Chemical Engineering Thermodynamics
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Lecture 15
The Concept of Entropy

Welcome back. Today's class we are going to extend the concept which you have learned in the last class that is the heat engine and Carnot cycle and then we will extend this to the concept of entropy as a property.

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So, we will start with a basic relation between the heat flow and the temperature as we have learned from the analysis in the last class and this will yield or this will lead to the Theorem of Clausius. So, as we learned from the previous analysis that we can write the ratio of the heat flow to and from the reversible heat engine of the absolute temperature of the reservoir, the heat is flowing to and fro.

$$\frac{Q_B}{Q_A} = -\frac{T_B}{T_A} \ or, \qquad \frac{Q_A}{T_A} + \frac{Q_B}{T_B} = 0$$

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

In differential form, $\frac{\delta Q_A}{T_A} + \frac{\delta Q_B}{T_B} = 0$

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Now, let us try to extend a bit to understand that how we can connect basically these ideas to something related to the paths. So, let me just try to describe this a bit more. So, let us consider generic reversible path on a P V diagram. So, this is state i and f. So basically, this is a reversible path from state i to f. Now we can draw path resulting from the adiabatic compression or expansion which originates from state i and f.

So, this is the one which originates from f and this is the one which originates from i and these are adiabatic paths as we have discussed in the Carnot cycle as well. So, this is the one original path which is a reversible one. These are the two adiabatic paths. Now what we can do is we can connect these two paths through a isothermal path g h that is the one which is this and one can show that the slope is going to be lower than the adiabatic path for the isothermal path.

That is something which one can show easily for the ideal gas as the working fluid for the reversible case. So, now the g is chosen in such a way that the W, the work which is done in this reversible original path is same as that for i g h f, so the area under the curve is the same as that for the case of the original one. Now as we know this that the energy is the state point, so essentially whatever the change in the energy here from i to f would be same as that for i to g, g to h and h to f.

So, that is the statement we have here. Now also since this is adiabatic then your heat i f in the original path must also be i g h f, as far as the, as far as the First Law is concerned. The reason
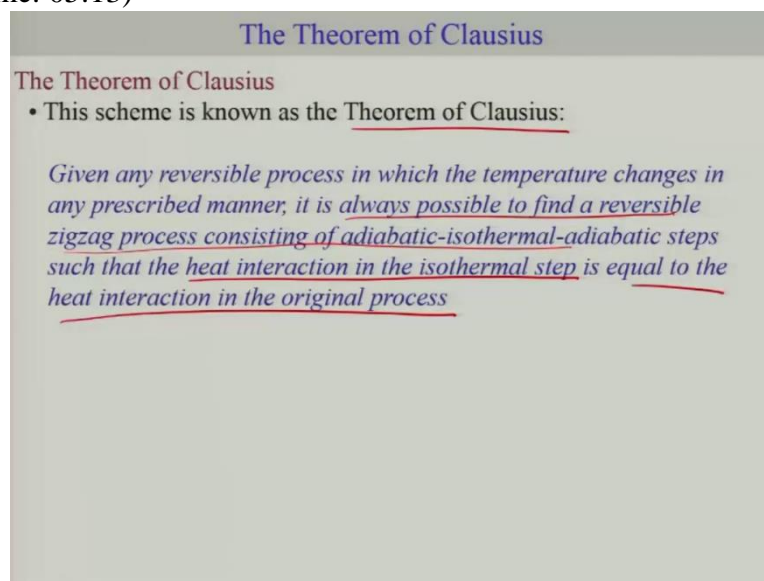
is, of course that since the work is same and total energy has to be same that means the heat has to be same, in this process.

Now since these are adiabatic, these two paths, that means the Q g h, the heat along this direction for this particular process from this to this should be same as that of the original, should be same as that of the original path, remember that.

So, what we did is very simple. We have delta E and that essentially we are saying Q plus W, since the work is same, so essentially and this is also same for the path because it depends on the state so that means Q i f should be same as, the original Q i f should be same as that of the new path, which consists of two adiabatic and one isothermal path. So, this is what we have got.

That finally that Q of g h that is the heat along the isothermal path must be same as that of the original path. So, this comes from simple analysis of reversible path and making use of adiabatic and isothermal paths, to represent that total process change from i to f.

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Now this scheme we often use known as Theorem of Clausius. It tells you that given any reversible process in which the temperature changes in any prescribed manner it is always possible to find a reversible zig-zag process consisting of adiabatic isothermal adiabatic steps as we have shown such that the heat interaction in the isothermal step is equal to the heat interaction in the original step. That is what we have proven, okay. So, this is the statement and this is what is called Theorem of Clausius. So, this is something which we can do for any

reversible process. So, let us now make use of the understanding of theorem of Clausius in order to define a property call entropy.

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So, consider the diagram to the right here this is a reversible cycle which we are considering from j, i, f, k, d ,c, f. Now consider this process from i to f and based on the theorem of Clausius, we can represent this as a combination of adiabatic and isothermal paths and that is what we are trying to do here, so this green line is basically 2 adiabatic processes and we draw from j to h in a way which basically is your isothermal process.

$$\frac{Q_{if}}{T_{if}} + \frac{Q_{CD}}{T_{CD}} = 0$$

$$\frac{\delta Q_{if}}{T_{if}} + \frac{\delta Q_{CD}}{T_{CD}} = 0$$

The Theorem of Clausius

The Theorem of Clausius
- This scheme is known as the Theorem of Clausius:

Given any reversible process in which the temperature changes in any prescribed manner, it is always possible to find a reversible zigzag process consisting of adiabatic-isothermal-adiabatic steps such that the heat interaction in the isothermal step is equal to the heat interaction in the original process

Entropy

Definition of Entropy
- Consider the diagram to the right
- Paths *i-f* and *c-d* represent processes, connected through adiabatic paths, within the reversible cycle *jifkdc*
- The inner path *ighfdbac* is a *Carnot* cycle, and therefore

$$\frac{Q_{if}}{T_{if}} + \frac{Q_{cd}}{T_{cd}} = 0$$

- We now make paths *i-f* and *c-d* infinitesimal …

$$\frac{\delta Q_{if}}{T_{if}} + \frac{\delta Q_{cd}}{T_{cd}} = 0$$

Now of course they certain we have to find out in such a way that it satisfies this [previous conditions on the as well as the theorem of Clausius is concerned. Now if you look at it essentially what you have now is a cycle here which is i, j, h and f. So this represents basically i to f and now if you look at this carefully this one, so what we have is the nothing but the Carnot cycle and therefore the heat here if is consider the heat here, the corresponding heat interactions with the surrounding during this process i, f let us assume this is Q i f and the temperature at this point is Tif.

Then essentially based on the Carnot cycle principle we know the ratio of the heat here and here is nothing but the ratio of the temperature and thus we can find out that this is indeed true for this Carnot cycle. Now for the infinitesimally small path so consider this i f is very small okay then we can write it in the way.

Now you can draw many such curves and many such isothermal adiabatic combination can be designed to represent this small paths here and essentially if you do that all the cycle then suddenly you will get it and if you integrate it over the cycle then this is going to be differential form small here and you can cover this across this cycle then this from j to k there could be one in particular integral which is sum of all this differential paths and that plus this should be the overall cycle but that has to be 0 because of the fact that this is entirely a reversible cycle

$$\int_j^k \left(\frac{\delta Q}{T}\right)_{rev} + \int_k^j \left(\frac{\delta Q}{T}\right)_{rev} = \oint \left(\frac{\delta Q}{T}\right)_{rev} = 0$$

And so, this is something which we can clearly see from this basic analysis. Now this result can be generated for any cyclic path proceed through j and k therefore what we can conclude that this term which we have obtained is conserved for any reversible cyclic process and that is nothing but a property because any property is conserved for any reversible process that means for example delta U for reversible process here from i to j here should be also zero and similarly for other property.

So that is a basic definition of the property and has this must be a property and that is what we defined as delta s and this is any property we define and this is we call it entropy and a differential form we define as d S is nothing but delta Q or del Q by T and that is at reversible but in general this is true by definition this is also true also for reversible as well.

$$\Delta S = \int \left(\frac{\delta Q}{T}\right)_{rev} \text{ and } dS = \left(\frac{\delta Q}{T}\right)_{rev}$$

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So, it is a first order in mass or it is not conserved quantity so entropy can be considered for the universe can be considered as delta S system plus delta Surrounding. So, it is an extensive property and hence it is simply a sum of difference sub system for universe sub systems are systems and surrounding and hence it is a simple addition of that for any natural or real process delta S must be greater than 0. In case it is completely reversible process that makes the sound and these are not being affected and, in that case, you will have delta S universe should be equal to 0

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

$$\Delta S_{universe} > 0 \text{ } for \text{ } any \text{ } real \text{ } or \text{ } natural \text{ } process$$

$$\Delta S_{universe} = 0 \text{ } for \text{ } a \text{ } completely \text{ } reversible \text{ } process$$

So, now let us look at again the same inequality which we know that from the same concept of the heat engine, so we have seen this part from the Carnot heat engine that del Q by T should be Q H by T H minus Q L by T L if you consider basically the heat, and this heat engine Q L, this is T H, this is T L, and this is work. So, if you consider this as a cycle, completely if we take a cycle here, it is nothing but we have shown that Q H by Q L is nothing but T L by T H.

So, this can be rearranged and if you write it down then this is nothing but the cycle. So if you look at it from this point of view this is also the same expression we are getting for reversible heat engine, because this is true for reversible heat engine but integral of this, cyclic integral of del Q is nothing but Q H minus Q, and that must be greater than 0.

Now, thus, for reversible heat engine of course this is also true. For irreversible or in general one can write that this must be less than equal to 0. Why? Because del Q by T here, this you can show that this part, this part has to be equal to, less than 0 for a generic expression. So, this particular inequality was first actually introduced, this you can prove it actually, so it was first introduced by Clausius and it is valid for all reversible or irreversible expressions.

$$Clausius\ inequality, \oint \frac{\delta Q}{T} \leq 0$$
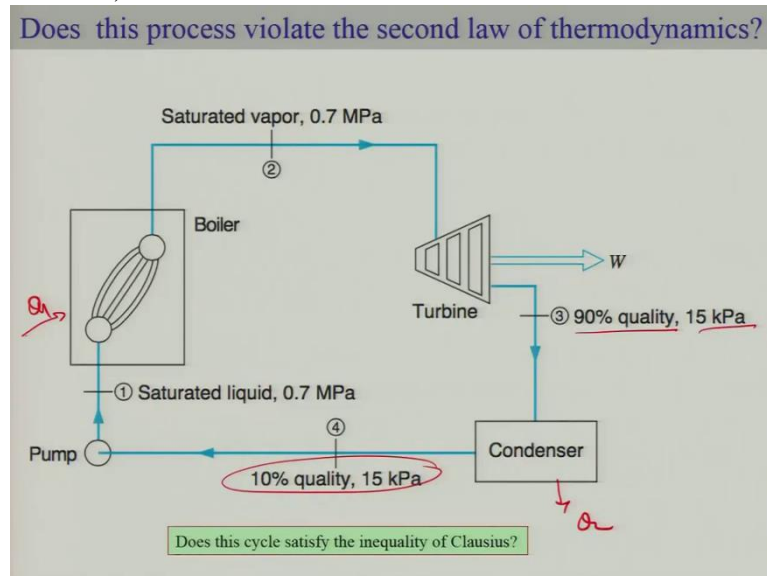
So, in fact it becomes a valuable tool to check whether The Second Law of Thermodynamics is being checked or is violated or is valid for a given process. So, if you look at this example, this example will illustrate that. So, for example you have this, kind of simple but basically where you have a boiler, which is heating of a saturated liquid and that saturated vapor comes at here and expansion occurs in turbine leading to the work and then you have this outlet of that.

It discharges the water at 90 percent quality, saturated system at a pressure 15 kilo Pascal goes to the condenser. It condenses and the outlet now is 10 percent quality, 15 kilo Pascal. Of course, it means some heat is being rejected here, and this is the boiler which means you have got Q H here. And there is a pump which basically pumps back the liquid and increases the pressure to the boiler pressure which is 0.7 mega Pascal.

So, the question is that, is this particular design good or feasible? So how do you check that? So that means one can check that this, or another question would be that this design violates the Second Law of Thermodynamics. That means does it satisfy the Inequality of Clausius?

Does this process violate the second law of thermodynamics?

$$\oint \frac{\delta Q}{T} = \int \left(\frac{\delta Q}{T}\right)_{boiler} + \int \left(\frac{\delta Q}{T}\right)_{condenser}$$

$$\oint \frac{\delta Q}{T} = \frac{1}{T_1}\int_1^2 \delta Q + \frac{1}{T_3}\int_3^4 \delta Q = \frac{{}_1 Q_2}{T_1} + \frac{{}_3 Q_4}{T_3}$$

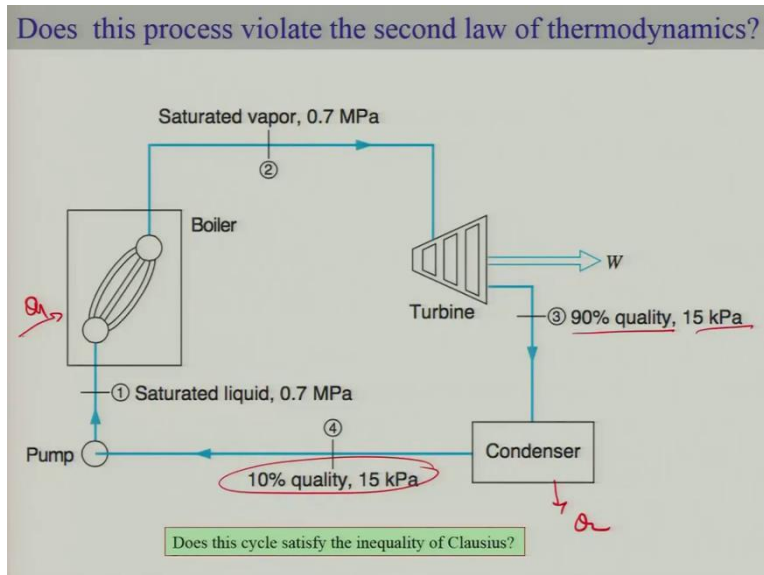Let us consider a 1 kg mass as the working fluid. We have then

$${}_1 q_2 = h_2 - h_1 = 2066.3 \text{ kJ/kg}, \qquad T_1 = 164.97°C$$
$${}_3 q_4 = h_4 - h_3 = 463.4 - 2361.8 = -1898.4 \text{ kJ/kg}, \qquad T_3 = 53.97°C$$

Therefore,

$$\oint \frac{\delta Q}{T} = \frac{2066.3}{164.97 + 273.15} - \frac{1898.4}{53.97 + 273.15} = -1.087 \text{ kJ/kg K}$$

Thus, this cycle satisfies the inequality of Clausius, which is equivalent to saying that it does not violate the second law of thermodynamics.

Does this process violate the second law of thermodynamics?

Saturated vapor, 0.7 MPa
② Boiler
Turbine W
③ 90% quality, 15 kPa
① Saturated liquid, 0.7 MPa
④ Pump Condenser
10% quality, 15 kPa

Does this cycle satisfy the inequality of Clausius?

So that is the question. So one can look at this basic cyclic interval of del Q by T and since they are two devices which interacts, which has a heat interaction so there is a boiler and a condenser, that is basically the assumption, this point here, we are ignoring other irreversibility associated with the other devices.

So, if you look at this part you can simply take out the temperature because it is a constant temperature, heating and similarly for the condenser so it is going to be 1 by T 1 integral of del Q and plus 1 by T 3. Now T 1 and T 3 are corresponding to the temperature here and here. So that will lead to this. So 1 Q 2 that means basically nothing but Q 1 to 2, the one which is from here to here, so that is associated with the boiler. This is the heat associated with the condenser or in the sense you can say this is Q L, this is Q H.

$$\oint \frac{\delta Q}{T} = \int \left(\frac{\delta Q}{T}\right)_{boiler} + \int \left(\frac{\delta Q}{T}\right)_{condenser}$$

$$\oint \frac{\delta Q}{T} = \frac{1}{T_1}\int_1^2 \delta Q + \frac{1}{T_3}\int_3^4 \delta Q = \frac{{}_1Q_2}{T_1} + \frac{{}_3Q_4}{T_3}$$

Now if you are considering 1 kilogram mass as a working fluid then we can consider, that means we can just simply look at specific properties and here the Q is nothing but the entire change in enthalpy because this is converting the saturated liquid to the saturated vapor. So essentially the latent heat is nothing but your change in enthalpy.

So, from the table you get this value 2066.3 kilo Joule per Kelvin and of course you know the T 1 because at this 0.7 mega Pascal from the saturated pressure table you will obtain the saturated temperature. So, this is nothing but T Sat at 0.7 mega Pascal. Similarly, you can look at again the steam table and now this is the condition where you are condensing, again condensation occurs at 15 kilo Pascal. You have to look at again the saturated pressure table and this is something we can obtain the phase transition from there.

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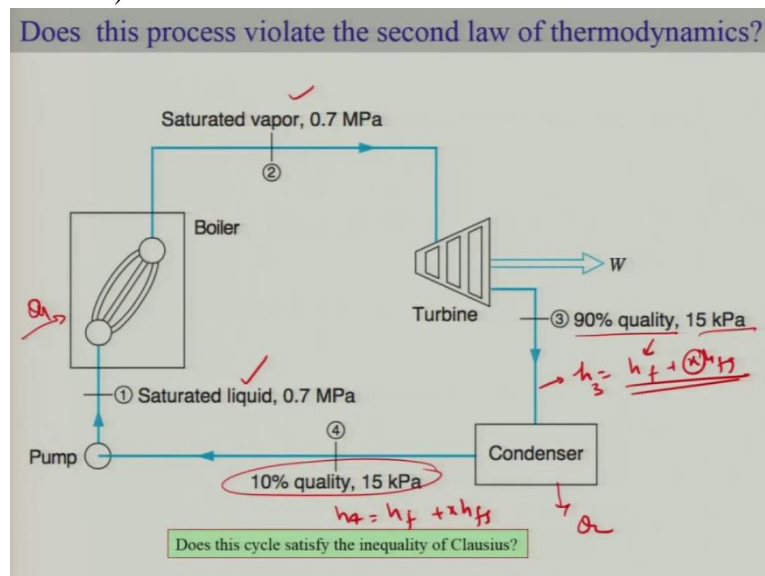
So, remember this is given 90 percent quality so essentially here H is going to be H f plus x H f g remember that. That you have to calculate the H at this condition using the quality here. So, quality is going to change from here to here. So, it is not complete phase transition as in the case of here, where it was saturated liquid to saturated vapor. So, you have to calculate H

3 in this way. Similarly, H 4 is also in the same way, H f plus H f g where x is now 0.1 and H f corresponds to the fluid enthalpy, specific enthalpy for this 15 kilo Pascal.

Does this process violate the second law of thermodynamics?

$$\oint \frac{\delta Q}{T} = \int \left(\frac{\delta Q}{T}\right)_{boiler} + \int \left(\frac{\delta Q}{T}\right)_{condenser}$$

$$\oint \frac{\delta Q}{T} = \frac{1}{T_1}\int_1^2 \delta Q + \frac{1}{T_3}\int_3^4 \delta Q = \frac{Q_2}{T_1} + \frac{Q_4}{T_3}$$

Let us consider a 1 kg mass as the working fluid. We have then

$_1q_2 = h_2 - h_1 = 2066.3$ kJ/kg, $\quad T_1 = 164.97°C$

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Therefore,

$$\oint \frac{\delta Q}{T} = \frac{2066.3}{164.97 + 273.15} - \frac{1898.4}{53.97 + 273.15} = -1.087 \text{ kJ/kg K}$$

Thus, this cycle satisfies the inequality of Clausius, which is equivalent to saying that it does not violate the second law of thermodynamics.

That is something which you can get from the table and T 3 is going to be fixed because T 3 again is going to be same as T Sat at 0.15 kilo Pascal. So, you have now the information of this. Now you can plug in this expression to see whether this value is greater than or less than 0. When you plug in these values, it turns out to be negative. In fact, that means this is correct. This cycle certainly satisfies the inequality of Clausius which is equivalent to saying that it does not violate Second Law of Thermodynamics. So, this is very useful tool to check the design is at least, you know in line with the laws of thermodynamics, particularly the Second Law of Thermodynamics using this Inequality of Clausius.

Entropy

Isothermal process

$T = 300$ K = const.

$\Delta S_{sys} = \frac{Q}{T} = 2.5 \frac{kJ}{K}$

$Q = 750$ kJ

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T}\right)_{int\,rev} = \int_1^2 \left(\frac{\delta Q}{T_0}\right)_{int\,rev} = \frac{1}{T_0}\int_1^2 (\delta Q)_{int\,rev}$$

$$\Delta S = \frac{Q}{T_0}$$

A cycle composed of a reversible and an irreversible process

Clausius inequality

$$\oint \frac{\delta Q}{T} \leq 0$$

Process 1–2 (reversible or irreversible)

Process 2–1 (internally reversible)

$$\int_1^2 \frac{\delta Q}{T} + \int_2^1 \left(\frac{\delta Q}{T}\right)_{int\,rev} \leq 0$$

$$\int_1^2 \frac{\delta Q}{T} + S_1 - S_2 \leq 0$$

Now let me just go bit to board and as we have defined that delta S is nothing but the integral of del Q by T so when you consider this piston cylinder geometry for example and let us assume

this is the constant temperature process, isothermal process. So, in that case we can consider the delta S of the system considering this internal reversible is nothing but del Q by T and since T is constant we can take out the T, it is nothing but the heat which is being supplied to the system, and if heat is, the Q is known, then you can simply write Q by T.

Now you consider another case where it is like you have a state 1 and 2, and process 1 to 2 occurs irreversibly or reversibly we do not know and the second one which is 2 to 1 reversible process always occur in the internal reversible process. 2 and 1 can be considered as internal reversible process. So, if you apply this Clausius Inequality you know this expression so this can be broken down in 2 parts, 1 to 2 and 2 to 1. So, this is what it is, 1 to 2 and 2 to 1 we know it is internal reversible, we know this internal reversible can be represented by simply that change in the entropy.

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T}\right)_{intrev} = \int_1^2 \left(\frac{\delta Q}{T_0}\right)_{inrev} = \frac{1}{T_0}\int_1^2 (\delta Q)_{intrev}$$

$$\Delta S = \frac{Q}{T_0}$$

$$Clausius\ inequality, \oint \frac{\delta Q}{T} \leq 0$$

$$\int_1^2 \frac{\delta Q}{T} + \int_1^2 \left(\frac{\delta Q}{T}\right)_{intrev} \leq 0$$

$$\int_1^2 \frac{\delta Q}{T} + S_1 - S_2 \leq 0$$

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

$$\Delta S_{sys} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}$$

And hence one can get a generic expression of the delta S here which is nothing but, the delta S must be greater than equal to del Q by T. So, this is the basic, the generic expression. That means this delta S we are talking about is nothing of the system. It is just the system. So basically, delta S system is nothing but S 2 minus S 1. It is this heat interaction term, which occurs at the boundary plus whatever the irreversibility associated with the process entropy generation, that is also part of that.

So, entropy change of a closed system, during irreversible process always greater than the entropy transferred due to heat transferred between the system and surrounding. Some entropy is generated or created during the reversible process and this generation is due, entirely due to presence of irreversibility. So, if you consider as generation, it is usually positive or 0. 0 is only for reversible process and certainly depends on the process.

Entropy of isolated system would be, this would be 0 and delta S isolated must be greater than 0 because S generation would be greater than equal to 0, and if it is reversible then this is going to be 0 and hence delta S isolated should be 0 for a system. So, it says that, if you look at this expression that entropy never decreases, it always increases and hence this is sometimes also called increase of entropy principle.

Now entropy is an extensive property. We know that. You can have many subsystems in a system and in that case the delta S Total can simply be the sum of all the entropy changes of the subsystem.

$$\Delta S_{total} = \sum_{i=1}^{N} \Delta S_i > 0$$

Now one can consider, let us say a system here. This is a open system and then immediate surrounding you can consider completely and surrounding plus system can be considered an isolated system. If we do that, okay in that case this is something which we are talking about universe and there this would be an equivalent of something called isolated system.
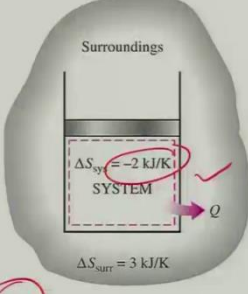
So, if you consider system and surrounding that would be together would form like an isolated system. So, you can apply all the analogies for the system plus surrounding together. Now let us look at again. The S generation, so what would be the S generation, S generation would be something which is the change in the total entropy, that would be the changes in the system, entropy plus delta S system entropy and that must be greater than equal to 0 as we have already discussed.

$$S_{gen} = \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \geq 0$$

So, for the case of irreversible process, this must be greater than 0. For the case of reversible process this would be 0. Of course, this is not possible if you get a negative value of S generation, it indicates that whatever the process you are working on, that is not feasible. So, the question is, can the entropy of the system decrease and is that possible?

Some remarks about Entropy

1. Processes can occur in a *certain* direction only, not in *any* direction. A process must proceed in the direction that complies with the increase of entropy principle, that is, $S_{gen} \geq 0$. A process that violates this principle is impossible.

2. Entropy is a *nonconserved property*, and there is *no* such thing as the *conservation of entropy principle*. Entropy is conserved during the idealized reversible processes only and increases during *all* actual processes.

3. The performance of engineering systems is degraded by the presence of irreversibilities, and *entropy generation* is a measure of the magnitudes of the irreversibilities during that process. It is also used to establish criteria for the performance of engineering devices.

Surroundings

$\Delta S_{sys} = -2$ kJ/K
SYSTEM

$\Delta S_{surr} = 3$ kJ/K

$S_{gen} = \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 1$ kJ/K

The entropy change of a system can be negative, but the entropy generation cannot.

Because what we are talking about the entropy of the complete system plus surrounding that must be greater than or equal to 0 but not necessarily the entropy of the system should be greater than equal to 0. So, this means you can have the system which can reduce the entropy of the, where you can have the process which can reduce the entropy of the system. Example will be heat transfer from the system to surrounding as in this case.

So, this is just a remark here that you know, entropy talks about the direction. Any process should proceed that increases the entropy that is S generation should be greater than equal to 0, the reverse is impossible. Entropy is a non-conserved property and there is nothing called conservation of entropy principle, and the irreversibility associated with S generation, that need to be minimized in order to have an efficient engineering device.
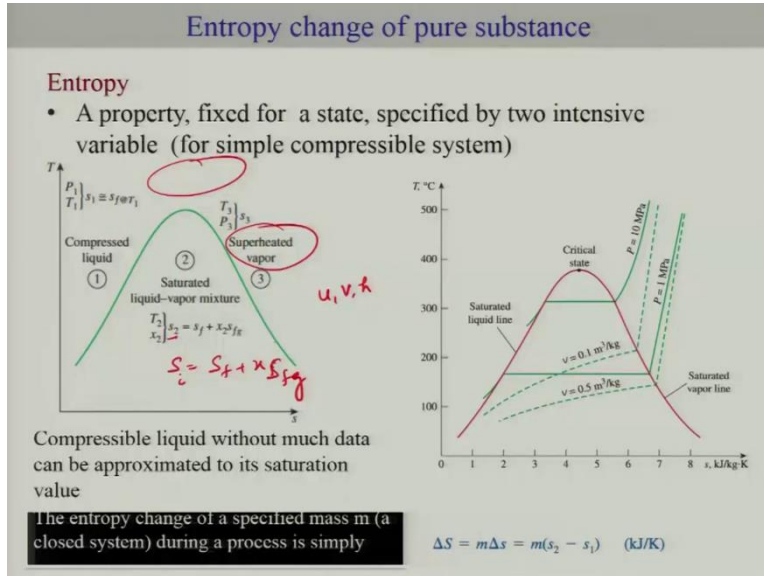
So, entropy also you can make use of the thermodynamic tables as for the case of enthalpies, our energies, our internal energies... So, one can also have these plots like temperature versus entropy and you will get these two, this kind of envelop which is nothing but binomial curves and here the same thing there is compressed liquid as we have seen for temperature, pressure and things like that.

Similarly, this is a superheated vapor. This is super-critical and this is saturated liquid in the same way as we have done for entropy, for enthalpy and internal energy. You would be also evaluating in this saturated system as simply as, of the system or particularly the state point, S f plus x of S f g, in the same way as we have done for other thermodynamic properties such as U, V, H and so forth.

Now one can also see this, if you look at these lines you will be seeing that you can plot T S and you can have these isobars, isochores, these are the typical lines, typical graphs for entropy which is useful to analyze for specific problems. So, I would not be going into details of this.
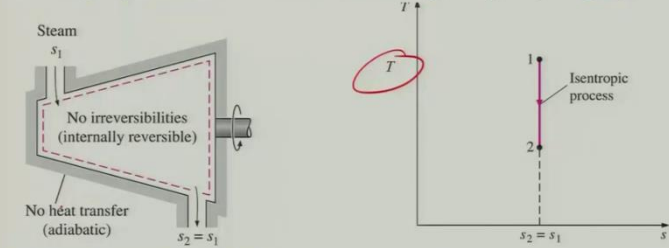
Some of you must have also gone through in your earlier class on Thermodynamics. Now entropy of fixed mass can be changed by two ways as we probably already guessed. One is of course the part is the heat transfer, that comes as del Q by T, that is heat transfer associated entropy change and another is S generation, that is the irreversibility.

So, if you have a reversible process and you have a adiabatic, process in that case the entropy cannot be changed for that particular fix mass, particular process and those kind of processes are called isentropic process. So usually, you have this kind of turbine and so, turbine which is often represented as an isentropic process, which is something like T, here from 1 to 2, the entropy is constant. So, the idea is that there is no irreversibility associated with that and there is no heat transfer and these are the two elements which make it isentropic process.

$$\Delta s = 0 \ or \ s_2 = s_1$$
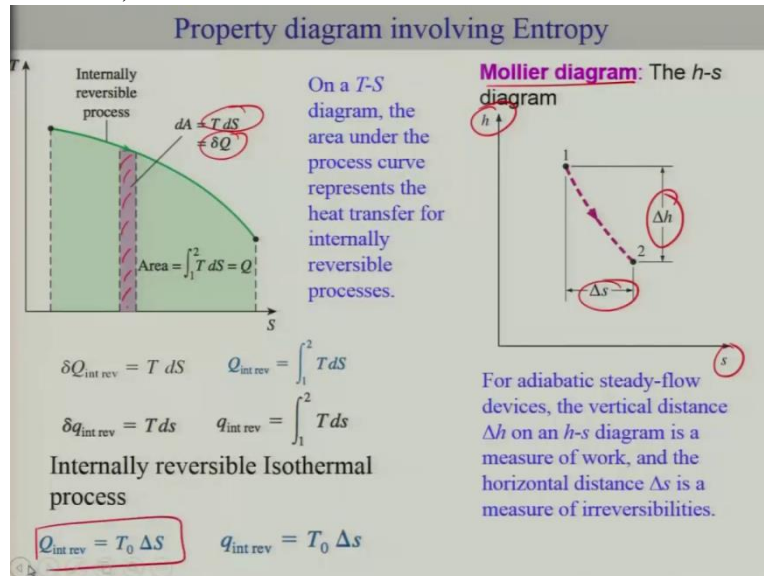
Now you can consider diagrammatic approach also to have analysis on the entropy-related, so here what I am doing is I am presenting this temperature versus entropy and this is the internally reversible process and this area here is nothing but T d S, because this is T versus S and this is nothing but d Q. So essentially the area of the curve on a T S diagram indicates the effective heat transfer for internal reversible process.

$$\delta Q_{intrev} = TdS \qquad Q_{intrev} = \int_{1}^{2} TdS$$

$$\delta q_{intrev} = Tds \qquad q_{intrev} = \int_{1}^{2} Tds$$
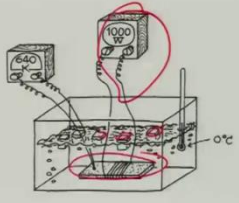
$$Q_{intrev} = T_0 \Delta S \qquad q_{intrev} = T_0 \Delta s$$

Now one can also use this Mollier diagram to gauge the process a bit. For example, you can see this h and h versus s and this is the process. So, delta s is associated with the irreversibility, associated with the process and delta h here is associated with the measure or with the work. So essentially this delta h is nothing but the measure of the work. Now looking back here we can write this Q internal thing simply as T 0 delta S, that is something which we have described early also.

So before I close I would like to go through two examples quickly and this is to illustrate our understanding how to solve such problems. So this is a problem on this bar of aluminum which is placed in a large bath of ice which is ice here you can see floating here, and there is water. Current is being passed here through the bar okay at this condition. At steady state there is power dissipation of 1000 Watt. So current is passed through a bar until, as I said there is a power dissipation of 1000 Kelvin which is really represented in this form.

This aluminum bar is also connected with the thermocouple and this reads at the temperature of 640 Kelvin. Film boiling occurs at the interface with a subsequent noisy collapse of the bubbles which is what you could see in the real experiment. The question is what is the entropy change of the bar, water and universe during this two-minute operation for this highly I reversible operation? So, assume there is ice remaining at the end of the two minutes. So, this is a very interesting practical problem. So, let us try to address this.

Before I try to address let me quickly go through the extension of the First Law for the case of reversible process where we represent del Q in terms of entropy. The First Law in the differential form is we know d E can be resonance the d U ignoring the kinetic energy and the potential energy, and del W considering only the boundary work is minus P d V. For internal irreversible we know that d Q is nothing but T d S. That is what we have shown. So, you can represent this First Law of Thermodynamics in terms of d U is equal to T d S and you can write S, d S as simply in this form. So, this is the alternative representation which may be very useful in our example.

$$Differential\ form\ of\ First\ Law, dE = \delta Q + \delta W$$

$$Simple\ system, dE = dU$$

$$quasi-static\ process, \delta W = -PdV$$

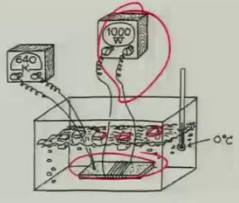$$internally\ reversilble\ process, \delta Q = TdS$$

$$Substituting, dU = TdS - PdV$$

$$Alternatively, dS = \frac{1}{T}dU + \frac{P}{T}dV$$

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Example

A bar of aluminum is placed in a large bath of ice and water. Current is passed through the bar until, at steady state, there is a power dissipation of 1000 W. A thermocouple on the surface of the aluminum reads 640 K. Film boiling is occurring at the interface with a subsequent, noisy collapse of the bubbles. What is the entropy change of the bar, water, and universe during 2 min of operation for this highly irreversible operation? Assume that there is ice remaining at the end of the 2 min.

The Combined First and Second Laws

Closed, Single-Phase, Simple Systems
- The First Law in differential form is

$$dE = \delta Q + \delta W$$

- For a simple system, $dE = dU$
- For a quasi-static process, $\delta W = -PdV$
- For an internally reversible process, $\delta Q = TdS$
- Making these substitutions gives

$$dU = TdS - PdV$$

- ** Really Important **, referred to as the combined First and Second Laws of Thermodynamics for a closed simple system
- An alternative representation is

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

So, consider that bar, aluminum bar does not change its volume. So, what is the entropy change of the bar, water and this. So, here the fact is that if you look at d S here, for the first part what we can assume that of course that there is no change in the V, and there is 2 minutes so it is hardly enough and we are assuming that, because of the fact that this is solid and effective changes in the internal of aluminum can be ignored.

So, we assume in this case is that aluminum bar does not change its entropy within 2 minutes. That is the assumption we made to solve the problem. Now what is the other thing we assumed for the case of ice water, that the delta V due to melting is negligible. So now we can find out delta ice water, this is going to be 1 by T d U plus P by T d V.

$$\Delta S_{ice-water} = \int \frac{1}{T} dU + \int \frac{P}{T} dV$$

This is interesting question. What becomes difficult is now how do you connect this, because this is highly irreversible process.

But then remember this, that this process at the end you have 2 state points and essentially even if it is irreversible, you can consider reversible, you can come up with a fictitious reversible path in order to obtain the state, changes in the state variables, changes in the thermodynamic

properties which are state dependent as in the case of d U and d V. So, what we can do is we can come up with some kind of, some kind of reversible process.

So, imagine or visualize some, so maybe we can come up with this reversible process between the same initial and final state, okay. So, what we can do is we can consider a system is contact in some external heat at the same T equal to 0 degree Celsius plus delta T which approximately is 0, which means it very small. So, the process whatever is happening, we consider that it is connected to some reservoir, this can be represented in terms of some reservoir

And which is 0 degree plus slightly higher value which is almost close to 0. That means it is very slow process and heat interaction occurs because of that. So, this is a reversible process. So that case, assuming this delta V is equal to 0, you have this goes to 0 and then your delta S is nothing but delta U plus T, which is nothing but Q by T, why, because T is constant.

Now Q is known this is the power 10 to the power 3 into 2 into 60, 2 minutes and temperature is of course 273. So, we can find out the value, 439 Joules per Kelvin and this is nothing but, this will be the same as universe because this is the change which we are occurring. So, delta S and delta, this would become, for your water ice water and that is same as delta S universe. So, of course, there are many problems which we can work on using this concept.

$$\Delta S = \frac{\Delta U}{T} = \frac{Q}{T} = \Delta S_{universe}$$

But just for the sake of illustration that we have made a very complex process a very simple analysis using gross approximation for the case of just analyzing the problem. So, I think this would be the end of today's lecture. We will continue this exercise in the next lecture with more examples, so I will see you in the next lecture.