Thermal Physics
Prof. Debamalya Banerjee
Department of Physics
Indian Institute of Technology-Kharagpur

Lecture-41
Topic-The Entropy Principle

Hello and welcome back to the first lecture of week 9 of this thermal physics course on NPTEL platform. Now in the last week we have been introduced to this concept of entropy, so far has been a pretty superficial concept although we have computed some of the entropy changes for some real process. But we are yet to understand what is the need of this quantity, we can of course do that mathematically it makes sense but why do we need that? So, this week let us try to understand the usefulness of entropy and what does it gives us, what does it tell us about the direction of a process? So, without further delay let us start with this.

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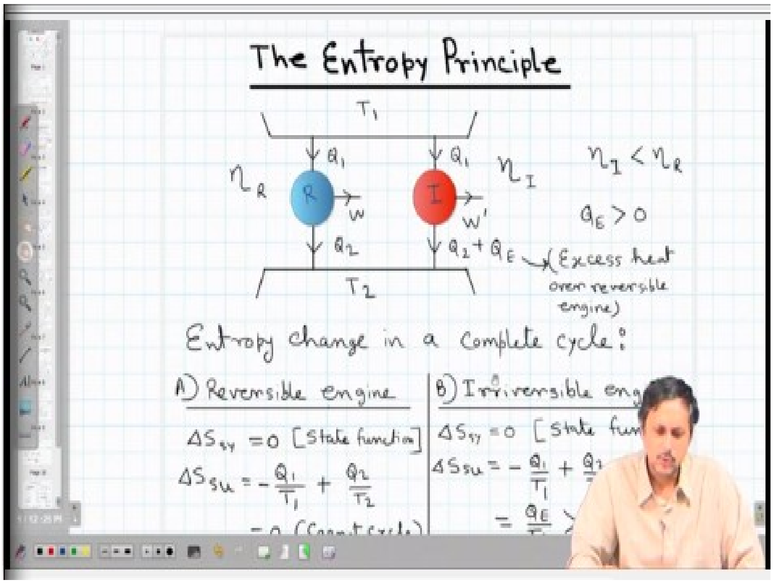

The Entropy Principle

$\eta_I < \eta_R$

$Q_E > 0$

Entropy change in a complete cycle:

A) Reversible engine

$\Delta S_{sy} = 0$ [State function]

$\Delta S_{su} = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2}$

$= 0$ (Carnot cycle)

B) Irreversible eng

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$\Delta S_{su} = -\frac{Q_1}{T_1} + \frac{Q_2}{}$

$= \frac{Q_E}{} >$

So, we will discuss at first a very important concept called the entropy principle. Now let us assume that we have 2 heat reservoir T 1 and T 2, of course T 1 is greater than T 2 I have not written that explicitly but this is understood. And we have 2 engines working side by side inside between the same 2 reservoirs. One is our reversible engine R and one is our irreversible engine I. So, that if both the reversible and irreversible engine let us assume they take Q 1 amount of heat from the hot reservoir.

And the reversible engine rejects Q 2 amount of heat to the cold reservoir, whereas the irreversible engine rejects Q 2 plus Q E amount of heat to the cold reservoir. And this is obvious because as by the Carnot theorem n I is less than n R, so that is why for same amount of heat intake because the efficiency is low the irreversible engine will dispose more heat into the cold reservoir, right.

So, that is why the amount I have just written this just for our own convenience, I have written this as Q 2 plus Q E the amount of heat that is going out to the cold reservoir. And this Q E is the excess heat over the other reversible engine which clearly tells you that Q E is greater than 0.

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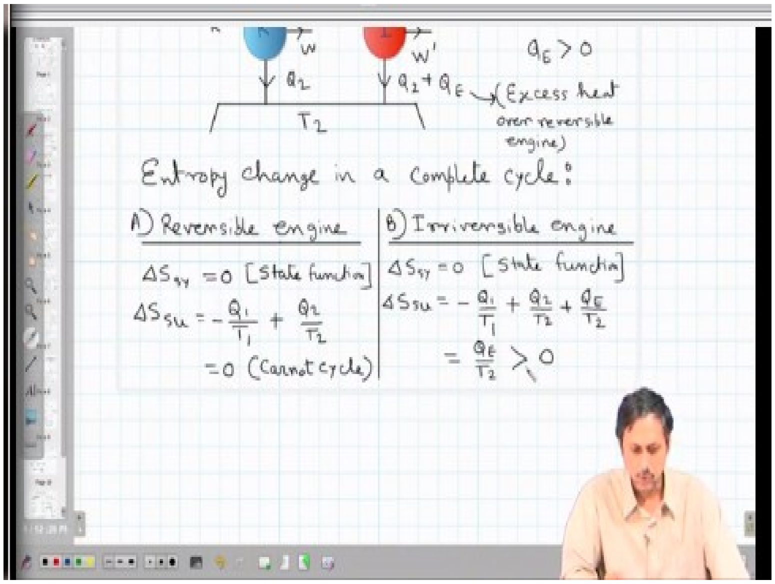

$Q_E > 0$

(Excess heat over reversible engine)

Entropy change in a Complete cycle:

A) Reversible engine

$\Delta S_{sy} = 0$ [State function]

$\Delta S_{su} = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2}$

$= 0$ (Carnot cycle)

B) Irriversible engine

$\Delta S_{sy} = 0$ [State function]

$\Delta S_{su} = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_E}{T_2}$

$= \frac{Q_E}{T_2} > 0$

Now if we now try to compute the entropy change in a complete cycle for both this reversible engine and the irreversible engine, what do we see? Now there are 2 parts, one is the engine, see the engine we do not know what is the operating system in this engine, we can have as we see that a reversible engine can be made using a number of different ideal objects, for example an ideal gas assembly a stretch to ware.

We have discussed that, we have not discussed that in much details but this is possible the whole idea of a Carnot engine is it does not depend on the working substance, so we can take anything. But whatever we do after a complete cycle the system, the working substance goes back to it is initial state that is the whole idea of a cyclic process that the system goes back to it is initial point.

So, that is why as and as entropy is a state function, the entropy change of the system after a complete cycle has to be equal to 0. And this is both true both for the reversible engine and for the irreversible engine. For reversible engine the pathway that it takes is all are reversible path, for a reversible engine all the pathway the cyclic path are irreversible path but irrespective the entropy of the system has to go back to 0.

Now let us come to the reservoir part. For a reversible engine the heat that is or the entropy change of combined both hot and cold reservoir, for hot reservoir we have an entropy loss of minus Q 1 by T 1 because heat is coming out of it. For the cold reservoir we have a entropy gain of Q 2 by T 2 and by Carnot theorem, not by Carnot theorem, for a reversible engine you have Q 1 by T 1 is equal to Q 2 by T 2 that we have discussed in details in the last week lecture, so this combination gives you 0.

So, for a Carnot cycle not only the system entropy change is 0 but after a complete cycle the reservoirs also have a net entropy change 0. Now for an irreversible engine system remains 0 because it is a state function for the surrounding. So, surrounding means the reservoirs actually. The entropy of the hot reservoir reduces by Q 1 by T 1, whereas the entropy gain of the cold reservoir is Q 2 by T 2 plus Q E by T 2.

Once again Q 1 by T 1 plus Q 2 by T 2 cancels out due to because it is a by virtue of this Carnot cycle this relation once again this gives you 0. So, the net change in the surrounding entropy is Q E by T 2 which is definitely greater than 0 because both Q E and T 2 are greater than 0. Q E is greater than 0 by the argument that reversible engine disposes of more heat and T 2 has to be a finite temperature because absolute 0 is not reachable.

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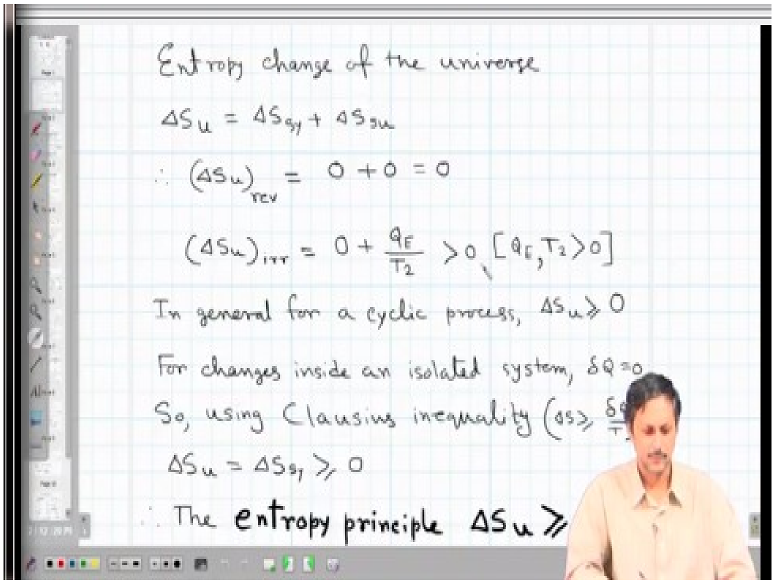

Entropy change of the universe

$\Delta S_u = \Delta S_{sy} + \Delta S_{su}$

$\therefore (\Delta S_u)_{rev} = 0 + 0 = 0$

$(\Delta S_u)_{irr} = 0 + \frac{q_E}{T_2} > 0, [q_E, T_2 > 0]$

In general for a cyclic process, $\Delta S_u \geqslant 0$

For changes inside an isolated system, $\delta Q = 0$

So, using Clausius inequality $(\Delta S \geqslant$

$\Delta S_u = \Delta S_{sy} \geqslant 0$

$\therefore$ The **entropy principle** $\Delta S_u \geqslant$

So, if we calculate the entropy change of the universe, in this case the entropy in universe means the system and the surrounding that means the engine and the reservoir, both the hot and the cold reservoir. For a reversible system the total change in entropy is equal to 0, whereas for a irreversible system the entropy change of the universe is delta Q by T E which is greater than 0.

Now in general for a cyclic process we can write delta S u is greater than equal to 0. Now that is for a cyclic process when it is interacting with the surrounding. What about for an isolated system? Let us say we have an isolated system in hand and for that let us say inside the isolated system there are certain irreversible processes going on. We will see some of the examples very soon, let me tell you.

Let us say I have inside a closed vessel which is thermally isolated, I am putting two chemicals together, so that and they are allowed to react. This reaction definitely we know there are exothermic or endothermic types of reaction, so the temperature of the whole system might go down or go up, we do not know. But something will happen, and of course chemical reaction is also a thermodynamic process, we will encounter that towards the end of the course when we will be discussing chemical potential. But does the entropy change? Question is whether the entropy changes or not?

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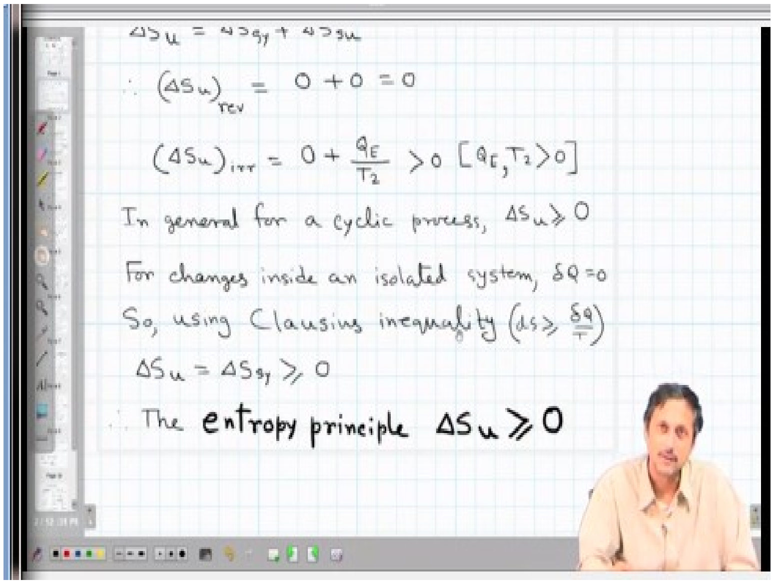

$\Delta S_u = \Delta S_{sy} + \Delta S_{su}$

$\therefore (\Delta S_u)_{rev} = 0 + 0 = 0$

$(\Delta S_u)_{irr} = 0 + \frac{Q_E}{T_2} > 0 \; [Q_E, T_2 > 0]$

In general for a cyclic process, $\Delta S_u \geqslant 0$

For changes inside an isolated system, $\delta Q = 0$

So, using Clausius inequality $\left(ds \geqslant \frac{\delta q}{T}\right)$

$\Delta S_u = \Delta S_{sy} \geqslant 0$

$\therefore$ The **entropy principle** $\Delta S_u \geqslant 0$

Now recall that the alternative form of Clausius inequality that delta S is greater than is equal to dQ by T. Or I should actually write d here, so ds is greater than equal to dQ by T. Now if dQ is equal to 0, that is for an isolated system this actually implies ds is greater than equal to 0. So, that means let it be a cyclic process where the system and the surrounding interacts or let it be an isolated system in both cases the entropy of the universe.

In this case this entropy itself is the entropy of the universe because the system is isolated, so for the thermodynamic consideration universe is that system only. So, the entropy of the universe always increases and this leads, the simple proof leads to a very important conclusion that is the entropy principle. A system is always driven towards the direction along which the total entropy of the universe increases.

And now you know why if we have a hot object and a cold object in physical contact with each other, why heat transfers from the hot object to the cold object and not the other way around. In the last lecture last part we have discussed about the energy change between 2 reservoirs, one at temperature T 1 and one at temperature T 2 and we have shown you that the total change in entropy is greater than 0.

This is precisely one special case of this entropy principle and for the most general cases we can write both for cyclic process and isolated system the entropy of the universe has to be greater than equal to 0. If the process is completely reversible we have an equality sign, if the process is irreversible we have this greater than sign.

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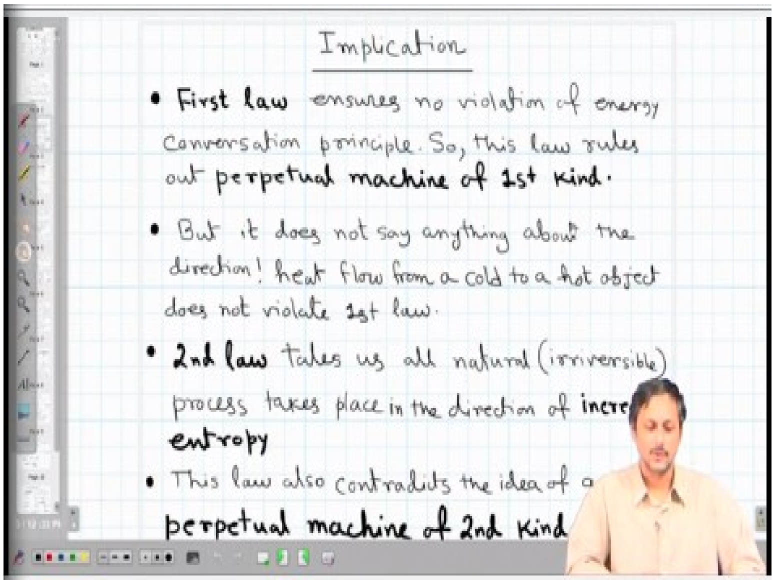

Implication

- **First law** ensures no violation of energy conversation principle. So, this law rules out **perpetual machine of 1st kind.**
- But it does not say anything about the direction! heat flow from a cold to a hot object does not violate 1st law.
- **2nd law** tales us all natural (irriversible) process takes place in the direction of **incre entropy**
- This law also contradicts the idea of a **perpetual machine of 2nd Kind**

Now this leads us to the following implication, I have already said something but let me tell in more details. Now first law of thermodynamics, this is actually a energy conservation law in the context to thermodynamics. In context of the systems we are interested in. Now that prevents the rules out the presence of perpetual machine of first kind, what is perpetual machine of first kind? Perpetual machine of first kind is a hypothetical machine that can work without any energy input.

Now first law says that is not strictly possible, strictly says it is not possible because you need to have energy, you need to have heat energy to change internal energy or perform work done or vice versa. So, if a machine is doing some work there has to be some source of energy, let it be it is internal energy, let it be some external source of thermal energy, whatever it is, or thermal or mechanical energy whatever that energy source has to be there.

So, first law of thermodynamics or that is to say the energy conservation principle objects or basically nullifies the concept of perpetual machine of first kind. Now it does not tell you which way a process should evolve. For example once again we have two objects a hot body and a cold body. So, we know that energy will be transferred from the hotter object to the colder object.

But going by the energy conservation principle if some amount of energy is rejected by the cold object and absorbed by the hot object energy conservation principle does not violate them, think of it. I have for example I have this particular object here, I know if I leave it from here it will drop. So, the gravity is pulling it down, why because the system wants to minimize the potential energy.

But if I going by first law I do not have any means to know that a system will drive towards energy minimal all the time. We know that by other observation by virtue of classical mechanic that is also once again there is an assumption, that system always wants to drives towards equilibrium minimum energy. But first law does not prevent us, for example what I mean to say is if I throw this object up, it will gain some potential energy and it will lose some kinetic energy, right.

So, this is an energy conservation that is taking place. Similarly but we know that at some point it will stop and start falling down again. But first law does not prevent this object to hang in mid-air; I mean it will not violate the energy conservation principle. But by virtue of concepts of classical mechanics we know that it will drive towards equilibrium, so that is why it will fall down.

Similarly first law of thermodynamics does not tell you sorry I should say energy conservation does not get violated if it hangs in mid-air but equilibrium gets violated. Similarly in thermodynamics if a colder object gives heat to a hotter object the first law is never getting violated but the second law does, why because we know that second law talks about the direction of a process in terms of increasing entropy.

So, once again this is the entropy principle that has to be followed in any process that is the final mathematical outcome of the second law of thermodynamics. So, we know by second law a process takes place or any natural process which are by nature irreversible takes place along the direction of increasing entropy. And also this law prevents us or contradicts the idea of a perpetual machine of second kind.

What is a perpetual machine of second kind? Perpetual machine of second kind says okay, let us say the first law is not violated we have an energy source. So, a ship is floating on the ocean; ocean is an infinite heat reservoir. So, the ship can extract energy from the ocean and run as long as it wants to. So, this is a machine which does not violate the first law of thermodynamics. Please remember, ocean will be giving energy, ship will be accepting the energy that is absolutely fine in terms of energy conservation.

But now we know second law prevents this because it also needs a cold reservoir, an engine cannot operate with only one reservoir alone. So, when we talk about perpetual machine of second kind we talk about machines which work with only one heat reservoir. So, second law thermodynamics prevents that, also it tells you the direction at which any natural process should occur is the direction along which the entropy of the universe increases.

So, individually if you take a part of the process you might find that entropy of a part of the system is decreasing. But as a whole, if you consider the whole universe the system and the surrounding with which the system is interacting the entropy principle must hold, so this is the implication of second law of thermodynamics.

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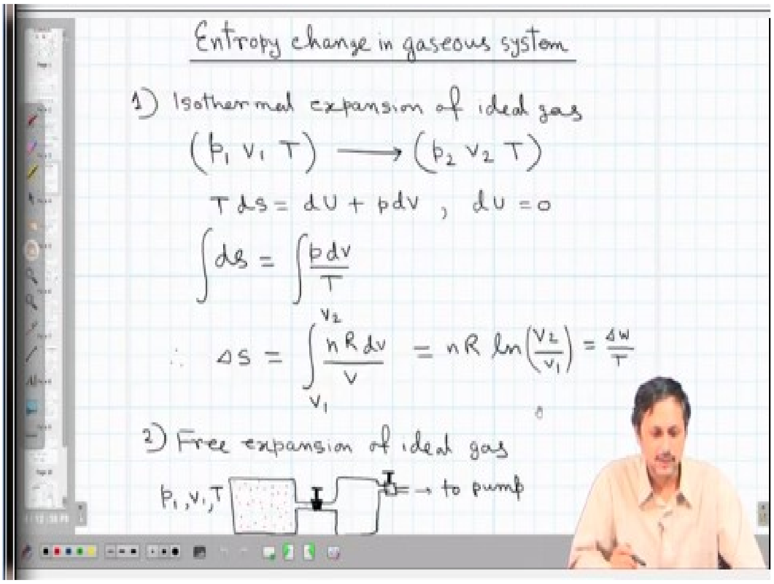

Entropy change in gaseous system

1) Isothermal expansion of ideal gas

$$(p_1\ V_1\ T) \longrightarrow (p_2\ V_2\ T)$$

$$T\,ds = dU + p\,dv \ , \quad dU = 0$$

$$\int ds = \int \frac{p\,dv}{T}$$

$$\therefore \Delta S = \int_{V_1}^{V_2} \frac{nR\,dv}{V} = nR \ln\left(\frac{V_2}{V_1}\right) = \frac{\Delta W}{T}$$

2) Free expansion of ideal gas

Now let us come back to these entropy changes, the calculation of entropy change we will focus on the gaseous system now. Because for most of the time we have taken these as examples and in we will continue doing so. So, let us focus on this isothermal expansion of an ideal gas, so it is going from p 1 v 1 T to p 2 v 2 T. So, during this process we have to compute the change in entropy.

We can write the first law as T ds = du + pdv because we know dq can be written as pdv and dw can be written as p sorry delta Q can be written as T ds and delta w can be written as pdv. And in this case because the temperature does not change du is equal to 0, so we have ds is equal to pdv by T which once again using the ideal gas equation p by T is n R by v, so delta s is equal to n R ln v 2 by v 1 which if you remember is exactly the expression of delta w divided by T.

Next comes a very important concept of free expansion of ideal gas. So, let us assume we have 2 chambers connected by a stop cork, stop cork is closed, we have gas at a pressure p 1, v 1 and at a temperature T and it is confined to only one chamber the other chamber is evacuated by means of a pump. Now what do we do? We open the stop cock, now on this side we have only vacuum, so there is no pressure on this gas or there is no resistance of this gas it will expand it will be an adiabatic process of course.

But for an ideal gas there are, okay, of course there is nothing called an ideal gas but for hydrogen or helium gases or argon gases at very low pressure and moderate temperature when it behaves almost like an ideal gas. It has been found that the temperature does not change in this free expansion process. So, what happens is finally it reaches to a state where the total pressure is something p 2, total volume is some v 2 this will be the volume of this compartment plus this compartment where the temperature does not change.

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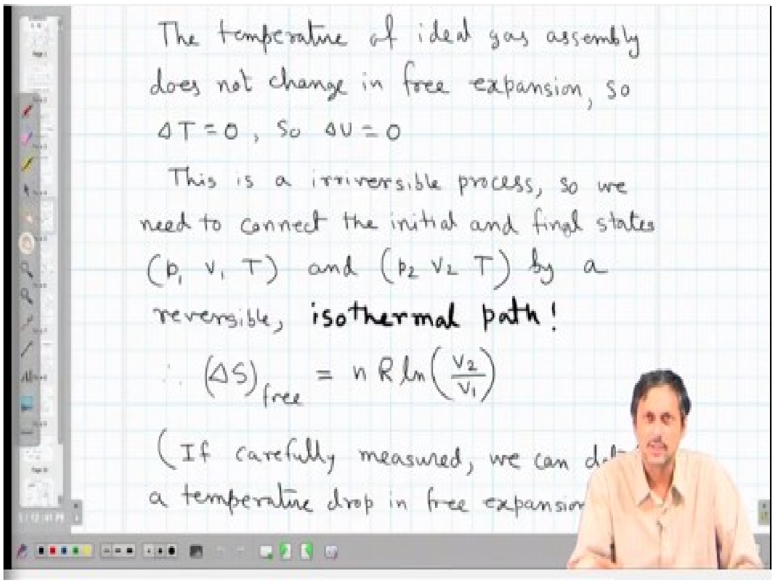

The temperature of ideal gas assembly does not change in free expansion, so

$\Delta T = 0$, So $\Delta U = 0$

This is a irriversible process, so we need to connect the initial and final states $(p_1\ v_1\ T)$ and $(p_2\ v_2\ T)$ by a reversible, **isothermal path!**

$$\therefore (\Delta S)_{free} = n R \ln\left(\frac{v_2}{v_1}\right)$$

(If carefully measured, we can d
a temperature drop in free expansion

Now we need to compute the entropy change in free expansion. Once again it is a totally irreversible process, so we cannot integrate, we cannot find and where to integrate along the free expansion. So, what we need to do is, we need to construct a reversible path between the initial and the final state. Initial state is p 1 v 1 T, final state is p 2 v 2 T, so it is exactly like the isothermal expansion of an ideal gas.

So, for a free expansion also we have to assume there is an isothermal reversible path exists between this initial and the final state. And we find that delta S free is equal to n R ln v 2 by v 1 exactly similar to what we have derived for an isothermal expansion of an ideal gas. Now later on it was found out if very carefully measured we can actually find out determine the minute drop in temperature and this has to do with.

So, basically this temperature drops because the internal energy is not exactly a function of temperature only, it also varies as volume, so we will come back to those once again later on. So, but for now you keep in mind that for free expansion of ideal gas your entropy change is n R r ln v 2 by v 1.

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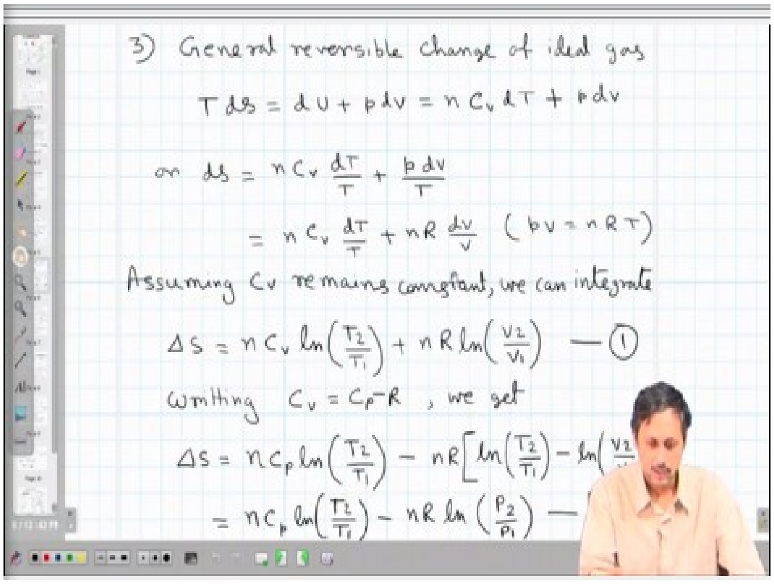

3) General reversible change of ideal gas

$$T\,ds = dU + p\,dv = nC_v\,dT + p\,dv$$

or $ds = nC_v \frac{dT}{T} + \frac{p\,dv}{T}$

$$= nC_v \frac{dT}{T} + nR\frac{dv}{v} \quad (pv = nRT)$$

Assuming Cv remains constant, we can integrate

$$\Delta S = nC_v \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right) \quad — ①$$

Writing $C_v = C_p - R$, we get

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right) - nR\left[\ln\left(\frac{T_2}{T_1}\right) - \ln(V_2\right.$$

$$= nC_p \ln\left(\frac{T_2}{T_1}\right) - nR\ln\left(\frac{P_2}{P_1}\right) \quad —$$

Now talk about a general reversible change in an ideal gas we write T ds = du + pdv and also du we can write nC v dT. So, the total equation is T ds = nC v dT + pdv, so ds = nC v dT by T + pdv by T. Now writing p by T once again as nR by v we can write this as nC v dt by T plus nR dv by v. Once again we have to assume that the specific heat at constant volume C v does not change during the temperature change for which we are integrating.

So, we can simply integrate this relation to get delta S = nC v ln T 2 by T 1 plus nR ln v 2 by v 1, that is let us call it relation 1. Now what we can do is we can write C v = C p - R and we get delta S is equal to nC p ln T 2 by T 1 minus nR ln T 2 by T 1 - ln v 2 by v 1. So, you see here we have nR ln T 2 by T 1, so this will be simplified to it will be T 2 v 1 by T 1 v 2. And once again this will be nothing but using this equation pv = nRT this will be nothing but p 2 by p 1.

So, delta S is equal to nC p ln T 2 by T 1 minus nR ln p 2 by p 1 let us call it relation 2. Of course we can keep on manipulating these relations and we can get more and more useful relation, some of those are useful, some of those are not so useful. But we will stop here, we will stop doing that.

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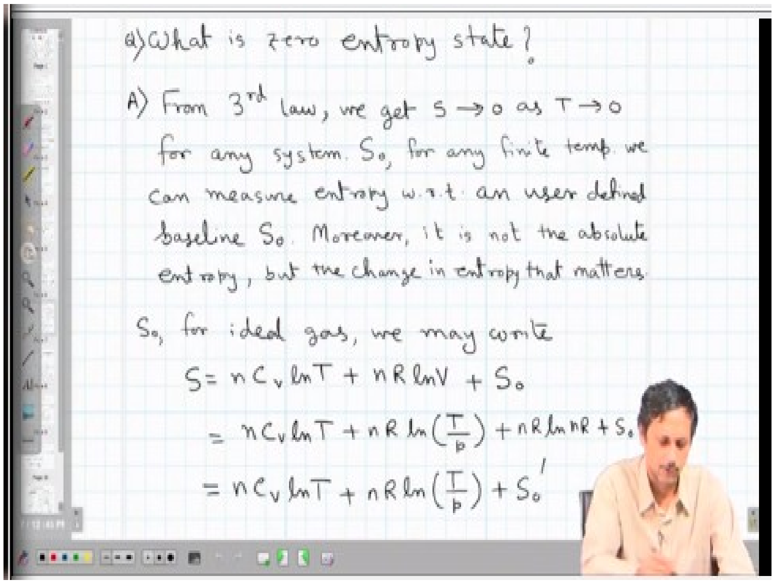

Q) What is zero entropy state?

A) From 3rd law, we get $S \to 0$ as $T \to 0$ for any system. So, for any finite temp. we can measure entropy w.r.t. an user defined baseline S_0. Moreover, it is not the absolute entropy, but the change in entropy that matters.

So, for ideal gas, we may write

$$S = nC_v \ln T + nR \ln V + S_0$$

$$= nC_v \ln T + nR \ln\left(\frac{T}{p}\right) + nR \ln nR + S_0$$

$$= nC_v \ln T + nR \ln\left(\frac{T}{p}\right) + S_0'$$

Instead what we are going to do is, we will talk little bit about zero entropy state. Now what is zero entropy state? You see in both these integrations we have not we wrote the entropy change just as delta S. So, is there any state possible for which we can define the entropy to be is equal to zero and we can integrate from there, is it a possibility? Now from 3rd law of thermodynamics which will be discussed towards the last part of this course.

We will see that S goes to 0 as T goes to 0. So, for any system, for any finite temperature we can measure the entropy change with respect to an user defined baseline S 0. So, what we have to do is we have to let us say the initial state we say that okay, so this is my the entropy of this initial state is S 0, now we compute the change and measure everything with respect to S 0. So, for ideal gas what we can do is, if we want to measure the absolute entropy of course absolute entropy is not possible.

But if we write delta S is equal to S minus S 0 instead of if we just want to write the entropy of the system, so we can write S is equal to nC v, so there like from this relation we do not have to write T 2 by T 1 because we are not integrating between T 1 and T 2. But we are integrating from some arbitrary point in the temperature scale to a certain temperature T. So, what we can do is we can simply write this as S = nC v ln T + nR ln V + S 0 which once again can be slightly modified to write nC v ln T plus nR ln T by p.

See, so V will be equal to nR T by p, so we can write this as nR ln T by p plus nR lon nR plus S 0 and please remember nR ln nR itself is a constant, so this plus this we can define a new constant and we can write S is equal to nC v ln T plus nR ln T by p plus S 0 prime. So, S 0 prime is our new reference point. Where, please remember we have not mentioned the starting point but there has to be some, so the starting point information all included in this particular constant here. Now what is the advantage of writing this expression in this particular form?

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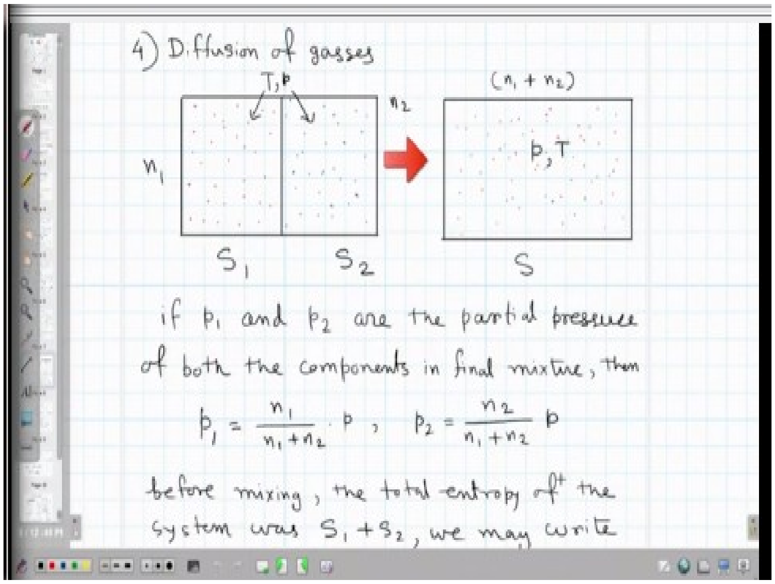

4) Diffusion of gasses

if p_1 and p_2 are the partial pressure of both the components in final mixture, then

$$p_1 = \frac{n_1}{n_1+n_2} \cdot p \, , \quad p_2 = \frac{n_2}{n_1+n_2} p$$

before mixing, the total entropy of the system was $S_1 + S_2$, we may write

The advantage is this. So, because next what we are going to discuss is the diffusion of gases. What is diffusion of gas? So, let us assume that we have two compartments in which we have two ideal gases one n 1 mole of one ideal gas and n 2 mole of another ideal gas and the wall between them is I forgot the exact terminology, so basically let us say we have a flexible wall between them, so that the pressure can equilibrate on both side. And of course that it has to be a diathermic wall as well.

So, let us say we have a flexible diathermic wall in between these two chambers, so that the pressure and temperature of both these sides, both these gas assembly are equal. Now, why we do that because we want to compute the entropy change arising out of pure diffusion of gases. If there is a difference in temperature there will be a entropy change due to temperature equilibrium, if there is a difference in pressure there will be a entropy change due to change in pressure. But here we assume that everything is same, so before and after the pressure and temperature does not change of this gas assembly.

What changes we initially had n 1 moles on this side, n 2 moles on this side, now we have n 1 plus n 2 moles mixed together. Now inside this mixture we have partial pressure of these 2 gases. And if you remember the Dalton's law of partial pressure, the partial pressure for the first gas the gas of type 1 will be p 1 which will be equal to p times n 1 divided by n 1 plus n 2 and p 2 will be equal to n 2 divided by n 1 plus n 2 times p. So, these are from the laws of partial pressure. Now before mixing using this relation we can compute the entropy of system 1 and system 2 and after mixing we can also once again use the same relation to compute the total entropy of the final state, so let us do that.

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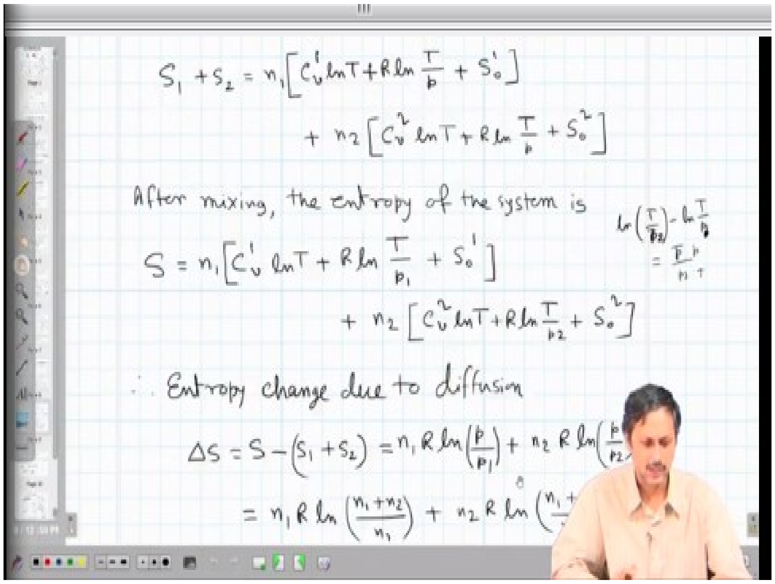

$$S_1 + S_2 = n_1\left[C_v^1 \ln T + R\ln\frac{T}{p} + S_0^1\right] + n_2\left[C_v^2 \ln T + R\ln\frac{T}{p} + S_0^2\right]$$

After mixing, the entropy of the system is

$$S = n_1\left[C_v^1 \ln T + R\ln\frac{T}{p_1} + S_0^1\right] + n_2\left[C_v^2 \ln T + R\ln\frac{T}{p_2} + S_0^2\right]$$

$\ln\left(\frac{T}{p_2}\right) - \ln\frac{T}{p}$

$= \frac{T\,p}{p_2\,T}$

∴ Entropy change due to diffusion

$$\Delta S = S - (S_1 + S_2) = n_1 R \ln\left(\frac{p}{p_1}\right) + n_2 R \ln\left(\frac{p}{p_2}\right.$$

$$= n_1 R \ln\left(\frac{n_1+n_2}{n_1}\right) + n_2 R \ln$$

So, we have S 1 plus S 2 which was the initial entropy is n 1 times C v 1 ln T plus R ln T by p plus S 0 1 plus n 2 times C v 2 ln T plus R ln T by p plus S 0 2. So, after mixing we have a system in which we have n 1 moles of gas with same C v 1 ln T plus R ln T by p 1 plus S 0 1 plus n 2 times this term remains the same we have R ln T by p 2 plus S 0 2. Now, entropy change due to diffusion will be S minus S 1 plus S 2.

Please remember that the first terms are exactly the same, so this term and this term will cancel out, this term and this term will cancel out which will leave us to this terms only which is n 1 R ln p by p 1 plus n 2 R ln p by p 2. Now going by this formula partial pressure p by p 1 is nothing but n 1 plus n 2 by n 1, p by p 2 is n 1 plus n 2 by n 2, so this is n 1 R ln n 1 plus n 2 by n 1 plus n 2 R ln n 1 plus n 2 by n 2. Now n 1 plus n 2 by n 1 is a quantity that is less than 1 because of course this is the total mole fraction, this is the partial mole fraction, similarly this is total, this is partial. So, this quantity is greater than 1 because this one is denominator is higher as compared to numerator.

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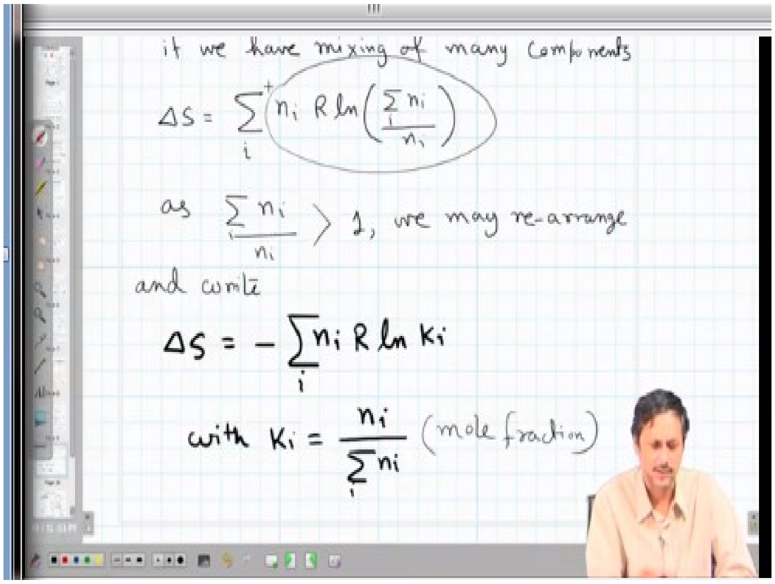

if we have mixing of many components

$$\Delta S = \sum_i n_i R \ln\left(\frac{\sum_i n_i}{n_i}\right)$$

as $\frac{\sum_i n_i}{n_i} > 1$, we may re-arrange

and write

$$\Delta S = -\sum_i n_i R \ln k_i$$

$$\text{with } k_i = \frac{n_i}{\sum_i n_i} \quad (\text{mole fraction})$$

But what we can do is, sorry this should be greater than 1. And we can rearrange the same expression as delta S = - n i ln k, where k is equal to n i divided by sum over n i, so this is basically the mole fraction. So, this is nothing but the mole fraction. So, if we have two such gases we have n 1 and n 2 and if we have n such gases they are mixed at same pressure and same temperature.

For each we can have a contribution of this type and finally the expression for entropy change will be delta S = -n i R ln k i, where k i is the mole fraction of individual components. So, these entropy changes please keep in mind that it is entirely due to the diffusion process, the mixing of different types of gases. So, we will come back to this once again when we will be solving problems.

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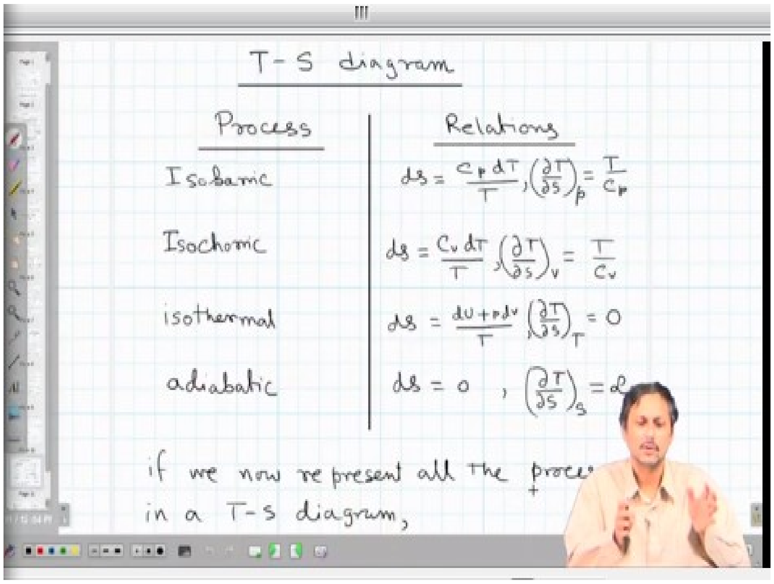

T-S diagram

Process	Relations
Isobaric	$ds = \frac{C_p\,dT}{T}, \left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{C_p}$
Isochoric	$ds = \frac{C_v\,dT}{T}, \left(\frac{\partial T}{\partial S}\right)_v = \frac{T}{C_v}$
isothermal	$ds = \frac{dU + pdV}{T}\ \left(\frac{\partial T}{\partial S}\right)_T = 0$
adiabatic	$ds = 0\ , \left(\frac{\partial T}{\partial S}\right)_S = \infty$

if we now represent all the proce
in a T-S diagram,

Now before ending today's lecture let us talk briefly about what is a T-S diagram. Now we have talked about pv diagram, pv these are conjugate parameters, pdv has a dimension of energy or the product pv has a dimension of energy. Similarly T-S is a set of conjugate parameter, the product T-S has the dimension of energy. So, let us try to look at this four processes isobaric, isochoric, isothermal and adiabatic.

And what are the slopes in this T-S diagram, of course we will have entropy in the x axis and T temperature in the y axis. So, in this case ds, for an isobaric case ds will be C p dT by T, so del T del S is equal to T by C p. And isochoric process del T del S with v constant will be equal to T by C v, isothermal will be del T del S is equal to 0 because in an isothermal process the temperature does not change. And an adiabatic process del T del S will be infinity because the entropy change is equal to 0.

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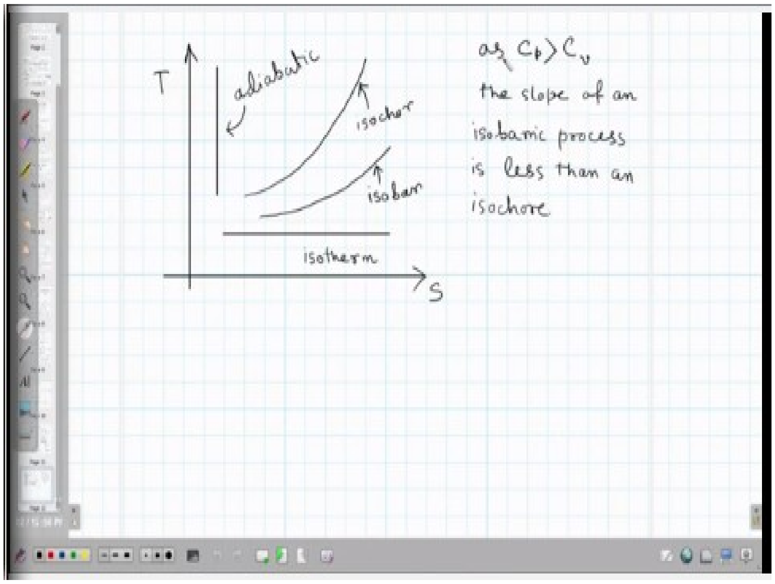

as $C_p > C_v$
the slope of an
isobaric process
is less than an
isochore

Now if we try to represent those in a T-S diagram where we have S in the x axis and T in the y axis. We have an isothermal process it becomes a 0 slope flat line, adiabatic becomes a slope like a vertical line. So, it is a horizontal line, it is a vertical line, isochor and isobar both looks something like this, whereas isobar has a lesser slope as compared to isochor because C p is greater than C v.

So, we will stop here today, we have talked about a very important concept called the entropy principle which is instrumental in determining the direction of any chemical process or any natural process in thermodynamics. And then we talked about the entropy change due to mixing of gases and finally we talked about T-S diagram which will be using in the next lecture in order to determine the efficiency of a heat engine, till then good bye.