Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 05
Second Law Of Thermodynamics (Contd.)

Well, good day to all of you again, so to continue with your discussions where we had left it in the last class I had started discussing the second law of thermodynamics and before that I had very briefly or quite rapidly glanced through the introductory concepts and the first law of thermodynamics you are requested to refer to any particular standard textbook go through the things which I have discussed in the class and in case if you have got any further doubts, me and my TAs' will be glad to clarify those particular doubts in our interactive and or question-and-answer session.

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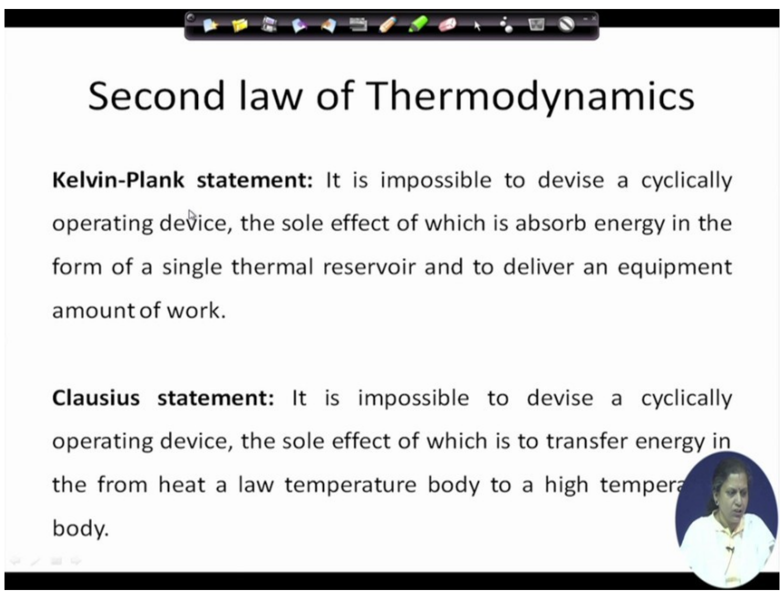

Yesterday I had started the second law of thermodynamics and I had given you the 2 statements the Kelvin plank statement and the Clausius statement and if you go through these 2 statements carefully just the way I was mentioning in the last class that most of the statements they have been developed with respect to heat engines and heat pumps.

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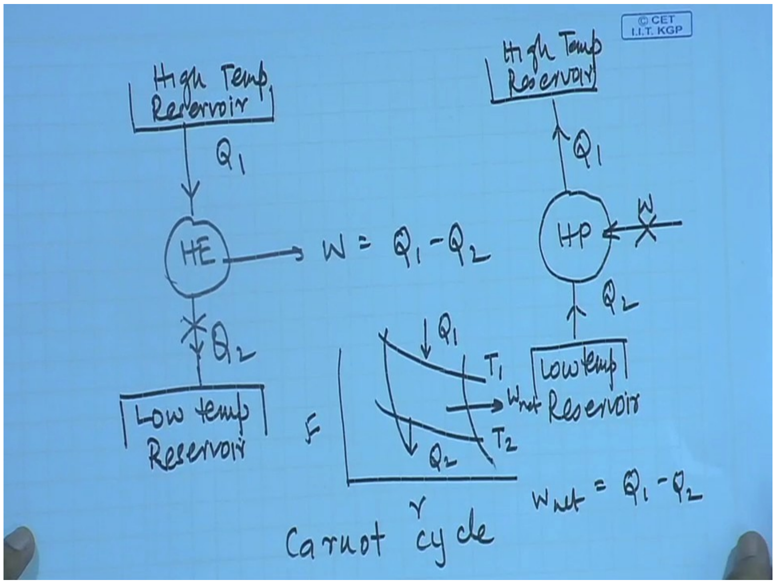

Now very briefly what is the heat engine? It is a cyclically operating device which converts heat to work, for this particular purpose what it has to do? It has to take up heat from a high-temperature reservoir, now what is a reservoir etc? Those things will get in any standard textbook and you are supposed to refer them. So therefore what a heat engine does is, it takes up heat from a high-temperature reservoir say Q1 amount of heat and it rejects heat to a low-temperature reservoir some amount of the heat and it does work with the remaining portion and so therefore this is what a heat engine is?

What does Kelvin Plank statement says? It says that it is impossible for a heat engine to operate without this particular portion or in other words we cannot convert the entire Q1 into W that we have already discussed in the last class that due to this reason heat is referred to as a low-grade energy while the reverse the entire W can be converted to Q1 but the entire Q1 cannot be converted to W there has to be a heat interaction with a low-temperature reservoir where some amount of heat has to be rejected and the remaining portion can be converted to W.

So therefore Kelvin plank statement says that this particular leg of the heat engine should be there and what does Clausius statement say? It suggests the feasibility of operation of a heat pump, heat pump is nothing but it is just the reverse of a heat engine what it does? Its basic purpose is to take up heat from a low-temperature reservoir and to pump that heat to a high-temperature reservoir and for this some amount of work has to be done on it without this particular amount of work it cannot take up the heat and reject it.

Just to be very brief heat pumps can be either heat pumps or a refrigerator the difference between the 2 being in the purpose fits their going to serve. The purpose of the heat pump is to keep the high-temperature reservoir hot and purpose of the refrigerator is to keep the low-temperature reservoir cold, so as a result in the case of refrigerator the high-temperature reservoir is the ambient and for the heat pump the low-temperature reservoir is the ambient, this is the basic difference between the 2.

What does Clausius statement say? Clausius statement says that for a heat pump to operate this much amount of work has to be done without this particular portion a heat pump cannot operate its quite evident because suppose a heat pump could have operated without this amount of work it automatically implies that heat can flow from a low-temperature to a high-temperature which we know it is not possible.

Now I leave it to you as an exercise to show that the Kelvin plank statement and the Clausius statement they are equivalent to one another and the violation of one automatically implies the violation of the other and after that what we did? We found out that the most efficient way of operating any particular process or any particular cycle is by a reversible process.

Well, so therefore a reversible process or a reversible heat engine cycle will definitely ensure that the heats taken up from the high-temperature reservoir and rejected to the low-temperature reservoir occurs under differential temperature difference or they occur under isothermal conditions.

So therefore these 2 processes should comprise of reversible isotherms in order to get the maximum efficiency. What we were discussing was that the Carnot cycle is the heat engine cycle which comprises or rather it is a reversible heat engine cycle which comprises of 2 reversible isotherms where the heat is being taken up from the high-temperature reservoir and heat is rejected to the low-temperature reservoir and the 2 isotherms are connected by 2 adiabats where the net work is performed such that the net work performed is equal to Q1 minus Q2, if anyone of these processes comprising the reversible cycle is irreversible then it becomes an irreversible cycle, okay.

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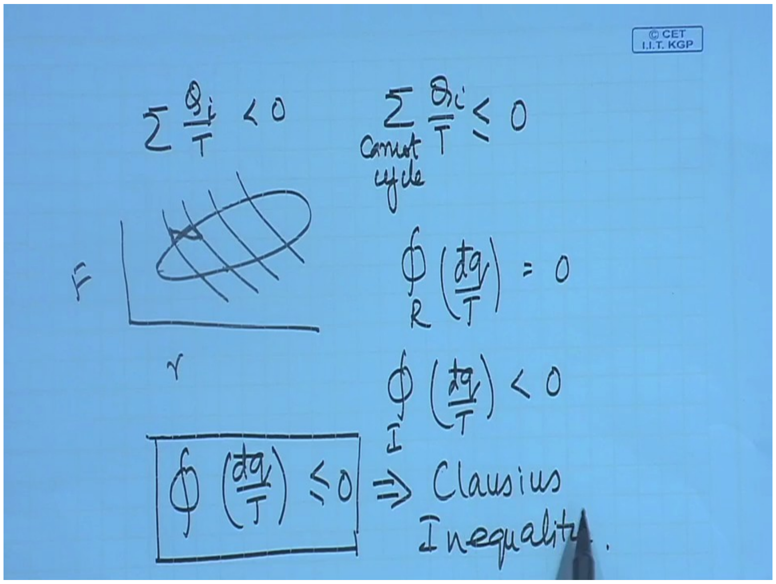

Now after this based on this cycle Carnot has proposed some very important propositions which we have already discussed in the last class and based on those particular propositions we had derived the Clausius inequality which states that in any particular cyclic or rather in any particular reversible cycle the quantity dq by T it disappears along a reversible cycle and that is less than 0 along an irreversible cycle, so therefore the 2 equations combined give us the Clausius inequality which we have derived in the last class.

Now I would just like to remind you that in order to derive this, what we did? We first based on the efficiency of a heat engine cycle we first derived this particular equation for a reversible and an irreversible Carnot cycle and then I had proposed that any particular reversible cycle can be broken into a series of Carnot cycle this was based on the supposition that any reversible process is equivalent to a reversible isotherm, a reversible adiabatic and another reversible isotherm. While this can be done again I leave it to you as an exercise for you to prove that any reversible process is equivalent to 2 isotherms and a reversible adiabat.

Now based on this any irreversible cycle can be broken down into a large number of adiabats and since we know that 2 adiabats can never coincide or can never intersect again why they cannot intersect? Is for you to find out and in case you have doubts we are going to clear it in the interactive session. So therefore for any cycle it can be divided into a large number of closely spaced adiabats with reversible isotherms connecting the different adiabats such that the entire reversible cycle can be broken into a number of Carnot cycle, for each Carnot cycle this particular equation or this particular proposition is applicable which gives for any reversible cycle dq by T is equal to 0 and in any portion of the cycle is irreversible then the term dq by T is less than 0.

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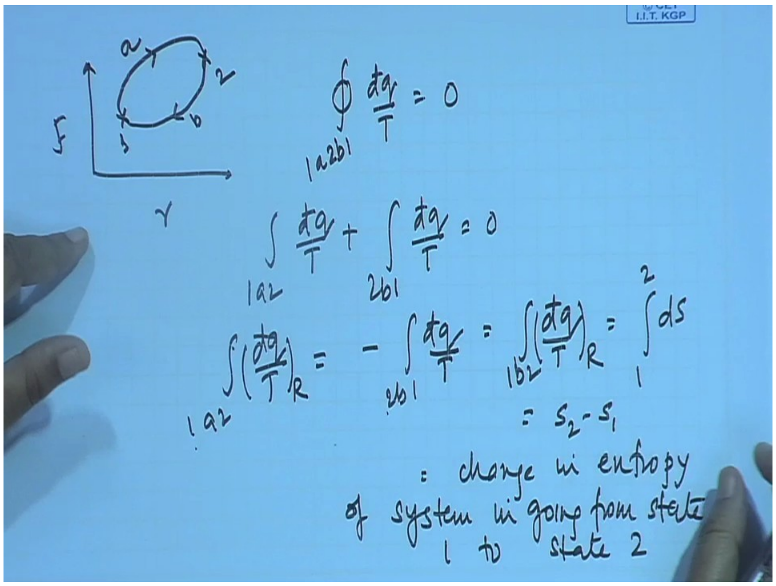

Now let us see what this particular Clausius inequality implies this gives rise to a very important relationship or it gives rise to a very important property which decides when a process is going to be irreversible or when a process is feasible and when it is not? Now let us see how it is done? Again based on a F-r plot maybe from state one to state 2 we devise a reversible process, so the process proceeds along 1a2 and the system comes back to its original state along another reversible process say 2b1.

As a result the system has undergone a cyclic reversible cycle 1a2b1. Just note that since it is a reversible cycle, so therefore all processes in the cycle are reversible so therefore each state the system has passed through in the course of this process is an equilibrium state therefore we can trace the path of the process by a solid line on the F-r plot. Now therefore for this reversible cycle from Clausius inequality what can we write? We can write 1a2b1 dq by T this is equal to 0.

What does it imply? It implies that 1a2dq by T plus 2b1 dq by T this is equal to 0 or in other words we can write it down as minus dq by T 2b1, now it is important to note that 2b1 is a reversible cycle, so therefore if we can reverse the heat interactions then the heat interactions along 2b1 is just the opposite of the heat interactions along 1b2, so therefore this is equivalent to 1b2 sorry dq by T.

So therefore we find that along this particular process 1a2 and 1b2 we find that the quantity dq by T reversible along path 1a2 is equal to the quantity dq by T along the reversible path 1b2, so therefore what does it imply? It implies that provided the path is reversible the quantity dq by T it is independent of the path followed it just depends upon the initial state and the final state.

So naturally when any quantity its change is independent of the path follows and depends only on the initial and final state. So naturally that particular quantity as we know, it has to be a property of the system. So therefore we find that although dq is a path function the term the quantity dq by T is a state function and this state function as we know this is defined by an entropy and therefore this particular quantity is nothing but equal to S2 minus S1 the change in entropy of the system in going from state 1 to state 2, change in entropy of system in going from state one to state to state two.

So therefore we have found this out. So therefore we find that for a reversible cycle we find that the quantity dq by T is equal to the change in entropy of the system in going from the same initial to the same final state now this was for a reversible cycle.

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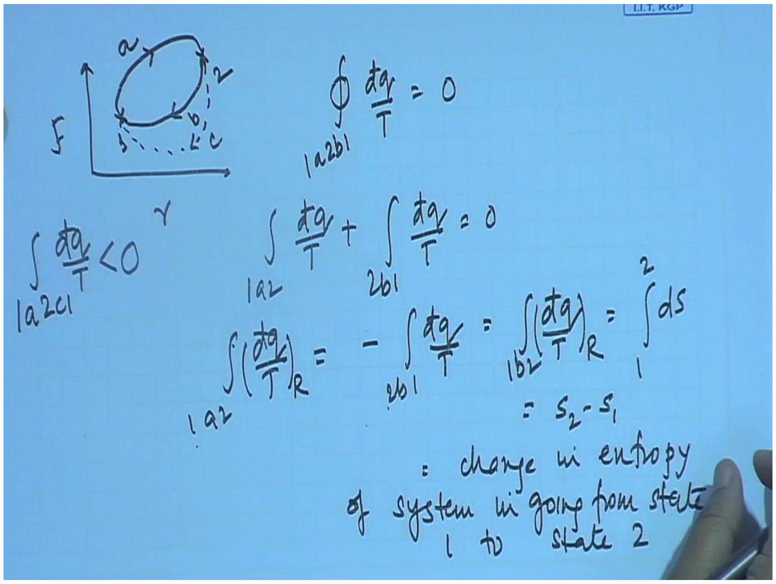

Now suppose I say that the system returns from state 1 to state 2 by an irreversible process say 2c1 since in this case the path is undefined there are several non-equilibrium states in the process. So therefore the curve joining it is depicted by a dotted line and not a solid line by the irreversible process.

Now for this particular case for the cycle say integral 1a2c1 for this case the quantity dq by T is less than 0 from Clausius inequality, isn't it?

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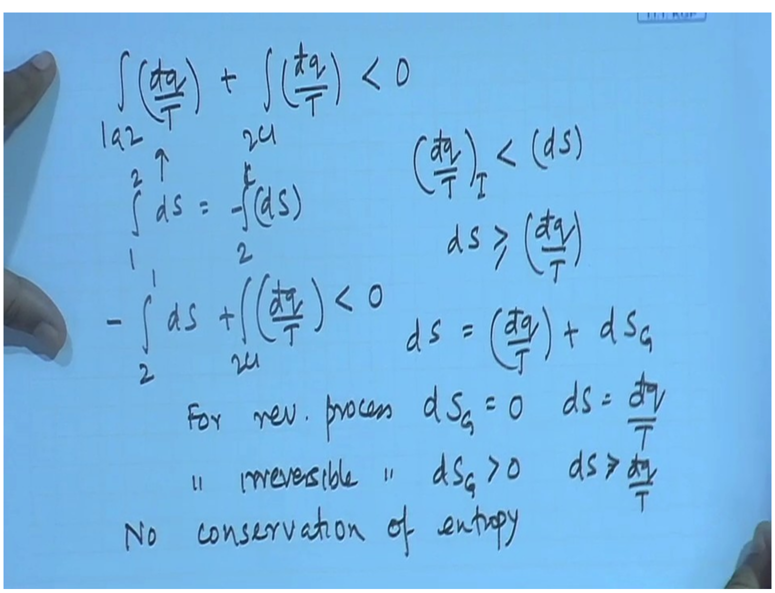

So elaborating this, what do we get? We get integral 1 a2 dq by T plus integral 2c1 dq by T this is less than 0 and we know that this particular quantity dq by T this is nothing but equal to integral 1 to 2 ds and we also know that if we just reverse the process or rather if we just reverse the heat interaction then the reverse process or in the reverse process the heat interaction just gets reversed. So therefore this is nothing but equal to integral 2 to 1 minus dS, isn't it?

So there because dS depends just on initial and final state and nothing else, so therefore instead of this particular term dq by T, can we not write it down as 2 to 1dS plus dq by T along 2c1 that is an irreversible process it is less than 0 or in other words dq by T irreversible is less than dS for that same change in states of the system say from an initial state to the same final state, so therefore in this particular case what do we get? We find out that the amount of or in other words dS is greater than equal to dq by T where the equal to sign it holds for a reversible process and greater than sign holds for an irreversible process.

In order to convert this particular inequality to equality we can also write it down as dq by T plus the amount of entropy which is generated as a result of irreversibility of the process. So therefore we find that for reversible process entropy generated due to the irreversibility equals to 0 and dS equals to dq by T and for an irreversible process dSG is greater than 0 and dS it is greater than dq by T.

So therefore this is what we get and we find that for a process to be feasible there has to be some amount of entropy generation which automatically implies that entropy of any particular system it keeps on increasing there is nothing like the conservation of entropy just as we have a conservation of energy there is nothing like the conservation of entropy and entropy is always generated during any particular irreversible process.

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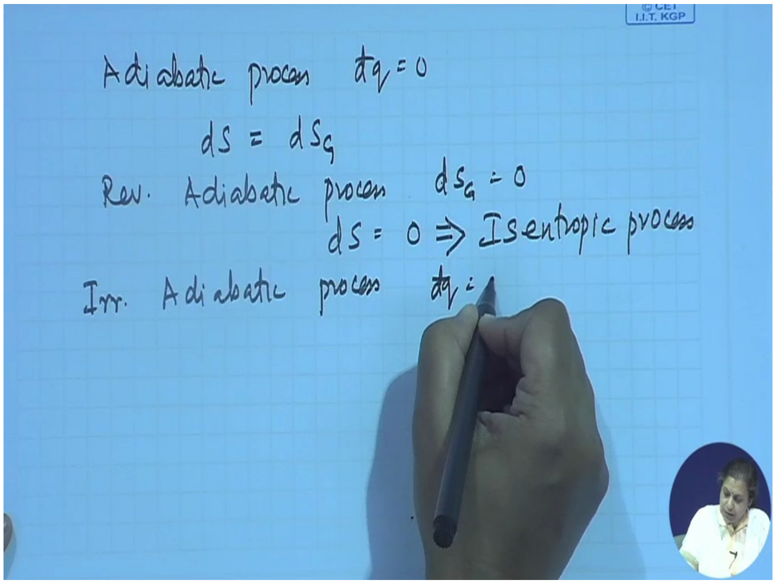

Now very interestingly suppose we take up an adiabatic process. For adiabatic process what do we have? We have dq equals to 0, so therefore dS which should be equal to dSG or in other words dS should be equal to dSG. When the process is reversible adiabatic then naturally we know that dSG equals to 0 and dS equals to 0 as a result of which we had already stated possibly you are aware of the fact that any irreversible adiabatic process is termed as an isentropic process because all the reversible adiabatic processes have to be accompanied by or rather can be depicted by dS equal to 0 when the process is not adiabatic what happens?

Sorry, when the process is irreversible, for an irreversible adiabatic process what do we get? For an irreversible adiabatic process definitely since it is adiabatic dq equals to 0, right?

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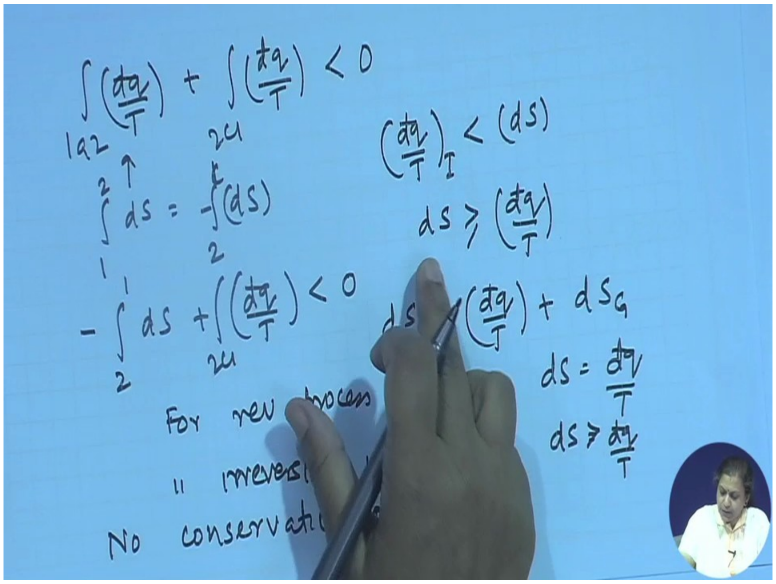

And from this particular equation then what do we get?

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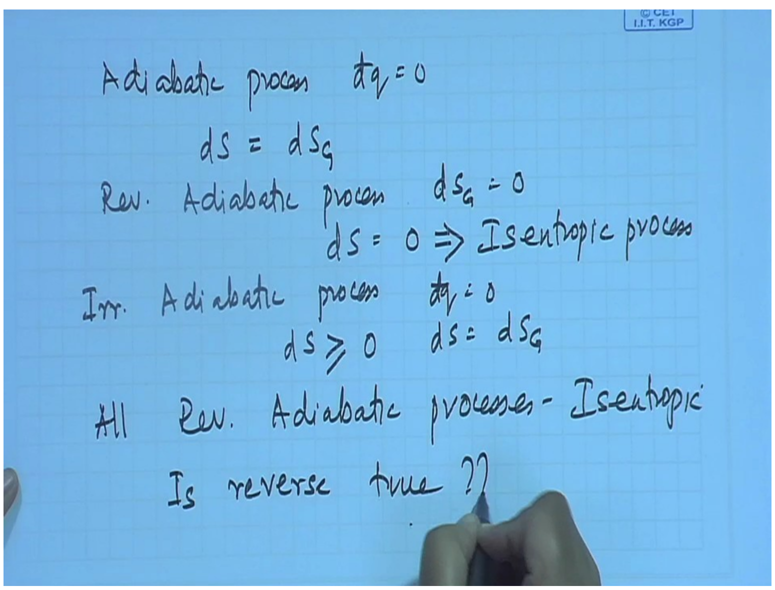

From this particular equation we get dS is greater than equal to 0, right? So therefore we find that when the process is irreversible adiabatic then in that case it is not an isentropic process although dq equals to 0 there is some amount of entropy generation which results in an increase in entropy of the process even when there is no heat transfer in this particular process.

So therefore from this what do we deduce? We deduce that all reversible adiabatic processes are isentropic. Now if I say that well, if you are convinced about this statement, is the reverse statement true? What do you think should all isentropic processes be reversible and adiabatic? Just let us give a thought at it, let us see that if this is definitely undisputed.

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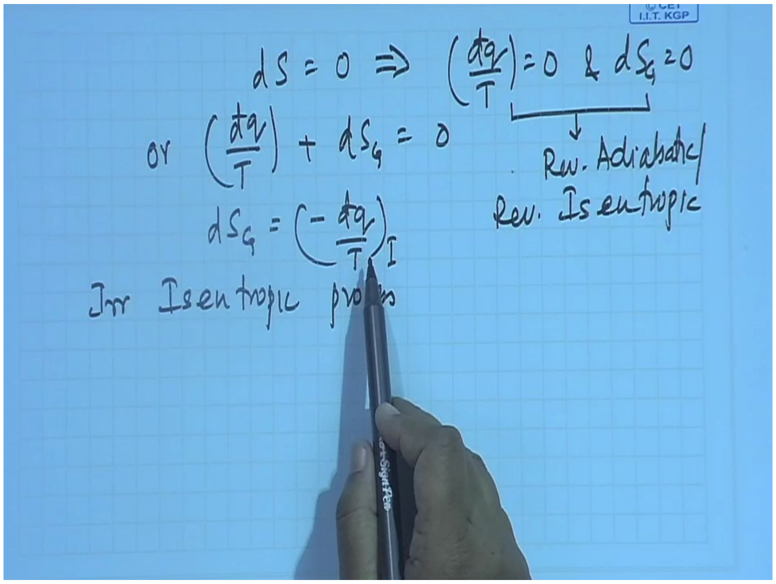

Let us see what happens for an isentropic process we know that for an isentropic process dS is equal to 0, now what does this imply? This implies that dq by T plus dSG equal to 0. This implies either dq by T equal to 0 and dSG equals to 0 or this particular thing when dS equal to 0 implies this then this suggests a reversible adiabatic or isentropic process this is an reversible isentropic process.

But we can also have an isentropic process with this being obeyed when this is obeyed under that condition what do we find? We find out that for an irreversible isentropic process is also possible where dSG is equals to minus dq by T what does it imply? This implies that we can have an isentropic process even when it is not reversible and adiabatic but under that condition the process has to be irreversible and there has to be entropy generation and this particular entropy generation has to be equal to the amount of heat which is lost by the system to the surroundings. So it implies 2 things, first thing is an irreversible isentropic process is possible only when heat is lost from the system to the surroundings, your reverse direction of heat transfer is not possible number 1.

Number 2 we find that only when the process occurs in such a way that the system loses heat at the same rate at which entropy is being generated then we can definitely have an isentropic process which is neither reversible nor adiabatic but it is isentropic. A classical example is maybe a liquid flowing through a pipe under where there is a lot of friction produced and the flow is such that the fluid loses heat to the surroundings at the rate at which the heat is produced due to friction.

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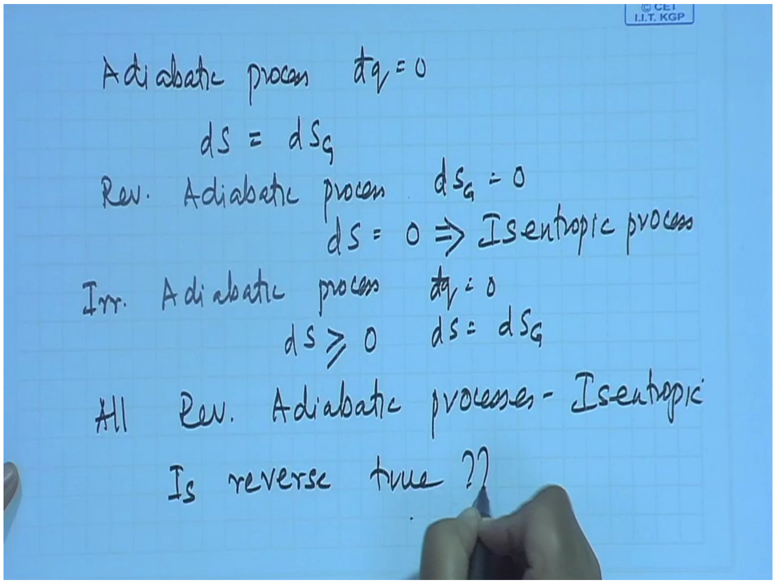

So therefore this is something very important for you to note and it is very important for us to remember that all adiabatic reversible processes are isentropic but all isentropic processes are not reversible, we can have isentropic processes but these have to be irreversible number 1 and number 2 for such processes to occur the system has to lose heat to the surrounding, heat transfer in the other direction is not possible. So this is one aspect which I wanted to discuss.

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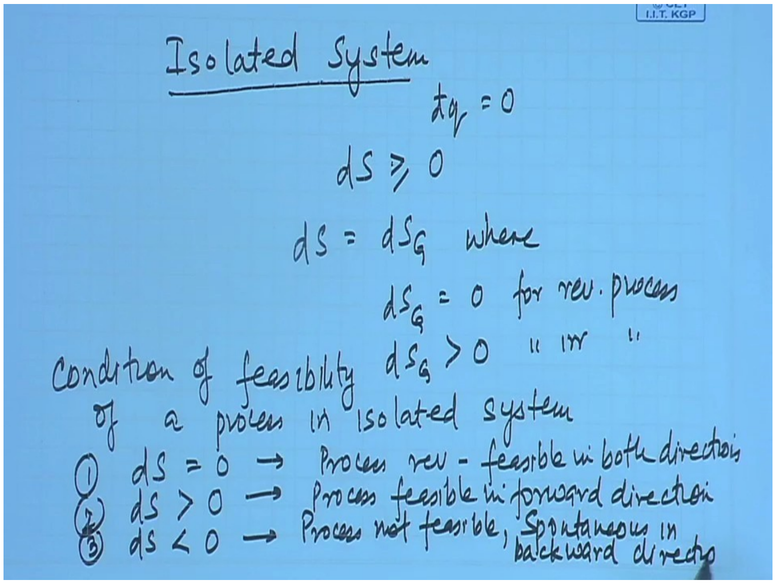

Now let us see what happens for an isolated system, let us take up an isolated system because again as I was telling that for most of the cases we would always like to refer to some sort of an idealization in order to find out how the system behaves under idealized condition? For an isolated system what do we have dq equals to 0 we know. So therefore for this particular case your dS has to be greater than equal to 0, agree?

So therefore for an isolated system we can have dS equals to dSG, where dSG equals to 0 for reversible processes, dSG greater than 0 for irreversible processes. So for this, what do we finally deduced? We deduce that in an isolated system entropy is always generated if any particular irreversible or feasible process occurs. So therefore from here what is the condition of feasibility of a process in isolated system? We find that if dS is equal to 0, we know that the process is reversible it is feasible in both directions that means both the forward and the backward process can occur.

If we note if we find that we calculate the entropy change of the isolated system when it is performing a process and we find that dS is greater than 0, then we know that the process is feasible in the forward direction but it is not feasible in the backward direction because in the backward direction dS will be less than 0 and suppose on calculation of dS you find dS is less than 0, what do you deduce? You deduced process not spontaneous or not feasible. It is spontaneous in the backward direction.

So from here we have deduced the criteria of spontaneity of any particular process in an isolated system the criteria of spontaneity is dS greater than equal to 0 where this equality sign is applicable when the process is feasible in both the forward and the backward direction and the greater sign it shows that the process is feasible in the forward but not in the backward direction and dS less than 0 it signifies that if the process has to proceed in the forward direction energy has to be applied to it but in the backward direction or in the reverse direction the process is feasible.

So we continue our discussions a little more discussions on entropy in the next class, good day.