Lecture – 21
Properties of a Pure Substance: Saturated states. Subcooled liquid. Superheated vapour

We start looking at the; we will take a we will do a experiments of thought experiment and try to see what happens.

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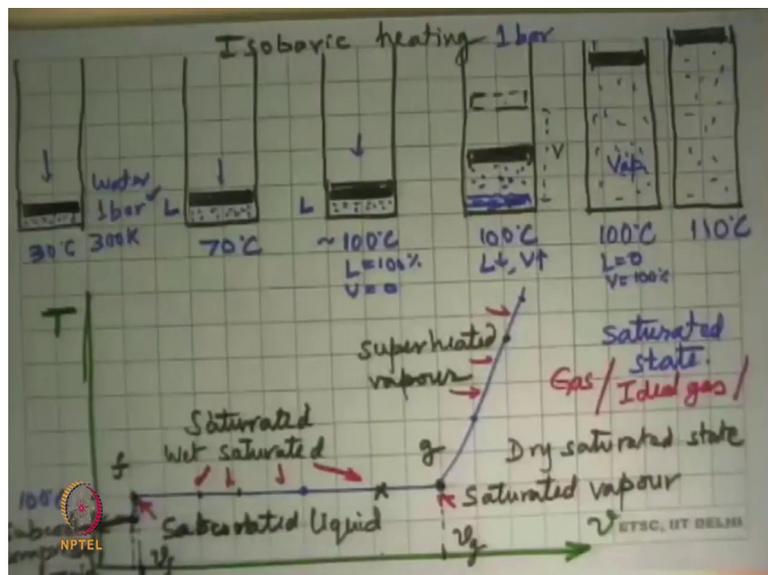
And what do I do is this. Then we look at a system that we have a cylinder piston arrangement and in that we have a substance which we will say is water and ambient conditions 1 bar say 300 into 10 k. And what we will do is we will figure out say now I will keep on heating it after a heating which sometimes we will stop. So, that there is equilibrium and then ask the question the pressure I am going to keep as one bar, what is the temperature that first question. The second question is what is the state of the substance or state of water inside this. So, what we are doing now is what we call isobaric heating.

In our first case we do isobaric heating and we know from experience nothing much is going to be happen. Water expands a little bit thermal expansivity of water is something we have learnt in school that comes in to play and because of that this water has

expanded a little bit and say it is reached say from 300 Kelvin say about 30 degree C. It reach say a temperature of 70 degree C. I am just putting a temperature, it could be 60, you can take 80, you can take 40 does not matter. But this thing could have happen the same 30 to 40 to 60 70 80; the liquid is still there. So, this was liquid, this is also liquid and its volume increase, but increase very very slightly.

We continue this heating and come to a point, we get to this point where this is still there and this is now close to say about 100 degree Celsius. Again we have only liquid over here and the pressure everywhere is still 1 bar; 1 bar is there everywhere ok. So, let us see what this states will look like on a plot. So, we make a plot where we have two axis there; x axis we will plot the specific volume on inverse of density and this side we will plot the temperature. And what we will see as these three points in that initially say it was here. The volume change was very small. So, the graph will not go like this, but it will go pretty much steep up like that and so, we get a series of states like that.

So, here is the point that we reached at 1 bar and all throughout this process we have the liquid. If at any state here say, take this case instead of heating we cool it; the liquid will contract a little bit because thermal expansion the opposite is happening and it will come back to these states and finally, come back to this state. Now what happens after we heated beyond 100 degree Celsius? What one sees is that the piston suddenly begins to move and move significantly.

So, it has come up there and here what has happened now? This amount of liquid that was there roughly that same liquid is there and now here there is vapour, the temperature same, what it mean? We get the heat transferred to the system. It converted some of the liquid into vapour phase, liquid is at 100 degree Celsius, vapour is at 100 degree Celsius. This is at 1 bar, this is at 1 bar; the specific volume of the liquid is this small the specific volume of this is much larger.

So, what we will do on this diagram, we say I just plot the total volume of this. So, when mass is the same volume has increased. So, specific volume meter cube per kg, that will increase and increase a lot without any change in temperature. So, this state will now start moving along the 100 degree Celsius line and say come over here. Then we do more heating and what we see that the piston goes up further. So, it comes to another point here, the liquid amount has now decreased a little bit; the rest of it is now vapour. The

liquid is at 100 degree Celsius vapour is at 100 degree Celsius specific volume has increased; pressure the temperature is the same. So, it will be in this state that is now here, we will show it by a point over there.

And then we continue heating this. We reach a point where the piston has gone up over there, pressure is still 1 bar and in this all we have now is a vapour, but the temperature is still 100 degree Celsius. So, this state we can make a plot and say this thing comes over here which means that at this point liquid is 0 and vapour is complete 100 percent. In all these cases, it was only liquid 100 percent, vapour 0. In this case as we kept heating little bit of as the piston kept rising more and more of the liquid went into vapour phase. So, liquid amount kept coming down, vapour amount kept increasing; the total mass of the system is still constant.

Now we come to the next state. We further heated the piston goes up, the vapour occupies all these, but now temperature has become say 110 degree Celsius. So, now, from this point to this point adding of heat started increasing the temperature of the system. Up to this point heating was increasing the temperature, but in this region heating of the substance was not changing its temperature, but changing its phase. So, this point would then show that temperature has increased, volume has also increased. So, it will go in this way and this way and we can get a point there and if you continue heating, this points will keep go increasing.

So, this is some example I have taken of water, but one can do a same thing with practically any substance. You can say take nitrogen at 77 Kelvin or say nitrogen at 1 bar pressure starting from 70 Kelvin. It will do the same thing take due time take a particular pressure and start from say 10 degree Celsius and start heating it will do the same thing. So, all substances under certain pressure and temperature conditions will have this behavior. In a minute we will see instead of 1 bar if I do it as point 1 bar, what will happen? If I do it at 10 bar, what will happen and 100 bar, what will happen? We will see those things.

So, now that we got all these states here what one can do is to join them by a line. So, you get one line there; a horizontal line over there and this line goes like that and this tells us a lot of things about the behavior of the such things. The most important thing is

that from this point to this point under these conditions what we saw here were the pressure was one bar temperature was 100 degree Celsius throughout.

Specific volume was changing, pressure and temperature neither of them were changing. So, this point where isobaric heating causes phase change to take place or isobaric cooling causes phase change to take place. These states are known as saturated saturation saturated states. These are very important concept. We will keep using it again and again and it does not have to be at 1 bar or for water. We have examples we get lot of substances including water at different pressures, it will have something like this.

Then we have these two points: this point and this point. At this point isobaric heating causes increase in temperature, at this point isobaric cooling causes decrease in temperature, at this point isobaric cooling no change in temperature; isobaric heating no change in temperature. So, what happens is that, if you are heating it increases the temperature. If you are cooling, it does not decrease the temperature.

Here if you cool, it decreases the temperature and if you heat, the temperature does not change. This is quite different from point like this. If you heat it, temperature goes up; you cool it, temperature goes down. Same thing here when you heat it, temperature goes up; you cool it, temperature comes down. These two points do not behave like that.

So, this is the point where you have vapour in this where heating makes it temperature go up else cooling makes the temperature remain same, but causes phase change. This is called a saturated vapour or sometimes dry saturated state that is one and this state with a substance is called this is a saturated liquid. So, saturated liquid means isobaric heating will cause phase change, saturated vapour means isobaric cooling will cause phase change. So, we have now two limits that have come up and then we have all states in between here where the pressure and temperature were both same specific volume kept increasing, all of these are saturated states or we may call it wet saturated or just plain saturated state.

And here all these states, this substance is said to be here superheated vapour and these states this is called either a subcooled liquid or a compressed liquid. So, several important things have come out from this small discussion. These are all subcooled liquid or compressed liquid states. This point in the saturated liquid state, this point the

saturated vapour state in between all these are wet saturated states and this points all these are superheated vapors.

Now let us take this problem further and say if keep heating, it what will happen? So, what this picture tells you that this keep on going up this way, specific volume will keep increasing, temperature will keep increasing, the super the vapour becomes more and more superheated until finally, we say it is starting to behave like a gas. When you heat it even more, it will start to behave as an ideal gas and further on either of two things can happen, but continue hypothesis may break down or the substance may begin to dissociate O 2 can break into O and O atoms.

So, we will not go to that part, but that is what will happen; if this heating work are continue for a long time. So, we are introduced five very important concepts; subcooled or a compressed liquid, superheated vapour, wet saturated state. In the wet saturated state as you can see from here, this whole state is called wet saturated, but the top part was saturated vapour and the lower part where the liquid was that liquid was saturated liquid. So, actually this is a mixture of this state plus this state. It is no new state as such.

I will come back to the question; we are just about to come there ok. So, this has happened here.

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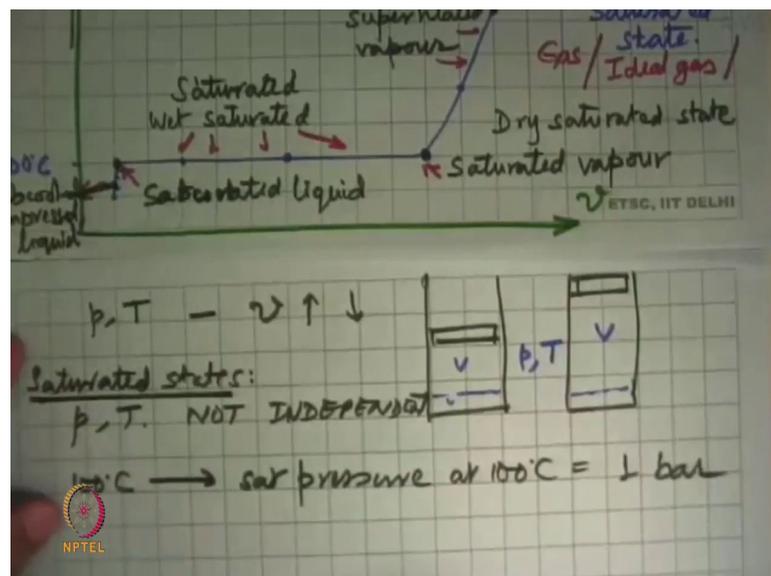
And now what happens is in the saturated state, the sub state has an interesting behavior and what we saw was that we heating pressure and temperature were the same, but specific volume keep kept increasing or decreasing whichever way you are heating or cooling it which means that if I say that this substance, I have two things two containers.

One is got this much volume, the other has this much volume and this has this much liquid and this much vapour and this has this much liquid and this much vapour and both are at the same pressure and temperature p and T and. So, if I say I know the pressure and temperature here, tell me what is the specific volume, we now have a problem because of the same pressure and temperature this specific volume is also possible, this specific volume is also possible.

So, what is telling us is that p and T are just not enough by themselves to tell us everything about the system and what we get is that in saturated states pressure and temperature are not independent of each other. There is a one to one correlation between pressure and temperature, but that is only the saturated state; that means, if you tell if you say what is the temperature say 100 degree Celsius. Then we can look up data that is already there and if the saturation pressure at 100 degree C is 1 bar. So, we have introducing a new concept that in a saturated state the pressure and temperature are known as the saturation pressure and saturation temperature.

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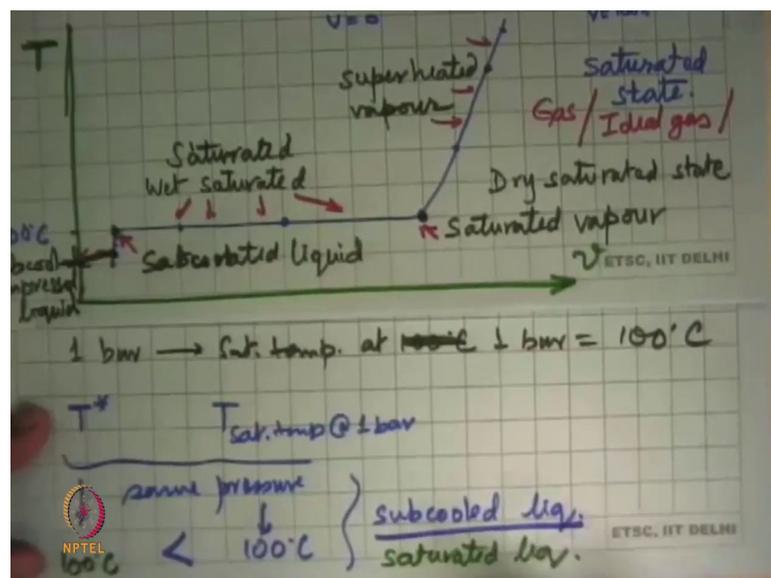
And conversely we can say that at 1 bar, what is the temperature at which phase change will start taking place. Therefore, that we say well tell me what is this saturation temperature at 100 degree C sorry at 1 bar and the answer is 100 degree Celsius.

So, by knowing the pressure we can know that corresponding temperature at which has saturated state can occur which means that it could be either saturated liquid, saturated vapour completely or any mass mixture of these two. So, this is what is happening. And now we say, but what happens in the other cases. So, for this one only needs to go to a table and these properties are well documented and say look for this material. This is the pressure, this the saturation temperature and the pressure in this case is 1 bar, in a minute we will see what happens every 10 bar point 1 bar or if the substance is different everything will fall in place.

What we will define now is this compared to the saturation properties what can I say about sub cooled and superheated states. So, what you are seeing is this that on this chart for a state which is over here, the temperature T or say, we will call it say that T star. This temperature and compare it with the saturation temperature at the same pressure. Saturation temperature at 1 bar, then this T star we are comparing in this case with 100 degree Celsius and we know from looking at it T star is less than 100 degree Celsius and that is the reason why this is called a subcooled state or subcooled liquid.

That means for the given pressure and temperature, the temperature is less than the saturation temperature at that pressure and very clearly it becomes that all the water we use and drink is temperature is 25, 30, 35 degree Celsius that would be here the pressure is 1 bar. The pressure saturation temperature at 1 bar is 100 degree Celsius and so, what we are dealing with everyday what we call water is actually subcooled liquid water. When water begins to boil we say that what is the temperature there and that time will say now our water is boiling, my T star is now 100 degree Celsius.

And that is why you keep seeing bubbles coming out because this temperature is not going up. You can make the gas stove or electric heater as big as you want, the temperature is not going to go up where the liquid will keep becoming vapour and vapour and (Refer Time: 20:45) everything will disappear. So, what we have produced at that point is a saturated state or a saturated liquid that saturated liquid becomes saturated vapour and vapour defused into the atmosphere that is what happens.

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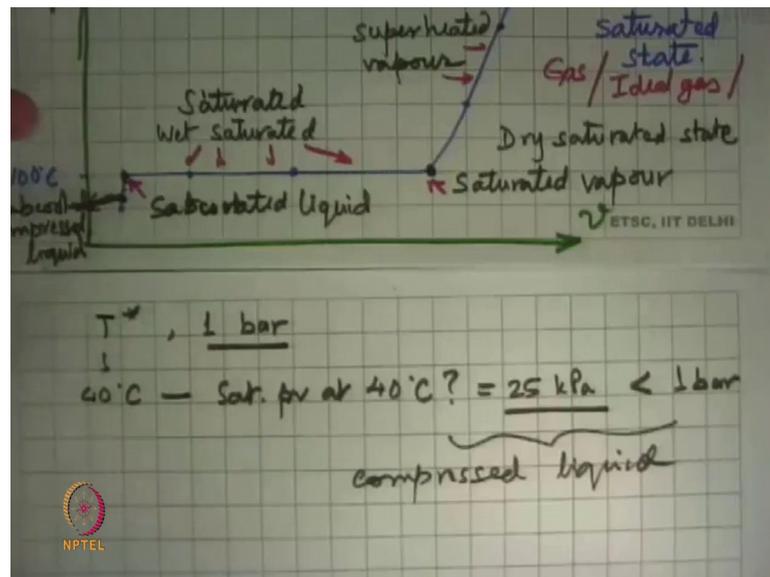
Now, we look at in another way and we say what is the pressure here to a saturation pressure at 40 degree Celsius here. So, we have T star and 1 bar and say T star were 40 degree Celsius. Then we say well what is the saturation pressure at 40 degree Celsius and you look up the table and just my guess is of the order of like about 25 or 20 25 kilo Pascal. I am just putting a number, there is of that order is not the exact. Now we compare this and this. This is less than the actual pressure at which it is. That means you have compressed it and that gives the name same state another name compressed liquid.

So, compressed liquid and subcooled liquid mean the same thing in one case, we are comparing the temperature with the saturation temperature at the pressure; in one case we are comparing temperature with saturation pressure in that temperature. So, that is the compressed liquid and we take that analogy into a further and we come to the super heated vapour state and what one sees here is that in all these cases the temperature is more than this temperature.

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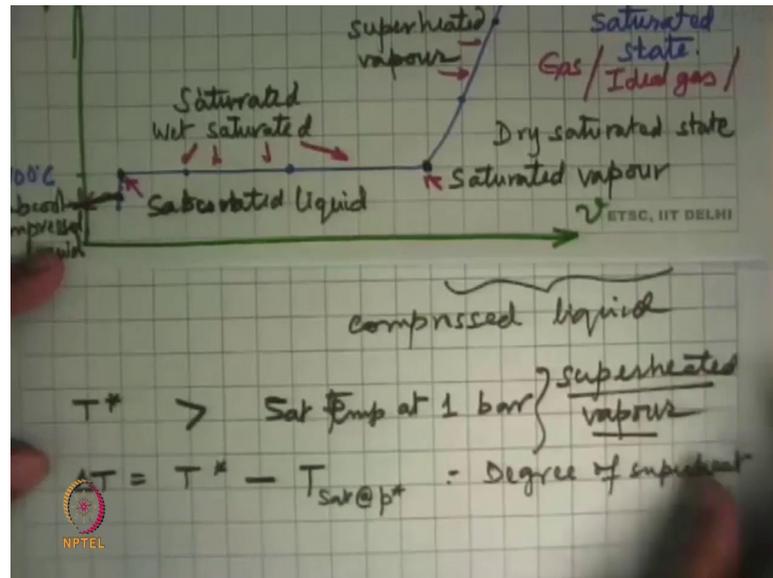
So, if the temperature T star at any state here is compared with the saturation temperature at that pressure at 1 bar. This temperature is more than the saturation temperature; this tells us that this is a superheated vapor.

So, a very simple thing that if I if someone says I have vapour at 1 bar and 200 degree Celsius tell me what is the state. When you (Refer Time: 23:21) look 1 bar the saturation temperature is 100 degree Celsius vapour that you have is 200 degree Celsius in the superheated state. So, the superheated vapour this is the way to find that out. We can define one more parameter here at the delta T which is T star minus the saturation temperature at that pressure and this is defined as degree of superheat.

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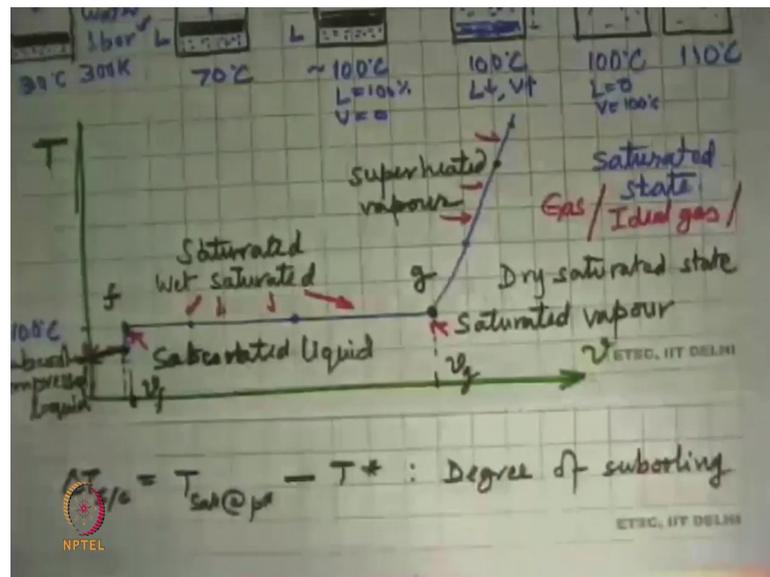
And similarly another delta T of subcooling, this is delta T superheated. If this is T saturation at T star minus T star, this is degree of subcooling. And in any saturated state the pressure and temperature will be the corresponding saturation properties of each other. So, we can say one more thing now that we are looked at specific volume. In this picture where we denote the saturated vapour phase by a subscript f and this by a subscript g fluid and gas. So, a specific volume at this point was this, specific volume here was this, specific volume here is this. This is called v g, this is v f.

Now these are fixed properties that once you say I have 100 degree Celsius what is the specific volume of the saturated liquid it is vf that is more in tables whereas, what is the specific volume of the saturated vapour in that case vg that is known in a tables. So, we can on that basis we know that all that states with a specific volume in between these two parameters.

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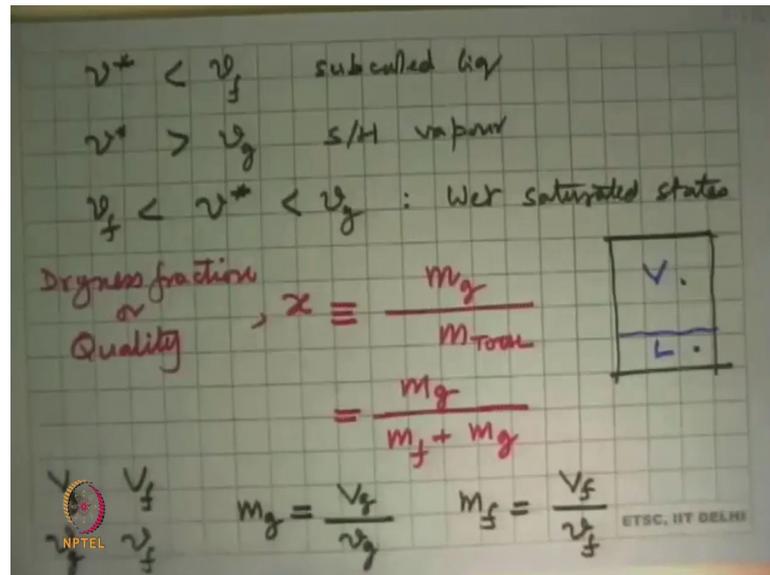
So, another way to decide whether it is a sub subcooled liquid or super heated liquid with that if the specific volume given is v star if v star is less than vf; that means, it is on this side this is subcooled liquid. If v star is greater than vg super heated vapour and if vf and vg are the limits within which v star lies, then these are all wet saturated states or simply we can even just say a wet state or a saturated state.

In this region super heated region, pressure and temperature are independent properties. In subcooled region again pressure and temperature are independent properties in this case they are not and this is the big change that has happened from what we have learned and we have to learn how to handle this because all your power cycles all refrigeration systems everywhere we encounter a saturated cycle. There very common ok.

So, let us now define one parameter by looking at any saturated state. So, behaviors of system, the closed one if you got certain amount of a liquid and certain amount of vapour and this is what is different between different saturated states with the proportion of these two. And so, we have to define something which tells us what is how much of liquid is there how much of vapour is there and for that we will define a new property which is called the dryness fraction or also known as quality.

The symbol is x it is defined as mass of the vapour divided by the total mass which is m g upon m f plus m g ok. So, this is the new definition that we are now putting in and let us see can we express it in terms of the specific gravities. And so, the small little exercise

that we can do by saying that the volume of the liquid is capital V g, volume of vapour sorry vapour is V g fluid is V f; its specific volume is v g, its specific volume is v f. And by definition we know that m g this is mass, this is volume of the gas divided by specific volume of the gas mf similarly is V f upon specific volume.

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So, remember that we are just looking at two things here. This is saturated liquid, saturated vapour. There in thermodynamic equilibrium specific to this thing and expert the fact that V is equal to V g plus V f and any substitute this into this we can get that the total volume if m g v g plus m f v f. And if it is by the definition of x which is m g upon m f plus m g, you can then put into this do little bit of simplification and what we get is that x is equal to 1 minus x times v f plus x times v g that is that tells us oh sorry this is v.

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I will defined v here v is V total upon m total. What it means is that if this is the whole system, then the dryness fraction of this is x and the specific volume of this is given by this expression. Over here x is equal to 0 it is a saturated liquid, over here x is equal to 1. So, dry saturated vapour, but taken together in this whole system they were dryness fraction which is in between those two numbers. So, we have x will always be between 0 and 1; x equal to 0 means saturated liquid, x equal to 1 means dry saturated vapour.

So, that is the independent property that we were looking at. We can get it from this and what it tells us is that now for saturated state T and p are not independent properties, but T and v is working because for if it is a saturated state no matter where it is, then we always be one unique point on this diagram. So, if that particular point happens to be here, you know that this is the specific volume this is the temperature and you can calculate x from here and we will see how to calculate how the other properties are. Similarly p and v, these are independent properties and once I do a similar type of a argument and we can show that h of the mixture is one minus x times h f plus x h g. The specific enthalpy can be calculated that way specific internal energy, you do exactly the same thing, specific entropy we do the same thing.

So, what we have we have come to point now where we say that I had independent properties called p T v and now we have added x u h s to that. And what we have said

that any two of this is applicable only for saturated state. So, the super heated vapour say x is equal to 1 x is not defined for states other than the saturated state.

So, if it is in any case for saturated state that is defined and these two are inter dependant, they are one and the same otherwise in general any two properties out of this will completely specify the state of the system. So, if I know u and h coding of the state is uniquely specified, we can go back to the property tables and get all the other values; pressure, temperature, specific volume specific control.

If p and s are given same thing, it is an independent. If the two independent properties the state is completely defined, we can calculate all the other properties If T and h are given, again the state is completely defined. We can get all the other properties the care that has to be taken as we have seen now.

If it is a saturated state p and T are not independent properties, they are one property and either of them with v or either of them with u or either of them with s or h, they will completely define the system or that x. So, they are the only thing that is not is p and T v and x is ok; x and h is ok, x and s is also ok. These all are independent properties, but then x is only for saturated state if you say that again ok.

So, now, we do the same experiment we did earlier, but we do it now instead of at 1 bar we say, we do the experiment at 10 bar and then we will do it of 100 bar 200 bar 300 bar, 500 bar portions what happens.

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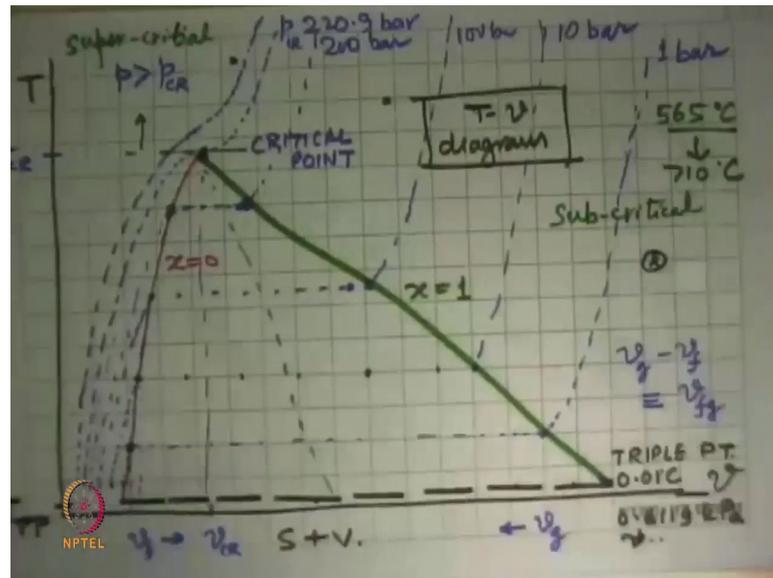
So, that is what we will make the plot now. This side is v and this side is T and the first chart that we got was at 1 bar. So, I will just reproduce that over here. This was 1 bar. Now what will happen if we do it 10 bar well you say that if I start form the same temperature 40 degree Celsius and increase the pressure to 10 bar, 200 bar or something like that those takes will go this way I am exaggerating a lot where in reality the change of volume of a liquid is very very small and you can see the plots whereas, particularly know difference between these densities just to illustrate the point I have pulled them out in reality, they are not that power of simple reason is cool.

We have learned liquid they are incompressible that is the manifestation. Now we heat this liquid and what we see is that this thing goes up here and the temperature at which the phase change begins is now increased. And the specific volume at which it is happening has also increased and it changes phase and it is somewhere here that it could becomes a completely a vapour phase and then from here it goes on this is 10 bar in between these we have all the saturated state. So, that is what 10 bar did v f moved become bigger v g decreased in quantity, but difference of these two v g minus v f this is often refer to as v f g.

And similarly for specific entropy for specific enthalpy and specific internal energy you can call this as specific volume of evaporation or specific enthalpy of evaporation; what we learned through school as latent heat. So, at what it tells us is that this steep that was

latent heat which was that much now become this much specific volume has also gone down. Now what happens if we increase the pressure further go to 100 bar; it comes over there when you have a series of state that come somewhere there and then you have the same behavior there.

So, the 10 bar 100 bar. Now let us go to 200 or some 200 bar200 bar. This will this will come up steeply come up over there and this will be here and from here this steep will go up there. So, this difference which specific volumes of vapour and (Refer Time: 40:47) keeps decreasing as the pressure increases 10 bar 100 bar 200 bar and then there is leap pressure for every substance at which this part becomes 0; that means, this curve which is coming like this as a point of inflection and continues like this.

That means, at this point the slope is zero this is what is called in the critical point. This is a unique property of every substance and so, all terminated that the critical point critical this temperature is called the T critical the corresponding pressure at which it happens is p critical the specific volume at which this happens is v critical specific enthalpy at which at that point is h critical entropy is s critical and like that this is unique point. And what it tells us is that if you do this isobaric heating at pressures for water, this is about 220.9 or 220.6 bar something like that and it even had pressures at 300 bar this line will go up and just continue like that; it will never come to a zero slope.

So, this is that all states where pressure is more than critical pressure and above this point temperature is more than critical temperature. And here we do not call it a compressed liquid or a super heated vapour we just call it a critical fluid or a dense fluid or a super critical fluid. Out stations core burning power plants that have been built now or have been built in the last 5 10 years in India they all had steam in the super critical state.

20 years back pressures were less than the critical pressure. Those were all sub critical units and the difference was that in a sub critical power plant, you got to design some part where the phase change takes place. In a super critical plant this issue is not there, but thermodynamic statue a very simple thing this has a very big implication on heat transfer and the mechanical design of the boiler itself.

We get completely different philosophies for this type of a boiler versus this type of a boiler. The first T locomotive that operated there pressures were like 3 bar, 4 bar somewhere here and over the last 100 120 years, this pressures have continuously gone

up temperatures have gone up where todays temperatures are of the order of 565 degree Celsius which is the super critical temperature and this is being pushed to 710 degree Celsius in power plants that we will be built maybe 7 8years from now.

So, from a thermodynamics is what is driving this whole thing because the efficiency goes cycle efficiency. So, this is the type of picture we get and now what we can do in this is that we join all these line points ok. These are all saturated liquid states at different pressures. So, we can say that these are all representing dryness fraction zero or this is a saturated liquid line and similarly we can join all these states on the other side like this. These are all the states where x is equal to 1 dry saturated vapour, saturated liquid in between this are all the wet states ok.

So, what it tells you that as we go from left to right, x goes from 0 to 1. So, in this one can draw a lines which are somewhat like this and somewhere these are constant dryness fraction lines x is equal to 0.6 is this much, x is equal to 0.7, x is equal to 0.3. They are like that. All the definitions that we had are valid for all these discussion. This is the saturated liquid left of this is a compressed liquid this side is super heated vapour in between we define the dryness fraction and the top this is the critical point.

So, upper limit of some sort have been set in the properties. As I am saying all of this is a huge exaggeration in the notes I have given some plots where all of this just goes becomes very very small. We can see that in books also that the effect of pressure on specific volume is very very small. So, that is as an approximation one can even say that water at 40 degree Xelsius and 1 bar have the same density as saturated liquid at 40 degree celsius. The next question comes up what happens below this? If I decrease the pressure to 0.1 bar 1 0 1 bar, will I get the same behavior? And the answer is that yes, you will get the same behavior until we reached a point which I will call here where these lines will end and this is what is called the triple point ok. So, the critical point on the top the lower limit of this is triple point.

And for water the triple point again is like a critical point is a unique value. Triple point for water is 0.01 degree Celsius triple point pressure is 0.6119 k P a and is under the specific volume of this. So, what the triple point line and all these states there all triple states triple point states which means that there will be solid plus liquid plus vapour existing on this line and if you go to temperature below the triple point temperature,

there is no possibility of a liquid you will only have solid plus vapour formation ok. So, this is one thing that comes out.

So, there is a limit at the bottom the triple point and the upper a critical point. If temperatures are between these two values and pressures are between the corresponding triple point and critical point pressures only those conditions, we can expect to see a wet saturated state. This is not easy that it will be always be there because at this temperature if we have this pressure; it is a super heated state.

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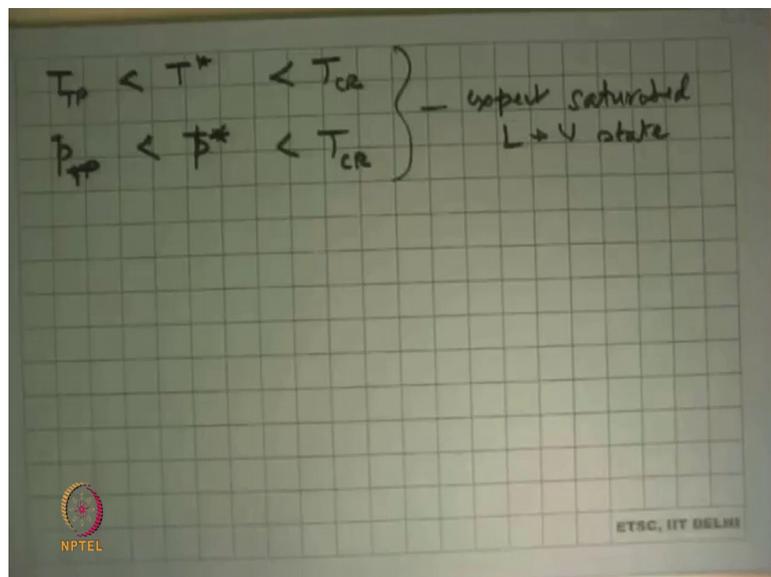
But if the pressure is between the so, if the given temperature is between T triple point and critical point and triple point pres[sure]- triple point pressure and the given pressure then we can expect a saturated state to be (Refer Time: 50:00) saturated liquid plus vapour state. At temperature below the triple point, we get saturated solid plus vapour phases. The other points where you get solid plus liquid phases so, that becomes the big picture of that what is called the T-V diagram and it gives us a ability to tell what will be the state of the substance once two independent properties are known. So, as you can locate that the state is say here we know it is wet saturated state, we can figure of where is the temperature what is the specific volume. And then calculate all the other properties also.

If the state happens to be here you know, this is Super heated state what is happening. If the state happens to be here, you know this is super critical fluid or a dense fluid you

know what that specific volume entropy (Refer Time: 51:08) So, this helps a very graphical way to very quickly visualize what states to expect for a given pair of properties provided specific volume is one of them ok. So, that is one thing that is come out.

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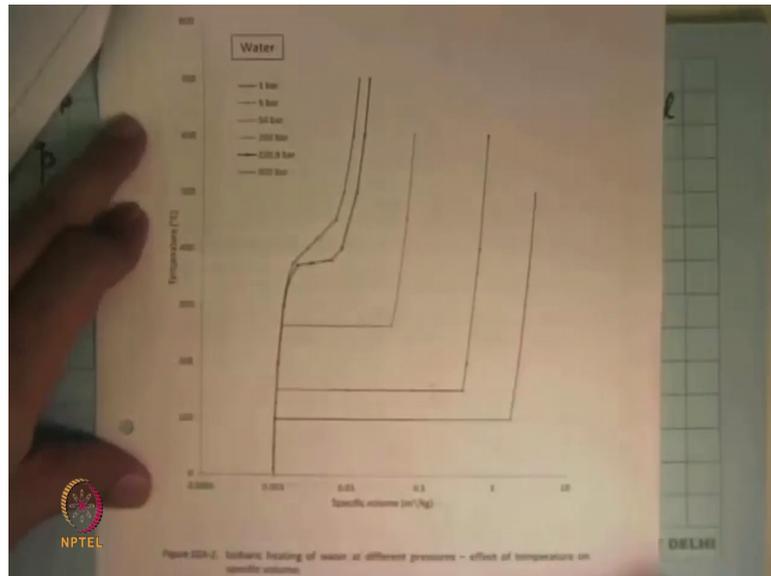
The real thing looks like this what I have put in the notes, this will be with you yeah. So, what I showed qualitatively? This is the actual numbers on this and the specific volume I have kept on the logarithmic scale whereas, temperature is a linear scale. And what you see what i just explain this is at 1 bar, this is at 5 bar, this is at 50 bar, then you have 220, this is a 220 bar and the top one 300 bar. And so, these are all the saturated vapour states these are all the saturated liquid states and what you see here is what I was just mentioning that the way I made the drawing qualitatively my free hand is quite unrealistic in what the actual numbers are.

We can see here all these points are practically on no manner that the effect of pressure although you have to 300 bar versus 1 bar this hardly any difference in the properties at low temperatures here. Only here that you start seeing some difference, but 100 degree Celsius the effect of pressure is very very little effect on the specific volume. That is why all these are collapsed on that these are all the saturated liquid forms and you could have again draw the complete thing, but you can drawn this point here get the saturated vapour line saturated liquid line and there is the critical point.

The next thing is that this is typical of all substances. You take oxygen, hydrogen, nitrogen, ammonia, sodium; any material they all behave like this. So, what we have learned is basic aspect which are very very generic and are applicable to every materials.