Chemical Principle 2
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Module 05
Lecture 32
Tutorial Problem – 03

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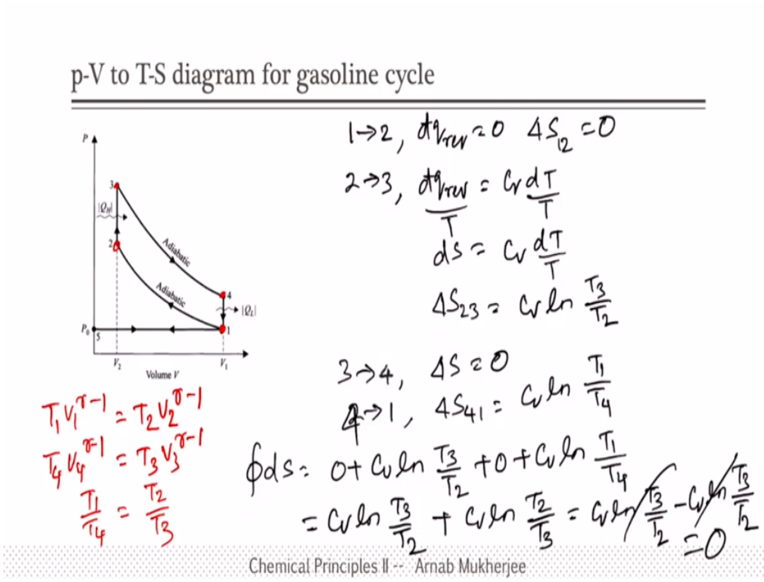

Now we want to do some problems as so see did with entropy calculations and we are going to start with a PV to TS diagrams for covert cycle right now we are going to do with for some other cycles and associated problems let us say we are going to calculate for gasoline cycles first, so in gasoline cycles first step want to two is n adiabatic step. In adiabatic step what happens is that DQ reversible is going to be zero so there for change in entropy is going to be zero, now two to three is an isochoric step in an isochoric step DQ reversible we know his CV DT, so therefore DQ reversible by T CVDT by T and therefore DS is CVDT by T and S two three is CVLNT and since we are going from T2 to T3 it should be T3 by T2 three to four is adiabatic step again so del S will be 0 and two to one is an isochoric step by the same logic S4 four to one, Four one will become CV LN T1 by T4.

Now what is the total change in an entropy total change in entropy in the whole cyclic process is sum of all these parts which is 0 plus CV LN T3 by T2 plus zero plus CVLN T1 by T4 now we have to invoke the relation between T3 T2 and T1 T4 so for that we need to put in a combined the relation of in adiabatic step one and two in which we can write T1V1 to the power gamma minus 1 is equal to T2 V2 to the power gamma minus one, why we can do that because one and two are connected by an diabetic path and all along the adiabatic path T1V1 to the power gamma minus one is constant, so therefore we can do that similarly one and three and four are also connected by an adiabatic path and therefore we can use three and four relation as T4V4 to the power gamma minus one is T3V3 to the power minus one we have done that before also now let us take the ratios of the this two so T1 by T4 since V1 and V4 is same is T2 by T3, so we have not done PV to TS diagram as of yet.

What right now we are doing is just to show that the overall entropy is zero first will do that and then we will talk about PV to TV diagram, CVLN T3 by T2 plus T1 by T4 I will write T2 by T3 so CVLN T2 by T3 which means CVLN T3 by T2 minus CVLN T3 by T2, because for LN case we can write that a LN X is minus LN of one by X and they cancel give zero, so overall entropy in the cyclic process we are getting to be zero, now we are going to show that how the PV and TS diagram will look like.

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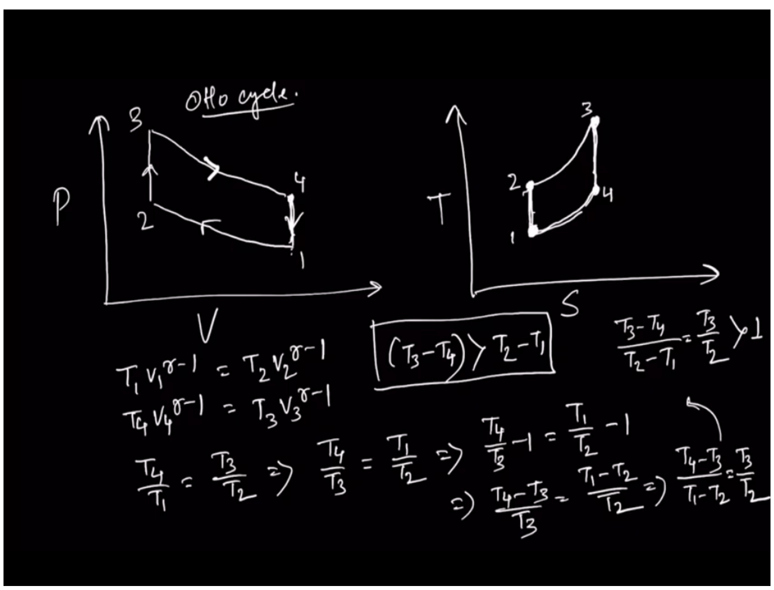

So this is our PV diagram where this is an isochoric step this is an adiabatic step this is an isochoric step one two three and four, now we have to understand one thing so when we write TS diagram then one to two is an adiabatic step, adiabatic compression so what happens in an adiabatic compression since DQ reversible is zero, entropy change is zero which we have to calculate between one and two however it is an adiabatic compression.

So therefore temperature increases so entropy does not change the temperature increases, so X make it little bit shorter for a reason, so now we have seen that del S12 is equal to zero, now two to three how do you calculate that so we know that two three DS is CV LNT, which means DS is DQ reversible by T which is CVDT by T and S is CV LNT, which means that S by CV is LNT and T is T2 the power S by CV, so the temperature increases exponentially with entropy, entropy by CV it is almost like let us say you can write Y equal to into the power X by A that kind of function only can also write into the power minus BX or plus BX you see B is nothing but one by CV, B is one by CV so it increases exponentially so we have to draw the same way, and then the three to four steps.

So this one two three so three to four step is of course entropy change is zero and temperature is decreasing because it is an adiabatic compression, now four to one step before doing four to one we want to do some calculations so I can write four to one step but there is any interesting fact about did that whether this line will be bigger than this line or smaller than this line can you tell me, so whether this changes so both two-two three and one to four little bit exponential but three and four the line three and four will be bigger or smaller so which means we have to see the temperature difference between three four and one two whether the same or not can you identify from this Otto cycle or not so now the question is that whether the line three four will be bigger than one two or not, so in order to do that we have to find this relation of the temperatures between one two three and four, so in order to do that.

Let us write that our adiabatic expression that T1V1 to the power gamma minus one is T2V2 to the power gamma minus one and T4V4 to the power minus one is T3V3 to the power gamma minus one taking the ratio we get T4 by T1 is equal to T3 by T2 now from there we can rearranged that and write by T4 by T3 is equal to T1 by T2 let us subtract one from both which is going to give T4 by T3 minus one is equal to T1 by T2 minus one which is going to give us T4 minus T3 by T3 is equal to T1 minus T2 by T2 which is going to give us T4 minus T3 by T1 minus T2 is equal to T3 by T2 following this till now, now four is lower temperature than thee and one is lower temperature than two, so we can write the energy and write it as T3 minus T4 by T2 minusT21 is equal to T3 by T2, now which is bigger T3 or T2 temperature so this is greater than one see this is greater than one that means T3 minus T4 is greater than T2 minus T1, so the temperature difference between three and four has to be larger than between one and two so this line will be smaller and this line will be bigger, this is very important you cannot do other way around because typically neglect the size of the line first of all the neglect how you do the TS it is has to be exponential and secondly what they neglect is the size of the height of the bars of the adiabatic changes, if you do it correctly that is what correctly but this is still not quantity in this qualitatively correct at least to show that the second one will be larger.

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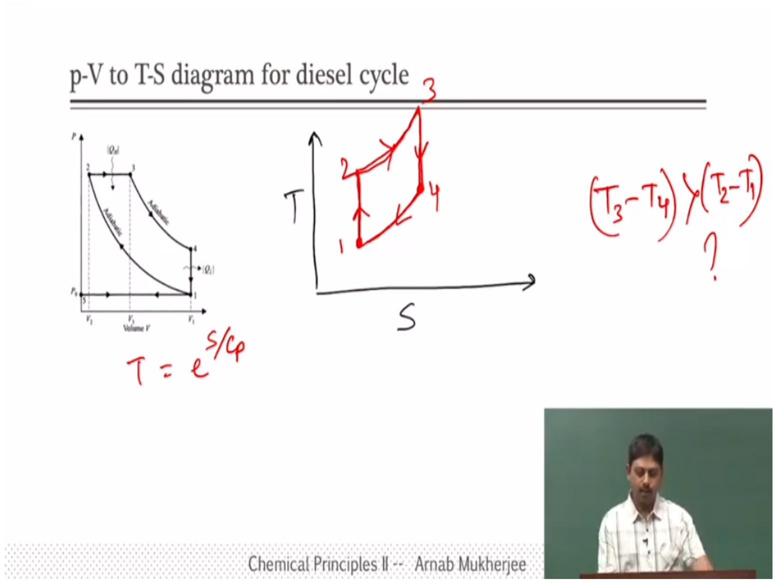

Now same for the gasoline but here we are going to do it little bit faster, so again from first step to the second step it should be straight one to two and then two to three is again it will be exponential but instead of T to the power S by CV, it will be T will be the relation between T is equal to T to the power S by CP and then there will be a line and it will be like this one two so this is again straight down, now you have to figure out write that the three four now is three minus four bigger that two minus one or not that you have to figure out, that will be a tutorial problem the same way we have done the gasoline cycle.

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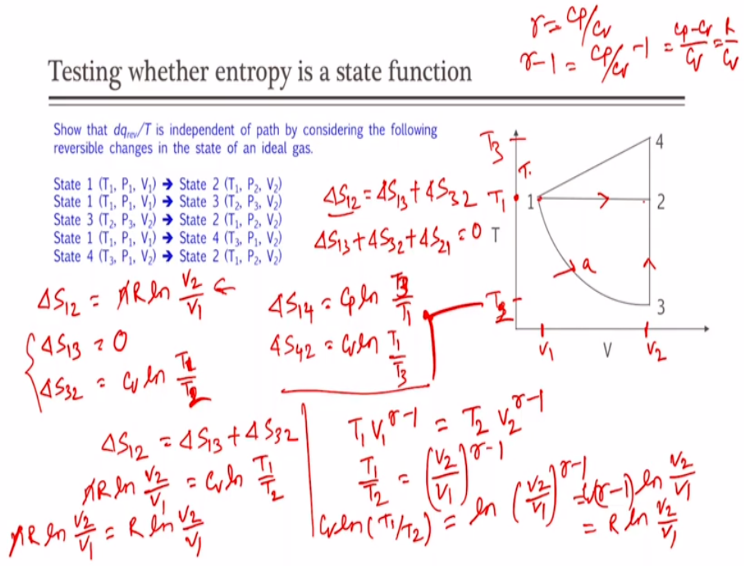

So now let us do some other tutorial problems so show that Q reverse by T is independent of path by considering the following reversible changes in the state of an ideal gas we already have done that for gasoline cycle that the reversible path is giving zero similarly if you used a diesel cycle also you can get that but this is a hypothetical cycle and for this is hypothetical cycle we can show that, so let's say the first one is state one is state two and so this is a TV diagram not a PV diagram not a TS diagram it is a TV diagram.

So therefore one has to be very careful while looking at it so one to two is an isothermal process but there is a change in volume which means an isothermal expansion process so the change in entropy of S1 to is going to be let us say a following reversible changes of and the state of an ideal gas let us take it to be in molecule ideal gas so NRLN V2 by V1 in the first steps state one to state three, now state one to state three this is although not mention I think this is an adiabatic step, so delta S13 since it is and adiabatic step of course it will be zero.

So we have calculated this one we have calculated this one now three to two, three to two will be the temperature is changing but volume is not change so it is a constant volume process so it is in a constant volume process what we get CVLN T2 by T1, so it should be CVLN T2 by T3, so we got a cyclic process so if you want to calculate a cyclic process however you have to be careful see we can come so if I go from one to two that is same as going from one to three plus three to two so we can write like S12 as delta S13 plus delta S32 or we can write that delta S13 plus delta S32 plus delta S21 is equal to zero in that case we are following the cycle in the same direction that is very important otherwise will not going to get, so here what we have to show is that this S12 which you have got here is same as some of them together which essentially nothing but just T2 by T3.

Now do we show that in order to show that, so one more step is remaining calculation of entropy of one to four now one to four is what kind of this thing is a constant pressure. So delta S14 one four is CPLN T4 by T1 and four to two temperature is changing pressure is changing volume is not so delta S42 is a as a constant volume process so CVLN T2 by T4, let us see four is four to two, two has a T1 temperature and starting with T3 temperature let us see if I have done correctly or not, so S12 volume is changing V1 to V2 that's fine S32 temperature is going from T2 to T1, so T1 by T2 it will be then one four is the temperature is T3 by T1 and four two is T1 by T3 so now it is fine because there are only three values.

So we should write that but it is already written here so that's why I was not writing but we can do that so this is because we can see that this is the same temperature so one and two will have the same temperature which is T1 this temperature is T1 and for the volume three two and four all have same volume and this volume is V2 and this volume is V1, so three will have a different temperature which is T3 and T4 has a different temperature now four has T3 temperature and the state three has a temperature T2.

So now will have to show that as delta S12 is equal to delta S13 plus delta S32, who is essentially means we have to show that NRLN V2 by V1 is CVLN T1 by T2, now again for that we are going to use the relation between this adiabatic process one and three, so one has T1 temperature and volume as V1, three has T2 temperature and volume as V2, once we do that then T1 by T2 become V2 by V1 to the power gamma minus one take LN on both side giving us LN of V2 by V1 to the power gamma minus one or gamma minus one LV V2 by V1 and what is gamma minus one so gamma is CP by CV so gamma minus one is CP by CV minus one which CP minus CV by CV which his R by CV.

So NRLN V2 by V1 is equal to if I multiply by CV on the left hand side I have to multiply by CV on the right hand side so which are going to get actually in this case of course we can take number of moles to be one, so it will be just one values and CV here we mean by CV bar otherwise will be NCV bar anything say that or we can write that enough so to make it simplified we can write as (())(18:23) CP minus CV is NR so we will take one mole for this calculation so it is RLN V2 by V1 and what is the right hand side CVLN T1 by T2, which is giving us this one which is giving us again RLN V2 by V1 right hand side RLN V2 by V1 so that means this two values are equal, so now we are going to erase this and show the other relation that one four and four two.

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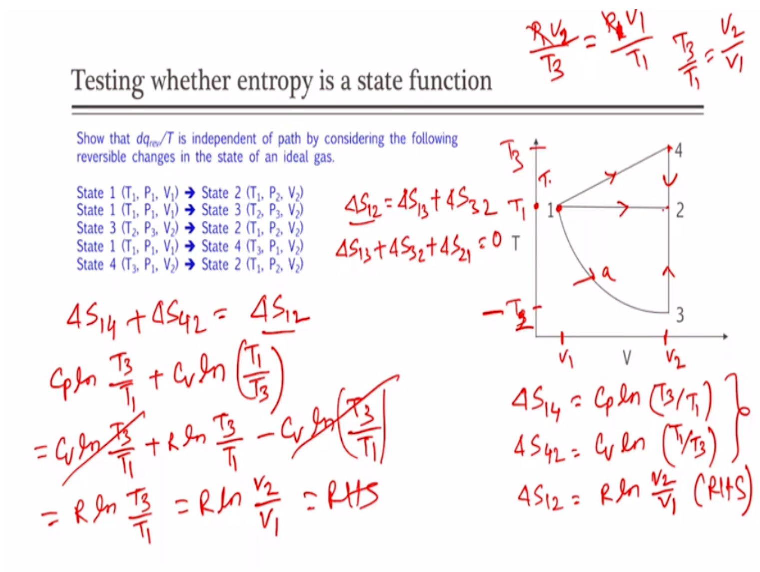

So the other relation says that delta S14 we are going by this path plus 42 is equal to delta S12, so what is delta S1, delta S14 again is as process where temperature changes pressure does not change and volume changes, so CPLN T3 by T1 delta S1, four two is a process where temperature changes pressure changes volume does not change, so CNLN four two so I have to say T1 by T3 and delta S12 is a process in which temperature is same pressure and volume changing which is now nothing but and isothermal expansion process which is RLN V2 by V1 now let us see left hand so right hand so this is our right hand side and left hand side is sum of these two let us sum both of them.

So CPLN T3 by T1 plus CVLN T1 by T3 that’s what you have to do which means we can inverted and write or we can just sum it and say that this is nothing but CVLN T3 by T1 plus RLN T3 by T1 because we know CPCV plus R and we can invert this LN relation and write minus CVLN T3 by T1, so this and this cancels each other giving us only RLN T3 by T1, but we know that T3 and T1 has a relation with V1 and V2, four and one pressure is constant so four has P1V2 by T3 is equal to P1V1 by T1, now P1P1 cancels giving us T3 by T1 is equal to V2 by V1, so this is nothing but RLN V2 by V1 which is our right hand side as well so which says that you know for this cycle the entropy for the whole cyclic path will be zero because what we have done is that we have not followed the cycle we have followed to pass from this point to this point again that is the same thing that says is that if is cyclic for then I will have to surprise you it will be zero, so we have done that

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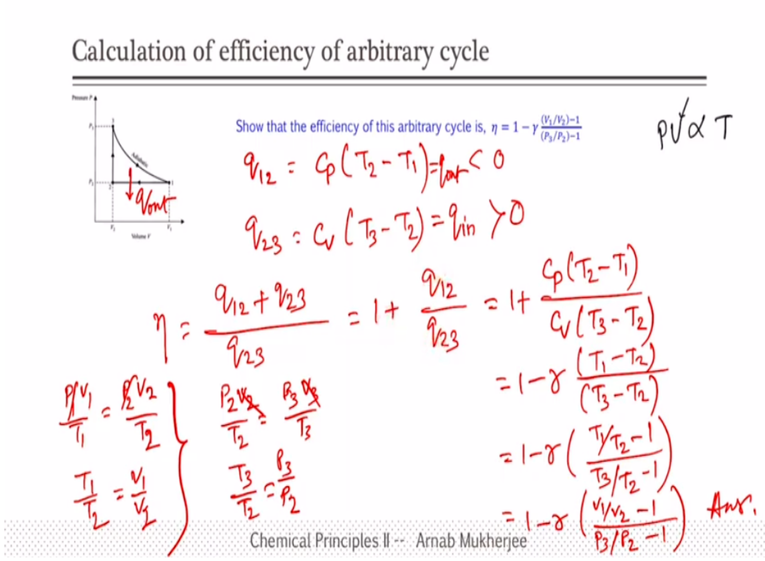

Now let us calculate efficiency of an arbitrary cycle so this is showing some arbitrary cycle where one to two is a constant pressure process two to three is constant volume process connecting by an arbitrary path C21 as an adiabatic process, so while I am doing that you should also try to do that we can pause the video and try to solve the problem and then look at it how it is working so calculation of efficiency is pretty simple because what all that we have to calculate that heat in and heat out so we are going to calculate that heat in port in first two step one two is a constant pressure process is be CP.

So when you calculate the heat changes CP it will be T2 minus T1 and then and in this case we know that it is a constant pressure compression process that means in this process volume gets less so the volume gets less you know the temperature has to be lower it is pressure is same remember it is an ideal gas, so pressure is getting lower, pressure is same volume is getting lower so temperature so PV by T is constant so pressure same volume getting lower temperature also has to be lower thus PV is proportional to T, PV is proportional to T a pressure constant so volume gets lower the temperature gets lower anyway, so now we know that so that this is negative quantity basically this is heat that is going out.

So this is nothing but Q out and two to three will be a Q (())(24:14) and this a constant volume so it will be T3 minus T2 this is our in step which is no greater than zero and three to one step is zero it is an adiabatic process, so what is the efficiency total heat change which is Q12 plus Q23 and what is the our input our input this Q23 that you have to understand, what is input and what is output otherwise we will not be able to put it in the efficiency calculation it input will go to the denominator which means is it is one plus Q12 by Q23 it is not minus because by the minus is there in the value itself Q12 so therefore just a plus just to written by earlier pint so it is one plus now Q12 is the this one CP, CP Q2 minus Q1 and this is CV T3 minus T2 I will write in such a way that you know T2 one side so one minus CP by CV is gamma and I took a minus so that I can write T1 minus T2 and T3 minus T2, now let us take T2 common from numerator and denominator giving me T1 by T2 minus one T3 by T2 minus one.

Now what is T1 by T2 that we have to figure out so T1 and 2 are related by constant pressure process so let us just use the formula SP1 V1 by T1 is equal to T2 V2 by T2, P1 and P2 are same so therefore T1 by T2 is V1 by V2, so we can write V1 by V2 here and let us check between three and two, so three and two are related by constant volume process, yes three and two are related by constant volume process, so we can write as P2V2 by T2 is P3V3 by T3, since volume is same V2 V3 is same so T3 by T2 will be P3 by P2 which means I can write one minus gamma T1 by T2 is V1 by V2, so V1 by V2 minus one T3 by T2 is P3 by P2 minus one, so this is our answer.

So it is pretty simple the efficiency calculation is not do this way just calculate the Q if you want to calculate the work done and all it will be very big and just calculate the overall change in Q and then essentially the this formula is always correct, it is always correct only when you have one input and one output if you have two input then both the inputs will go in the denominator and the numerator will have everything so that is why you be careful it is better to have total heat divided by heat input that is a definition and that is we should stick to,

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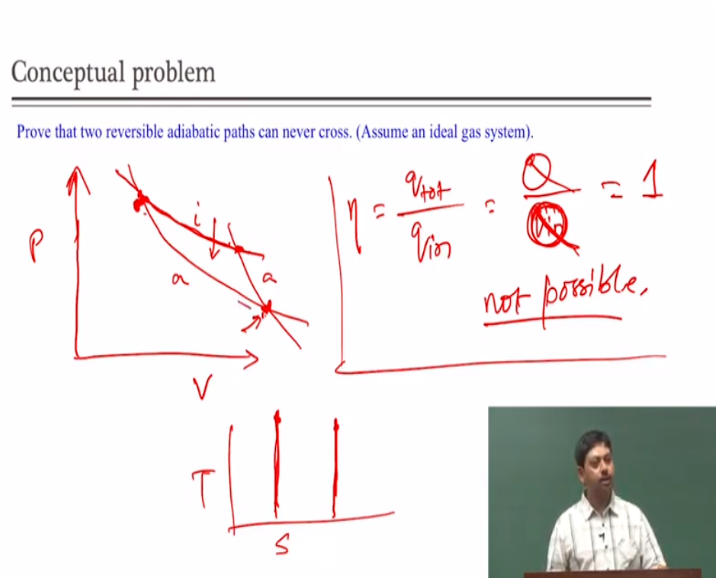

Now this is conceptual problem that is says that show that to adiabatic paths can never cross now how do you think about that so let us say I have a PV diagram and I have an isothermal path, isothermal is not drawn that way but let me just draw it once more it is have an isothermal path and have two adiabatic path connecting so this a adiabatic and this is isothermal let us say, say it is possible what will happen can you tell me what will happen, if this is a case let us calculate the efficiency it is we know that Q taught by Q in what is Q in.

So Q cannot be in through any of this adiabatic process, so this is the Q in, let us say this is some value Q and what is Q taught because Q taught total Q is only that Q because there is no other place which is one, which is not possible, if two adiabatic path cross than you can always join them by an isothermal path and that would violet second law of thermodynamics therefore two adiabatic path cannot cross for ideal gas you can obviously show that because this if two adiabatic crosses then this two will have some relation with T and V, these two also will have some relation with T and V and those both the relations cannot be satisfied because the temperature is same here that is another problem because let us say this volume is V so these V and T has some relation and this because the volume is different here so temperature will be different here compared to here, you are getting my point.

So when you have this relation between this and this since the volume is same between this step and this step temperature will be different here because the volume is changing differently compared to this point, so this temperature and this temperature will be different and therefore but it is not possible because we are joining them by Islamabad is there is another way of thinking but anyway so this is sufficient to show that if they cross you can always join them by an isothermal path and then it will violet this (())(30:01) so that is why two adiabatic can never cross and you can thing upon the TS diagram also, so in our two adiabatic if they have the different temperature in TS diagram they cannot meet so this is T this is S this temperature is increasing here.

So this is between an adiabatic path if another adiabatic path is there which has a different temperature and different entropy then they can never meet, it has to have same entropy otherwise they cannot meet and that is why they cannot cross because if you cross at some point they will have to have same entropy and same temperature because their is a state function both entropy and temperature at this point they have the same value but it can never have same value unless it is a same path if you start from here it will follow the same path so that is the another way of thinking.