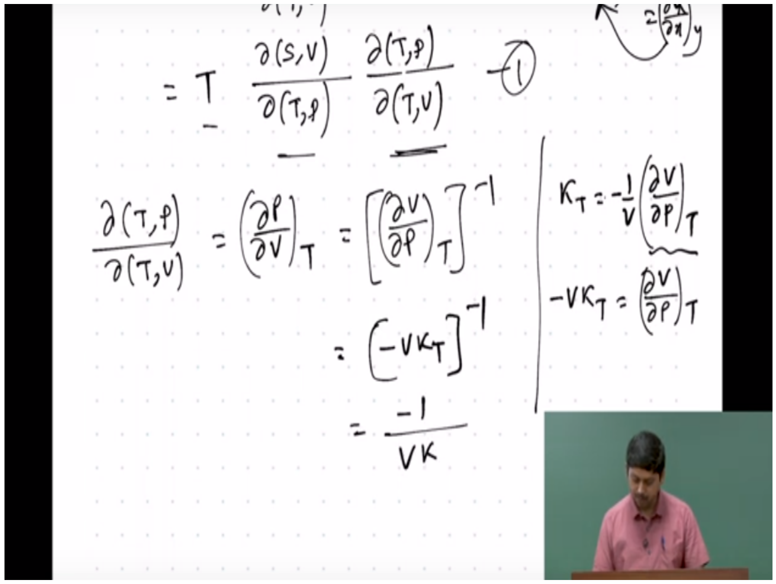
Once we have all the steps, now let us see that how to convert one form to another, so for that we will take a famous example of CP minus CV, so we know that CP minus CV is equal to R for ideal gas, so what will be the value for any realistic system it is not R in general it is only R in case of an ideal gas, so in order to understand that will go to the general formula of CP and CV, so you know CP is T del S by del T at a constant P and CV is T del S by del T at constant V.

(Refer Slide Time: 00:56)



So we can start with any of that and see the whether the other one is coming up or not, so we will start with CV, so CV is T del S by del T at a constant V, now since we have that we can immediately write the Jacobean for as is V and TV, we have explained that so whenever these V comes we can usually do that because it is that form where you remember UV by del XY if V and Y are same then we can write as del U by del X as a constant Y, so we are just from here we are writing this one, now once we have that we need to bring PT remember because we also need to bring P further reason that there is a CP term which you involves as you can see that CP term involves a P so we need to bring PT, so we got PT here and then you have to multiply with PT and we have DV already here in order to make.

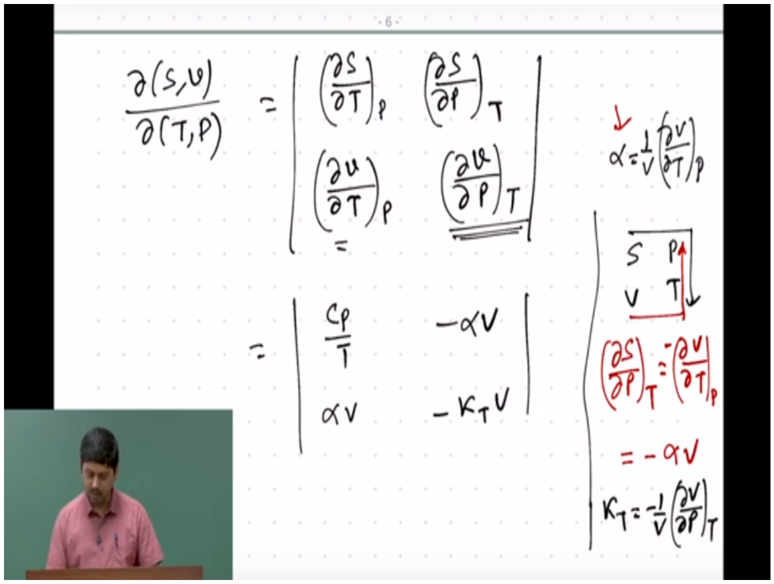
(Refer Slide Time: 02:10)



So this is fine you can also multiply with TP instead of PT if that makes life easier, so I will do that with TP instead of PT for a reason TP and here also I have to do the same thing TP less number of calculation nothing else , so now I have this three terms here one two and three, so let us call that equation one and I will do it separately, so first M is just T we do not anything let us do this one, so del TP by del TV is nothing bur del P by del V at a constant T now by definition you know whenever you see that it is nothing but inverse of del V by del P at a constant T the inverse of that.

Now what is del V by del p at a constant T it is in you know you are using pressure at a constant temperature and therefore the volume will reduce, so del V by del P, so you know from the definition that isothermal compressibility K_T is minus one by V del V by del P at a constant temperature so therefore this quantity is minus V K_T is del V by del P at a constant temperature, so I can write that as minus V K_T and inverse of that which means it is nothing but minus one by V $K_{T,}$ So you keep it as equation two and then we start with the middle term this term we are going to start with is V and T.

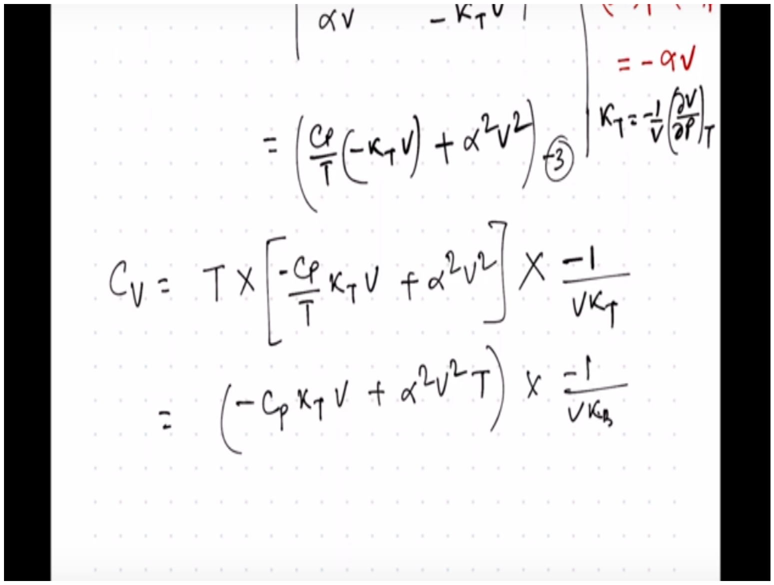
(Refer Slide Time: 03:46)

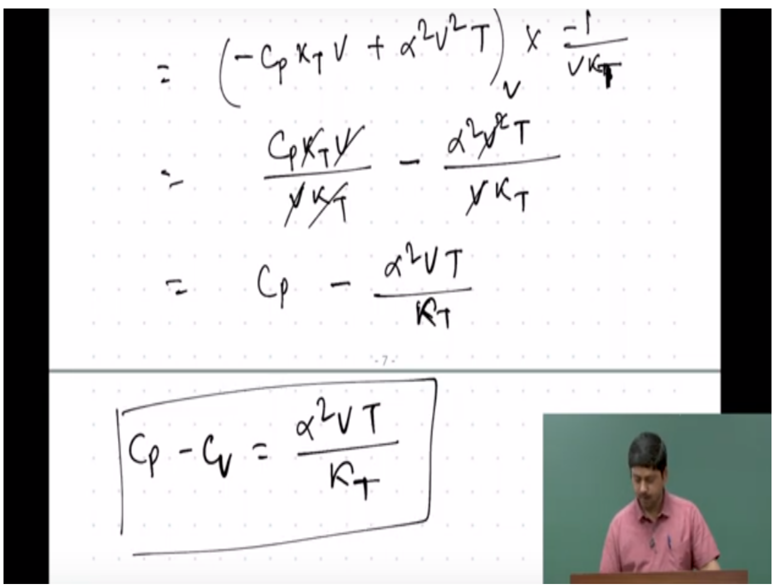


So del S V and del TP they are nothing in common, so we have to write in a matrix form as this, so del S by T s a constant P then del S by del P at a constant then del V by del p at a constant P and del V by del P at a constant T, so this is the matrix that we got and you have evaluate each of the matrix, Now we see that we got the CP term here del S by del T at a constant P is nothing but CP by T and we got isothermal co-efficient of thermal expansion here as you know that alpha is one by V del V by del T at a constant P which means this quantity is nothing but alpha V this quantity.

Now on the right hand side I have del S del P at a constant T and that is not immediately understandable but we can use the Maxwell relation here SP TV and we know that del S by del P at a constant T which is coming down is del V del T at a constant V which is going up, so therefore we can write del S by del P at a constant T is nothing but minus of del V by del T at constant P minus F, now what is del V by del T at a constant P again we are talking about a thermal expansion which is one by V del V by del T you look at here minus of this quantity is minus alpha V if you compare with this quantity you can see that it is nothing but minus alpha V, so you can write minus alpha here and del V by del P which again isothermal compressibility as you know that isothermal compressibility is K_T which is minus one by V del V by del P at a constant T so this quantity is minus K_T into V.

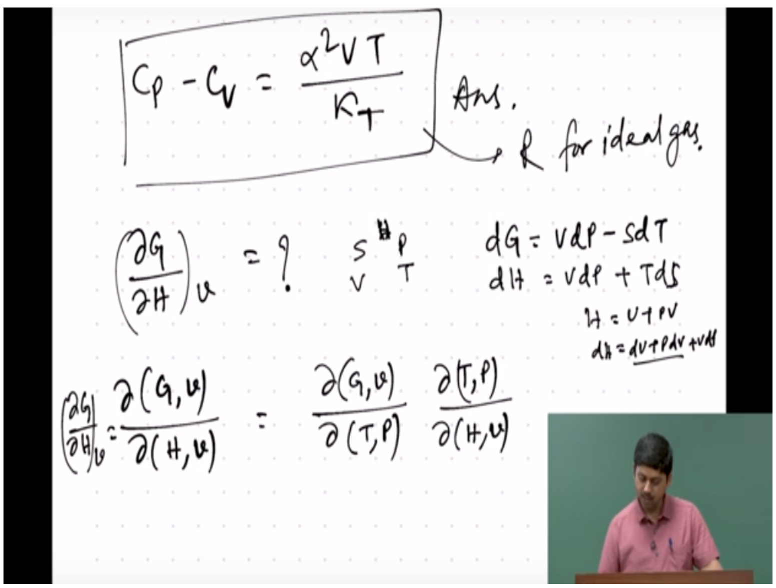
(Refer Slide Time: 05:46)

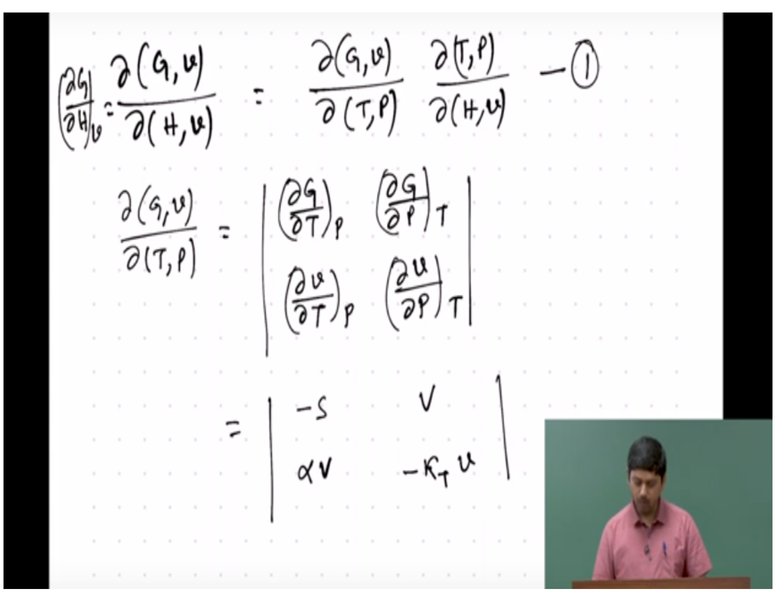




Now I have all the four quantities now let us multiply that and see what we get CP by T minus K_T V minus-minus becomes plus alpha square V square, now let us called that equation three, so from all the equation what we get is CV equal to T multiplied by this quantity CP by T or you can just say write minus CT by T K_T into V plus alpha square V square multiplied by go to equation two minus one by V K_T minus one by V K_T, now what we say we just multiply with T first, so we see it is minus CP K_T V plus alpha square V square into T and then into we will not jump this steps, So now we will multiply with the K_T we get minus-minus plus CP K_T V by V K_T minus alpha square V square T by the K_T, now V K_T cancels giving us CP minus V and V square cancels giving me V so minus alpha square VT by K_T, so now therefore CP minus CV is alpha square V T by K_T and that is what the answer is you see it is almost straight forward I just took from one and went to the other and you know it was very-very smooth that way so the thing is that you can do many such thing okay one thing you can prove that this quantity is equal to R for ideal gas you can try that to yourself.

(Refer Slide Time: 07:55)



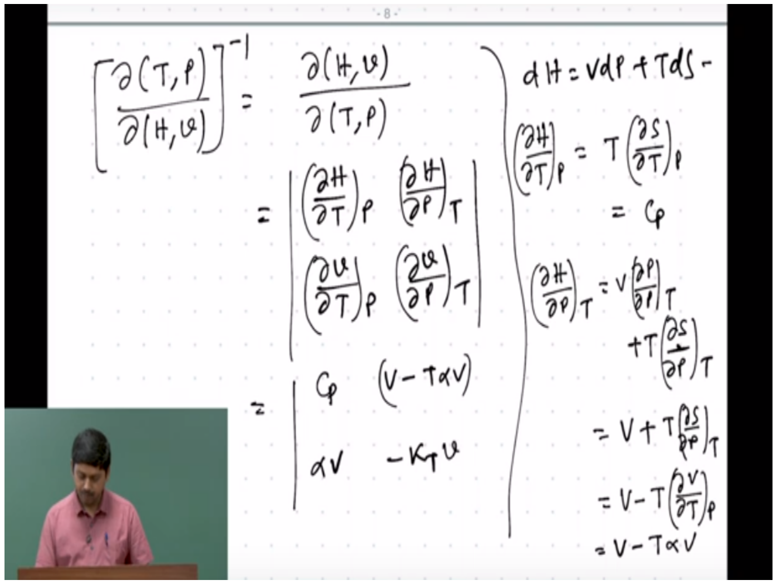


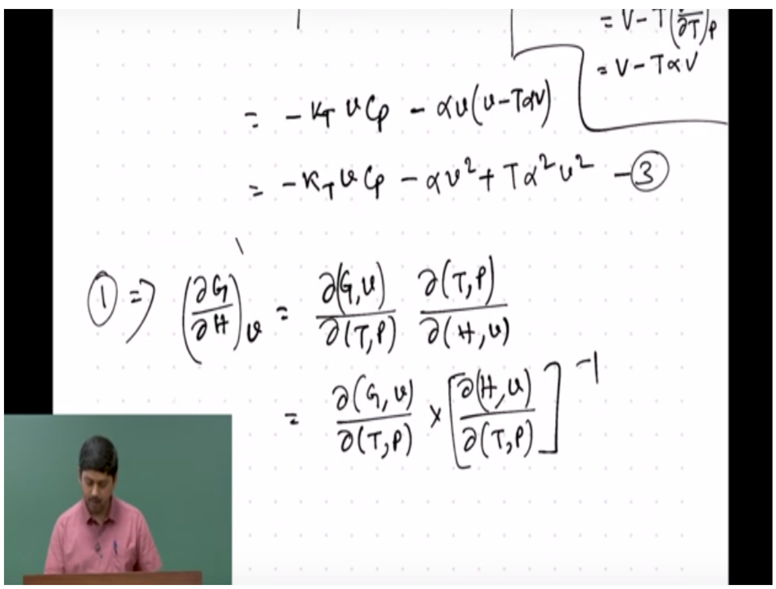
Now we can do one more which is shown in the mathematica will let us go back, so let us do this one let us do delta G by the crazy one delta H at a constant V let us see this one, so shall we get that particular answer or not let us try so delta G by delta H at a constant V is how much let us see first itself we can write delta GV by delta HV, and then we write delta GV by delta TP delta TP by delta HV, now once we have that we need to know certain quantities of G so del G equal to VDP minus SDT, so therefore it advantageous for us if we have T and P quantity so this is particularly fine and for H it is VDP plus TDS I guess.

So remember our SP TV thing SPTV and H is a function of S and P, so these are the variable that we get also we can remember that H is nothing but U plus PV and therefore DH is DU plus PDV plus VDP and U plus PDV DU is DQ plus DW, so TDS minus PDV, so TDS plus VDP, so that is perfectly alright so these are the things that we will need, so these are the things that we will need in order to calculate that so this is a product of these two quantities, so now let us separate them and write so del GV by del TP is equal to del G by del T at a constant P and del G by del O at a constant T del V by del T at a constant P del V del P at a constant T.

So this is let us say equation number one and then we are taking only the first term of the equation number one, now del G by del T at a constant P let me see if I wrote it correctly, now del G del T at a constant P is how much you can get that from here del G by del T at a constant P is minus S, so this is nothing but minus S and then del G by del P at a constant T is nothing but V and del V by del T at a constant P we know against is isothermal co-efficient of thermal expansion alpha V and this quantity del V by del P it is minus K_T into V you got all the four for the first term and this going to give as K_T SV minus alpha V square.

(Refer Slide Time: 11:51)





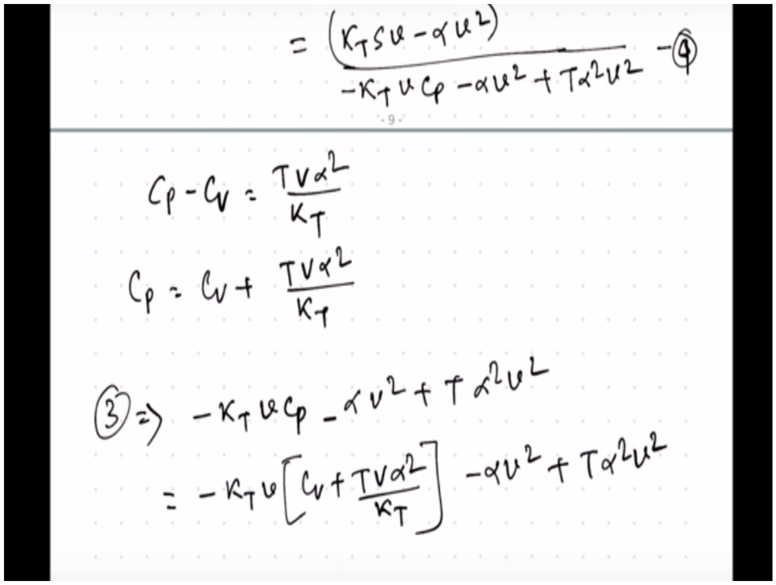
Now right hand side del TP by del HV, del TP by del HV is of course inverse of that quantity ,so we are going to do this one HV or first of all we are going to write the inverse itself as DP because we are taking inverse because we want H to be in the numerator now for H what are the variable that are important as I said DH is V DP plus TDS, so both S and P are important but let us see with T itself we can get something or not, so we can write that del H by del T at a constant P del H by del P at a constant T del V by del T at a constant P del V by del P at a constant T, we need to get el H by del T and del H by del P.

So we can get that easily from this equation for example from this equation itself we can get that let us take a derivative with respect to T at a constant P once we do that this quantity becomes first one term becomes zero because it such a constant P, so the second one gives us del S by del T at a constant P and T del S by del T at a constant p is nothing but CP, so the first term is CP, now let us take a derivative with respect to P, so del H by del P at a constant T is the first terms is giving us V del P by del P at a constant T which will be only plus T del S by del P at a constant T.

So now V plus T and del S by del P at a constant T we have to use Maxwell relation we are going to do that, so now again we are going to remind you that it is SPTV, so del S del P at a constant T is minus of del V by del T at a constant P you have used the Maxwell relation here, so what is the del V del T at a constant P you know is this co-efficient of thermal expansion again, so therefore it is V minus T and the del V by del T is co-efficient of thermal expansion but alpha into V, so it will be T alpha V, so CP V minus T alpha V, now what is del V by del T again coefficient of thermal expansion multiplied by volume and that is minus K_T into V, so we got all that.

So we got minus K_T V CP minus alpha V into V minus T alpha V which is minus K_T V CP minus alpha V square plus T alpha square V square let us see if I am okay T alpha square V square, so we got two quantities this was our one and this is the second one, so let us say I write as two and this one I write as three, so now our original equation was the one from one we get that in order to do this particular derivative, which is del G by del H at a constant V was product of two quantities del GV by del TP multiplied by del TP by del GV by HP and this we wrote as del GV by del TP multiplied by del HV by del TP inverse, now we got this quantity as this one so and the.

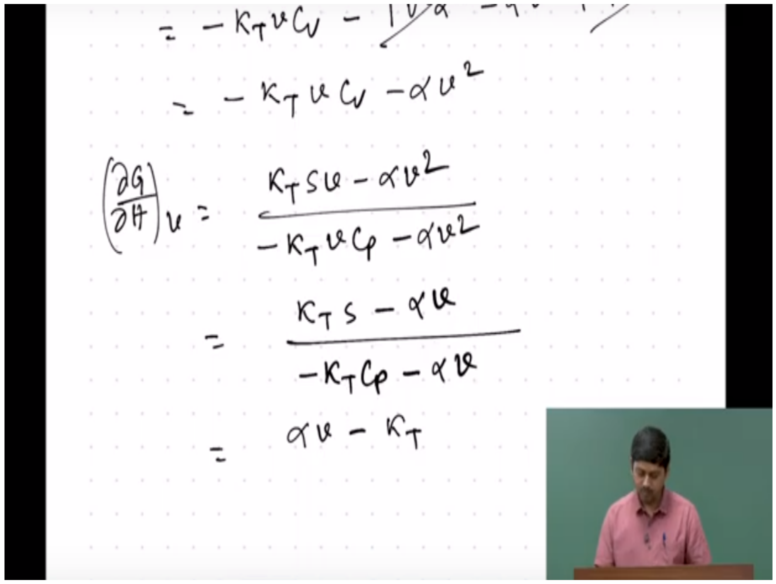
(Refer Slide Time: 16:47)

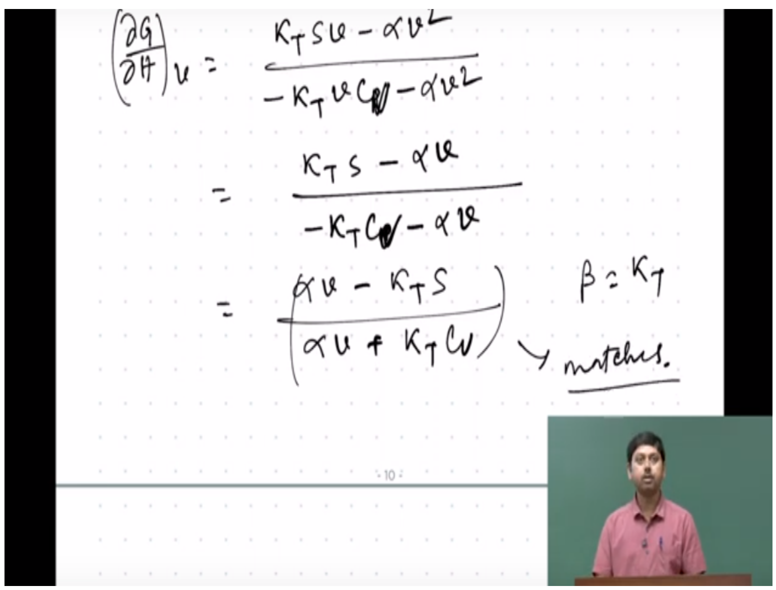


So now we write from equation two and three del GV by del TP we got K_T as V minus alpha V square let me see and then this inverse quantity I have to divide by the whole thing minus K_T V CP minus alpha V square plus T alpha square V square because the quantity that we got we have to take the inverse of that and that is the inverse that we got, so which means.

So now see in order to match the result which is here we have CV here so let us convert CP to CV just to match the result otherwise it fine just to see whether it is coming there or no, so we know that CP minus CV is TV alpha square by K_T so therefore CP is CV plus TV alpha square by K_T, so from three we can write that now from three we can just write from two itself from three this equation three this will be four then, so sum three we can write minus K_T V CP, CP minus alpha V square plus T alpha square V square equal to minus K_T V CV plus TV alpha square by K_T minus alpha V square plus T alpha square V square.

(Refer Slide Time: 18:40)





When you multiply that we get minus K_T VCV minus K_T K_T cancels we get T V square alpha square minus alpha V square plus T alpha square V square, let me see minus K_T V minus CV K_T V K_T K_T cancels minus TV square alpha square, so now this two term cancels giving us minus K_T VC V minus alpha V square, so therefore the result is little bit simpler is that K_T SV minus alpha square, so therefore del G by del H at a constant V is K_T is V minus alpha V square divided by minus K_T V CV minus alpha V square at least one we can go and K_T S minus alpha V divided by minus K_T CP minus alpha V, now if I see the expression mathematica it is says I take minus on both sides.

So I get alpha V minus K_T into S by K_T CP plus alpha V or alpha V plus capital CV just for the sake of symmetry alpha V plus O this is CV not CP, and let us see the mathematical result now so they say alpha V minus beta into S and their beta is our K_T remember then alpha V plus beta into CV into K_T CV, so this matches with matches with that of mathematica you see that starting with any derivative we can actually convert it to one which can be measurable of thermal expansion volume can be measured and then of course if you entropy cannot be measured we can again express entropy in term of other quantities or entropy is also can be measured as you know that from the derivative of free energy with respect to temperature.

So therefore all of these things are measurable and we can actually get that what if enthalpy is change and the free energy what will be the change in the free energy of enthalpies change at a constant volume, so that is really-really interesting and intriguing that we can do that with the standard techniques that are there that if these thing will be very-very difficult to do so some of the derivatives will take more time with Jacobean but thing is that since it is logical and you can go step you know directly step by step without remembering anything you should be able to finish it within the time that is what I so but you need more practice and we are going to some practice problem after this of there of changing thermodynamic derivatives from one to another along with some other problems related to the free energy itself.