Introduction to Molecular Thermodynamics

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Lecture - 02
Review of Classical Thermodynamics (Contd.)

Hello. Welcome back to the Review of Classical Thermodynamics part 2. So, we have already discussed the first law of thermodynamics, where we have seen that an energy function has been defined which is a internal energy.

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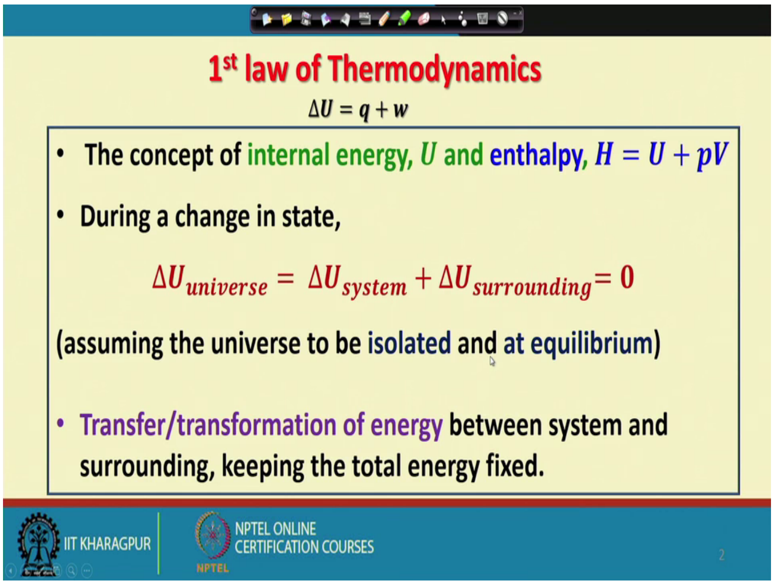

1st law of Thermodynamics

$\Delta U = q + w$

- The concept of internal energy, U and enthalpy, $H = U + pV$
- During a change in state,

$$\Delta U_{universe} = \Delta U_{system} + \Delta U_{surrounding} = 0$$

(assuming the universe to be isolated and at equilibrium)

- Transfer/transformation of energy between system and surrounding, keeping the total energy fixed.

And we have given it a symbol U. And it was discussed that the change in internal energy can be carried out in two different ways. First you can talk about supplying heat to the system or withdrawing heat to the system and making the system work or extract some work from the system. So, the different informations that we get from the first law are as follows. First it introduces the very important concept of internal energy and also it introduces another energy function enthalpy which is defined as a sum of internal energy plus a term an additional term, which is comprised of pressure and volume.

We will come back to the importance of enthalpy as an energy function, but let us now go back and see how a change in state is described within the first law of thermodynamics. If we assume that the universe is composed of the system and its surrounding, then during a change in state there may be some change in the internal energy of the system. And associated with that there may be some change in internal energy of the surrounding.

Now if you assume that the universe is isolated and is always at equilibrium, then by the first law of thermodynamics I would say that delta U universe which is the summation of the changes in the system internal energy and the surrounding internal energy that must remain equal to 0. Or in other words when the universe is isolated and at equilibrium, then its total internal energy remains constant. And therefore, the first law suggests that when a system is undergoing some change in state, it can transfer some amount of energy between itself and the surrounding whereas, the sum of internal energy of the system and the surrounding remains the same.

So, of course, the first law of thermodynamics tells us a lot, but there are a lot more that it does not. And let us have a look at the limitations of the first law of thermodynamics.

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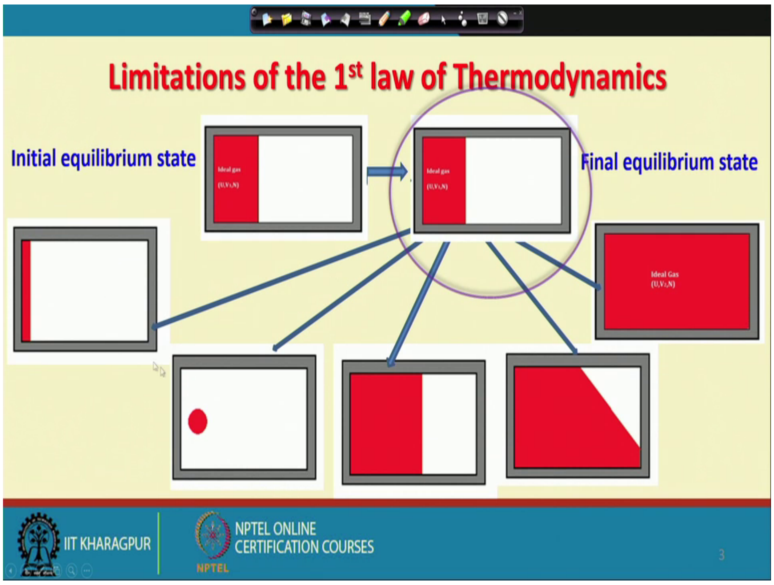

Limitations of the 1st law of Thermodynamics

And try to understand why we needed a second law at all. So, in this case I am going to concentrate on a very simple system. This particular system is contained within a rigid impermeable box as shown by this grey area, and there are two compartments inside this system. In the initial equilibrium state as we have seen before the right hand side compartment is highly evacuated and the left hand side compartment is filled with an ideal gas. So, in the initial equilibrium state we have prepared the system like that, and if we do not disturb the system it remains in this state. Now we are planning to disturb this system and how do we disturb this system? We are going to withdraw this separator without adding or extra or withdrawing energy from the system, and then the system finds itself ready to undergo a change in state now what will happen.

There are many different possibilities under such circumstances and these are the many different possibilities that are highlighted over here. When the gas undergoes a change in state it may so happen that it compresses, and compresses and goes to one edge of the system and remains here. It may so happen the gas in the new equilibrium state calls up in a ball. So, once again this is a compression of the gas. But obviously, the final state as you see here and the as you see here they are different.

In other words there are possibilities that the gas may undergo expansion. So, it may undergo expansion in such a way that it expands up to here maybe half way through the box and stops. It may expand a little more, but still it stops when still some area is yet to be filled or it may go all the way expand and fill up the entire box. So, the question is which one is the final equilibrium state, our experience with the real world experimental system says that the gas would expand it will not undergo compression as shown here, it will not stop in during the expansion, where it would fill halfway or maybe 75 of the box.

The final equilibrium state is going to be when the gas expands, and fills that entire box. And the first law of thermodynamics does not tell us why it expands the first law of thermodynamics is entirely silent on why the compression process may not be possible. And also it does not tell us even if expansion is happening why should the gas fill up the entire box as we see in the real walled experiments there is something farther that we have to bother about in the second law of thermodynamics.

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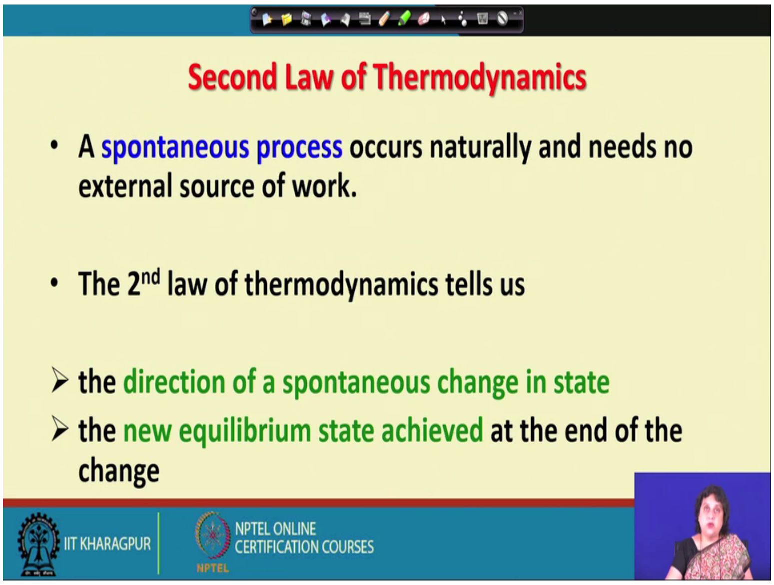

Second Law of Thermodynamics

- A spontaneous process occurs naturally and needs no external source of work.
- The 2nd law of thermodynamics tells us
  - the direction of a spontaneous change in state
  - the new equilibrium state achieved at the end of the change

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First the second law of thermodynamics says as we have already seen, a spontaneous process occurs naturally and needs no external source of work. And it also tells us that the direction of a spontaneous change in state can be predicted and also the new equilibrium state achieved at the end of the change that also can be predicted. So, what else does the second law of thermodynamics two?

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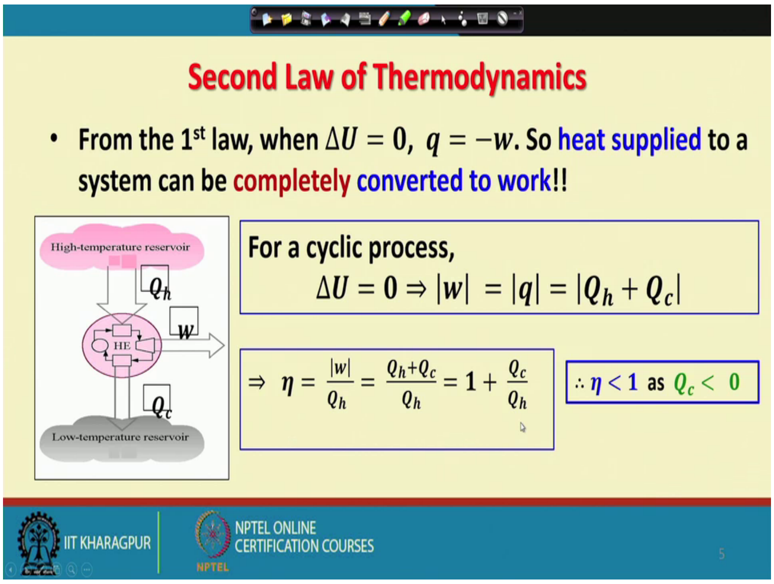

Second Law of Thermodynamics

- From the 1st law, when $\Delta U = 0,\ q = -w$. So heat supplied to a system can be completely converted to work!!

For a cyclic process,

$$\Delta U = 0 \Rightarrow |w| = |q| = |Q_h + Q_c|$$

$$\Rightarrow \eta = \frac{|w|}{Q_h} = \frac{Q_h + Q_c}{Q_h} = 1 + \frac{Q_c}{Q_h}$$

$$\therefore \eta < 1 \text{ as } Q_c < 0$$

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It also brings to us the crucial problem of harnessing energy from a given change in state. And this is another aspect where the first law of thermodynamics is not doing enough. If we have a look at what the first law of thermodynamics say.

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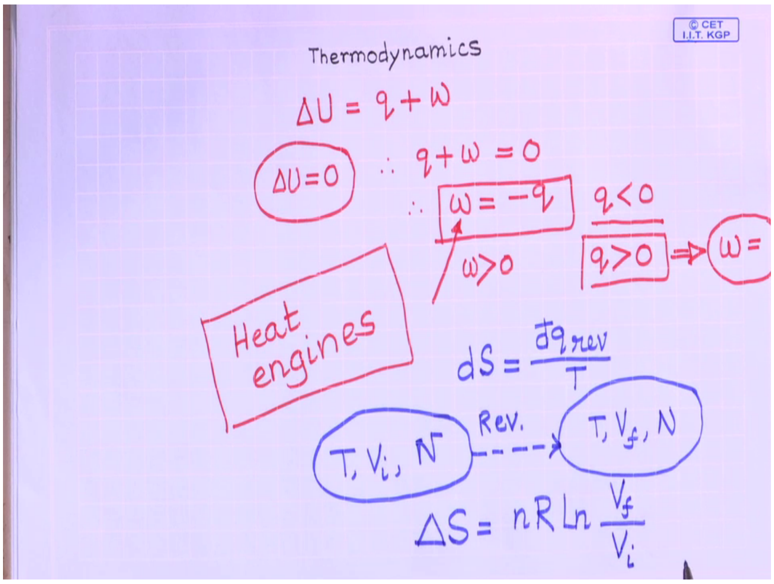

Thermodynamics

$\Delta U = q + w$

$\boxed{\Delta U = 0}$ $\therefore q + w = 0$

$\therefore \boxed{w = -q}$ $q < 0$

$w > 0$ $\boxed{q > 0} \Rightarrow w =$

Heat engines

$dS = \frac{đq_{rev}}{T}$

$T, V_i, N \xrightarrow{\text{Rev.}} T, V_f, N$

$\Delta S = nR \ln \frac{V_f}{V_i}$

We have already seen that the change in state introduces a change in internal energy of the system, whereby I have delta U is equal to q plus w. Now if it so happens that delta U is equal to 0 this means that I must be having q plus w equal to 0, this also means that w would be equal to minus q. Now this means that if I am doing work on the gas, then w is less than greater than 0 by the sign convention I have introduced in the last class and correspondingly I will have q must be less than 0. Now what does this correspond to q less than 0, it corresponds to the heat lost by the system

Or in other direction you can say that if q is greater than 0 that is the system gains heat this implies that for the condition where delta U is equal to 0, I must be having w equal to whatever heat has been supplied to the system. Now is this possible, this was very interesting you could see that you induce a system, you heat up a system and you convert the entire heat into doing some external work, and this is the purpose this is the purpose that would be served by what are known as heat engines. Now you must have come across heat engines while studying thermodynamics, since this is a review class I am going to look up some brief description of what a standard heat engine does.

For the maximum efficiency one introduces a heat engine that operates reversibly between a high temperature reservoir and low temperature reservoir. So, what it does is it undergoes a cyclic process. Initially it extracts Q h amount of heat from the hot reservoir, and in the final stages it rejects Q c amount of heat to a low temperature or cold reservoir. And in this process while going back to its initial state it does w amount of work on the surrounding. So, it is our interest that we are going to have maximum amount of work available being done by this reversible heat engine with the input of Q h that is the amount of heat absorbed at the high temperature reservoir. Now once again this is a cyclic process.

And therefore, delta U is equal to 0 and this also means that the amount of work that can be extracted this is equal to the modulus that is the amount of heat that is supplied from the first law of thermodynamics. Now what is the total amount of heat supplied in this system? That is Q h the amount of heat that has been exchanged at the hot reservoir plus Q c the amount of heat that has been exchanged at the low temperature reservoir. You must realize that Q h and Q c each of these quantities may be positive or negative depending on whether the heat is being gained by the system, that is my heat engine or it is being rejected by the system ok.

Now, what is the consequence of? This consequence is that we are going to describe the efficiency of the heat engine as the amount of the magnitude of the work done by it divided by the input. So, output divided by input; for the maximally efficient engine eta must be equal to 0. Now I look at what the expression of eta is, and I find that eta is 1 plus Q c by Q h. Now this means that eta will always be less than one why is that so? That is because Q c is the amount of heat rejected by the heat engine to the low temperature reservoir therefore, by the sign convention that we have adopted here it is a negative quantity and if Q c is a negative then this is going to be less than one because of the presence of a fraction with a negative sign here.

So, what we find is the second law of thermodynamics is telling us something that the first law did not tell us. It tells us that well there should be some preferred direction for a spontaneous change in state, and during this change in state if you are interested in harnessing the energy you cannot do it with 100 percent efficiency, even when you are working under the conditions that a maximum work can be extracted during the change in state.

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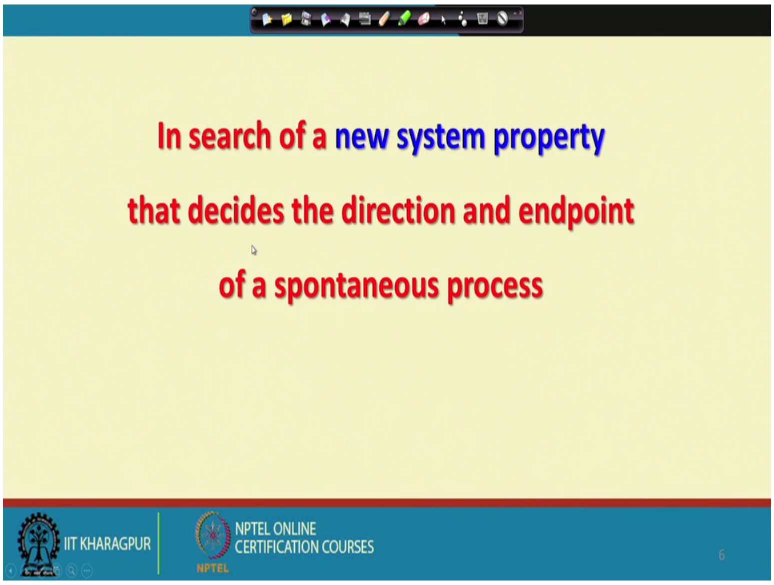

In search of a new system property

that decides the direction and endpoint

of a spontaneous process

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Then obviously, the challenge was to look for a new system property that decides the direction and endpoint of a spontaneous process.

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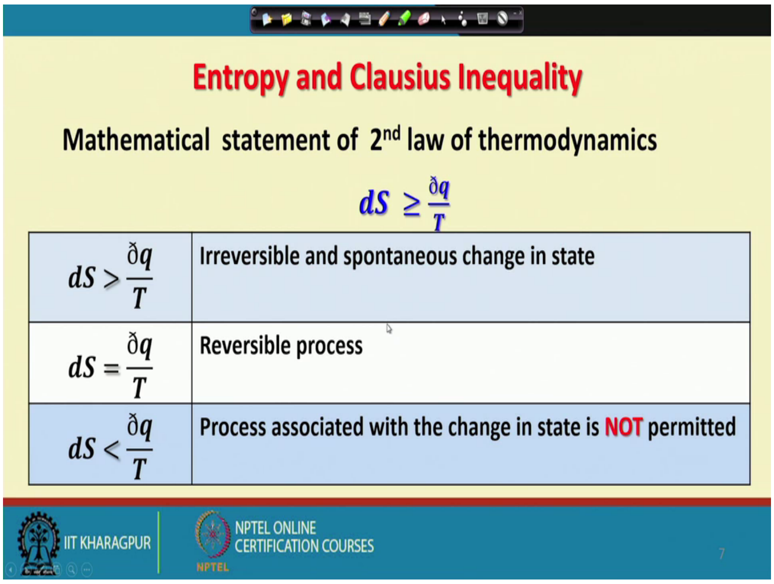

Entropy and Clausius Inequality

Mathematical statement of 2nd law of thermodynamics

$$dS \geq \frac{\eth q}{T}$$

$dS > \frac{\eth q}{T}$	Irreversible and spontaneous change in state
$dS = \frac{\eth q}{T}$	Reversible process
$dS < \frac{\eth q}{T}$	Process associated with the change in state is NOT permitted

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And this is where the second law of thermodynamics introduces the concept of entropy. I will present to you sure directly the mathematical statement of the second law of thermodynamics, in terms of a relationship that is known as the clausius inequality. Let us say I have an a system which is an initially in equilibrium and then it is induced to undergo a change in state.

And if this change in state is infinitesimal and is associated with an exchange of heat dq at a thermal reservoir maintained at a temperature T, then the clausius inequality says d S must always be greater than or equal to this ratio del q by T. And here the inequality sign is having different implications. It says that when d S is greater than this ratio then we are essentially looking at irreversible and spontaneous change in state, as this system goes from an entropy value of S to S plus d S. If it so happens that the process associated with this change in state is not permitted, which me it is not spontaneous it must be associated with this relationship that d S is less than this ratio.

So, what happens a system when it starts from an equilibrium state, it changes its entropy which is d S and it will go in the direction where d S increases, and till it reaches this equality that d S is equal to del q by T. Now this mathematical relationship is perhaps best understood when we apply it to a real system.

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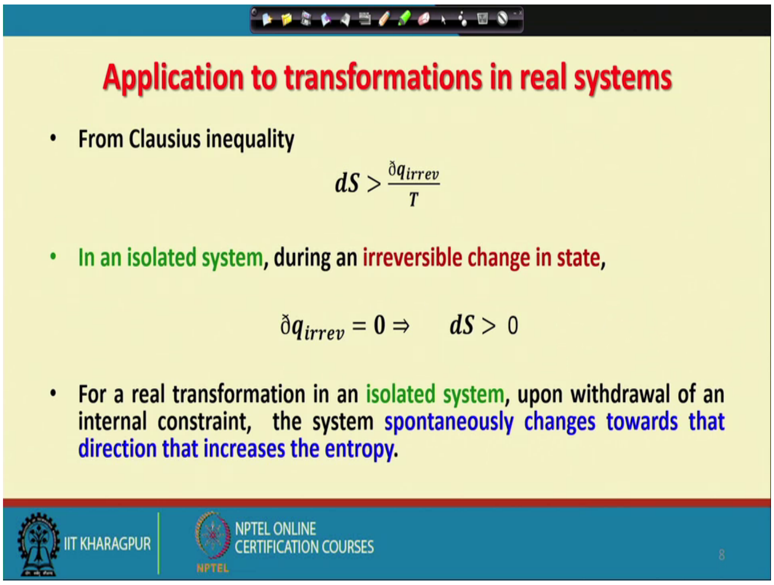

Application to transformations in real systems

- From Clausius inequality

$$dS > \frac{\eth q_{irrev}}{T}$$

- In an isolated system, during an irreversible change in state,

$$\eth q_{irrev} = 0 \Rightarrow \quad dS > 0$$

- For a real transformation in an isolated system, upon withdrawal of an internal constraint, the system spontaneously changes towards that direction that increases the entropy.

So, let us have a look at what it means by applying the clausius inequality to a real system where a spontaneous process is happening. So, the clausius inequality tells us that d S would be greater than del q irreversible by T. Now if I have an isolated system will there be any heat exchanged between the system and the surrounding during this change in state. The answer is no and this means that if the system undergoes a change in state under isolated condition then d S must be greater than 0. So, for a real transformation in an isolated system, upon withdrawal of an internal constraint the system spontaneously changes towards that direction that increases entropy.

So, this is the implication of the second law of thermodynamics as far as understanding the direction of spontaneous changes of state is concerned. But once again to understand this entire framework, let us take an example and a simple one. So, this is the system that I am talking about which I have already explained, and from your previous exposure to a thermodynamics. You probably know that, this is essentially the system used in joules experiment the celebrated experiment carried out by joule where the ideal gas is placed in one part of the insulated box.

And then on the other hand on the right side there is an absolute vacuum and a change in state is induced by withdrawing this separator, and allowing the gas to expand.

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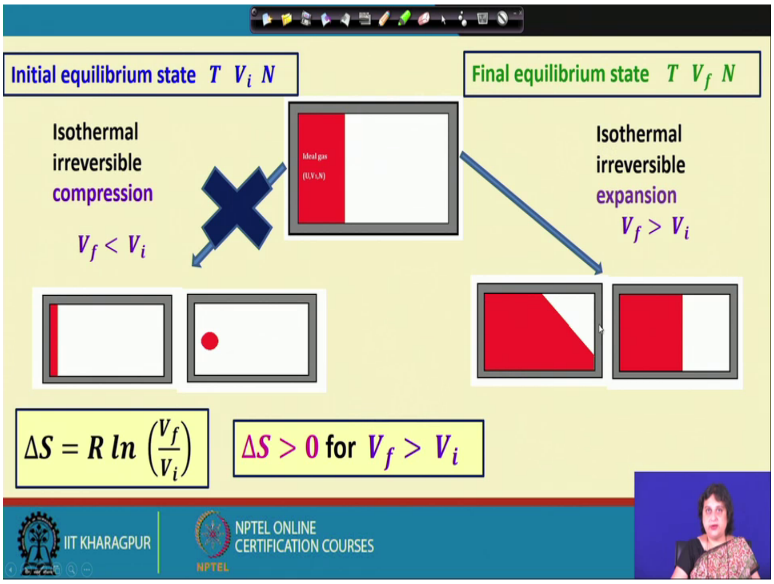

Initial equilibrium state T V_i N

Final equilibrium state T V_f N

Isothermal irreversible compression $V_f < V_i$

Isothermal irreversible expansion $V_f > V_i$

$\Delta S = R\,ln\left(\frac{V_f}{V_i}\right)$

$\Delta S > 0$ for $V_f > V_i$

Now if you use an ideal gas then you will see that the gas will expand and under the experimental conditions, there will be no change in the temperature of this system recorded if you use an ideal gas here. So, basically we are looking at the change in state whereby the system undergoes starts from this initial equilibrium state characterized by these three variables temperature T volume of this ideal gas V i and N is the number of particles constituting the ideal gas. And we are looking at the change in state whereby it reaches the final equilibrium state with the same temperature and the same number of particles, but a different volume that is designated as V f. Now the question is if this gas undergoes compression, this compression will be against a 0 pressure because this part is maintained under high vacuum.

So, these are the possible equilibrium states final equilibrium states. So, the process with which they are going to be reached would be nothing, but an isothermal irreversible compression. It is isothermal because experimentally you do not see any change in a temperature as you go from the initial to the final equilibrium state. Its irreversible that is because this compression is happening against a 0 external pressure, it is a constant external pressure it happens rapidly and in a single step and it is a compression, because the initial volume is greater than whatever the final volume that we have drawn here.

What is the other option? The other option is the gas undergoes an expansion process. So, once again the associated process is an isothermal irreversible expansion, whereby the final volume irrespective of what the final state is going to be greater than the initial volume. What second law of thermodynamics tells us in order to decide in which direction this change of state would go, look for the change in delta S that is the change in entropy between the final state and the initial state, as the system goes from the initial state of temperature T, initial volume Vi and the number of particles N to the final equilibrium state characterized by the temperature T, the same temperature T volume V f and the same number of particles, but here you must be very very careful while calculating the entropy, because entropy is defined in terms of the reversible process connecting the initial and the final state.

So, we know that d S is equal to d q reversible divided by T therefore, for the given initial and the final states I cannot really look for the irreversible process to find the delta s, I will have to look for the fictitious reversible process that will take the system from this initial state to this final state. And this is something that you must be knowing from your initial exposure to thermodynamics, and the result is going to be delta S that is equal to n R L n the final volume of the gas V f divided by the initial volume of the gas. So, this is exactly what we are going to look at here.

So, delta S in this case if I use one mole of the ideal gas it is going to be R l n a ratio of final volume of the gas divided by the initial volume of the gas, and where as usual r is the universal gas constant. This also says that the entropy will increase with the change in state, if and only if the final volume is greater than the initial volume. So, this is exactly what is written here. Now as we understand that as the system proceeds in a direction where the final volume is less than the initial volume, there will be a decrease in entropy as the system passes from the initial to the final state.

And therefore, by the second law of thermodynamics, this is not the preferred direction of change in state. Pn the other hand this is the case where the final volume is greater than the initial volume, as a result delta S is positive in this direction. And therefore, we must conclude that the ideal gas we will spontaneously expand under the given experimental condition.

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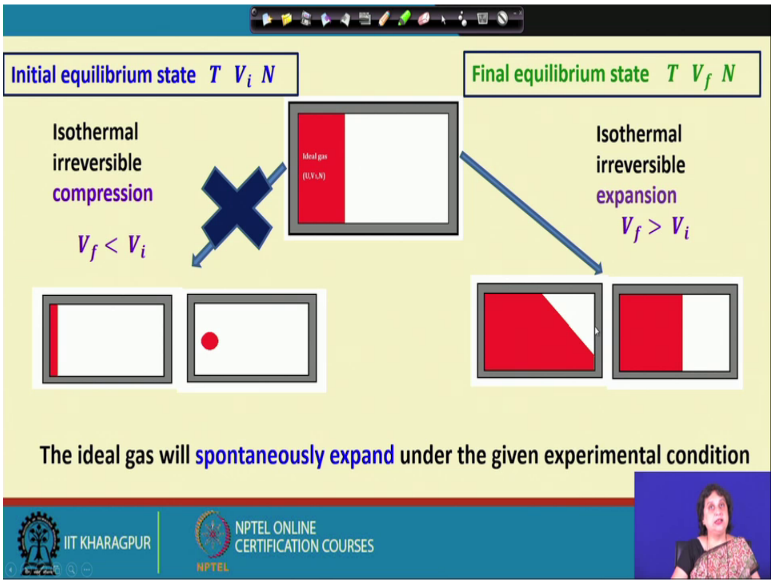

Initial equilibrium state T V_i N

Final equilibrium state T V_f N

Isothermal irreversible compression

$V_f < V_i$

Isothermal irreversible expansion

$V_f > V_i$

The ideal gas will spontaneously expand under the given experimental condition

So, we once again have this single step where I am representing the change in entropy as entropy of the final state minus entropy of the initial state. We have rejected the possibility of compression of the gas, now we are left with a choice between this kind of a state or this kind of state or the experimental observation, where the gas will go and fill up the entire volume.

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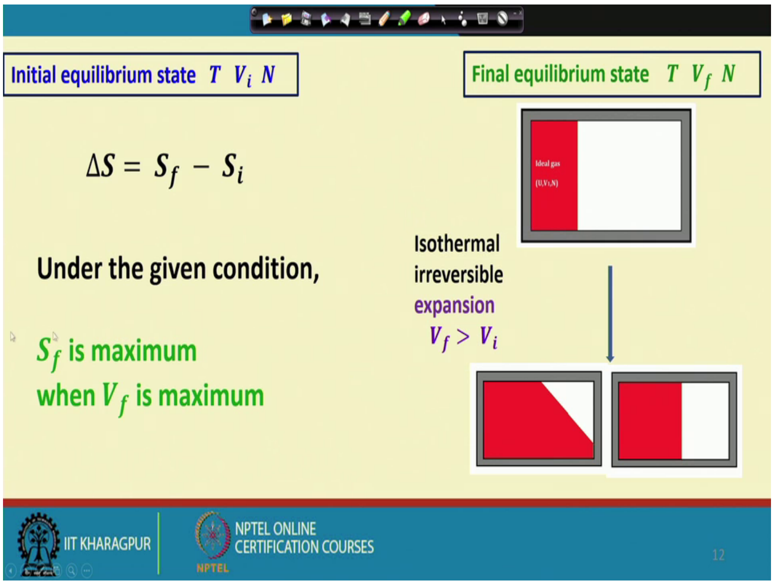

Initial equilibrium state $T\ V_i\ N$

Final equilibrium state $T\ V_f\ N$

$$\Delta S = S_f - S_i$$

Under the given condition,

S_f is maximum when V_f is maximum

Isothermal irreversible expansion $V_f > V_i$

So, what does the second law of thermodynamics say when this gas expands, where will it stop what would be the final equilibrium state; under the given condition you see that the final entropy of the system is maximum when the final volume of the gas is maximum under the given condition. So, what is the maximum volume of the gas? When it fills up the entire box, therefore the entropy change in an isolated system is summarized by this particular picture.

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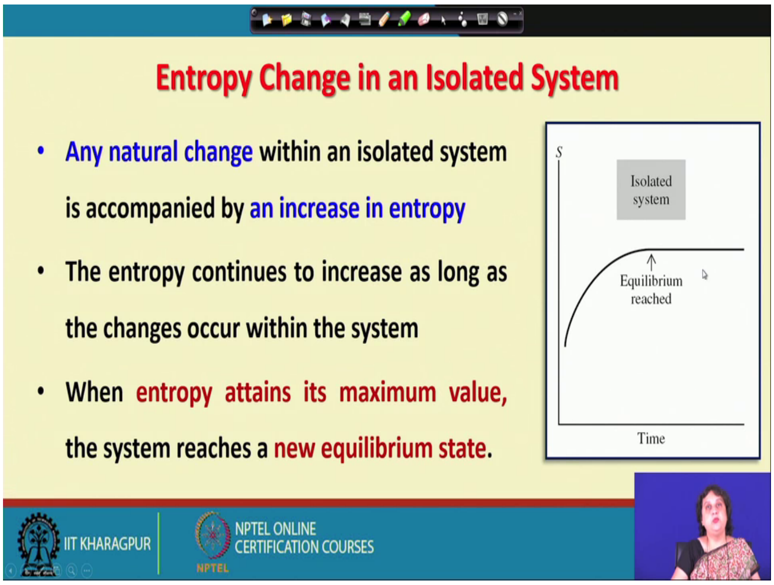

Entropy Change in an Isolated System

- Any natural change within an isolated system is accompanied by an increase in entropy
- The entropy continues to increase as long as the changes occur within the system
- When entropy attains its maximum value, the system reaches a new equilibrium state.

You started from somewhere here and then you allowed the system to evolve with time. Now the why is it that I am talking about time because I have an irreversible process which goes very fast and this is how the instantaneous value of entropy is going to change and as you see that in the direction of spontaneous change in state, it is going towards a maximum value? And of course this is the direction of any natural change and the entropy would continue to increase as long as the changes occur within the system.

And finally, when the entropy attains its maximum value, there will be no further change and the system would reach a new equilibrium state.

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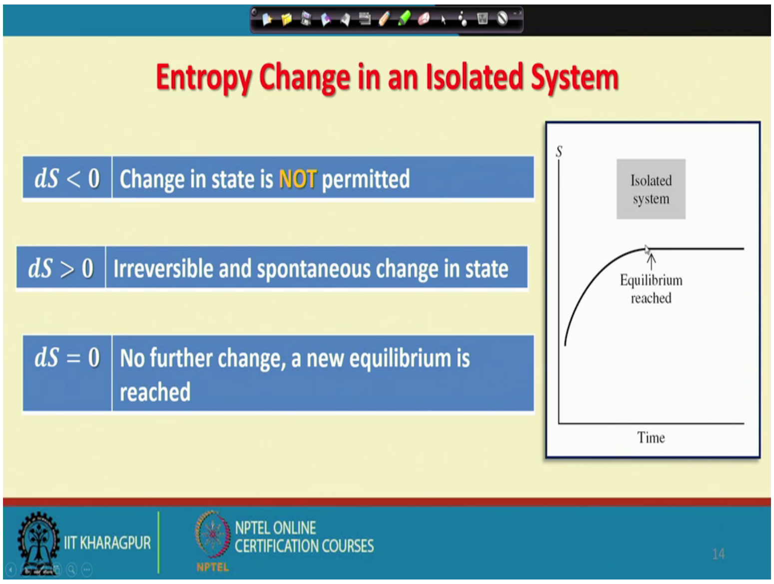

Entropy Change in an Isolated System

$dS < 0$	Change in state is NOT permitted
$dS > 0$	Irreversible and spontaneous change in state
$dS = 0$	No further change, a new equilibrium is reached

So, now that we know this we understand that d S would less than 0, for if I choose any point here when the maximum value has been reached, and there is a infinitesimal perturbation of the system. So, that there is a infinitesimal change d S of the system. Let us say the perturbation is such that d S is less than 0, which means that the system is being transformed towards this direction, this change in state will not be permeated. If I am here somewhere here and I am slightly part of being the system the system will spontaneously go to increase the entropy of the system and when it reaches this plateau.

There will be no further change and therefore, the final equilibrium state is going to be characterized by a constant value of the entropy of the system and that is a maximum under the given experimental condition just as we have seen the entropy of the gas becomes maximum when it fills up the entire box.

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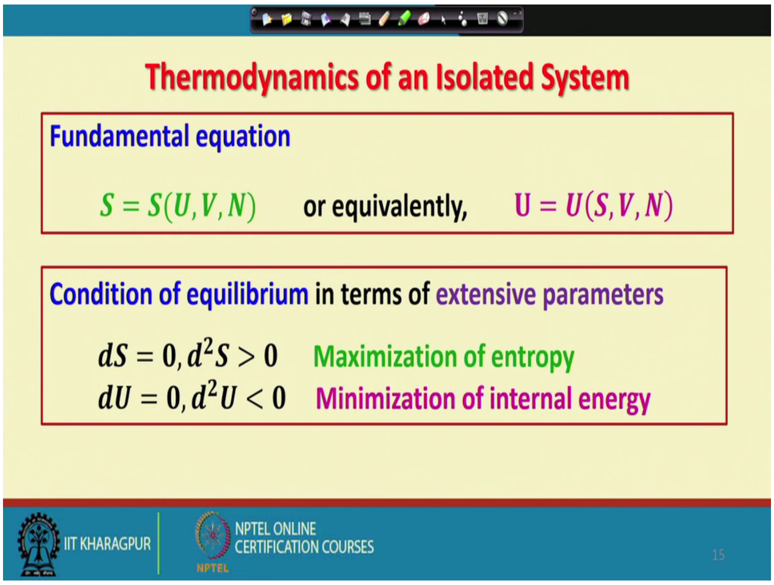

Thermodynamics of an Isolated System

Fundamental equation

$S = S(U,V,N)$ or equivalently, $U = U(S,V,N)$

Condition of equilibrium in terms of **extensive parameters**

$dS = 0, d^2S > 0$ Maximization of entropy

$dU = 0, d^2U < 0$ Minimization of internal energy

So, this is the summary of thermodynamics of an isolated system, I can start by describing the thermodynamic state of a system either by specifying some constant value of the internal energy volume and the number of particles, in that case entropy is going to be a function of these three independent variables. Equivalently just because for an equilibrium state is also has a constant maximum value. You can define the equilibrium state of the system in terms of entropy volume and number of particles.

In that case internal energy is going to be dependent on these three independent variables and correspondingly the condition of equilibrium, can be stated in terms of these two extensive parameters U and S. There will be a maximization of entropy when the system undergoes a change in state, and which is a new equilibrium state and if the system undergoes a change in state and arrives at a new equilibrium state in that final equilibrium state there will be a minimization of the internal energy. And the within this framework thermodynamics also introduces the concept of intensive variables. What are the two most common intensive variables that we know about; temperature and pressure.

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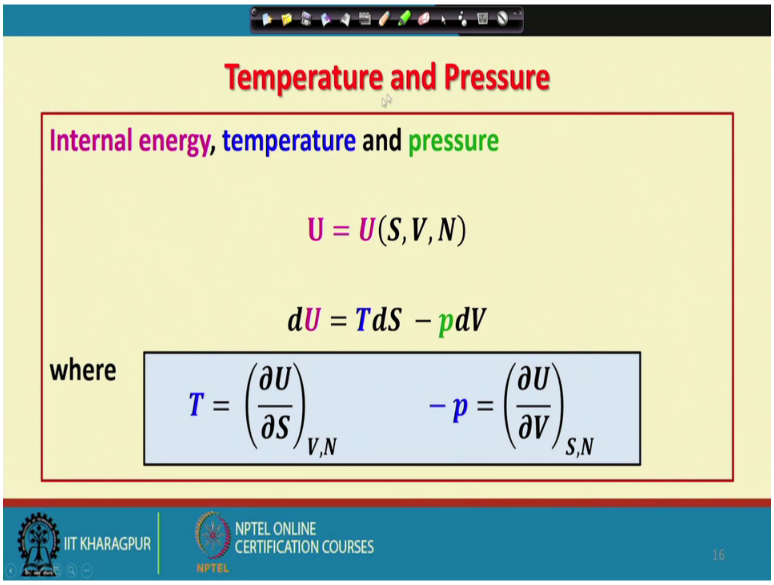

Temperature and Pressure

Internal energy, temperature and pressure

$$U = U(S,V,N)$$

$$dU = TdS - pdV$$

where $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ $\quad -p = \left(\frac{\partial U}{\partial V}\right)_{S,N}$

So, let us have a look at if I am expressing you as a function of S, V and N in that case I can very easily write the d U is equal to TDS minus pdV. So, what is it that I am doing here, I will start from an equilibrium system which is characterized by a constant value of entropy a constant value of volume and a constant number of particles. Now I keep the number of particles same and I change the state of this system by allowing s to change from s to s plus d s.

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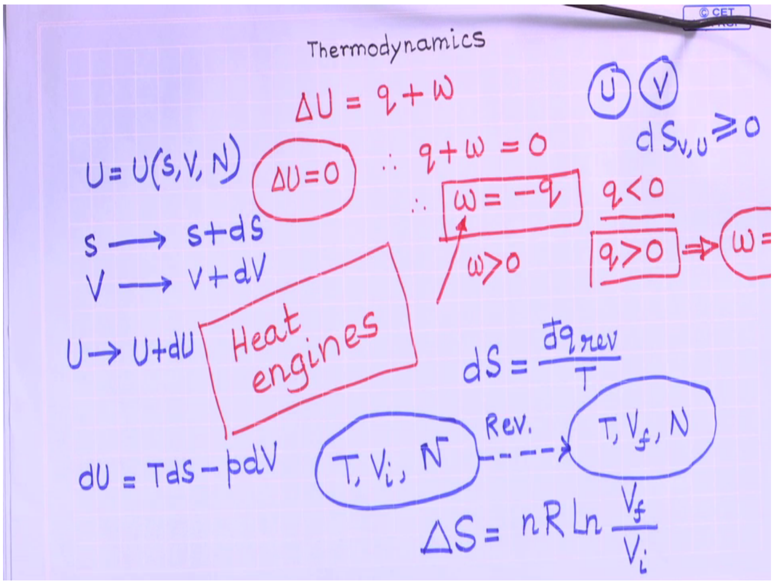

Thermodynamics

$\Delta U = q + w$

$dS_{V,U} \geq 0$

$U = U(S,V,N)$

$\boxed{\Delta U = 0}$ $\therefore q + w = 0$

$\therefore \boxed{w = -q}$

$q < 0$ $\quad w > 0$

$\boxed{q > 0} \Rightarrow$

$S \longrightarrow S + dS$

$V \longrightarrow V + dV$

$U \rightarrow U + dU$

Heat engines

$dS = \frac{đq_{rev}}{T}$

$dU = TdS - pdV$

$T, V_i, N \xrightarrow{Rev.} T, V_f, N$

$\Delta S = nR \ln \frac{V_f}{V_i}$

So, s goes from s to s plus d S this is the change in entropy, V in the initial state acquires a new value v plus d V in the final state, and the question is since U is a function of S,V and N. Obviously, the value of U in the initial state will now change to U plus d U. So, can I predict what d U is.

Of course I can predict what d U is d U is equal to TDS minus pdV and here temperature T is defined as a derivative of U with respect to s under constancy conditions of V and N and negative of pressure is nothing, but the derivative of U with respect to volume, under the condition that entropy and the number of particles remain constant.

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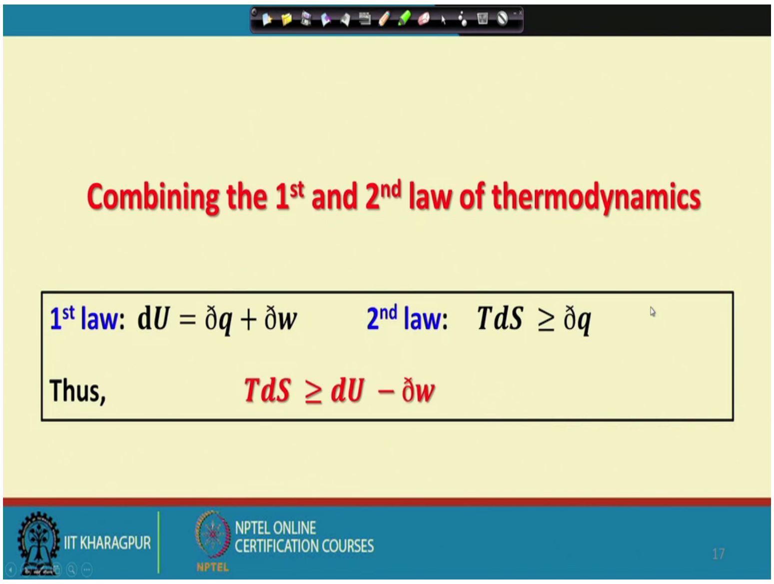

Combining the 1st and 2nd law of thermodynamics

1st law: $dU = \eth q + \eth w$ 2nd law: $TdS \geq \eth q$

Thus, $TdS \geq dU - \eth w$

And this actually has been arrived at by combining the first and the second law of thermodynamics. In the first law the mathematical statement is d U for infinitesimal process is a summation of d q and d w and TDS this is greater than or equal to d q and this is just another way of writing the clausius inequality. So, combining the two of them what we get is TDS greater than or equal to d U minus T w. And that tells us that this combination can be used not only to describe isolated systems, but also in the spontaneity and equilibrium conditions in non-isolated systems as well.

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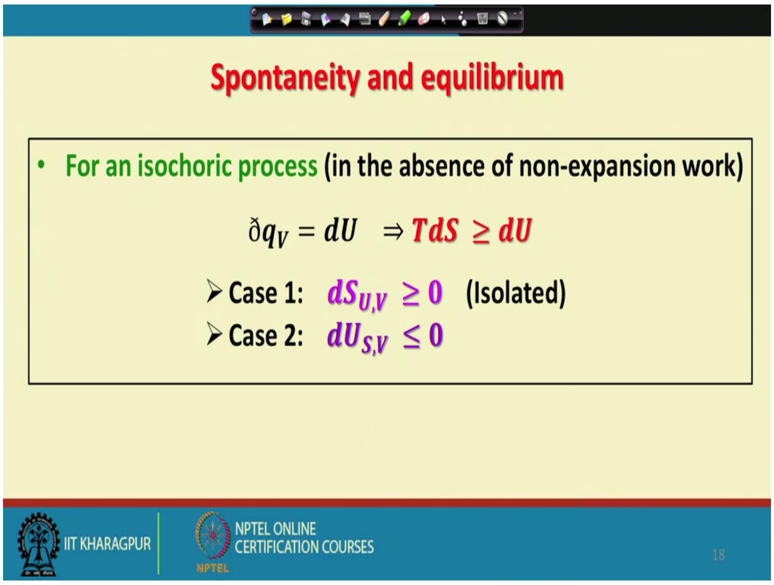

Spontaneity and equilibrium

- For an isochoric process (in the absence of non-expansion work)

$$\eth q_V = dU \quad \Rightarrow TdS \geq dU$$

➢ Case 1: $dS_{U,V} \geq 0$ (Isolated)

➢ Case 2: $dU_{S,V} \leq 0$

So, here I am showing you just one example of how the condition of spontaneity and equilibrium, may be predicted by combining the first and the second law of thermodynamics. So, under isochoric process the volume is constant. So, there will be no pressure volume work done. And therefore, dqv would be equal to d U and the consequence is that, the combination of the first and the second law of thermodynamics tells us that TDS must be greater than d U.

Now you can carry out several experiments one of which is you start from an initial state, which has some internal energy U and you keep it fixed, and you keep v also fixed and in the under such condition d S U, V that is going to be greater than or equal to 0 why is that. So, that is because if I have an isolated system. Then having a constant U this goes to 0 and therefore, d S under such condition must be greater than or equal to 0, similarly we can talk about what happens to U if I keep s and v constant and there will be a small perturbation under such condition this will be leaning to d U s v less than or equal to 0.

In the next class we will look at how non isolated systems can be treated to understand the direction of spontaneous change and state, and attainment of equilibrium and we were going to introduce the generic formalism of thermodynamic potentials. You have come across many energy functions while dealing with thermodynamics: internal energy, enthalpy, Helmholtz, free energy and Gibbs free energy. What we are going to do is we will next see how these different free energies are relevant to different experimental conditions, and what would be the ideal way of describing equilibrium states of non-isolated systems.

Thank you.