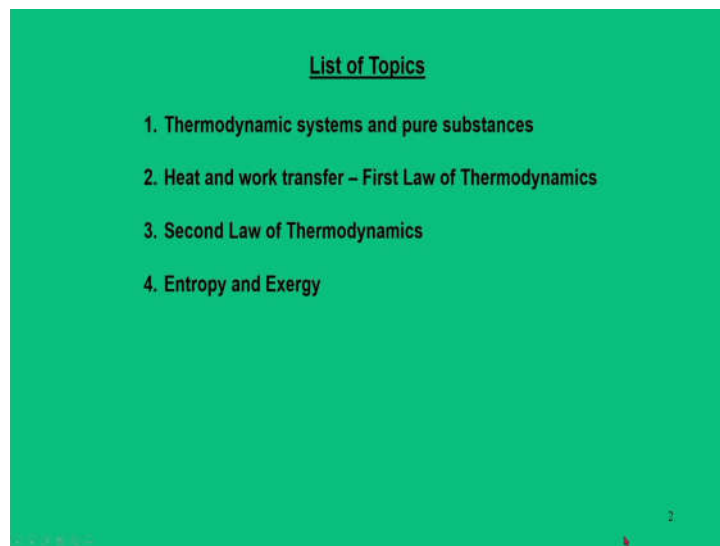


Applied Thermodynamics
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Module - 01
Review of Basic Thermodynamics
Lecture - 04
Entropy and Exergy

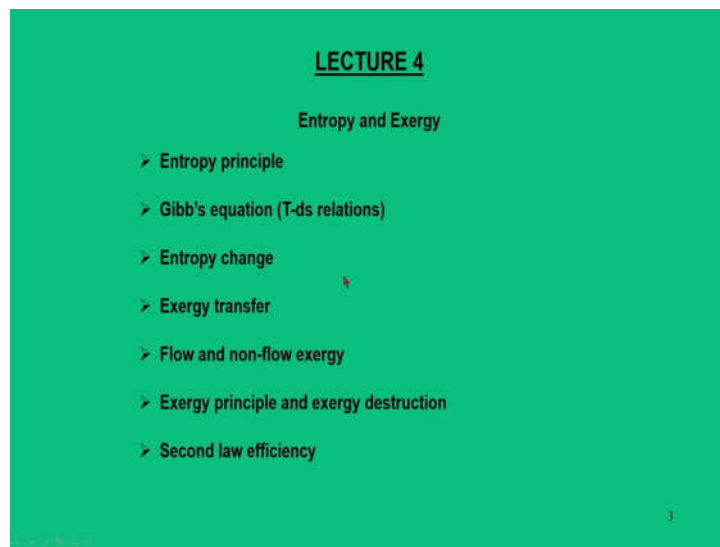
Dear learners, greetings from IIT Guwahati. We are in the MOOCs course that is Applied Thermodynamics, 1st module Review of Basic Thermodynamics.

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So, previously, we have covered three lectures of this module; thermodynamic systems and pure substances, heat and work transfer mainly dealing with the first law of thermodynamics, then last class we have elaborately discussed about second law of thermodynamics, but another important aspect of this second law of thermodynamics is the concept of entropy and exergy and this part, we are going to cover today.

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So, under this lecture that is entropy and exergy, we are going to cover the following topics: entropy principle, then we have Gibb's equation, many a times we know it as T-ds relations, entropy change; how you are going to calculate actually the entropy change during a process.

The next part would be the concept of exergy, how the exergy transfer takes place typically the exergy means work potential of energy and we will show that how it is different for work, for heat and for mass transfer. Similar to that the way we calculate the energy transfer in a closed system and open systems, we will also calculate the flow exergy and non-flow exergy that means, flow exergy for an open system and non-flow exergy for an closed systems.

Then, we have exergy principle and exergy destruction, this is something reverse of entropy principle where entropy always increases and exergy principle means it always decreases and the last part which is a second law efficiency is another concept that we drop in normally, when you deal with the efficiency after covering the first law, we use the word efficiency and that efficiency normally referred as first law efficiency.

But after covering the concept of second law of thermodynamics entropy and exergy, we are going to see that how a second law efficiency is different from the first law efficiency. So, this is the overall picture or spectrum for this today's lecture.

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Entropy

- The second law of thermodynamics leads to expressions that involve inequalities involving reversible/irreversible heat engines/refrigerators.
- Another important inequality is the "Clausius inequality" involving cyclic integral of ratio of heat and absolute temperature.
- The cyclic integral of ratio of heat and absolute temperature in a reversible process is assigned a new thermodynamic property (entropy). It is an abstract property to measure the randomness/disorderness of a system.

Process 1-2
(irreversible)

Process 2-1
(internally reversible)

Clausius inequality: $\oint \frac{\delta Q}{T} \leq 0$; $\oint \left(\frac{\delta Q}{T} \right)_{\text{rev}} = 0$

Entropy $(ds) = \left(\frac{\delta Q}{T} \right)_{\text{rev}}$; $\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{rev}}$

Isothermal heat transfer process: $\Delta S = \frac{Q}{T_0}$

So, if you have just brief review of last lecture, it was mainly deal with the second law of thermodynamics, its statements that is Kelvin Planck statement and Clausius statement and we also gave the concept of heat engine and refrigerators.

The entire idea was how we are going to extract heat from the low temperature reservoir and for a heat engine, we expect that we want to convert work output from a heat source. So, this is the very basic philosophy of heat engine and similarly for refrigerator and heat pump, the input requirement is work, but we can make use of the fact that whether you are extracting heat from a low temperature sink, or we are rejecting the heat to a high temperature source.

So, these are the two concept which was used in the refrigerator and heat pump. The another significant remark of second law is the directionality of a process. So, to quantify this directionality, we use the concept of entropy. So, it is basically a parameter or property of a system that decides whether a process is going to occur in certain direction or not.

By evaluating that property, we can say that which direction the process is going to occur, what is the irreversibility that is occurring in that process so, all these evaluation is possible. Another significant remark of second law is the concept of inequality. The first law says that its energy audit, whatever energy comes in that goes out, but in the second law, we say that it is not possible to convert all the energy if it is available in heat form.

So, only some part of heat is going to be converted and that is through heat engine. So, that is the reason the upper limit or Carnot efficiency was specified. So, again this is a concept of inequality that means, that entire heat is not going to be converted so, some part has to be lost to the surroundings.

So, this inequality that involves gives the concept of reversible and irreversible nature of heat engines and refrigerators. Another important inequality is known as Clausius inequality and that Clausius inequality gives the concept of entropy. How? What the Clausius inequality says that the cyclic integral of ratio of heat to absolute temperatures.

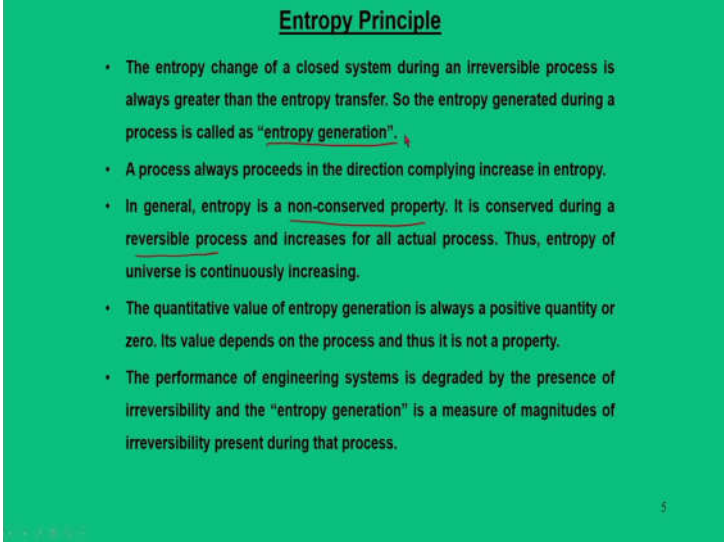
So, cyclic integral of heat to absolute temperature mean $\oint \frac{\delta Q}{T}$. So, let us say consider a process where state can change from 1 to 2 maybe internally; one may be an internally reversible process another cyclic process that can be from 1 to 2, it is going in a cycle so, it is a irreversible process. One is having an internally reversible process, other is irreversible process.

What the Clausius inequality tells? It tells about the parameter that what happens to the heat transfer during that cyclic process. So, this is something like a cyclic process so, we call this as $\oint \frac{\delta Q}{T}$ and it has been proved that in a cyclic process, this $\oint \frac{\delta Q}{T} \leq 0$ and if the process happens to be internally reversible, then it is equal to 0.

So, this is another inequality that comes in from the second law of thermodynamics and that we call as a Clausius inequality. Now, if that process is internally reversible, then Clausius defined it as a parameter called as entropy. So, $dS = \left(\frac{\delta Q}{T} \right)_{intrev}$.

So, once we know this so, $\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{intrev}$ and if the process happens to be an isothermal process that occurring at T_0 , then $\Delta S = \frac{Q}{T_0}$ can be easily computed by knowing the heat transfer.

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Entropy Principle

- The entropy change of a closed system during an irreversible process is always greater than the entropy transfer. So the entropy generated during a process is called as "entropy generation".
- A process always proceeds in the direction complying increase in entropy.
- In general, entropy is a non-conserved property. It is conserved during a reversible process and increases for all actual process. Thus, entropy of universe is continuously increasing.
- The quantitative value of entropy generation is always a positive quantity or zero. Its value depends on the process and thus it is not a property.
- The performance of engineering systems is degraded by the presence of irreversibility and the "entropy generation" is a measure of magnitudes of irreversibility present during that process.

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Now, next aspect is the entropy principle. So, the entropy principle means that in a naturally occurring process, first thing is that we want to quantify that how much entropy transfer takes place number one, by considering that entropy transfer, we are going to predict whether the process is reversible or irreversible process and third aspect is that that entropy change or excess of exergy whether it is a positive quantity or negative quantity. So, all these things are answered what we typically call as an entropy principle.

And in fact, all these points which I will be talking about is the corollary of second law of thermodynamics. A more detailed derivations are available in the books, but somehow, I am just going to give you the brief concept of entropy principle. So, what does it say? That the first one is that the entropy change of a closed system during an irreversible process is always greater than the entropy transfer.

So, the entropy generated doing a process is called as entropy generation; that means, an irreversible process always encounters entropy generation. A process always proceeds in the direction complying the increase in the entropy. So, if process goes in a direction in which the entropy increases and unlike, when we say energy, energy is a conserved property by first law.

From the second law, entropy is a non-conserved property, this is the most important because entropy is a non-conserved property, but at a certain instant, it is conserved what is that instant? So, only during the reversible process it is conserved. So, it is conserved

only during a reversible process and always increases for all actual process. So, entropy of universe is continuously increasing. Many a times, we call this is a law of entropy.

The quantitative value of entropy generation is always a positive quantity or a zero. Its value depends on the process and thus it is not a property. Entropy generation depends on the process, but entropy is a property and entropy generation is not a property.

The performance of engineering system is degraded by the presence of irreversibility and the entropy generation so, and entropy generation is a measure of magnitude of irreversibility present during that process. So, these are the some concept of this entropy generations. Now, let us see what is that entropy generation mean for us.

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Entropy Principle

- The increase in entropy principle does not imply that the entropy of the system can decrease. The entropy change can also be negative.

$$\oint \frac{\delta Q}{T} \leq 0 \Rightarrow \int_1^2 \left(\frac{\delta Q}{T} \right) + \int_2^1 \left(\frac{\delta Q}{T} \right)_{\text{atmos}} \leq 0 \Rightarrow \int_1^2 \left(\frac{\delta Q}{T} \right) + (S_1 - S_2) \leq 0 \Rightarrow S_2 - S_1 \geq \int_1^2 \left(\frac{\delta Q}{T} \right)$$

$$\Rightarrow (\Delta S)_{\text{total}} > 0$$

$$\Rightarrow (\Delta S)_{\text{total}} = (S_2 - S_1) = \int_1^2 \left(\frac{\delta Q}{T} \right) + S_{\text{gen}}; \quad S_{\text{gen}} = (\Delta S)_{\text{total}} + (\Delta S)_{\text{surroundings}} \geq 0$$

Irreversible process: $S_{\text{gen}} > 0$; Reversible process: $S_{\text{gen}} = 0$; Impossible process: $S_{\text{gen}} < 0$

Now, let us give some mathematical background to it. That mathematical background comes by the fundamental principle what we call as increase in the entropy principle.

So, what it says that increase in the entropy principle does not imply that entropies of system can decrease, entropy change also can be negative, but when you deal with the entropy principle, always system and surroundings they are always taken into account. So, that is the first thing that we need to understand.

So, let us give some mathematical background to it. So, we start from the Clausius inequality which says that $\oint \frac{\delta Q}{T} \leq 0$. So, if you want to make it equal so, I have made it

in two ways, one that a process goes from 2 to 1 and then from 1 to 2. So, from 1 to 2, the process is irreversible so, I can write δQ by T , other way is that when the process returns from 2 to 1 so, it is an internal irreversible process.

So, this is the first assumption we make that while going, it goes in a irreversible manner, it can be reversible or irreversible, while coming it is always a reversible process. So, in

that sense, $\int_1^2 \left(\frac{\delta Q}{T} \right) + \int_2^1 \left(\frac{\delta Q}{T} \right)_{intrev} \leq 0$ and since we are not known whether the process is reversible or irreversible, we keep the integral as it is when the process goes from 1 to 2 and for the 2 to 1 process, we can write this as entropy change that is $S_1 - S_2$.

So, in other words, this tells us that $S_2 - S_1 \geq \int_1^2 \left(\frac{\delta Q}{T} \right)$. So, this $S_2 - S_1$ we call this as a

ΔS for an isolated system and this is this value is always a positive quantity so, it is a greater than 0. Now, when we say this as system, another way of interpreting this particular system as this so, we write this $(\Delta S)_{system} = (S_2 - S_1)$ and this is nothing but

$\int_1^2 \left(\frac{\delta Q}{T} \right) + S_{gen}$ that means this particular term I want to make it an equal way.

And from this equation we can calculate the $S_{gen} = (\Delta S)_{system} + (\Delta S)_{surroundings}$. So, this particular term is nothing, but the entropy change for the surroundings. So, from this, we can tell that $S_{gen} \geq 0$. So, by quantifying this S_{gen} , S_{gen} is nothing but the total ΔS involving system and surrounding.

And from this equation, one can find out that maybe this particular relation is more appropriate when you deal with these particular expressions. So,

$(\Delta S)_{system} + (\Delta S)_{surroundings} > 0$. So, we can say it is a isolated system, when there is involving system and surrounding, it is always greater than 0.

But this entropy principle say that entropy of the system can increase or decrease. For example, a system may have many subsystems and within them, there may be change in the entropy of each subsystems. So, if there are N number of subsystems within a system, then total entropy change is greater than 0. So, this ΔS is greater than 0.

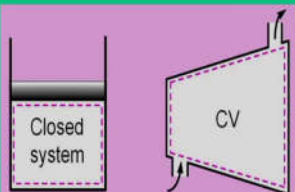
Now, it tells about that S generation is always greater than 0, but within the system, this may be positive, this may be negative. So, if these are the system involving number of sub system and these constitute the surroundings your total entropy change could be 0, but within the sub system, there can be positive or negative depending on the heat interaction among the sub systems. So, this is one part.

Second aspect is that it gives another important consequence that is for an irreversible process, S generation, entropy generation is always greater than 0 that we get it from this expression. For a reversible process, we say S generation is equal to 0 that is there is no entropy generation and there is no such process which occurs in a nature for which S generation, entropy generation is less than 0; so, this we consider as an impossible process.

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Gibb's Equation

- The combination of first and second law of thermodynamics leads to two fundamental T-ds relations for a closed stationary system containing a simple compressible substance. These relations are called as Gibbs equation.
- These relations are valid for both reversible/irreversible process and both open/closed system.



$T ds = du + P dv$ ✓
 $T ds = dh - v dp$ ✓

First law: $\delta Q_{\text{system}} - \delta W_{\text{system}} = du$
 $\delta W_{\text{system}} = p dV$
 Second law: $\delta Q_{\text{system}} = T ds$
 $\Rightarrow T ds = du + p dV$ & $T ds = dh + p dv$
 $h = u + pv \Rightarrow dh = du + p dv + v dp$
 $\Rightarrow T ds = dh - v dp$

$\rightarrow du = dh - h du = v db$

The next topic is the Gibb's equations. After considering the first law and second law, there is some mathematical relation that was proposed that those relations are typically known as T-ds relations. This T-ds relation when it was proposed, these are proposed by famous scientist and they are known as Gibb's equations.

Let us bring the first law and second law together and find out the consequence because the first law talks about internal energy and enthalpy for an open system and closed system. For closed system, first law gives you a property about internal energy, for an

open system the first law gives the concept of enthalpy and from the second law, we get another property called as entropy.

So, the question is that are they related or whether is there any relevance between these two laws or is there any relevance among these properties? To answer these questions, we have to recall famous Gibb's equation and commonly known as T-ds relations.

So, what the first law tells that for internal reversible process $\delta Q_{\text{int rev}} - \delta W_{\text{int rev}} = dU$ and these are the path functions. So, it is exact differential where U is internal energy which is a property.

Now, since it is an internal reversible process so, $\delta W_{\text{int rev}} = p dV$. Now when you deal with the second law, $\delta Q_{\text{int rev}} = T ds$. So, from the second law, we get these equations.

By putting this δW and δQ in this first law so, we get the famous relation one is $T dS = dU + p dV$ or simply we can write in unit mass basis and in a unit mass basis, this turns out to be $T ds = du + p dv$. So, it is a specific entropy and specific internal energy and specific volume.

Now, you also recall that there is a term enthalpy for a open system, we write it as $h = u + pv$ and so that we can express another relations involving enthalpy. So, from this equation, we can find out $dh = du + pdv + vdp$. Now, from here, we can find out $du = dh - pdv - vdp$. When we put this in this first equation, we get second relation $T ds = dh - v dp$.

So, there are two relations, one is $T ds = du + p dv$ and $T ds = dh - v dp$. So, first term involves internal energy, second term involves enthalpy. Now, what is the significance of this equation is that irrespective of the fact, we have told that this entropy, internal energy and specific volume and enthalpy, all these are the property of the systems. When we say property of the system, they depend on the end state, they do not depend on how the process is going to occur.

So, irrespective of the fact these two equations holds good for any kind of process that is either it can be used for open or closed systems or it is valid also for reversible as well as irreversible process because it only depends on the end state. So, this is the very

important significance when we combine first law and second law through Gibb's equations.

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Entropy Change

- Depending on the phase of pure substance, the property table and Mollier diagrams are used to measure the entropy change.
- A process during which the entropy remains constant is characterized as "isentropic process".
- Area under the process curve on a *temperature-entropy* diagram represents the heat transfer during an internally reversible process.

$$dh = \frac{dh}{T} + \frac{p dv}{T} = c_p \frac{dT}{T} + \frac{p dv}{T} \quad \& \quad pv = RT \Rightarrow s_2 - s_1 = c_p \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right)$$

$$dh = \frac{dh}{T} + \frac{v dp}{T} = c_p \frac{dT}{T} + \frac{v dp}{T} \quad \& \quad pv = RT \Rightarrow s_2 - s_1 = c_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{p_2}{p_1} \right)$$

So, this is all about the conceptual thing. Now, let us see that how we are going to calculate the entropy change in our real applications. So, there are situations that the flow process involves pure substance, flow process can involve gas flow; so, all these things we are going to calculate the entropy change.

Now, let us say that what happens in a pure substance. So, in a pure substance, a typical diagram that represents in a temperature entropy diagram; so, there is a dome and across the dome we have this critical point that is the peak of the dome and this dome separates the saturated liquid and the saturated liquid vapor mixtures, other part of the dome that separates saturated liquid vapor mixture and super-heated vapor and within the domes, it is only the saturated liquid vapor mixtures.

Now, if you are in the region 1 that is the complete liquid regions, if you want to calculate the entropy at state 1 so, for that state, we require either one parameter that is the temperature or pressure at which the liquid is available. So, we can write entropy at state 1 is equal to liquid entropy at temperature T_1 .

Now, when we are in the dome 2 and region 2 that is in the saturated liquid vapor mixture, you require two parameters that is temperature or pressure and a dryness

fraction that is x_2 . So, by knowing the T_2 , we can find out what is the entropy of saturated liquid and saturated vapor and knowing the value of x_2 , we can calculate the entropy at state 2. So, you require these two parameters.

And when you are in the region of super-heated vapor so, we require two parameters, pressure and temperature. These temperature we can refer to super heated table. So, find out the entropy at state 3. So, this is how we calculate the entropy when we are dealing with the pure substance and mostly, we use it for water.

Another consequence of this temperature entropy diagram is with respect to enthalpy entropy which is normally known as Mollier diagram and this Mollier diagram is extensively used for steam power plant where it is used extensively to find the different state conditions of turbines, boilers.

Now, if the process is isentropic in this temperature entropy diagram, we represent the process as 1-2; it is a vertical straight line and why I am saying this? In over the period of time, you will be dealing with the temperature entropy diagram exhaustively and when you say it is a isentropic process it means in a TS diagram, it is a vertical straight line.

And many situation you want to calculate the entropy change either for a reversible or irreversible process and this entropy change we are looking at if it is not a pure substance if it is gas, then we can directly use the T ds relations.

From this T ds relations and using the equation of state, then we can easily calculate the entropy change based on the state point temperatures 1 and 2 and corresponding either specific volume or pressure. So, from this, we can calculate the entropy change, but we have to know that the C_p and C_v of the gas.

$$s_2 - s_1 = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right); s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right)$$

So, this is how the entropy change is calculated involving working fluid either it can be a pure substance, or it can be a gas.

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Exergy

- The first law deals with *quantity* of energy in the form of work/heat/mass transfer. The second law is concerned about the *quality* of energy and its degradation during a process through entropy generation.
- Exergy is a measure of work potential dealing with maximum useful work that could be obtained from a system at a given state in a specified environment. It is a property of the system which is also called as "availability or available energy".

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The next important topic that we are going to discuss is the exergy. Till this point of time, we talked about energy, we talked about work transfer, heat transfer, but another word that we are coming back is the exergy. Now, when you deal with heat or work transfer, always we will deal with the system, system means what that particular system is capable of.

Now, when the system is capable of on its own, but during that calculation of heat or work transfer, we did not take into account about the environment that means, with which the system is interacting. Now, always the system is interacting with a environment.

Now, the environment has its own potential. For example, if you look at the atmosphere, the atmosphere has a pressure of 101kPa or temperature is about 300K. So, it means that this environment is not at its absolute value. So, actual absolute value could be a 0 pressure or 0 Kelvin temperatures. So, this is how the second law talks about.

Now, the question is that when the system is undergoing a heat or mass transfer or heat transfer or work transfer, it is always interacting with the environment and these environment is not at its absolute state, it has some potential that means, it has some pressure P_0 and temperature T_0 that we call as a reference state.

Now, during the process of heat and work interaction that means, it spend some energy in overcoming the work or resistance that is occurred due to the environment state that is is atmospheric state. So, the first law or second law does not account for this fact.

So, to bring the concept of the exergy, it always accounts that where is your environment state. So, when is 10kJ of heat is rejected or 10kJ of work is coming out of the system or work is done by the system; so, during this process, it also includes the resistance offered by the environment that is not taken into account while dealing with the work transfer or heat transfer.

Similarly, when the heat transfer takes place, always we encounter that environment is at 30°C not at 0K. So, to account this fact, the concept of exergy is introduced. So, this concept of exergy is nothing, but a measure of work potential. So, what does they say that the first law deals with the quantity of energy in the form of work, heat or mass transfer, second law is more concerned about the quality of energy and its degradation during a process through entropy generation.

But exergy is a measure of work potential that deals with maximum useful energy that could have been obtained from a system at a given state in specified environment; so, that is more important that brings environment into picture. So, when we say ambient condition, it is referred as dead state.

So, it is the property of a system, many books call it as a availability or available energy, but that is old practice, but new way of representation of this availability or available energy is the exergy. So, basically the total energy is divided into two parts, one is the exergy other is the unavailable energy which is typically waste.

Now, during a system, exergy can in similar way to the energy comes into a system either through mass, through heat or through work and when it goes out, it also goes out as a mass or heat or work.

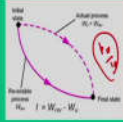
During this change, measure a ΔX of the system and by difference between these two, we call this as a X destroyed, but remember while talking about this fact, we also say that atmosphere at ambient condition as pressure p_0 and T_0 and we say its a ambient. So, that means, in this process of exergy calculation we also take ambient into picture, but when

you deal same thing with respect to energy, we do not take ambient into picture or in our calculations.

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Exergy

- A system will deliver the maximum possible work as it undergoes a reversible process from the specified initial state to the state of its environment (i.e. dead state). It represents the useful work potential of the system known as 'exergy'.
- A system reaches the 'dead state' when it is in thermodynamic equilibrium with the environment.
- Exergy is the upper limit on the amount of work a device can deliver without violating the laws of thermodynamics.
- Exergy is a property of the system-surrounding combination not the system alone.
- Exergy transfer by work can be expressed by accounting boundary.



Work = $f(\text{initial state, process path, final state})$

Boundary work: $X_{\text{avail}} = W - W_{\text{lost}}; W_{\text{lost}} = P_0 (V_2 - V_1)$

All other forms of work: $X_{\text{avail}} = W$

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Now, when we talk about energy transfer, we say mass, heat or work. Similarly, we can also calculate the exergy due to mass, heat and work. So, how we are going to calculate? So, for that some of the things that we need to remember that a system will deliver maximum possible work as it undergoes a reversible process.

So, basically, when it is a work transfer, work transfer is maximum when it is a reversible process when the system goes from initial state to the state of environment that means, the final state is nothing but your dead state and when it is a dead state, when you calculate the work transfer that is the reversible work that is possible. So, this represents the useful work potential known as exergy.

So, now under what situation we call the system to be dead state? So, when it is a dead state, when it is the thermodynamic equilibrium with the environment and in this case, the exergy is the upper limit of work of a device that can deliver without violating the second law of thermodynamics.

Another way of representing is that exergy is a property when you deal with the system surrounding combinations not alone whereas, energy is the property of the system, but

exergy is the property of system and surrounding combination. Exergy transfer by work can be expressed by accounting the system boundary.

So, for example, if you look at this particular figure that a system goes from initial state to final state and in this process, it can go as a reversible work or it can go as a irreversible manner and irreversible manner we call this as actual process and in the reversible process, we said reversible work. Now, in the both the cases system is interacting with surroundings that is p_0 and T_0 .

Now, these surrounding when this it is interacting, when it goes in a reversible manner that means, we have extracted, the reversible work out of the system and system has reach the final state or maximum possible work by involving surrounding into pictures that means, it has reach the surrounding conditions, but when it goes as a actual process, we call this as useful work and it is always less than the reversible work. So, in between the difference is nothing, but irreversibility.

So, this is what the exergy talks about that this is the work transfer and actual reversible work transfer that is exergy and, but this is the useful work transfer and difference between these two is nothing but the irreversibility or we can say exergy destruction due to work only.

So, this is how we have specified that here the work transfer we call this as boundary work and this is nothing but actual work minus surrounding works so, that means, while calculating exergy we involve surrounding work.

$$X_{work} = W - W_{surr}; W_{surr} = p_0 (V_2 - V_1)$$

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Exergy Transfer

- Regardless of temperature and pressure of the environment, work potential (exergy) of kinetic energy of a system is the kinetic energy while work potential of potential energy is the potential energy itself.
- Exergy can be transferred to/from a system in three forms: heat, work and mass flow. It is recognized when it crosses the system boundary.
- Heat is a form of disorganized energy and only a portion of heat can be converted to work. So, the heat transfer at a location with certain absolute temperature is always accompanied by "entropy and exergy transfer". In adiabatic system the exergy transfer as heat is zero.
- The exergy transfer by mass are proportional to the mass. For closed system the exergy transfer by mass is zero.

HEAT SOURCE
Temperature: T
Energy transferred: Q
Exergy: $(1 - T_0/T)Q$

$x_{KE} = KE = \frac{V^2}{2}; x_{PE} = PE = g h; X_{heat} = \int \left(1 - \frac{T_0}{T}\right) \delta Q = \left(1 - \frac{T_0}{T}\right) Q$

$X_{mass} = m\psi; \psi = (h - h_0) - T_0(s - s_0) + \frac{V^2}{2} + gz$

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Now, another way the energy is available in the form of heat and in the form of kinetic energy, in the form of potential energy; then in that situation what is the how we are going to calculate the exergy? So, for that we call this as exergy transfer through kinetic energy; so, exergy transfer by kinetic energy is the kinetic energy itself, exergy transfer due to potential energy is the potential energy itself.

But when you talk about exergy transfer by heat; so, here you have to bring into picture the Carnot efficiency because we cannot take complete heat into work. So, there is a limit that is imposed that is through Carnot efficiency. So, that is what this particular integral comes. So, exergy due to heat we can limit it to $\left(1 - \frac{T_0}{T}\right)Q$. So, there is a limit for the exergy transferred due to heat.

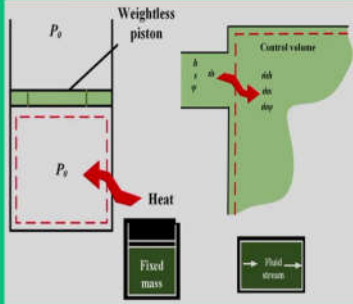
And when we calculate mass exergy due to mass that is $X_{mass} = m\psi$ and ψ is nothing but since it is a flowing work so, we can represent in the form of enthalpy difference. So, here, the h_0 , s_0 and T_0 they represent the atmospheric condition in the dead state. So, this is all about what we find out exergy transfer by various terms.

$$\psi = (h - h_0) - T_0(s - s_0) + \frac{V^2}{2} + gz$$

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Non-flow and Flow Exergy

- A closed system may possess kinetic and potential energies as well as internal energies based on which exergy can be calculated.
- The exergy of a closed system is either positive or zero.
- A flowing fluid has an additional form of energy called as 'flow energy'.



$$x_{kin} = KE = \frac{V^2}{2}; x_{pot} = PE = g h$$

$$x_{heat} = \int \left(1 - \frac{T_0}{T}\right) \delta Q = \left(1 - \frac{T_0}{T}\right) Q$$

$$x_{mass} = m \psi$$

$$\psi = (h - h_0) - T_0 (s - s_0) + \frac{V^2}{2} + gz$$

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Then, what else it is remaining? And there is another concept called flow exergy and non flow exergy. So, also in the first law and second law, we deal with the closed system and open system. So, a closed system is referred as a fixed mass system and open system is referred as a flowing stream and they involve both work transfer, heat transfer and all these things.

And for a closed system, when we actually calculate exergy, we call as a non-flow exergy and when you deal with the flowing stream, we call this as a flow exergy. So, likewise this is how it is represented as flow exergy.

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Non-flow and Flow Exergy

Fixed mass

Fluid stream

Closed system (non-flow exergy)

$$X = (U - U_0) + p_0(V - V_0) - T_0(S - S_0) + \frac{1}{2}mV^2 + mgz$$

$$\phi = (u - u_0) + p_0(v - v_0) - T_0(s - s_0) + \frac{1}{2}V^2 + gz = (e - e_0) + p_0(v - v_0) - T_0(s - s_0)$$

$$\Delta X = X_2 - X_1 = m(\phi_2 - \phi_1)$$

$$\Delta X = (U_2 - U_1) + p_0(V_2 - V_1) - T_0(S_2 - S_1) + \frac{1}{2}m(V_2^2 - V_1^2) + mg(z_2 - z_1)$$

$$\Delta\phi = \phi_2 - \phi_1 = (u_2 - u_1) + p_0(v_2 - v_1) - T_0(s_2 - s_1) + \frac{1}{2}(V_2^2 - V_1^2) + g(z_2 - z_1)$$

$$\Delta\phi = \phi_2 - \phi_1 = (e_2 - e_1) + p_0(v_2 - v_1) - T_0(s_2 - s_1)$$

Open system (flow exergy)

$$\psi = (h - h_0) - T_0(s - s_0) + \frac{1}{2}V^2 + gz$$

$$\Delta\psi = \psi_2 - \psi_1 = (h_2 - h_1) - T_0(s_2 - s_1) + \frac{1}{2}(V_2^2 - V_1^2) + g(z_2 - z_1)$$

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And here, elaborate expressions have been given for a closed system. When we deal with the closed system, it is a non-flow energy so, that is represented by ϕ that involves internal energy change, work transfer and entropy transfer and also the kinetic energy and the potential energy. So, the closed system exergy, non-flow exergy is defined by $\phi = (u - u_0) + p_0(v - v_0) - T_0(s - s_0) + \frac{1}{2}V^2 + gz$ and finally, they are expressed as $(e - e_0) + p_0(v - v_0) - T_0(s - s_0)$.

And if a closed system undergoes a change of state so, we can write that $\Delta\phi = \phi_2 - \phi_1$. So, this environment conditions gets nullified as $\Delta\phi = (e_2 - e_1) + p_0(v_2 - v_1) - T_0(s_2 - s_1) + \frac{1}{2}(V_2^2 - V_1^2) + g(z_2 - z_1)$. So, this is how we define the closed system exergy that is for fixed mass system.

And similarly, when you deal with the flow exergy that is open system, instead of internal energy it is replaced with an enthalpy. So, finally, we can express as flow exergy $\psi = (h - h_0) - T_0(s - s_0) + \frac{1}{2}V^2 + gz$ and change in the exergy in a flow process that is $\Delta\psi = \psi_2 - \psi_1$. So, these are the derivations are available in the book, but here I have just touched upon the important mathematical things that we are going to use in solving the problems.

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Exergy Principle and Exergy Destruction

- The exergy of an isolated system during a process always decreases and in the limiting case, of reversible process, it remains constant.
- In an actual process, exergy never increases and is always destroyed.

No heat, work or mass transfer

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Another important concept we are dealing with the exergy principle or exergy destructions. So, this is similar to entropy principle where entropy always increases, but this particular thing is almost reverse of entropy. So, if I say that the exergy of an isolated system during a process always decreases and in the limiting case, in reversible process its constant whereas in entropy, it always increases.

In an actual process, exergy never increases and it always destroyed and based on this, we say that $\Delta X_{\text{isolated}}$ always less than 0 or exergy destroyed is always greater than 0, this is in a reverse of entropy principle.

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Exergy Principle and Exergy Destruction

- The decrease in exergy principle is applicable to any kind of system undergoing any kind of process since the system and its surroundings can be enclosed by a sufficiently large arbitrary boundary across which there can be no heat, work and mass transfer. So the system and surroundings constitute an isolated system.
- The decrease in exergy principle does not imply that the exergy of a system can not increase. It can be positive or negative during a process. But the exergy destroyed can not be negative.

$$X_2 - X_1 = -T_0 S_{gen} \geq 0$$

$$\Delta X_{isolated} = (X_2 - X_1)_{isolated} \leq 0$$

$$X_{destroyed} = T_0 S_{gen} \geq 0$$

Reversible process: $X_{destroyed} = 0$

Irreversible process: $X_{destroyed} > 0$

Impossible process: $X_{destroyed} < 0$

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So, we call as a exergy principle or exergy destructions, this is the just opposite statement of entropy principle. The decrease in exergy principle is applicable for any kind of system undergoing a process since the system and its surroundings can be enclosed by sufficiently large arbitrary boundary across which there can be no heat or work transfer. So, such a system constitute an isolated system.

And the decrease in the exergy of principle does not imply that exergy of a system cannot increase. It can be positive or negative during a process. But exergy destroyed cannot be negative. So, it is a positive quantity. So, from this, the exergy principle tells that change in the exergy that is $X_2 - X_1 = -T_0 S_{gen} \geq 0$ and this $\Delta X_{isolated} = (X_2 - X_1)_{isolated} \leq 0$.

So, in other words, we can say this particular difference as $T_0 S_{gen}$, S_{gen} is always a positive quantity; so, exergy destroyed is always greater than or equal to 0. Now, in a reversible process exergy destroyed is equal to 0; Irreversible process, exergy destroyed is greater than 0 and for an impossible process, exergy destroyed is less than 0. This is just opposite statement of entropy.

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Second Law Efficiency

- Thermal efficiency and Coefficient of performance are the measure of indicative measures for heat engines and refrigerators. Many a times, they are referred as "first law efficiency".
- A realistic quantification is to define "second law efficiency" which is the ratio of actual efficiency to the maximum (reversible) possible efficiency under same operating condition.

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The last or most important segment of this exergy is to discuss about the second law efficiency. Now, when you deal with the efficiency by taking the first law, many a times we call this as a first law efficiency that point of time you talk about either heat engine or refrigerator.

Now, when you define this efficiency, first category of efficiency we define that when certain quantity of heat is extracted from a source, and based on which some quantity heat is rejected to the sink and out of which we get work transfer. So, from this we say efficiency of the heat engine is W_{out}/Q_{in} , this is the first aspect.

Now, if such a system is reversible process, then the heat and work has no role; so, we can say the limiting case is put by Carnot efficiency that is efficiency of the Carnot cycle becomes $1 - \frac{T_2}{T_1}$ where T_2 is the sink temperature and T_1 is the source temperature. Now, this is with respect to a particular engine.

Now, let us say that we are going to compare two engines A and B, both are operating at same sink temperature and, but the source temperature is different that is one is operating at source temperature of 600K other is the 1000K. So, from this, we can calculate that for engine A, based on the things that actual efficiency is 30%, but maximum possible efficiency or reversible efficiency that we can find out which is Carnot efficiency which is about 50%.

But when we are dealing with engine B, the actual efficiency is 30%, but the reversible efficiency is 70%. Now, the question is that which is a better engines? And of course, the source temperature are different and this is at higher energy potential, but this is at lower energy potential. So, to overcome this, we define a second law efficiency which is a realistic quantification which is defined as the actual efficiency of the engine to this reversible efficiency.

So, for the first engine, we can calculate the reversible second law efficiency as 60% whereas, the second engine the second law efficiency is 100%, in that case, we say that the engine B is more efficient than engine A and that means, it is performing close to a value of its potential whereas, engine A has potential, but it is not performing to its best possible efficiency value.

So, this is the way we say the quantification of second law efficiency as the ratio of actual efficiency to the maximum possible efficiency under same operating conditions.

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Second Law Efficiency

- Second law efficiency is also expressed as the ratio of useful work output to the maximum (reversible) work output.
- A more general description of second law efficiency is the ratio of exergy recovered to the exergy supplied during a process.
- For heat engines, the exergy supplied is the decrease in exergy of heat transferred to the engine (difference between exergy of heat supplied and exergy of heat rejected). But, the exergy of heat rejected at surrounding temperature is zero. So, the net work output is the recovered exergy.
- For refrigerator or heat pump, the exergy supplied is the work input. In heat pump, the recovered exergy is the exergy of heat transferred to the high temperature medium. In refrigerator, it is exergy of heat transferred to low temperature medium.

Heat engine (work producing device): $\eta_2 = \frac{W}{Q_{in}}$ & $\eta_1 = \frac{W}{W_{rev}}$

Refrigerators and Heat pumps (work consuming device): $\eta_2 = \frac{COP}{COP_{rev}}$ & $\eta_1 = \frac{W_{rev}}{W}$

$$\eta_2 = \frac{X_{recovered}}{X_{supplied}} = 1 - \frac{X_{rejected}}{X_{supplied}}$$

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So, there are many ways that we define the second law efficiency. So, after considering the exergy, after considering the work transfer, there are many expressions one can device these things. For heat engines, we can define the second law efficiency in two manners, one is efficiency of actual engine to the reversible efficiency other way of representing is that actual work or useful work to the reversible work.

So, for work consuming device, we can represent the second law efficiency as actual COP to the reversible COP or ratio of reversible work to the useful work. And in terms of exergy, we can also define the second law efficiency as exergy recovered to the

exergy supplied that is $1 - \frac{X_{destroyed}}{X_{supplied}}$ and this is the way we define the second law efficiency.

So, first statement says that it is useful work output to the maximum work output. It is the exergy recovered to the exergy supplied during a process and for a heat engines, the exergy supplied is nothing, but the decrease in the exergy transferred to the engines. But in refrigerator and heat pump, heat supplied is the work input.

So, for heat pump, recovered exergy is nothing, but exergy transferred to the high temperature medium and for refrigerator, exergy transferred is nothing, but the heat transfer to the low temperature medium.

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Numerical Problems

Q1. A heat source at 530°C loses 2 kJ of heat to sink. Determine the heat transfer process which is more irreversible: (a) sink at 230°C; (b) sink at 480°C.

$$\text{Case-I } (\Delta S)_I = (\Delta S)_{H1} + (\Delta S)_{Sink}$$

$$= -\frac{Q}{T_H} + \frac{Q}{T_{L1}}$$

$$= -\frac{2000}{803} + \frac{2000}{503} = 1.48 \text{ J/kg.K}$$

$$\text{Case-II } (\Delta S)_{II} = -\frac{Q}{T_H} + \frac{Q}{T_{L2}}$$

$$= -\frac{2000}{803} + \frac{2000}{753} = 0.16 \text{ J/kg.K}$$

$$(\Delta S)_{II} < (\Delta S)_I \Rightarrow \text{Case-II} \rightarrow \text{More irreversible}$$

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So, with this, we conclude all the contents of the module 1. Now, towards the end of this we are going to solve few numericals. So, the first numerical problem is about the entropy. So, here the question that is given that we have a heat source which is available at 530°C and it ejects 2kJ of heat and there are two situations; case I and case II where the sink is at one case is 230°C and other case is 480°C.

Now, question is which process is more reversible, case I or case II? So, to start with, the first thing that we are going to do is you have to represent all the temperatures into Kelvin. So, T_h is becomes 803K and for the case I, T_1 is 503K and for case-2, T_1 is 753K. So, let us calculate one by one what is the heat transfer during the process.

So, first thing you have to calculate the total entropy. So, for case I, we have to calculate

$$(\Delta s)_I = (\Delta s)_{sys} + (\Delta s)_{surr} = \frac{-Q}{T_h} + \frac{Q}{T_{I1}} = \frac{-2000}{803} + \frac{2000}{503} = 1.48 \text{ J/kg-K} \cdot$$

And for case II, we can write $(\Delta s)_{II} = \frac{-Q}{T_h} + \frac{Q}{T_{I2}} = \frac{-2000}{803} + \frac{2000}{753} = 0.16 \text{ J/kg-K} \cdot$

So, what we have found is $(\Delta s)_{II} < (\Delta s)_I$. So, this means entropy change in the second process is less. So, this means case I is more irreversible. So, this is how we quantify the nature of irreversibility occurring in a process.

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Numerical Problems

Q2. A piston-cylinder device contains 0.03 kg of steam at 1 MPa and 300°C. Steam expands to final state of 0.2 MPa and 150°C. by doing work. Heat losses to the surroundings is 1.2 kJ. Determine, (a) the exergy of the steam at the initial and final state; (b) exergy change of the steam; (c) exergy destroyed; (c) second law efficiency.

Ans

State-1 $\rightarrow P_1 = 1 \text{ MPa}, 300^\circ\text{C}$ Steam $\rightarrow u_1 = 2793.2 \text{ kJ/kg}, u_1 = 0.2579 \text{ m}^3/\text{kg}, s_1 = 7.1239 \text{ kJ/kg}\cdot\text{K}$

State-2 $\rightarrow P_2 = 0.2 \text{ MPa}, 150^\circ\text{C}$ Steam $\rightarrow u_2 = 2576.9 \text{ kJ/kg}, u_2 = 0.9596 \text{ m}^3/\text{kg}, s_2 = 7.2740 \text{ kJ/kg}\cdot\text{K}$

Environment $\rightarrow T_0 = 300 \text{ K}, u_0 = 104.88 \text{ kJ/kg}\cdot\text{K}, s_0 = 0.001 \text{ m}^3/\text{kg}\cdot\text{K}, s_0 = 0.3674 \text{ kJ/kg}\cdot\text{K}$

(a) $X_1 = m [(u_1 - u_0) - T_0 (s_1 - s_0) + P_0 (v_1 - v_0)] \quad m = 0.03 \text{ kg}$
 $\Rightarrow X_1 = 21 \text{ kJ}$
 $X_2 = 15.24 \text{ kJ}$

(b) $\Delta X = X_2 - X_1 = 5.76 \text{ kJ}$
 $X_{destroyed} = (X_1 - X_2) - W_{k} = 0.46 \text{ kJ}$

(c) $\eta_2 = \frac{W_k}{X_1 - P_0} = \frac{5.3}{5.76} = 92\%$

(d) $Q - W = \Delta U \Rightarrow W = Q - \Delta U$
 $W_k = -P_0 - m(u_2 - u_1)$
 $\Rightarrow W_k = 5.3 \text{ kJ}$

The second problem we are dealing with exergy. So, here, we are talking about a situation piston cylinder device that contains certain quantity of steam that is 0.03 kg of steam at 1MPa and 300°C. Now, this steam goes to final state 0.2MPa and 150°C by doing work that means, there is a work transfer and during this process, heat is lost to the surroundings is 1.2kJ.

So, you have to find out the exergy of the steam of the initial and final state, exergy change of the system, exergy destroyed and second law efficiency. So, in fact, here we have to involve two things, one is the first law we have to calculate, second thing that is most important is that we have to calculate the property value of the steam at the states. So, the property value of state 1, state 2 and since it is a exergy transfer, you have to look into environment. So, before you start the solutions, first thing you have to do state 1, state 2 and environment. So, these properties we are going to look at. So, the state 1 is p_1 1MPa and 300°C steam. So, we have to use super-heated steam table to find its property. So, those values can be noted and since it is a piston cylinder device so, it is a closed system; so, we have to concentrate on internal energy.

So, we can note down this internal energy value from the super-heated steam table u_1 as 2793.2 kJ/kg and specific volume v_1 which is 0.2579 m³/kg, we also require entropy s_1 is 7.1229 kJ/kg-K and similarly for the final state that is p_2 0.2MPa and 150°C steam. So, we can find out u_2 as 2576.9 kJ/kg, v_2 as 0.9596 m³/kg, s_2 is 7.2795 kJ/kg-K.

And environment, here we have to make an assumption as if that environment is p_0 as 100 kPa and T_0 as 300K. So, if although it is not in the data so, this is the realistic approximation we can take and we say it is a dead state. So, under this dead state, we can find out u_0 as 104.88 kJ/kg, v_0 as 0.001 m³/kg, s_0 that is entropy at dead state 0.3674 kJ/kg-K. So, once we know this data, let us answer the question one by one.

First question, initial state exergy and final state exergy. So, by definition, we can write $X_1 = m[(u_1 - u_0) + p_0(v_1 - v_0) - T_0(s_1 - s_0)]$. So, here m is given as 0.03 kg. So, by putting this numerical value, we can find out X_1 as 21kJ and similarly, $X_2 = m[(u_2 - u_0) + p_0(v_2 - v_0) - T_0(s_2 - s_0)]$, we can calculate X_2 as 15.24kJ. So, the first question it is answered, initial state and final state.

Second question exergy change, exergy change means $\Delta X = X_2 - X_1$ that is 5.76 kJ. The next thing exergy destroyed. So, exergy destroyed means you also say that it is doing work. So, you have to take work transfer into account. So, here, you have to involve the first law. So, by first law, we can write $Q - W = \Delta U$. So, from this, we can find out what is W .

So, here I will represent this W as W_u that is useful work. Here heat is lost so,
 $w_u = -1.2 - m(u_2 - u_1) \Rightarrow w_u = 5.3\text{kJ}$.

So, from this, we can find out $X_{Destroyed} = (X_1 - X_2) - w_u = 0.46\text{kJ}$. The last part of this answer which is second law efficiency that is nothing but $\eta = \frac{w_u}{X_1 - X_2} = 92\%$, So, second law efficiency is 92% that means, the process is close to a reversible process.

If the second law efficiency is 100%, it is a completely reversible process. So, with this, I conclude for discussion today, thank you for your attention and from the next session onwards, we will go to another module and we complete the module 1 that is first module of this course applied thermodynamics.

Thank you for your attention.