Thermodynamics of Fluid Phase Equilibria
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Lecture – 09
Review of entropy

Welcome back. In this lecture, we will be reviewing the concept of entropy. So, let me start with the inequality of Clausius.

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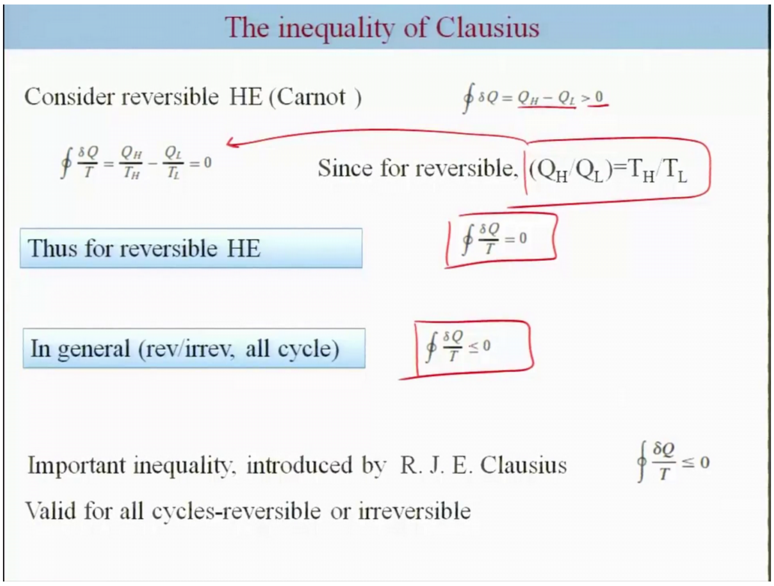

Let us consider first reversible heat engine case, which we have discussed in our last lecture, this is nothing but a Carnot heat engine. For Carnot heat engine; we know that QH by QL is equal to TH by TL and as well as we know that for a cyclic process, your delta Q is nothing, but QH minus QL which is going to be greater than 0.

Now, based on this reversible type of concept, you can write it in this way where the del Q by T for a cycle is nothing, but QH by TL minus QL by TL and that has to be 0. So, for a reversible heat engine you have a condition that this must be equal to 0.

Del Q by T should be equal to 0, in general whether it is a reversible or irreversible for all cycle we can write in this way and this is nothing, but your inequality of Clausius. So, in order for a process to occur this particular inequality must satisfy and this was proposed by Clausius and is valid for all cycles, whether is reversible or irreversible for both the cases it will be valid.

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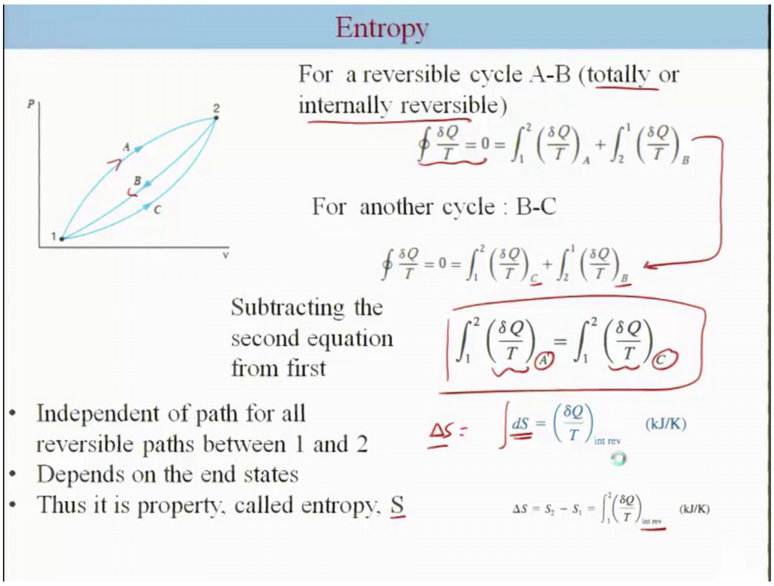

Now let us consider Process processes which changes the state condition on a from 1 to 2 and this is drawn on a P v diagram.

So, if you consider reversible cycle A and B which a could be totally or internally reversible, we can write down the cyclic value of d ki d Q by T equal to 0, because of the reversible cycle and if you are following 1 to 2 or A plus 2 to 1 on B that could be one particular cycle ; similarly you can take another cycle and you can write the same expression but now on C and B. Using 2 relation you can show clearly that this pointer 2, whether you go from or whether you take a path of A or you have taken the path of C, this should be same in order to have the same value of 0 ok; which essentially means that this term is basically independent of the path and this term which we call it as dS.

Because of the differential Q which essentially means that the delta S from 1 to 2 is independent of whichever path you take, if you integrate it you get basically delta S. So, this is independent of the path only depends on the final state point and this is nothing but the principle of the property ok, that the property depends only on the state condition. So, change in the property also depends only on the initial and a final condition not on the path. So, that is what we defined as the considering this is reversible, we make use of this internal reversible in a condition that this is true assuming that you have reversible process, now so for the case of let us say isothermal process ok.

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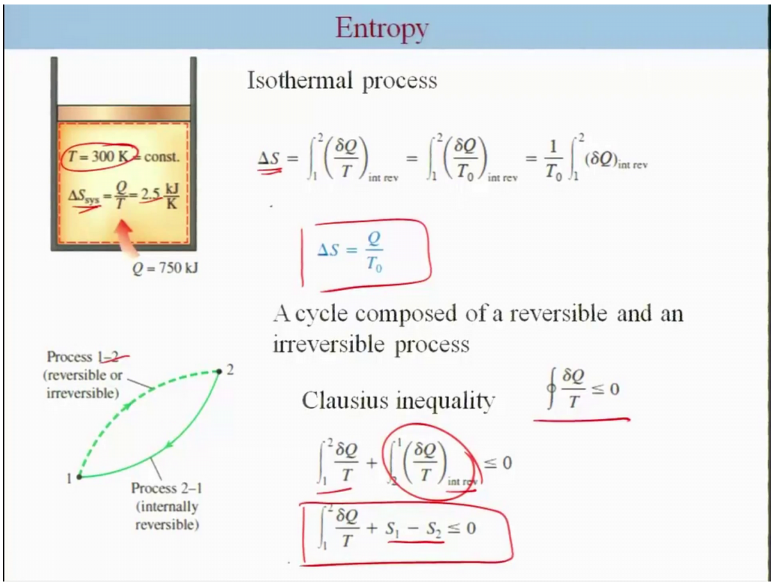

Where the heat is being supplied and temperature is fixed your delta S uh, in this case of the system will be nothing but since the temperature is fixed will be nothing but simply Q by T 0.

So, for the case of here 750 divided by 300 Kelvin, it comes out to be 2.5 kilo joules per Kelvin. Now let us consider again a cycle. Now in this case you have a reversible and an irreversible process which constitute the cycle. So, we will be making use of the process inequality.

So, let us say 1 to 2 could be reversible or irreversible and 2 to 1 is basically reversible or internally reversible. So, considering this you have 1 to 2 plus 2 to 1 which is internally reversible and this for this we know this is going to be delta S1 minus S2.

So, we can now make use of this expression in order to rewrite in this form ok.

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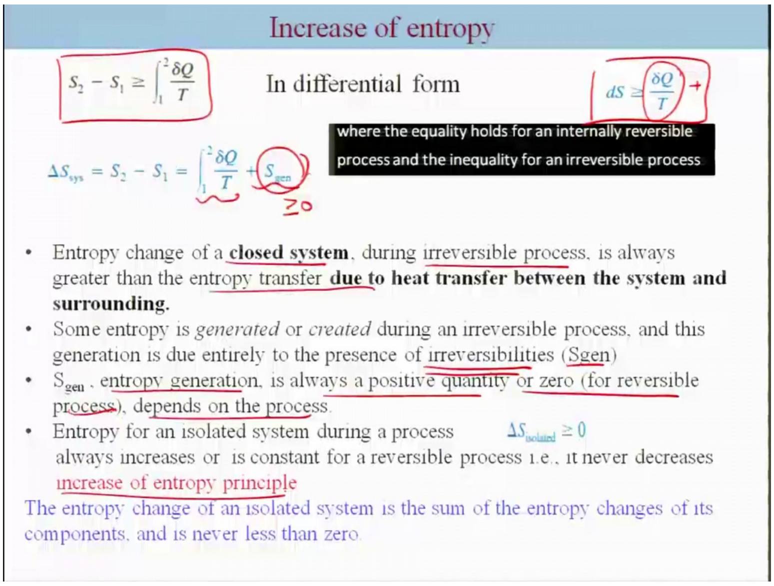

That means, S2 minus S1 is greater than equal to 1 to 2 del Q by t. So, in the differential form 1 can write d S greater than equal to del Q by T. So, which essentially means that entropy is increasing ok, it is not just equal to this but there is another additional terms which are coming which is we call it as generation.

So, for the case of a closed system entropy change during irreversible process is always greater than the entropy transfer due to heat transfer between the system and surrounding ok. So, this is the heat transfer due to heat transfer between the system and surrounding.

So, for the irreversible reversible process there is a certain S generation which is due to irreversibility's that is S generation. Now S generation or entropy generation is always a positive quantity or 0 for reversal process and it depends on the process. Entropy for an isolated system during a process is always greater than equal to 0 that means, because if I isolated you have this would be 0. So, S generation is always greater than or equal to 0 and thus delta S isolated will be greater than equal to 0.

So, in other word, the entropy never decreases entropy always increases or remains constant and this is the concept of increase of entropy principle.

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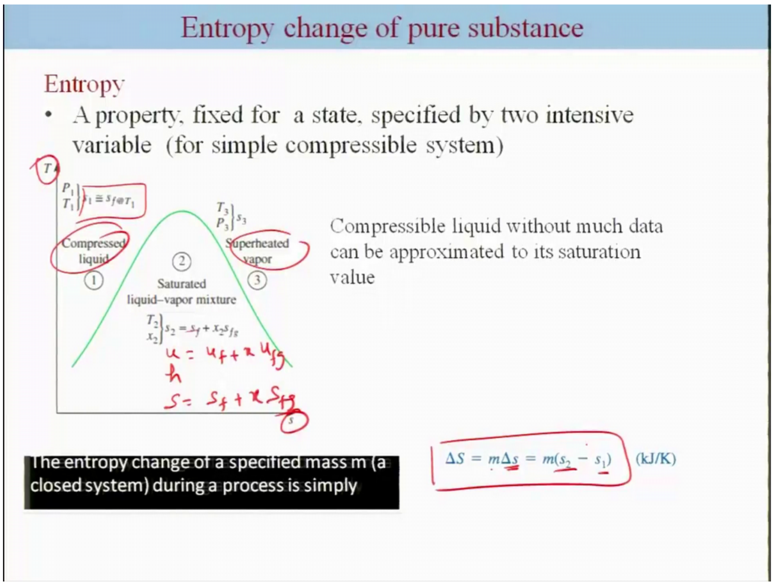

So, as we know based on this the entropy is a property and similar to the other properties you can also make use of thermodynamic tables, the graphs steam table and so forth to understand or to calculate the changes in entropy as in the case of a changes in internal energy or enthalpy ok.

So, this is an example of TS diagram temperature versus entropy specific entropy diagram, so this is be the green line is basically nothing, but vapor liquid equilibrium. So, this is your compressed liquid this is your superheated liquid this is your 2 phase system liquid and vapor in a similar case as you have done that for u for h ok.

If the quality is given for any point in this 2 region 2 you can find out s by simply saying u of f plus x u of f g similarly you can also write s as s f plus x s f g ok. And if you do not have information for the compressed liquid we will make use of the similar approximation as done for enthalpy, that s is nothing but s of saturated fluid at T1 for a given state point.

The entropic change of a specific mass m during a process is simply nothing, but small m multiplied by delta small s. So, this you can connect get it from the tables ok, similar to what you have done that for delta u or delta h ok.

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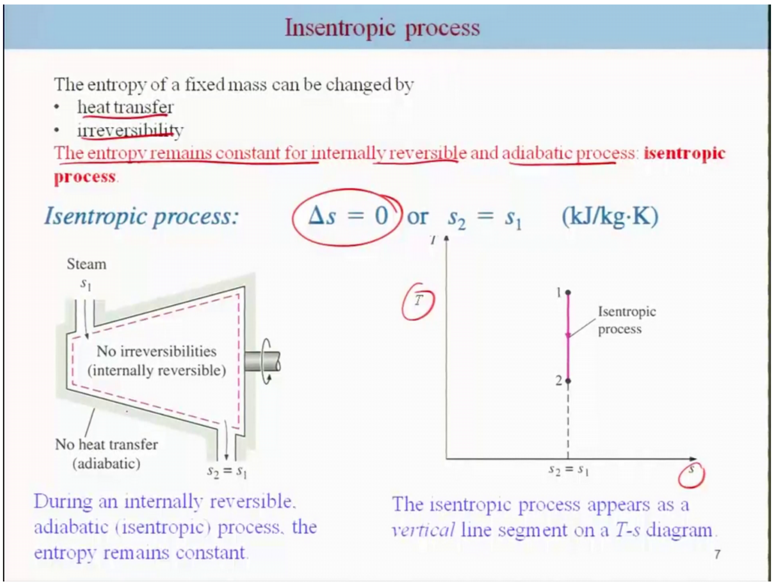

Let me just summarize here the entropy, as I said the entropy changes are due to heat and if there is a flowing condition due to the mass also you can have the entropy change.

So, for the case of a fixed mass the entropy change is due to the heat transfer and due to irreversibility, for the case of a internally reversible system the entropy will remain constant or the entropy remains constant for internally reversible and adiabatic process; that means, when you do not have any heat transfer and when there is no irreversibility delta S is equal to 0 and this is typically used for turbine case, which we approximate it to isentropic process in this case on a temperature s plot the vertical draw from 1 to 2 would indicate the expansion at a constant entropy ok. So, this will be the process for the case where you have adiabatic process and internal reversible process. So, this is for fixed mass ok.

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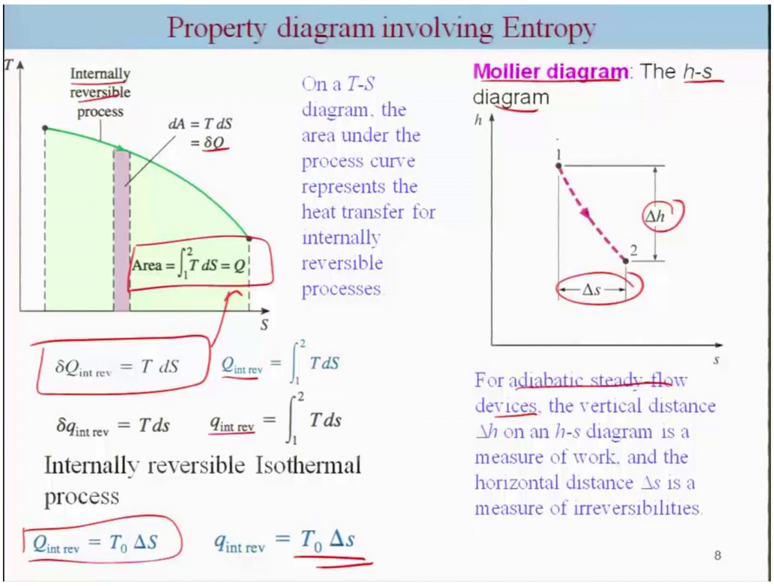

So, we can also represent entropy on or entropy changes on a TS diagram for a process, internal reversible process as depicted here represented by the green line from this point to that point; area under the curve is basically associated with the heat supplied to the system and the differential area would be nothing, but d a is equal to T ds is nothing, but del Q. For the internet reversible process del Q is nothing, but T T ds and from here of course, this information can be extracted ok.

So, you can find out the heat supplied or heat associated with this by just integrating this T ds, you can divide by the mass to get in specific per unit mass values, for a constant temperature system it will be simply T 0 delta S .

One can also make use of h s diagram which is a Mollier diagram for processes involving adiabatic steady flow in such case the drop in delta h measures the work associated with this steady flow devices and increase in the delta S is measures, the irreversibility associated with the device ok.

So, this is often also used in order to explain the irreversibility's of the devices ok. Now having done some exercise on this we can take this information particularly for the internal reversible expression of del Q and T ds and plugging in the relation at the first law.

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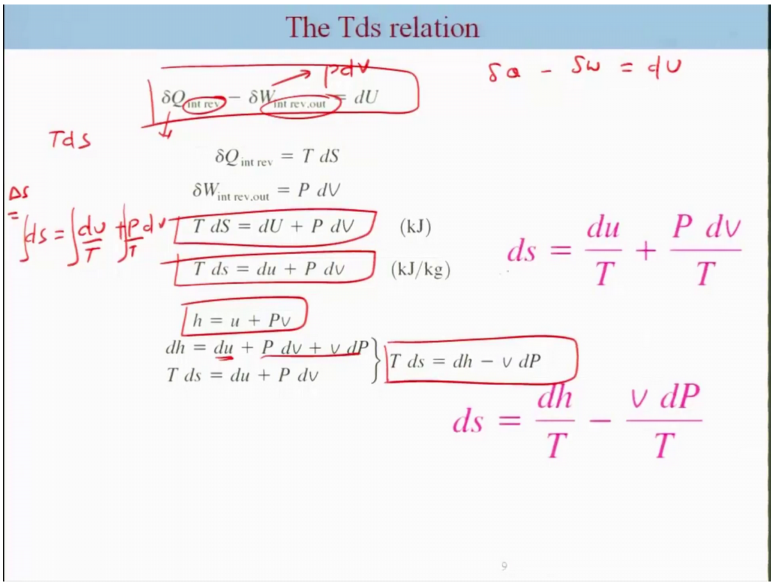

So, what we are considering is del qs heat supplied minus the work done by the system, is basically the change in the internal energy of the system now we considering internally reversible system ok. So, here we can make use of a T ds and here we can make use of only the boundary work which is associated with the system.

So, if you do that you have this relation which you get or in the per k g you can write it in this form. Now from here we can find out the d s by taking dividing by T and you can find delta S by integrating it ok, now you can also make use of the expression of enthalpy and write this expression instead of u you can rewrite in instead of u you can rewrite this expression in terms of h.

So, h is equal to u plus P v in other word d h is equal to d u plus P d v plus v d P you can write d u now as d h minus this term and thus you can get this expression. So, from here as I said we can find out ds in terms of changes in the d u or changes in the u and v. Here in this case ds is changing can be related to changes in the h and P.

So, if you integrate it and if you know the relations of the internal energy or enthalpy in terms of the pressure in the volume, you should be able to find out the change in the entropy for the simple cases it is easy ok.

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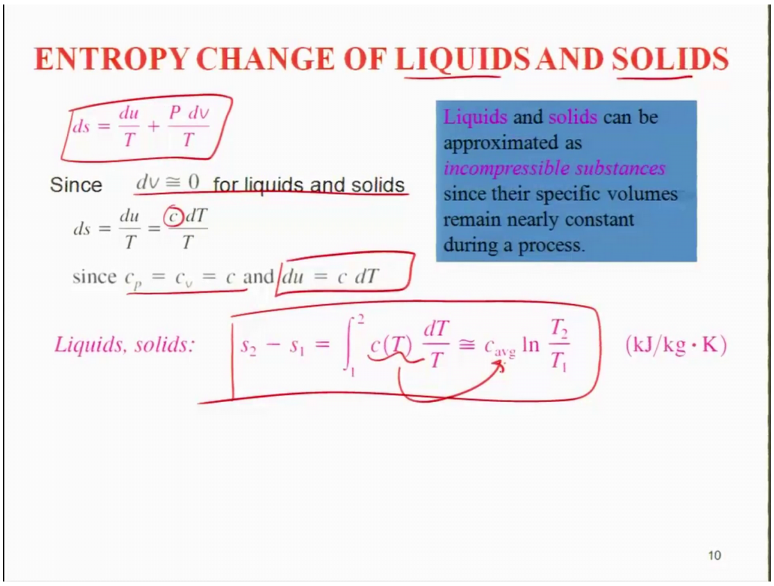

So, let us take at the some simple examples.

So, for the case of a liquid and solid for the case of a liquids and solid, we can consider that the volume hardly changes and thus your d v is equal to 0; in that case if you take out this expression in terms of u ds is equal to d u by d T d s is equal to d u by T, it can be simply written as C because for the case of liquid and CP you can approximate CP is equal to Cv is equal to C and thus d u is nothing, but C times d T and thus you can get this expression of the delta S in this form where C can be taken out as an average for the case of idle gas you can write du as dv Cv d T and d h as CP dT.

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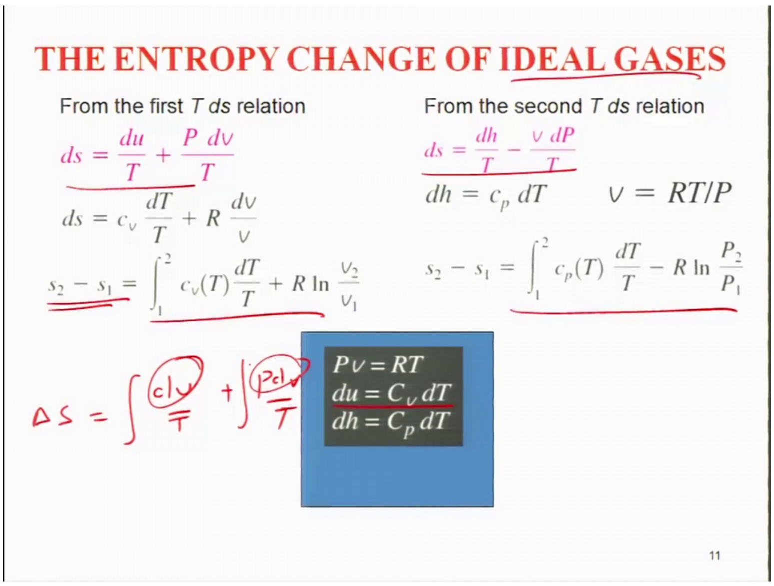

Now, this you have 2 expression one is here and the another 1 is here which is based on h you can plug in this appropriately in order to find delta s here ok. So, you can get this expressions in a very simple way, but in general if you want delta S you should be able to integrate this term separately.

For the case of u and similarly you can do that for the case of h and what we need is basically relation of this and since this is something which we are going to focus more in the later part of the course, making use of the volumetric property in order to create this kind of changes in delta S and other thermodynamic properties ok.

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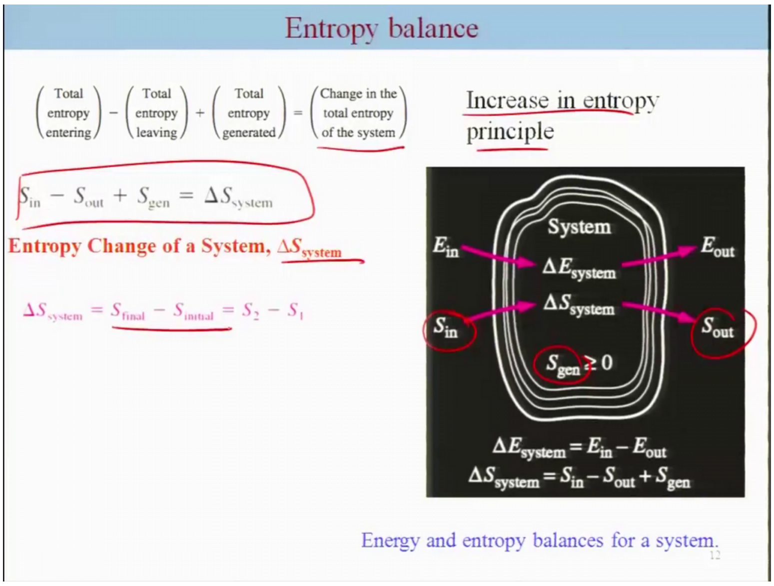

So, let us focus now on the entropy balance. Now entropy balance for a given system can be represented in this schematic form where the total entropy entering which is S in minus total entropy living out plus total generation, should be the change in the total entropy of the system ok. In other word on a simpler way S in minus out plus S generation is equal to delta S system and this is basically nothing but the increase in entropy principle.

Whereas delta S system is nothing, but s final minus S initial now what are the different mechanism of entropy transfer? Now beside heat transfer you can have also the due to the mass for the open system .

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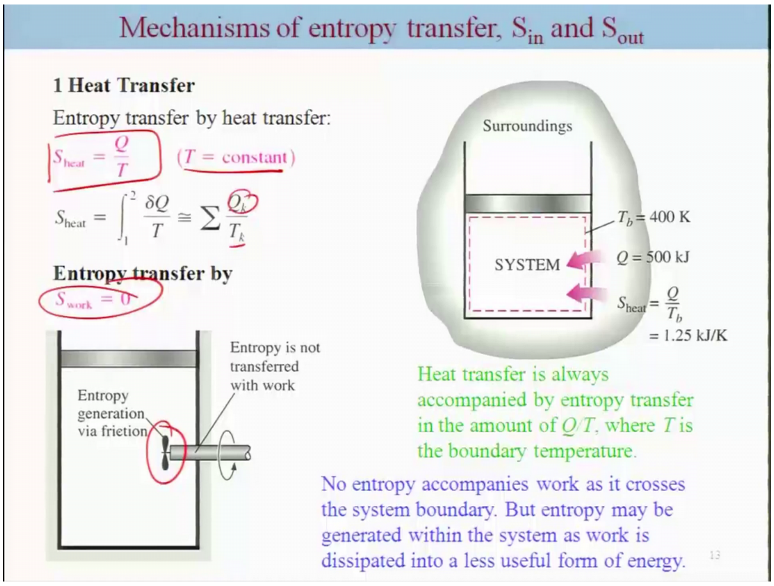

So, S heat for a constant temperature is simply Q by T that is due to the heat entropy transfer by the heat, if the temperatures are changing across the boundary you can also make use of summation of heat at different part of the boundary and this will be your T Q k divided by T k summation of that. Entropy transfer due to the work which is ordered form of energy is not; is it going to be 0 anything which is associated; while for example, considering the shaft the entropy is being generated only due to the friction associated with this.

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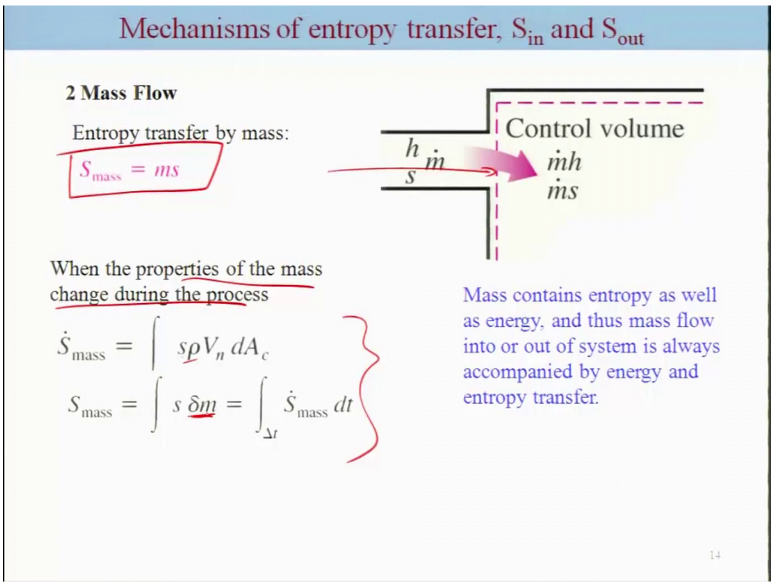

So, in addition to the heat transfer you have also due to the entropic transfer due to the mass ok. So, of the fluid is flowing it also bring in entropy into the control volume and that is can be written as simply S mass is equal to m times the specific entropy. And if it if the property of the mass changes during time you can make use of these expressions, which is well known it is S times density times the volumetric normal velocity multiplied by the cross sectional area or in general S mass is equal to s times the differential mass which can be written in this form.

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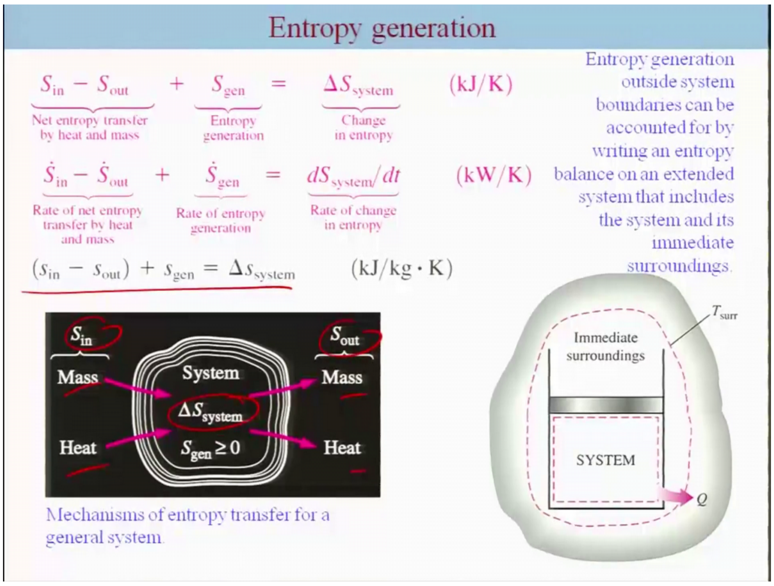

So let me get back to the again the entropy balance here as I said is S in minus S out plus S generation is equal to delta S system, S in minus S out is due to the entropy transfer by heat and mass ok.

This can be written in to rate form and this is what we have written also earlier. So, in summary S in is due to mass and heat S out is due to mass again heat and delta S system the change is due to the changes in the s m S out plus the S generation.

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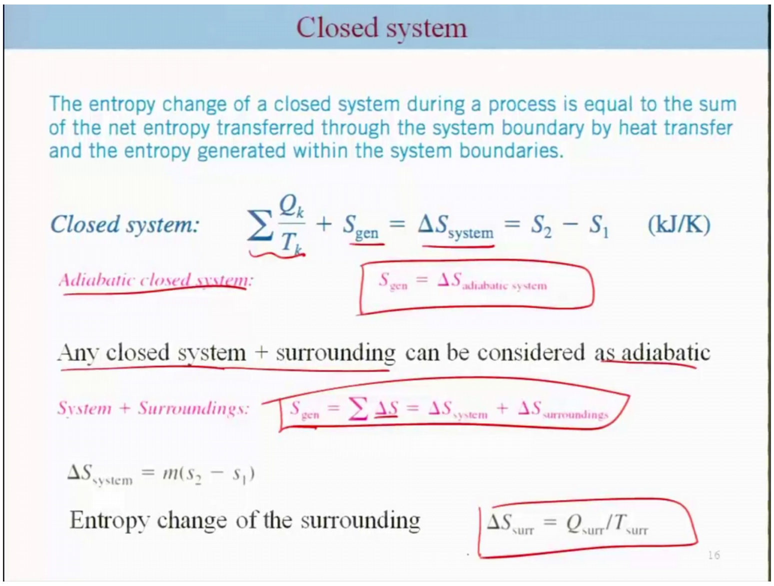

For a closed system we can we can write down S in minus S out, simply as due to the heat transfer there is no mass entropy due to the mass transfer and thus this can be written as summation of Q k by T k plus S generation is equal to delta S system ok.

So, for adiabatic close system when the heat is also 0, supply then S generation is nothing, but delta S of system which is adiabatic. For any closed system plus surrounding we can consider that to be an adiabatic in other word S generation is basically nothing, but summation of delta S system plus surrounding. If we consider system plus surrounding as a combined system which can be considered as adiabatic, then this expression holds and delta S surrounding would be nothing, but Q surrounding divided by T surrounding.

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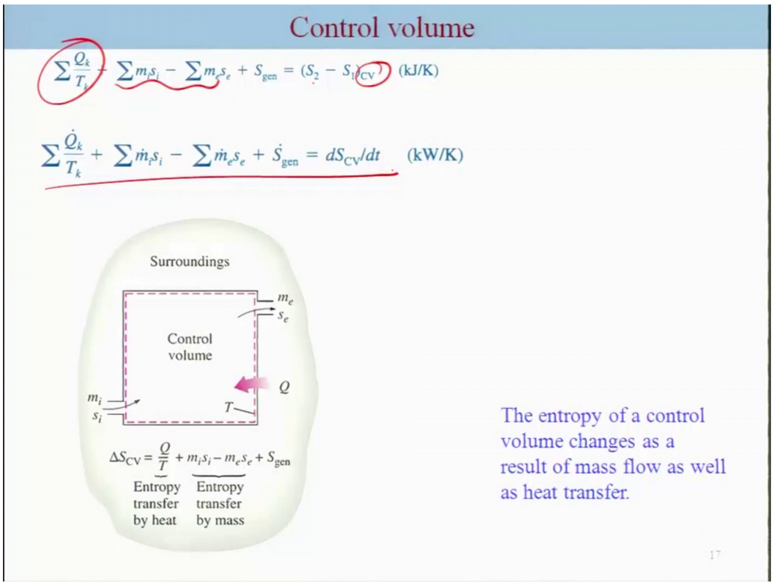

For the case of control volume beside the heat you have to consider the mass element here and the rest of the terms are straight forward; whereas, of course S2 minus S1 would be of the control systems you can write this in terms of rate expression as well ok.

So, this is something which I expect that you have already gone through earlier it is just recap. So, let me just try to finish this particular lecture by working on this example.

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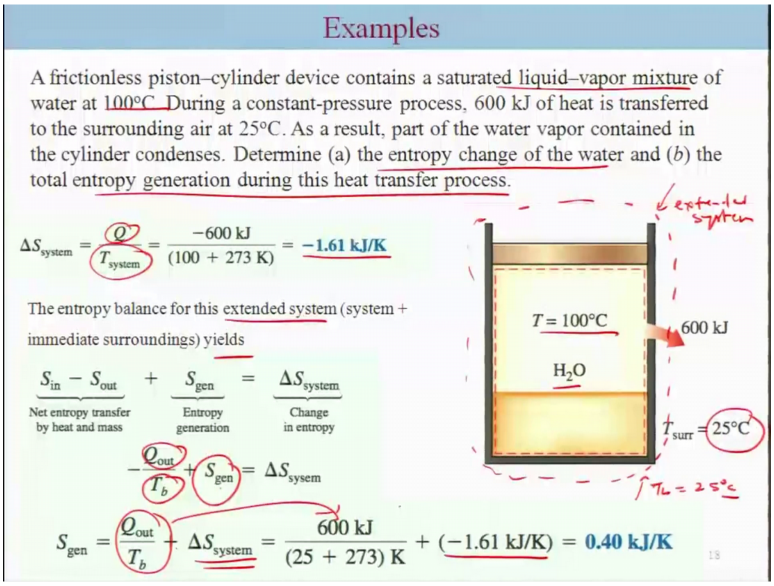

So, here we have a frictionless piston cylinder device which contains a saturated liquid vapor mixture of water at 100 degree Celsius, during a constant pressure process 600 kilo joules of heat is transferred to the surrounding at 25 degree Celsius as a result part of the way water vapor contains in the cylinder condenses ok. So, some part of the vapor condensed to the liquid and what we have to find out the entropy change of the water and the total entropy generation during this heat transfer process.

So, for the case of a delta S system, we will simply consider the Q which we know and the T system because it is a saturated liquid vapor mixture the temperature remains constant, so this is 100 plus 273 Kelvin and the Q is minus 600 which turns out to be this.

Now, for the case of total entropy generation, we have to also find out entropy generation outside or particularly the surrounding as well. So, the way we are going to do is we are going to consider a combined extended system where system plus surrounding is extended system.

So, this is extended system, such that here T b or the boundary is 25 degree Celsius. So, in that case if you consider the total energy total entropy balance, you have S in minus S out there is no S in only the heat is being transferred. Now at the boundary of extended system this is Qout divided by T b which is 25 degree Celsius plus S generation is equal to delta S system, S generation is a total entropy generation. So, you can rewrite you can write in this way S generation is Q out plus T b plus delta S system. Now delta S system we know and this entropy generation or the entropy due to the heat is can be written as in this way.

So, this plus delta S system which we have already calculated will give us the total entropy generation during this heat transfer process. So, the idea is basically to make use of extender system in order to calculate this. So, I hope that this quick exercise and as well as quick recap of second law of thermodynamics and beside the earlier contents which we have covered the basic definition of the system ah; then the first law of thermodynamics, open system close systems and how to make use of the balances energy and then the introduction of the entropy and finally a very quick example.

With this I hope that you are now well warmed up in order to take more fundamental aspect of the thermodynamics which we will be starting from next lecture onward with the basic thermodynamics or calculus related to thermodynamics.

So, with this I will stop here and we will see you in the next lecture.