Statistical Mechanics
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Lecture – 04
Entropy, Clausius Inequality
Thermodynamic Processes and Systems

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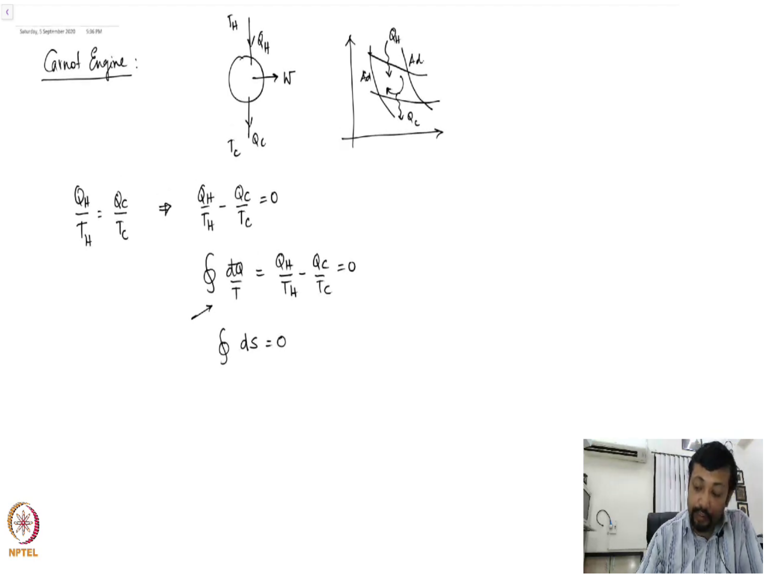

Carnot Engine :

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C} \Rightarrow \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0$$

$$\oint \frac{dQ}{T} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0$$

$$\nearrow$$

$$\oint ds = 0$$

Now, when we looked at the Carnot engine, if you recall the Carnot engine it takes an amount of heat Q H at a temperature T H dumps an amount of heat Q C to the cold reservoir and does an amount of volt w and surprisingly enough when we analyze the Carnot engine all the processes in the Carnot engine is reversible, what we found out was Q H over T H is equal to Q C over T C.

So, then we argued that this relation we can write down in this particular more simplified form and not a more simplified form, but you simply write down we write it down in this way and as it turns out since when we looked at the processes for the Carnot engine, there were two adiabatic process and there were two isothermal process. So, let us just do it properly.

And heat was taken in this part; heat was taken in this part and no heat transfer was allowed in the adiabatic processes which were this. And therefore, it follows that if for the whole cycle if we write down an integral d cut Q over T and if we evaluated this integral for the whole cyclic process in this way, then we would simply come up with Q H T H minus Q C T C and that would be 0.

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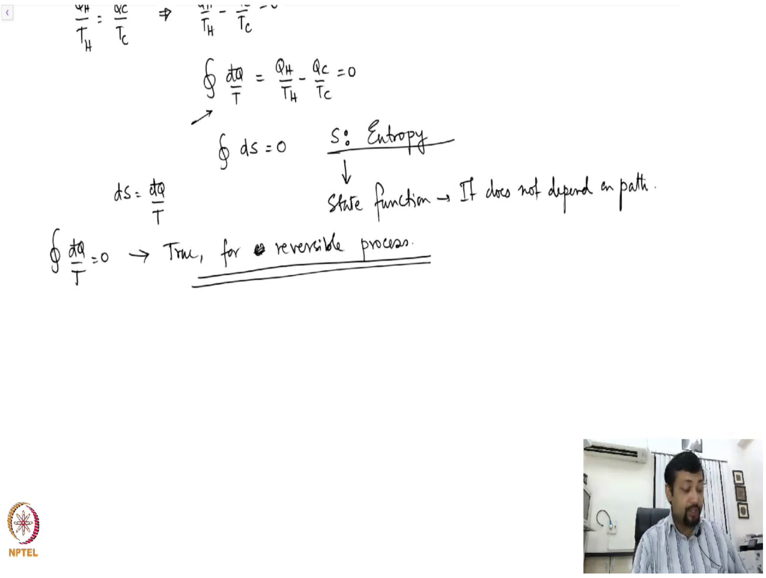

$\frac{Q_H}{T_H} = \frac{Q_C}{T_C} \Rightarrow \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0$

$\oint \frac{dQ}{T} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0$

$\oint ds = 0$ S: Entropy

State function → It does not depend on path.

$ds = \frac{dQ}{T}$

$\oint \frac{dQ}{T} = 0$ → True, for reversible process.

So, clearly it appears that this equation can be written down in this particular form, but now I have introduced d S is equal to d cut Q by T. The implication of this equation is that this quantity S is now a state function. Since I have taken down the system taken the whole system the Carnot engine in a cycle and therefore, I find that the no change there is no change in the quantity S and this is what we called entropy.

And I find out that there is no change in the entropy because the system comes back to its original. Therefore, I conclude to this original starting thermodynamic state and therefore, I conclude that this is a state function and it does not therefore, it does not depend on path. But you see in the whole argument whatever we did this integral 0 is true for reversible processes. In Carnot engine all the processes are reversible and therefore, it is kind of an idealized engine and so, this integral is valid.

Now, what I my natural question is if I remove this restriction that if my processes are not reversible then what happens? So, what happens to this inequality? And that is what we want to find out.

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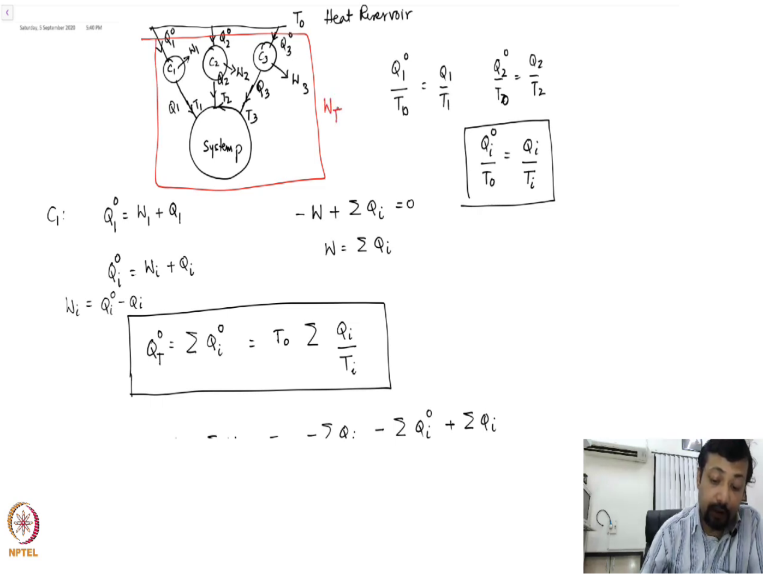

So, imagine that I have a system that works in a cycle. So, we will call this cycle as p and this is my system and this system receives an amount of heat Q 1 at temperature T 1 it receives amount of heat Q 2 at temperature T 2 and then again let us say it does it with Q 3 it receives an amount of heat Q 3 at temperature T 3 and so on and so forth.

Now, what I can do is for further analysis I can direct all this heat to a Carnot engine which extracts some amount of heat from the heat reservoir at a temperature T naught. So, therefore, I operate a Carnot engine which extracts Q 2 0 amount of heat, here I operate a Carnot engine which extracts Q 1 0 amount of heat and here I operate a Carnot engine which extracts Q 3 0 amount of heat does some work so on and so forth.

Correct. So, let us these are all my Carnot engines and there is no loss in generality in writing it down in this particular way, now I want to look at the energy conservation. It obviously, means that Q 1 0 is equal to W 1 plus Q 1 and for the Carnot engine C 1 and similarly for the Carnot engine C 2. So, the general relation would be Q i 0 is W i 0 plus Q i right.

The work done by the system is simply minus. So, if I want to write down the energy conservation for the system then the work done by the system in the whole cycle plus Q i must be 0 and therefore, W is sum over Q i right. What is the total amount of heat taken from the reservoir? The total amount of heat that is taken from the reservoir is sum over Q i 0.

Now, remember for all of these Carnot cycles, I can again write down the relations Q 1 0 over T 1 over T 0 is Q 1 over T 1 and again for the second one also I can write down sorry this has to be T 0 is Q 2 over T 2 because it is taking a heat Q 1 0, Q 2 0, Q 3 0 and so on from the temperature T naught from the hot reservoir and it is dumping heat Q 1, Q 2, Q 3 at temperatures T 1, T 2, T 3 respectively.

So, the general relation becomes Q i 0 over T 0 is equal to Q i over T i. I am going to use this relation. So, this means that this I can write down T naught sum over Q i 0 sorry sum over Q i over T i right. So, what is the total work done?

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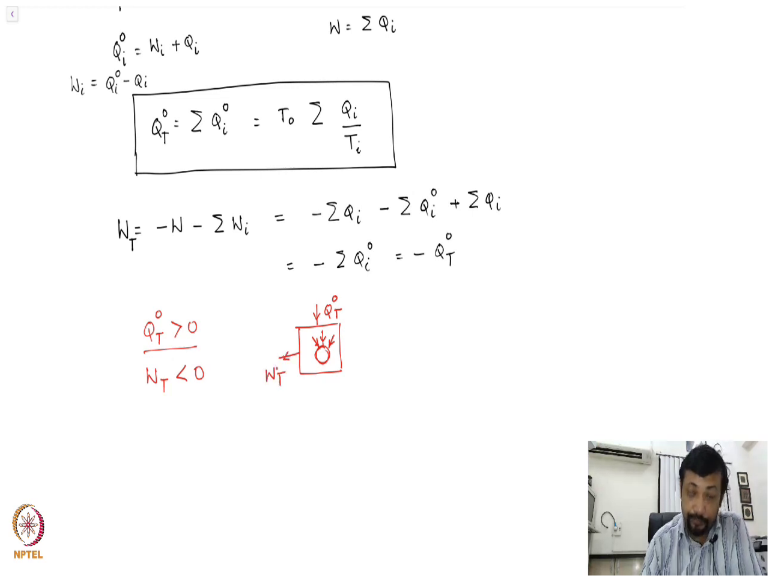

$W = \sum Q_i$

$Q_i^0 = W_i + Q_i$

$W_i = Q_i^0 - Q_i$

$$\boxed{Q_T^0 = \sum Q_i^0 = T_0 \sum \frac{Q_i}{T_i}}$$

$$W_T = -W - \sum W_i = -\sum Q_i - \sum Q_i^0 + \sum Q_i$$
$$= -\sum Q_i^0 = -Q_T^0$$

$$\frac{Q_T^0 > 0}{W_T < 0}$$

The total work done is minus W plus we will put a subscript because work is the energy which is flowing out of the system therefore, in our convention it should be minus W i. So, minus W is minus sum over Q i and then we will write down this as minus sum over Q i 0 plus sum over Q i this follows from here where I can recast this equation as W i is Q i 0 minus Q i.

So, I have once I have this relation therefore, it follows that this is sum over Q i 0 which is minus Q T total. Now what one can do is one can think of this as a whole kind of a system which is doing in work W T right. If that is the case then it follows that if Q T 0 is positive then W T is negative. What does this mean?

This means I have this box I have the system inside it where it is receiving all this amount of heat, but as the whole system what it does? It takes Q T 0 amount of heat enters this box just take an system plus Carnot engine is taken together because its positive and it is doing an amount of work W T.

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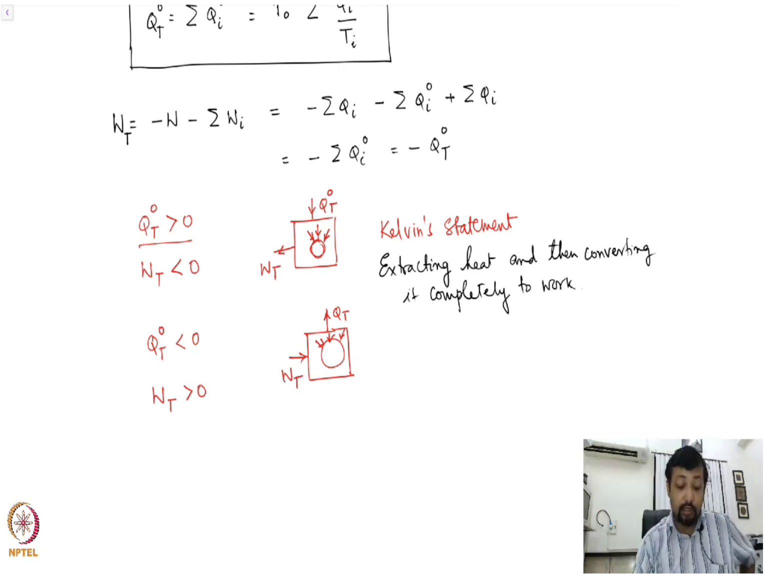

$Q_T^0 = \sum Q_i^0 = T_0 \sum \frac{Q_i}{T_i}$

$W_T = -W - \sum W_i = -\sum Q_i - \sum Q_i^0 + \sum Q_i$

$= -\sum Q_i^0 = -Q_T^0$

$Q_T^0 > 0$

$W_T < 0$

Kelvin's Statement

Extracting heat and then converting it completely to work

$Q_T^0 < 0$

$W_T > 0$

But this, what about the other one? Let us just look at the other one where Q T 0 is negative; that means, W T 0 is positive. Here of course, what happens is the arrows get reversed. So, W T and then Q T. Now, the problem with the first thing is that if you allow this then you violate Kelvins statement why?

How do you violate Kelvin statement? Well, because you are extracting some amount of heat you are extracting it heat and then converting it to work completely to work in contrast, this does not violate right this because there is no thermodynamic principle that says I cannot convert work into heat.

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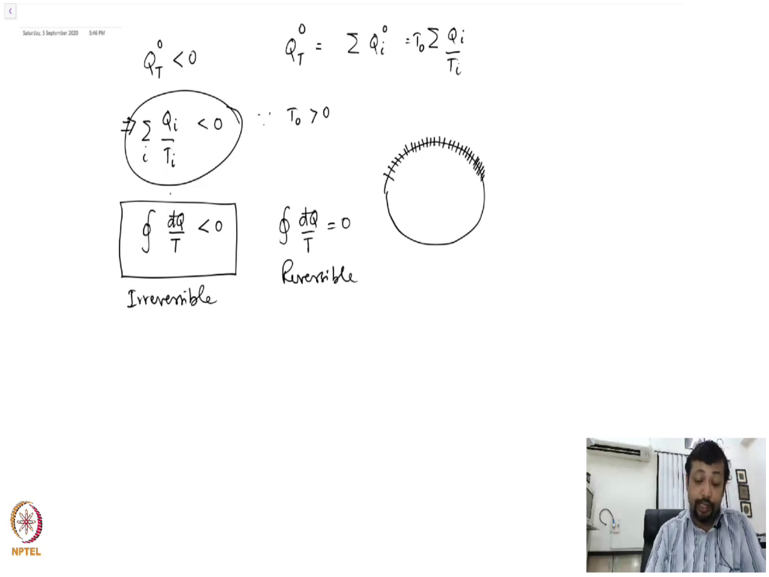

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$Q_T^0 < 0$

$Q_T^0 = \sum Q_i^0 = T_0 \sum \frac{Q_i}{T_i}$

$\Rightarrow \sum_i \frac{Q_i}{T_i} < 0 \quad \because T_0 > 0$

$\boxed{\oint \frac{dQ}{T} < 0}$

Irreversible

$\oint \frac{dQ}{T} = 0$

Reversible

Therefore, it follows that Q T 0 must be less than 0, but what is Q T 0? Q T 0 is sum over Q i 0 which is sum over t 0 Q i over T i this implies that Q i T i sum over I must be less than equal to 0.

Well in this particular case it must be just less than 0, but we will combine right. Since T naught is positive quantity. Once you have this relation you can imagine that all these heats now are infinitesimal heats therefore, I can write it down in the more general case where I have infinitesimal. So, I have the system and the heat transfers are infinitesimal that happens at different temperatures. So, I can generalize this as less than 0.

So, whenever the processes in the system involved are not reversible processes, the most. So, in the reversible case we saw that d cut Q over T is equal to 0 reversible and for irreversible processes this integral must be less than 0. If I want to convert this sorry not convert this, but combine these two it follows the general for any arbitrary process I must have d cut Q is less than equal to 0.

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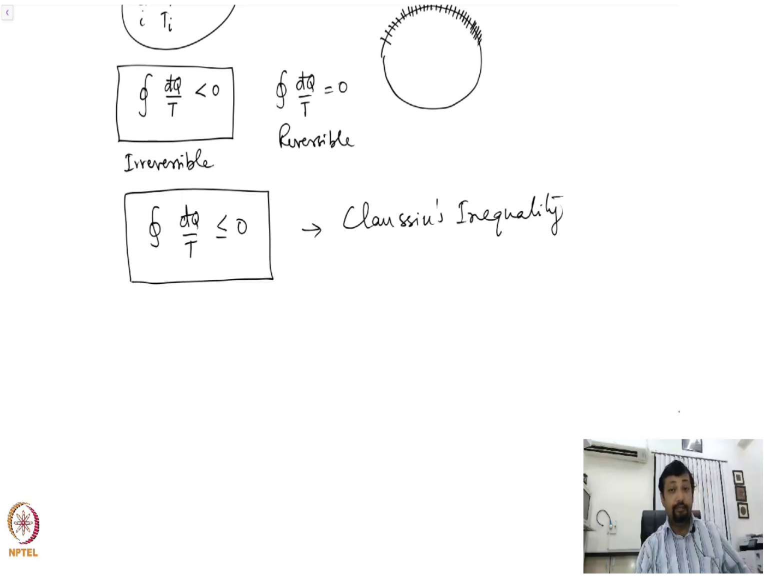

$i \quad T_i$

$$\boxed{\oint \frac{dQ}{T} < 0}$$

Irreversible

$$\oint \frac{dQ}{T} = 0$$

Reversible

$$\boxed{\oint \frac{dQ}{T} \leq 0} \rightarrow \text{Claussiu's Inequality}$$

So, this quantity is called not this quantity, but this inequality is called Clausius's inequality and it is very very important in thermodynamics.

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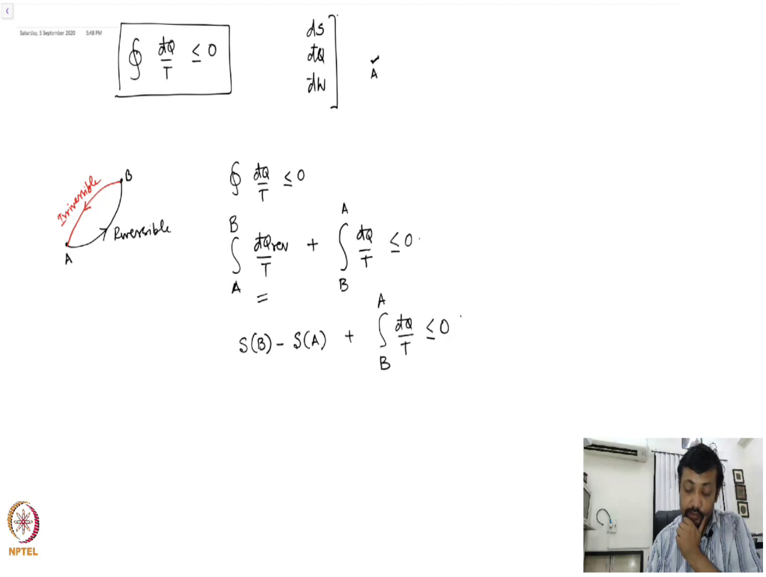

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$$\boxed{\oint \frac{\bar{d}Q}{T} \le 0}$$

$$\left.\begin{matrix} dS \\ \bar{d}Q \\ \bar{d}W \end{matrix}\right] \quad \overset{\checkmark}{A}$$

$$\oint \frac{\bar{d}Q}{T} \le 0$$

$$\int_A^B \frac{\bar{d}Q_{rev}}{T} + \int_B^A \frac{\bar{d}Q}{T} \le 0$$

$$=$$

$$S(B) - S(A) + \int_B^A \frac{\bar{d}Q}{T} \le 0$$

So, Clausius’s inequality tells me that Clausius’s inequality tells me that d cut Q by T must be less than 0 right. Now, one thing I want to make clear over here that see in thermodynamics whenever we doing the formulations of we always say that d S d kept Q d cut W what does this mean?

This means that there are always infinitesimal changes or quantities we are talking about and this essentially means that if I take have the thermodynamic state and then I take a thermodynamic state to a state which is very very close to A, an infinitesimal change in its macroscopic parameters.

How much change in infinitesimally changing or how much amount of heat to a; is the system taken is there does the system take or give off that is d cut Q? How much amount of work does it do that is your d cut W so on and so forth right. Now imagine that you take the thermodynamic take a thermodynamic system from the state A to a state B right and you do it via a reversible process.

You bring it back from B to A via an irreversible process, but then I know that for the whole cycle from A to B and B to A. So, you are going like this and coming back like this and then for the whole cycle d cut Q by T must be less than equal to 0. Now let us write it down in the more explicit form.

So, I have d cut Q reversible over T plus B to A d cut Q over T must be less than equal to 0, right. But I know what this quantity is. For a reversible process I can define this as S B minus S A right plus B to A d cut Q over T is less than equal to 0.

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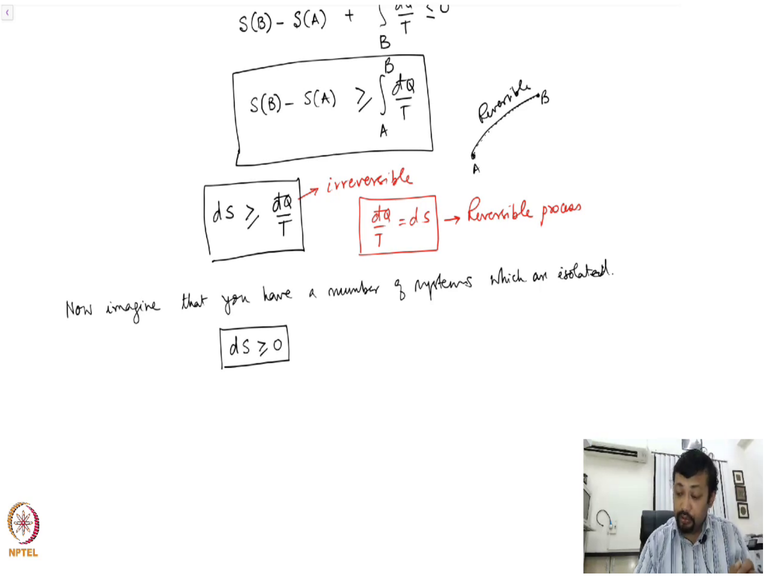

$$S(B) - S(A) + \int_{B} \frac{\bar{d}Q}{T} \leq 0$$

$$\boxed{S(B) - S(A) \geq \int_{A}^{B} \frac{\bar{d}Q}{T}}$$

$$\boxed{dS \geq \frac{\bar{d}Q}{T}} \rightarrow \text{irreversible}$$

$$\boxed{\frac{\bar{d}Q}{T} = dS} \rightarrow \text{Reversible process}$$

Now imagine that you have a number of systems which are isolated.

$$\boxed{dS \geq 0}$$

So, this follows thus S B minus S A is greater than equal to. If I want to write down this relation in a differential form I will write down d S is greater than d cut Q by T. Remember that this d cut Q that you have write down written down is for irreversible processes.

So, let us just and the relation d cut Q over T is equal to d S is valid only when you are considering a reversible process. So, this entropy what does this let us be more explicit about this. This entropy or any other thermodynamic parameter if I have a reversible process between A and B, then the entropy is defined for all the thermodynamic state points which lie on this curve if this is reversible.

In contrast, if it is an irreversible process this essentially means that it is only defined at A and B otherwise it is not. So, therefore, I have this particular relation d S which is greater than equal to d cut Q by T. Now imagine that you have a number of systems which are isolated or you can also think about adiabatic system. So, these systems are isolated which means there is no universe no path nothing around it.

And therefore, when they you bring them together. When you bring them together you see they are adiabatically insulated then essentially this means that there is no heat exchange and if there is no heat exchange this means that d S must be greater than equal to 0. So, this is a very very important consequence, it tells you that when the systems come to a joint equilibrium they kind of go to the maximum entropy state they go to the maximum entropy state.

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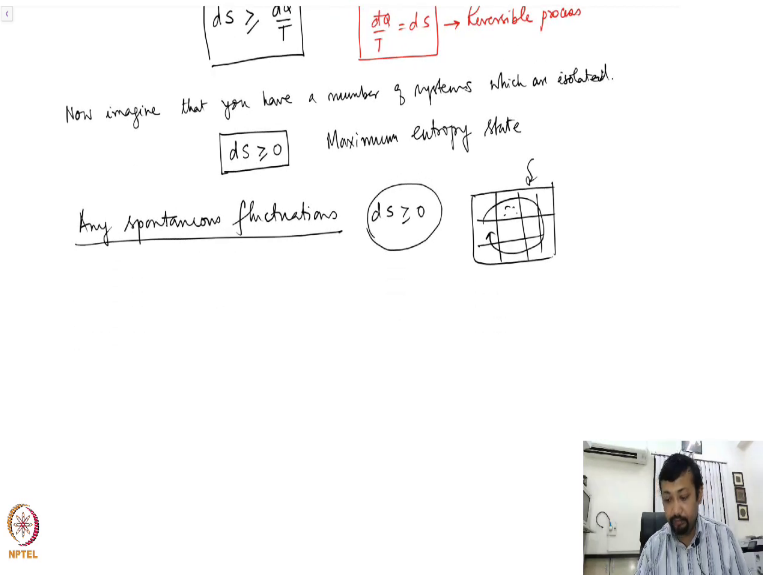

$\boxed{ds \geq \frac{dQ}{T}}$ $\boxed{\frac{dQ}{T} = ds}$ → Reversible process

Now imagine that you have a number of systems which are isolated.

$\boxed{ds \geq 0}$ Maximum entropy state

Any spontaneous fluctuations $ds \geq 0$

Of course, this also has to mean that the system is isolated system right. So, your joint equilibrium or the final thermodynamic state is the one which has the maximum entropy. So, any spontaneous fluctuation; why do we say a talk about any spontaneous fluctuations? Because your system which is made up of smaller subsystem is insulated from the outer world. So, therefore, there is no heat that no energy which flows out.

So, anything that can happen inside is a spontaneous change. So, any spontaneous fluctuations in this system must will give you d S greater than 0. So, which means that if they want to come to a joint equilibrium then they has to be they have to maximize their entropy right.

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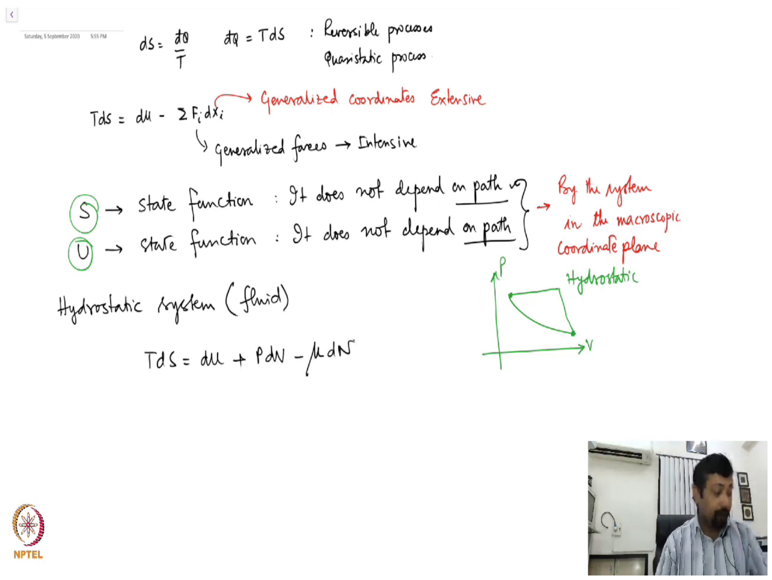

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$dS = \frac{đQ}{T}$ $đQ = TdS$: Reversible processes

Quasistatic process

$Tds = du - \sum F_i dX_i$ → Generalized coordinates Extensive

↳ generalized forces → Intensive

S → State function : It does not depend on path

U → State function : It does not depend on path

→ By the system in the macroscopic coordinate plane

Hydrostatic

Hydrostatic system (fluid)

$TdS = dU + PdN - \mu dN$

So, I know that d S is d cut Q by T. So, in principle therefore, it follows that d cut Q by d S and this is true for all reversible processes or quasi static processes which are necessarily reversible. So, therefore, I can write down rewrite down my 1st law as T d S is equal to d u minus sum over F i d X i.

If you have forgotten what this means the F i is my generalized forces which are intensive in nature and these are my generalized coordinates which are extensive in nature. In addition to that now I have the information that the quantity S is a state function, the entropy is a state function it does not depend on path.

Similarly, U is also a state function. We have seen that when we wrote down the 1st law that is to say that this also does not depend on the path. So, whenever you see when I write down path, you are familiar with trajectories in mechanics where you plot X and t and you said this is the path the particle takes, but here this is the path that is referred that is essentially the path which is taken by the system in the macroscopic coordinate plane.

And we have seen such examples where we had if we have a pressure volume for a hydrostatic system, we have seen that this can be the path, this can be a path, this can be a path, so on and so forth. So, all of this refers to the path that we are talking about and both S and internal energy does not depend on the path.

If it is a reversible process it only depends on the end points right.So, for a hydrostatic system we will just write it down quickly, for a hydrostatic system which is essentially a fluid my 1st law equation is d u plus P d v minus mu d N.

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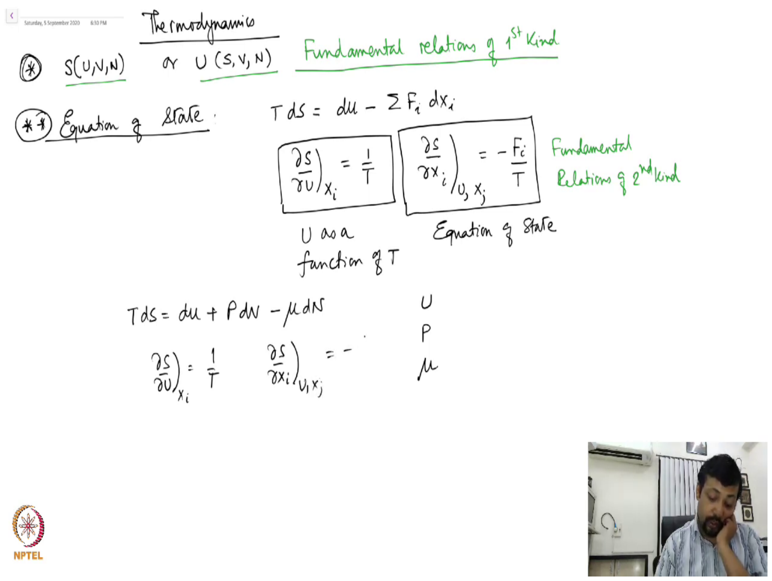

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Thermodynamics

(*) $S(U,V,N)$ or $U(S,V,N)$ Fundamental relations of 1^{st} Kind

(**) Equation of State

$$T\,dS = dU - \sum F_i\,dx_i$$

$$\boxed{\left.\frac{\partial S}{\partial U}\right)_{x_i} = \frac{1}{T}} \quad \boxed{\left.\frac{\partial S}{\partial x_i}\right)_{U, x_j} = -\frac{F_i}{T}}$$

Fundamental Relations of 2^{nd} kind

U as a function of T

Equation of State

$$T\,dS = dU + P\,dV - \mu\,dN$$

$$\left.\frac{\partial S}{\partial U}\right)_{x_i} = \frac{1}{T} \qquad \left.\frac{\partial S}{\partial x_i}\right)_{U, x_j} = -$$

U

P

μ

Now, in thermodynamics U, V, and N or U as a function of S, V, N these are called let us just highlight this a little bit and write it down as fundamental relations of first kind and these are the most powerful relations that you can have. For example if you know either S as a function of U, V, N or U as a function of S, V, N you can invert either of this and then essentially you can calculate the heat taken the change in entropy the work done all of this provided you know this.

The second one is of course, what we call the equation of state. Now the equation of state is if I write down like this way d u minus F i d X i, then you clearly see that del S del U the derivative holding all the coordinates fixed must be equal to 1 by T.

Similarly, del S del X i sorry this is del X i holding u and X j with j not equal to X i must be minus F i over T. This equation is called an equation of state and this relation is going to give you U as a function of T. So, clearly I have two approaches given this relation I have nothing to worry about for any thermodynamic processes that is given to me I can evaluate this.

The second route is this one, where you are rather not given the fundamental relation. So, let us these are called fundamental relations of second kind. If you are given the equation of state, then you necessarily can reconstruct back the entropy the fundamental relation that is always possible, but you have to know all the equations of state. So, if you write down the for the hydrostatic system which is for fluid T d S is d u plus p d v plus sorry minus mu d N.

In this particular case you have to know U as a function of T P as a function of v and n and t and also mu if you know all of this then you can reconstruct back this how well that is very easy because you know that del S del U is equal to 1 by T. X i are fixed and similarly you can use these relations these two derivatives you can integrate out to write down this as so, in one case let us be explicit here.

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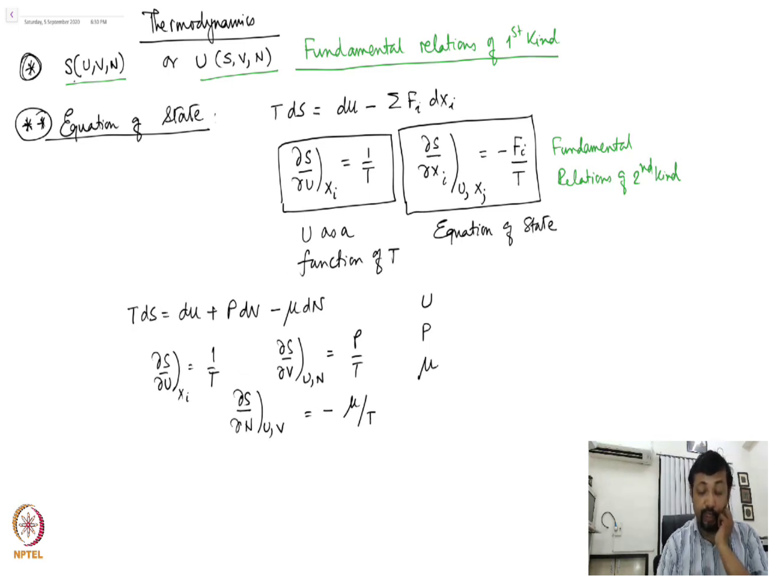

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Thermodynamics

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Fundamental Relations of 2nd kind

U as a function of T

Equation of State

$$T\,dS = dU + P\,dV - \mu\,dN$$

U

P

μ

$$\left.\frac{\partial S}{\partial U}\right)_{x_i} = \frac{1}{T} \qquad \left.\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T}$$

$$\left.\frac{\partial S}{\partial N}\right)_{U,V} = -\mu/T$$

Since, I have already written down the 1st law. So, del S del V is e U constant and N constant is P by T and del S del N U constant and V constant is minus mu by T. So, you can replace this over here and integrate out to determine S as a function of U, V and N right.

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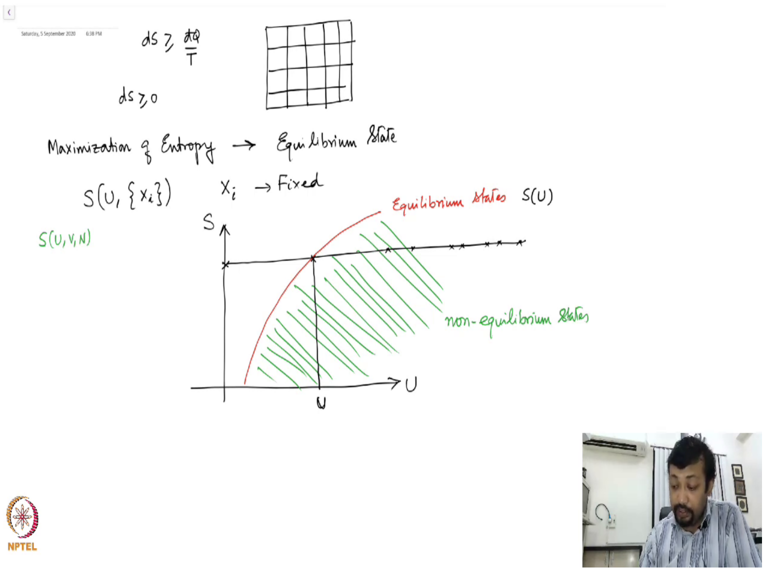

$dS \geq \frac{đQ}{T}$

$dS \geq 0$

Maximization of Entropy → Equilibrium State

$S(U, \{X_i\})$ X_i → Fixed

$S(U,V,N)$

So, we will come back to all of this a little later, but I want to discuss something. So, we have seen that d S must be greater than equal to d cut Q by T for the any general process right.

This means, that if I have a system which is adiabatically strained which means there are no possibilities of heat exchanges and it comprises of subsystems which are in equilibrium themselves and are brought together then since there is no heat exchange possible any spontaneous change within itself can only lead to a maximization of the entropy.

So, we see that the maximization of entropy leads to a thermodynamic equilibrium state correct? But now I know that the entropy is a function of U and X i. This is my fundamental relation of type 1. So, for a hydrostatic system I know that we have seen that S is a function of

U, V and N. See the forces are not appearing here, the F i's are not appearing, it is always the generalized coordinates right.

So, it follows let us take a system where I have fixed the X i's and I am only interested in looking at the in this plane. Now, let us draw a line over here. All the points on this line corresponds to the equilibrium states and all the points below this line essentially comprises of your non equilibrium states. So, these are your non equilibrium states. Can you find out why these are your non equilibrium states?

And all the points on this red line or red curve is essentially is the equation S as a function of U, where X i's are held fixed right. Now imagine that I fix the entropy of the system. If I fix the entropy of the system I have also fixed the coordinates of the system then you see there are several thermodynamic states are possible correct, but none of these are equilibrium state. The equilibrium state always corresponds to the minimum energy, the one which has the minimum energy of all the states.

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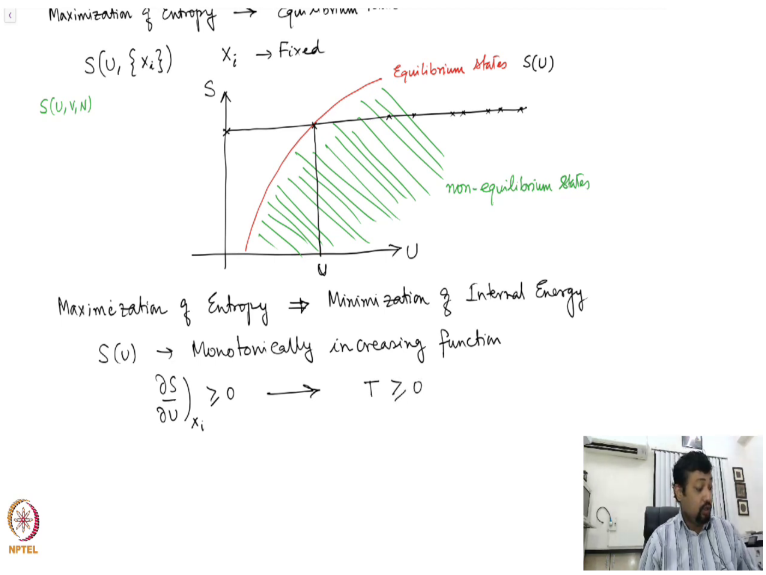

Maximization of entropy → equilibrium

$S(U, \{X_i\})$ $X_i \to$ Fixed

Maximization of Entropy ⇏ Minimization of Internal Energy

$S(U) \to$ Monotonically increasing function

$$\left.\frac{\partial S}{\partial U}\right)_{X_i} \geq 0 \longrightarrow T \geq 0$$

In other words, essentially this means that your maximization of the entropy of entropy is equivalent to minimization of internal energy. Of course, the point in here is that I have cheated a little bit you will see why. Now this is only possible you see when S is a monotonically increasing function of U. So, when S of U is a monotonically increasing function.

And this is where I have cheated because I have drawn a monotonically increasing function right. Clearly if you had this like this or in some other way then this would not have been possible and the property of the monotonically increasing function would mean that del S del U must be greater than 0. See X i’s are held fixed I have also held fixed, but this essentially means that the temperature must be positive.

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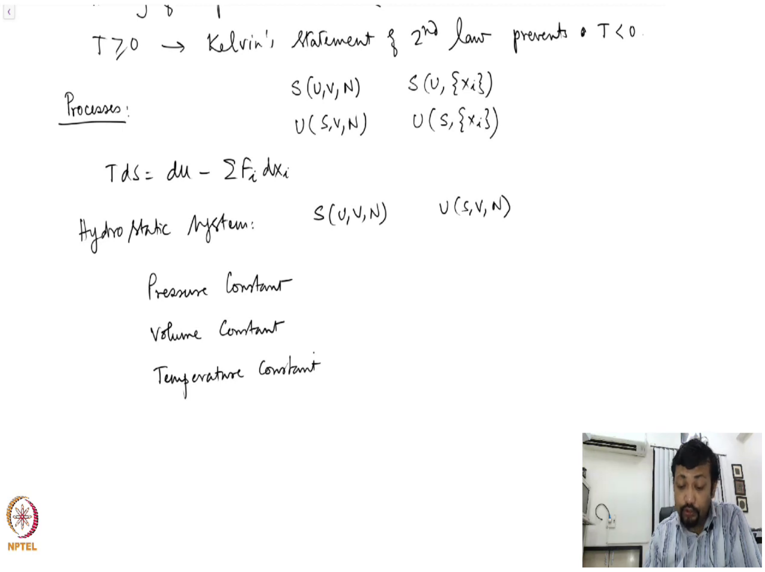

$T \geq 0 \rightarrow$ Kelvin's statement of 2^{nd} law prevents $T < 0$.

Processes:

$S(U,V,N)$ $S(U,\{x_i\})$

$U(S,V,N)$ $U(S,\{x_i\})$

$T\,dS = dU - \sum F_i\,dx_i$

Hydro Static System: $S(U,V,N)$ $U(S,V,N)$

Pressure Constant

Volume Constant

Temperature Constant

So, positivity of the temperature implies maximization of S and minimization of U are identical and the same thing that you are doing right. This holds because your temperature is positive. Your temperature is positive because Kelvin's statement of 2nd law prevents a negative temperature right.

So, everything is kind of falling in place and there is nothing. So, this more or less now we are done with thermodynamics or rather we have learned of what are the guiding principles in thermodynamics, now I want to apply this right.

So, for that we have to look at processes and as we said before that S as a function of U, V, N for hydrostatic system or equivalently S as a function of U of X i. These are or U as a function of S, V, N for a hydrostatic system, U as a function of X i are the fundamental relation. So, if I know this I know everything.

And since you see when we formulated the thermodynamics thermo dynamical principles, we are always writing down differential change and therefore, partial calculus would give us all the answers we want to look at. So, any thermodynamic process you can imagine must obey the 1st law and the 2nd law right which in sum therefore, should be d u minus sum over F i d X i right.

We will take the example of the hydrostatic system where S is a function of U, V, N or U as a function of S, V, N. Now let us look at processes. So, how can you take the thermodynamic system from A to B? There are several ways. You can keep pressure constant, you can keep volume constant, you can keep temperature constant.

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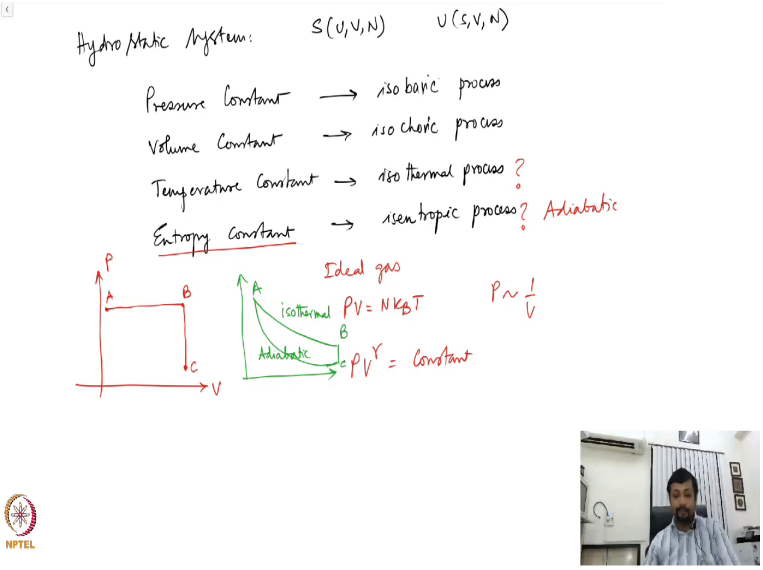

Hydro Static System: $S(U,V,N)$ $U(S,V,N)$

Pressure Constant → iso baric process

Volume Constant → iso choric process

Temperature Constant → iso thermal process ?

Entropy Constant → isentropic process ? Adiabatic

Ideal gas

$PV = NK_BT$

$P \sim \frac{1}{V}$

$PV^{\gamma} = \text{Constant}$

Usually particle number is always held constant. So, we will not talk about an explicitly unless we want to and you can also keep entropy constant right. This is what is known an isochoric process this is known an sorry I will say you know other way around.

This has to be an isobaric process, this has to be an isochoric process and this has to be an this is what is called an isothermal process, this is isentropic process. You have to realize that depending on the thermodynamic coordinates that you choose this processes look different. So, if I for example, take the PV diagram, let us use a different color now.

So, if I use a P V diagram now an isobaric process is where you take the system from A to B right where your pressure is held constant and isochoric process would be this one where you take from B to C, where your volume is constant. Now clearly what is an how does an isothermal process or an isentropic process look? For an isentropic process for this you have to know the type of system you are looking at.

If I look at an ideal gas, then I know that P V is N K B T. So, therefore, I know that if it is an isothermal process then pressure must go as 1 by V. If it is an isentropic process where the entropy is constant which means it is an adiabatic process no heat exchange that would also mean that P V to the power gamma is equal to constant.

So, these are the kind of curves you expect as you take it from in the P V diagram and we have seen the example of that in the Carnot engine. One of them was like this the other one was slightly steeper right. So, this is isothermal and this is adiabatic. So, you take the system from B and C right.

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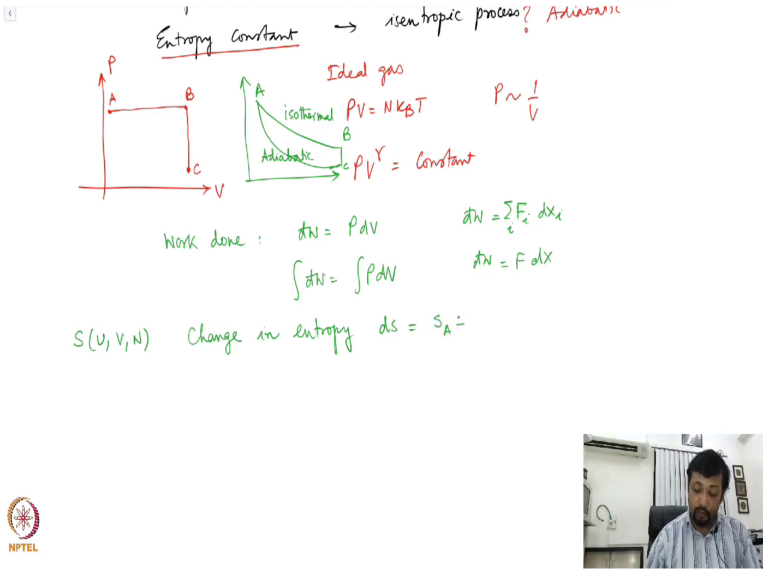

Entropy constant → isentropic process? Adiabatic

Ideal gas

$PV = NK_BT$ $\quad P \sim \frac{1}{V}$

PV^γ = Constant

Work done : $đW = PdV$ $\quad đW = \sum_i F_i\, dx_i$

$\int đW = \int PdV$ $\quad đW = F\,dX$

$S(U,V,N)$ Change in entropy $dS = S_A$ ÷

The work done for this particular system is P d V. In general is F i d X i sum over i. If you have one force then it is just F 1 sorry if you have just one thermodynamic coordinate; for example, here I have only one extensive coordinate for the hydrostatic system which is the volume because n is typically (Refer Time: 36:32) then this is the case is the work done.

And therefore, the total work done would be integral d cut W which is integration P d V right. So, these are the nitty gritty details calculational details of how you calculate the work done the heat exchange changed so on and so forth in this system. Given S as a function of U, V, N now typically whenever.

So, whenever we will give illustrations we will only concern ourselves with hydrostatic system, then change in entropy is d S it is a state function. If it is taken from A to B, then I know that this is S A minus sorry it is going to be S B minus S A.

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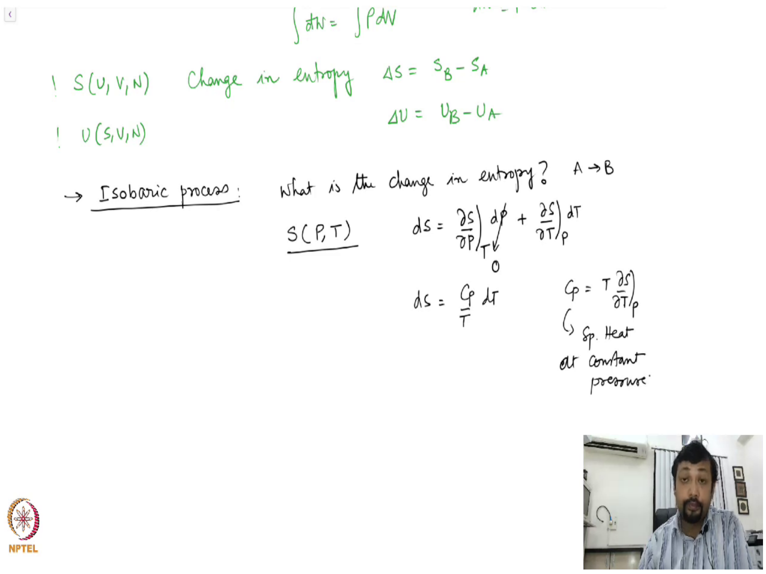

$\int dW = \int P dV$

! $S(U, V, N)$ Change in entropy $\Delta S = S_B - S_A$

! $U(S, V, N)$ $\Delta U = U_B - U_A$

→ Isobaric process: What is the change in entropy? A → B

$S(P,T)$ $$dS = \left.\frac{\partial S}{\partial P}\right)_T \underset{0}{dP} + \left.\frac{\partial S}{\partial T}\right)_P dT$$

$$dS = \frac{C_P}{T} dT$$ $$C_P = T \left.\frac{\partial S}{\partial T}\right)_P$$

↳ Sp. Heat at constant pressure.

The change in entropy let us say is going to be delta S is going to be S B minus S A. If you know this relation then of course, you know u as a function of S, V, N, then the change in internal energy would be U, B minus U, A provided you know these relations right. If I have an isobaric process I can ask what is the change in entropy. As the system goes from A to B, I am not constraining myself to an ideal gas for any arbitrary system.

The answer is very simple and here in your partial calculus help us entropy is a state function. Therefore, here you see that I have an isobaric process. In the isobaric process the pressure is held constant. Therefore, the temperature and the volume can change for a hydrostatic system.

So, what I am going to do is I am going to write down S, take S as a function of P and T, I will not worry about following.

You have to understand also that not all the three equations of states are independent because you can eliminate between them, only two of them are independent quantities and that is typed down very closely and that is because of your Gibbs-Duhem relation, but we will come to that. So, if I write down S as function of P and T then d S by rule of partial derivative is temperature constant d P plus del S del T pressure constant d T.

But look I have it is an isobaric process and I have held pressure constant therefore, d P must be 0. So, it follows d S is C P d T sorry C P by T d T, where C P is T del S del T, pressure constant is a specific heat at constant pressure right.

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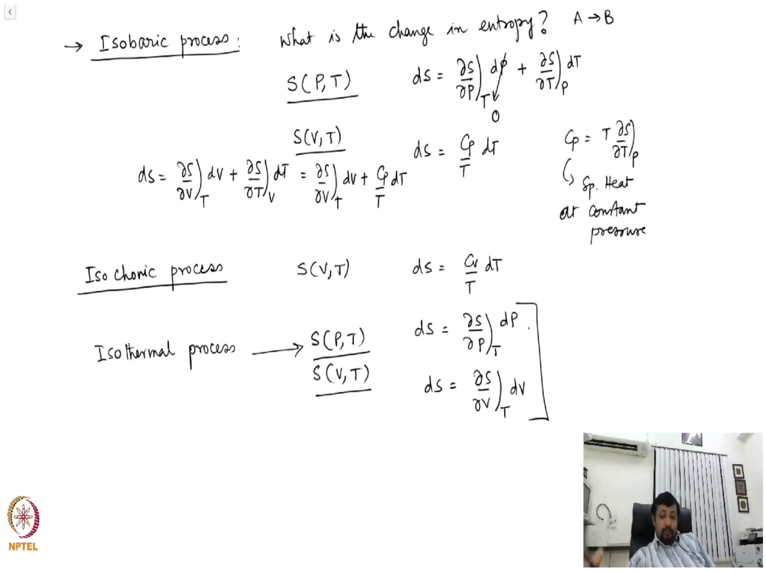

→ Isobaric process: What is the change in entropy? A → B

S(P, T)

$$dS = \left.\frac{\partial S}{\partial P}\right)_T \underset{0}{dP} + \left.\frac{\partial S}{\partial T}\right)_P dT$$

S(V, T)

$$dS = \left.\frac{\partial S}{\partial V}\right)_T dV + \left.\frac{\partial S}{\partial T}\right)_V dT = \left.\frac{\partial S}{\partial V}\right)_T dV + \frac{C_p}{T} dT$$

$$dS = \frac{C_p}{T} dT$$

$$C_p = T \left.\frac{\partial S}{\partial T}\right)_P$$

↳ Sp. Heat at constant pressure

Iso choric process S(V, T)

$$dS = \frac{C_v}{T} dT$$

Isothermal process → S(P, T), S(V, T)

$$dS = \left.\frac{\partial S}{\partial P}\right)_T dP.$$

$$dS = \left.\frac{\partial S}{\partial V}\right)_T dV$$

If you are looking at an isochoric process, you can do the same thing if I ask you what is the change in the internal energy right. If you are looking for an isochoric process, then you will write down this as V comma T and you will see that d S is C V T d T and the heat taken out is just T d S which is just C V d T. In this case it is c p d t right.

For an isothermal process your temperature is held constant. So, you can take either as a function of P and T or V and T you can also take here as a function of V and T, but here you have to note that if you in the isobaric process if you take S as a function of V and T then your d S is del S del V temperature constant d V plus del S del T volume constant d T.

This is equal to del S del V temperature constant d V plus C p by T d T. Please note that your d V is non zero because your pressure is held constant, but not the volume and you have to somehow manipulate this derivative. We will do it later on once we have introduced Maxwell's relations and so on and so forth.

Now, for then isothermal process coming back to it I can either have S as a function of P and T or S as a function of V and T in which case since d T is going to be 0 a priori I know it is going to be del S del P temperature constant d P del S del V volume sorry d S is going to be del S del V temperature constant d V depends on what information is given to you. So, if I if you are asked to calculate the change in entropy given that your pressure doubles.

Then, you are going to use this first relation S as a function of P and T and if it is for you are given the information that your volume doubles or volume halves in the isothermal process what is the change in entropy or how much heat is taken then you would precisely do it the second way you take the second relation. So, you essentially get the general idea of how to deal with thermodynamic processes and thermodynamic systems.

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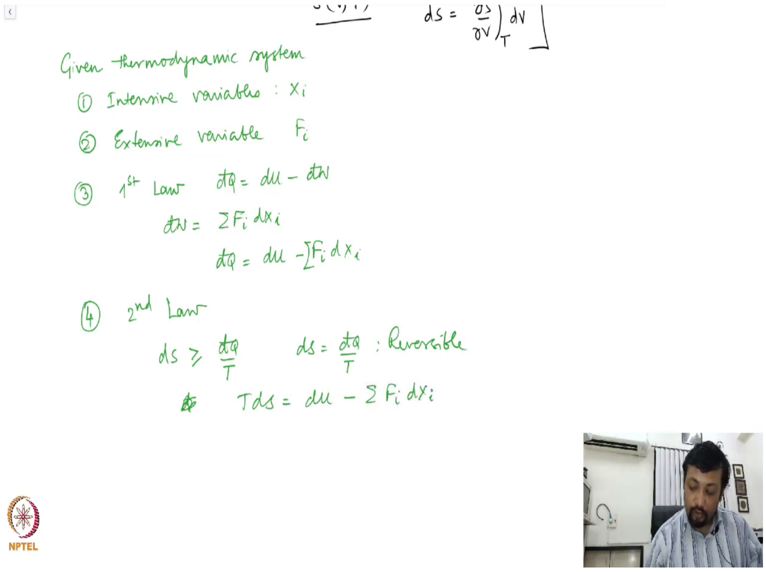

$ds = \left.\frac{\partial s}{\partial v}\right)_T dv$

Given thermodynamic system

① Intensive variables : X_i

② Extensive variable F_i

③ 1st Law $\bar{d}Q = du - \bar{d}W$

$\bar{d}W = \sum F_i dx_i$

$\bar{d}Q = du - \sum F_i dx_i$

④ 2nd Law

$ds \geq \frac{\bar{d}Q}{T}$ $ds = \frac{\bar{d}Q}{T}$: Reversible

$Tds = du - \sum F_i dx_i$

Again, let us just very quickly summarize that for a given thermodynamic system I have a set of intensive variables and a set of extensive variables. X i F i 1st law is delta Q or we will write it down in the differential form d cut Q is d u minus d cut W; d cut W is F i d X i so, that d cut Q is equal to d u minus F i d X i.

If you have two coordinates two terms is going to come three coordinates three times its going to comes so on and so forth. And then enters the 2nd law that tells you that d S must be greater than equal to d cut Q by T, if it is a reversible process then you have d S is d cut Q by T and therefore, you have T d S is equal to d u minus sum over F i d X i.

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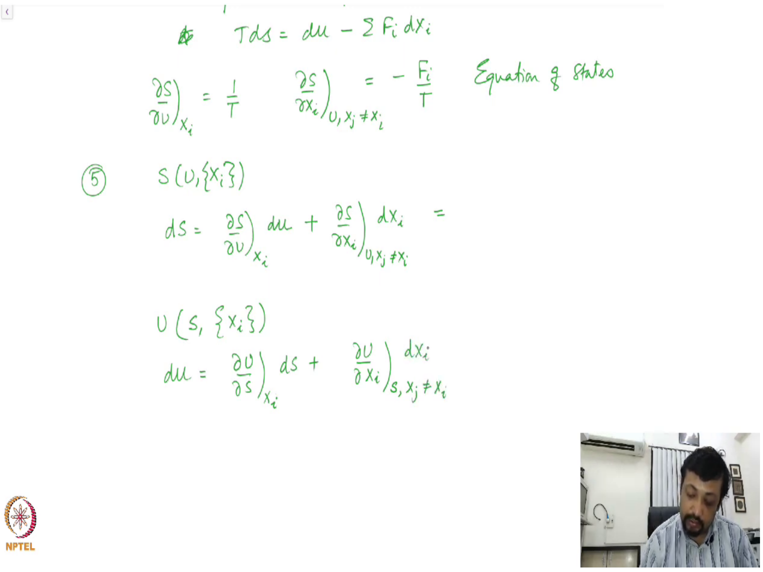

$$T\,ds = du - \sum F_i\,dx_i$$

$$\left.\frac{\partial S}{\partial U}\right)_{x_i} = \frac{1}{T} \qquad \left.\frac{\partial S}{\partial x_i}\right)_{U, x_j \neq x_i} = -\frac{F_i}{T}$$

Equation of states

⑤ $S(U, \{x_i\})$

$$dS = \left.\frac{\partial S}{\partial U}\right)_{x_i} du + \left.\frac{\partial S}{\partial x_i}\right)_{U, x_j \neq x_i} dx_i =$$

$U(S, \{x_i\})$

$$du = \left.\frac{\partial U}{\partial S}\right)_{x_i} dS + \left.\frac{\partial U}{\partial x_i}\right)_{S, x_j \neq x_i} dx_i$$

Once you have written down this differential form of the 1st law you immediately say that del S del U X i's all the coordinates held constant must be equal to 1 by T and del S del X i U and X j which is not equal to X i sorry which is not equal to X i held constant would be minus F i over T right and these are your equation of states.

If you are given S as a function of U and X i, then you can write down d S as del S del U X i held constant d u plus del S del X i u and X j not equal to X i held constant d X i right and then you can immediately relate it with these derivatives.

You can of course, have the other way around where you have U as a function of X and X i in which case d u is del U del S all the coordinates are held constant d S plus del U del S not again an S, but rather the coordinates X i with the entropy and X j not equal to X i held constant d X i.

And then you can immediately compare once again you can immediately compare it with the 1st law and see that del U del S X i held constant must be T and del U del X i entropy X j not equal to X i must be equal to F i over T.

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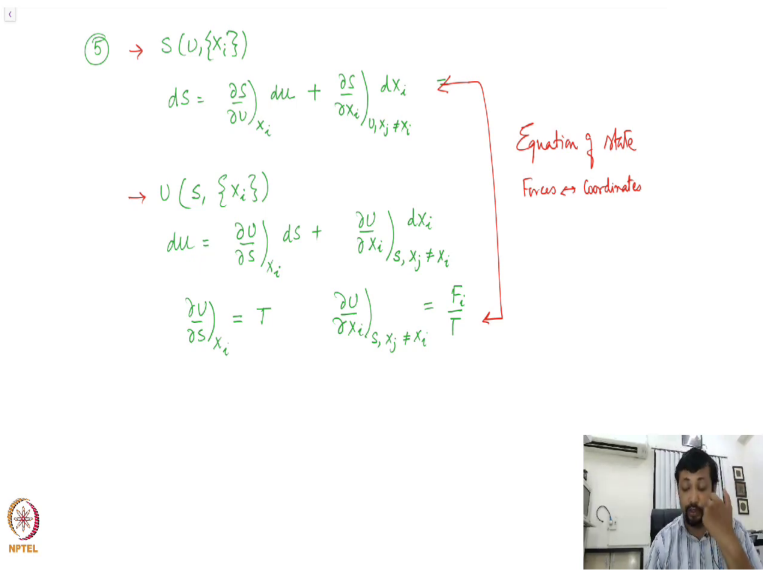

⑤ → $S(U, \{X_i\})$

$$dS = \left.\frac{\partial S}{\partial U}\right)_{X_i} dU + \left.\frac{\partial S}{\partial X_i}\right)_{U, X_j \neq X_i} dX_i$$

→ $U(S, \{X_i\})$

$$dU = \left.\frac{\partial U}{\partial S}\right)_{X_i} dS + \left.\frac{\partial U}{\partial X_i}\right)_{S, X_j \neq X_i} dX_i$$

$$\left.\frac{\partial U}{\partial S}\right)_{X_i} = T \qquad \left.\frac{\partial U}{\partial X_i}\right)_{S, X_j \neq X_i} = \frac{F_i}{T}$$

Equation of State

Forces ↔ Coordinates

So, essentially given these two relations you can derive the equation of state that relates the fundamental that relates the forces with the coordinates right for a for an ideal gas this would be like P v equal to N K B T and U is equal to three half N K B T ok. So, now, we have mostly covered this part.