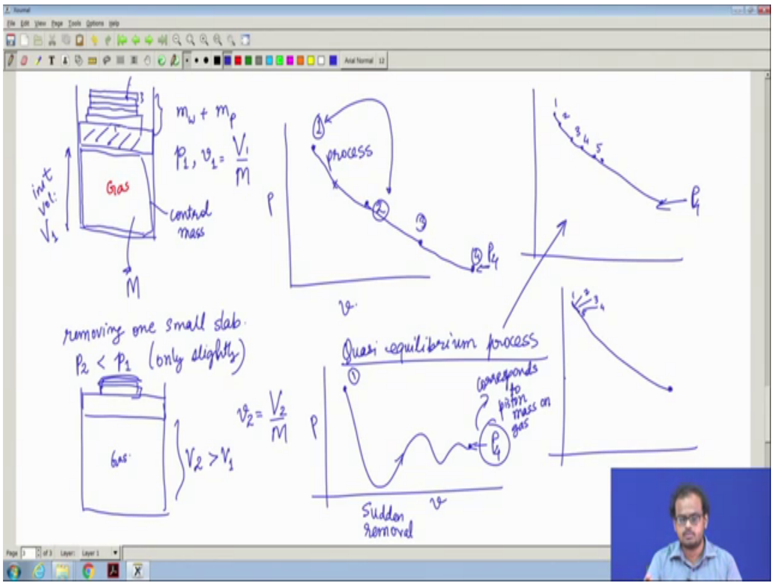
Concepts of Thermodynamics
Prof. Aditya Bandopadhyay
Department of Mechanical Engineering
Indian Institute of Technology, Kharagpur

Lecture – 02
Properties of Pure Substances

So, hello and welcome to this lecture, in which we will consider the definitions of a process and we will see what a quasi equilibrium process means and then study what the Properties of Pure Substances are.

(Refer Slide Time: 00:37)



So, let us consider again the prototypical image that of a piston cylinder arrangement ok. So, this confines some gas for example. Let say is not confining a gas and I mean does not matter really, confines some substance. So now, suppose this piston is loaded with a bunch of deeds, it is loaded with small slabs of weight which can be removed and replacement as required. So now, whatever the amount of mass we have here, plus the mass of the piston mass of weights plus mass of piston it is the total mass acting on the substance, the gas in this case ok.

So, the pressure is defined as P 1 and it is occupying some, so suppose we know that the total mass of the gas is equal to M, initial volume if it is V 1, then the specific volume V 1 is equal to capital V 1 by mass it is this specific volume. So, this is the initial state this is known as the initial state this is the property of the gas ok.

Now, suppose I remove one of the two or more of these small slabs, suppose I remove just one slab the pressure has decreased slightly, P 2 has decreased slightly. And in this the fact that the pressure has reduced, so it means there is lesser load on the gas and the gas is free to expand, there is more space for the gas to go; so all this is common sense, we know this from common experience.

So, if this initial volume was V 1 because of the removal of one of the mini slabs, it will occupy now volume V 2 which is just larger than V 1. And thus the specific, so because it is a control mass, this is a control mass the specific volume V 2 is equal to capital V 2 by the mass. The mass is fixed there are intending the amount of mass is fixed it is the same gas ok.

So, essentially we have initiated a change from P 1 V 1 to P 2 V 2. If we draw it on the P v diagram it was at a higher pressure and then because of the removal of the mass it reduces the pressure and increases the volume. So, I have exaggerated and shown it like this. Now suppose I remove one more plate, one more slab it goes here I remove even one more it goes here.

So, this is how we are able to transition from one point to the second point to the third point to the fourth point. And, going from 1 to 2 the gas is said to be undergoing a process. But, how exactly can I know what the intermediate stage 1 to 2 is? I do not exactly what is going on in between the stage. So, this brings us to a very important idea of a quasi equilibrium process.

So, we assume that the amount of slabs are infinite; that the same mass is made up of infinitely many smaller slabs and we remove the finest slab possible so that, while going from state 1 to state 2, the difference in pressure is so less that it is almost close. So, if I have even lighter slabs then point 1 point 2 point 3 point 4 point 5. If I have even smaller slabs, then something may be like 1 this is 2, then 3, then 4, then 5 and so on, you get the idea.

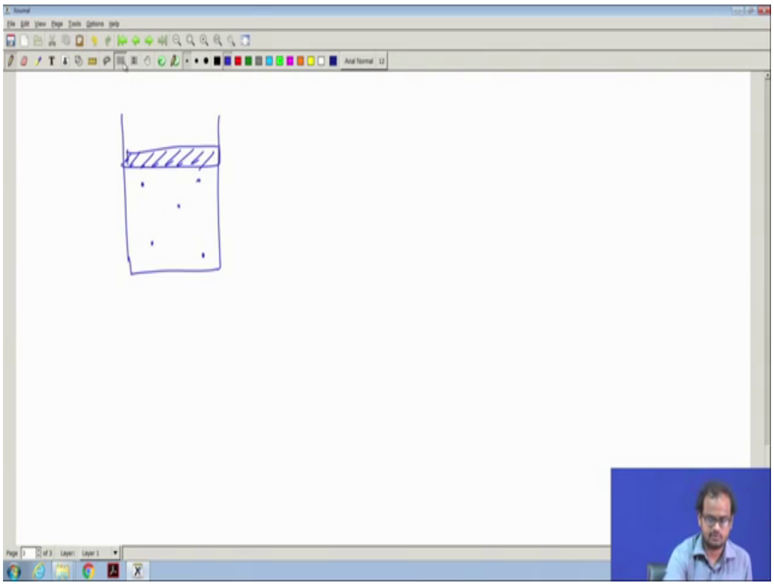
You can make more number of steps to go to the final state, we eventually go to a final state, but we make sure that the system is not disturbed from its initial condition too much. If I were to remove all the slabs in one go, then suddenly the piston would see that suddenly all the mass has been realized and the piston would fly off and we do not have any information about what the process is happening during that non equilibrium process, this kind of process is called as a non equilibrium process.

So, suddenly if it is removed, the P suddenly reduces the V suddenly increases. So, the initial state is known. But, may be the final state is may be something like this it goes to the final state it oscillates may be the piston oscillates and goes to the final state may be. We do not know exactly the nature of how the states will be it is difficult to measure.

So, quasi equilibrium process is a slow process which disturbs the equilibrium very slightly ok, it disturbs the equilibrium very slightly so that between each step it is locally inequilibrium. So, here if the pressure is P 4, the pressure is P 4. Basically if you remove all the slabs, the only thing that is exerting a force on the gas is the piston. And so, in this case the final pressure must correspond to that of the piston, this final pressure should correspond to piston mass acting on the gas.

So, that mass of piston divided by the area will give us the pressure the final pressure. The final pressure in all of cases will be the same, but in the case of non-equilibrium process we will not be able to decide exactly how the system went from the first state to the final state. But, in the case of quasi equilibrium process we can carefully remove part by part the masses which are loading the piston, we will get to the final state we will know each intermediate step there is no question of non-equilibrium.

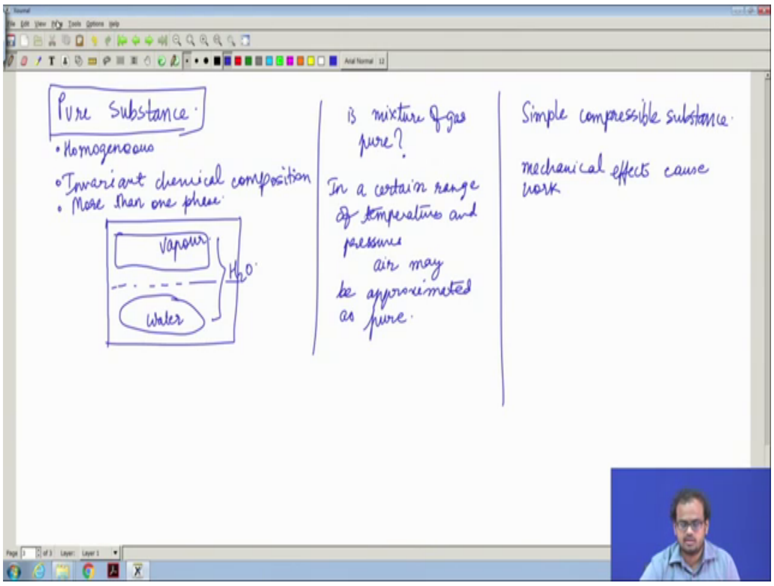
(Refer Slide Time: 08:39)



Essentially implying that the pressure in this point and the pressure in this point this point this point everywhere would be equal. The system is instantaneously able to equilibrate to the small disturbance that we have created; this is called as a quasi equilibrium process. The word itself helps us to understand what the process should be like, it is a quasi equilibrium it can never be in equilibrium ok.

If a process if a state is in equilibrium, there will be no tendency for it to move because it is by definition in equilibrium. So, every process inherently as to have some deviation from equilibrium, but the deviation if it is small, the system relaxes very quickly to the new a state and we say that in the system is undergoing a quasi equilibrium process ok. Let us now focus on the definition of a pure substance we want to know what a pure substance is.

(Refer Slide Time: 09:49)



Pure Substance.

- Homogeneous
- Invariant chemical composition
- More than one phase.

is mixture of gas pure?

In a certain range of temperature and pressure air may be approximated as pure.

Simple compressible substance.

mechanical effects cause work

A pure substance is something which is homogeneous and has an invariable chemical composition throughout. So, it needs to be homogenous and invariant chemical composition. So, by this we mean that, if we consider small vessel if there is some liquid water and some water vapour ok. So, the system, the there can be more than one phase, there can be more than one phase. So, it is homogeneous in the sense that the whole system is comprised only of the H 2 O, the chemical composition throughout is simply H 2 O it is not changing its chemical composition ok.

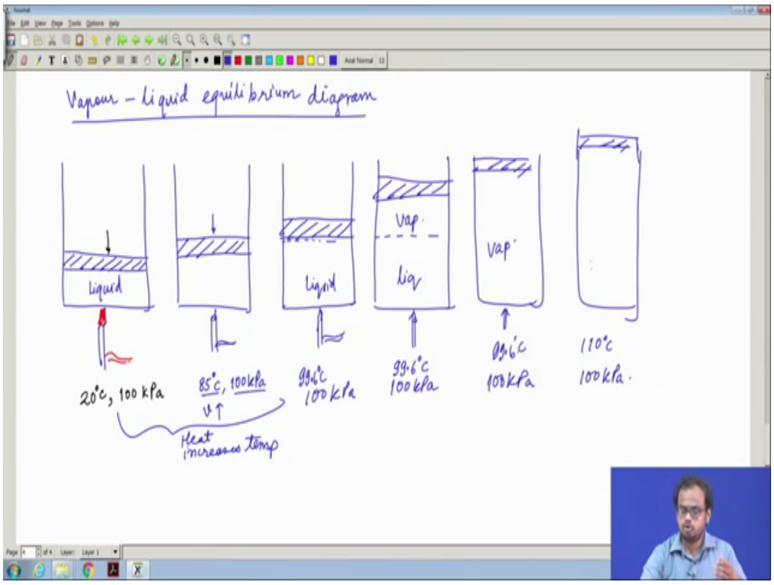
So, each phase has a same composition; however, if we had may be C O 2 dissolved here, then we would not call this as a pure substance because, we have an additional component in this system. So, pure a substance is something which needs to have the same invariant phase. So, is a mixture of gas a pure substance. So, gas say for example, air, air is a mixture of many gasses. So, is it a pure substance. So, as long as we do not have phase change, so if we consider air as whole it is composed of fixed percentage of gases, unless you have phase change those fractions remain more or less fixed if you work in a certain range of temperature.

So, given a certain range of temperatures and pressures, air may be approximated as a pure substance ok. So, for a pure substance, we need homogeneity. So, there is no heterogeneity in the domain, it is uniform in space except few changes the phase, so it is homogeneous in the vapour phase, it is homogeneous in the liquid phase, this homogeneous is everywhere, in the liquid phase the properties are homogeneous there can be more than one phase and the chemical composition should be invariant.

So, this is the most important definition. What is a simple compressible substance? Simple compressible substance refers to those substances, in which only mechanical effects of pressure and all this cause some work to be done. The system is not affected by the presence of electric fields, magnetic fields and so on ok. In many cases, actually in the generation of very very low temperatures, where various exhorting effects those are used because at low temperature the physics changes drastically.

So, in those kinds of conditions things are no more simple compressible ok. One has to account for all those kinds of additional effects in which the magnetism, there direct properties of the substances are exploited to achieve some kind of phase changer property change ok. So, but in this course we will deal mostly with a simple compressible substance; so, only the mechanical so for example, pressure work and all this. We apply pressure on a piston because work on the piston this kind of things where, refer to a simple compressible substances.

(Refer Slide Time: 14:59)



So, let us consider a vapour liquid equilibrium diagram. Let us consider a piston cylinder arrangement as shown. There is some weight of the piston and there is some liquid water and then you start heating. So, suppose the initial condition of the water is 20 degree Celsius and may be its imposing a pressure of 100 kilo Pascal's.

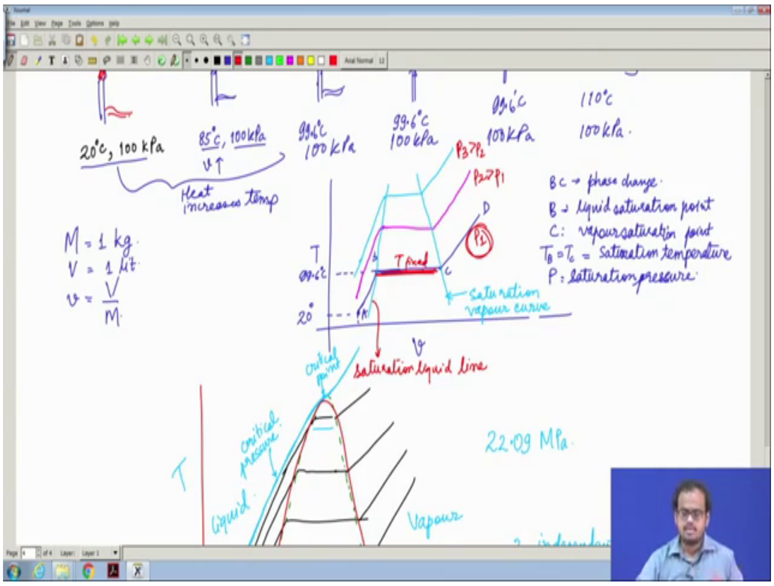
So, just for your reference the atmosphere pressure is 101.325 kilo Pascal. This is one atmosphere. So, this is being heated. So, from common sense we know that because of the heating, there will be a change slight change in volume. So, there is a slight increase in the volume, the temperature increases. So, the temperature increases to may be 85 degree Celsius, but the pressure is remaining the constant remaining constant because you are not adding additional weights on the system. So, pressure remain constant, we have essentially added heat and thus a temperature has increased the volume is also increased.

Now, this goes on upon till the temperature reaches something close to 100 degree Celsius because we know at that point what is try to boil. So, I draw the situation under approximately 99.6 degree Celsius. So, there is some generation of vapour in this state some small amount of vapour is generated.

So now, as more and more heat is given we know that heat is absorbed as latent heat and liquid starts to transition to a vapour phase. So, vapour occupies far more volume than a liquid So, suddenly the volume increases by a huge margin, so the volume increases like this but temperature remains locked because we know everything is now latent, it keeps on absorbing heat, but the heat is absorbed to change the phase it is not used to increase a temperature, upon till the boiling point it was used to increase the temperature.

But now is effecting a change in phase and so there is some vapour some liquid. So, it heat keeps on the temperature keeps on remaining constant up until the point all the liquid has been converted vapour. After this, if you keep on adding, so at all the points, the pressure is 100 kilo Pascal. So, to have the quasi equilibrium process we are heating it in a very slow manner So, after this now the temperature again starts to increase and the specific volume also starts to increasing if I take a larger temperature say we comes 110 degree Celsius ok. So, the volume then keeps on increasing. So, what has happened?

(Refer Slide Time: 19:15)



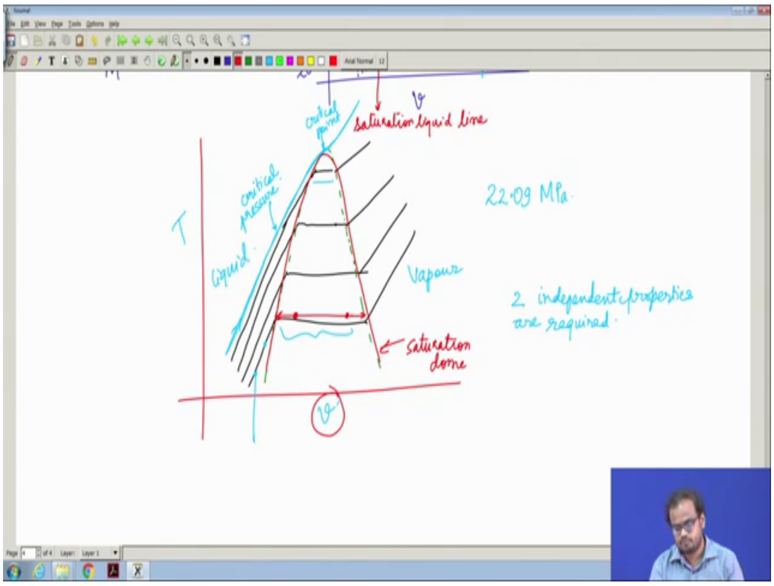
If I try to draw this, in a T versus V diagram, initially I was at some temperature 20 degree Celsius and some specific volume So, I know the total mass of the liquid, total mass of the liquid is suppose 1 kg. So, initial volume is may be 0.2 meter cube ok. So, then the initial condition actually we cannot chooses randomly, because at this conditions the initial volume will be fixed. So, initial so density is approximately 1000 kg per meter cubes. So, for 1 kg it is approximately 1 liter ok.

So, thus we can find out the specific volume as the total volume by the mass. So, this is that initial condition. So, now we keep on adding heat, we are going slowly. So, these are some intermediate step that we are shown, intermediate step 1 2 3 4 5 6. So, we keep on adding heat the temperature keeps on increasing up until a point, where the temperature becomes equal to 99.6 degree Celsius. Then there is no increase in temperature, but there is an increase in the volume, keeps on increasing up until all the vapour is found, all the liquid has converted into vapour and then again the temperature starts to increase.

So, in if I call this A B C and D, C to C is phase change, point B is the liquid saturation point, point C is the vapour saturation point ok. The temperature at which the phase change is beginning T of B equal to T of C is called as a saturation temperature. And the pressure at corresponding to the saturate temperature is called as the saturation pressure alright.

So, this is how process has occurred. Now suppose I do the same process at a higher pressure, how will it look? It will start somewhere over here, then it goes here, then may be it goes like, this goes like this and at even higher pressure, it goes like this. So, I were to join the locus of this points, I obtain 2 distinct curves; this one is called as the saturation vapour curve or line, this one is called as a saturation liquid line corresponding to higher pressure this keeps on happening ok. So, let us now see what happens when we keep on increasing the pressure.

(Refer Slide Time: 23:43)



All the line seems to merge, then there occurs point where there is no more scope, there is no more scope to have any saturation and so the system goes directly from liquid state to vapour state. So, this is vapour, this is liquid in order to go from liquid to vapour we had to pass through this saturation zone.

However add a certain pressure, we directly transition from liquid to vapour. So, what do you really call the thing? There is no its just called as a fluid there is no were to call it a liquid or a vapour So, this corresponding pressure is called as the critical pressure it is the pressure below which we cannot form liquid you need to achieve some lower pressure in order to have this two phase business going on without having a pressure lower than this you are always in that fluid zone where it is simply one homogeneous fluid fluid vapour thing going on liquid vapour thing going on ok. So, this point is called as the critical point.

So, for water, the critical pressure is 22.09 mega Pascal, above this pressure there is no liquid water, it is all just one fluid. So, for pure substances, the minimum amount of properties required are 2, 2 independent properties are required. In this case for example, the temperature and volume, they were two independent properties in this case temperature and volume also we can specify the system in terms of temperature and pressure.

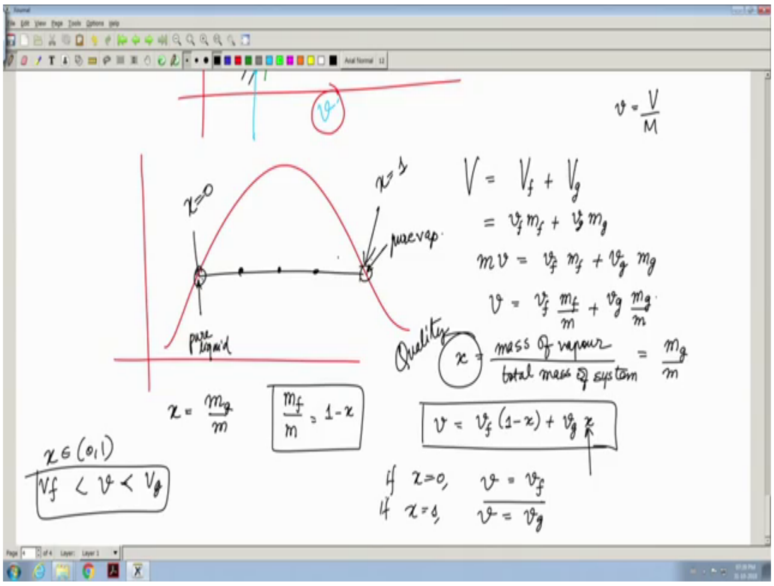
However for a given pressure in this zone, there is no change in the temperature, the pressure is also fixed, the temperature also fixed, but the specific volume is changing. So, we can only choose any one of temperature or a pressure, because corresponding to a fixed pressure, corresponding to a fixed pressure there is a unique temperature inside the saturation dome. This zone inside is called as the so, this is called as the saturation dome.

Inside the saturation dome for a given for a given pressure, this temperature is fixed and thus inside the dome we cannot specify temperature and pressure as 2 independent properties, outside the dome we can; obviously, specified temperature differently, pressure differently. You can have liquid heated to some temperature, but at some other pressure we can decrease the pressure increase the pressure for a liquid, but the moment goes into a saturation zone for a given pressure, it cannot change the temperature.

So, inside the saturation dome, the independent property that is required at this stage that we know is the specific volume. The specific volume helps us to understand exactly what state the fluid is in, is it in this state, this state or which state? So, the specific volume is what helps us to identify the property of the pure substance in saturation dome. Again outside the saturation dome, the pressure and temperature can vary independently, I need not keep the pressure fixed, it is only inside the dome where if the pressure is fixed the temperature is fixed, but the pressure is a saturation pressure the temperature is a saturation temperature, I cannot independently vary the saturation temperature and saturation pressure; given a saturation pressure, saturation temperature is fixed, here I can vary it.

So, we can have a gas at some pressure and some temperature we can cool the gas. Temperature can reduce at the same pressure no problem, but the moment becomes 2 phase, the moment it reaches the saturation dome, we cannot do that. So, inside the dome how can we do a calculation?

(Refer Slide Time: 29:21)



$$v = \frac{V}{M}$$

$$V = V_f + V_g$$
$$= v_f m_f + v_g m_g$$
$$mv = v_f m_f + v_g m_g$$
$$v = v_f \frac{m_f}{m} + v_g \frac{m_g}{m}$$

$$x = \frac{\text{mass of vapour}}{\text{total mass of system}} = \frac{m_g}{m}$$

$$x = \frac{m_g}{m} \qquad \boxed{\frac{m_f}{m} = 1-x}$$

$$\boxed{v = v_f(1-x) + v_g x}$$

$$x \in (0,1)$$
$$\boxed{v_f < v < v_g}$$

If $x=0$, $v = v_f$
If $x=1$, $v = v_g$

How do we really define the property? So, here it is pure liquid, here it is pure vapour. So, the total volume is a total volume occupied by the fluid plus total volume occupied by the liquid and we know that the specific volume is equal to total volume by the total mass. So, this is equal to volume specific volume of the fluid multiplied by the mass of the fluid plus volume occupy specific volume of the, so this should be g, so fluid and gas, this is the convention this will be v g times m of g. So, the volume occupied by the gas is equal to specific volume of the gas multiplied by the mass of the gas ok.

So, total volume is equal to total mass multiplied by the net specific volume of the mixture of the gas. So, suppose the point is here, it is the mixture of this and this, the properties of mixture of this property and this property. So, this is equal to v f m f plus v g m g. Let us divide everything by the mass, so the specific volume of the state is equal to specific volume of the fluid times mf by m plus specific volume of the vapour times m g by m.

So, if we define the quality x as the mass of vapour divided by total mass of system, then the specific volume of that mixture is equal to v f times, so this quantity this is essential equal to m g by m mass of vapour. So, vapour means gas. So, this is x so; obviously, 1 m f divided by m will be equal to 1 minus x. This is very easy to show. If x is equal to m g by m then m f will be 1 minus x. So, v f times one minus x, plus v g times x; so, this is how the property x is able to quantify where the point x actually lies. So, if x is equal to 0, then v is equal to v f. So, it is in the fluid.

So, this point corresponds x equal to 0. If x equal to 1, then v equal to corresponds to v g. So, this point is x equal to 1. So, you put simply x equal to 1, you put simply x equal to one you see this term goes. So, it simply become v g. So, for any other condition x lies between 0 to 1, v is less than v f and so v is less than v g and greater than v f So, this is the mixture So, this how you find out the mixture, the mixture property.

So, in the later classes we will see how to find the energy in the similar manner. The important thing is this quality, inside the dome we cannot specify the temperature and pressure independently and thus we must specify the quality of the substance. The quality if it is 0, then it is said to be pure liquid the quality if it is equal to 1, then it said to be pure vapour. Anything in between specifies where the point lies. The pressure and the quality can be one of ways it can be specified, the temperature and the quality or the temperature and the specific volume.

Once we know the specific volume, we can also find out the quality. We will see all this in due course of many various examples, but the point is inside the dome the pressure and temperature cannot be varied independently. They have to be bounded because during that phase change, the temperature is locked given a pressure, given a pressure the temperature is locked we cannot play with that anymore.

So, we conclude the lecture here. Professor Suman Chakravarthi will help you to read the thermodynamic tables, how to make the sense of properties which are available in various books. So, the reference book is Sonntag Fundamentals of Thermodynamic by

Sonntag (Refer Time: 34:14). It is very compressive book and this will be distributed through the online portal as well.

Thank you, I will see you next time.