Course on Phase Equilibrium Thermodynamics
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Lecture 11
Tutorial

Hello everybody, so by this time what are the things that we have covered? We have covered the introduction part the first Law and the second law. Before we proceed further I would like to do a few problems on these particular topics and then proceed and the problems which I will be dealing with today, they will be primarily confined to the things which we have already covered and I would also like to mention that the assignments along with these problems will be consulted while preparing the question papers for your final examination.

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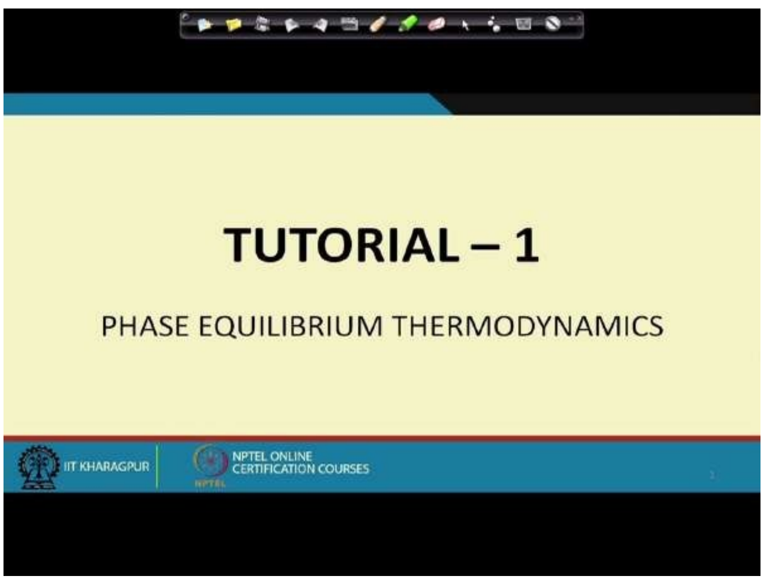

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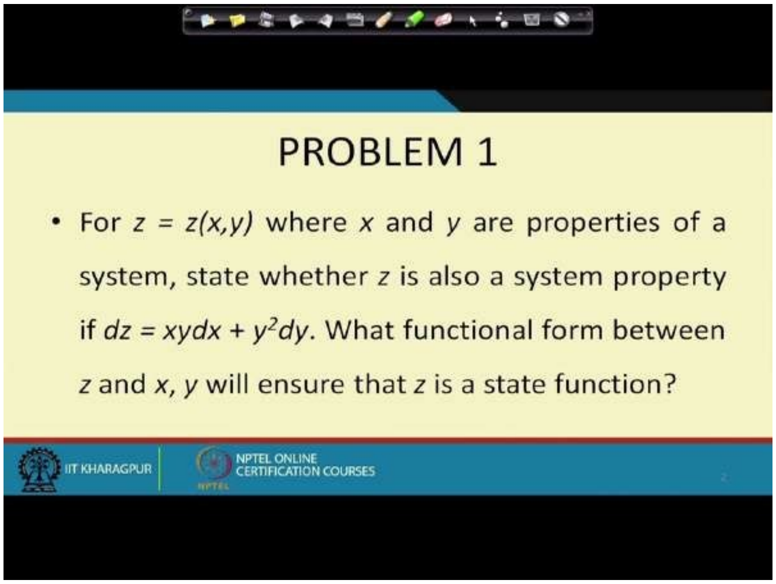

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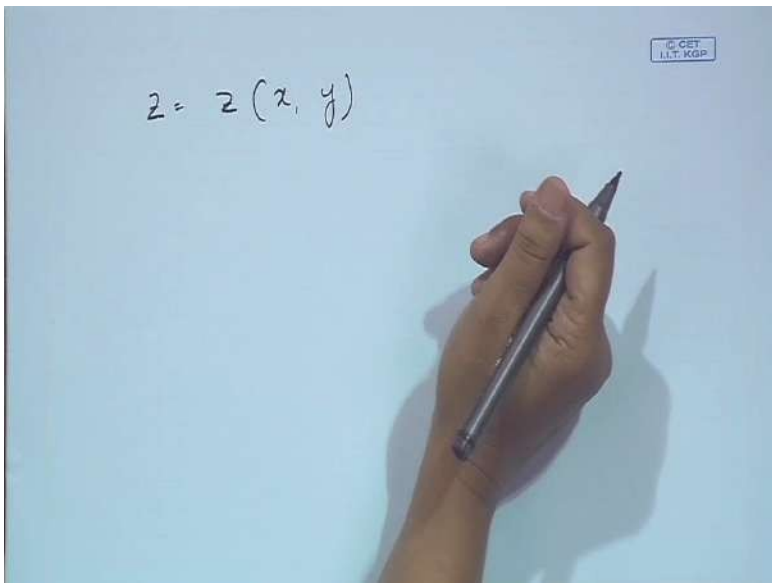

Now let us go to the first problem here, let us see what the first problem is? The first problem is that, well, there are 3 properties of the system, right? One property is, it can be PVT or anything first property say is z and we have expressed z as a function of 2 other properties x and y just to keep matters general I have mentioned these at z, x and y they can be PVT they can be something, now the thing is that we know that x and y are properties of the system, right?

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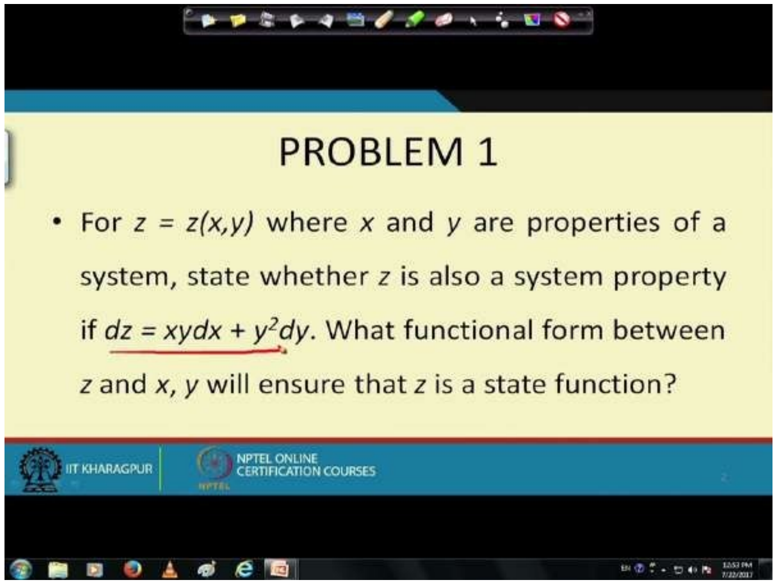

And this is the equation of state of the system, the equation of state which relates z with x and y and there is we have mentioned one particular equation of state and what is it given? It is given that whether this particular function form is fine if all the 3 parameters x, y and z have to be properties of the system, how do you go about it? We know that an equation of state relates the different properties of the system.

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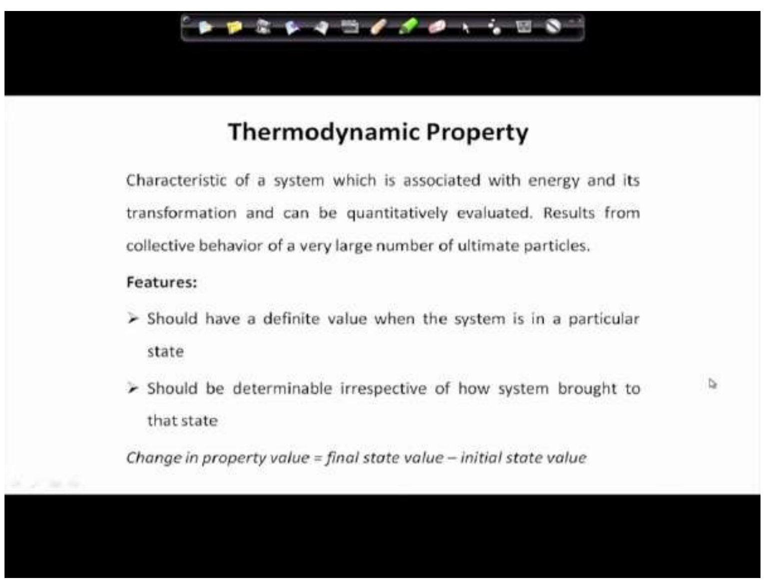

How do we define properties? If you recall one of my slides you will see that we had defined properties of the system as the characteristic of a system which is associated with energy and its transformation and we had mentioned a few features of the system, what is it? Firstly it should have a definite value when the system is in a particular state it should we determinable irrespective of how the system is brought to that particular state.

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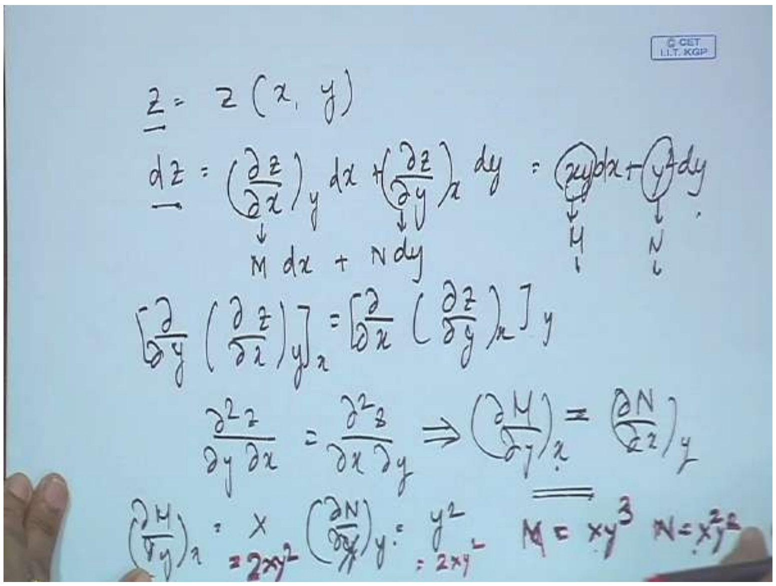

Or in other words it is independent of the path followed in moving from one state to the other, it depends upon the initial state and the final state. So therefore suppose I write down dz equals to say it is a function of x and y. So it should be del z del x at constant y dx plus del x del y at constant x dy, right? Now where this should be an exact, since it is an exact differential we can always write it down as M dx plus N dy.

Where M is del z del x at constant y, N is del z del y at constant x. Now suppose we double differentiate this equation, so in that case suppose we are differentiating it in the form del del y of del z del x at constant y this should be equal to del del x of del z del y at constant x this is at constant y this is at constant x. It should hardly matter whether we are differentiating z with x first or with y first or in other words both the things del 2 z del y del x should be equal to del 2 z del x del y, isn't it?

If this has to hold true only then we can say that z is a property of the system, now for this to hold to, what does it imply? It implies that del M del y at constant x should be equal to del N del x at constant y. So what do we need to know? The equations which have been proposed in this particular case, the equation is xydx plus y square dy.

So therefore this is nothing but M we have denoted this as M this as N. So what do we require to do in order to find out whether z is a property or z to be a property dz has to be an exact differential, if dz is an exact differential then the order of differentiating z with respect to x and y is not going to matter del 2 z del y del x should be equal to del 2 z del x del y and this automatically implies that del M del y at constant x should be equal to del N del x at constant y.

So for the equation of state which is provided, we just need to verify this particular thing. Once we verify this we find that this holds true then we can always say that this particular equation of state is thermodynamically consistent. So let us see what is del z del N del x at constant y under this particular condition? Here we find that del M del y at constant x this is nothing but equal to X, right? And what is Del N del x at constant y this is equal to y square.

So therefore we find that this is not equal to this and therefore this is not a proper equation of state or this is not a proper functional form between x, y and z in order to ensure that z is a property. So therefore what is the question? What will be a proper functional form? Now in order to get a proper functional form we need to suggest corrections either in M or in N or in both such that this equation is valid.

Now this can be done in a number of ways for example suppose I suggest or suppose we propose that M is equal to say xy cube, N is equal to x square y square I have changed both of them. Now for this particular situation what is del M del x del y at constant X let us see? This is nothing but equals to 2xysquare, let me write it in a different pen, if we propose M equals to xy cube N equals to x square y square.

For that case we find del M del y at constant x is going to be 2xy square similarly del N del x at constant y is also going to be 2xysquare. So therefore this can be one particular equation of state relating x, y and z we have obtained this by modifying both the terms.

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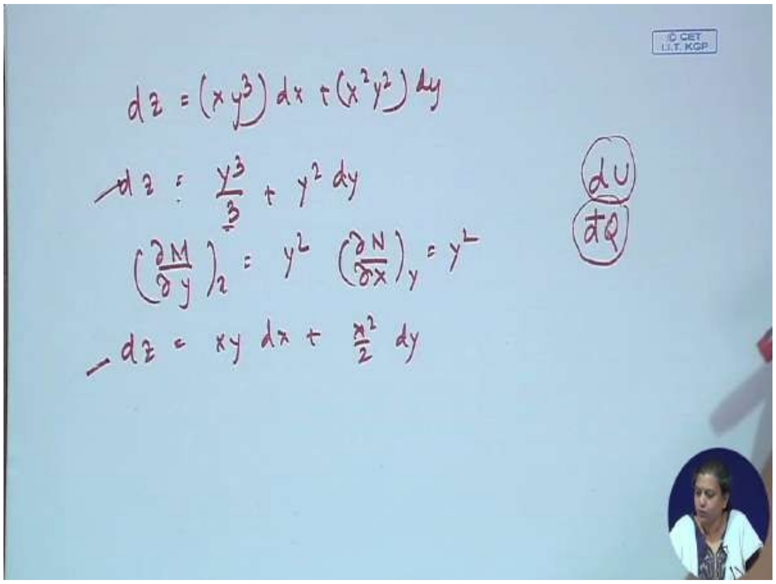

So therefore a correct equation of state in this case can be xy cube dx plus x square y square dy but please remember this is not the only equation of state that we can use. We can use some other equation of state as well, for example suppose we suggest that dz equals to y cube by 3 plus y square dy, what do we get in this particular case? We get del M del Y at constant x is equals to y square del N del x at constant y equals to y square. So therefore this can also be a equation of state where we have just modified one term and kept the other term, this term is kept constant only this term has been changed.

In the same way, we can also write it down as say xy dx plus x square by 2 dy. So this can also be an equation of state, right? So therefore we will find that for any particular property it is important to remember that the differential has to be an exact differential and if you recall I had repeatedly requested you in order to differentiate between exact and inexact differentials. Exact differentials I had shown by d, inexact differentials by a cut d dQ, dW in this way, du in this way you can very well understand the difference while this depends upon the path this is just a state function. So therefore it’s immutual how we perform this u, it is just important that initial and final states are the same.

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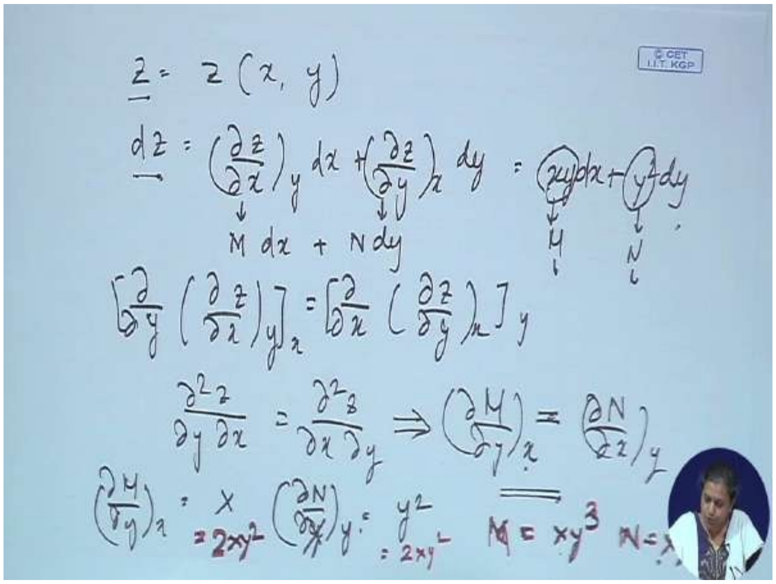

And the equation of state that cannot be anyone equation of state connecting the 3 variables this can be one equation of state, this can be one equation of state where I have just changed one parameter and along with that this can also be an equation of state, this can also be in equation of state. So therefore this is one thing which I wanted to emphasize upon that how you are going to find out whether any equation of state is thermodynamically consistent or not?

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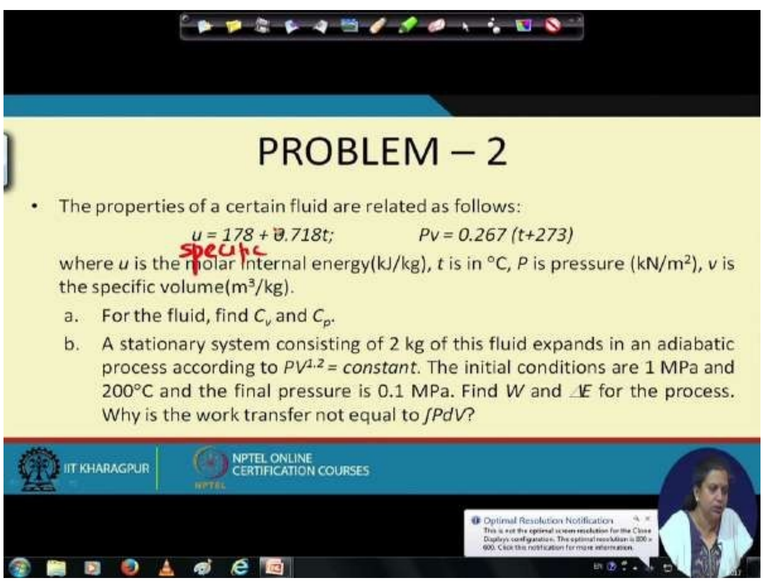

Now let us go to the second problem, what is the second problem? We had expressed internal energy or rather to be more specific it's wrongly written it is the specific internal energy, I am sorry about it. It should be the specific internal energy. So therefore we have a equation relating the specific internal energy with the temperature which automatically suggests us number of things. The first thing is internal energy is a function of temperature only in this particular case and the equation of state for that particular fluid.

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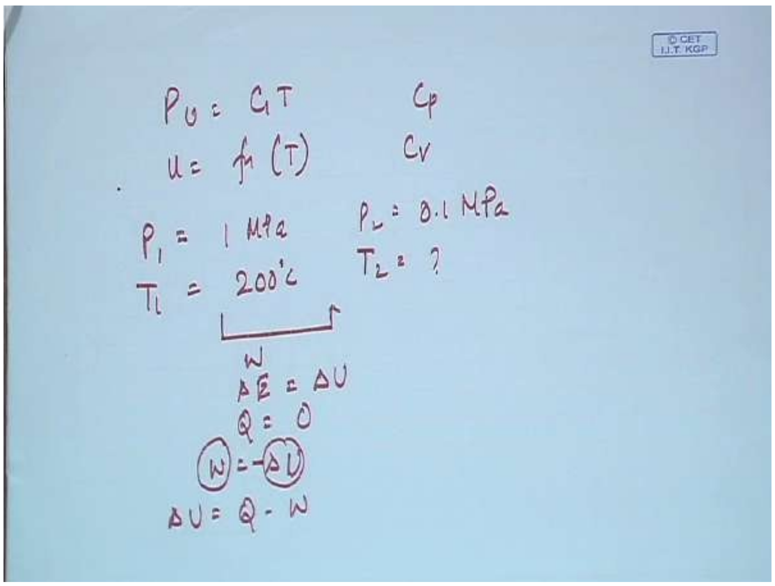

Mind it, it's not specified that it is a gas or a liquid, it is just a fluid, the equation of the state for that particular fluid is also suggested. If you find equation of state it is something of Pv equals to a constant into T, right? But the constant is not equal to R in this case. So therefore it possibly is not an ideal gas but it can be represented by an equation of state for a gas and we also observed that as it seems it is Pv equals to say C (t) or C1T, so therefore since it resembles the equation of state of an gas that is why u has been expressed in this case as a function of temperature only.

Now what are you required to find out here? You are first required to find out Cp and Cv for this particular gas or for this particular fluid and then you are supposed to compute some change of state for this particular fluid from some initial state to some final state, what is the initial state? The pressure of the initial state is given it is 1MPa and the temperature of the initial state is given the final pressure P2 is also given and what are you required to find out?

In going from this state to this state you are required to find out the work done and the energy change in this particular process it's delta E but for this case delta E will be equal to delta u. So therefore and since it's given that it is an adiabatic process we know for this particular process Q equals to 0 and therefore we know from first law W will be equal to delta U or delta E in this particular case. So therefore we find that the problem reduces to finding either W or delta U, right?

Now there is a small thing which you need to consider Delta U equals to Q minus W from our sign convention, if you follow our sign convention then in that case your W will be equal to minus of delta U or Delta U will be equal to minus of W, this you need to keep into consideration. So for this particular change in state the T2 is not given, so you can compute either the Delta U or you can compute the work done if you find one, you need to find the other.

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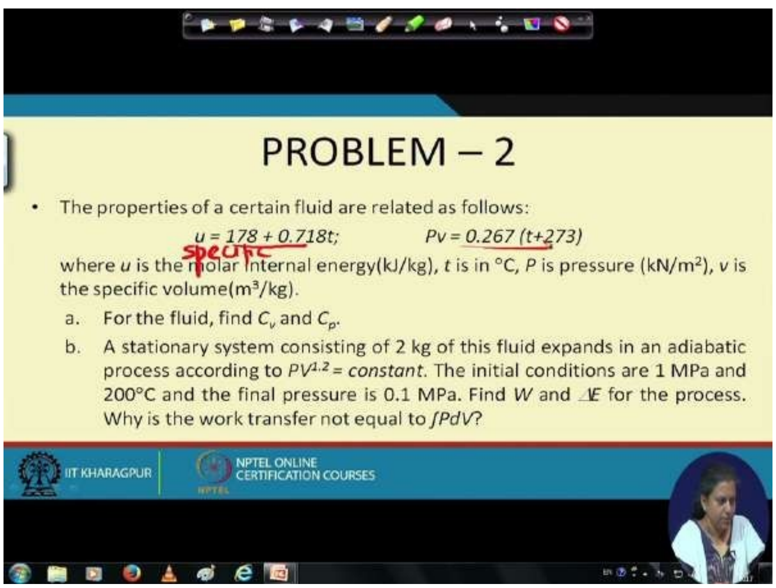

In order to compute this particular change in state what is given? You have the equation of state and you have a relationship relating the specific internal energy with the temperature, you have these 2 things in mind. If you observe the equation of state you find that t is in degree plus centigrade which automatically implies that this is nothing but the absolute temperature of the system. Now we can do the first part first or even in the first part is not giving you will find that unless you find out Cp or Cv one of them, it is difficult for you to compute the second part.

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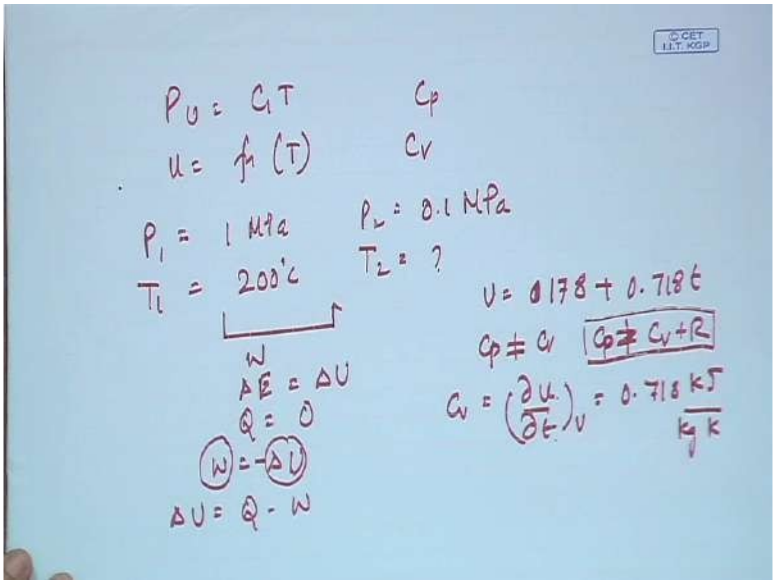

So let us first let us concentrate on the first part and then we will see how the information we have gathered from the first part helps us to find out or solve the second part of the problem, what is given here? Let me write it down it's given u equals to 178 plus 0 .718t degree centigrade we need to find out Cv in this particular case. By definition what is the specific heat at constant volume?

We know that for most of the cases Cp will not be equal to Cv, if we knew that it was an ideal gas we could have found out Cv and we could have computed Cp as Cv plus R, in this case it is difficult to do because we do not know or rather this equation is not an ideal gas equation as is quite evident. So therefore in this particular case we cannot use this particular, in this case this equation is not going to be applicable. How to find out Cv?

Cv by definition is del u del t at constant v, isnt it? So therefore if we differentiate this equation with respect to t, what do we get? We get 0.718 kilojoules per kg degree Kelvin whether it is going to be kg or moles or whether it is going to be joules or calories that all depends upon the units in which u and t has been specified.

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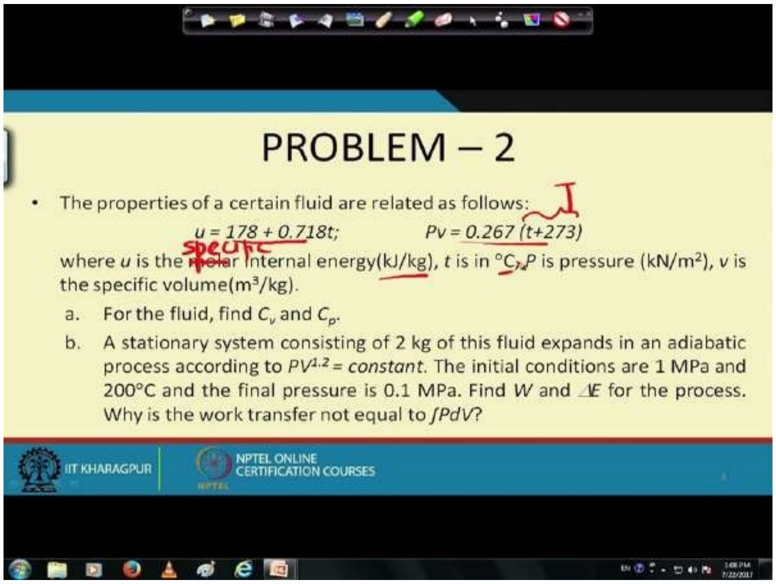

In this particular case if you observe we find that the specific internal energy has been specified in terms of this kilo joules per kg t is in degree centigrade, so the unit of Cv is as given.

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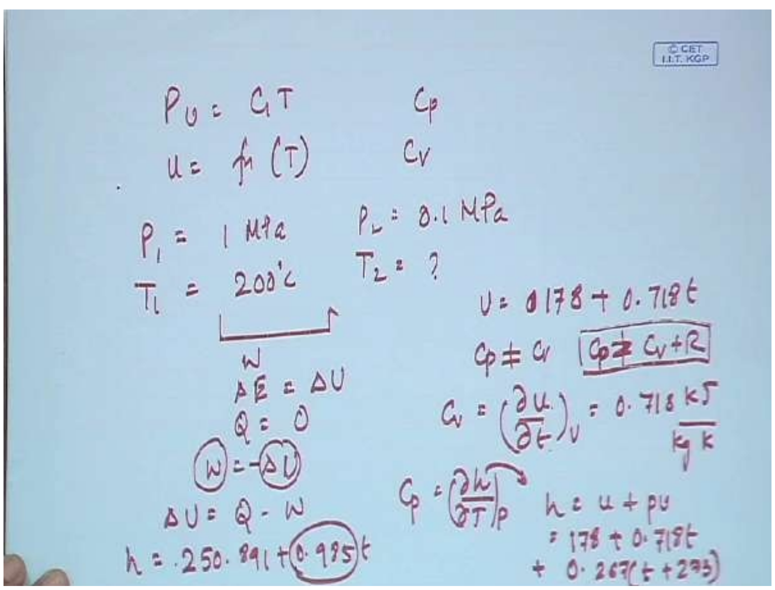

How to find out Cp? What is Cp by definition? Del h del T at constant P, what is this h? This is nothing but equals to u plus pv, right? What is, if from the problem what is u? u is nothing but equals to 178 plus 0.718t. What is pv equals to? This is going to be 0.267 into t plus 273, so therefore from this equation can you not express h in terms of temperature? What is the equation?

I will just write down here in this particular equation we will find h is nothing but equals to 250.891 plus 0.985t, isn't it?

So therefore from here we can find out that h if you differentiate h with respect to t, what do you get? You get the Cp value.

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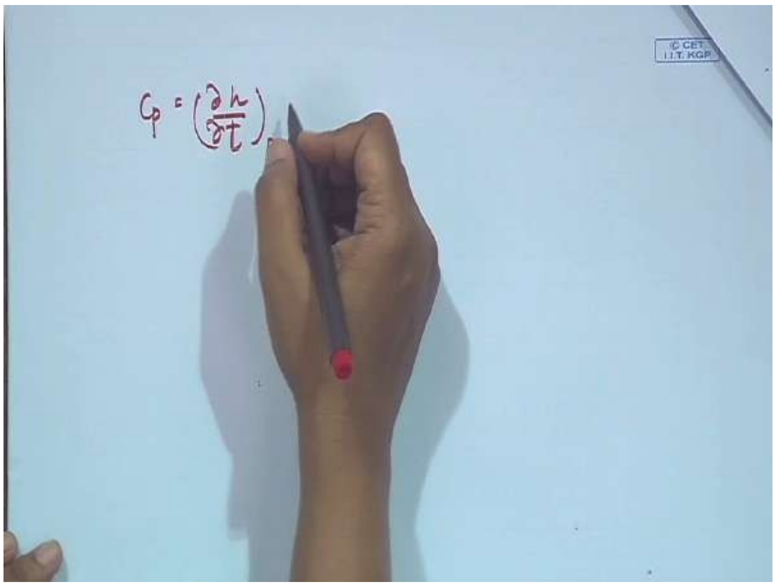

So in this particular case what is the Cp value that you are getting? Cp which is nothing but equal to del h del t at constant P, please remember small t is for degree centigrade capital T is for degree Kelvin, from here we get this to be 0.985 kilo joules per kg Kelvin there is another interesting thing that I would like to mention in this particular case.

We notice that in this particular case what is Cp minus Cv equals to? Cp minus Cv if you subtract one from the other what do you get? You get this is equal to, sorry your Cv was equal to 0.718, so this is 7, this is 6, this is 2 it is 0.267, what is this 0.267?

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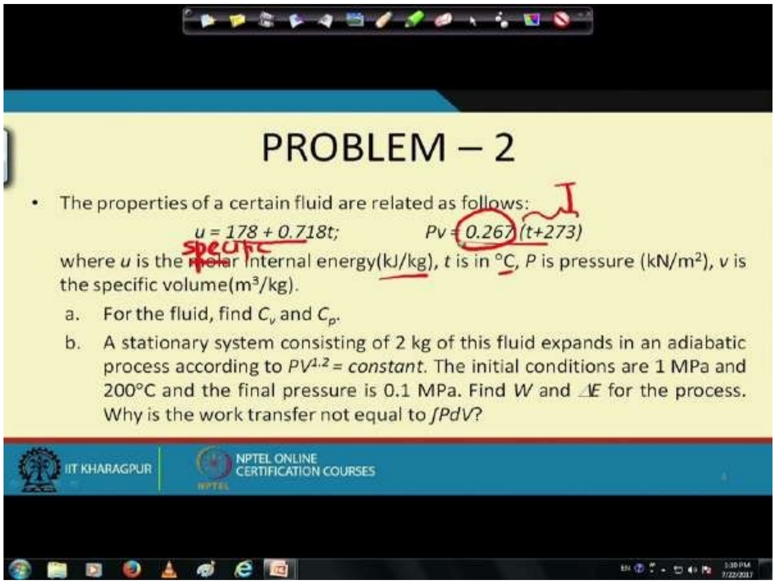

Just refer to this problem you will find this is the constant C1T which would have corresponded to R for an ideal gas equation. So therefore what does it imply?

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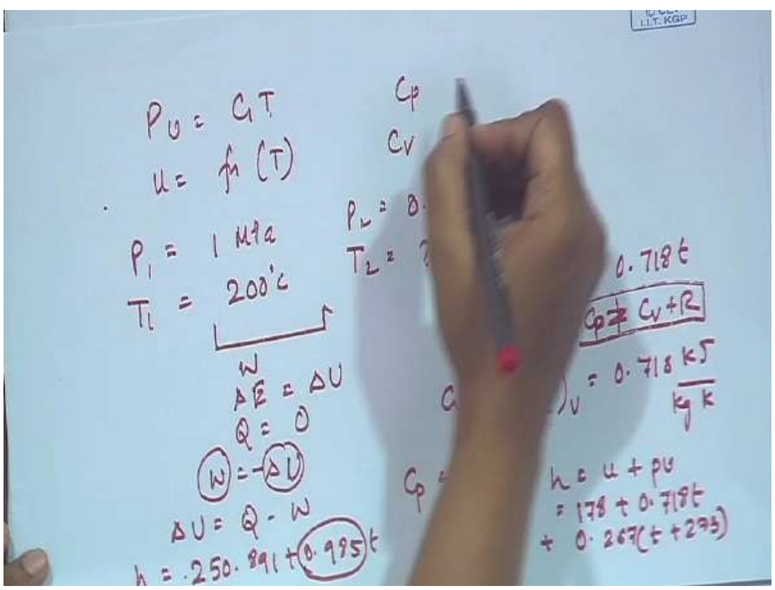

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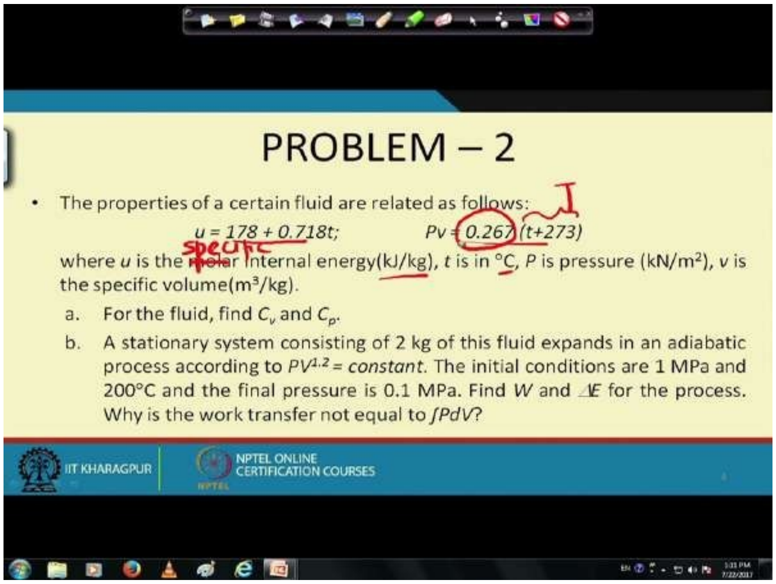

It implies that if you have a equation of Pv equals to C1T, then in this particular case Cp minus Cv will always be equal to the constant which is C1, for an ideal gas this constant C1 reduces to R, right? But here the very common tendency which I find among students is they just see you have to find out Cp, Cv. u is given, so they find out Cv and then they simply add it up with R and try to find out Cp but did not notice that it is applicable only for an ideal gas and for no other situation.

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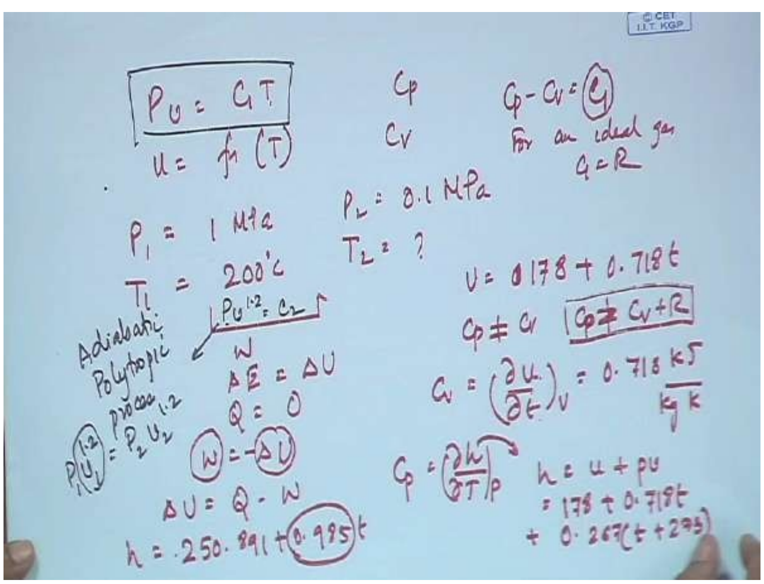

Now let us come up to the next part of the problem, now for this part of the problem there are initial conditions given final condition is given the process is specified, what is the process? The process occurs according to this particular, this particular equation, right? And what is this equation? This equation as you know this equation is for a polytropic process, isn't it? It is already mentioned it is adiabatic, so it is an adiabatic polytropic process that we are going to deal with this, fine.

So for this process if you know you know P1v1 to the power 1.2 should be equals to P2v2 to the power 1.2 the initial conditions are given you need to find out the final conditions but if you wish to use this equation you will find the equation is in terms of Pv whereas initial conditions are given in terms of P and T which is quite understandable as I have already mentioned that pressure and temperature are the easily measurable and more accurately measurable variables.

So for that what do you need to do? You simply need to convert or express v in terms of t and for that you need to use this particular equation.

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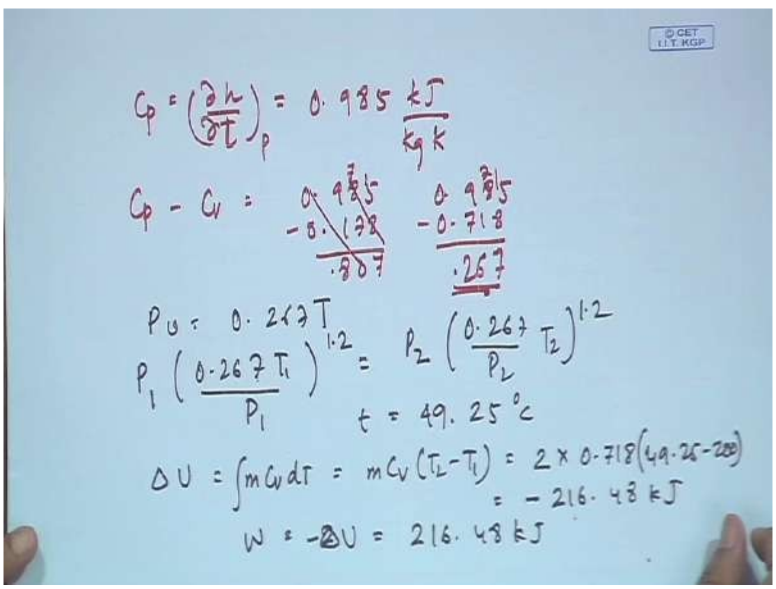

So therefore how do we go about this then? We know that Pv equals to 0.267 into capital T say, okay. I just make it first for convenience. So P1 0.267T1 by P1 to the power 1.2 should be equals to P2 0.267 by P2 into T2 whole to the power 1.2, so by this equation I could actually relate the pressure temperature of state one to the pressure temperature of state two. I can solve this out and I can find out the temperature t it comes out to be 49.25 the temperature in degree centigrade comes out to be 49.25 centigrade.

So once I know and I can always compute delta u for this particular case, what is it? It is mCvdT, right? Integral of this or in other words since Cv remains constant. So it is T2 minus T1, m you already know it's given 2kgs, Cv you have already found out from the previous problem it is 0.718, you know T2 by this time you know T1 by this time, so therefore it is 49.25 minus 200 which gives you minus 216.48 kilojoules.

As a result you know W it is nothing but equals to minus of delta u which is nothing but equals to 216.48 kilojoules. Now this is one particular process of doing it, you can also do it by first computing W and then computing u that can also be done.

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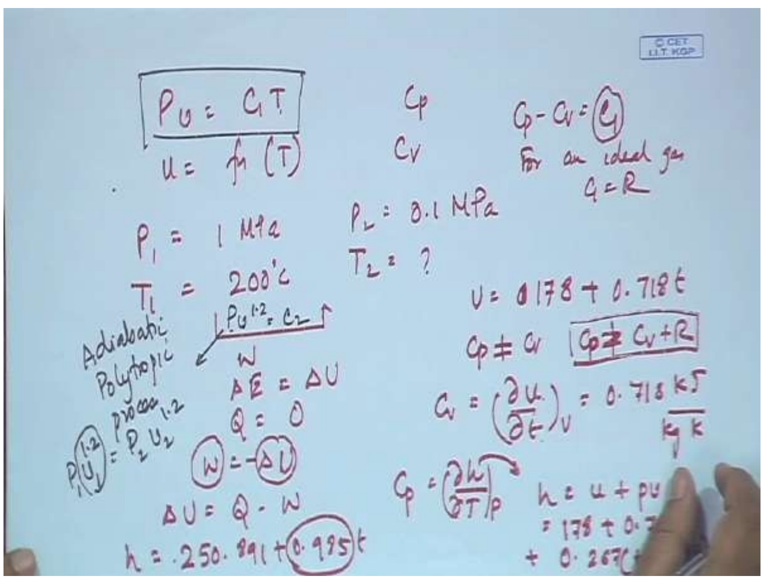

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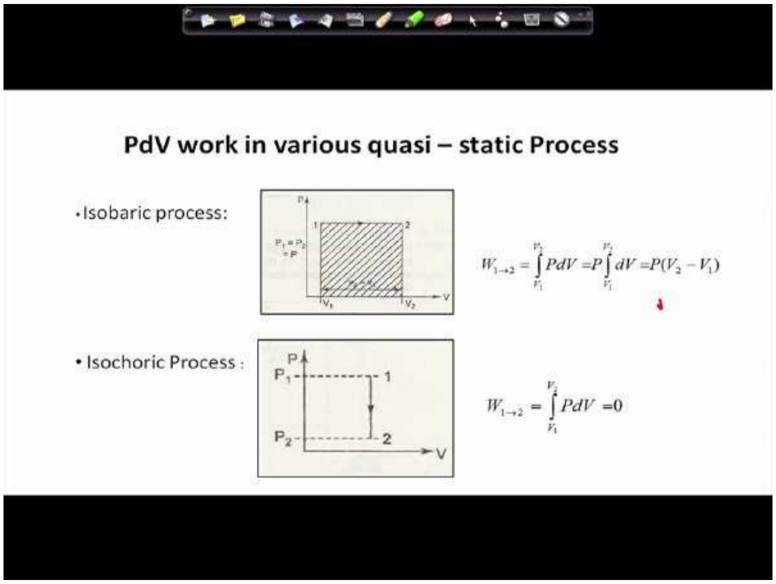

You know that the process is an adiabatic polytropic process, now if you recall that when we were discussing these particular things I had already discussed the PvT work in various quasi-static processes. I have discussed PvT Work for an isobaric, isochoric, isothermal and then adiabatic process, in fact this is specifically not an adiabatic process this is a polytropic process it becomes adiabatic when this n becomes equal to gamma, right?

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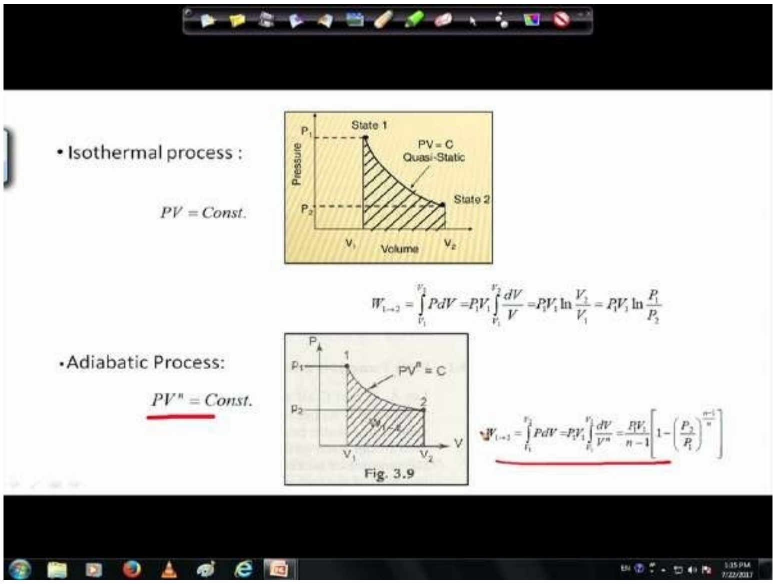

So can we not use this particular equation here in order to find out, if we can use this particular equation here, this particular equation, this is the equation so can we not use this particular equation in order to find out W. We can do it, right? But again in order to use this equation you know P1, you do not know V1.

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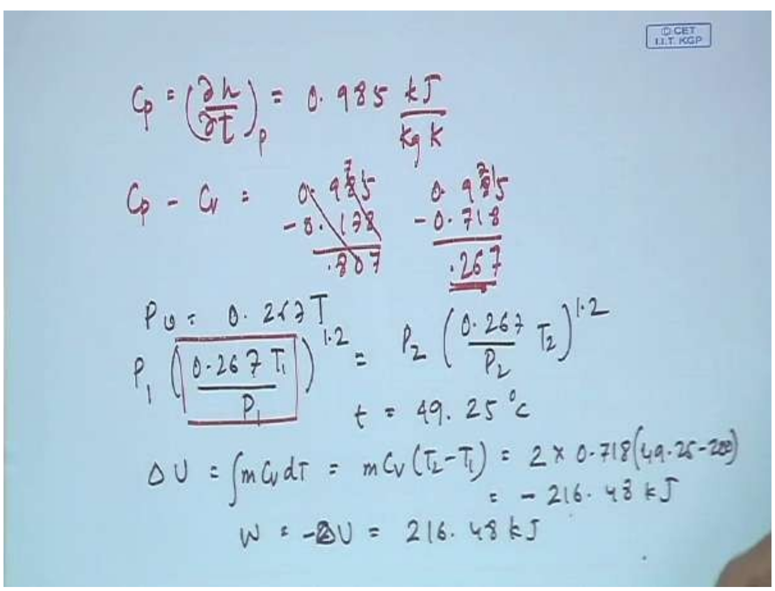

So you again have to express V1 in terms of temperature in terms of temperature, where V1 in this particular case I have already written down your V1 is nothing but this part, isn't it? So therefore you can substitute V1, n is nothing but 1.2, P2 and P1 both are known to you so therefore you can find out W in this case and equate this W with Delta u.

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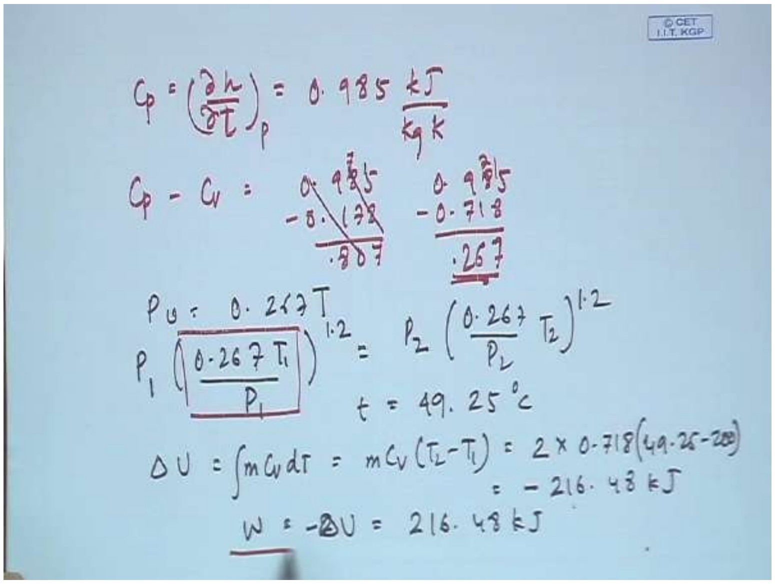

I give it as an exercise to find out W independently from this equation and compare the value with the W which you have obtained by equating this with Delta u. Just to show that once the path is specified no matter how you do the computation? The work done will be the same for both the cases.

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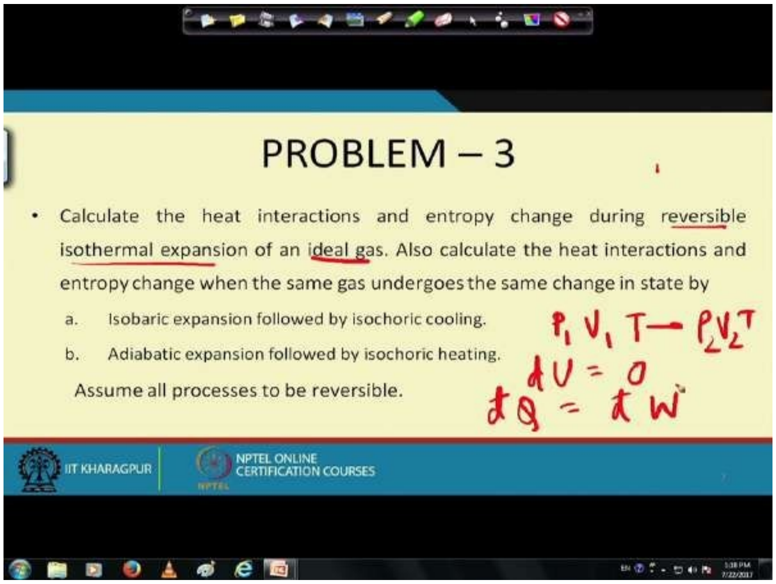

Now we move on to the third problem, let us see what the third problem is? This is also another problem in order where we perform some particular change of state and from that particular change of state we try to find out the heat interactions and with that one additional thing also we would like to find out in this particular case the entropy change, right? What is the process that we have devised? This system is an ideal gas and for an ideal gas what is the process? It is a reversible isothermal expansion.

So if it is a reversible isothermal expansion, what does it imply? It implies that the change of state it will be from P1V1 temp T to say P2V2 T, isn't it? And for this particular change of state since it is an ideal gas we know that since T remains constant for an isothermal process du is equal to 0. So therefore for this process we know dQ is going to be equal to dW. So therefore to find heat interactions we can find out the work done, from the work done can find out the heat interactions.

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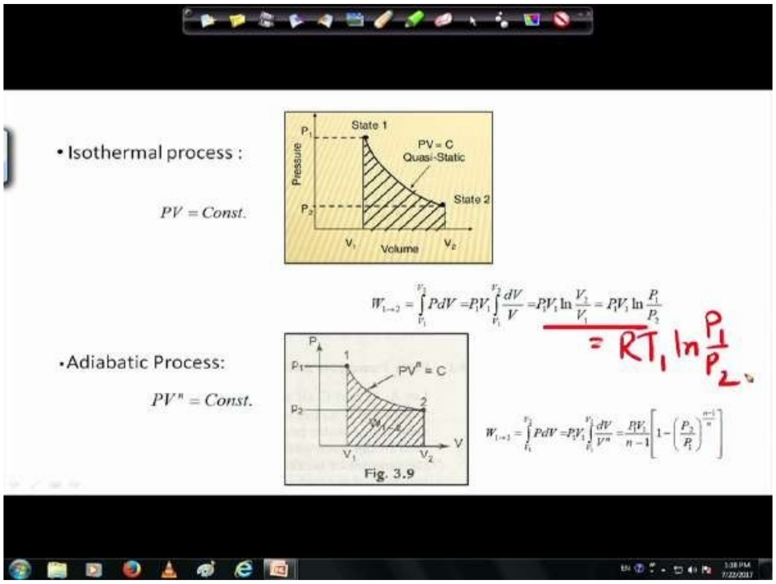

For an isothermal process again if we go back to the equations which I had shown for an isothermal process Pv equals to constant and this is the expression for the work done, isn't it? So therefore in this particular case P1V1 is nothing but equals to RT1. So therefore this can also be written down as RT1 ln P1 by P2, agreed? So therefore we can find out the work done and this will be equal to the heat interactions under this particular process.

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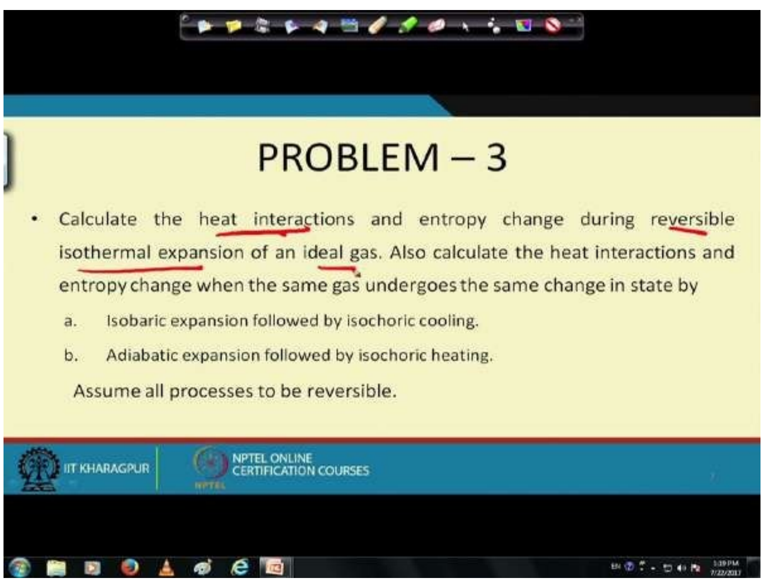

So accordingly in order to find out the heat interactions for reversible isothermal expansion ideal gas you have already got the expressions we had already derived the expressions.

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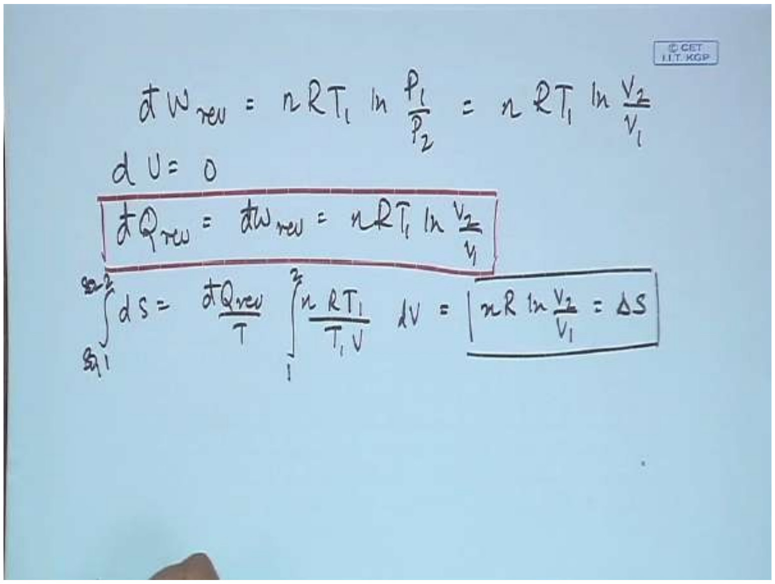

So for this particular case your dW reversible was equal to as I have shown you it was nRT1 ln P1 by P2 or else you can also write it down as n RT1 ln V2 by V1, right? We know that ideal gas dU equals to 0. So therefore dQ reversible will be equal to dW reversible will be equal to n RT1 ln V2 by V1, right?

But here we are required to find out the entropy change as well, if you recollect what is dS? It is nothing but equal to dQ reversible by T in this particular case T remains constant. So therefore in this case if you substitute it, we will find out that this is n RT1 by T1V dv which is nothing but equal to, if you integrate this particular equation say from state one to state 2 say S1 to S2 or in other words just from state 1 to state 2.We need to integrate this also from state 1 to state 2, so therefore this gives us n R ln V2 by V1 this is equals to delta s for this particular process, right?

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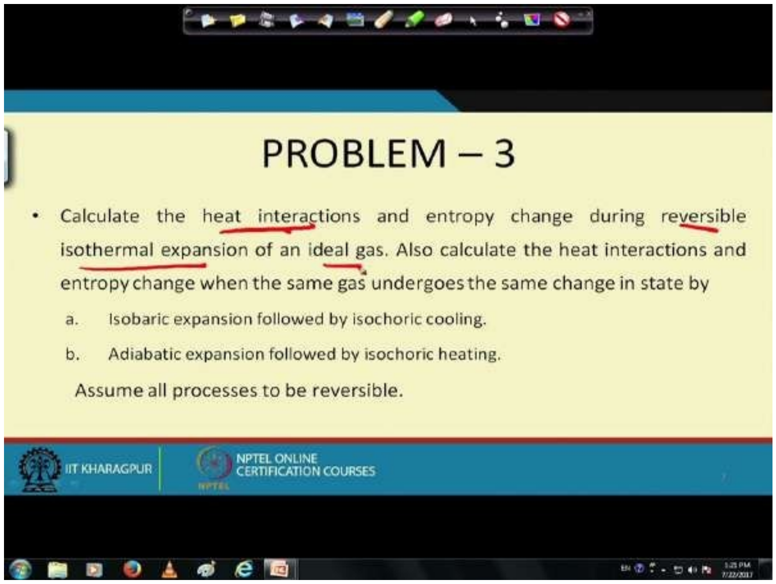

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But this was pretty simple but the problem does not end here we are required to find out the heat interactions then the entropy changes for 2 other processes which provided the initial and final states are the same. What are the 2 other processes? The 2 other processes are isobaric expansion followed by isochoric cooling, adiabatic expansion followed by isochoric heating and all the processes have to be reversible.

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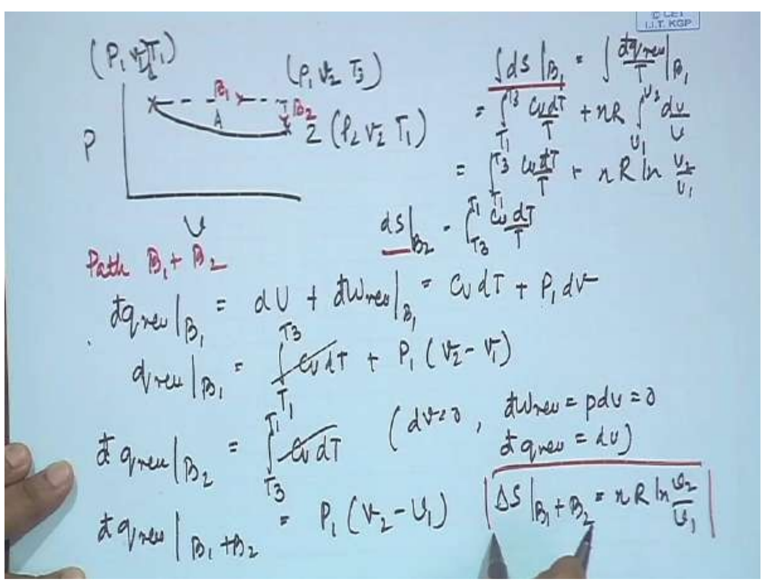

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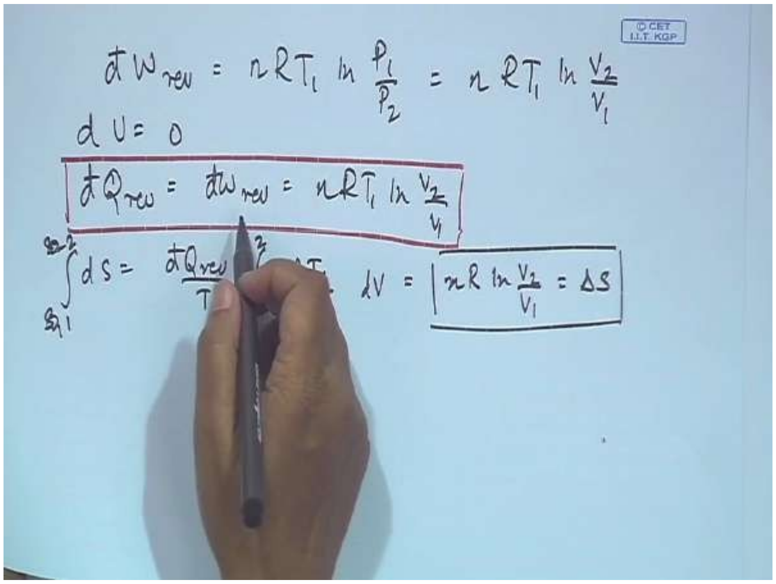

So if we just plot it, simply for ease of your visualization this was state 1, this was state 2 this was the process which we performed this was P1V1, this was P2V2 say T1 here also it was T, this process we have already performed and we have found out the heat interactions and the entropy changes in for this particular case this is say process A, what is process B? Isobaric expansion so that means pressure P is constant

This is isobaric expansion followed by isochoric cooling, right? So the process B is, you proceed in this way and you proceed in this way. Now for this particular process it comprises of 2 processes say B1 and B2, for this particular B1 plus B2 we can very well write down dq reversible along B1, what is this? This is du plus dW reversible along B1, what is dU in this particular case? This is an isobaric, this is dU is going to be CvdT plus dQ reversible under this case. So therefore this is going to be P1dv, isn't it?

So therefore q reversible along B1 this is going to be your integral and here if I specify the states it is going to be P1, all of these are small they are molar P1 v2 and say T3. So therefore this has to be integrated from T1 to T3 CvdT plus P1, V2 minus V1, agreed? So this is a q reversible for this particular path.

What is dq reversible for B2? In this particular case we have integral T3 to T1 CvdT, since this is an isochoric process so naturally dv equals to 0, so naturally dW reversible which is equals to Pdv will be equals to 0, right? So therefore in this particular case what do we have? We have dq reversible equals to dU. So therefore automatically we find that when such a situation arises the heat interaction behaves or can be evaluated from this as a state function as it is.

So now what is dq reversible for the entire process B1 plus B2? You add this and this with this, when you add you will find that in this case the integration was performed from T1 to T3, in this case it is performed from T3 to T1. So therefore since we have just the initial and final states are the same we are just reversing it. So therefore these 2 cancel out and we find this is equals to P1 into V2 minus V1, I am sorry I am repeatedly writing it s capital. So therefore this is dq reversible.

What is the entropy change now let us see? Entropy change ds along B1 it is going to be integral of this integral this is dq reversible by T along B1, right? So therefore dq reversible T along B1, I need to integrate this I need to integrate this, so therefore what does it amount to T1 to T3 CvdT by T plus nR integral V1 to V2 dv by v, agreed which is nothing but equals to T1 to T3 CvdT by T plus n R ln V2 by V1.

What is ds along B2 tell me? This is nothing but T3 to T1 CvdT by T, right? Now add this particular (ds) and this particular (ds) to get the delta s along path B1 plus B2, what is this? This is equals to n R ln V2 by V1.

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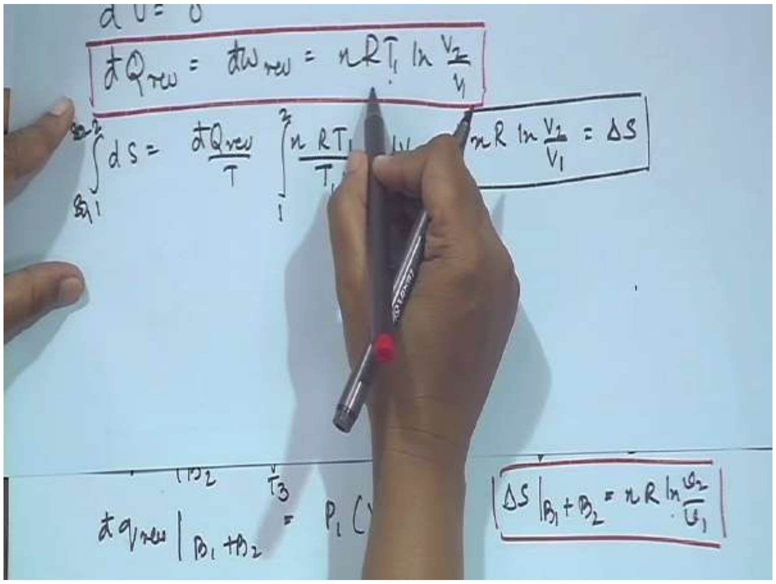

Compared this with the del delta s that you had obtained for an isothermal process, what do you find? You find that the delta s for both the cases are the same but we find that the dq for this process and the dq for this process they are not the same.

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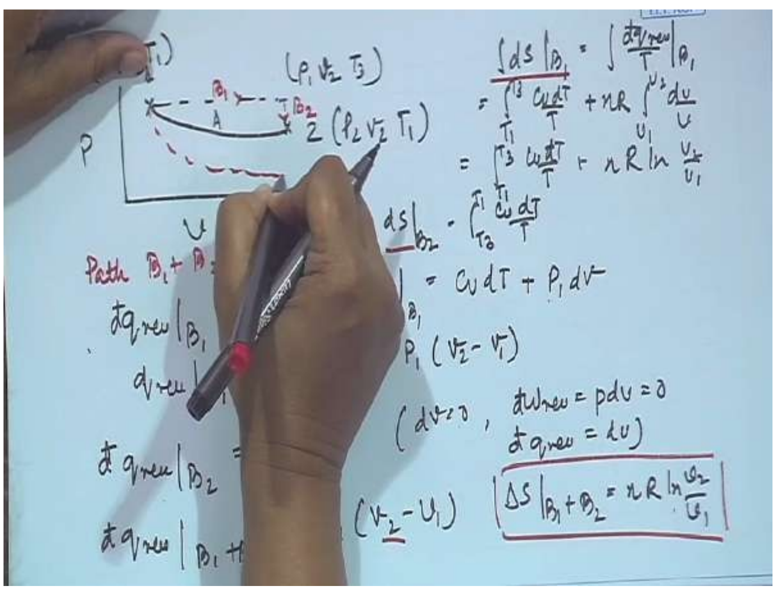

Again you can repeat it for the next process which is given, the next process is nothing but your adiabatic expansion, say for the next process what is it? This is basically the adiabatic expansion followed by the isochoric heating. So therefore here we start from P1V1T1 along a process say

C1 to arrive to P3V2T2 and then from there we come to this process. For this process also, we can proceed I believe you could have done it on your own.

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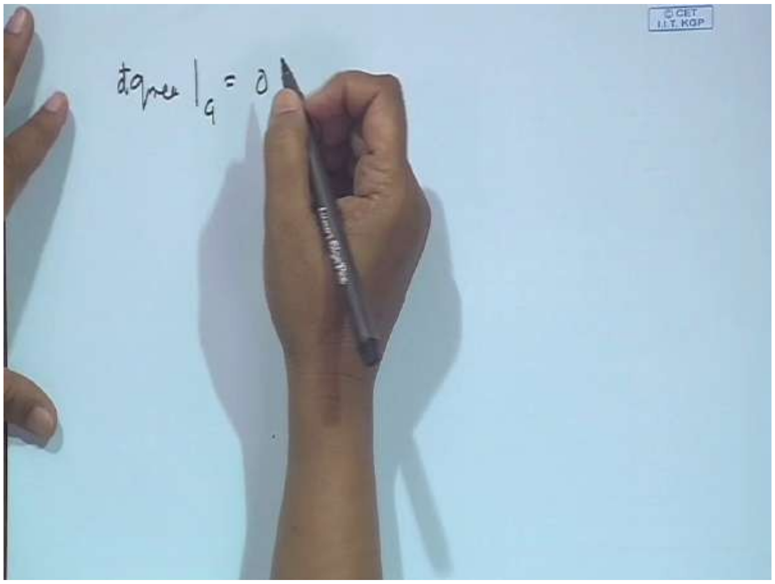

But suppose we work it out say dq reversible along C1 that is equal to 0 because it is adiabatic, so therefore dS along this process it is going to be 0, dQ reversible along C2 is nothing but du which is equal to CvdT again since for an isochoric process dW equals to 0 I have already told you. So therefore what is q reversible along C1 plus C2? It is just CvdT, right? What is dS for this process let us see? This is going to be integral T2 to T1 CvdT by T, right?

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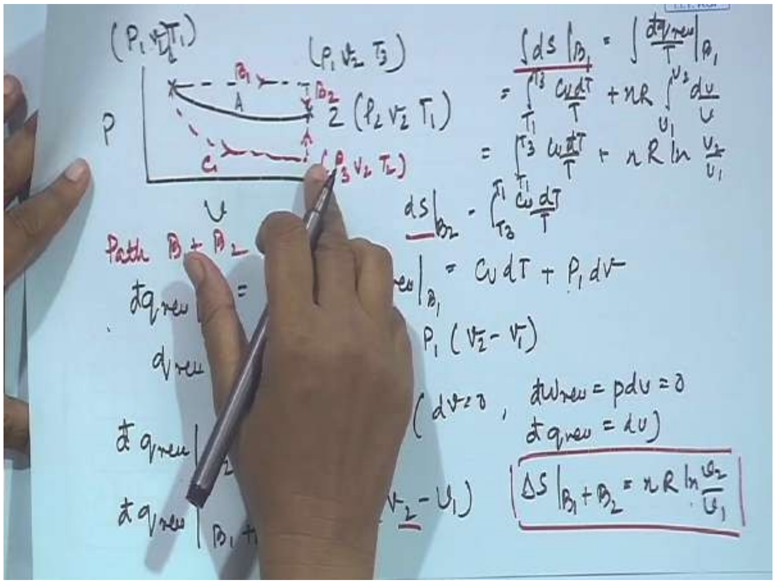

And we can also for this particular path C1, say for this particular path C1 we can also write that CvdT equals to minus nRt dv by v, why? Because du equals to minus w since dq equals to 0, right? So therefore instead of the CvdT by T, can we not substitute it with minus V1 BY V2 nR dv by v, which gives us minus nR ln v2 by, in this particular case there was a minus, very sorry so it becomes a plus so therefore this is ds in this particular case, right?

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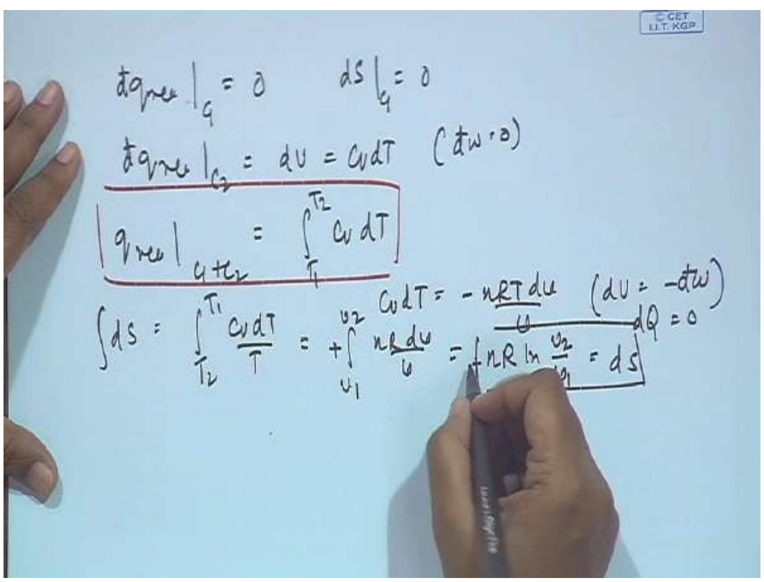

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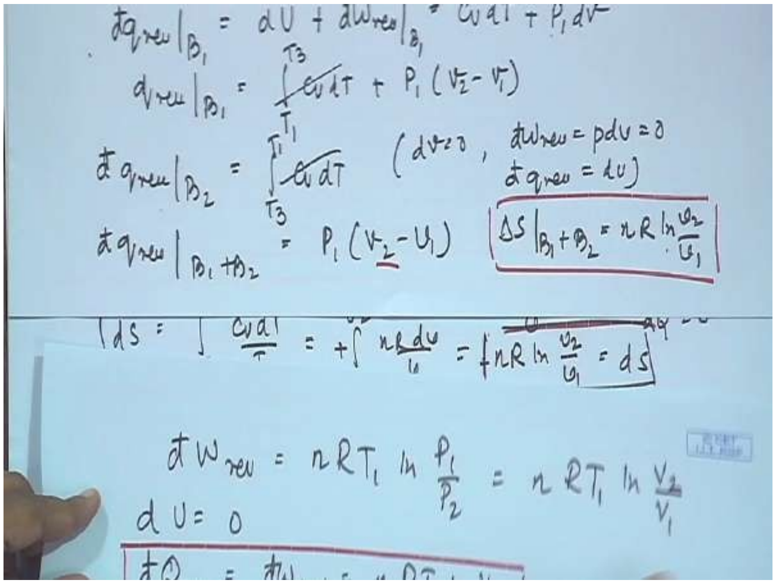

Again if we compare the q reversible and the ds's what do we find? I can just superimpose it on this and if you observe all the 3 what do you find? For this particular path this nR ln v2 by v1, for this path it is nR ln v2 by v1, in this case also it is the same which automatically implies delta s is a property of the system and no matter what path we follow, provided the paths are reversible we know that delta s it is going to be the same provided the paths are reversible.

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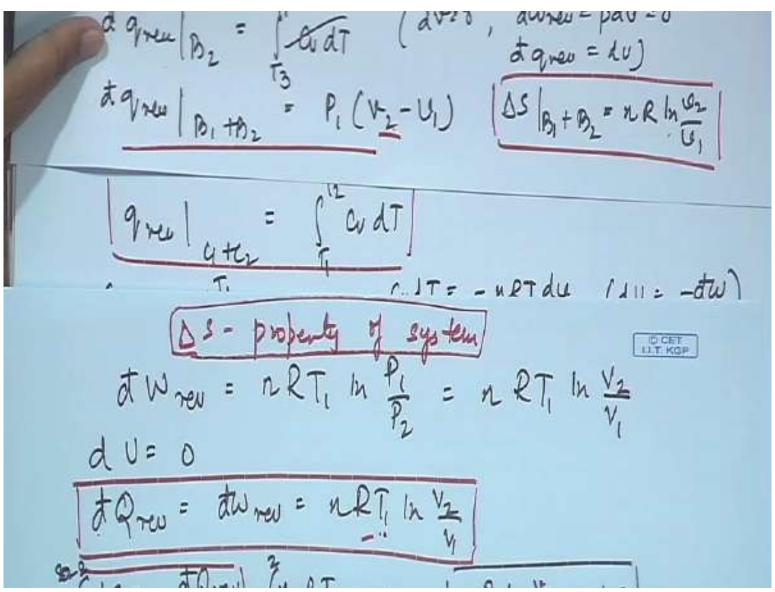

On the contrary we find delta s from this particular formula that ds equals to d, we find it from this particular formula but here even if you are finding it from a path function it is a property but the heat computed for all the 3 cases this is for case 1, this is for case 2 and this is for case 3 this is for case 3 we find that the heat interactions along the three-paths they are different. Although the entropy change is the same for all the 3, thank you very much and I look forward to further interactions while we proceed in this particular course, thank you.