Engineering Thermodynamics
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Lecture – 22
Properties of a Pure Substance: Vapour pressure curve. Reference state

The next drawing that we will extract from what we have learnt is what is called the vapour pressure curve.

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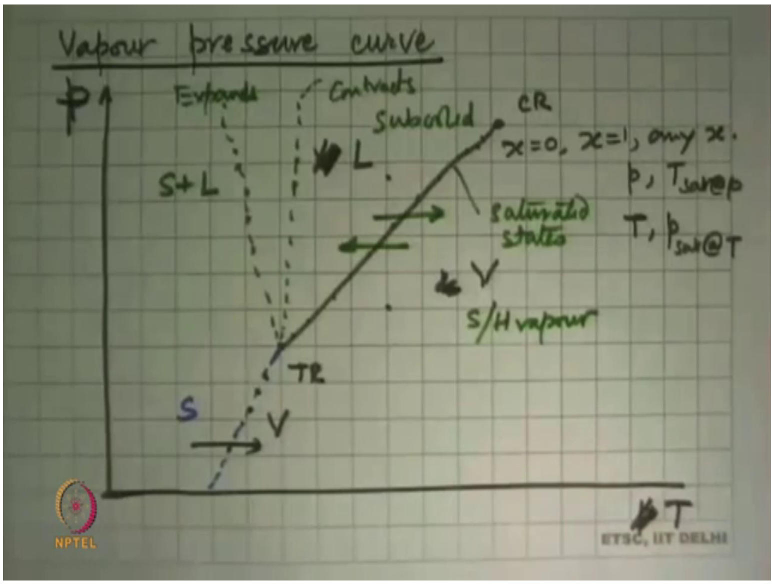

And what we have plotting here, I am just plotting which were in your nodes, this side is pressure, this side is temperature as we will translate the same diagram into this form as what are the states that are possible for a period of pressure and temperature specifications this diagram interpreting one line from these lines.

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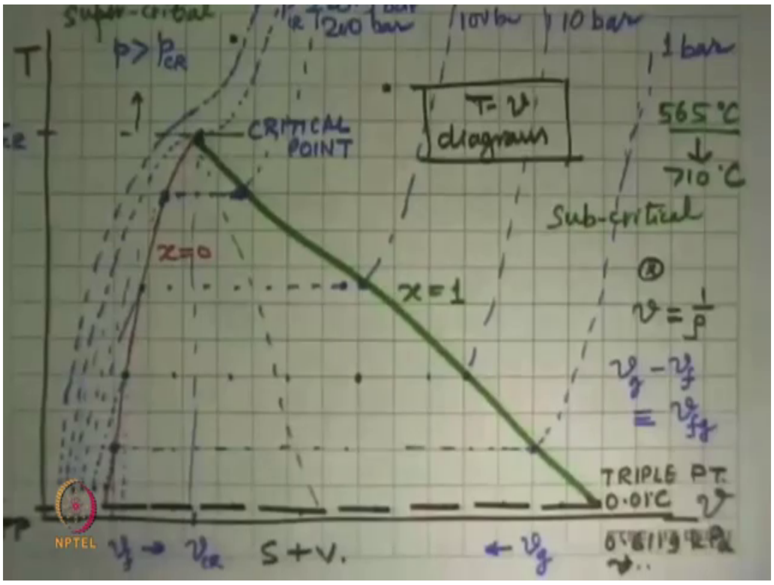

What you see here is that a one bar its saturation temperature was this much, at 10 bar saturation temperature was this much 100 bar because this much. So, in the saturated state between critical point and triple point, this is temperature, this is pressure and this will be in vapour, this is liquid ok. So, this line represents states, where there is a equilibrium between solid and vapour. So, heated this way there is sublimation in this case any process that goes from left to right is vaporization across this line is condensation.

In the role line remains now line between liquid and solid state and here we get two types of lines one a line that can either go in this way or a line that can go that way. And the slope of these lines are pretty much close to 90 degrees very difficult to make out any difference here. So, these are two different types of substances, this is a substance that contracts on solidification and this is the one that expands on solidification. So, these lines represents there lines where you have equilibrium between a solid and the liquid state ok.

So, this types of an induction all types of states that are possible and this vapour means this is superheated vapour, this liquid means it is a sub cooled liquid and they are solid in this and this line is saturated states all saturated states. So, that is the vapour pressure curve and the way it actually looks like it is there in the most (Refer Time: 03:44) way ok, this one.

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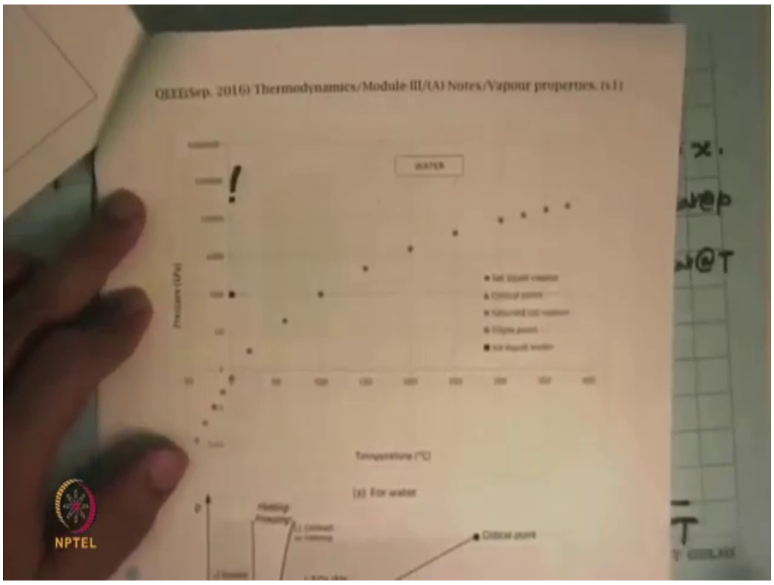

So, this is the actual part for water and you can see the stain here is in degree Celsius this side is pressure and logarithmic claim 0.01 kilo Pascal to 1 lakh kilo Pascal this line this is well saturated line liquid vapour line.

These points are solid liquid lines solid vapour line and this is ice or solid ice on this side solid phase and here there is liquid phase. So, you can see that actually what I have drawn is again a part in exaggeration just to bring out the point, in the fact is that this line is very steep and for other substances of this line we will go slightly back, it is not going to be very much different from this particular line where it is not like they are we cover like in very sharp under surface here.

So this is the real thing that what is looks like a chart and lastly we have a complete handle on liquid vapour saturated states. We now need to look at how we can construct a bigger picture out of this for instance, we take this picture and say took my I will instead of making it on two axis on a piece of paper, I make T v and a third axis normal to the paper which is P. So, we have an x y z system and every state point can be located uniquely in that state. Another reason we do it a simple was from experiments we measured p v T.

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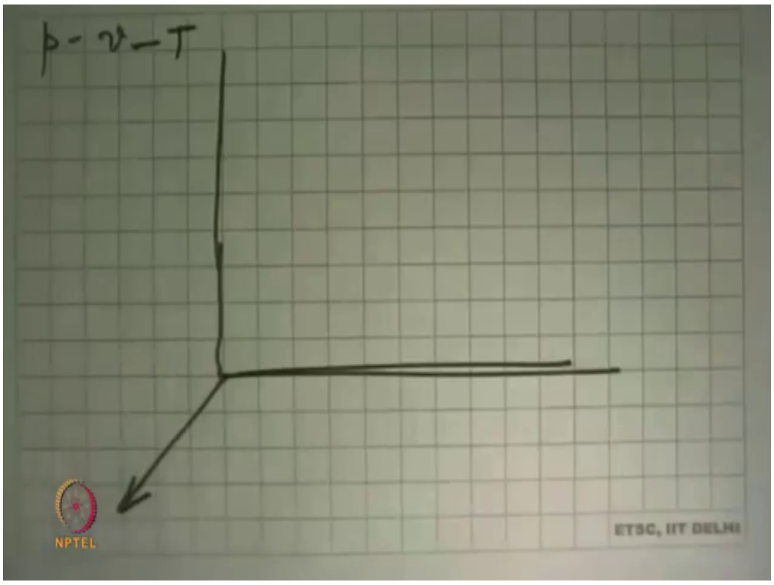

And now we try to make a plot and.

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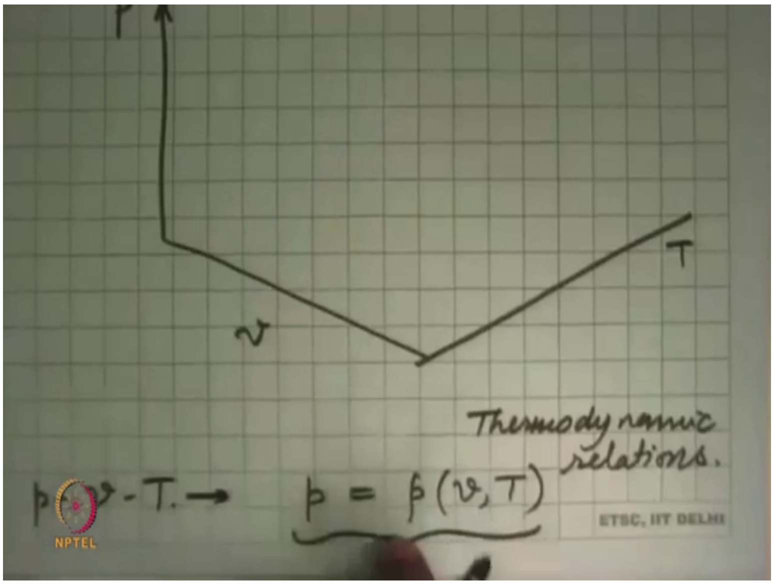

Pressure here, temperature there and specific volume over there and what we have doing is a simple thing.

We got lots of data from different researchers across the world over the last 70 80 90 years of p v and T and that only data we have for thermodynamic properties and we plot it on this curve. So, it will become 3D surface and this surface looks little bit complicated means.

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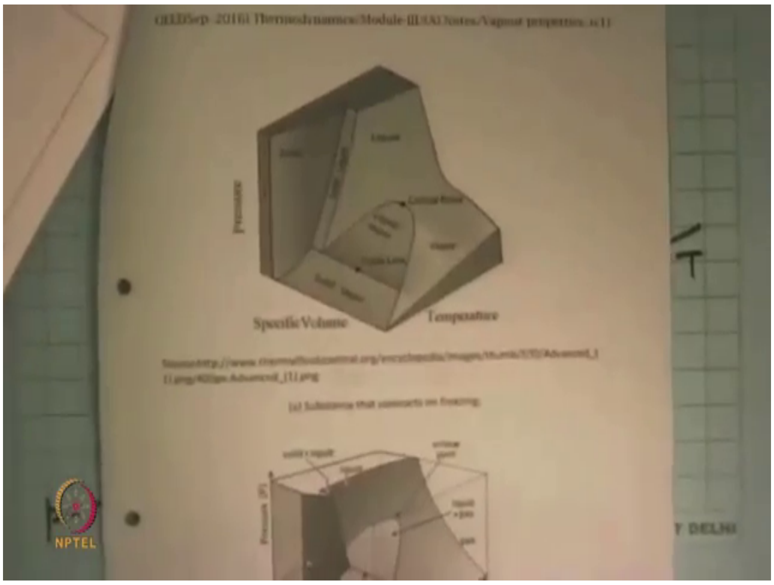

So, the first one here this is on the nodes, this is temperature this is specific volume this is pressure. And what we have been drawing was T versus v, we know show it here that everywhere or rotted slice is T versus v at that pressure.

So, we are start-up those curve one over the other and join them by a three-dimensional surface. So, in that an inclined surface which is a solid vapour phase vapour line a critical point which have this shape and as we go up and keep taking stresses this T v diagram became 0 and beyond that, if this surface is liquid dense liquid and this side is super-heated vapour. And this side is solid plus liquid equilibrium, this side is solid and this is true for a substance that contraction freezing. Now, water as we know is one of the very few exceptions to this room and instead of this curve being here the rest of the curve be the same this line flips and comes into the back and that what you see in this particular picture at the bottom ok.

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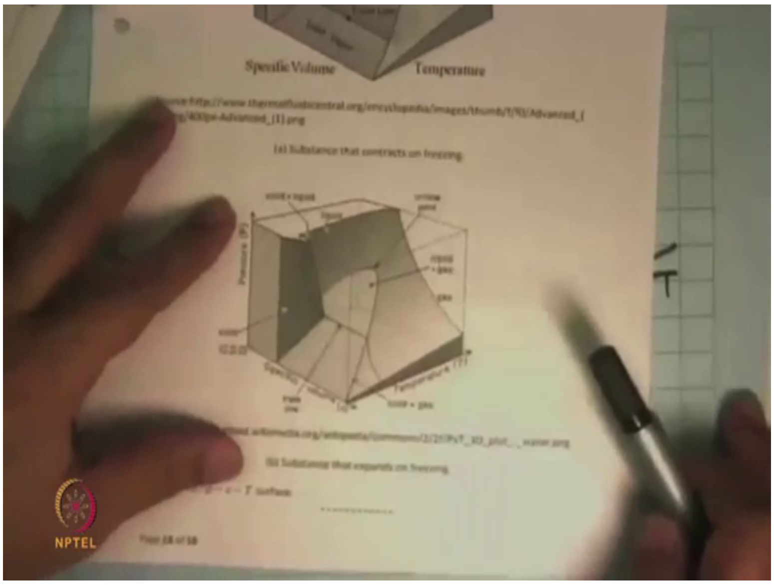

This is the triple line critical point, this is the shape, this surface little here represents solid plus liquid equilibrium, this is solid that side is this surface represents liquid this surface represents vapour. So, this is the surface plot, it does not look like a very nice surface. So, little bit complex it not a full three d thing in the sense, that only point on these surfaces are realisable by that material, this is what is called the PVT surface.

So if we have this surface we then pick an equation to this. So, p as a function of v and T and then we do something which were look at in very much detail in the earlier part, which is to use thermodynamic relations. I have given all these details in module three the third part of the nodes, may really do not need to go into great detail as for as this part goes it is not part of this basic course. But what it tells us basically is that all the relations that we wrote down are related to one of the in some differential form of the other. Until that differential form that we explained using this equation to get all the other values of all the other properties. So, that what we have this. So, in there are questions we will take questions, where there is the few more points that are need to make.

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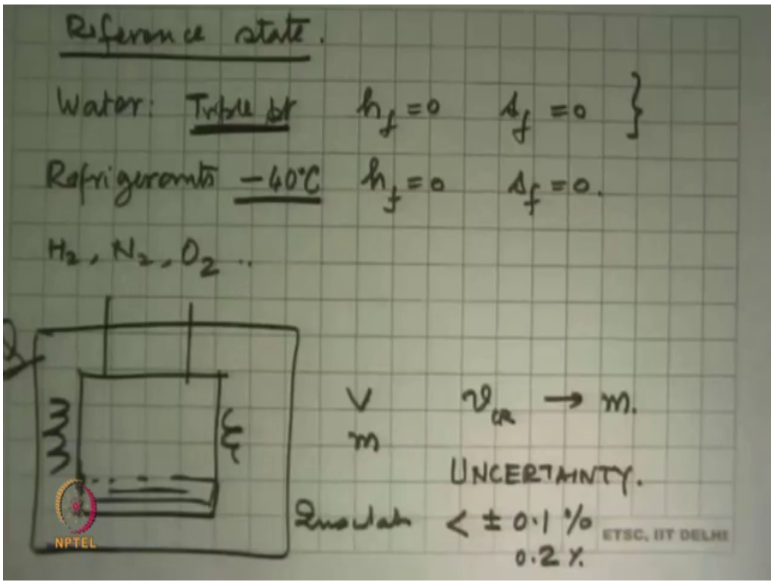

In making the properties I put in numbers we need a reference state and what have been done over the past many years in that we select the state. So, that values of u h s and all they are somewhat nice manageable numbers and it is not that all of the numbers are 10000 15000 20000. So, at different materials have a different reference state for water we say that are in the triple point h f is equal to 0 s f is equal to 0.

For most refrigerants we say that instead of triple point there we say minus 40 degree Celsius h f is said to 0 s f is said to 0 and for cryogenic materials hydrogen nitrogen oxygen hey somewhere is in the three point we set it to 0 or for material like helium we can reference it to even 0 Kelvin. Thing is that long as we are dealing with differences of enthalpy or differences of entropy, this sets reference point does not matter, but we can go to compare something with water with say a refrigerant there that reference points of entropy are different, then we cannot make the same picture. And show that in the next lecture how that difference comes here. So, we will stop here and take questions now if the first question.

The question is s H is equal to C p t 2 minus T 1 is this that question valid for all processes are only for constant pressure processes; similarly for c v in the case of calculation of between energy volume. I will come to this tomorrow when we look at the properties of ideal gases then I will clarify this here is a questions why ok. Please tell us why it is called compress liquid? I have just mentioned that is called compress liquid because the pressure at which the water is in more of than the saturation pressure at that temperature. So, the set is compressed it will be compressed into a liquid phase that the reason.

Then there is another question why specific volume of liquid is decreasing as we are increasing the pressure ok. The question is why are these points going like this when we increase the pressure. Now if you look at it the other way by looking at density, when you take water and compress it its volume goes down it becomes denser. So, density increases and specific volume is one upon density. So, you can see there that when we increase the pressure the specific volume has increase now decreased. So, there density has increased that is the reason ok. If there is we are talking T versus v we are talking t versus v with the help of experimentation results here, but is it possible to conduct experiment critical pressure and temperature to get various properties ok.

So, we have question is how did we these people now these properties? So, what they did what they did took around vessel, we have equated it and they put a certain amount of and liquid in it. This vessel then had heaters around it and this whole system were then insulated and within this they were instruments. So, pressure and temperature, the volume of this vessel was known, the mass of fluid that we put into it was known and because measure pressure and temperature and that is how the experiment were done. So, once you want to create a critical state, what we now know is that is the volume is known.

We know what is the specific volume at the critical state and these two will tell us what is the mass that I should put in this to generate a critical state ok. So, would it use it said that done, the critical state at least the mathematically its look like a singularity, which it is. And at that point almost all the equation that are develop also stand in behaviour as differential equations. So, now, there is a believe that yes critical point is there, but to exactly get to back pressure and exactly that same temperature and say that it is at the critical state, even within the experiment (Refer Time: 15:32) is its very difficult.

But this is the way one would produce the critical state you know substance. Now having said that I add one more thing, since this was the experimental data every experimental data has something within which is called uncertainty. It arises from the basic idea that we just involved there is no such thing as exact measurement. So, pressure was not exactly measured, temperature was not exactly measured neither was mass neither was stilled volume, and we quantify how much was the what you may call the error the limits of error is do not is the uncertainty and all these experiments also it is in say specific enthalpy is less than plus minus like 0.1 to 0.2 percent.

Because extremely difficult to do such good quality experiments, and that is why we believe those numbers and that is why you and I use it in solving problems and professional engineers use that in doing all engineering. But inherently it is never exact ok, what is saturated liquid lines ok. Here question is what is saturated liquid line on this diagram and I will show T v diagram and tomorrow I will along to it and we will make t s diagrams, p h diagrams any combination of those diagrams everywhere we will get a locus of points which correspond to x equal to 0 or it is the saturated liquid, that line we joins all the points of x equal to 0 is called the saturated liquid line.

So, this line is the saturated liquid line, this is the saturated vapour line why does the critical state of a substance occur? This are the questions why there the substance exhibit a critical state top? And as I have mentioned this is two of all substances you take copper, you take zinc sodium whatever you have in my everywhere you will see these things, but the thing is that this thing happens because we are now increase the pressure to a point, where the difference between what is the vapour and what is the liquid has gradually decreased and disappear that you have the critical point is actually telling us. So, in instead of here below the critical pressure at any point there were the distinct thing which is called the liquid where the intermolecular spacing was something.

It become a vapour where the intermolecular spacing suddenly increased. This does not happens to get a point because if increase the pressure so, much that this in 90 that we saw has disappeared. It continuously shows a behaviour of one type only, where the intermolecular spacing is now fairly tight and very close and it does not show that because any ability to become a vapour by getting the molecules very far apart. So, by that is where this thing happens here. And of course, if pressures are more than the critical point pressure there is actually no hope.

Because now, we are compress it so much molecules are so, close to one another they have more chance to get away from which I was how solid liquid and vapour exists in equilibrium ok. So, is the question was, how is it that you can have a solid vapour liquid equilibrium where rather how do we get triple point ok. So, many word of say the question says here, we talk of triple point or denotable point when we talk about solid state.

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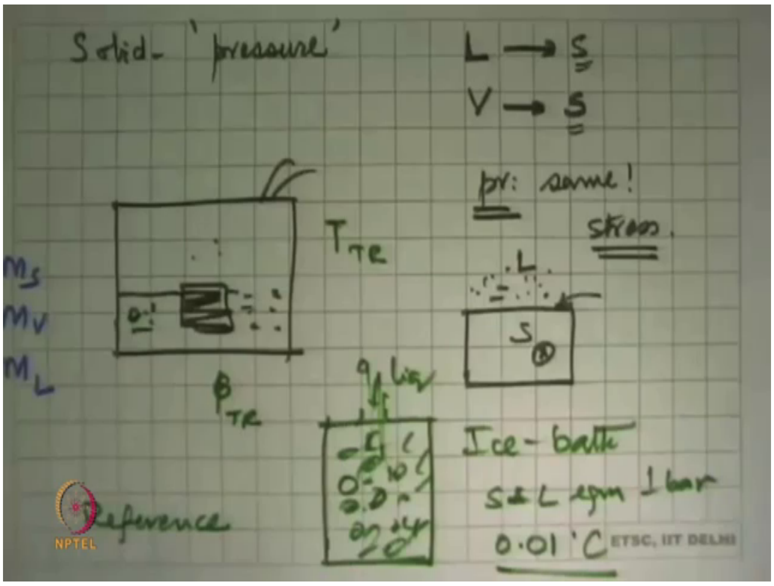

So, far I liberally use the term pressure ok. So, what it means is that either I have a liquid state with we are cooling and we get a solid and here liquid we know that if we the pressure everywhere will always be constant.

Because if the fluid seems to be the vapour the pressure everywhere is the same, the no way these substances start becoming a solid at that point where they have become a solid the pressure everywhere in the solid is going to be the same. That we know from our knowledge of solid mechanics and stress analysis that pressure is not defined for a solid.

So, the only thing that we can say then is that if the solid was made at the particular pressure, we will get that temperature the pressure inside will be go to stress inside which is the same pressure. If you further cool it may not be the same pressure because stresses will develop, and stresses will call internal average stresses to be different then what the hydrostatic pressure was.

In such a situation if we have a solid in contact with the liquid, the only thing that make sense is pressure at the surface or the interface of the solid and the liquid. So, this is solid this is liquid only here it make sense we cannot talk of pressure inside the solid we only talk a stresses. So, this is one question, the second thing the question is how can a solid liquid and vapour can existing equilibrium. The think of it like this like you have a vessel into it you put some solid say ice out of that there is water we evacuate this now you only have vapour in this. And if we allow it to cut equilibrium and we get that pressure here is you have if we cut the triple point pressure peak triple point.

Hope the pressure everywhere is that and the temperature everywhere is the triple point pressure, then all these three we will coexists together and we explore this in one very important way not in thermodynamics, but in all measurements of temperature explain need to answer. What we can do is and we can do this small experiment yourself take a thermos flask, first ice into it pack it as much you can and then pour a little bit of tap water in it, what will happen? The temperature of the water which was say at 25 30 degree Celsius we will go down.

Some of the ice will melt and you keep measuring the temperature by putting an instrument in this means, here temperature going down it start going to 3 degrees 2 degrees 1 degree. At that point what you do is, you drain out that water and if you have cold water or some drain out some of the water or keep that water there and put more ice in it and then again let it come to an equilibrium. Once you do that what you have finished is a solid plus liquid equilibrium at 1 bar pressure means temperature is 0.01 degree Celsius which is the triple point temperature of water.

So, this is the very easy you know very reliable way to generate a very well-known temperature in laboratory and this is an excellent reference temperature, where any instrument with the thermocouple or an alcidine will always require a temperature difference against which you measure a change in a property. Triple point with an this is what is called an ice bath. This is a simple and an extreme reliable way of generating 0.01degree Celsius. You have in equilibrium solid and liquid the vapour was at 1 bar, but that does not matter too much once you have close so, that something exist in equilibrium and equilibrium remember, there are three issues that come up here we have mass of the solid mass of the vapour mass of the liquid.

And as long as each one of these is in the triple point state, you can have any combination of these masses in this. We cannot just define drainage fraction, but now it is a three way thing to be define here the question is such could you explain importance of critical point in engineering field of application ok. Quickly as I do this analytic tomorrow again, what is the importance of critical point temperature?

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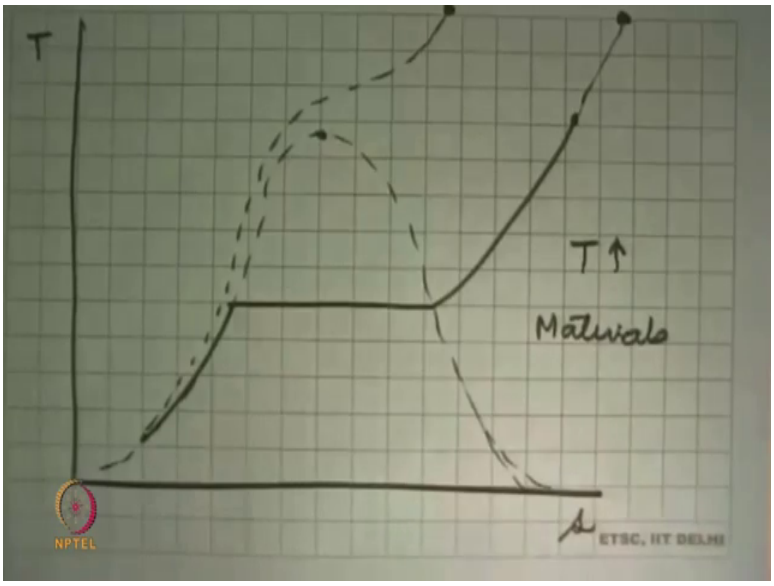

As I mentioned we are designing say there is a I am going to jump the down it, tomorrow I am going to show this. So, this is the temperature and a entropy diagram.

The saturation do not looks like this. If it designed something to generate superheated steam we have to design something that will heat the liquid part, then we design something that will do the evaporation where this is the big fractals taking place the fractals means a big volume change and then super heating part. So, the design of the boiler becomes three part design, but it is a super critical boiler this will go off like that which means I do not need to design three different things, only one thing. The reason why we design it is that, when we use steam at this condition versus a steam at this condition with thermodynamic efficiency of this our cycle built around this is going to be a much more means thermodynamics efficiency of this cycle.

So, that is the reason why traditionally pressures have gone up temperatures have gone up and we are coming to super critical pressures and temperatures, the limiting factor go, thermodynamics is at you can go as I as you want in temperature, but we do not have materials. So, we making a boiler that can with stand such high temperatures at high pressures for 20 30 years, that is the challenge. So, with that mean its conclude the session, tomorrow we will pick up look at some more of the property diagrams take some more examples and then we will go on to see what is the ideal gas behaviour.