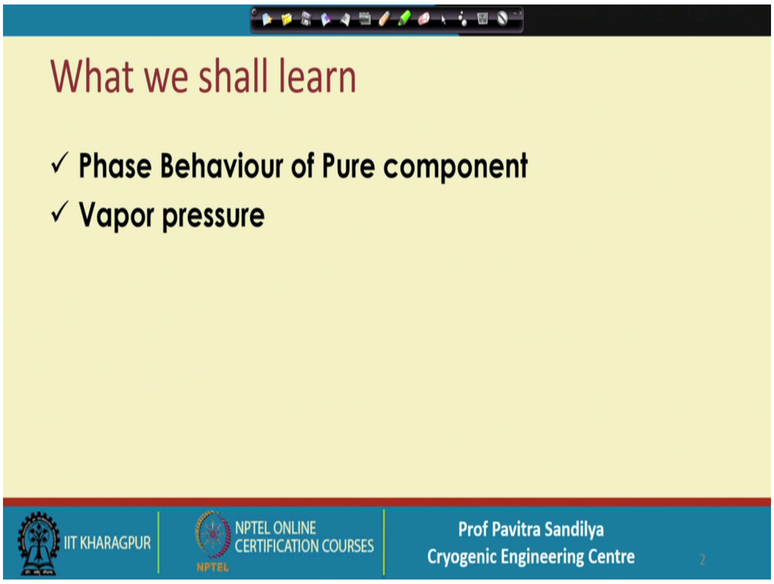
Upstream LNG Technology
Prof. Pavitra Sandilya
Department of Cryogenic Engineering Centre
Indian Institute of Technology, Kharagpur

Lecture – 04
Pure Component Phase Behavior

Welcome back. Now, we shall learn about the Phase Behavior by which we mean that how the different phases of a given mixture or a species distribute themselves at a given temperature and pressure at equilibrium. Why do we need to an equilibrium? Because equilibrium gives us the maximum possible extent a system can work under a given operating condition. So, in terms of the separation processes when we talk of equilibrium, we get the maximum possible separation under a given set of operating conditions.

Similarly, equilibrium has different significance under different contexts. Now, this equilibrium behavior can be there for the pure components as well as for a mixture of components. First let us go to see the equilibrium phase behavior for the pure components.

(Refer Slide Time: 01:32)

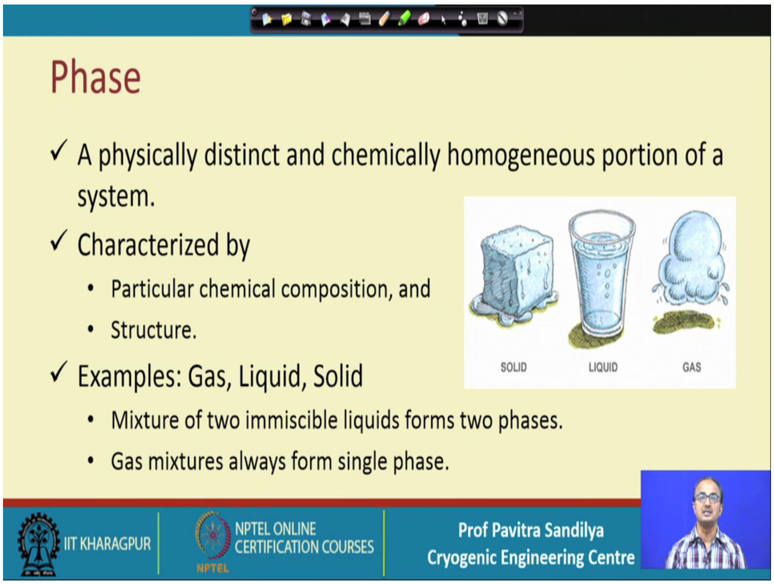


What we shall learn

✓ Phase Behaviour of Pure component
✓ Vapor pressure

In this lecture we shall learn a phase behavior of pure components and how to calculate the vapor pressure which is needed to analyze the phase behavior of pure component.

(Refer Slide Time: 01:50)



Phase

- ✓ A physically distinct and chemically homogeneous portion of a system.
- ✓ Characterized by
  - Particular chemical composition, and
  - Structure.
- ✓ Examples: Gas, Liquid, Solid
  - Mixture of two immiscible liquids forms two phases.
  - Gas mixtures always form single phase.

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Prof Pavitra Sandilya Cryogenic Engineering Centre

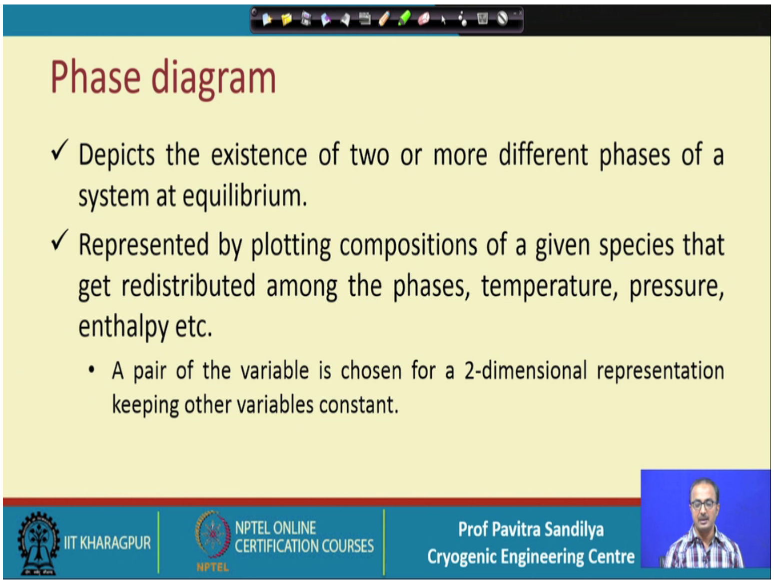
First let us see how do we define a phase. Thermodynamically a phase is defined as a physically distinct and chemically homogeneous portion of a given system. That means, it is should have a given physical identity by our naked eye and it should have a uniform composition all throughout the system. A phase is characterized by its chemical composition and some sort of structure, structured by structure I mean, depending on the bonding between the various species or molecules, we may have solid liquid gas etcetera, and examples are gaseous phase liquid phase and solid phase.

Now, let us see this common example in which we have taken water. Water can exist in three types of phases; that is solid ice and the liquid water and vapor, this moisture in the air or the clouds the vapor phases of water. We have to understand the difference between the state of the matter and phase. The states again are can be gas, liquid or solid, but phases for a given state may be one or more.

For example, when we talk of two immiscible liquids, we have one state of matter; that is liquid, but two phases; example say oil and water. Whenever we are having oil and water we know that they are immiscible, they cannot mix between each other. So, we shall be having oil and water if we take them in a given container. Oil we know that is lighter than water, so it will float over the water. So, they will make two phases.

All the gas mixture will always form a single phase, whatever gas we might be having. Suppose in air you are spreading say carbon dioxide, it will mix and will they will form a single phase.

(Refer Slide Time: 04:21)



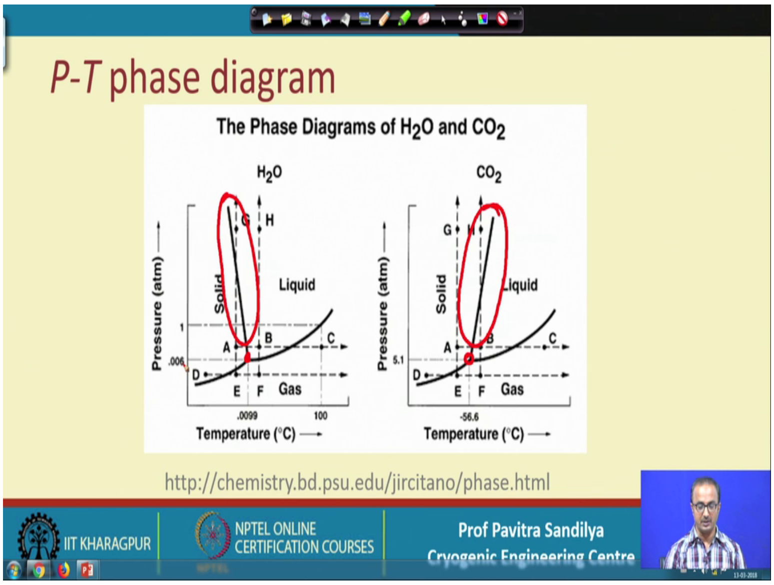
Phase diagram

- ✓ Depicts the existence of two or more different phases of a system at equilibrium.
- ✓ Represented by plotting compositions of a given species that get redistributed among the phases, temperature, pressure, enthalpy etc.
  - A pair of the variable is chosen for a 2-dimensional representation keeping other variables constant.

Now, let us come to the phase diagram of a pure component. Now what it depicts? A phase diagram shows the existence of two or more phases of a system at equilibrium. We make the phase diagrams always for equilibrium. And how we depict them, we depict them by plotting the compositions of a given species that get distributed among the phases, temperature, pressure, enthalpy, entropy such kind of properties, such kind of thermodynamic properties we use to represent the phases and when we talk of a 2 dimensional representation on a paper, we choose any pair from among these set.

Now, we may choose temperature pressure, we may choose temperature entropy, we may choose the temperature density or temperature specific volume, pressure volume etcetera. So, we may have different types of representations of the phase diagram.

(Refer Slide Time: 05:31)



P-T phase diagram

The Phase Diagrams of H_2O and CO_2

http://chemistry.bd.psu.edu/jircitano/phase.html

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Prof Pavitra Sandilya Cryogenic Engineering Centre

Now, let us take some examples of these various types of representations of the phase diagram. First let us see the pressure temperature phase diagram. Here we have shown two typical P T diagrams in short; first is for the water H 2 O and second is for carbon dioxide.

Now, here we see, even though these two phase diagrams look similar, but there is slight difference in the upper portion; that is this line and this line; otherwise all the phase diagrams have some typical points. For example, both the phase diagrams has these two points common, they are the triple points. By triple point with mean that where the three phases coexist the solid, liquid and vapor phases coexist.

And in case of water we have some typical value like 0.0099 degree centigrade and 0.006 atmosphere, as the triple point temperature and triple point pressure and this is unique for a given component. Similarly for water, for carbon dioxide, we have minus 56.6 degree centigrade as the triple point temperature and 5.1 atmosphere as the triple point pressure.

And what is the significance of this triple point that it decides that whether the particular component will be staying in the vapor phase or solid phase. Now, below the triple point you can see from these two curves that we have only the solid phase and the gaseous phase.

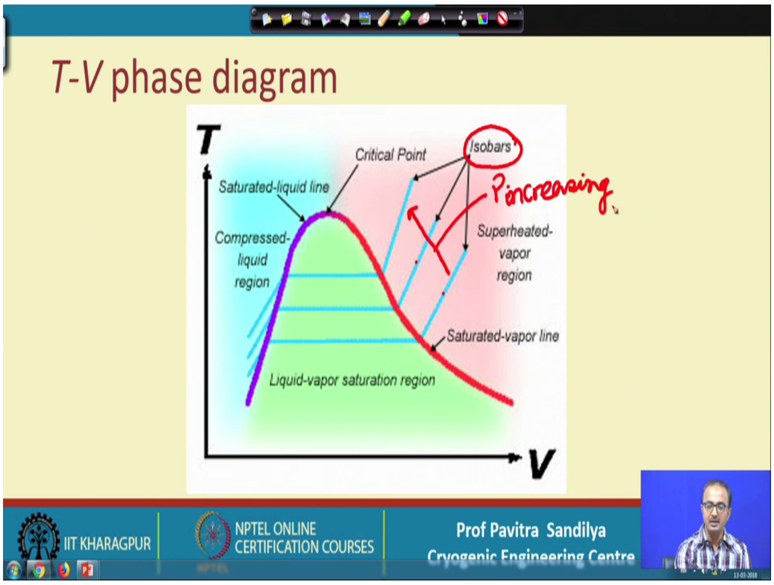
Now, let us see what happens with water. In case of water we will see our atmospheric pressure is about one atmosphere. So, under one atmosphere if I am changing the temperature; that is I am heating the water at the given pressure, I find that at lower temperature below the 0 degree centigrade, we have only solid that is ice and as I cross 0 degree centigrade I find we land up with liquid water. And if I still further increase the temperature I find liquid gets converted to water vapor.

So, under no condition at atmospheric pressure we shall have the direct conversion from solid to vapor phase. On the other hand if I look at carbon dioxide, we find that the triple point pressure is 5.1 atmosphere. So, at the ambient pressure of one atmosphere we find that at lower temperature, if I have solid carbon dioxide and if I keep heating it up and as it crosses this phase line, we find that we go to directly to the vapor phase without going through the liquid phase.

So, this is the significance of the phase diagrams which tells us about how the state of a given species would change by changing is pressure and temperature conditions. here one thing to be noted is this that there are three lines we have we here. Now these three lines like this line and this line here, they are demarcating the two different phases. Like for example, the line between the solid and the gaseous phase is the sublimation line.

Sublimation means the direct conversion of a solid into vapor state. We know some examples like iodine, like solid carbon dioxide, they can get converted from directly from the solid phase to the vapor phase without going through the liquid phase. Then we have another line between the solid phase and the liquid phase; that is the fusion line or the condensation line. And similarly we have the between liquid and the gas; that is the vaporization line. So, this way we have different types of lines which are demarcating the various states of the matter.

(Refer Slide Time: 10:07)

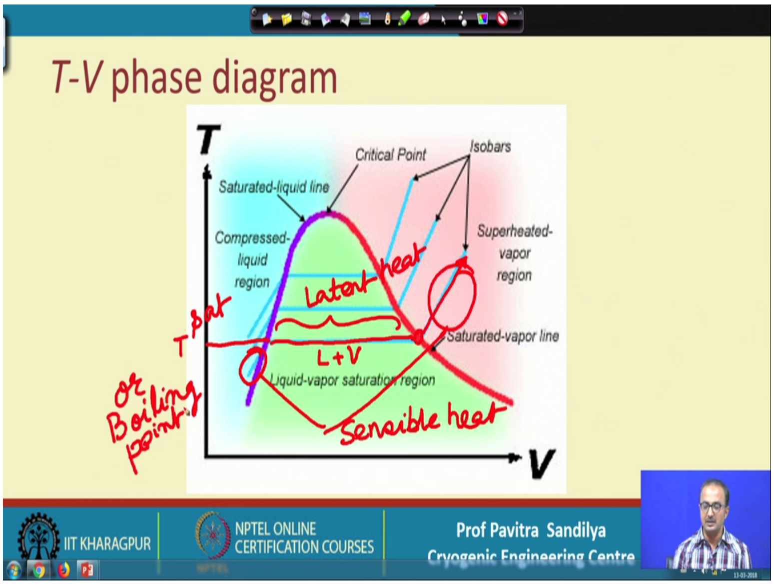


T-V phase diagram

Next we go to the T V diagram. Here I have shown some a typical temperature versus volume or more correctly specific volume. This is interesting. Now here you will see that we have different lines and these different lines represent different isobars, meaning that they are representing the phase change behavior at a constant pressure, and as we move from bottom to top the pressure is increasing.

Now, let us see what happens at a given pressure. Suppose we start with a liquid state; for example, we start with water. Now, as I heat up the water at constant pressure which we can easily do at our home or laboratory by keeping the vessel open to atmosphere, so it will be at constant pressure. So, at constant pressure if I heat water I will find that initially the temperature of water will increase due to sensible heat transfer and then at one temperature I will find, the temperature stops increasing, but we will find that this water will be going through two phase, two phase region.

(Refer Slide Time: 11:32)



T-V phase diagram

IIT KHARAGPUR

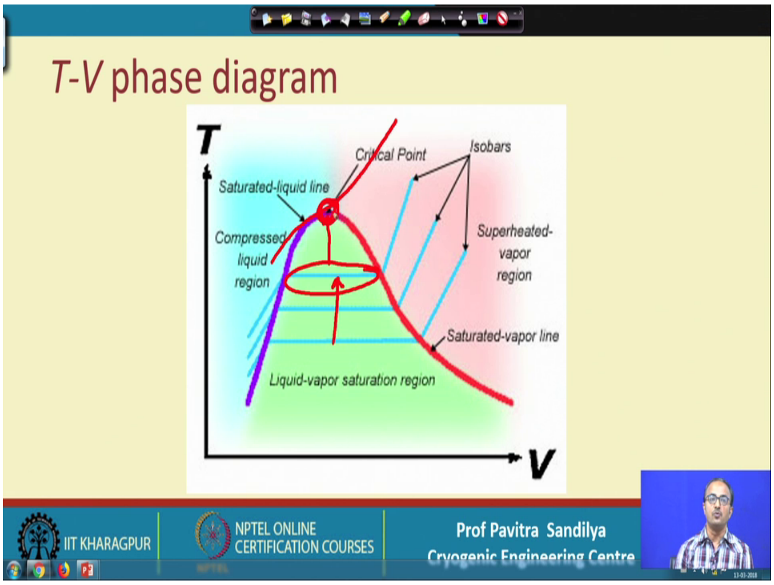
NPTEL ONLINE CERTIFICATION COURSES

Prof Pavitra Sandilya
Cryogenic Engineering Centre

So, within this two this line we have both the liquid and vapor phases, and during this conversion of the liquid to vapor we will find that there will not be any change of the temperature. And ultimately at this point we will find the last drop of the liquid water will get converted to vapor and then this vapor will again start going, its temperature will start increasing due to the sensible heat transfer.

So, in this region and is this region we have the sensible heat transfer; whereas, in this region we call it the latent heat transfer. Means there will not be any expression of the heat transfer, because it is being consumed for the phase change ok. Now this temperature at which this phase change is taking place is the, we call it the saturated temperature T sat, T sat or for the liquid vapor transition it is same as the boiling point temperature at a given pressure. And as we can see from the diagram, this boiling point temperature keeps increasing with the rise in the pressure.

(Refer Slide Time: 13:04)


T-V phase diagram

IIT KHARAGPUR

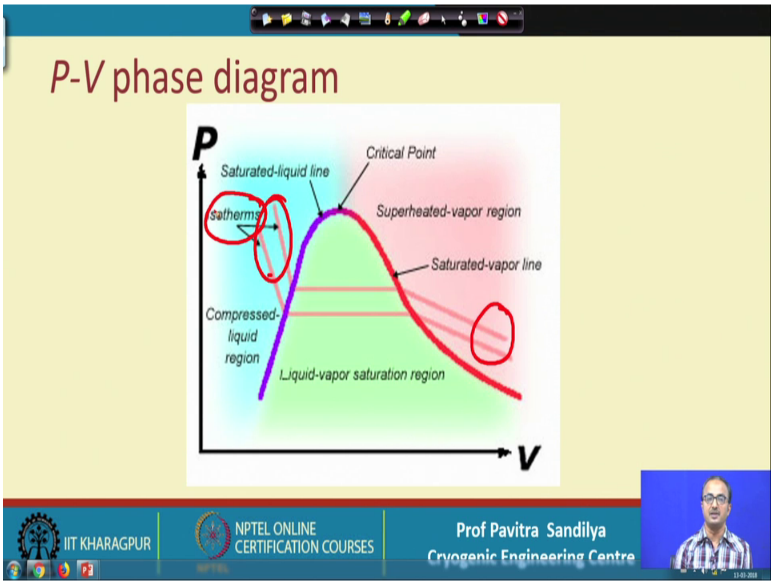
NPTEL ONLINE CERTIFICATION COURSES

Prof Pavitra Sandilya
Cryogenic Engineering Centre

So, we can make such kind of isobars for different pressures, and as we move up the pressure we find that the region of the two phase keeps on shrinking. And ultimately as did still move up at higher pressure we find the two regions merge and we get a conversion of the liquid to vapor phase without any clear demarcation of the two phase region, and this particular temperature pressure is called the critical point temperature and critical point pressure.

So, this critical point decides whether we shall be having a two phase region or only a single phase region when we are heating a particular liquid to at a constant pressure.

(Refer Slide Time: 14:03)

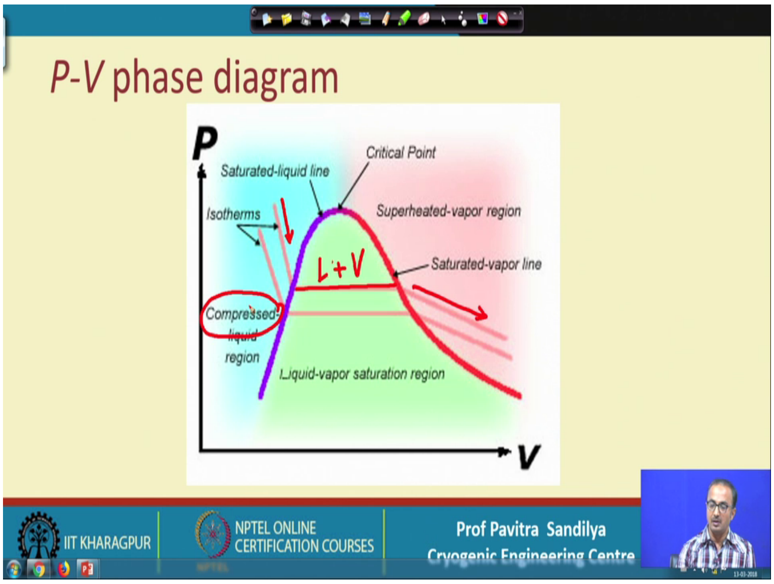


P-V phase diagram

IIT KHARAGPUR
NPTEL ONLINE CERTIFICATION COURSES
Prof Pavitra Sandilya
Cryogenic Engineering Centre

Next let us see another diagram; that is the P V diagram. In this P V diagram we know that we are again sorting the pressure versus volume and this pressure versus volume we see that we have again at, unlike in case of temperature at higher temperature we have vapor, at lower temperature we have liquid at a given pressure. In case of pressure at higher pressure we have the liquid. Whereas, at lower pressure we have the vapor at a given temperature, and in this case these lines are representing the isotherms; that is the constant temperature line.

(Refer Slide Time: 14:58)



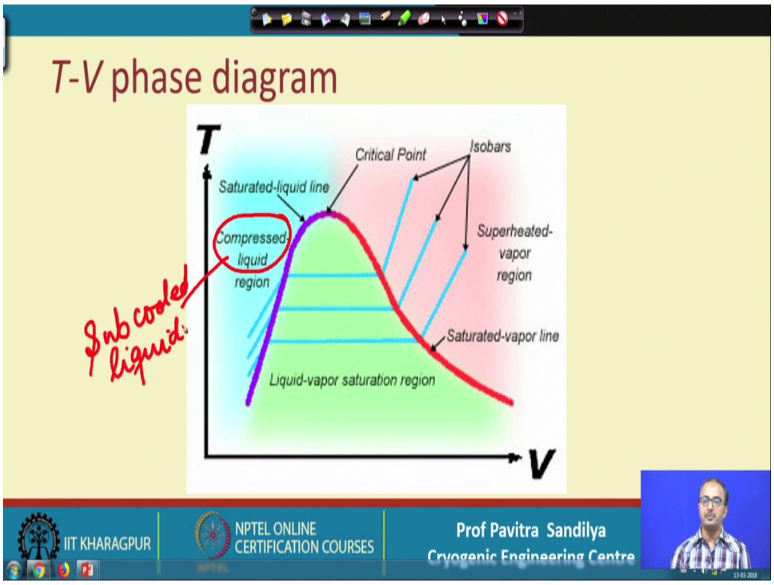
P-V phase diagram

IIT KHARAGPUR
NPTEL ONLINE CERTIFICATION COURSES
Prof Pavitra Sandilya
Cryogenic Engineering Centre

So, in this case if I look at the phase behavior at a given temperature, we are starting with say liquid and if I keep decreasing the pressure, I will find that initially there will be the volume will keep on changing, volume will keep on increasing a bit and then we will find that at certain pressure, there is no change in the pressure. But the volume is still increasing; that means, we are having the two phase, two phase region, two phase region, and if I still decrease the pressure we will find we are having the vapor. So, from a liquid state it has gone to the vapor state.

Now, in these two diagrams the common thing is this, there is this transition of the pure component from the liquid to the superheated vapor via a two phase region. In case of these P V characteristics, this liquid is called the compressed liquid.

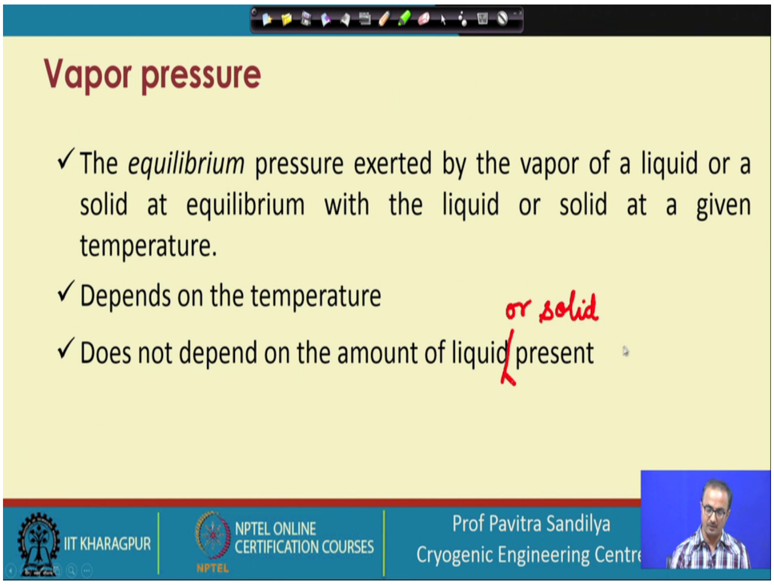
(Refer Slide Time: 16:11)



T-V phase diagram

Now in case of the temperature, volume phase diagram the we same. Similarly we have a compressed liquid region, but these also called sub cooled liquid. So, compressed liquid or sub cooled liquid represent the same state of the material.

(Refer Slide Time: 16:50)



Vapor pressure

- ✓ The *equilibrium* pressure exerted by the vapor of a liquid or a solid at equilibrium with the liquid or solid at a given temperature.
- ✓ Depends on the temperature
- ✓ Does not depend on the amount of liquid or solid present

And lastly we have the vapor pressure. Before I go to vapor pressure let me tell you that, as I told you earlier that other then P T P V and T P diagram in some literature you will also find we are using the temperature entropy representation or the enthalpy pressure representation. And in these diagrams you will find we have host of other constant design processes like isobars, isotherms and etcetera ok

So, in different literature you will find different types of representations of this pure component phase behavior, but ultimately all of them will represent the three states of matter; that is liquid, then liquid vapor mixture region and then the superheated vapor region. After learning all this we come to a very important concept; that is vapor pressure. So, first let us see; what is the vapor pressure.

Vapor pressure is the equilibrium pressure; that is exerted by the vapor of a liquid or a solid at equilibrium with the liquid or solid at a given temperature. It means that if I keep a closed system. Closed system means, a system where it is possible to exchange energy between system and the surroundings, but not the mass. In such a system I put a liquid, liquid will start evaporating at any given temperature pressure and it will reach in equilibrium with its own pressure. If it reaches equilibrium then the pressure we are reading is the vapor pressure of the liquid and that given temperature.

Similarly, the same thing may happen to the solids which are sublimating. For example, naphthalene, for example, iodine, they can also exert their vapor pressure. Other non sublimating solids also exert, but their vapor pressures are generally neglected at the ambient conditions. So, this vapor pressure decides that whether the particular liquid or solid will undergo a phase change at a given set of temperature pressure conditions or not.

Now, we have to understand that this vapor pressure is a function of the temperature, with increase in temperature the vapor pressure of a liquid or solid increases, and it does not depend on the amount of the liquid or solid present in the system; that is it is independent, this is independent of the amount of the evaporating liquid or the sublimating solid, it only depends on the temperature. So, this vapor pressure is an intrinsic property of the particular system, which does not depend on the amount of the system.

With this we come to the end of some basic knowledge about the phase behavior of a pure component and the vapor pressure. This knowledge will be used later on to predict the phase behavior of a mixture of components

Thank you.