Introduction to Molecular Thermodynamics
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Lecture - 01
Review of Classical Thermodynamics

Welcome to the course Introduction to Molecular Thermodynamics. And in today's lecture, we are going to review the fundamental principles of classical thermodynamics.

Now the primary goal of classical thermodynamics is to study the equilibrium properties of a system. So, there is no thermodynamics; in thermodynamics there is no dynamics, and we are interested in time dependent properties of a system in equilibrium. So, the first question that arises is what is a system in equilibrium? A system in equilibrium is something where the measurable properties are not changing with the system.

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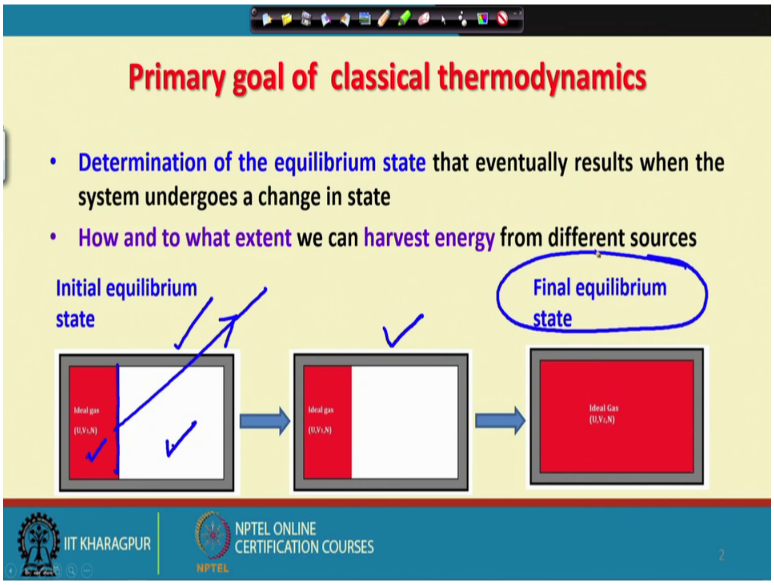

Primary goal of classical thermodynamics

- Determination of the equilibrium state that eventually results when the system undergoes a change in state
- How and to what extent we can harvest energy from different sources

Specifically the goal of thermodynamics is determination of the equilibrium state that eventually results when a system undergoes a change in state.

But, why should we be interested in a change in state? We of course remember the famous story of James Watt watching a boiling kettle and how he observed that the steam could lift the lid of that boiling kettle. So, basically what we are looking for a different ways in which we are going to harvest energy from different sources, and use it for our own benefit. So, these are the two primary goals which we try to attend in thermodynamics.

And let me now go over and try to define schematically the typical way in which change in state is visualized, in the case of a thermodynamic process. First of all let me have this initial equilibrium state. When you have an initial equilibrium state you have prepare the system in such a way that if no external perturbation is provided the system will be left as it is and its properties will not change with time.

So, here we have one particular system that is in this contained in this box, it is surrounded by a rigid insulated wall and we have two compartments here. In the first compartment as you see on the right this is under high vacuum and there is to say practically no molecules in there and we have the other red compartment, where we have put some gas maybe some ideal gas and this system if not perturbed externally will remain as it is. What we do next is we perturb this initial equilibrium state. As I said there are two compartments here one here another one here and there is a separator as you can see over here. I am going to remove this separator and when this separator is removed what does the system face? It faces this kind of a situation where the gas is now faced with the choice of undergoing a change in state.

Then the question that we ask is, what will happen when the system undergoes this change in state or in other words what is going to be the final equilibrium state as the system undergoes this change in state. From our experience we know that this ideal gas is next going to fill up this entire box and once it has filled up this entire box, it will not undergo any further change in state and if I go and measure in its properties it will be independent of time. If no further external perturbation is provided, and this means that you have passed from an initial equilibrium state to a final equilibrium state. And the question that you ask is during such a process, can I harvest energy for some useful purpose.

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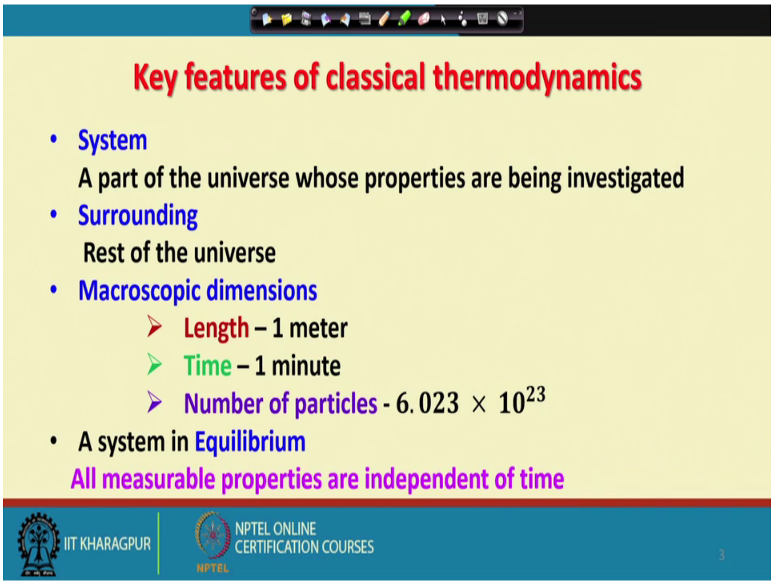

Key features of classical thermodynamics

- **System**
  A part of the universe whose properties are being investigated
- **Surrounding**
  Rest of the universe
- **Macroscopic dimensions**
  - **Length** – 1 meter
  - **Time** – 1 minute
  - **Number of particles** - 6.023×10^{23}
- A system in **Equilibrium**
  All measurable properties are independent of time

Now, let us talk about the key features of classical thermodynamics. First what is the system that we are talking about? I have already shown you some schematic diagram, but let me define in the most general terms what I mean by a system. It is a part of the universe, whose properties are being investigated. So, it may be a box or a cylinder full of some kind of a gas, it may be a closed vessel full of some liquid that you are interested in or it may be a block of solid. And the next one that we would like to talk about is what we mean by the surrounding of the system, because this also is very important in understanding the property of the system.

So, since system is only a part of the universe and most of the cases, we assume the rest of the universe as the surrounding to the system. And we also must mention that the systems that we are interested in have macroscopic dimensions, by which I mean that if you have a block of solid, it will have a typical length of one meter time off, and the if you are looking at the time dependent property of such a system, it will be typically measures in seconds or a few tens of minutes or even a few hundreds of minutes, but the time scale over which you will be following the properties of the system, will typically be in minutes.

And then I must mention this very very important that the number of particles is going to be very very large and therefore when a system is in equilibrium when any such system is an equilibrium, you are basically trying to make an observation or the measurement of the system from time to time let us say once every minute or maybe once every ten minutes or so, and trying to measure some kind of property of that system that you are interested in.

Now, I would like to highlight once more that I am talking in terms of a macroscopic property; a macroscopic system, which is comprised of a very large number of particles and the system is in equilibrium and all my measurements are done typically within about a minute, and all the properties of the system thus measured are independent of time.

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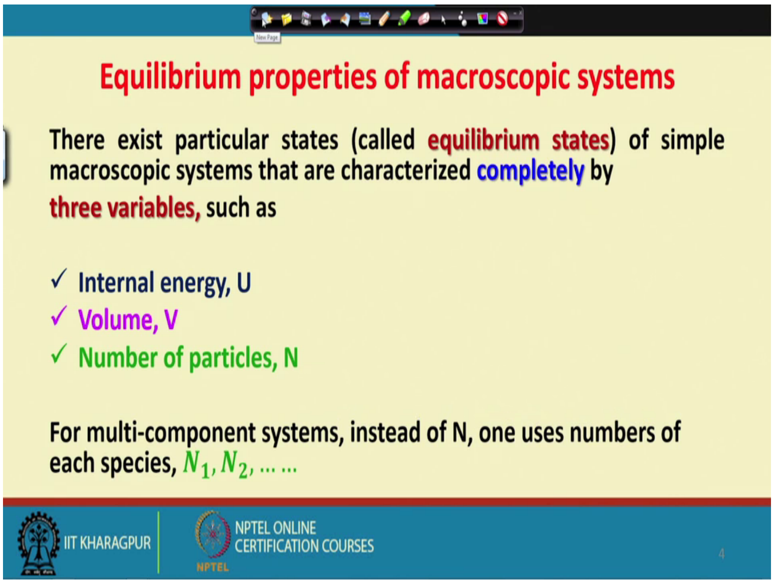

Equilibrium properties of macroscopic systems

There exist particular states (called equilibrium states) of simple macroscopic systems that are characterized completely by three variables, such as

- ✓ Internal energy, U
- ✓ Volume, V
- ✓ Number of particles, N

For multi-component systems, instead of N, one uses numbers of each species, $N_1, N_2, \ldots \ldots$

So, those are the properties that we are interested in when we are studying or describing a system using classical thermodynamics. Now when we talk about the equilibrium properties of a macroscopic system, the base fundamental statement of thermodynamics is that, there exists a particular state that is called the equilibrium state of simple macroscopic systems that are completely characterized by only three variables.

Now this is probably the most important property of the entire subject area of thermodynamics. Think about it you have typically Avogadro number of particles, and these particles are making up a block of the substance which is something that I can see with the naked eyes I can make measurements of on it in the real world, and I am trying to describe the equilibrium state of the system in terms of just three variables and that is probably why thermodynamics is so, successful in describing such systems.

Now, what are these three variables? To start with the first quantity that we can talk about is the internal energy, the second one volume and the third the number of particles. You may argue that why these three as we will see later that this three variables actually give you a unique representation of the system which is the simplest one that is an isolated system a system that is not interacting with the surrounding you may also ask.

If what happens if I have a multi component system in that case instead of N, that is a number of particles of a single type you are going to have difference as species. So, specie 1 will have the number of particles equal to N 1, specie you will have number of particles N 2 and so on and so forth. So, with this in mind that thermodynamics is actually giving us a very simple description of a very complicated situation, we next go and try to see how do we think of the system and its interaction with the surroundings.

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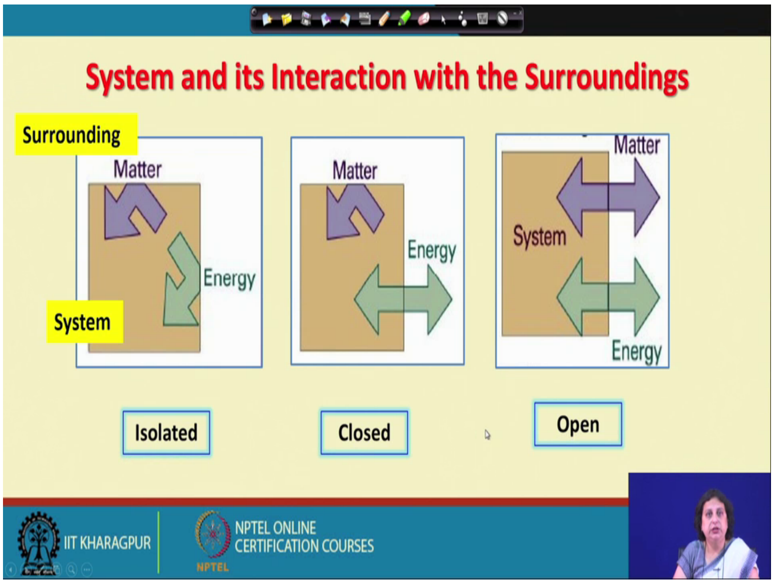

System and its Interaction with the Surroundings

So, here we go. So, first let me point out that this is my system and this white portion is my surrounding. Now the system is surrounded by a wall that is completely insulated as a result of which it cannot exchange energy volume or matter with its surrounding; and we would call such scenario as describing an isolated system. It may so happen that the wall is of such nature, that it allows exchange of energy between the system and the surrounding.

In that case we call the system a close system please note that the system is incapable of exchanging either volume or matter with the surrounding. And there is a third scenario where you have the system exchanging energy, and the matter across the wall separating it from the surrounding. So, in that case we will call such system an open system.

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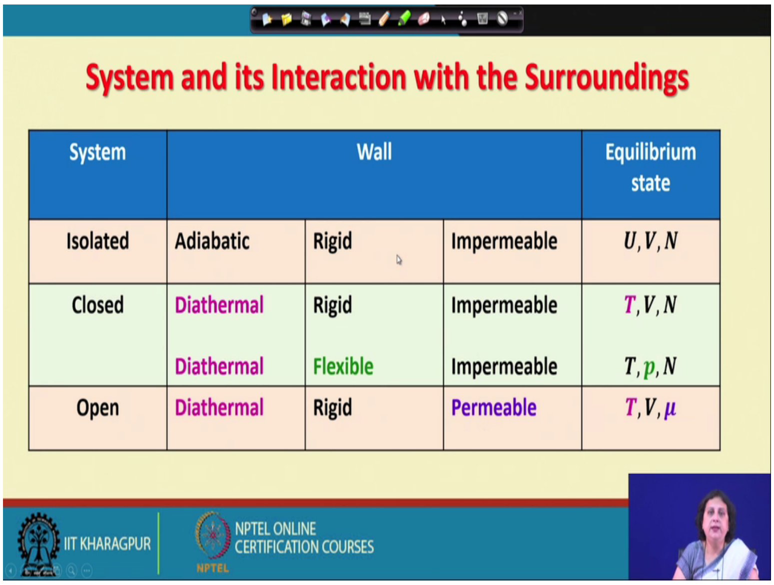

System and its Interaction with the Surroundings

System	Wall			Equilibrium state
Isolated	Adiabatic	Rigid	Impermeable	U, V, N
Closed	Diathermal Diathermal	Rigid Flexible	Impermeable Impermeable	T, V, N T, p, N
Open	Diathermal	Rigid	Permeable	T, V, μ

So, thermodynamics tells us that there are different ways of monitoring the system and its interaction with the surrounding by varying the property of the wall that separates the system from its surrounding. So, take the isolated system, if I have an adiabatic wall that is rigid and impermeable to the substance that is there inside the box I will be having an isolated system isolated from the surrounding and I can very easily describe the equilibrium state of the system by assigning specific values of its energy U the volume of the box v and the number of particles present in the system.

On the other hand, when I have a closed system I may design the wall to be diathermal, which means it allows exchange of energy between the system and the surrounding. If I keep this wall rigid and impermeable, still then what you think would be a good description of the equilibrium state? Since the system can exchange energy with the surrounding. Therefore, when the system attains an equilibrium its temperature is going to be equal to the temperature of the surrounding, and this constant temperature is then a very good descriptor of the equilibrium state, instead of its total energy. So, the equilibrium state and such condition will be described in terms of these three variables T temperature V a volume and N a number of particles.

You may also think that well in addition to the diathermal wall. Let me make at least one of the walls flexible so that the system can exchange volume with the surrounding. Of course, you can do it by attaching a piston and in that case it is understandable that the equilibrium state will be described in terms of temperature pressure and the number of particles. And if you have an open system you may still design the system with a rigid wall, but maybe diathermal and permeable. Let us say that its supporter's wall in that case the equilibrium state is going to be defined in terms of temperature volume and another system property which is known as the chemical potential.

Now, when we go for understanding the interaction between the system and the surrounding; the next thing that becomes important is if the system has interacted with its surrounding and attained an equilibrium state in that case what are the different kind of equilibrium states that we can think of the first one that we can think of is the thermal equilibrium.

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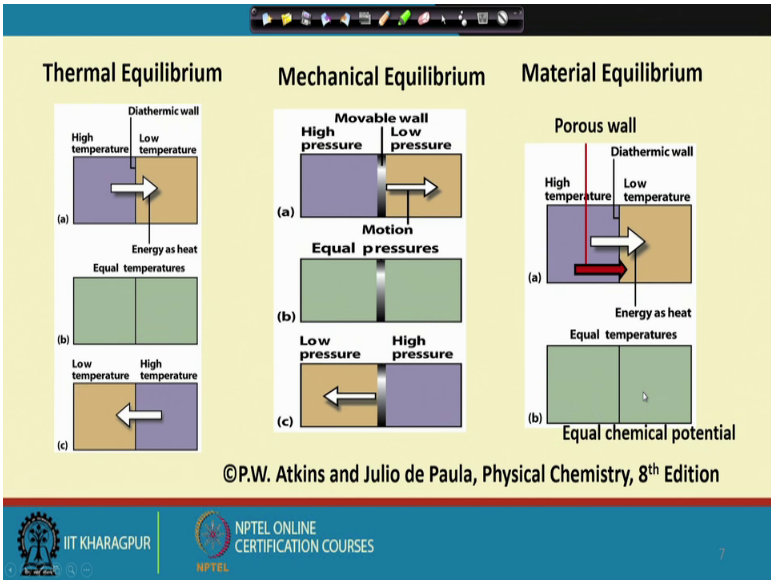

Thermal Equilibrium

Mechanical Equilibrium

Material Equilibrium

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So, this is the case where we have let us say this is the system and this is the surrounding, and the system and the surrounding they are exchanging energy as heat and this wall is a diathermal wall or diathermic wall, and the system will go on exchanging energy with its surrounding till both the parts attained equal temperatures. Under such condition I will say that the system and its surrounding are present in thermal equilibrium with each other.

The next scenario that I will highlight over here is, when the system is distinguished is when the system is separated from its surrounding by a movable wall. And I can move this in this direction if there is a high pressure in the system and the low pressure in the surrounding, then this will spontaneously move to this direction and when will the motion of this movable wall stop. It will stop when on both sides of it that is between the system and the surrounding the pressures are equal, we would then say that a system has attained a mechanical equilibrium with its surrounding. The other scenario is generally known as material equilibrium or equilibrium with respect to matter flow.

So, if I have a porous wall which is diathermaled in nature as well, and if this system is maintained at a high temperature and the surrounding at a low temperature then there will be the transfer of heat from the higher temperature to lower temperature, till the two the system and the surrounding acquire equal temperatures. In the addition if I make this walls porous. There will be transfer of matter from- let us say the system to the surrounding and this transfer will continue till the chemical potential is equal in both the system and the surrounding.

So, these are the three types of equilibrium that we come across in the real world and thermodynamics introduces us to the concept of giving a precise definition of how to get from experiments the condition of equilibrium under such circumstances.

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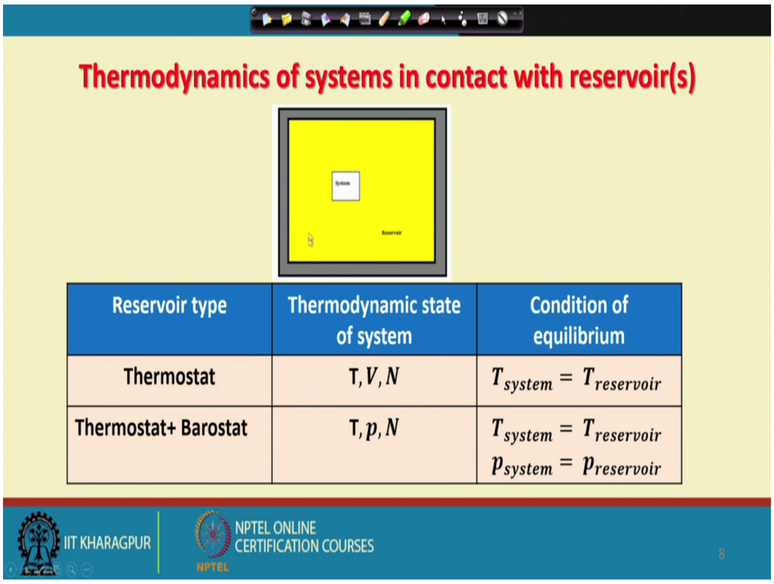

Thermodynamics of systems in contact with reservoir(s)

Reservoir type	Thermodynamic state of system	Condition of equilibrium
Thermostat	T, V, N	$T_{system} = T_{reservoir}$
Thermostat+ Barostat	T, p, N	$T_{system} = T_{reservoir}$ $p_{system} = p_{reservoir}$

So, let us say that you have kept your system in contact with a thermal reservoir. So, this is a schematic representation, where you have a system and you can vary the property of the wall surrounding the system to control its interaction with the reservoir. So, if this wall is diathermal rigid and impermeable, then the reservoir can be taken as a thermostat. So, under this condition as I have already mentioned the equilibrium thermodynamic state of the system will be given by temperature volume and the number of particles and the condition of equilibrium is that that the temperature of the system is equal to the temperature of the reservoir .

On the other hand a more common and system is where this wall is diathermal as well as flexible, but impermeable in that case this reservoir is going to act as a thermostat plus a barostat, and the thermodynamic state is going to be defined in terms of temperature pressure and the number of particles and then the condition of equilibrium will be that the temperature of the system is equal to the temperature of the reservoir, pressure of the system is equal to the pressure of the reservoir. And then we come across this very important concept of equation of state. So, what is the equation of state?

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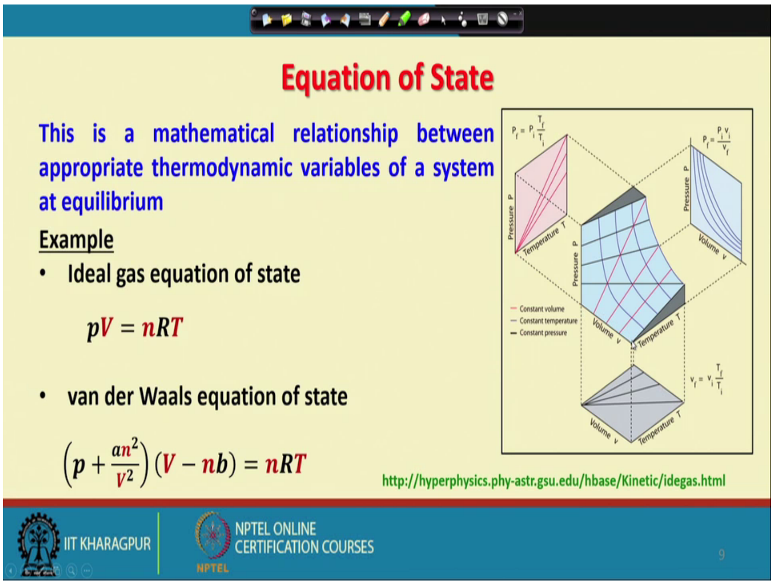

Equation of State

This is a mathematical relationship between appropriate thermodynamic variables of a system at equilibrium

Example

- Ideal gas equation of state

$$pV = nRT$$

- van der Waals equation of state

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/idegas.html

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This is a mathematical relationship between appropriate thermodynamic variables of a system at equilibrium.

So, what I have here is something that is giving me interesting relationships, why do I need them? I need them because I am interested in finding out how to handle these systems under different conditions. So, do I know of an example of course, you know from your high school days you have come across these equations of states for gases, the first one is the ideal gas equation of state. So, I am sure all of you have seen this equation which connects the pressure volume temperature and the number of moles or the number of particles of the ideal gas for an equilibrium state. And this ideal gas equation of state also demonstrates the very fact that.

You require only three variables to define the equilibrium state of the gas have a look at this because of the existence of this kind of a mathematical relationship, you can always have N expressed as a function of pV and T or T expressed as a function of pV and n and so on and so forth therefore, you require only three variables to describe the equilibrium state of a system. Now if I come to the van der Waals equation of state, this is something that has been obtained from experiments to describe the properties of real gases. And here also you see because of the existence of this kind of an equation of state, you require only three variables to describe the properties of the system.

In fact, what you have here is the existence of an equation of state under various conditions, can tell give you a lot of information regarding what would be the predicted property of the state. If for example, you are having an ideal gas and you can vary three variables independent of each other pressure, volume and temperature and this blue surface is showing you the way in which an equilibrium state will be defined in terms of these three variables. Therefore, from here you can project it in different directions and see for example, how volume is going to vary as a function of temperature or pressure is going to vary as a function of temperature keeping the third variable constant.

Now when we talk about thermodynamics, of course I have already mentioned to you that we are interested in thermodynamic processes that take the system from one equilibrium state to a final equilibrium state.

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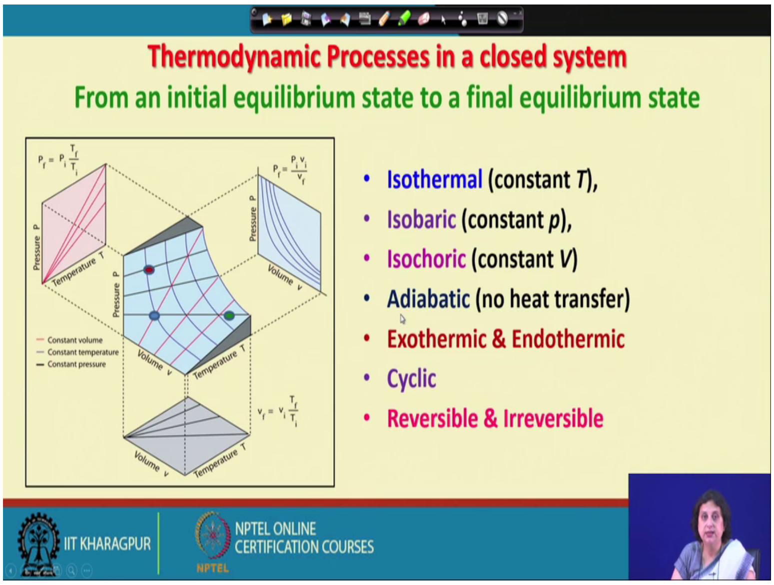

Thermodynamic Processes in a closed system

From an initial equilibrium state to a final equilibrium state

- Isothermal (constant *T*),
- Isobaric (constant *p*),
- Isochoric (constant *V*)
- Adiabatic (no heat transfer)
- Exothermic & Endothermic
- Cyclic
- Reversible & Irreversible

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I would like to mention here all the points that you see in this surface that represents the equation of state for an ideal gas these are equilibrium states, because they obey these points have been generated from the ideal gas equation. So, this equation this point or this point they represent equilibrium state of the ideal gas. And there may be a very large number of processes, and I am all of you know about these isothermal isobaric isochoric processes which may be adiabatic processes, exothermic or endothermic processes, cyclic reversible or irreversible processes.

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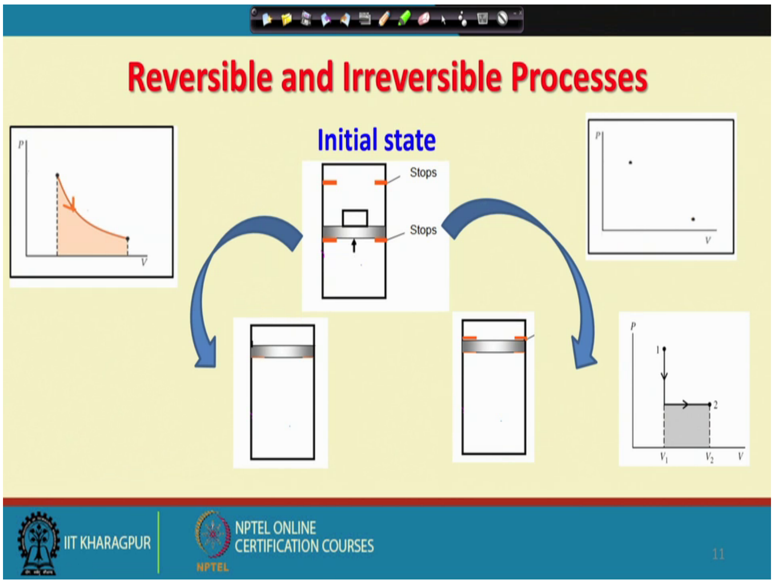

Reversible and Irreversible Processes

Initial state

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And what I would like to mention here is something that if you prepare a system in an initial state. So, let us say that I have a cylinder, which I have prepared in an initial state by putting a piston over here and there is some weight holding the piston here and there are some stops over here, and on this side of the piston we have some gas now I can induce this system to undergo a change in state by withdrawing this stops. When I withdraw this stops the system will equilibrate in a final state which looks like this, I have taken away the stops I have taken away the mass and the piston has moved and this separation has got stopped at the position of this final braces over here.

If I could carry out this process in a very slow manner I would say that I am looking at a reversible process. And under such condition if I come up with a pressure volume indicator diagram, this is my initial state, this is my final state and since I have maintained equilibrium all throughout the process, all the points in this curve they represent intermediate equilibrium states. And therefore, the pV indicator diagram includes all the states, that have been covered in going from the initial state to the final state. But on the other hand if I carried out this process very very fast, I would have reached some other final state, but in this case it would be an irreversible change where the initial and the final states are the only two equilibrium states that I talked about.

I did not allowed the system enough time to equilibrate with its surrounding. And therefore, as you are already that under such circumstances this is going to be the work done in this process, while in the reversible process we are going to have the area under this curve as the amount of work done during a reversible change.

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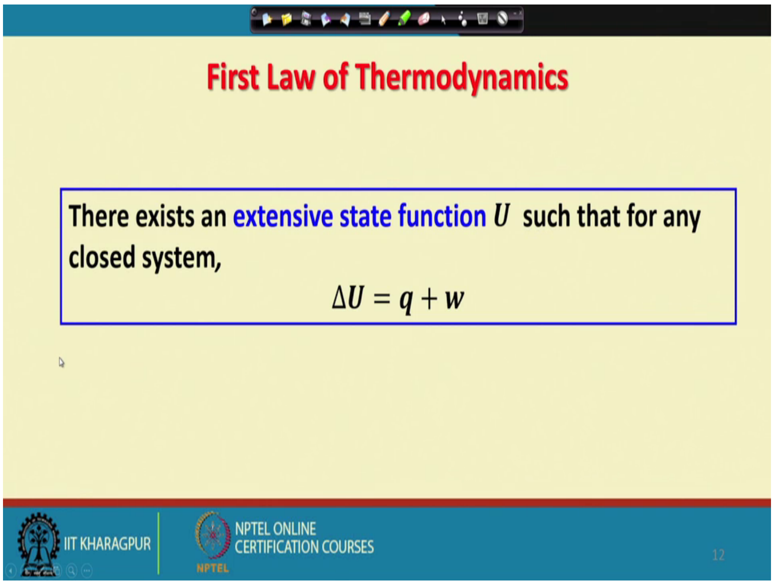

First Law of Thermodynamics

There exists an **extensive state function** U such that for any closed system,

$$\Delta U = q + w$$

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Now this brings us to the laws of thermodynamics; and the laws of thermodynamics are quite well known to the students, that is what I will issue. So, I will give a quick look at what the first law of thermodynamics tell me the first law of thermodynamics, introduces to us an extensive state function which I will represent as U and term as the internal energy.

It says that this is a function it undergoes a change in value delta U during a change in state and delta U is equal to q plus w, where q is the heat exchanged and w is the work done during the change in state.

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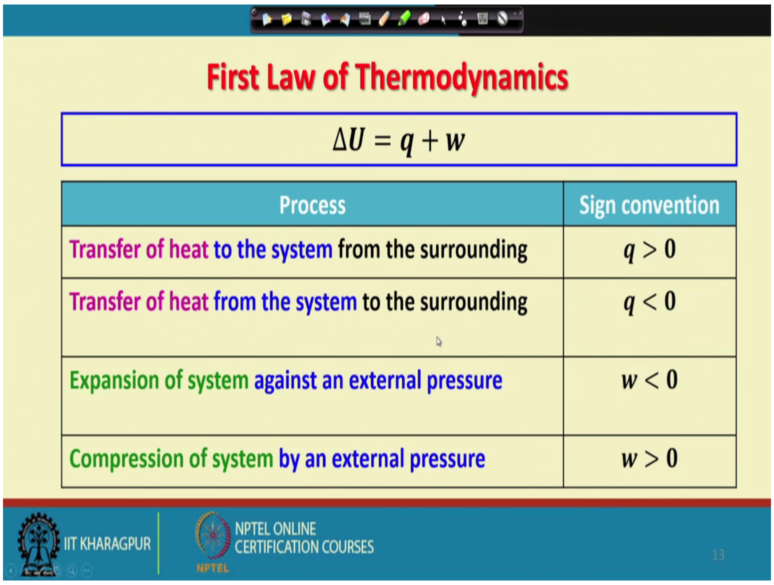

First Law of Thermodynamics

$$\Delta U = q + w$$

Process	Sign convention
Transfer of heat to the system from the surrounding	$q > 0$
Transfer of heat from the system to the surrounding	$q < 0$
Expansion of system against an external pressure	$w < 0$
Compression of system by an external pressure	$w > 0$

So, when we know about the first law of thermodynamics. So, basically we understand that the internal energy of a system can be changed in two different ways, either by transferring heat or by allowing the system to do work or by doing work on it. So, when heat is transferred to the system from the surrounding; usually the sign convention that is q is positive. So, it contributes to the increase in delta U increase in the internal energy and if heat is transferred from the system to the surrounding U will decreases. So, q will be assigned a negative value.

Similarly, if the system expands it uses of its internal energy to do work against an external pressure. So, w the work done by the system decreases U and it is less 0, and in similarly compression of system by an external pressure that would be associated with increase in internal energy and w is greater than 0 . So, this also says that I do not really have to have a finite process I can also have an infinitesimal change especially when I am talking about the reversible processes.

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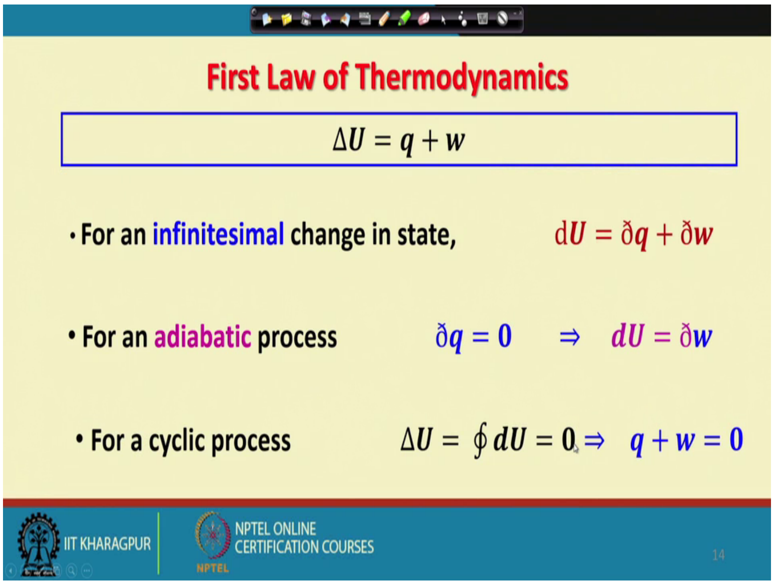

First Law of Thermodynamics

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

- For an infinitesimal change in state, $dU = \eth q + \eth w$
- For an adiabatic process $\eth q = 0 \Rightarrow dU = \eth w$
- For a cyclic process $\Delta U = \oint dU = 0 \Rightarrow q + w = 0$

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So, for an infinitesimal change dU that is the differential exact differential of the state function U, this is a sum of two in exact differentials this is the infinitesimal amount of heat exchanged between the system and the surrounding. And this is the infinitesimal amount of work done during the change in state.

That takes the system have from a state having internal energy U to an internal energy U plus dU. If you have an adiabatic process then the q would be equal to 0 as a result I will always have dU is equal to dw and for a cyclic process. The system comes back to the same initial state. So, the initial and the final states are the same as a result delta U which is a state function that would be equal to 0, which means that for every such process q plus w is going to be equal to 0.

And it is also understood from the first law of thermodynamics that the absolute magnitude of internal energy cannot be measured rather when we study a chemical. Any thermodynamic process we are measuring the change in internal energy.

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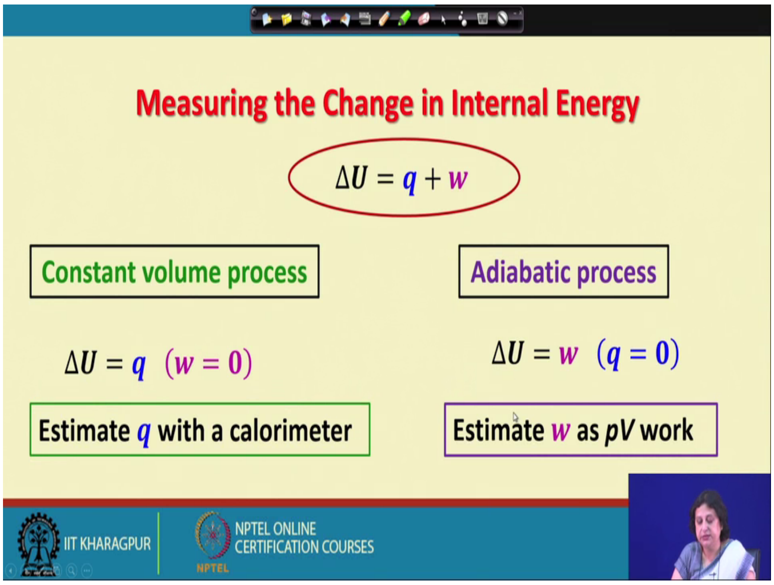

Measuring the Change in Internal Energy

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

Constant volume process

$\Delta U = q \quad (w = 0)$

Estimate q with a calorimeter

Adiabatic process

$\Delta U = w \quad (q = 0)$

Estimate w as pV work

So, this now we can do in a either a constant volume process, where delta U is estimated as q and typically a calorimeter is used to estimate q or you can have an adiabatic process where delta U is measured in terms of the amount of work done during the process, and if it is a pV work once again it can be measured it brings us to the end of our discussion of the first law of thermodynamics, now we know what is an equilibrium state of a system. Also we know how an initial equilibrium state can move over to some final equilibrium state by some kind of process, and you can design this processes depending on the different conditions like an isothermal process, an adiabatic process, a reversible process and irreversible process and so on and so forth.

And the first law of thermodynamics tells us that there is some function, which we call the internal energy this is a capability of one given system to do some external work and therefore, this is the quantity that we are interested in. Now U is a system property if I have an isolated system, then you will have a finite value. And as long as I do not change the property of the system it will remain fixed at its equilibrium value.

Now if I induce a change in state you will change. So, what are the ways in which U can be changed? First law of thermodynamics tells us: there are two ways in which you can change the internal energy of a given system. One is the supplying some heat to it or extracting some heat from the system or by doing some work either by the system or on the system. And this tells us that interaction of the system with its surrounding is possible only when the system is undergoing a change in state.

But first law of thermodynamics does not tell you if a system will go in a particular direction; so that is when the second law of thermodynamics comes into the picture. And, we are going to talk about the first law as well as the second law of thermodynamics in characterizing the macroscopic systems in our next lecture.

Thank you.