Indian Institute of Technology Kanpur

National Programme on Technology Enhanced Learning (NPTEL)

Course Title Engineering Thermodynamics

Lecture – 24 Applications of Second Law of Thermodynamics: Entropy 1

> **By Prof. D. P. Mishra Department of Aerospace Engineering**

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Let us start this lecture with a thought process basically about entropy, entropy is a nonconserved property, based on clausius inequality, unlike the widely used term, energy, entropy provides a measure of disorderness, of matter, that with time increases to lead a descent and effective life, by organizing our work in proper line, one can follow the path of least entropy, by consuming in our life list energy.

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By using CI, we have shown that 2nd law of TD
leads to a property of system known as "Entropy".
Applying CI to two cycles 1A2B1 & 1A2C1

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\int_{1}^{2} \frac{dQ}{T} = 0 \Rightarrow \int_{142}^{2} \frac{dQ}{T} + \int_{2m}^{2} \frac{dQ}{T} = 0 \quad \text{(1)}
$$

$$
\int_{142m}^{2} \frac{dQ}{T} = 0 \Rightarrow \int_{142}^{2} \frac{dQ}{T} + \int_{2c1}^{2} \frac{dQ}{T} = 0 \quad \text{(2)}
$$

Eq.(1) - Eq.(2) gives $\int_{2B1}^{2} \frac{dQ}{T} = \int_{2C1}^{2} \frac{dQ}{T}$
Exact differ, dQ/T is a point function. \Rightarrow It must be a property.
dS = Entropy Change = dQ/T

So if you look at the last lecture we basically discuss about the clausius inequality which will be useful for a cyclic operating device right, but in the real situation we need to what we call use for the non cyclic processes, we will have to do the similar have done for the first law of thermodynamics we will take a cyclic process and let us say the cyclic process, you know process moves from state 1 to the state 2 through the path A and it comes back from state 2 the state 1 through the path B and this is let us say reversible right. And similarly we can say that this is also there is another cyclic I mean between the state to one can think of the 1A2C1 there is another cycle.

So now we can basically apply the clausius inequality for the two cycle that is 1A2B1 and 1A2C1 right if you do that what you get we will guess basically we know the cyclic by the clausius inequality the cycle integral of the $dQ/T=0$ because it is a reversible process right and that is what, that is basically dQ/T for the path A $1A2+$ the dQ/T for the path to be 1 is equal to 0 and if we take for the other cycle that is 1A2C1, I mean if we decompose this path that is basically dQ/T for the path $1A2+$ the dQ/T for path $2C1=0$.

Now if we just, if we subtract this one right what you will get, we will get even if you just subtract this one so this will be cancelled it out and this is minus right. So what will say, we will say that basically that is dQ/T for path 2B1=dQ/T for the path 2C1, what it indicates that that the dQ/T is basically independent of the path, because as we have just now seen that for the two different paths that is 2B1 and 2C1 dQ/T is same right.

So this is, we can call is basically a property and that we will be considering as a property because it is a point function it does not depend on the path. And that is nothing, but what we call entropy change or the like that is nothing but $dS=dQ/T$. If you recall we did in the similar way we have defined the internal energy for the first law of thermodynamics and we are defining the entropy by using the second law of thermodynamics right.

So here what we have done we have used the clausius inequality and also shown that the second law of thermodynamic leads to the property of a system known as entropy right. So by that way and we can really define what you call the entropy change.

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And then we can say that you know B $S_2/DS_1 = dQ/2$ for the reversible right path. So this is your basically reversible path from state 1 to the state 2 and this also can move like from 1 to 2 in a reversible path like I have shown it as a dashed line. And dQ/T can be integrated along the internal irreversible path to give the value of entropy change we have already seen that, that is basically $S_2-S_1=dQ/T$ and for the reversible process is equal to the change in internal, and change in entropy for the irreversible process keep in mind this is basically irreversible process right.

That means we can find out the entropy change for an irreversible process between two state by considering at a reversible process in other words you can substitute an irreversible process right with an internal irreversible process right, and so far the state is same so therefore entropy change will be same. So in other words change in entropy for an irreversible process term very easily by dividing suitable imaginary reversible process between two states.

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And let us look at the entropy change of certain process like we know that change in entropy is equal to dQ/T for reversible process only and as I state earlier that entropy is a state function. So the entropy change is dependent only on its initial and final state it does not depend on the path taken by the system whenever it is interacting with surrounding, basically it is a independent of the path, but it is dependent on the, what you call state or the point between who is the system undergoes a changes.

So by analyzing the irreversible process right, in other words what we call like for analyzing irreversible process right we need to substitute this irreversible process by imaginary equivalent reversible process, and so that we can calculate the entropy change, you know between two states whenever system is interacting with its surrounding.

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So for that will have to do I am just restating the same thing let us look at the entropy change for heat interaction. So let us take an example that is temperature of a large reservoir remains almost constant and 350 Kelvin when a paddle wheel is rotated for one hour by using a 125 watt motor, and we need to estimate the change in entropy of the reservoir if the paddle wheel is operated in a very slow manner, you know so that it will be one can think of you know reversible kind of things.

So if you look at this is our system I mean the thermal reservoir and which is at 350 and you are giving some 125 watt it is a very big reservoir so that there is no change, much change in the temperature and you are using a motor for that. And of course you can consider that you know it is an irreversible process why because you cannot take it whatever the work, you know being done on this you cannot really produce again to the come that to, you know like if this work is being done on the this thermal reservoir and that same amount of work cannot be make the motor to run if you consider you know like other way around.

So therefore it is an irreversible process, but we can consider that imaginary reversible process and that is this whatever the work you are giving is equivalent to the some heat energy during the reversible process dQ and therefore the change in entropy will be dQ/T for the reversible process in this case th what is the dQ is nothing but the work done, work done is 125 what you call watt and that is run for the one hour right.

And if you look at this is of course 125 watt, but here I have taken the kilowatt so therefore it will be 3600 right one hour kind of seconds, so they divide by 350 will be giving to 1.29 kilo joule per Kelvin right, so that will give the entropy change for this thermal reservoir although it is an irreversible process we have considered that as a reversible process considering that work is converted into heat and then you can done in such a way that there is no change in temperature of the thermal reservoir then we can estimate.

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So if you look at the heating or cooling of the matter is basically is an irreversible process and the irreversible process can be considered as basically imaginary reversal process between state 1 and 2 like you consider let us say between a process you know let us say this is PV and this is one process like which is state going to one to two, but I can consider is as a you know some imaginary process like I can say this is constant pressure and then it can be what you call a constant volume process and it can go to the constant pressure process you know like equate you know and we can say this is a this is your isobaric process which is reversible and this is isochoric process reversible right reversible isochoric process so heating and cooling is a can be consider as a basically isobaric and isochoric process.

And as to the first law of thermodynamic we know that dQ is equal to dU for the isochoric process right and for isobaric process dQ is equal to dH we have already learnt so for isobaric process we can find out the entropy change is nothing but your dQ by T and which is nothing but your change in this dQ is equal to because dQ is we know that dQ is equal to dH so therefore that will be mCP dT and we will take C_P is not really function of temperature for the further this thing so or you can assume is evidence EP so that if we integrate this thing will get mCPl and T_2 by T_1 .

If that is you are considering that as a reversible process and you are finding out the entropy change similarly for the isochoric process you can have dQ by T and then we know that dQ for isochoric process is nothing but you are what we call equal to dQ and that is mCVdT and then /T you will give when you integrate it will be $mC\ln T_2/T_1$ keep in mind that this we are saying that C_V is constant it is not a function of temperature so by this process you can find out the entropy change for what you call for the isochoric process and isobaric process.

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Example: Estimate the
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\triangle S
$$
 if 1 kg of H₂O at 30°C is
heated to 80°C at 10⁵ Pa. $C_{B,H2O} = 4.2$ kJ/kg K.

$$
\frac{dS}{dS} = \int_{1}^{2} \frac{dQ}{T} = \int_{1}^{2} \frac{dH}{T} = \int_{1}^{2} C_{p} \frac{dT}{T} = C_{p} \ln \frac{T_{2}}{T_{1}}
$$

$$
= 4.2 \times 10^{3} \ln \frac{(273 + 80)}{(273 + 30)}
$$

$$
d\hat{S} = 0.6415 kJ/kgK
$$

And let us take an example that we need to find out the entropy change if 1 kg of water at 30 $^{\rm o}$ C is heated to 80 $^{\circ}$ C at 10 power 5 Pascal and the C_{P} of water is given so what we will do we will basically you know find out that dS s is equal to dQ / T and that we have seen this is a what you call we can consider that this process is isobaric process because there is no change in pressure right and then that is dQ is equal to dH and that is nothing for $C_P dT$ because we can consider this is 1 kg so mass is basically 1 kg in this case mass is 1 kg.

So mass is 0 will not consider so that is CPln T_2/T_2 and CP is given to you so therefore that will be what you call 4.2 x 10 / 23 this is kilo Joule therefore I have taken this ln 273 / T and 80° because allure to use the Kelvin and 30 $^{\circ}$ so you will get this is basically change in entropy 0.64 15 kilo joule per kg Kelvin and you can consider this as a basically per unit mass kind of thing so I could have used this as a small s you know small s this is nothing but a small less we use per unit mass right and if you want to find out basically this thing that change in entropy that is nothing but your ΔS will be 0.6 for 15 kilo Joule per Kelvin that easier because mass is given 1 kg so you just multiply.

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So let us say that you know we need to find out entropy change for an ideal gas and which is going from state 1 which is at P_1 V₁ T₁ to P_2 V₂ T₂ let us say that we are having this point what you call state 1 here and stay to hear like this is we can say that it is an irreversible process right and we need to find out entropy between this state 21 and state 2 so how to go about it and this

state a of course I volatile told you that is $P_1 V_1$ and T_1 and state to is your $P_2 V_2 T_2$ right so how will go about it basically.

What we will do we will have to substitute this imaginary as a substitute this is reversible path by certain reversible path right for example I can say that these are the two isotherms right one is temperature T_2 other is T_1 and I can say that this is basically you know path is one is we are saying this imaginary path the irreversible path there is between state 1 and state 2 can be consider like you know substituted by two reversible path one is I so very that is 12 and then it will go with the again reversible isothermal to the state 2 right.

I can do that I am like because so far interpret calculation is concerned I can substitute these two things so and similar way I can say there is another one you know which is between state 18 can be I mean also the same thing because the entropy change between state1 state 2 will be not dependent on the path whether these paths say if I say this is you know this path or this path and again this you know between that I can say that it will be having to what you call path we are saying it can take place one is isochoric path that is Oracle here and then it will return back to the state to with the isothermal reversible isothermal process and this also reversible ice occurring right.

So we can estimate by this way that entropy change between state one and state to at this point we are calling it as a be right.

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So what we will do the for the path 1a right that is your 1_a 2 write this path which is nothing but your between entropy change between the state 1 to 2 consists of isobaric 1a and isothermal a2 both are reversible okay so for the change in entropy for the path 1a is equal to dQ by T and this is the isochoric process therefore dQ is equal to dH and dH dQ is equal to d H for because this isobaric process so dQ is equal to dH and dH is nothing but your C_P dT is equal to C_P and dT right so I will put it here and when you say that C_P you know is constant so therefore when you integrate it between 1to 2.

I will get Cpln T_2 / T_1 is it fine so similar way we can find out the entropy change between the path a22 right that is nothing where dQ / T and we know other for the isothermal process that is du + Pdv and for isothermal temperature is not changing so therefore this will be 0 right and that is nothing but Pdv / T and we can integrate between the state 1 to 2 and this is an ideal gas you know so therefore I can write down Rln V_2 / V_a cannot write down because in this case I can use ideal gas law that is what you call R / dV write this is equal to R / V and then you integrate it here and then you will get Rln V_2 / V_a .

Now we need to connect this volume at a station a two-volume at station 2 right how will do that we will have to use the ideal gas law that is $P_2 V_2$ is equal to Pa V_a and Pa is nothing but you P_1 the pressure at a because this isobaric process so is equal to P_A is equal to P_1 and therefore we can write down V_2 / Va is equal to P_1 by P_2 so if you know add this thing then we can get the change in entropy for the a22 for the path a_2 a₂ is equal to - Rln P_2 / P_1 keep in mind that we are just changing the ratio therefore minus sign comes over.

So when you add this thing put these values here like change in entropy between state 1 to 2 is equal to entropy change for the path 1_a + entropy change / path a to write when you substitute these values you will get an expression here that is change in entropy between state 1 to 2 is equal to C_{P} ln T₂ by T₁ – Rln P₂ by P₁ right so you can now evaluate you know for the what you call the entropy change for an of course an ideal gas that we have considered hereby substituting the irreversible process between state 1 to 2 with reversible isobaric followed by the isothermal process in this case we have seen.

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And let us consider the other way around that is for the path you know 1b2 the change in entropy is equal to isobaric process for path 1 sorry the isochoric process for the path 1b plus the isothermal process b2 right, so what we will do, we will do evaluate then similar way the change in entropy per 1b is nothing but dq/dT and this for isochoric process what it would be, it will be change in internal range and that is nothing but your C_v dT/T and when we integrate it between station 1 to b is it not it that is $C_v \ln T_1$, $C_v \ln T_2/T_1$ because why it is $C_v = T_2$ right.

So for the path b2 the change in entropy will be equal to basically du+Pdv that is nothing but dq/T and in this case that is what is the isothermal process therefore that will be 0 and using ideal gas law we can find out that is nothing but your Pdv/T when you integrate I mean you can substitute this by the vertical PT=R/V and then integrate that thing is R ln v_2/v_1 so you can add all this thing together you will find out that that is basically change in entropy is equal to C_v ln T_2/T_1+R ln v_2/v_1 keep in mind that this is basically integrated this b_2 is integrated between b_2 to b_2 and $v_b=v_1$ right, vv this is $v_b=v_1$ right.

So we will get an expression you know we have already seen that this is for the expression for which is in terms of C_v and of course the ln T_2/T_1 and R ln v_2/v_1 and equation 1 which we had derived earlier for the isobaric process followed by the reversible isothermal process are you know are in terms of C_p and $\ln T_2/T_1$ -R $\ln P_2/P_1$. So these are equation two are different is it different can it be or it will be same right, I think I will leave that an exercise for you to prove

that equation1=equation 2 in principle it should be now I will leave that an assignment for you people to do that. (Refer Slide Time: 27:28)

So entropy change for a pure substance we need to evaluate for our problem because you know like entropy is a property we know thus the value of entropy is basically dependent on the state of the system and once it is state of the system is fixed so there it can be fixed. For example, like you know if you look at like this is the T_s diagram if you look at this is your compressed liquid right.

And for the compressed liquid what we will do if you know the P_1 and T_1 from the saturated steam table corresponding to the saturated liquid point you can find out s_1 you know that is the liquid is equal to s_1 you can find out very easily and similarly for the superheated steam or the superheated vapor it can be steam it can be refrigerant also right, so you can find out basically at a particular pressure that is let us say P_3 and T_3 you can evaluate s3 from the superheated steam table or the very end table right.

But if the mixture is in between like it will be some different quality right, so you need to know this quality and then if you know the entropy at the saturated liquid point and there you know the change in entropy between the saturated vapor point and the liquid point then you can evaluate what will be in trouble provided you know the what you call either temperature or the pressure any one of them saturated condition and also the quality.

So if you look at like let us say there is a what you call sublimation that means the let us say there is a ices which is converted into liquid then change in entropy will be heat of sublimation divided by the temperature which the sublimation occurs right. Similarly for the vaporization you can find out change in entropy is basically heat of vaporization divided by the temperature at which vaporization occurs.

So we will take a very simple example like 500 grams of ice is melted to water at 0˚Cby heating it slowly right by heating it slowly and we need to determine the entropy change. So what we will do we will have to change in this entropy you know during this melting process is equal to h_{sf}/T_{sf} , h_{sf} will be given interval and which happens to be 333.4 kJ/kg right and then you will use the temperature it is occurring at 0˚C so in Kelvin that will be 273.15 and you know these grams and then you will get the you know if you substitute these values you will get 0.6kJ/K that is the entropy change during this melting of ice.

So we love to now look at basically interpret change for an irreversible process right and we will have to see how we can handle we can take a control mass system which undergoes a reversible cycle 1A what you call 1A 2B1 this is a reversible cycle right, and we will consider a for that we will apply this what you call classes in equality which is equal to that one equal to dQ/T for the path $1A 2+dQ/T$ for the path $2B 1=0$ right, for this path.

And we will take an irreversible cycle that is basically I can represent this as a dot dash line you know this is basically a dashed line and then that will be the path is what we call the cycle is 1A2C1 right and we can apply the classiest inequality and that is dQ/T for the path 1A2+dQ/T for the path to see one which is irreversible path of course this is the same you know reversible path so that cycle become irreversible any one of the path is a reversal mean cycle will be reversible.

So what we will do we will just subtract this one right and if we subtract this one that what will happen like if I subtract this one this is minus and this will be can cancelled it out so you will get dQ/T for the path to be 1-dQ/T for the path 2C1 is greater than 0 right, and what he says that dQ/T for the path 2B1 is basically greater than the dQ/T for path 2C1 right, that is the change in entropy.

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So as the process 2B1 is reversible right, so therefore the change in entropy for the path what you call 1 to 2 is greater than the dQ/T for the path to see one right we are just restating because they

say reversible therefore I can say dQ/T is nothing but your entropy change. In general we can write down the change in entropy is basically greater than dQ/T for an irreversible cycle or reversal process right and the equal to dQ/T for the reversible process.

So we can basically say that this is a generalized equation that $dS=dQ/T$ for the reversible process and change in entropy is greater than the dQ/T for an irreversible process. For an isolated system right we can say that $dQ=0$ from this relationship we can say that dS change in entropy will be greater than equal to 0 right for an isolated person that means there would not be any what you call energy interaction and also there would not be any what you call heat interactions right so that is an isolated system.

So therefore entropy of an isolated system increases or remains constant right, but in if you look at first law of thermodynamics we have seen the energy of an isolate system can what will happen in case of an isolated system energy is conserved. In this case need not to be right entropy is not a conserved property so the process can never occur in the direction of decreasing entropy so then we can say that whenever there is a entropy change is equal to zero the process is reversible and if the entropy change is greater than zero it is an irreversible process right. So this is basically known as the principle of entropy increase that means entropy of the if you look at the an isolated system always maybe increase or it may remain constant but it cannot really decrease if it is not debated if you know it cannot never be will be less than that.

So this principles is a very important one like which will be says and people says also the entropy of the what you call whole universe is increasing all the time, so when the change in entropy is less than zero that means the process is impossible it is not possible to have a process where the entropy will be less than because it is violating the principle of entropy increase.

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Entropy Generation

For an irreversible process for the same dO and T $dS > \frac{dQ}{T}$; $dS = \frac{dQ}{T} + S_G$ S_G = Entropy generation due to irreversibilities (Friction, mixing, unstrained expansion, dQ with finite $S_G \ge 0$ $S_G = 0$ for reversible process dT, etc) $S_G > 0$ for Irreversible process The value of S_G is always a positive quantity or zero. Is S_G a property of system? Certainly no as its value depends on the process.

So for an irreversible process which is operated you know for the same DQ 1 T then we know that $D > DQ / T$ right. So what we can say we can write down ds = $DQ / T + SG$ and this AG is nothing but entropy generation that is for an irreversible process and for reversible process what will be this SG what will be this as S_G will be 0 for a reversible process and this irreversibility's is basically being caused either due to friction or mixing or understand expansion or heat addition you know with a finite temperature difference you know temperature gradient is more the irreversibility will be more but we have seen that quasi steady state where you know the gradient is very, very small you can call it as a an irreversible process right.

Which you can call it as a reversible process if the gradient is infinitesimally small, so as I told that $S_G \ge 0$ and $S_G = 0$ for a reversible process and $S_G > 0$ for an irreversible process and the value of S_G is always positive quantity or it will be 0, so question then arises we have learned that entropy is a basically property of the system right yes or no. Now is this is e a property of a system can it be actually it cannot be okay because it is dependent on the path what if we will be taking so therefore it cannot be a property of the system that is the entropy generation.

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So how do we use the principle of entropy increase for a non adiabatic system because what we have seen is basically we are saying okay $DQ = 0$ then we talk about it but how we will do that so what we will do as I told that entropy is an extensive property hence it is additive in nature right, so therefore if I say that isolated system right if I take an isolated system that means there is no energy or the in interaction and it may have subsystems like let us say sub system one two or three it may be n number of substrate systems then total entropy change is basically summation of entropy change for the e sub system will be greater than equal to 0 right.

Then if you know that I mean one can really find out let us consider another example there is a system right if I consider this contains some let us say gasps and then it is interacting with the surrounding both the work or the heat interaction will be taking place right and I want to find out what will be the entropy change between the system and the surrounding right I do not know like what is happening what we will do we will take this as a surrounding hear what I have shown here this is basically surrounding and then put together this is an isolated system it means if I consider this as my system boundary right.

In this case Q and W in this case right the $Q = 0$ W = 0 but the system is embedded inside this I am taking both the system and surrounding as a isolated system and if you do that then you can easily calculate what will be the entropy change and then one can do that. So we can say the total entropy for an isolated system you know will be change in entropy of the system plus surrounding will be greater than equal to 0 right, and if I know this what is happening system and if I know that what will be the then we can find out what will be the surrounding right kind of things and then we can evaluate.

And this concept is being used you know if you look at isolated system is being used very often to calculate the entropy change where you know you can sub certain things are not known.

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Hence, 2nd law of TD indicates direction/feasibility of process. $_{b}$

So the entropy change if we look at as I told basically for a isolated system will be considering both system and surrounding greater than 0 and this is the general expression for the increase of entropy fins entropy principle and if I consider that same you know I am saying that there is entropy change is in the system right and that is minus kilo joule per Kelvin and this is your surrounding right, this is your surrounding basically all this thing and there is entropy change for the surrounding in five kilo Joule per Kelvin.

So in this case what is that system entropy is less than zero right in this example and change in entropy is greater than zero, so total entropy what it would be total entropy will be basically will be greater than zero because if you add together what will be it will be change total entropy in this case when you add in this example the total will be equal to 1kilo Joule Kelvin which is greater than zero right.

So therefore that indicates that the increase of entropy principle, so if you just say that you know if the total entropy is equal to 0 then we call it as a reversible process and if you say total entropy is equal to greater than zero it is easy reversible process if it is total entropy is less than zero is impossible process. Hence the second law of thermodynamics indicates what you call direction is the feasibility of process that means whether the process is possible or not it stipulates right.

So I think this is the way what we can think of applying the vertical entropy increase principle for calculating the various entropy and then find out whether the process is possible or not, and I will just tell you basically quality of energy by that can you say that from this you know.

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Whether the what is the quality of energy for example if I take the certain amount of heat is being taken from what you call the source a temperature T_H and then it rejects this heat engine reject the Q_L amount of it to the temperature 300 Kelvin of course producing w amount of it and keep in mind this is basically a reversible heat engine. Now and if I so now question arises how do we can increase the thermal efficiency of this Carnot engines consider reversible heat engine basically Carnot engine and however the actual heat engine what is the way of means of doing that right if I look at I will take some example.

For example we know that efficiency is equal to 1- T_L / T_H right and if I take this what you call T_H as 1200 Kelvin and of course the low temperature is 300 Kelvin that is a sink what will be efficient efficiency is basically 75% further for a Carnot engine if I take the 900 instead of 1200 if I take 900 in 66.6 if I take 600 Kelvin right it will be 50% right, what is we can infer from this that means if I am taking this higher source temperature I am getting higher efficiency for the same sink temperature right that is from the Carnot cycle and that will be true for the other irreversible engine as well because this Henry reversible ending.

And suppose I will say that now there is a heat engine where you have to change the sink temperature by delta T let us say and you will also experiment and change the temperature a source temperature as by δT if you look at efficiency wise in which case it will be higher what I will suggest that you please look at this problem and I am giving this as an assignment, so that you can check which one will be higher which one will be lower and why it is so.

But from this example if you look at what we are learning from here that means if the heat energy available at a higher temperature then its quality will be higher as compared to the energy which is available at the lower temperature that means if you look at quality of the things will be both on increasing with the increasing of the temperature at which thermal energy is a little right, so will be a you know coming back to this quality of energy little later on whenever we will be talking about the availability and other things.

So we will stop over here we have learned basically that how we have used the entropy increase principle to evaluate the entropy for the not only for the reversible process but also called an irreversible process right and we now in a equipped with a tool for what we call estimating the entropy change and also the predicting whether this process is possible or not so if you look at the first law of thermodynamics is basically talk about the quantity it will give a quantitative evaluation and the quality of the energy being stipulated by the second law of thermodynamics that we have also done thank you very much I will stop over here.

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> **NPTEL Team Sanjay Pal**

Ashish Singh Badal Pradhan Tapobrata Das Ram Chandra Dilip Tripathi Manoj Shrivastava Padam Shukla Sanjay Mishra Shubham Rawat Shikha Gupta K. K. Mishra Aradhana Singh Sweta Ashutosh Gairola Dilip Katiyar Sharwan Hari Ram Bhadra Rao Puneet Kumar Bajpai Lalty Dutta Ajay Kanaujia Shivendra Kumar Tiwari

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