Chemical Principles II
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Tutorial Problem - 13

So we have learned how to change one (thermo dynic vareb) one thermodynamic derivative to another thermodynamics derivative using Jacobian technique and I have shown some usefulness in terms of finding out CP minus CV, a general expression of CP minus CV and also an arbitrary partial derivatives of del G by Del H at a constant V, I guess. So the point is that we can do whatever partial derivative it is using the Jacobian technique and that will make our life much simpler and will help us also to find out useful quantities.

For example you know joule coefficient or joule Thomson coefficient and things like that. So we are going to go and do some more thermodynamic derivatives you know it is called reduction of thermodynamic derivative, so we are going to go and do some more reduction of thermodynamic derivatives and see that how we can easily you know use them and you know convert them and we get more accustomed to that.

So we will do some more problems to help you understand that things better.

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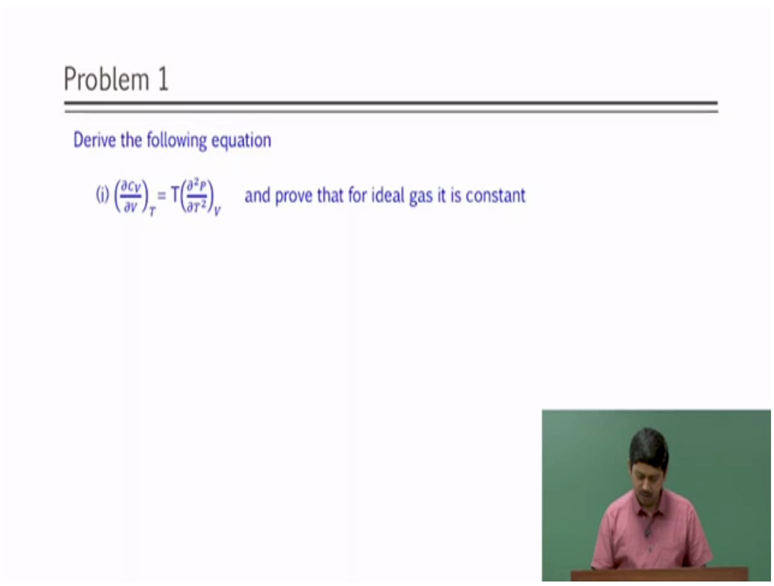

So today is problem that we are going to do is that problem number 1 has these derivations that derive this following Del C V by Del V so I am going to do it here.

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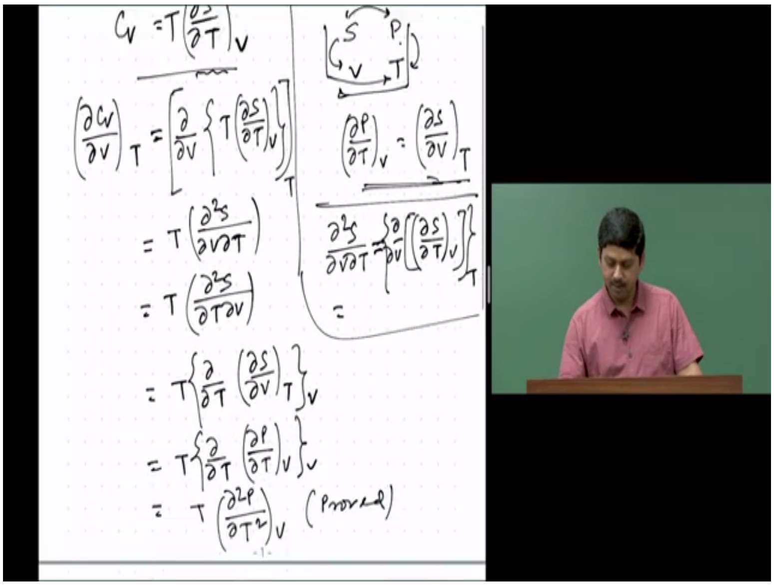

So the first one is prove Del C V by Del V at a constant T is equal to T del 2 P del T 2 by V, ok. So we have to do in this (pra) problem Del C V by Del V at a constant T is equal to Del 2 P by Del T 2 at a constant V. Now we will start with the definition of C v, C v is Del S by Del T, T Del S by Del T at a constant V, so we know that. So once we start with that we will have to see whether we can get the right hand side expression or not but before we do that let us also understand that if we get these things from somewhat from the Maxwell relation or not.

So we write Maxwell relation S P T V and we see that we can get either Del S by Del P or we can get Del S by Del V or Del P by Del T, so Del P by Del T we can get though ok, that is a important thing, so Del P by Del T you can get and we know that from Maxwell relation that Del P by Del T at a constant V is we have to do this way is Del S by Del V at a constant T, ok.

So that is fine we have that however we see in this particular formula it is just interchange it is Del S by Del T at constant V but we need Del S by Del V at a constant E so they are not exactly same, so we will try to see whether we can get that or not. So now before you get that so C V definition is this one, so therefore if I take one more derivative Del C V by Del V T if I do that then essentially I have to take the derivative of this entire quantity at a constant temperature.

Now if I want to do that then you see that T becomes a constant, so T will come out and it will give me Del 2 S by Del V Del T which by notation means this is a shorthand notation Del 2 S by Del V Del T, the shorthand notation is Del S by Del T at a constant V and then the whole thing taking a derivative with respect to V at a constant T, so that is equivalent to writing as Del S Del 2 S by Del V Del T.

Now we know that S is exactly differential, so therefore we can write that as Del 2 S by Del T del V as well, now once we do that we can write T Del Del T Del S by Del V at a constant T and this whole thing at a constant V. now we know that Del S by Del V T from Maxwell relation is nothing but Del P by Del T V and whole thing is at a V constant V which then proves our point that it is nothing but Del 2 P by Del T 2 at a constant V and that is what we wanted to show.

You see the Jacobian cannot be used in this particular case because Jacobian will take the derivative to the heat capacities like C P, C V and then alpha and Kappa T but here we wanted a conversion of relation and the way I understood that we have to do the this formula for exact differential is when I look into Del P Del T as this one then I realize that which means that the V and T are interchange and then I have done that, so you have to do that as well.

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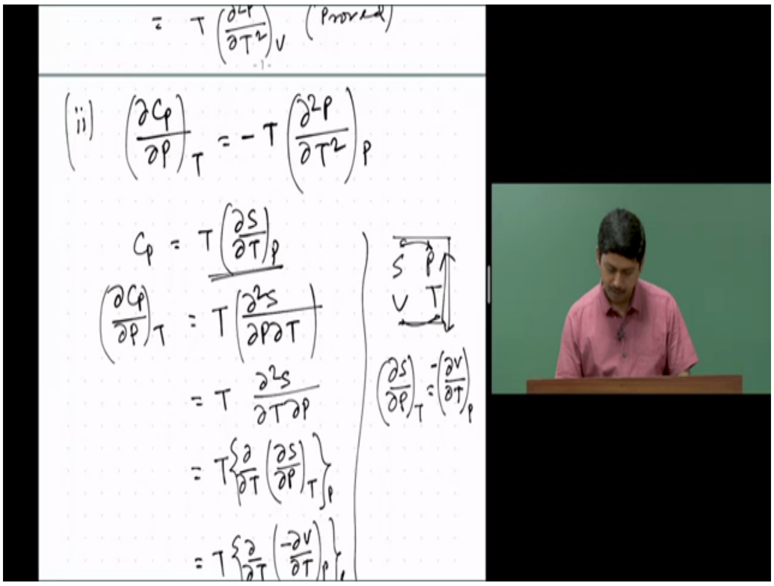

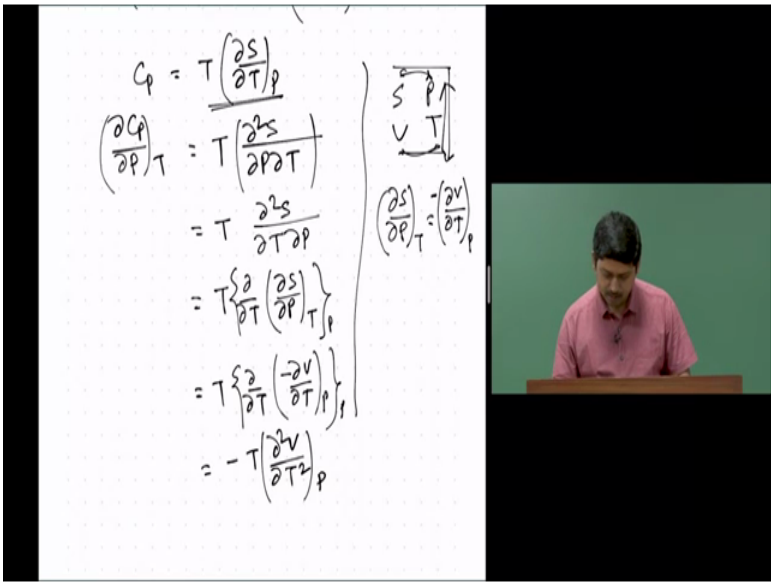

So now go to the second problem, we have to show that Del C P by Del P at a constant T is minus T Del 2 P by Del T 2 at a constant P. so again I think it is very similar to the problem above just let us write C P as T Del S by Del T at constant P that is the CP and we need to do the derivative of this particular one, so we need to do Del C P by Del P at a constant T which means we have to take the derivative of this quantity at a constant T, so T will come out and we will get Del 2 S by Del P Del T, ok.

So again it is a shorter notation Del 2 S by Del P Del T meaning first we will take the derivative with respect to T at a constant P then the whole thing at a constant with respect to P at a constant T. So this is same as since it is exact differential as Del S Del P which again means that first derivative with respect to P at a constant T then with respect to T at a constant P. So again we just going to look at the Maxwell relation S P T V and we know that Del S by Del P is Del P by so Del S by Del P is Del V by Del T we know that, so but there is a plus and minus thing as you can see from my arrows, so Del S by Del P at a constant T is Del V by Del T at a constant P but with a minus.

So it will be T Del Del T Del S by Del P at a constant T and the whole thing it is at the constant P which is T Del Del T and Del S by Del P at a constant T is minus del V by Del T at a constant P which is and the whole thing is at a constant P which is minus T Del 2 V by Del T 2 at a constant P. Now but I think it is written question is given wrongly it should be V not P, ok.

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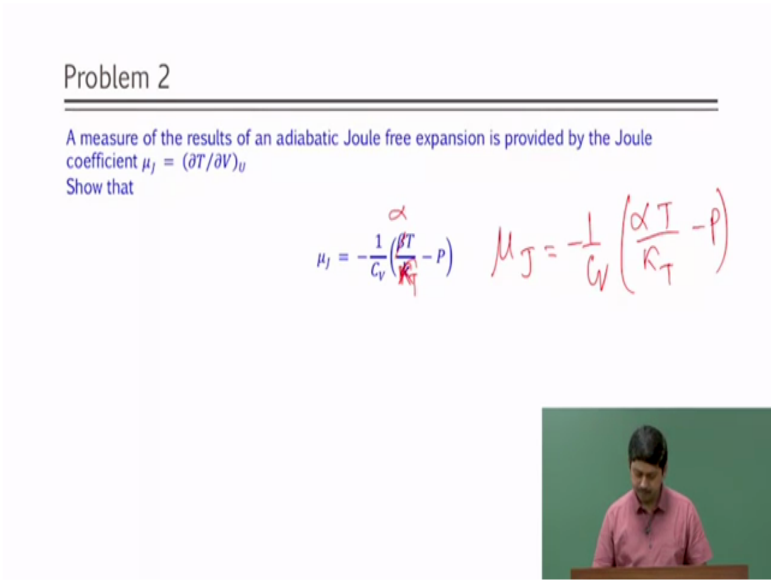

So we will let us go to the next problem, so next problem says that a measure of the results of adiabatic joule free expansion is provided by the joule coefficient mu j, show that mu j is equal to 1 by C V, so this is nothing but alpha because alpha is the coefficient of thermal expansion and this is a cup and this is nothing but Kappa T minus P, so I will just write it clearly, so mu j show that mu j is 1 by C V alpha T by Kappa t minus P.

So let us see if that is the thing we can show or not.

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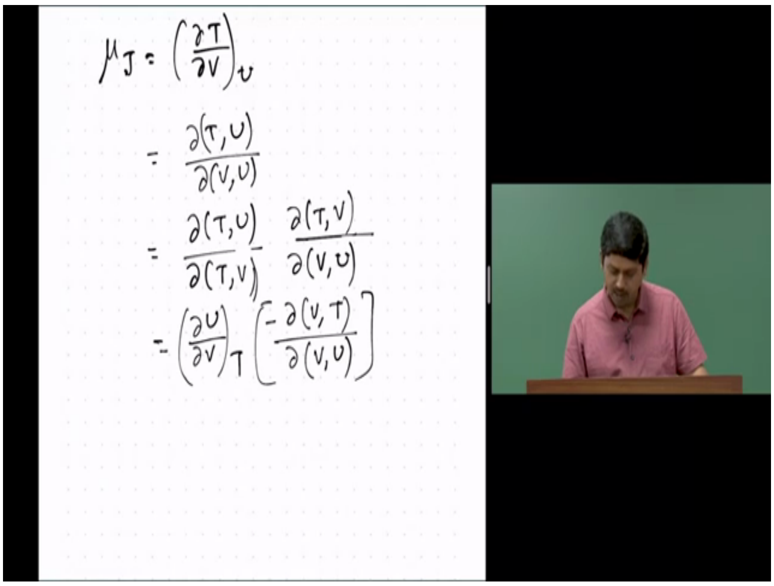

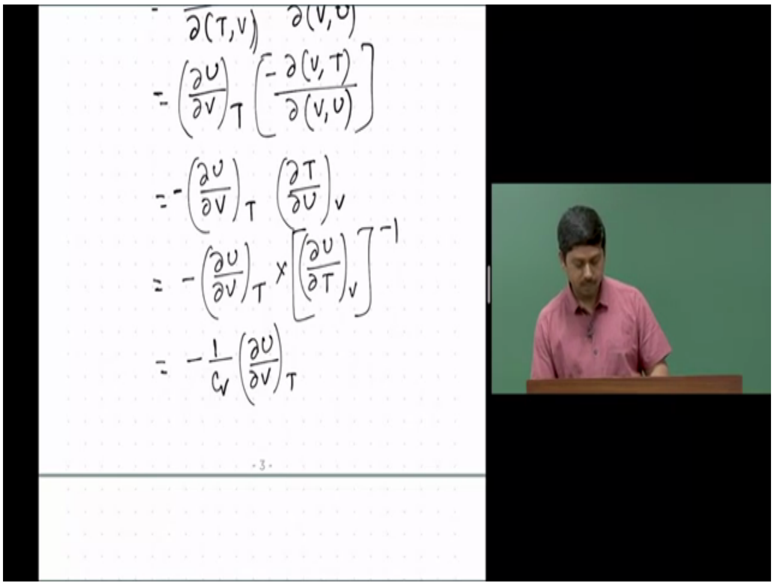

So by definition you see mu J is Del T change in temperature with respect to change in volume at a constant U, so you know in this particular case we have to use the Jacobian because we have to bring the U in the numerator, so it is Del T U by Del V U, I can write that and then I can take as Kappa T U by Del T P and I have to multiply by Del T P and Kappa V U.

Now this one the left hand side gives us Del U by Del P at constant T, so instead of T P let us change it to V because V is good for always U, so use a natural variable is V and T, so let us change it to V so instead of P I will just put V, so yeah and that also is good because here also I am getting V common. So now we can write that as Del U by Del V at a constant T multiplied by I take a minus and then I Del V T by Del V U and you know why the minus is because I switched the numerator positions T and V.

Now Del U by Del V T do you remember what it is? So U is a natural variable is PdV ok, so U is TdS minus PdV so that does not help us because a Del U by Del V at a constant S only we would have got T but Del U by Del V at constant T is given so that does not help us, so we will deal with that later on. So now just let us continue Del U by Del V T or I will put a minus here and that gives us Del T by Del U at a constant V, so which is Del U by Del V at a constant T multiplied by Del U by Del T at a constant V inverse which as you know is C V, so this is minus 1 by C V Del U by Del V at a constant T that is what we got, that is what the joule coefficient is.

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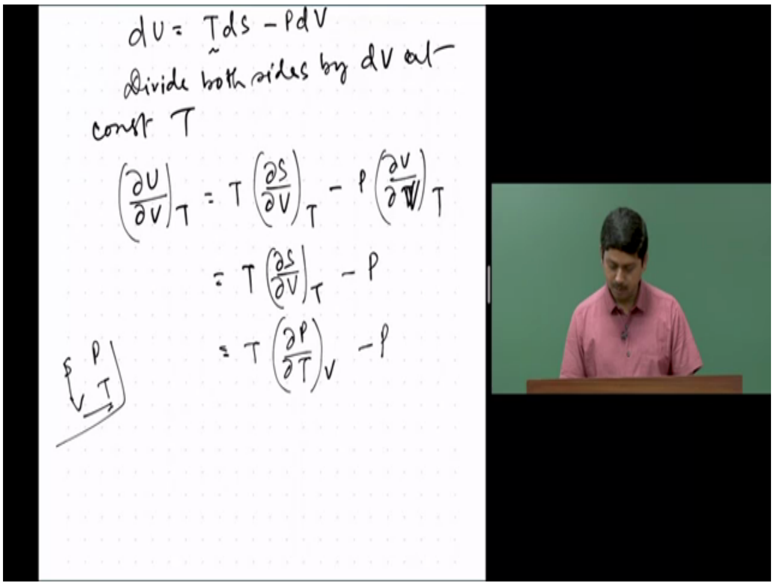

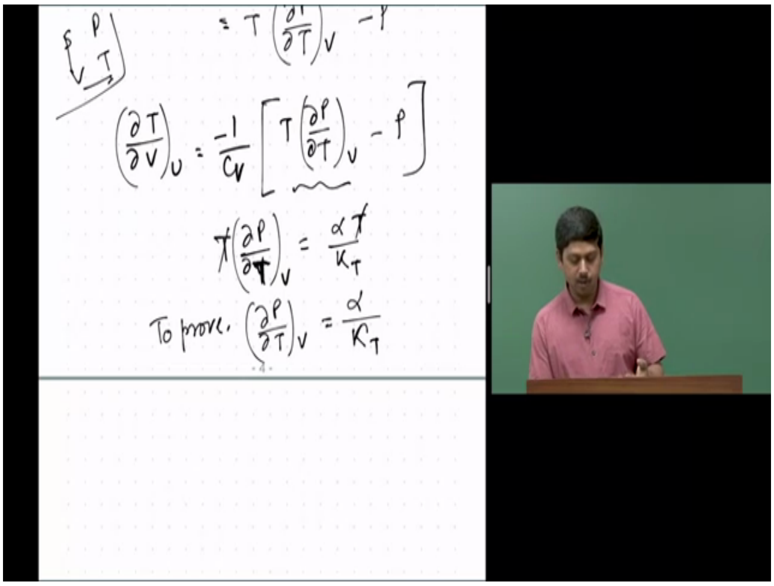

Now we have to do Del U by Del V at a constant T, so we will start with this expression dU equal to TdS minus PdV. Now we cannot do directly from here Del U by Del V at constant T because T is not a variable here, so T is just a parameter so therefore we have to divide both sides by dV and now at constant T, so what you are going to get from there is Del U by Del V at a constant T is T Del S by Del V at a constant T minus P Del V by Del V at a (cons) Del V by Del V at constant T which is T Del S by Del V at a constant T minus P, say I am getting back minus P.

So now what else see we also have got now I have to just do Del S by Del V and that I will now use formula for or Maxwell relations so S P T V, so you see Del S by Del V is at a constant T is nothing but Del P by Del T at constant V minus P. So this also we got but that does not help us in getting the Alpha and Kappa T because in alpha and Kappa T we know, so this much we got.

So now if I just write my Del T by Del V at a constant U I have already got minus 1 by C V T Del P del T V minus P, now I have to prove that this quantity T Del P del T V is equal to alpha T by Kappa, so in fact T is also common, so I have to prove Del P Del T sorry it was T Del P Del T V is Kappa T I will just rewrite is it again I have to prove Del P Del T V is alpha by Kappa T, this what I have to proof then I can prove the whole relation because everything else is fine with this.

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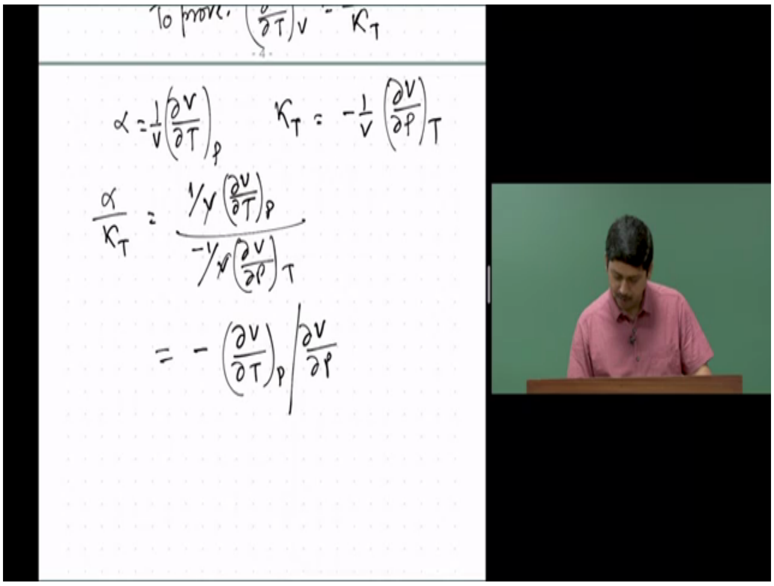

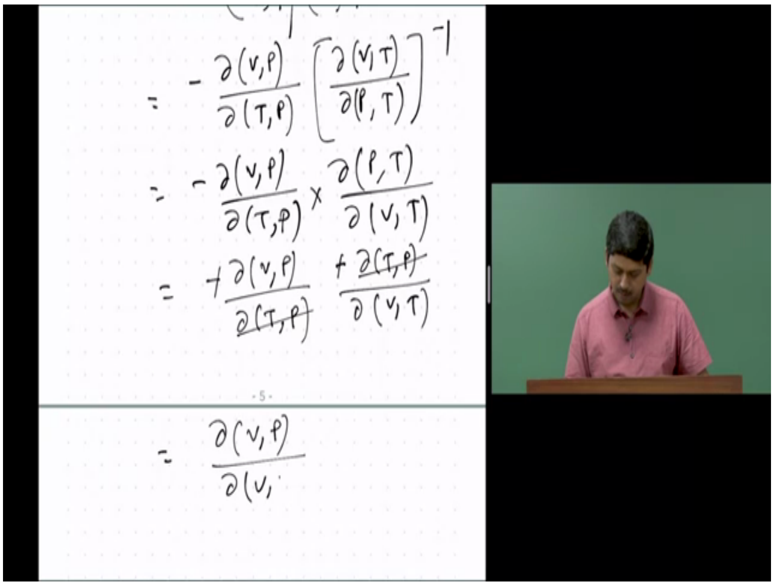

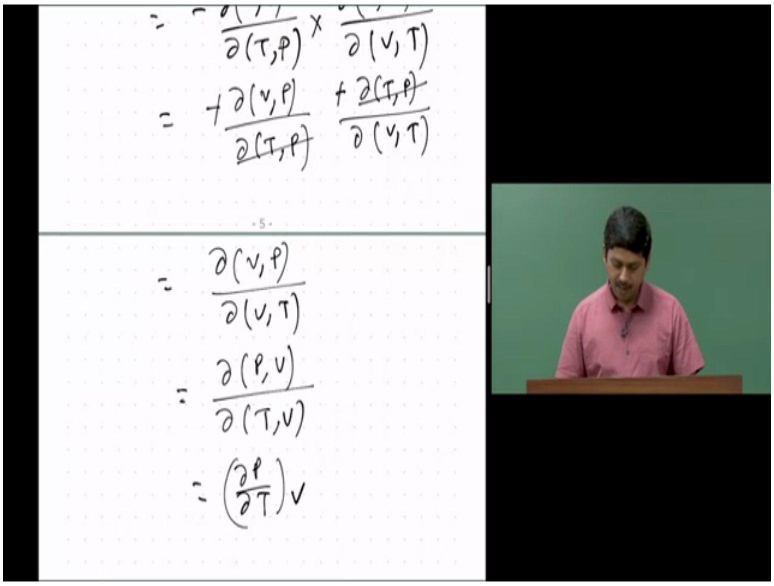

Now we know what is alpha, alpha is coefficient of thermal expansion, so Del V Del T at a constant pressure 1 by V and we know what is Kappa T right minus 1 by V Del V Del P at a constant T, so alpha by Kappa T is 1 by V Del V Del T at constant P by minus 1 by V Del V Del P at a constant T, 1 by V 1 by V cancels each other there is a minus sign we will have to deal with that, now Del V Del T at a constant pressure Del V no I will just take by sign Del V Del P at the constant T.

Now I am going to used a Jacobian technique minus Del V P by Del T P and divided by Del is not a good way of writing it, so I will put an inverse Del V T by Del P T inverse meaning just I will just change it Del V P Del T P multiplied by Del P T by Del V T. Now there is a P T so I am not going to change that V P Del T P I will going to change take a minus and say T P Del V T, now Del T P Del T P cancels giving us and minus minus cancels giving us Del V P by Del V T which is nothing but Del P V by Del T V which is nothing but Del P by Del T at constant V.

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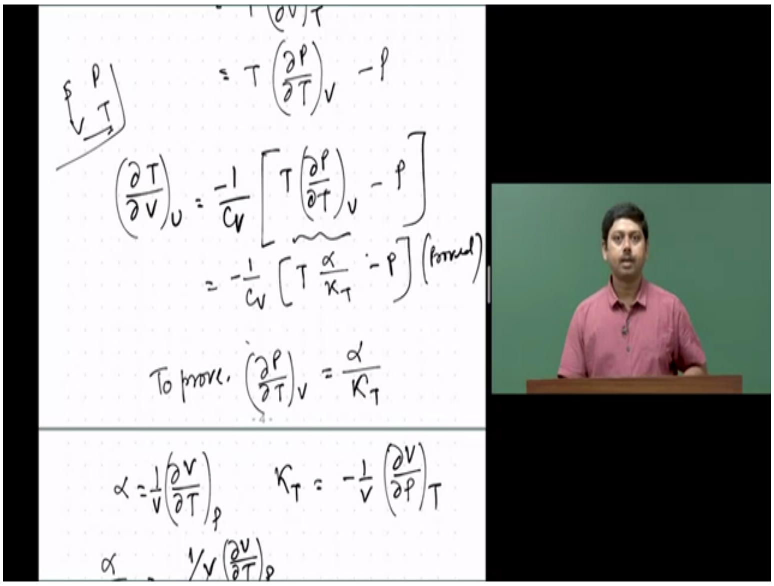

So now I am coming back and I see that I can write this whole expression I am going to just remove this part, now I am going to whole expression I am going to write as T alpha by Kappa T minus P and proved, ok.

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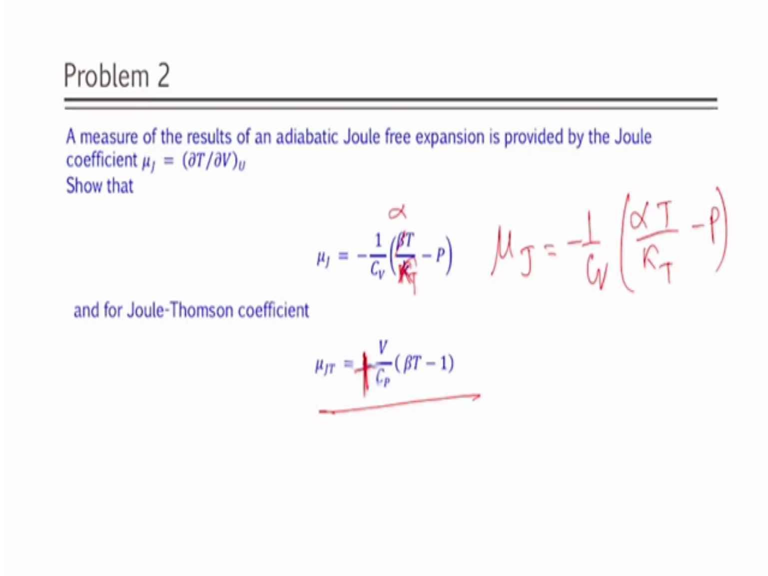


$$= \left(\frac{\partial \ \ }{\partial T}\right)_V$$

$$\mu_{JT} = -\frac{V}{C_p}(\alpha T - 1)$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial(T,H)}{\partial(P,H)} =$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial(T,H)}{\partial(P,H)}$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$dH = dU + PdV + VdP = TdS + VdP$$

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P + V\left(\frac{\partial P}{\partial T}\right)_P^{\to 0}$$

$$\mu_{JT} = \frac{\partial(T,H)}{\partial(P,H)} = \frac{\partial(H,T)}{\partial(H,P)} = \frac{\partial(H,T)}{\partial(T,P)}\,\frac{\partial(T,P)}{\partial(H,P)}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

S P
V T

$$= -\frac{\partial(H,T)}{\partial(P,T)} \times \left[\frac{\partial(H,P)}{\partial(T,P)}\right]^{-1}$$

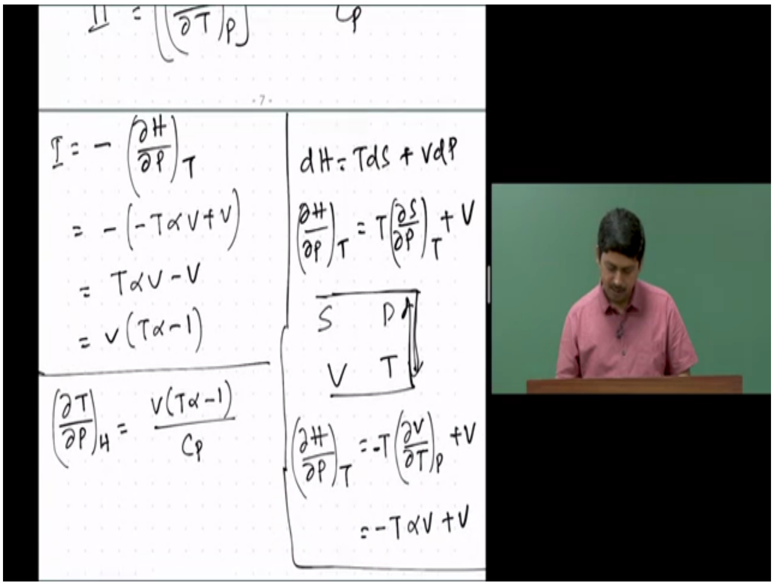
$$= -\left(\frac{\partial H}{\partial P}\right)_T \times \left[\left(\frac{\partial H}{\partial T}\right)_P\right]^{-1} \quad -(1)$$

$$= I \times II$$

$$II = \left[\left(\frac{\partial H}{\partial T}\right)_P\right]^{-1} = \frac{1}{C_p}$$

$$I = -\left(\frac{\partial H}{\partial P}\right)_T$$

$$dH = TdS + VdP$$



Now for joule Thomson coefficient we have to show that mu JT is equal to minus V by C P, so this beta is alpha actually it suggests a notational issue V by C P alpha T minus 1. Now so joule Thomson coefficient is as you know that it is change in temperature with respect to pressure at a constant enthalpy, so this one we have to show as the one that is mentioned here since H is held as constant we have to bring the H in the numerator and we can do that by taking this and immediately we need something.

So for example we need the C P and you know just we can just do a back calculation and just find out that what C P is C P is Del S by Del T at constant P, so we need some S somewhere and alpha is also there, so yeah but we need the S and T and pressure so that you have to just remember and also we have to remember our H, H is nothing but H is U plus P V so it is dU plus PdV plus VdP and dU plus PdV as you know is nothing but TdS, so TdS plus VdP is Del H.

So we just keep that those things in mind and continue our derivation, so mu JT is Del T H by Del P H we can take the H on the left hand side, so Del H T by Del H P. So now what do you want as a derivative so for example if I do Del H by Del T we can do Del H by Del T at constant P yeah that we can do here so for example we do from this above expression del H by Del T at a constant P will give us T Del S by Del T at constant P plus, so I am doing with respect to T right so V Del P by Del T at constant P, so that goes 0, so Del H by Del T at constant P is nothing but that, so we need that.

So we can do this Del H T and so we need with respect to temperature at a held at constant pressure, so that means we need this so Del H P by Del T P we need that, so H P is here for sure so T P is not here, so let us let us write that Del T P multiplied with Del T P and Del H P, so you see I wanted to bring Del S by Del T at constant P and I just that is that is why I multiplied with T P in the numerator and denominator.

So now what I am going to see is what is the left hand side? So I can just take a minus sign and rewrite it Del H T by Del P T multiplied by Del H P by Del T P inverse, left hand side will give us Del H by Del P at a constant T and this is going to give us Del H by Del T at a constant P and inverse of that. Now this one what is Del H by Del P at constant T? So let us figure out from that, so Del H by Del P at a constant T I have to take the differentiation again so if I do that this equation from this equation Del H by Del let me see a Del H by Del P, Del P at a constant temperature is T Del S by Del P at a constant temperature plus V because Del P Del P will cancel.

So now when we do SP T V ok, so this so this will be a little bit longer not just simple once we will do that more carefully in the denominator ok so first just write this one. So we are going to do individually all that ok, so let us do both of them separately, so let us write that as equation 1 and just write that as term 1 into term 2, now term 2 is by definition is very simple that is Del H by Del T P inverse we have shown that that is nothing but Del H by Del T P is nothing but T Del S by Del T P which is nothing but C P, so this is nothing but C P so we can write as 1 by C P so you got as you can see we got our 1 by C P right there from the term 2.

Now term 1 term one is minus Del H by Del P T, so for that what we need is we need to write again dH as TdS plus VdP take derivative with respect to P on both sides, so Del H by Del P at a constant T is T Del S by Del P at constant T plus V because Del P by Del P will be 1. Now once we have that we have to use Maxwell relation S P T V and we know Del S by Del P at a constant T is Del V by Del T at a constant P.

So Del H by Del P at a constant T is T Del V by Del T at a constant P plus V, now what is Del V by Del T at constant P? So yeah so this and ok and it will be a minus sign because as you can see that this is going down and this going up so there will be a minus here, so that will be minus T now what is Del V by Del T? So we can say coefficient of thermal expansion multiplied by V, so this will be alpha V Plus V so we got the whole thing so that means this term 2 our term 1 which is this is equal to minus of this quantity minus T alpha V Plus V which is going to give us T alpha V minus V or V T alpha minus 1, ok.

So now we put together whatever our answer was our answer that we wanted is Del T by Del P at a constant H is equal to V T alpha minus 1 divided by C P did you get that? So the way it is written is minus V by C P, so minus V by C P 1 minus yeah so I think that we have made a mistake with minus somewhere let us see where did I let us see we start with this Del T by Del P at a constant H this is not a problem this part is fine here I have interchanged P and T, so this this part is fine so 1 is having the minus, now 2 the side 2 that is T P H P H P T P, so 1 by C P is fine.

Now minus Del H by Dell P T, now Del H by Del P T is written here, so I guess we got the thing right although there is there difference with just a minus, so the question was little bit wrong so this is correct the question was wrong, so this should be plus and not minus, so I got the answer so we will stop here and we will continue.