Course on Phase Equilibrium Thermodynamics
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Lecture 01
Introduction

Hello everybody welcome to the first-class on phase equilibrium thermodynamics, now you must have all gone through the introductory video and you more or less know what you should be expecting from this class. Now before I go into the details concerning phase equilibrium thermodynamics it is very important to understand exactly the individual words comprising the title of this particular subject. What is phase? What is equilibrium? And exactly what does thermodynamics in general deal with? And how do we use the laws of thermodynamics in order to predict phase equilibrium or rather in order to predict the conditions of phase equilibrium and to predict the properties of different systems when they are undergoing some change from one equilibrium state to another.

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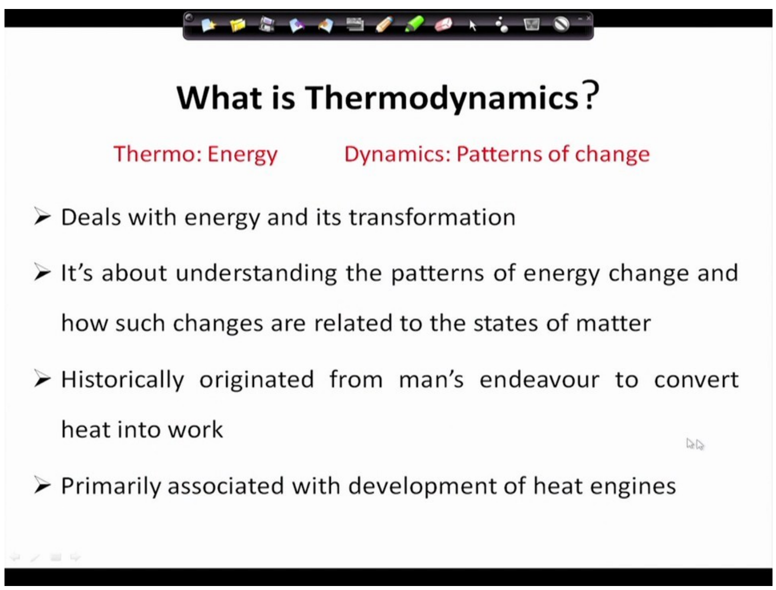

Now let us come to the first thing regarding on the most generalized the topic what is thermodynamics? Now if you look at the word thermodynamics it basically means the patterns of change of the different energies, so therefore it primarily deals with energy and its transformation. It is about understanding the patterns of energy change how such changes are related to the states of matter. Now historically this particular subject developed from man's endeavor to convert heat into work.

Because man found that there is a lot of thermal energy all around, so he was trying to extract useful work from the enormous amount of thermal energy around and therefore in this particular endeavor he came across some very unique properties of heat energy and also he tried to, also he found out how much amount of heat can be converted into useful work and the interrelations between heat and work etc.

And since it was primarily rather it primary developed due to man's endeavor to convert heat into work, so therefore we find that most of the developments at least for the first and second law they are associated with the development of heat engines and heat pumps but let me tell you that these particular whatever relations etc has been developed they are applicable for any particular kind of work it will and for any particular kind of system which may not be only applicable for only heat engines and heat pumps.

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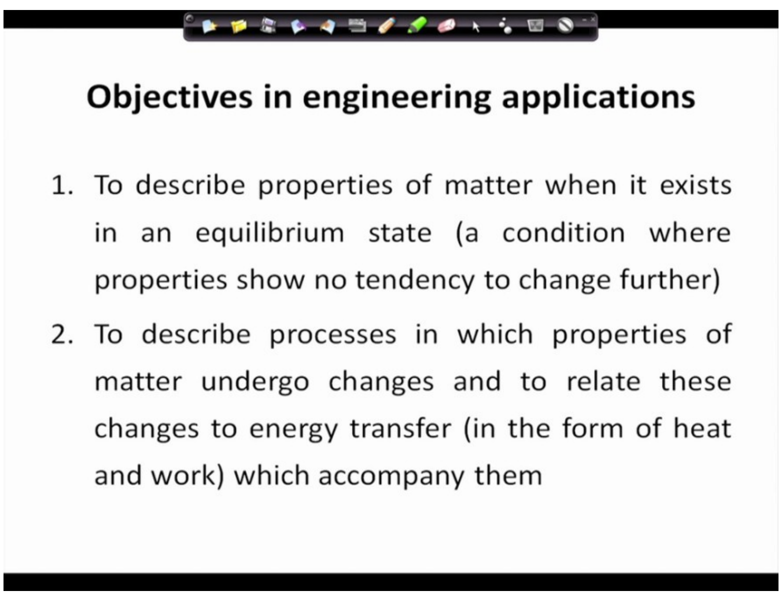

Now as far as the engineering aspects are concerned the primary objectives of thermodynamics can broadly be generalized into 2 categories the first is to describe properties of matter when it exists in an equilibrium state and to describe processes in which the properties of matter undergo changes and to relate these changes to the energy transfer which have brought about this particular changes. Now therefore these are the 2 forms.

First we have to understand rather we have to in order to find out the properties we have to first identify one particular content of matter where they are going to concentrate and whose properties we are going to find out and then from that particular portion of mass on which we are concentrating when that undergoes some particular changes why will it change? Only when it interacts with the surroundings due to some amount of energy interaction between that particular portion of matter and the remaining portion.

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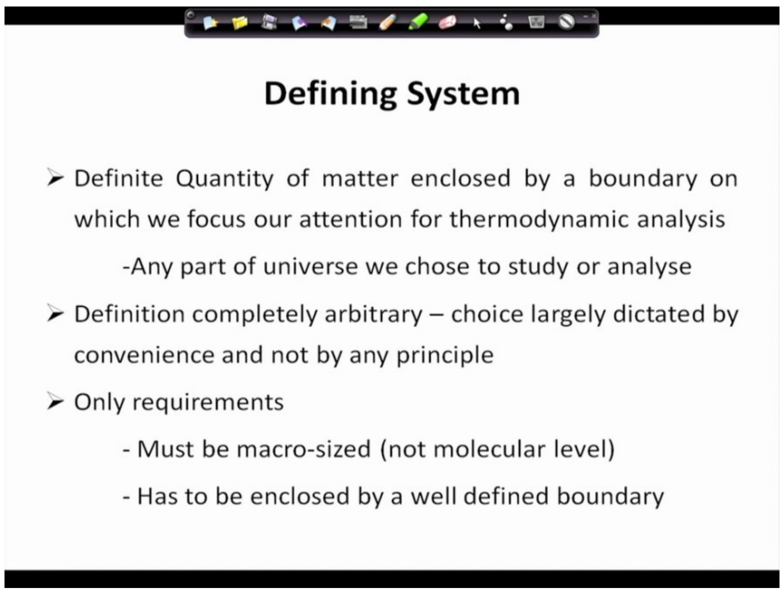

Well, that portion of matter undergoes some change in its state which will be manifested by a change of some of its characteristics which we are going to estimate experimentally or theoretically and relate these changes of the properties or characteristics of that particular content of matter with the energy interaction it had with its environment or with its surroundings. So therefore the first thing in thermodynamics is we need to identify some particular quantity of matter which is enclosed by a well-defined boundary on which we are required to focus our attention for thermodynamics analysis.

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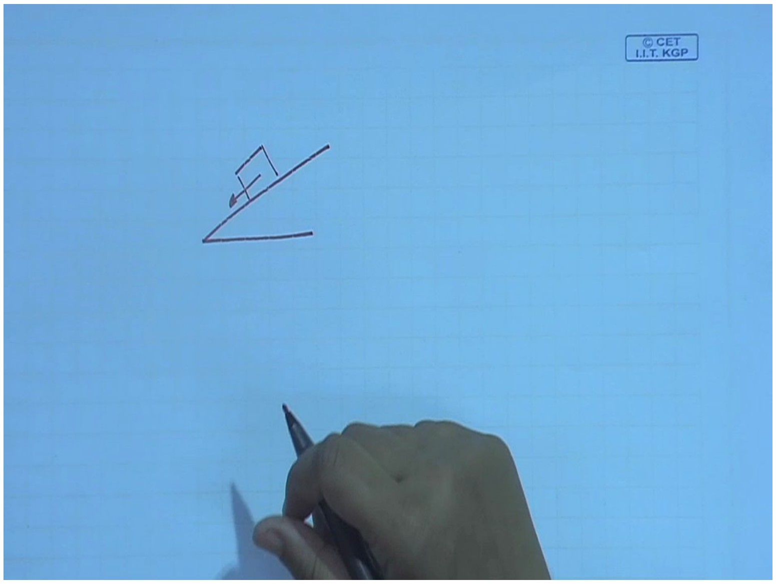

Just like in physics if you want to perform any particular analysis say for example you we can find out that maybe there is an inclined plane and the body is trying to fall across the inclined plane. We would like to find out the acceleration of the body and the displacement of the body may be fent it starts from the rest or fent is given some particular amount of force in the beginning. So in order to perform any sort of analysis on this particular or in the order to perform the physical analysis what we first need to do is we need to perform or rather we need to make a free body diagram of the body and or in other words we need to separate the body from its surroundings make the free body diagram and then start the physical analysis.

In the same way when we are going to define our, or rather when you are going to perform any thermodynamic analysis we have to first identify that portion of matter which is affected by due to some particular changes and then after we identify that particular portion of matter we perform the or rather we try to find out how it is interacting with its environment? Anything outside what we have considered as the system is its surroundings and the first thing which you should be remembering is that defining a system can be completely arbitrary but its choice as we will be seeing shortly its choice is largely dictated by convenience there is no particular principle.

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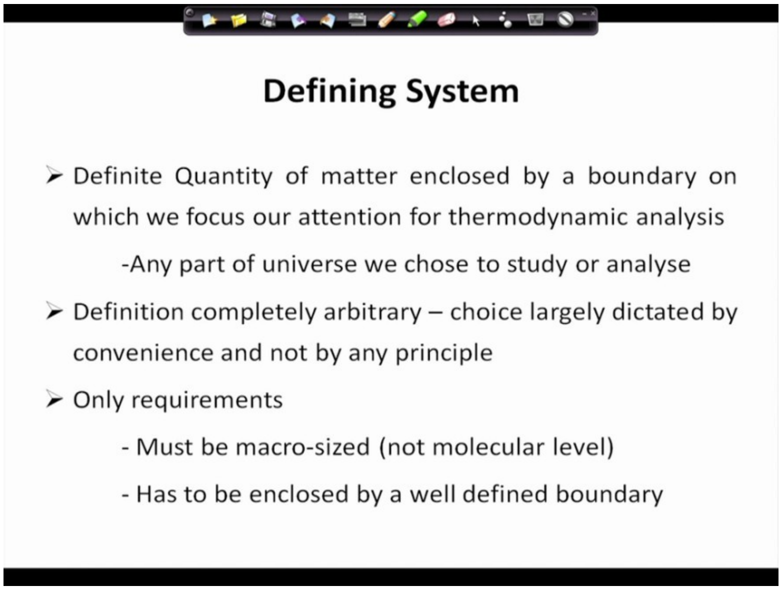

The only requirements of selecting a system is firstly it has to be macro size it cannot be something of a molecular level because we are dealing with classical thermodynamics and it has to be enclosed by a well-defined boundary, the boundary can be real, the boundary can be imaginary, the boundary can coincide with the outside boundary of the system that we have considered, the boundary can be adiabatic, the boundary can be diathermal, it can allow the flow of mass intake, it might not allow the flow of mass into it.

It can have all, it can be flexible, it can be rigid, it can assume a wide variety of sizes, shapes, configurations etc but it has to be a well-defined boundary which separates the system from the surroundings and depending upon the nature of the boundary as you all know because it assume that you have a preliminary idea of thermodynamics, so therefore depending upon the nature of the boundary you know a system can be isolated it can be closed it can be open.

In isolated system to be very honest is actually it is ns idealization or it is an approximation in Cruces we hardly get isolated systems in our real life or in practical applications a Thermos flux can be considered a close approximation of an isolated system. Mostly we deal with close systems which interfere, the system interacts with the surroundings by flow of energy into and out of it or open systems which fed the boundary allows flow of both mass as well as energy across its boundary.

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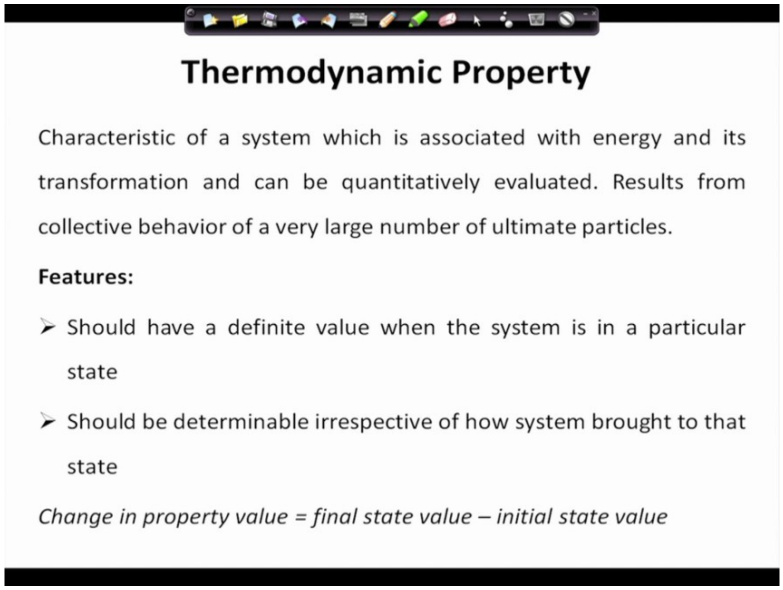

Now once you have defined system you know that you are supposed to perform your analysis on this particular system, now how to identify this system? We have to identify it by means of a number of properties just like if you want to describe your friend to someone you will be describing your friend by means of some of his or her characteristics how tall, whether that person wears a specks or not, whether he is short or tall or whether he is fair, whether he has got any identification marks etc. In the same way when we define a particular thermodynamic system we are going to characterize that particular system by means of some particular properties. Now there can be a huge amount rather there can be a large extent of properties by which we can characterize a particular system.

Now as far as thermodynamics properties are concerned we are we usually refer to those particular characteristics which are associated with energy and its transformation firstly they can be quantitatively evaluated and mostly we find that since we are dealing with macro systems which are made up of a large number of ultimate particles I am not going to refer to them as atoms, molecules, ions nothing because they can be anything.

I would be referring to the smallest portion of my system as ultimate particles, which is the smallest subdivision of my system which retains the characteristics of the system. So therefore the properties which are manifested of the system they are actually the result of a collective behavior of a very large number of ultimate particles you can very well understand that when since we are dealing with phase equilibrium thermodynamics which is the part of classical thermodynamics which deals with macro sized systems.

We are not going to relate or rather we are not going to deal with thermodynamics at its molecular level or the statistical thermodynamics as it is called, since we are dealing with classical thermodynamics, so usually we are going to deal with those particular properties which are associated with energy and its transformation. We are comparatively fewer in number and there are some characteristics which a thermodynamic property possesses.

What are these? The first property is it should have a definite value when the system is in a particular state. Quite naturally when I see that the system existing in a particular state it means that it has a definite set of its different properties. It has a definite temperature, it has a definite pressure, it has a fixed volume and so on and so forth we will be coming across other properties in our due course. And remember one thing when we define the properties of a system in a particular state it is irrespective of how that system has come to that particular state?

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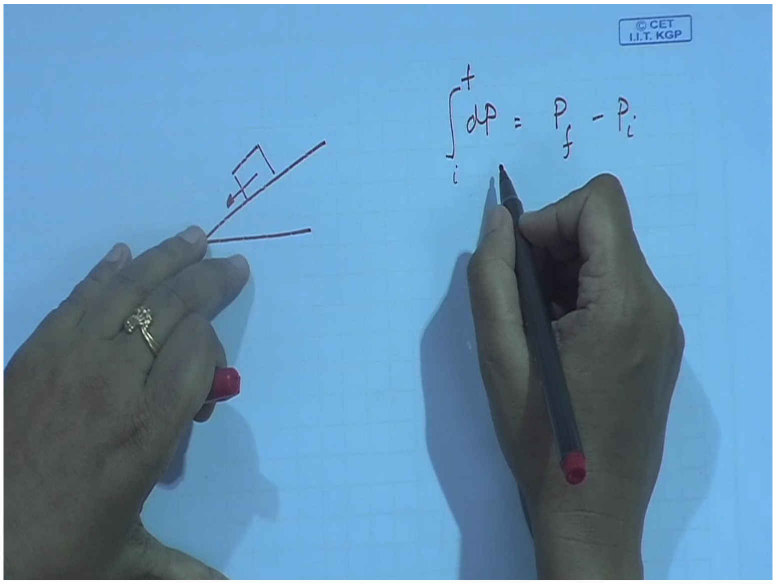

It can take up any path it can start from any other initial state but when it has come to some particular state say I or some particular state F, no matter what was the initial state? No matter how it has come from the initial state it is going to have the same properties. So therefore what I mean to say is the properties of a system they are state functions they define the state of a system they are determinable irrespective of how the system was brought to that particular state and when any particular system is undergoing a change of state from say one particular state i to another state f then the change in the property dP is equal to Pf minus Pi. It does not matter in what path the system had used in traversing from state i to state f as a result we say that the properties are usually exact differentials.

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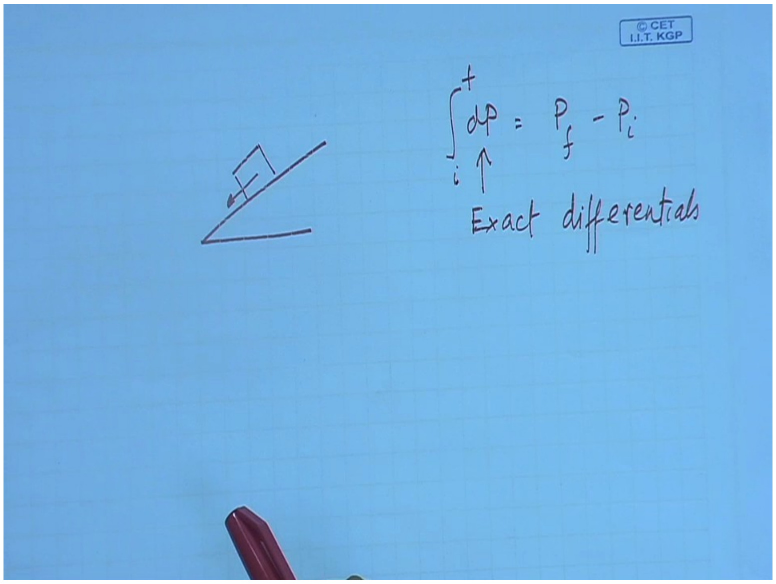

Well, it is very good that you have identified it. Let me tell you some other things that although I have told you that the thermodynamic properties they are the collective behavior of a large number of ultimate particles which are characterizing that or rather which are making up that particular system we need to remember that while thermofile for determining thermodynamic properties it is not important to understand or consider the structure of matter and usually there are very few variables which can be used to describe the state of matter and while on the other hand the ultimate particles in order to characterize them we need to know the structure of matter and therefore for each and every particle we need to know its position its momentum its velocity, so a large number of variables are required for complete specification of the state of the ultimate particles but when the ultimate particles are completely random and they are manifesting their average characteristics which are manifested as thermodynamic properties, so for finding out this thermodynamic properties it is not important to understand this structure of matter or we need not go to the molecular level.

Now when I am mentioning that well, we have a particular system it should be characterized by some particular properties when it is in a definite state it automatically implies that the whole system should possess one set of properties or in other words, when a system is in some particular state and I want to measure the temperature by inserting a thermometer I should be getting the same temperature no matter where I insert the thermometer in the or if I insert the thermometer in different parts of the system.

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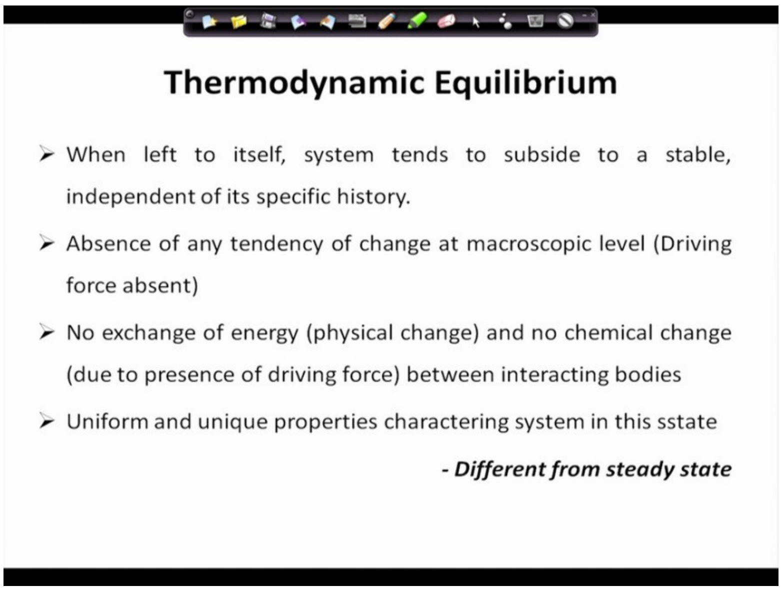

So therefore what I mean to say is that a particular state of a system is meaningful only when it is an equilibrium state and then the next question comes is what is an equilibrium state? In other words how do I define an equilibrium state? We should remember one thing, if we leave a system to itself if we do not disturb a system it will finally attain a some particular state where it does not change on itself, more importantly it does not have any tendency to change by itself.

This tendency to change or not having the tendency to change is much more important than the fact that it does not change, what do I mean by this? I mean that suppose you have a wall, a wall does not move you are pushing it very hard, right? It resists the movement but there is some particular unbalanced force which is acting on the wall, fine. So therefore there are 2 things which bring about the change in property of this system.

First, is there has to be some particular unbalanced force which will bring about this change and the system it resists that particular unbalanced forces when it cannot resist then it undergoes some particular change. The important thing about equilibrium is that the system or the body does not have any unbalanced force acting on it as a result of which there is not only that there is absence of any change there is absence of any tendency of change at the macroscopic level.

So therefore under such a condition there is no exchange of energy and there is no chemical change between the that different bodies which are interacting with one another and as a result of which we find that the whole body, it is in some particular state where it exhibits the same properties throughout thus the properties neither change with position nor they change with time. Now you have to remember, as I was telling you when left to itself all systems they come to this state of equilibrium. Suppose you throw a stone, as small children you must have thrown stones in the river and you must have found ripples.

The ripples continue for some time and finally they die out and the pond comes or returns to its quiescent state. In the same way whenever you are performing any particular change you find that there is some disturbance in the system the disturbance continues and then after a time the system returns to its quiescent state under which there is no unbalanced forces neither there are any unbalanced mechanical forces nor there are any unbalanced chemical forces nor there are any unbalanced thermal forces. So therefore the body is completely at peace with itself and with the surroundings, this particular state is known as an equilibrium state.

Now when we talk of thermodynamic equilibrium it's very important for you to remember that when a body simultaneously satisfies thermal, mechanical and chemical equilibrium only under that condition a body is said to exist under thermodynamic equilibrium. Mechanical equilibrium means equality of pressure at all positions or points of the body as well as with the surroundings. Thermal equilibrium means equality of temperature at all positions of the body and with the surroundings.

Chemical equilibrium means equality of chemical potential, possibly you are not aware of this word, we are going to deal in greater details with this particular word and you will find that after a few lectures chemical potential is going to be our companion throughout the entire course on this particular subject of phase equilibrium thermodynamics. Any how it is sufficient for you to remember at this moment that equality of chemical equilibrium between the system and the surrounding it guarantees chemical equilibrium.

After a few lectures I will be taking up one particular class where I am going to prove that equality of temperature, equality of pressure and equality of chemical potential they are the primary constants the primary requirements for attainment of thermodynamic equilibrium. Now before I proceed I have one question for you as I was telling you that the thermodynamic equilibrium is a state where the system does not change its property with position or time.

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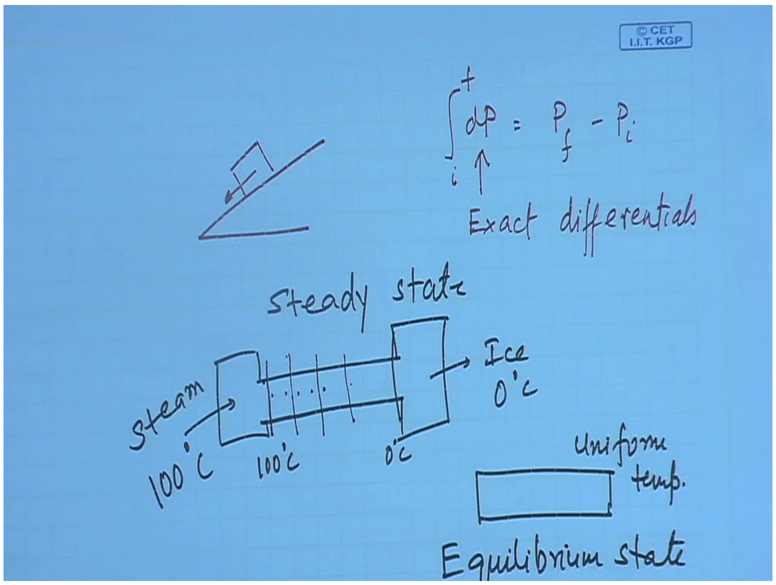

This particular aspect distinguishes an equilibrium state from a steady-state; can you just identify what is a, what differentiates a steady-state and an equilibrium state? I will just give an example which will help you to understand the difference between the 2. Say we have got a copper rod, right and that particular copper rod we arrange it in such a way that one part of the copper rod it is immersed in say steam at 100 degrees centigrade.

And the other part of the copper rod you have immersed in ice at 0 degrees centigrade will keep the copper rod in this particular manner for quite a sufficient time what happens, we find that the end of the copper rod which is immersed in steam, that particular end it has a temperature of 100 degrees centigrade. The temperature as you proceed it keeps on decreasing, finally the temperature at the other end is 0 degrees centigrade.

So therefore you find that after sometime you find that when you put a thermometer at different locations you record the same temperature but this temperature is not same for different locations it varies with position. The rod under this condition is said to be at steady-state. Now what you do?

You simply remove the steam jacket as well as the ice jacket and you keep the rod as it is in the air after sometime you find that the whole rod has assumed some particular uniform temperature and this particular temperature does not change, it's the same throughout the rod and it does not change with time. Under this condition the rod is in an equilibrium state.

Now when some particular or other let it be here, so therefore when we have any particular system in an equilibrium state it has a fixed set of properties when it goes to another equilibrium state it is again characterized by another set of properties. Now there are different equations of state which relate the different properties of the system and from these equations of state we can predict some properties in terms of the other properties. For example the most common equation of state which you know by this time is the ideal gas equation. So from that equation you know that if suppose you know the pressure and temperature of the gas in a container and if you know that the gas is in equilibrium state then without measuring the volume just by using ideal gas equation you can find out its volume you can find out its mass and so on and so forth. You can find out the number of moles of the gas etc.

Now it is important to remember that some system is in equilibrium state there are a minimum number of properties which can be varied without changing the state of the system or in other words, there are a minimum number of properties which must be specified in order to completely define the state of the system. And these numbers of properties are related to the number of phases present in then system and the number of components present in that system by a very famous rule which is known as the Gibbs or rather Gibbs phase rule.

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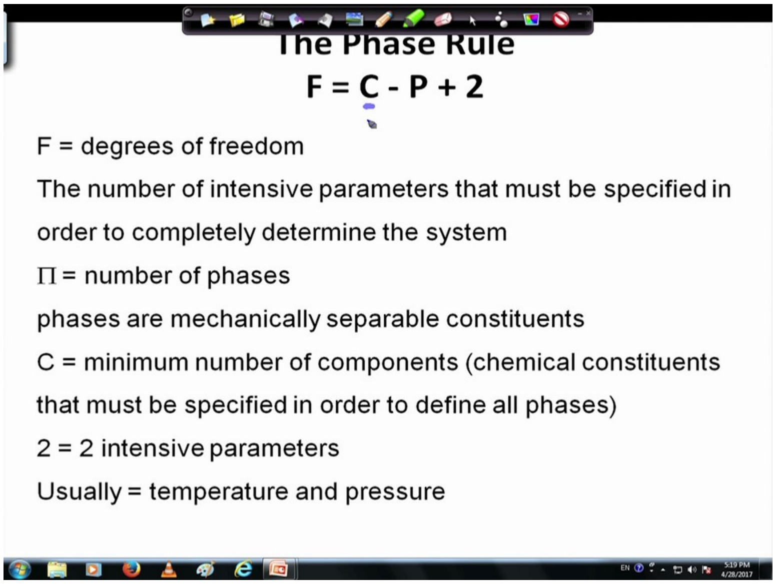

The rule as it is as stated here the rule states that the number of intensive properties which can be specified that is equal to the number of components which are present minus the number of phases plus 2 this 2 usually refers to the temperature and pressure conditions. So therefore from here what do we know? Suppose we have water in a container it is a single phase system, single component system so therefore for this water there are 2 properties which can be independently varied other 2 properties which if you mention the state of the water is completely specified they are its temperature and its pressure. This same water if it is kept in equilibrium with its vapor.

Suppose there is a container we have water and water vapor above it and the 2 phases are in equilibrium with each other, so in this case you tell me what are the minimum number of interns or rather what are the minimum number of properties which must be specified. C is 1 here P is 2 here, when there was just water in the container we could independently vary its temperature and pressure. Now if this water is kept in equilibrium with steam then we find that temperature and pressure they are no longer independent of each other they become interdependent.

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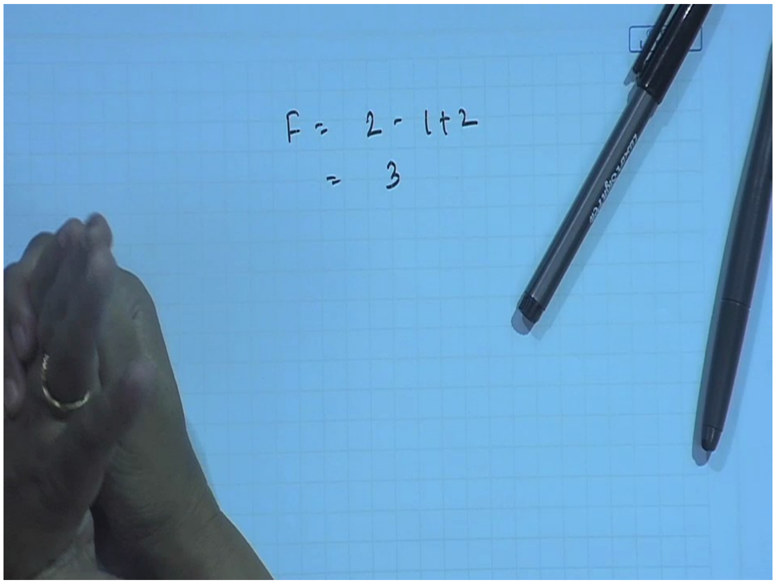

So either you specify its temperature or you specify its pressure the other gets fixed automatically, with this water you mix up alcohol ethanol say, okay. This ethanol water mixture now it has 2 components it has one phase so therefore in this particular case we find that what is going to be F? For this particular case you tell me when we have an ethanol water mixture we have 2 components, so therefore in this particular case what do we have we know that we can vary 3 properties independently.

What are the 3 properties? The temperature of the mixture, pressure of the mixture, composition of the mixture or in other words the mole fraction of at least one component of the mixture. Same ethanol water mixture when it is kept in equilibrium with its vapor, right? So therefore in a container we have an ethanol water mixture in equilibrium with its vapor, now under this condition what do we have? Can we vary 3 properties at will or in this case we find for the 2 phase 2 components systems we can just vary 2 properties independently.

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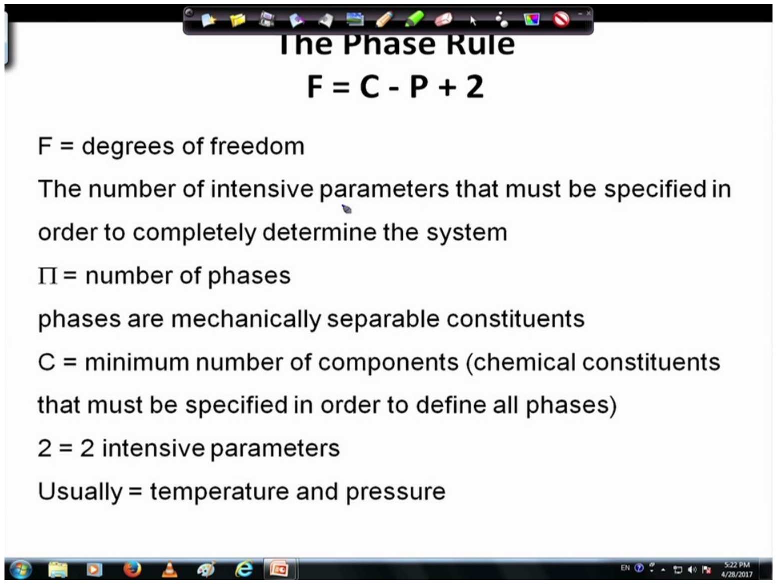

So we can either vary the temperature and composition of one of the phases automatically the pressure and the composition in the other phase gets fixed or in other words we can vary temperature and pressure the compositions gets fixed etc. So therefore the phase rule is something very important it is a very powerful tool in order to deal with phase equilibrium thermodynamics. There are just 2 things which you need to remember when we are dealing with this phase rule the first thing is F refers to the number of intensive parameters as is mentioned in this particular slide, so therefore it has nothing to do with the total amount of mass or the total amount of volume it just deals with the intensive properties. Well, I forgot to mention when I was mentioning properties that properties they can be intensive they can be extensive all extensive properties when divided by the total number of mass or the moles they result in intensive properties.

So therefore the phase rule it states that if we have a ethanol water mixture then we can vary 3 properties and that is true if we have 99 percent ethanol 1 percent water or 1 percent ethanol 99 percent water, so therefore the important part to remember about phase rule is that it is definitely a very powerful tool when we are dealing with phase equilibrium thermodynamics but it has it deals with intensive variables number 1 and it has nothing to do regarding the proportion of the 2 phases.

Well, so we stop here at the moment until the next class we continue our discussions on the introductory aspects of phase equilibrium thermodynamics.