Introduction to Aerospace Propulsion

Prof. Bhaskar Roy
Prof. A.M.Pradeep
Department of Aerospace Engineering
Indian Institute of Technology, Bombay

Module No. # 01
Lecture No. # 12

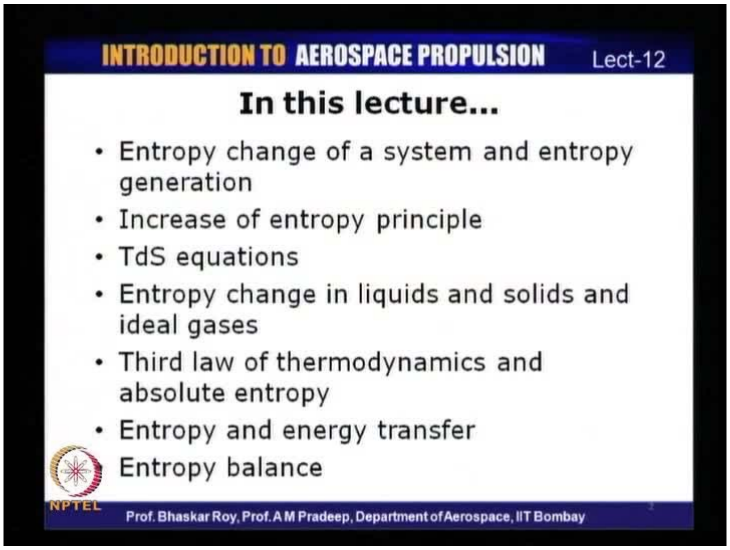
Increase of entropy principle, third law of thermodynamics, absolute entropy, perpetual motion machines

Hello and welcome to lecture 12 of this lecture series on Introduction to Aerospace Propulsion. We have been, over the last several lectures, understanding some basic concepts of thermodynamics and we have already got an introduction to the zeorth law, the first law and the second law of thermodynamics.

We shall continue our journey in understanding thermodynamics and basic concepts of thermodynamics. Because, as I have mentioned several times, thermodynamics is a very fundamental subject that forms an important aspect of analysis of engineering systems which involve heat and work.

As aerospace engineers we are always interested in trying to maximize performance of, for example, an aircraft or an engine for that matter. So, in order that we understand how we can improve the efficiency of many of these systems, it is important for us to understand the basic concepts or basic principles underlying the performance or the operation of these engineering systems.

(Refer Slide Time: 01:53)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

In this lecture...

- Entropy change of a system and entropy generation
- Increase of entropy principle
- TdS equations
- Entropy change in liquids and solids and ideal gases
- Third law of thermodynamics and absolute entropy
- Entropy and energy transfer
- Entropy balance

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

In the lecture we were discussing the second law of thermodynamics and entropy as a consequence of the second law of thermodynamics.

Today we shall discuss a little further about entropy. Also we shall explore what the third law of thermodynamics is, which is again a consequence of entropy.

So what we shall discuss in today’s lecture is the following: we shall begin our lecture today with discussion on entropy change for a system, as well as we shall discuss what is known as entropy generation.

Then we shall discuss increase of entropy principle. Then we shall derive two equations which are very important, which shall help us in determining entropy change for a given process. These are: the TdS, that is, temperature differential change in entropy equations-TdS equations, then we shall derive expressions for entropy change in liquids and solids as well as entropy change for ideal gases.

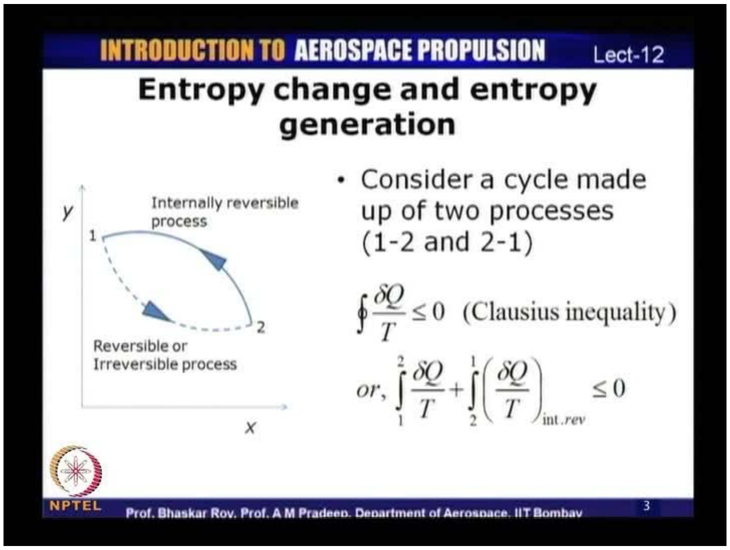
Subsequently, we shall be discussing the third law of thermodynamics and absolute entropy. Then we shall talk about entropy and energy transfer, what the significance of entropy is and energy transfer of a certain process. Towards the end of the lecture we shall discuss what is known as entropy balance. So these are some of the aspects. As you can see, they are all related to entropy and I think I mentioned in the last lecture that entropy is a very basic concept and obviously a very important concept in the understanding of performance of systems, and entropy is one parameter which helps us in identifying whether a certain process is feasible or not.

So in today's lecture, we shall try to look at how we can use entropy to analyze a certain system and a certain process, and how entropy helps us in understanding whether a certain process is possible or not or how is it that we can improve the performance of a certain system.

We will begin our lecture here today with a discussion about entropy change as well as entropy generation for a certain system. Now, in the last lecture, if you recall, we had discussed the Clausius statement. Clausius statement was basically on the Clausius theorem, which states that the cyclic integral of dQ by T should be greater than or equal to 0.

In the last lecture we were discussing the Clausius inequality; the Clausius inequality is basically a statement which states that, or you can actually derive it for any process, the cyclic integral of dQ by T is less than or equal to 0.

(Refer Slide Time: 04:49)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy change and entropy generation

- Consider a cycle made up of two processes (1-2 and 2-1)

$$\oint \frac{\delta Q}{T} \le 0 \quad \text{(Clausius inequality)}$$

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

NPTEL Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

We shall take this a little further and find out that how you can generalize it for a certain process. If you recall, I had mentioned that Clausius inequality is valid for any process whether it is reversible or irreversible and so on. So the equality of cyclic integral dQ by T is valid only if the process is reversible, for all other processes it is the inequality which holds. Let us take a look at a certain process, which is what I have represented here. Now, in this process, which is plotted in terms of some co-ordinates x and y which could be pressure, volume, temperature entropy or so on.

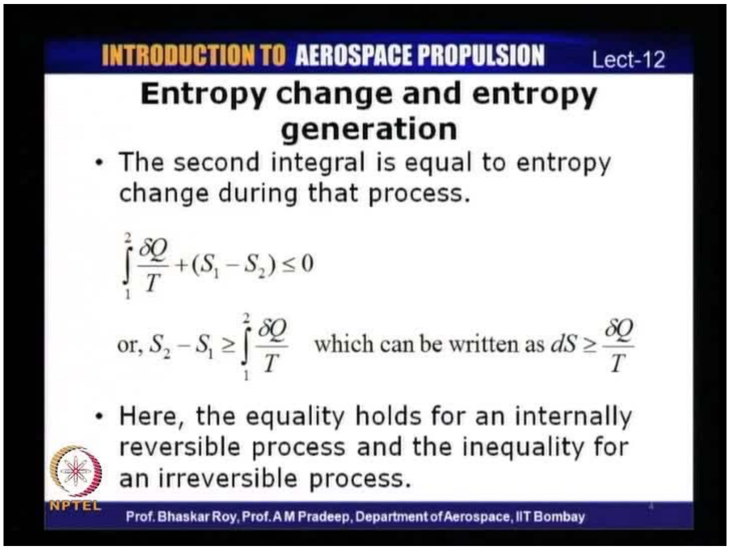
Let us look at two different processes here, which occur from state 1 state 2.

The first process, let us say, is from state 1 to state 2. It could be either a reversible process or it could be any irreversible process and as a system goes from state 2 to state 1 it is an internally reversible process.

So here we have a cycle which consists of two processes- 1 - 2, 2 - 1. Which is which could be any process- a general process, a reversible or it could be irreversible.

Process 2 - 1 is an internally reversible process. As I mentioned about Clausius inequality, the cyclic integral of dQ by T for this particular cycle should be less than or equal to 0. Or, if you were to cyclic integral we have integral 1 to 2 dQ by T, which is for the general process plus integral 2 to 1 for dQ by T for the internally reversible process. So this, according to the Clausius inequality, should be less than or equal to 0.

(Refer Slide Time: 06:11)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy change and entropy generation

- The second integral is equal to entropy change during that process.

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

or, $S_2 - S_1 \ge \int_1^2 \frac{\delta Q}{T}$ which can be written as $dS \ge \frac{\delta Q}{T}$

- Here, the equality holds for an internally reversible process and the inequality for an irreversible process.

NPTEL

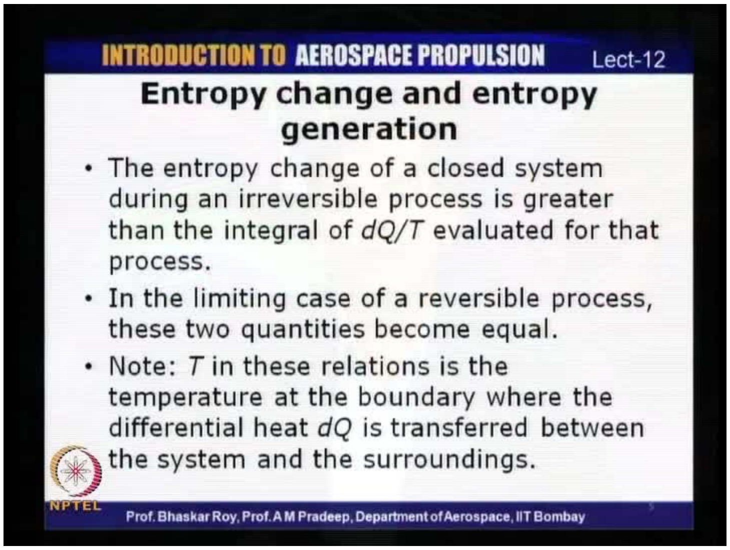
Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

This second integral that we see here is applicable for an internally reversible process. In the last lecture, I had also mentioned that for an internally reversible process, integral dQ by T should be equal to the change in entropy. So integral 1 to 2 dQ by T plus S 2 minus S 1 or S 1 minus S 2 as in this case, should be less than or equal to 0 because the final state is S 1. For the second process, or we can express this as S 2 minus S 1 is greater than or equal to integral 1 to 2 dQ by T. Or in general terms dS is greater than or equal to delta Q by T.

Here we have an expression, which states that the change in entropy for any process will always be greater than or equal to dQ by T.

These equalities and those you see here will be valid only if the process is internally reversible; for all other processes the inequalities sign will be valid. So dQ by T, which is the ratio of the change in heat transfer to the temperature at which the heat transfer is occurring, is always less than or equal to the increase or change in entropy. So, dS is greater than or equal to delta Q by T is an expression which is valid for all processes. If you consider an internally reversible process, then, it is the equality which is valid. That is- dS change in entropy will be equal to dQ by T. For all other processes it is the inequality which is valid. So, for all processes in general we can write that the change in entropy will be greater than or equal to dQ by T.

(Refer Slide Time: 08:51)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy change and entropy generation

- The entropy change of a closed system during an irreversible process is greater than the integral of dQ/T evaluated for that process.
- In the limiting case of a reversible process, these two quantities become equal.
- Note: T in these relations is the temperature at the boundary where the differential heat dQ is transferred between the system and the surroundings.

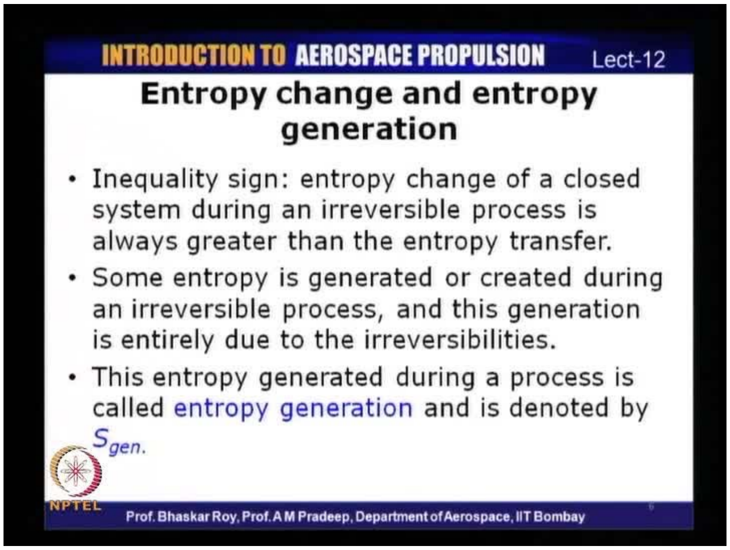
NPTEL

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

This is a general expression, which is valid for any process whether it is a reversible process or it is an irreversible process and so on. As a consequence of this we can see that for an irreversible process what happens to this increase in entropy that we see that across any process. If you have dQ by T the dS is always greater than dQ by T; which means that there is a certain amount of additional entropy which is getting formed as the process proceeds. We will understand now, what this additional entropy is that we are talking about. We will very soon name this as what is known as the entropy generation.

So entropy change during an irreversible process, especially if it is a close system, is always greater than the integral of dQ by T, which is evaluated for that particular process.

(Refer Slide Time: 09:46)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy change and entropy generation

- Inequality sign: entropy change of a closed system during an irreversible process is always greater than the entropy transfer.
- Some entropy is generated or created during an irreversible process, and this generation is entirely due to the irreversibilities.
- This entropy generated during a process is called entropy generation and is denoted by S_{gen}.

NPTEL

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

So the limiting case of this is a reversible process. a reversible process is during a reversible process this the equality sign will be evaluate that dS will be equal to dQ by T

This equality is valid only if the process is a reversible process. Now, I mentioned that this dQ by T- the temperature that we talked about- in this, dQ by T is basically referring to the temperature at the boundary where this differential heat is getting transferred between the system and the surroundings. So the temperature that we referred to in dQ by T is basically the temperature at the boundary, that is, where the differential heat transfer delta Q or dQ is transferred between the system and the surroundings.

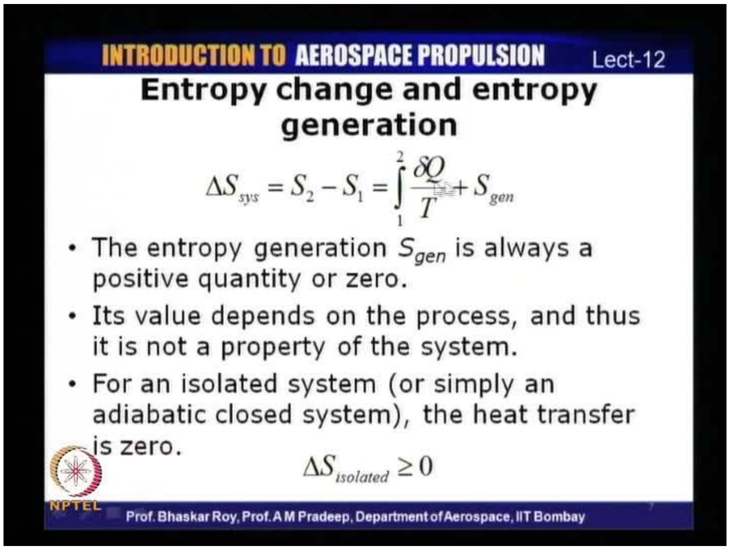
So, dQ by T is basically valid for that particular process wherein entropy heat transfer takes place between the system boundaries and the surroundings.

Now, as regards the inequality sign for an irreversible process, the entropy change is always greater than the entropy transfer. It means that there is always a certain amount of entropy which is getting generated or getting created during an irreversible process; this is primarily because of the irreversibilities in a process.

We have already discussed about irreversibilities that can take place, in the last lecture. Like irreversibility dot due to friction, reversible due to heat transfer between finite temperatures and so on.

So all these irreversibilities put together or one or more of these irreversibilities might occur during a certain process. It is these irreversibilities that lead to an additional creation or generation of entropy.

(Refer Slide Time: 11:45)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy change and entropy generation

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

- The entropy generation S_{gen} is always a positive quantity or zero.
- Its value depends on the process, and thus it is not a property of the system.
- For an isolated system (or simply an adiabatic closed system), the heat transfer is zero.

$$\Delta S_{isolated} \geq 0$$

NPTEL

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

So this generation of entropy, which takes place during a process is known as entropy generation. It is usually denoted by symbol S subscript gen, which means entropy generation.

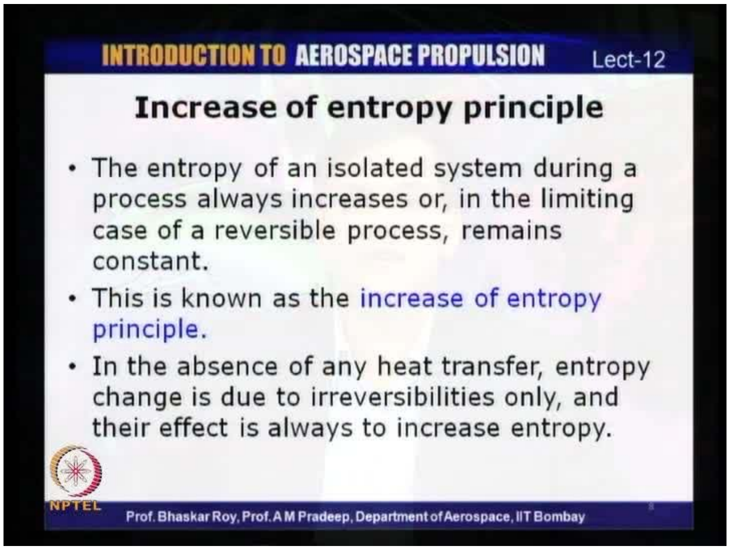
So for any real life processes we will always have or if there some amount of irreversibilities that we have discussed and. So irreversibilities always accompany, or any irreversibility in a process will always be accompanied by, some amount of entropy generation; which is the reason why for an irreversible process there is always a certain amount of en entropy generation. That is the reason for the inequality- that delta S will be greater than delta Q by T. This inequality is what leads to the generation of entropy. It expresses it in the form of an equation: delta S, that is, the delta S of the system is equal to S 2 minus S 1, that is, change in entropy which is equal to integral 1 to 2 delta Q by T plus term, which is the entropy generation S gen.

So entropy generation is always a positive quantity for irreversible processes and it can become 0 only if the process is reversible. Which means that, for all real life problems or for all real life processes which are irreversible in nature, there is always a certain amount of entropy generation coming as part of the process itself.

And the value of this entropy generation depends upon the process itself; it is not a property of a system. So it is very important to understand here, that entropy generation is not a point function. It depends upon the type of process and the nature of the process; therefore, it is a path function. It depends upon how the process takes place.

If you look at an isolated system, for example, an isolated system is one which has no interaction between the system and the surroundings, which means that it has to be an adiabatic closed system- then the heat transfer is 0. We know that across an adiabatic system there is no heat transfer, so heat transfer being 0 the delta S, that is, change in entropy for the isolated system is greater than or equal to 0. So, for an isolated system, which we shall look at little later as well, there is always a certain amount of entropy generation that accompanies the process itself. So when we consider the entropy generation during a certain process it is that for all real life processes that we are familiar with that is always a certain amount of entropy gen that is generated during the process

(Refer Slide Time: 14:43)



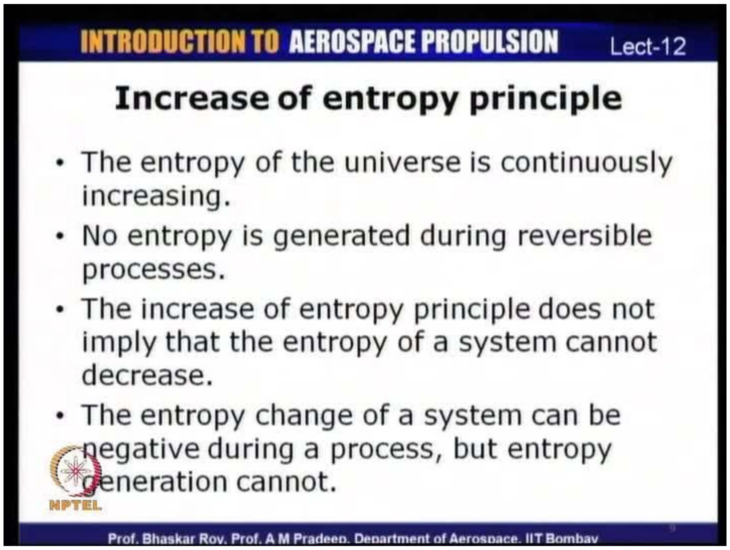
INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Increase of entropy principle

- The entropy of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant.
- This is known as the increase of entropy principle.
- In the absence of any heat transfer, entropy change is due to irreversibilities only, and their effect is always to increase entropy.

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

(Refer Slide Time: 18:27)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Increase of entropy principle

- The entropy of the universe is continuously increasing.
- No entropy is generated during reversible processes.
- The increase of entropy principle does not imply that the entropy of a system cannot decrease.
- The entropy change of a system can be negative during a process, but entropy generation cannot.

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

As I mentioned, this entropy generation depends upon the nature of the process itself; it is definitely not dependent on the initial and final state alone. So, entropy generation being a function of the nature of the process, it definitely qualifies to be called a path function. It depends upon the nature of the process; all real life processes will involve certain amount of creation of entropy. It is important for us to understand that entropy generation is accompanied by or is a byproduct of any real life process. For any real life processes we encounter on a day-to-day basis, there is always a certain amount of entropy increase or entropy generation that should be part of all the real life processes. Which means that there is always a certain amount of entropy that is getting generated.

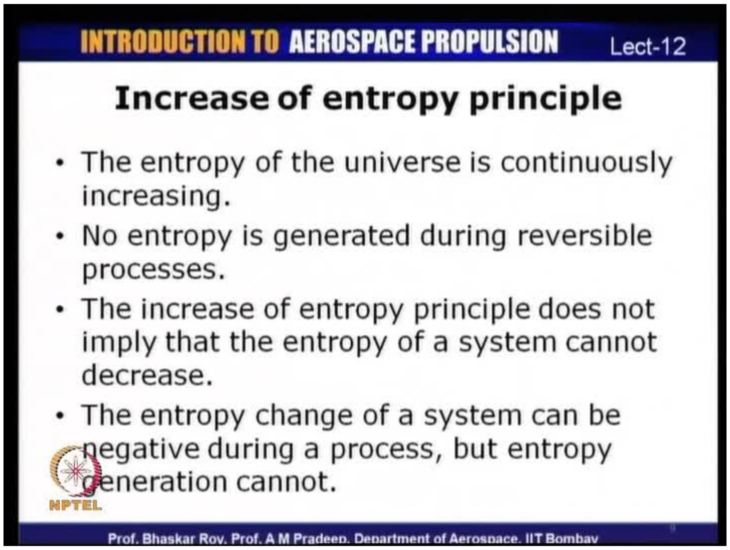
So, if you look at the whole universe as an isolated system, then the entropy of an isolated system will always increase and only in the case of reversible process will it remain constant. This means that there is always a certain increase in the entropy of an isolated system. So the universe as a whole constitutes an isolated system; which means that there is always a continuous increase in the entropy of the universe, and this is basically known as the increase of entropy principle.

So increase of entropy principle is valid for all the irreversible processes. The only limiting case is that of a reversible process, which obviously is an idealized process wherein the entropy remains a constant. In the absence of any heat transfer, entropy changes basically only due to irreversibilities because of friction or surface tension.

another effects So all these irreversibilities basically lead to entropy change if there is no heat transfer and the effect of irreversibility is always to increase the entropy; so irreversibilities will always cause an increase in entropy.

The entropy of an isolated system as we have just seen- it increases. Or, the only limiting case of this is that entropy can be constant. The change of an entropy can be constant only for a reversible process. For an isolated system the entropy, if the system consists of irreversible processes, will always increase. If you consider the whole universe as an isolated system this means that the entropy of the universe is continuously increasing. Because we come across so many irreversible processes, in fact all the processes that we are aware of are irreversible, because of the presence of irreversibilities. Therefore, there is an entropy generation associated with any irreversible process; this means that the entropy- the change in entropy- of an irreversible process always increases. If the universe is to be considered as an isolated system, entropy of the universe is continuously increasing and this is what is known as the increase of entropy principle.

(Refer Slide Time: 18:27)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Increase of entropy principle

- The entropy of the universe is continuously increasing.
- No entropy is generated during reversible processes.
- The increase of entropy principle does not imply that the entropy of a system cannot decrease.
- The entropy change of a system can be negative during a process, but entropy generation cannot.

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

Now, if you look at a process where there is no heat transfer, it means that the only reason for increase of entropy during this particular process would be other irreversibilities, like friction or surface tension and so on. So, in the absence of heat transfer during a certain process, entropy increases due to the presence of other irreversibilities, which accompany normal day-to-day processes.

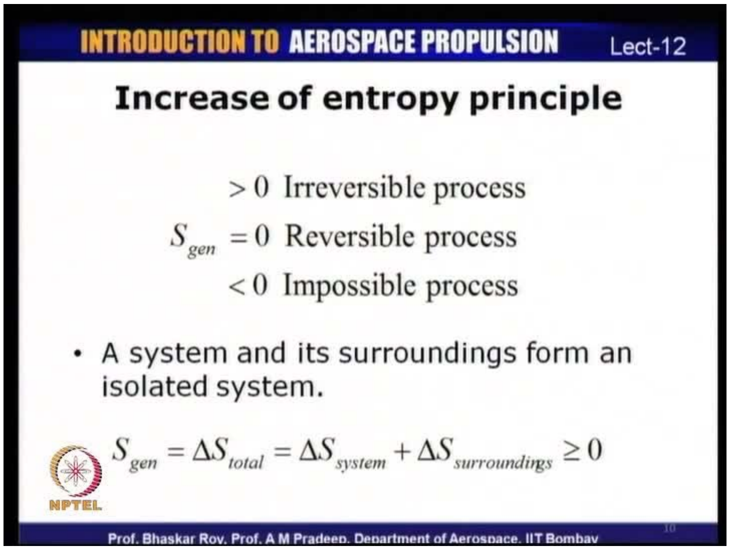
Increase of entropy principle basically states that, if you consider an isolated system because of the presence of irreversibilities within the isolated system, the change in entropy is always greater than 0 or there is always an increase in entropy during such processes.

As I mentioned, because if you can actually consider the whole universe as an isolated system, which is basically not interacting with any other system, the entropy as per the increase of entropy principle, it would mean that the entropy of the universe is continuously increasing. And during a reversible process, we have seen that there is no change in entropy; or the entropy remains a constant during a reversible process. So, there is no increase in entropy associated with a reversible process. But, as all the real life processes are irreversible in nature, there is always a certain amount of entropy that is generated during these processes.

A consequence of the entropy principle is that entropy of an isolated system will always increase. But this does not mean that entropy of a system cannot decrease. Well, entropy of a system can definitely decrease, but it has to be compensated for by a corresponding increase in entropy during some of that part of the system interaction with the surroundings. In fact, the increase in entropy during that particular interaction would be greater than the decrease in entropy of that particular system.

Entropy generation basically is what is being implied by the increase of entropy principle; that, it cannot be negative. It means that, though entropy change can be negative during a certain process, entropy generation can never be a positive quantity. So there is always entropy generation associated with all irreversible or real life processes. Increase of entropy principle implies that you can always have certain processes wherein there is a certain decrease in entropy locally, but there has to be a corresponding increase- in fact a greater increase- in entropy elsewhere; so that there is a net increase in entropy during that particular process. So, to summarize this entropy generation or increase in entropy principle, basically, increase in entropy principle states that entropy generation or S gen is greater than 0 for irreversible processes; entropy generation S gen will be equal to 0 for reversible processes; an entropy generation less than 0 implies that particular process is impossible or infeasible.

(Refer Slide Time: 20:30)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Increase of entropy principle

$$S_{gen} \begin{cases} > 0 & \text{Irreversible process} \\ = 0 & \text{Reversible process} \\ < 0 & \text{Impossible process} \end{cases}$$

- A system and its surroundings form an isolated system.

$$S_{gen} = \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$

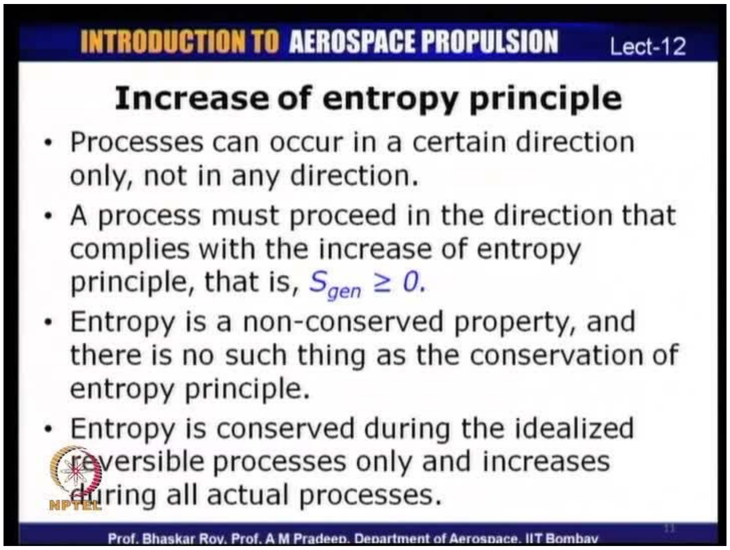
Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

10

So, entropy generation less than 0 implies the infeasibility of a particular process, entropy generation equal to 0 is basically valid only for reversible processes and an entropy generation greater than 0 is what is valid for all real life processes or irreversible processes.

If you consider a system and it surroundings put together, you can actually form an isolated system by considering the part of the surroundings which are close to the system. So, system plus the immediate surroundings can actually be considered- are approximated as- an isolated system. For such a system, entropy generation is equal to the net change in entropy, which is basically equal to change in entropy of the system. Plus, change entropy of the surroundings can be greater than or equal to 0- this, as per the increase in entropy principle

(Refer Slide Time: 21:06)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Increase of entropy principle

- 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, $S_{gen} \geq 0$.
- Entropy is a non-conserved 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.

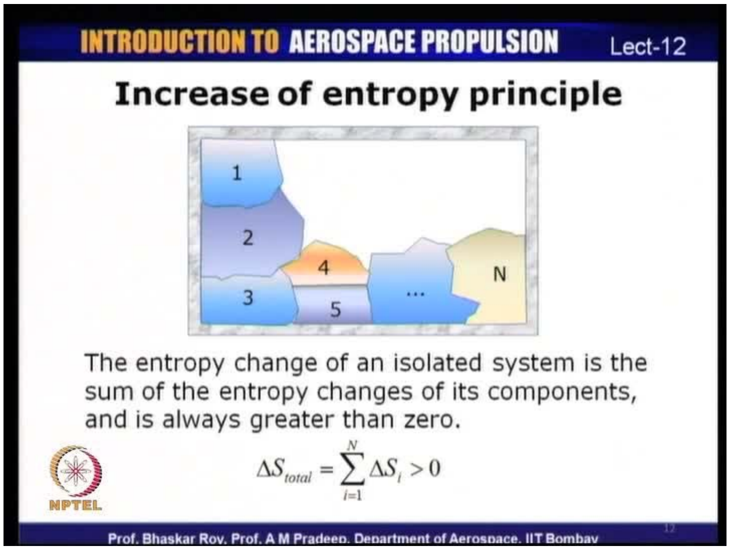
Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

Let us look at what the consequences of increase in entropy principle are. Basically, entropy principle states that: processes can occur only in a certain direction; it cannot occur in any arbitrary redirection, it can occur only in a direction which leads to an increase in the entropy generation. So processes must always proceed in that direction where the entropy generation is greater than or equal to 0; where the equality is only valid for reversible process. It means that, as a consequence of the increase of entropy principle, there is always an entropy generation which accompanies any reversible process.

Another interesting aspect is that, unlike energy, entropy is not a conserved property; which means, there is nothing like a conservation of entropy principle. Because entropy can be generated but it obviously cannot be destroyed for real life processes. So, there is always a creation or generation of entropy, unlike energy, which is a conserved quantity. You cannot create energy; you can only transfer energy from one form to another- entropy is something which is generated.

And the conservation of entropy is valid in struts sense only for idealized reversible processes. And for all actual processes there is an increase- a continuous increase- in entropy associated with irreversible processes.

(Refer Slide Time: 22:58)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Increase of entropy principle

The entropy change of an isolated system is the sum of the entropy changes of its components, and is always greater than zero.

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

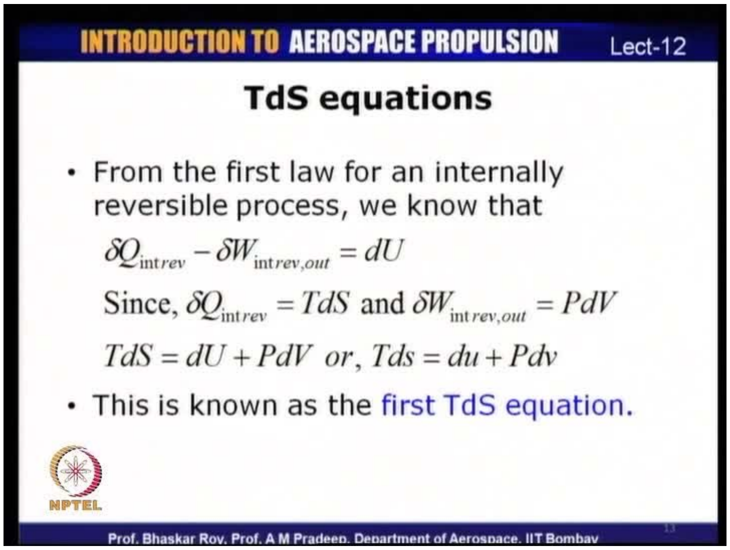
Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

So unlike energy- conservation of energy- principle, there is nothing like conservation of entropy principle because entropy is not a conserved quantity. It does not- well- it can actually be created during all actual or irreversible processes.

Now let us look at some examples of applying increase of entropy principle to a group of systems. So, what is shown here, enclosed within the walls of this particular system are several sub-systems. Let us say this is an isolated system. What you shown by this bounding box here, this isolates this particular system from the rest of the surroundings making it an isolated system.

This isolated system comprises of several sub systems, which are named 1, 2, 3, 4 and so on up to N. So there are N number of sub systems which constitute this isolated system. The net change in entropy of this entire system- this isolated system- will be equal to the net change in entropy of these individual systems; which means that, delta S total, that is, the entropy change of the entire isolated system will be equal to the summation i equal to 1 to N delta S of the individual systems. And each of them are, well, the total enthalpy or total entropy of this particular isolated system will be greater than 0; even though you may have certain systems within the isolated system which may have entropy decrease. But that will be compensated by an even more increase in entropy elsewhere, and as a consequence of this delta S of this particular isolated system will be always greater than 0. This again is as a consequence of the increase of entropy principle.

(Refer Slide Time: 24:40)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

TdS equations

- From the first law for an internally reversible process, we know that

$$\delta Q_{\text{int}\,rev} - \delta W_{\text{int}\,rev,out} = dU$$

$$\text{Since, } \delta Q_{\text{int}\,rev} = TdS \text{ and } \delta W_{\text{int}\,rev,out} = PdV$$

$$TdS = dU + PdV \;\; or,\; Tds = du + Pdv$$

- This is known as the first TdS equation.

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

We have been looking at entropy and increase of entropy principle as applied to an isolated system, reversible processes, irreversible processes and so on.

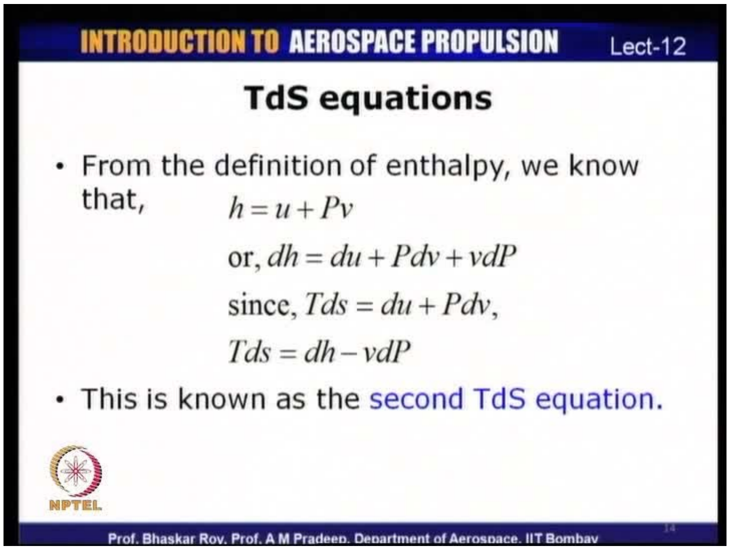
What we shall do now is to try and derive expressions for calculating entropy for different processes. We shall derive expressions for entropy change for liquids and solids, as well as entropy change for ideal gases. Before we do that, we need to understand or be familiar with what are known as TdS expressions or TdS equations- where T is the temperature, dS is change in entropy. Now TdS equations form the basis for deriving expressions for entropy change in solids and liquids as well as for ideal gases.

Now, to derive TdS equations, we will have to go to the first law of thermodynamics, apply that for a particular system, and then express the internal energy and enthalpy in terms of the corresponding properties of a particular system. So we can actually derive expressions in terms of the product of temperature and the change in entropy.

From the first law, as we are aware, that delta Q minus delta W is equal to dU.

Let us say the process is internally reversible; so delta Q internally reversible process minus delta W internally reversible out, that is, it means that work output is equal to dU. Now, for an internally reversible process, we are aware that delta Q internally reversible is equal to TdS because dS is dQ by T for internally reversible processes. Similarly, the work output delta W is equal PdV. So if you substitute these in the first equation- in the first law equation- we get TdS is equal to dU plus PdV or per unit mass; it can be expressed as T times ds which is in small s, which means entropy per unit mass is equal to change in internal energy per unit mass du plus p times dv, where v is the specific volume. So this is known as the first TdS equation

(Refer Slide Time: 27:37)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

TdS equations

- From the definition of enthalpy, we know that, $h = u + Pv$

  or, $dh = du + Pdv + vdP$

  since, $Tds = du + Pdv$,

  $Tds = dh - vdP$

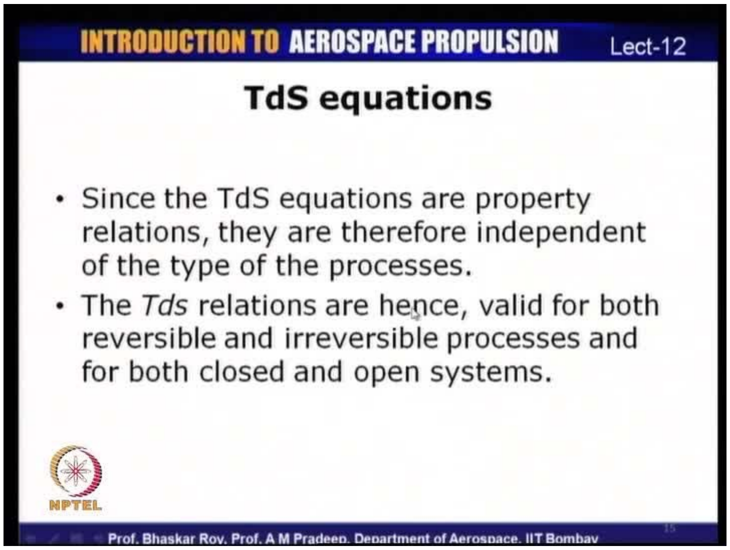
- This is known as the second TdS equation.

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay 14

So TdS equal to dU plus PdV is the first TdS equation. Similarly we can derive what is known as the second TdS equation, that is, if we substitute, instead of internal energy, we have enthalpy. An enthalpy, as we know, is u plus pv, so dh will be equal to du plus PdV plus vdP. So you can get an expression in terms of du is equal to dh minus vdP. So, that we will substitute in this first law expression and then we can derive what is known as the second TdS equation. Let us do that here. As enthalpy is a combination, property h is equal to u plus Pv, dh is equal to du plus Pdv plus vdP, and since we have already derived the first TdS equation- dS is equal to dU plus PdV, we can substitute for dU, that is, internal energy in terms of enthalpy. Therefore we get Tds is equal to dh minus vdP and this is known as the second TdS equation.

So the first TdS equation in terms of the internal energy, pressure and specific volume, the second TdS equation is in terms of enthalpy, specific volume and pressure; so TdS is equal to dU plus PdV is the first TdS equation and Tds is equal to dh minus vdP is the second TdS equation.

(Refer Slide Time: 28:48)



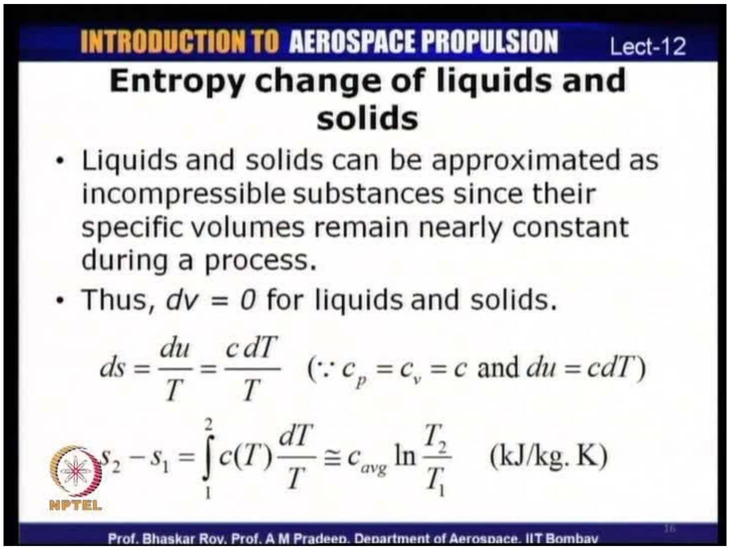
TdS equations

- Since the TdS equations are property relations, they are therefore independent of the type of the processes.
- The *Tds* relations are hence, valid for both reversible and irreversible processes and for both closed and open systems.

As you can see, both the TdS equations are in terms of properties of a system. First equation is in terms of internal energy, pressure and volume; second equation is in terms of enthalpy volume, well, specific volume and pressure which means, in TdS equations are themselves property relations; they are again independent of the nature of the processes and therefore it does not matter what type of process we are looking at. TdS equations are valid for all these processes; therefore, they are valid for both reversible and irreversible processes as well as for closed systems and open systems. So, TdS expressions or TdS equations are general equations which can be used, which are valid, for any process irrespective of whether they are reversible, irreversible, open systems or closed systems.

What we shall do now is derive expressions for the entropy change for liquids and solids as one component and separately for entropy change of ideal gases. We are considering liquids and solids in one group because of one property; both liquids and solids can be approximated or are considered incompressible. Since they are incompressible, there is no change in the specific volume- dv will be equal to 0. We will use that property in deriving expression for change in entropy for liquids and solids.

(Refer Slide Time: 30:08)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy change of liquids and solids

- Liquids and solids can be approximated as incompressible substances since their specific volumes remain nearly constant during a process.
- Thus, *dv* = *0* for liquids and solids.

$$ds = \frac{du}{T} = \frac{c\,dT}{T} \quad (\because c_p = c_v = c \text{ and } du = c dT)$$

$$s_2 - s_1 = \int_1^2 c(T)\frac{dT}{T} \cong c_{avg} \ln\frac{T_2}{T_1} \quad (\text{kJ/kg. K})$$

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

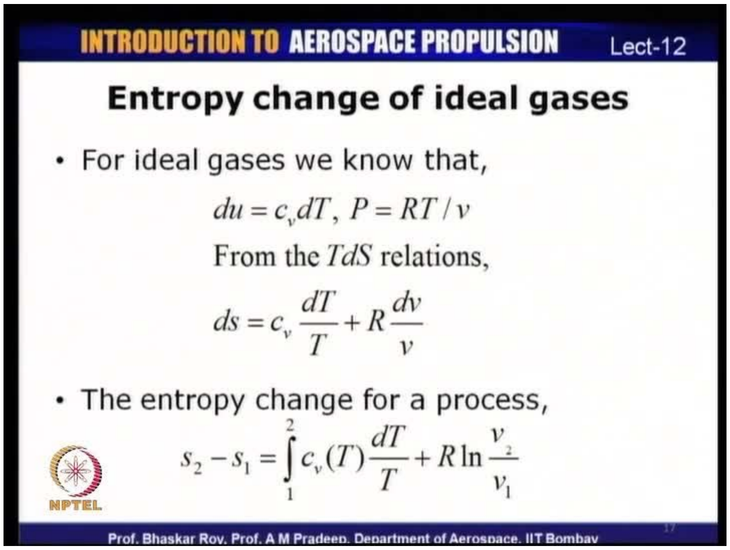
16

If you look at liquids and solids, we know that the change in specific volume is 0 because we can approximate liquids and solids as incompressible substances.

Since dv is equal to 0, we have change in entropy ds is equal to du by T- this is again coming from the TdS equations. TdS was du plus PdV and dv is equal to 0, therefore TdS is equal to du or ds is equal to du by T which is again equal to cdT by T; for liquids and solids the specific heat at constant pressure and specific heat at constant volume are the same- c p is equal c v which is equal to c.

Therefore, du is equal to cdT. Therefore, if you were to integrate entropy change for a process, s 2 minus s 1 will be equal to integral 1 to 2 c of T because c is a function of temperature dT by T, and in most of the common applications we would assume an average specific heat between temperatures T 1 and T 2. So this can be approximated as c average log T 2 by T 1 where c average is the average specific heat for this particular process between the temperatures T 1 and T 2. Therefore, entropy change which involves liquids and solids will be during a particular process is equal to the product of the average specific heat during that process multiplied by log of T 2 by T 1, which is again in kilo joules per kilo gram kelvin because it is entropy per unit mass.

(Refer Slide Time: 32:04)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy change of ideal gases

- For ideal gases we know that,

$$du = c_v dT, \; P = RT/v$$

From the TdS relations,

$$ds = c_v \frac{dT}{T} + R\frac{dv}{v}$$

- The entropy change for a process,

$$s_2 - s_1 = \int_1^2 c_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1}$$

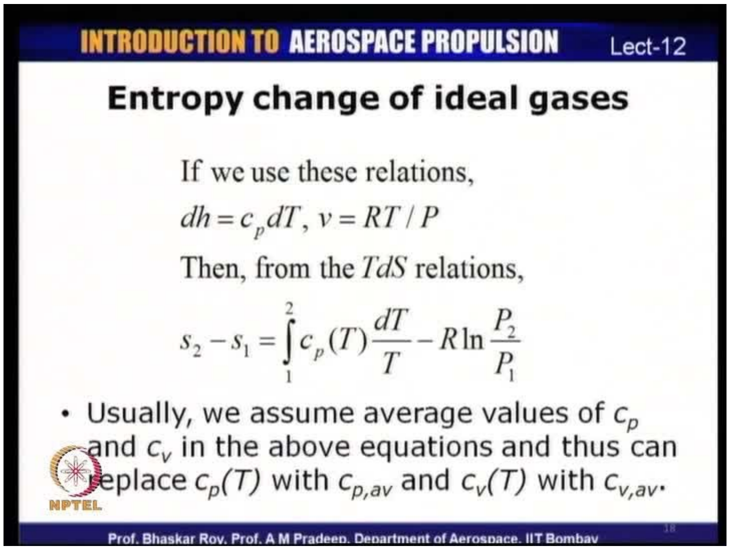
Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

17

So this is the entropy change for a process which involves liquids and solids. Now what about ideal gases? Let us also look at entropy change for ideal gases. For ideal gases, we have already seen that change in internal energy, that is du, is equal to c v dT and we can express the pressure in terms of temperature and specific volume as- v is equal to RT by v.

So, from the TdS equations, TdS is dU plus PdV; so we substitute for du and P here to get ds is equal to c v dT by T plus R times dv by v which is coming from the ideal gas equation, that is, the state equation as well as du is equal to c v dT. If you were to integrate this for a process, we get the change in entropy during that particular process; so s 2 minus s 1 will be equal to integral c v of T, which is specific heat at constant volume, which is again a function of temperature multiplied by dT by T plus R times log of v 2 by v 1.

(Refer Slide Time: 33:27)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy change of ideal gases

If we use these relations,

$$dh = c_p dT,\ v = RT/P$$

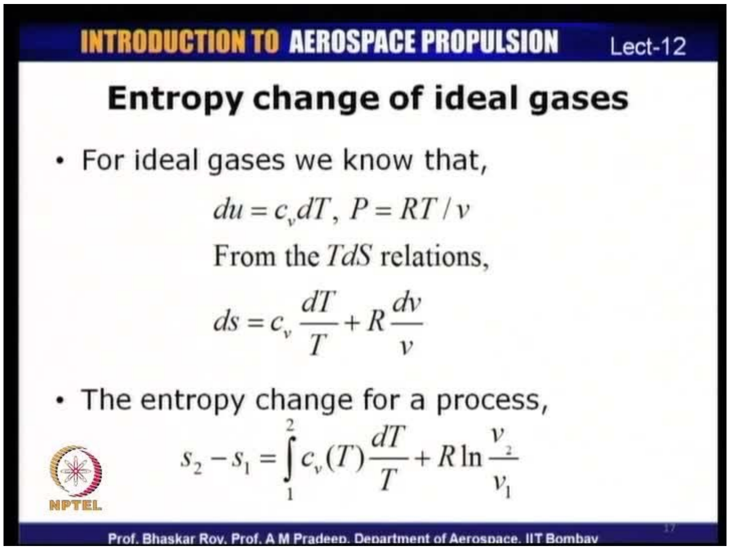
Then, from the TdS relations,

$$s_2 - s_1 = \int_1^2 c_p(T)\frac{dT}{T} - R\ln\frac{P_2}{P_1}$$

- Usually, we assume average values of c_p and c_v in the above equations and thus can replace $c_p(T)$ with $c_{p,av}$ and $c_v(T)$ with $c_{v,av}$.

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay 18

(Refer Slide Time: 33:40)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy change of ideal gases

- For ideal gases we know that,

$$du = c_v dT,\ P = RT/v$$

From the TdS relations,

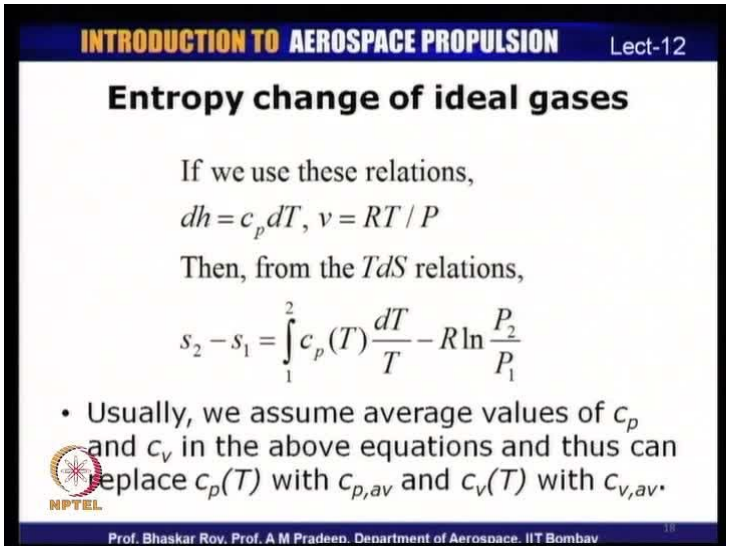
$$ds = c_v\frac{dT}{T} + R\frac{dv}{v}$$

- The entropy change for a process,

$$s_2 - s_1 = \int_1^2 c_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1}$$

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay 17

(Refer Slide Time: 33:48)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy change of ideal gases

If we use these relations,

$dh = c_p dT$, $v = RT/P$

Then, from the TdS relations,

$$s_2 - s_1 = \int_1^2 c_p(T)\frac{dT}{T} - R\ln\frac{P_2}{P_1}$$

- Usually, we assume average values of c_p and c_v in the above equations and thus can replace $c_p(T)$ with $c_{p,av}$ and $c_v(T)$ with $c_{v,av}$.

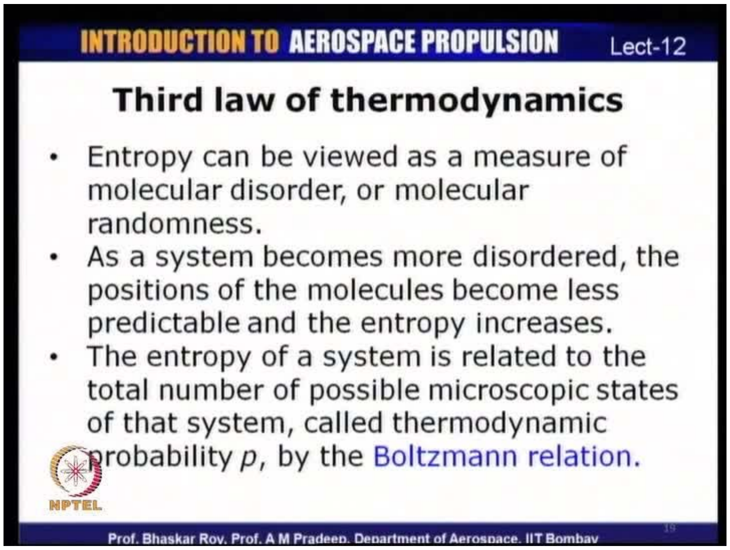
Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

So entropy change for a process involving an ideal gas will be: s 2 minus s 1 is equal to integral c v dT by T plus R log v 2 by v 1; which we will again simplify as- if you are to assume that c v- if you assume an average value of c v- then we get c v times log T 2 by T 1 plus R times log v 2 by v 1. Now, let us also derive an expression for the specific heat at constant pressure. So for an ideal gas, again, the change in enthalpy dh is equal to c p dT and v is equal to RT by P.

Again, if we use the TdS equations- the second TdS equation- we get TdS was dh minus VdP; therefore, s 2 minus s 1 is equal to integral 1 to 2 c p of T, that is, c p is a function of T dT by T minus R log P 2 by P 1. These two expressions, that is, the first equation which we derive for entropy in terms of heat at constant volume and the second equation in terms of specific heat at constant pressure- both of these equations are primarily valid for ideal gases.

Now, as we have done for solids and liquids as well; here, again we can assume an average value of c p and average value of c v for the range of temperatures for which we are calculating the change in entropy. Then we substitute c p of T as c p average and c v of T as c v average, where these average parameters are averaged over the range of temperatures for which this particular process has been carried out.

(Refer Slide Time: 35:32)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Third law of thermodynamics

- Entropy can be viewed as a measure of molecular disorder, or molecular randomness.
- As a system becomes more disordered, the positions of the molecules become less predictable and the entropy increases.
- The entropy of a system is related to the total number of possible microscopic states of that system, called thermodynamic probability *p*, by the Boltzmann relation.

NPTEL

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

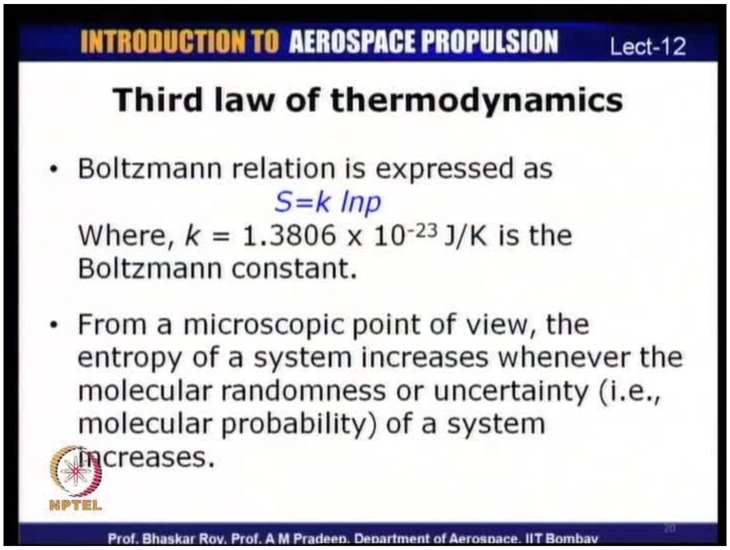
19

So c p average, c v average refers to the average specific heats at constant pressure and constant volume during that given process. This is how we can actually calculate the change in entropy associated with a process involving liquids and solids as well as change in entropy for processes involving ideal gases.

What we shall look at next is what is known as the third law of thermodynamics. Before we understand the third law of thermodynamics we need to also be familiar with what is known as the Boltzmann's equation. As I mentioned a few times in the last lecture, as well as in today's lecture, that entropy is sometimes we would or is often we would as a measure of the molecular disorder or molecular randomness.

As system becomes more disordered, the positions of the molecules become less predicted or predictable; therefore, the entropy increases. If you were to apply this for different states of a system like liquids, solids and gases- we know that, in the case of a gas the number of molecules in a given area, in a given volume, is much more rarefied than in solids or in liquids. Therefore, as a system changes its phase from solid to liquid to gas, the entropy - corresponding entropy - of that system also increases; because, the randomness associated with the molecular motion is the highest in the gaseous phase as compared to solids or in the liquid phase. So, as a system moves from solid to liquid to gaseous phase, the entropy associated with that particular system also increases. So Boltzmann basically expressed entropy in terms of the probability associated with particular molecules as well as a certain constant, which we now call the Boltzmann's constant.

(Refer Slide Time: 37:38)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Third law of thermodynamics

- Boltzmann relation is expressed as
  $S=k\ lnp$
  Where, k = 1.3806 x 10^{-23} J/K is the Boltzmann constant.
- From a microscopic point of view, the entropy of a system increases whenever the molecular randomness or uncertainty (i.e., molecular probability) of a system increases.

NPTEL

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

20

So Boltzmann basically related entropy of a particular process to the total number of molecules - the probability of the total number of molecules - in a particular state, which is known as the thermodynamic probability p. So the expressions in terms of entropy in terms of the probability times a constant is referred to as the Boltzmann's expression or Boltzmann's equation

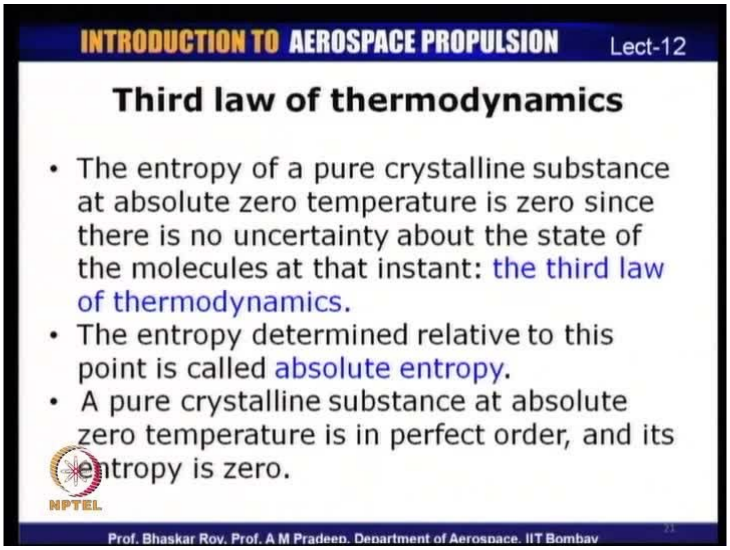
he Boltzmann's expression or equation is basically expressed as the entropy S is equal to k times log of p where k is a constant, which we now know as the Boltzmann's constant, which is 1.3806 into 10 raise to minus 23 joules per kelvin and p is basically the probability of the thermodynamic probability, which is basically the total number of possible microscopic states of particular system- the probability associated with that. So, that is known as the thermodynamic probability.

S is equal to k times log of p is the Boltzmann's equation. So Boltzmann basically stated that entropy is proportional to this particular probability and the proportionality constant is the Boltzmann's constant which is 1.3806 into 10 raise to minus 23 joules per kelvin.

This is the Boltzmann's equation and interestingly Boltzmann wanted this equation to be engraved on his tomb; it is still there on his tomb. The Boltzmann's equation has been engraved on his tomb or his resting place.

From a microscopic point of view, if you look at the Boltzmann's equation, the entropy of a system increases with the molecular randomness or uncertainty. So if you look at a system in different states, like in solids liquids or gases, the molecular probability is the lowest as you look at gaseous phase; correspondingly, the entropy associated with that particular gaseous phase is the highest.

(Refer Slide Time: 39:14)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Third law of thermodynamics

- The entropy of a pure crystalline substance at absolute zero temperature is zero since there is no uncertainty about the state of the molecules at that instant: the third law of thermodynamics.
- The entropy determined relative to this point is called absolute entropy.
- A pure crystalline substance at absolute zero temperature is in perfect order, and its entropy is zero.

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

If you look at the third law of thermodynamics, which is again a consequence of the Boltzmann's equation, the entropy of a pure crystalline substance will become 0 only at temperature of 0 kelvin; which is the absolute 0 temperature. Third law of thermodynamics states that an entropy associated with the particular system or a process can become 0 -or which is primarily true for a pure crystalline substance- it can become 0 only at absolute 0 temperature, because at absolute 0 temperature there is no uncertainty about the state of the molecules at that instance.

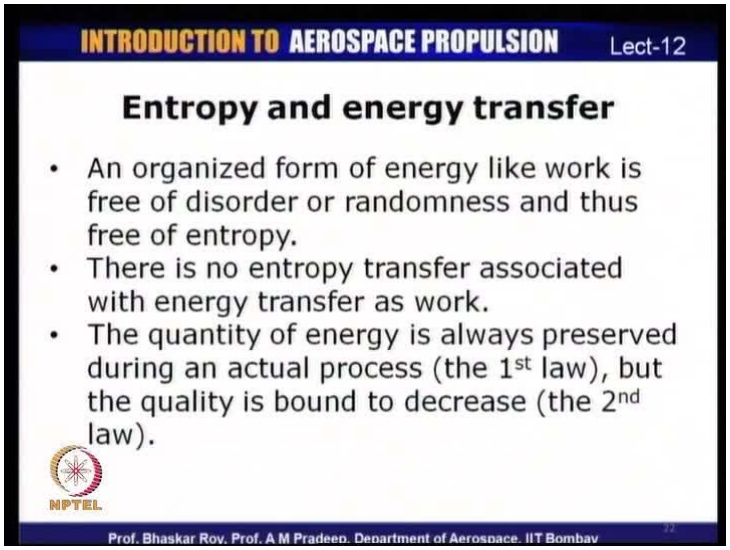
So when you have 0 kelvin temperature, when this pure state of the pure crystalline substance is at absolute 0 temperature, that is 0 kelvin, there is no uncertainty about the state of the molecules at that instant. Because there is no uncertainty about the state of the molecules, the entropy becomes 0 at that particular instant, that is, at absolute 0;

which means that at any other temperature you will always have a certain amount of entropy associated with a particular system. This particular entropy that we referred to is known as the absolute entropy; so the entropy of a particular system at absolute 0 temperature is the absolute entropy. So, obviously that should be the reference state for calculating entropy for any process or any particular system.

But, as we have already discussed, it is impossible for us to achieve absolute 0 temperature or at least we have not been enable to do that so far. So how do you calculate the absolute entropy of a particular process? Well, it is obviously impossible to determine the entropy at its absolute state, but that does not really matter because as engineers we are only interested in change in entropy of a particular process; we are not worried about the absolute entropy of a particular system in a particular state. Therefore, we are only worried about changes in entropy and usually entropy is calculated with reference to certain reference temperature, which need not necessarily be absolute 0.

A pure crystalline substance, as we have seen, as per consequence of the third law of thermodynamics is one where the entropy becomes 0. So a pure crystalline substance at absolute 0 has 0 entropy and therefore, there, it is basically in perfect state of equilibrium and therefore its entropy is 0 at absolute 0.

(Refer Slide Time: 41:54)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy and energy transfer

- An organized form of energy like work is free of disorder or randomness and thus free of entropy.
- There is no entropy transfer associated with energy transfer as work.
- The quantity of energy is always preserved during an actual process (the 1st law), but the quality is bound to decrease (the 2nd law).

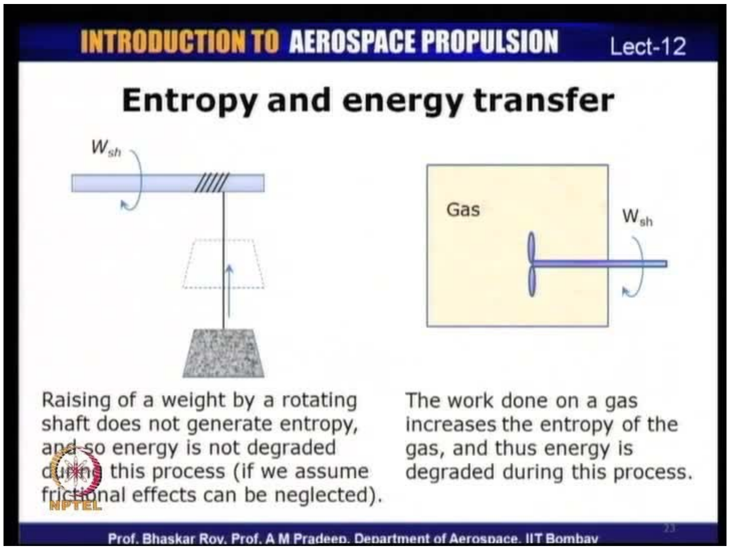
Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

We have already discussed about energy transfer; we have mentioned that energy transfer can take place in different forms of work, heat and mass. Entropy is unlike energy; there is also certain amount of entropy transfer which takes place along with work.

Work is basically an organized form of energy and therefore work is free of disorder or randomness; therefore, it is free of entropy. Which means that there is no entropy transfer associated with energy transfer as work. That is, if you are considering in a process which involves energy transfer as work, there is basically no entropy transfer associated with that particular process.

We have already seen that, as a consequence of the first law of thermodynamics, quantity of energies is always preserved or conserved during an actual process- that is known as the conservation of energy principle. But there is always a decrease in quality, which is as a consequence of the second law of thermodynamics; that during a certain process there is always a decrease in quality of the energy associated with that process.

(Refer Slide Time: 43:07)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy and energy transfer

Raising of a weight by a rotating shaft does not generate entropy, and so energy is not degraded during this process (if we assume frictional effects can be neglected).

The work done on a gas increases the entropy of the gas, and thus energy is degraded during this process.

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

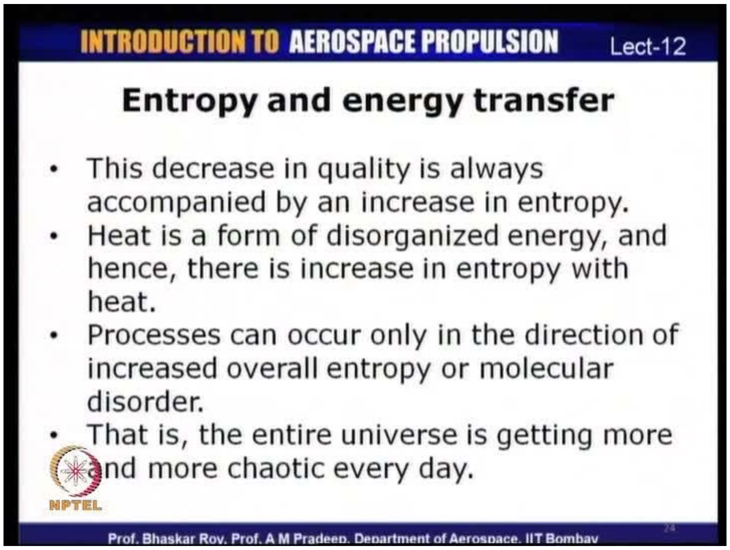
Let us look at this example. Well, that’s two examples. Here one is considering a raising of a weight by shaft movement. So, if you rotate this particular shaft by applying a certain work, that leads to raising of this particular weight against gravity. It is possible, as I mentioned, that the entropy associated with work is 0, then you might wonder that it should be possible for you to regain that work which you have spent in raising this weight; that is perfectly possible. Because, if you now leave that or drop the weight from this height then that will lead to generation of work output or shaft work output which you had spent in raising this weight. This is the reason why there is no entropy associated with a work transfer process.

Well, if you look at, on the other hand, here there is definitely a work done on the system. You may wonder that work is a there is no entropy change associated with work transfer process, so there should be no change in entropy during this process as well; which is not really true here, because if you do work on the system which consists of a gas, the work done gets dissipated in the form of heating of the gas; so it is not just work that is getting transferred into heat. Since work getting transferred into heat is a low grade energy, there is an entropy associated with heat; though, there is no entropy associated with work, which is a high grade energy because it is getting transferred or degraded into low grade energy as heat. It is not possible to get back the work after the work has been done on the system in the second case.

In the first case on the other hand, work was not transferred or converted into heat and therefore there was no degradation of energy associated with that work; so it was possible to recover the amount of work done by, let us say, dropping the weight. You will basically get back the work that was spent. Whereas, on the second case, that is, the second example, work was transferred or converted into heat, which is a low grade energy and there is an entropy associated with that; so you cannot transfer or convert heat into work directly as we have discussed earlier and that requires certain special devices which are known as heat engines.

So, entropy basically is associated with certain forms of energy interactions. Work is one form of energy interaction to which, that is, no entropy is associated with that. There is always a certain amount of entropy associated with a decrease in quality; so in the second example that we just discussed, that is, work getting transferred into heat, there is a decrease in quality of the energy and therefore there has to be an increase in entropy during that process.

(Refer Slide Time: 46:03)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

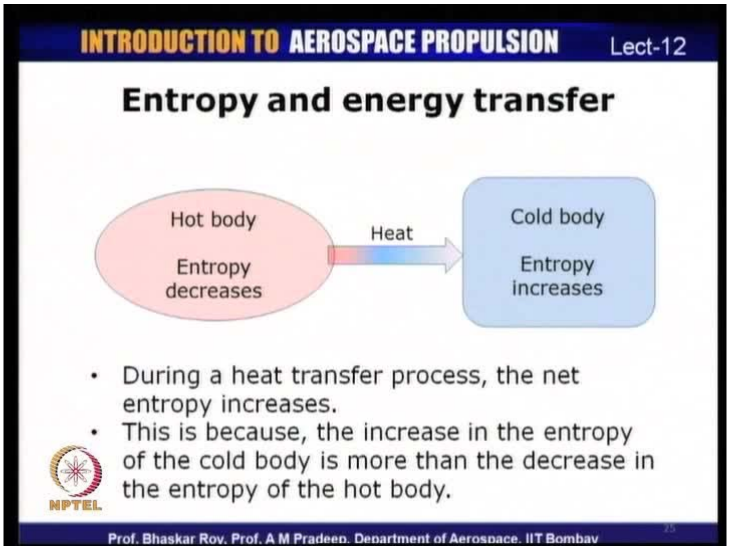
Entropy and energy transfer

- This decrease in quality is always accompanied by an increase in entropy.
- Heat is a form of disorganized energy, and hence, there is increase in entropy with heat.
- Processes can occur only in the direction of increased overall entropy or molecular disorder.
- That is, the entire universe is getting more and more chaotic every day.

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

Heat is a form of disorganized energy and there is always increase in entropy associated with heat. So processes can occur only in that direction which leads to increase in overall entropy or molecular disorder of a system. In some sense, I mentioned that increase of entropy principle also states that there is increase in entropy of the whole universe, well, this means that the entire universe is getting more and more chaotic day by day. That is because entropy can be equated or can be compared to that of disorder of a particular system and since the entropy of the universe is increasing this also should mean that the amount of cures or the disorder of the universe is also increasing day by day. So the whole universe is getting more and more chaotic day by day- as per the increase in entropy principle.

(Refer Slide Time: 46:59)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy and energy transfer

- During a heat transfer process, the net entropy increases.
- This is because, the increase in the entropy of the cold body is more than the decrease in the entropy of the hot body.

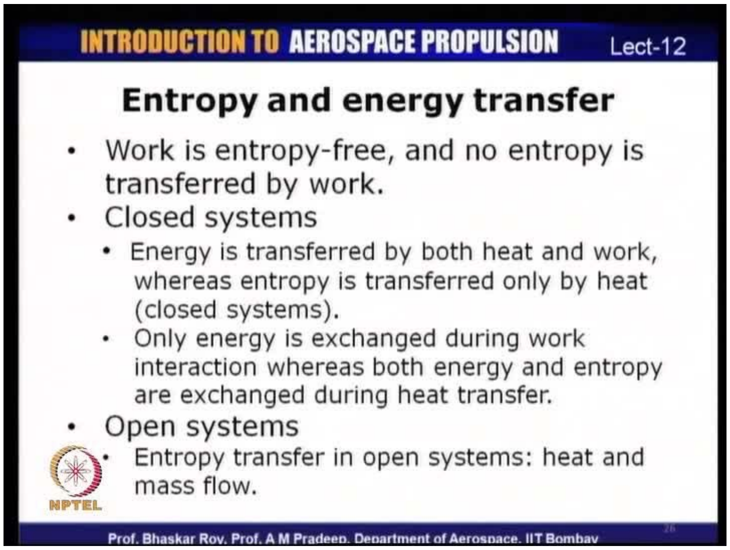
Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

Now let us look at another example of a heat transfer or entropy transfer. Here we have a hot body which is transferring heat to a cold body. Since there is heat transfer from the system- from the hot body- the entropy of this hot body decreases and heat is transferred to the cold body; therefore, entropy of the cold body increase.

We have also discussed that entropy is not a conserved quantity. It means that entropy decrease of the hot body is not equal to entropy increase of the cold body; in fact, the entropy increase of the cold body will be higher than the entropy decrease of the hot body. Therefore, there is a net increase in the entropy of this process; basically because it involves heat transfer and there is always entropy associated with a heat transfer process. Unlike work, and if you had considered these two different bodies interacting through work interaction, the entropy change would have been 0, because there is no entropy change associated with work. Because work happens to be a high grade energy, which has lesser disorder in it. So entropy associated with work is always equal to 0.

As I mentioned, work happens to be an entropy free energy interaction, but obviously in day to day life we will always have processes which involve interactions besides work: it may also have a heat interaction. So heat interactions between the system and surroundings are inevitable. That means, that there is always a certain amount of entropy which is possible during any actual or irreversible process; however, if the process involves only work interaction, obviously the entropy associated with that will be 0.

(Refer Slide Time: 48:56)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy and energy transfer

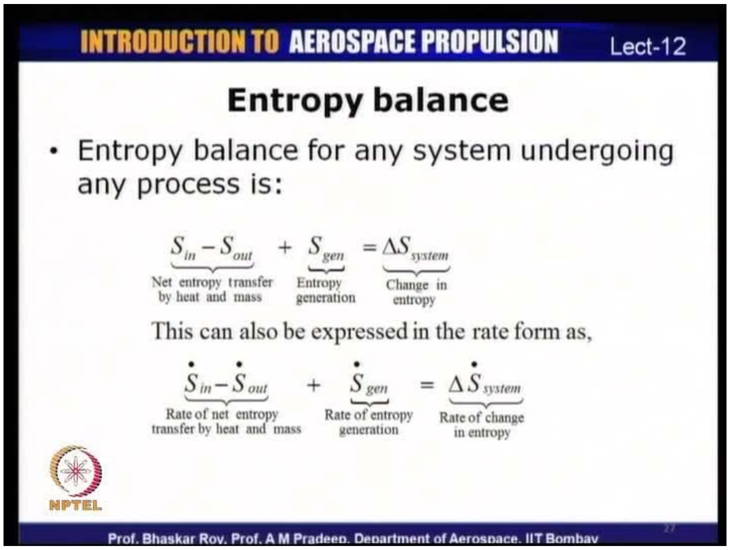
- Work is entropy-free, and no entropy is transferred by work.
- Closed systems
  - Energy is transferred by both heat and work, whereas entropy is transferred only by heat (closed systems).
  - Only energy is exchanged during work interaction whereas both energy and entropy are exchanged during heat transfer.
- Open systems
  - Entropy transfer in open systems: heat and mass flow.

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

Now let us look at what happens - basically - what happens to entropy and energy when you look at closed systems and open systems. If you look at closed systems, energy, as we have discussed, is transferred by both heat and work; however, there is no entropy associated with work. For closed systems, the only mechanism for transfer of entropy is by heat. In closed systems, entropy is transferred only by heat. During work interaction on the other hand, there is only energy interaction and during heat transfer there is both energy as well as entropy transfer across the system boundaries.

If you look at an open system on the other hand, entropy is transferred through heat as well as mass flow. Again, in the case of open systems, there is no entropy associated with work; so, entropy transfer in open systems occurs through two modes: could be either heat or it could be through mass flow. On the other hand, for closed systems entropy, transfer takes place only through heat- there is no entropy associated with work.

(Refer Slide Time: 50:33)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

Entropy balance

- Entropy balance for any system undergoing any process is:

$$\underbrace{S_{in} - S_{out}}_{\substack{\text{Net entropy transfer}\\ \text{by heat and mass}}} + \underbrace{S_{gen}}_{\substack{\text{Entropy}\\ \text{generation}}} = \underbrace{\Delta S_{system}}_{\substack{\text{Change in}\\ \text{entropy}}}$$

This can also be expressed in the rate form as,

$$\underbrace{\dot{S}_{in} - \dot{S}_{out}}_{\substack{\text{Rate of net entropy}\\ \text{transfer by heat and mass}}} + \underbrace{\dot{S}_{gen}}_{\substack{\text{Rate of entropy}\\ \text{generation}}} = \underbrace{\Delta \dot{S}_{system}}_{\substack{\text{Rate of change}\\ \text{in entropy}}}$$

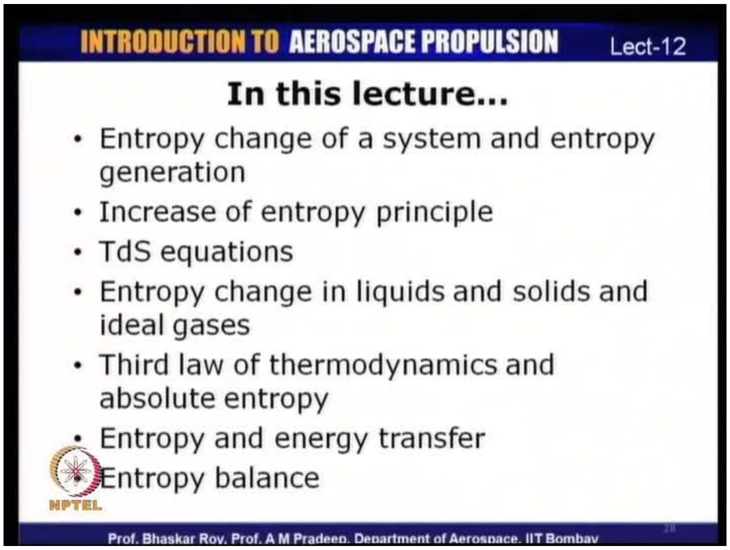
NPTEL

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

So, that leads us to what is known as the entropy balance. If you were to look at what is the entropy- net change in entropy- associated with a process- whether it is a closed system or a an open system and what is the entropy balance associated with that.

Entropy balance is basically looking at what the amount of entropy- net change in entropy- associated with a particular process is. If you consider this equation that is stated here- S in minus S out is basically the net entropy transfer by heat and mass, which means that this is basically for an open system. Plus the entropy generation should be equal to the change in entropy of the system; so net change in entropy of a system will be equal to the sum of the net entropy transfer, which could be either by heat and or mass plus the entropy generation. You can also express this in a rate form: so rate of net entropy transfer by heat and mass plus the rate of entropy generation will be equal to rate of change of entropy of a system. So net change in entropy will be equal to sum of two parameters: one is the entropy transfer, which could be by heat and mass, and the entropy generation.

(Refer Slide Time: 51:23)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

In this lecture...

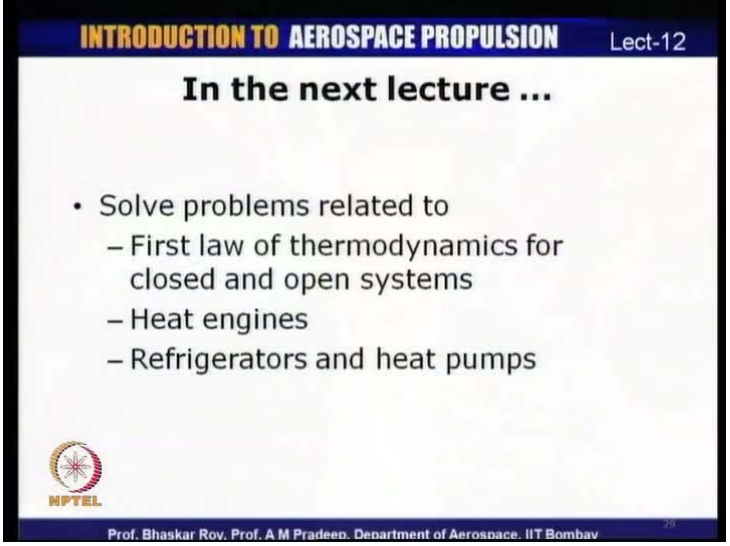
- Entropy change of a system and entropy generation
- Increase of entropy principle
- TdS equations
- Entropy change in liquids and solids and ideal gases
- Third law of thermodynamics and absolute entropy
- Entropy and energy transfer
- Entropy balance

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

Let us recap what we had discussed during this lecture today. We had basically started the lecture with a discussion on entropy change of a system and entropy generation. We had discussed that, during a certain process, during an irreversible process there is always a certain entropy which is created or generated during the process, so entropy generation can never be less than 0. It can - in the limiting case - become equal to 0 for reversible processes, but for all irreversible processes entropy generation will be greater than 0.

Then we discussed about what is known as the increase in entropy principle, which states that entropy of an isolated system will continuously increase. So if you consider the whole universe as an isolated system, entropy of the universe is continuously increasing- that is the increase in entropy principle. Subsequently, we derived what are the TdS equations, that is, product of temperature and change in entropy equations in terms of change in internal energy du and change in enthalpy dh; using this as a basis we have derived equations for calculating entropy change in processes involving solids and liquids as well as in processes involving ideal gases. Then we discussed about entropy change for an isolated system leading towards what is known as the third law of thermodynamics, which is also something Boltzmann’s equation stated.

(Refer Slide Time: 53:54)



INTRODUCTION TO AEROSPACE PROPULSION Lect-12

In the next lecture ...

- Solve problems related to
  - First law of thermodynamics for closed and open systems
  - Heat engines
  - Refrigerators and heat pumps

Prof. Bhaskar Roy, Prof. A M Pradeep, Department of Aerospace, IIT Bombay

Which basically states that entropy of a pure crystalline substance at absolute 0 temperature is equal to 0, so, that entropy, which is associated with this particular state is known as the absolute entropy. Then we discussed about entropy transfer and energy transfer: we discussed that the entropy associated with work transfer is 0 whereas for all other energy interaction there is a certain amount of entropy that is associated which is what leads to certain amount of entropy generation.

Towards the end of the lecture we were discussing about entropy balance, which was- net change in entropy of a system is equal to the change in entropy transfer due to either heat or mass plus the entropy generation. So this is what we had discussed in today’s lecture. What we shall be discussing in the next lecture is that, we shall solve certain problems- we shall basically have a tutorial session. We will solve problems related to first law of thermodynamics applied for closed and open systems. We shall also solve problems associated with heat engines, refrigerators and heat pumps. So this we shall take up during the next lecture that would be lecture 13.