Engineering Thermodynamics

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Lecture - 23
Properties of a Pure Substance: Saturated states

Good afternoon, this is the second lecture on properties of a Pure Substance.

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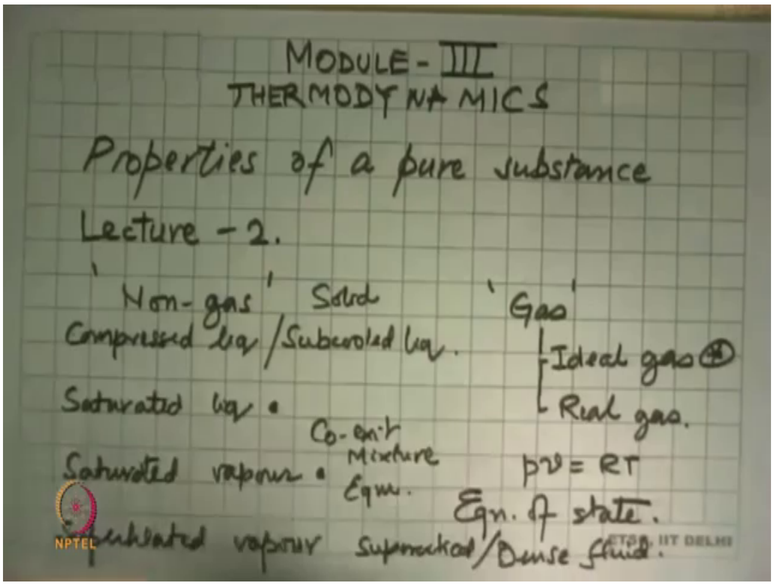

MODULE - III
THERMODYNAMICS
Properties of a pure substance
Lecture - 2.
'Non-gas' Solid
Compressed liq / Subcooled liq.
Saturated liq •
Saturated vapour • Co-exist Mixture Eqm.
Superheated vapour Supercritical / Dense fluid.
'Gas'
Ideal gas ⊕
Real gas.
$pv = RT$
Eqn. of state.

What we do today is revise what we learnt yesterday and then we will carry on to see different types of property charts that are there, how we can show states and what are some of the common processes that can be shown on those charts. After that we will go to the idea is to what happens, when use the temperatures or the degree of super heat increases a lot and that takes a saying through this discussion one ideal gas. So, we will reach that point where we will begin the discussion on ideal gas today.

That is what to revise what we learnt yesterday was that the substance can exist in what broadly we called two categories, ordinary called a not a gas or a non gas and a gas. And within gas we have the most idealized situation which we call the ideal gas and then a real gas that deviates from this thing this is the easiest thing to work with in thermo dynamics for the equation of state is very simple and that is the central idea of all this discussion on properties of a substance as to how can I get property all the properties for a given state, I have one two or there are minimum two independent properties are specified.

Then we went through a discussion about how a materials behaves and we took the example of water at ambient conditions and looked at what happens to it when you do isobaric heating. And then we came across that substance can exist in many stages we say that there is a compressed liquid, which can also be called as a sub cooled liquid, then we came across saturated liquid, saturated vapour and superheated vapour.

And then something which is beyond this, we call it is the supercritical fluid or the dense fluid. So, we learnt that substance can exist in so, many states beginning from ideal gas which is one asterisk, to real gas super-heated vapour saturated vapour, saturated liquid, compressed liquid and if you go below temperatures below that, then you may have the solid phase. Then we came across something which says that this and this the saturated liquid and saturated vapour can co-exist as a mixture as a phase mixture in equilibrium.

So, any mass fraction of liquid and vapour as if it is corresponding to the saturated state it will be there in equilibrium.

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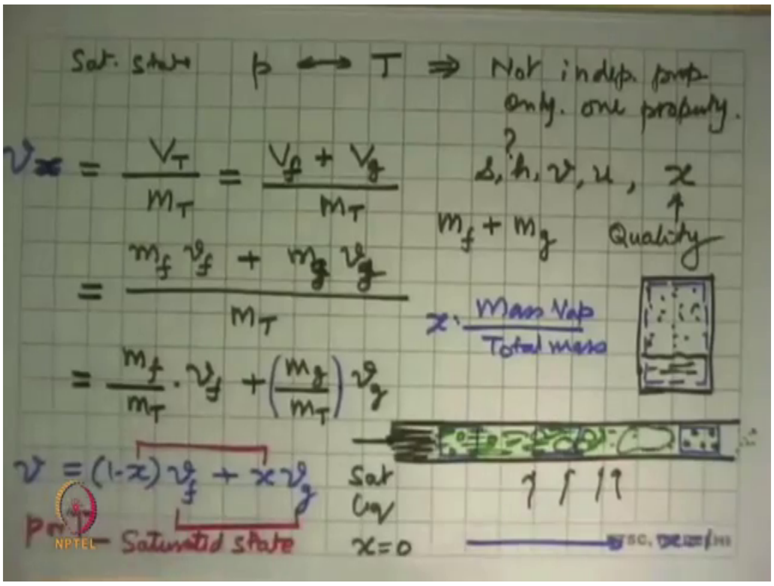

Sat. state $p \leftrightarrow T \Rightarrow$ Not indep. prop only. one property.

s, h, v, u, x

$m_f + m_g$

x ↑ Quality

$$v_x = \frac{V_T}{m_T} = \frac{V_f + V_g}{m_T}$$

$$= \frac{m_f v_f + m_g v_g}{m_T}$$

$$= \frac{m_f}{m_T} \cdot v_f + \left(\frac{m_g}{m_T}\right) v_g$$

$$x = \frac{\text{Mass Vap}}{\text{Total mass}}$$

$$v = (1-x) v_f + x v_g$$

Pr — Saturated state

Sat Liq $x=0$

Then we said that in saturated state pressure as a one to one correspondence with temperature and vice versa; which implies that these two are not independent properties, but basically only they are only one property. And to quickly specify the state, we need some more information. That information can come either from data on s or h or v or u let me introduce one more parameter that will complete this definition of the state, which we called x then dryness fraction or the quality.

And the way we define x is at x is equal to the mixture volume divided by the total mass of the substance in that. What do we mean by this we can call it is a V total upon m total meter cube per kg. We took one example yesterday and we said that to (Refer Time: 05:29) vessel there is so, much liquid sitting here, the upper space is filled with vapour then what is the dryness fraction. And for that we define the system boundary as this one and this is the dryness fraction we are not defining for this. Its not necessary that this is the only way in which a liquid and a vapour in a saturated state can existed 1 another.

Another example is a tube, which has been heated that the evaporator of a refrigerator or evaporator and air conditioner and at the entry of this this have been put saturated liquid dryness fraction is 0. And we ask that the liquid was completely occupying the space inside the tube, what happens to this liquid as it gets heated and it shows on the tube. Now as some heat is added it forms small vapour bubbles which are largely floating in saturated liquid. As more heat is given these bubbles become bigger and they still the liquid around this and even more heating takes place, this bubble start to occupy largest place in the tube and the liquid is now is smaller amounts in a very irregular fashion.

And then we could have a state when there is lots of vapour, small amounts of liquid as fine droplets and finally, only vapour. For physically this is what happens in the tube, but we can always pick up a state at that point and say what is the dryness fraction here or what is the dryness fraction here. So, you could have dispersion of vapour bubbles inside a large liquid or at the other extreme fine droplets moving around in vapour, this is also what happens in stream turbines where these operating in the wet state and is between its very irregular behaviour and we cannot really is write equations and solve of and say what is the answer.

But qualitatively we assign if I take a element here what is the dryness fraction. And we know that as this heating takes place x goes from 0 x equal to 1 and then is more heating takes place temperature raises and it is then a super-heated steam. So, these are decide ways in which one can encounter this thing, which is a mixture of a liquid vapour liquid and a vapour in a saturated state.

In all cases the definition relates to the definition as per the system is concerned this is the system here, this whole thing is a system over there and this is what we write and we can then write that this total volume is volume occupied by the liquid, then f plus volume occupied by the gas the vapour divided by the total mass; the total mass is mass of the vapour mass of the liquid plus mass of the vapour.

The volume itself we can write in terms of specific properties, this is m f into v f which is a specific volume of the vapour. So, that is the volume occupied by the vapour and similarly mass or sorry the liquid mass of the vapour multiplied by the specific volume of the vapour this is the volume occupied by the liquid sorry this is g vapour divided by the total mass.

And then we broke this we can break this up, that this is mass of the fluid which is a liquid divided by total mass multiplied by specific volume of the liquid plus mass of the vapour divided by mass total mass of the mixture multiplied by specific volume of the vapour. And here we define this property that this ratio mass of vapour divided by the total mass this is our dryness fraction sorry this is v, this this is v this is x, there is the specific volume of the mixture that is what we are trying to convey.

So, this is equal to this becomes 1 minus x times v f plus x v g. So, the specific volume of this mixture or this mixture or this mixture can be calculated by a relation where we know the dryness fraction we know specific volumes or the two faces. So, although this equation looks like we have three variables on the right side, we have x coming here and these two coming here. But since these corresponds to a saturated state, they are basically only one variable which means that either we know the pressure or we know the temperature and then from the property tables we can go and pick up v f and v g.

So, we are basically looking at only one variable here and one variable over there that is what we need we need two things and that is what we can get from here. We can recast this equation and right x is equal to as a function of specific volume.

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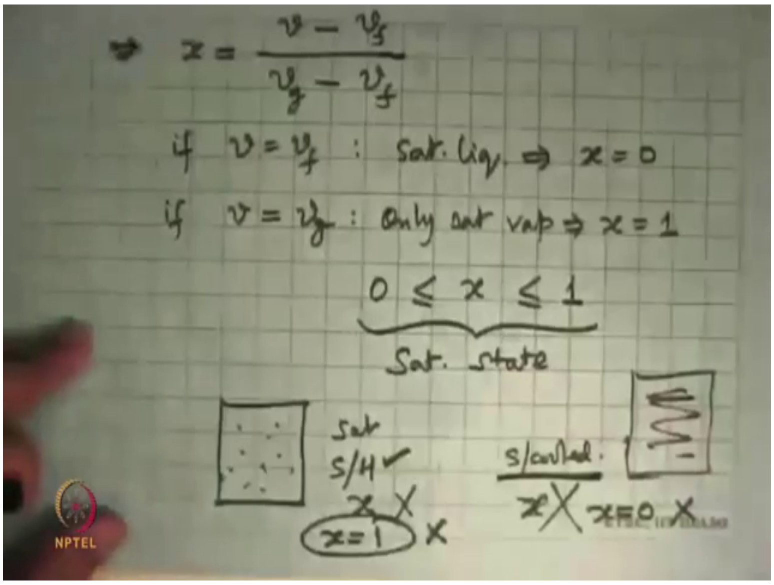

$$\Rightarrow x = \frac{v - v_f}{v_g - v_f}$$

if $v = v_f$: Sat. liq. $\Rightarrow x = 0$

if $v = v_g$: Only sat vap $\Rightarrow x = 1$

$$\underbrace{0 \leq x \leq 1}_{\text{Sat. state}}$$

And if we do that we get the answer like x is equal to v minus v g v f upon v g minus v f. That is how we can calculated and what it tells is that if v is equal to v f; that means, the entire volume is occupied by the saturated liquid state then x is equal to 0.

And if v is equal to v g; that means, there is only saturated vapour then x is equal to 1. And in all applications x we take a value between these two and this and all these that define only if we have a saturated state. So, it say that we have you know vessel or any system, we only have the liquid if it is saturated liquid its dryness fraction is 0, but if it is sub cooled liquid then this dryness fraction is not defined as so, sub cooled liquids even its not a saturated state. So, x is not defined.

And similarly the other extreme; that means, we have only vapour in this if it is saturated vapour then we have x is equal to 1, but if this is super-heated vapour then x is not defined. Sometimes somebody we will write x is equal to 1 even though it is a super-heated state that is wrong and same thing if sub cooled liquid is there ones I known there is only liquid there since only liquid is there, so, x is equal to 0.

That is incorrect because state sub cooled and for that dryness fraction is not defined. So, it need to take care of this what they had also mentioned is that we got this property relation for in terms of specific volume, but the same thing also applies for all the other properties. So, if you want to know that for this mixture, what is the specific enthalpy of this mixture?

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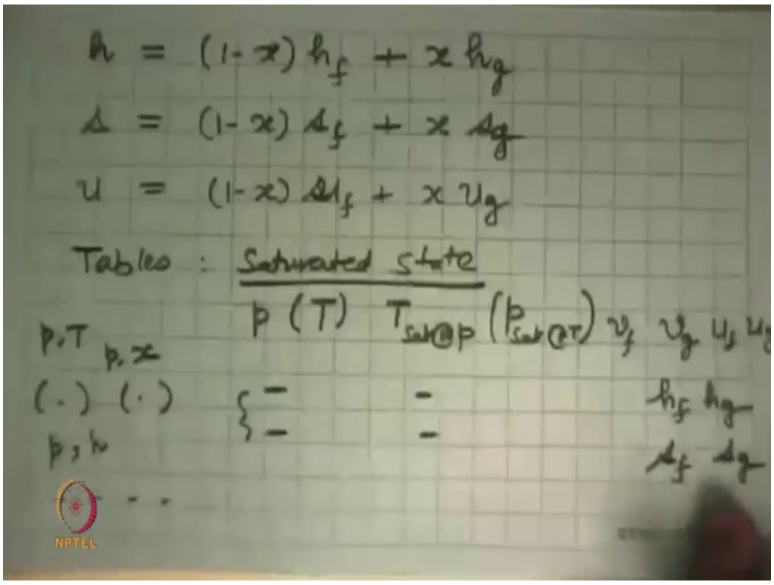

$h = (1-x)\, h_f + x\, h_g$

$s = (1-x)\, s_f + x\, s_g$

$u = (1-x)\, u_f + x\, u_g$

Tables : Saturated state

p (T) $T_{sat@p}$ $(p_{sat@T})$ v_f v_g u_f u_g

h_f h_g

s_f s_g

Then we can say that h is equal to 1 minus x times h f plus x times h g and we say what is the ask the question what the specific entropy of this system? Then s is equal to 1 minus x s f plus x as s g and the second thing we can use for u; u is equal to 1 minus x u f plus x u g yes. So, how do we get values of u f and u g? We discussed that a little bit yesterday and what we have this tables and then computer programs also to help us with that, given examples on the tables that table is having will be saturated state. And in this table the first column would could be either pressure or in some cases it could be the temperature.

If the pressure is given then after that follows a temperature column, which is the saturation temperature at this pressure T sat at this p. If the temperature is the first entry and the second column will be p sat at that temperature. So, we will have a entry here and entry here like this or these two entries and after that you will find that there is an entry for v f v g then u f u g h f h g s f and s g. So, all one needs to do is pick up where the pressure or temperature is, and you get all the saturation state properties coming over here that is of u g changes in between.

If these are discrete values all has to do interpolation alternately you can use either software packages or it can go online and their online things where you say, the gas input two independent properties. And when you input those two properties and they will give options, you may want to input pressure and temperature or pressure and dryness fraction or pressure and specification enthalpy, you pick that option put those two values it will tell you all the other properties that we are talking of over. So, everything comes out.

One can also write these equations and integrated with a program that then people do it when you are doing complete analysis of thermodynamics systems, you want to frequently call properties and you need that. So, you write a small subroutine and get it of it.

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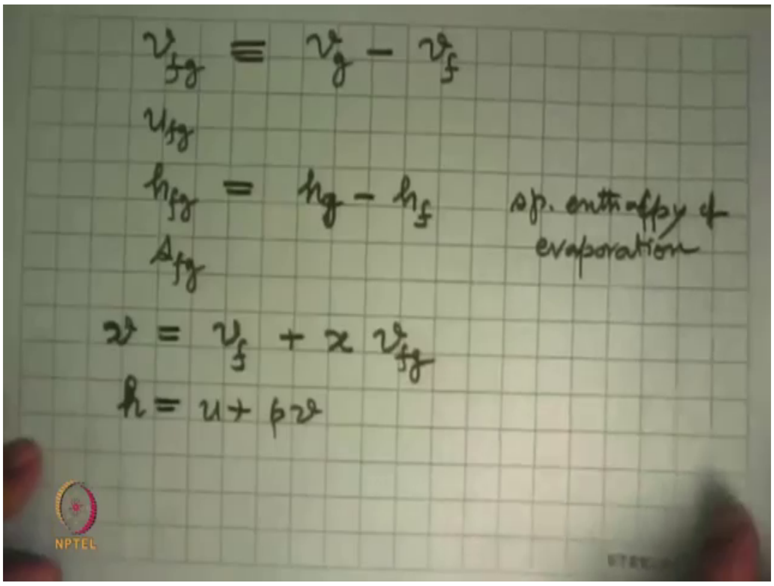

$v_{fg} = v_g - v_f$

u_{fg}

$h_{fg} = h_g - h_f$ sp. enthalpy of evaporation

s_{fg}

$v = v_f + x\, v_{fg}$

$h = u + pv$

Then one more definition that comes in and that has to do with the first that we define a new term v f g as v g minus v f; that means, the specific volume change during the phase change and similarly we can define u f g, h f g and s f g or just write down one of these this is h g minus h f and just got a specific enthalpy of evaporation. And its value at 1 bar or water what you are learnt in school usually have 540 calories for gram or be equivalent in joules per the gram.

So, if we want to express the value of x say v we can write that v f plus x, v f g write another way or writing the same equation or in the ordinary equation that we wrote where we defined dryness fraction in this way, this we can further write as v minus v f upon v f g in. In many cases the tables will give values of these also, but they have many cases where they may not give these values and the reason would be that if you want that we can just calculated from the values of h f f that what we get and in the tables this property relation also is always true h is equal to u plus p v the property relation we have already seen. So, in some cases even u may not be given only h would be given. So, the in many engineering application h is what is used very frequent.

So, either find that there is no properties for u given, no need to done it we can we know that h is given p and v are given from there we can calculate. So, let us now look at from property diagrams we also saw yesterday something that we plot it.

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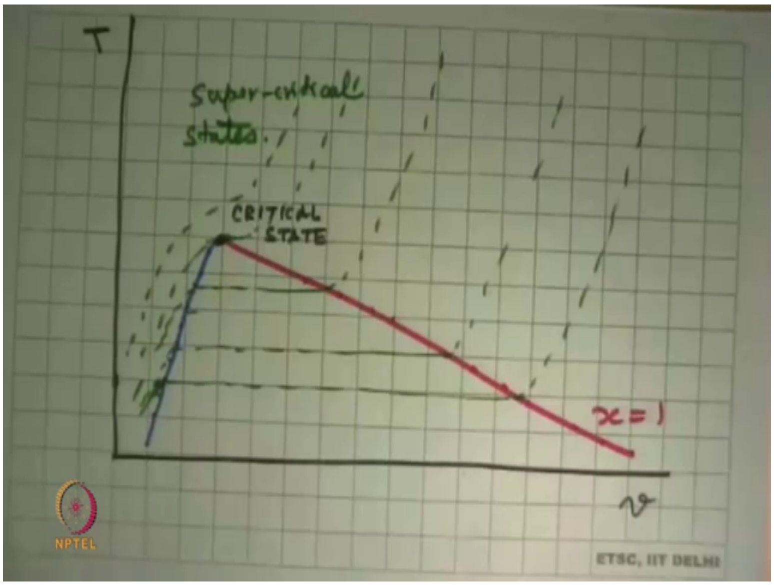

That how does this whole thing depend on the pressure at which this vapours are seen and we came across two different set of lines. You are making temperature on this axis and specific volume on this side and we came out saying that there is a line which is like this, there each point represents x equal to 0 this is the saturate liquid there. And then we said that there, the other part of this line which goes there where points on this there represents dry saturated vapour and we define one thing which is this point here, as a point where the differentiation between vapour and liquid phase disappears and all we are left it is one state this is called the critical state.

And all properties at the critical state for a given substance are unique, they have just listed out separately. And last time we looked at start that it is started with 1 bar what happens and we made pictures something like this. Then I have the pressure kept increasing we said that this goes up and we start seeing lines over there and similarly further increase in pressure this side is there and all the states over there. The critical state there is the point of interaction here and then it continues at pressures greater than the critical pressure we do not see any phase change this is what is called the super critical fluid.

And all states in this region that we have above the critical pressure and above the critical temperature, we have got super critical states. So, we looked at T v diagram and now would let us look at the T v diagram for some other substances ok.

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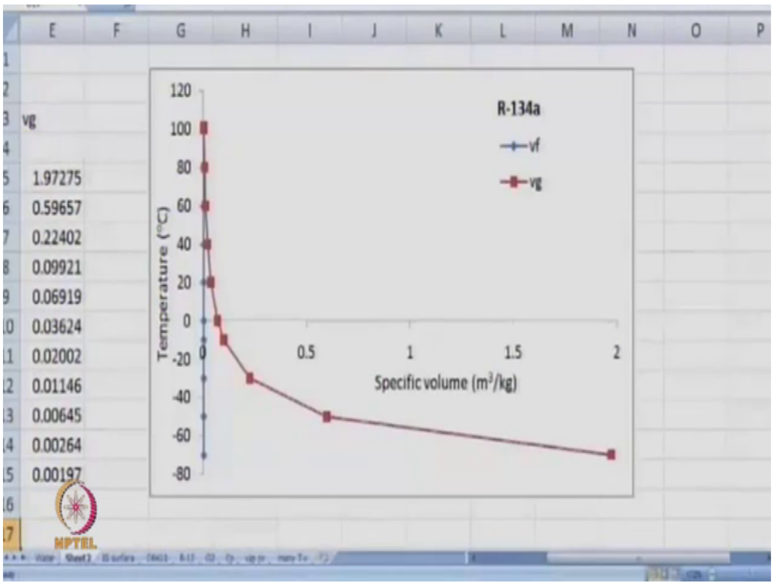

vg
1.97275
0.59657
0.22402
0.09921
0.06919
0.03624
0.02002
0.01146
0.00645
0.00264
0.00197

So, let us look at this picture first. I have plotted what I have explained by free hand over there, these are real numbers for a substance which is a refrigerant R 134 a this is a common refrigerant which you now see in refrigerators and some air conditioners. On the y axis is temperature in degree Celsius on the x axis is specific volume in meter cube per kg.

These are real numbers what you see is that these this line here going all the way up this is saturated liquid states and they are all pretty much like a vertical line, telling us that the specific volume change, but temperature is quite negligible. But when you go to the saturated vapour state we see this line coming here and you can see a very large change in the specific volume, something which was like 0.001 or 0.002 of that order has now become at least 100 times bigger its now 1 over here and goes up to 2.

So, the first thing to know is that in many of the cases there is a very lot change in specific volume that accompanies this exchange process. Water at ambient conditions when it changes states from liquid to vapour each specific volume increases the almost thousands times. So, the huge increase in volume that takes place.

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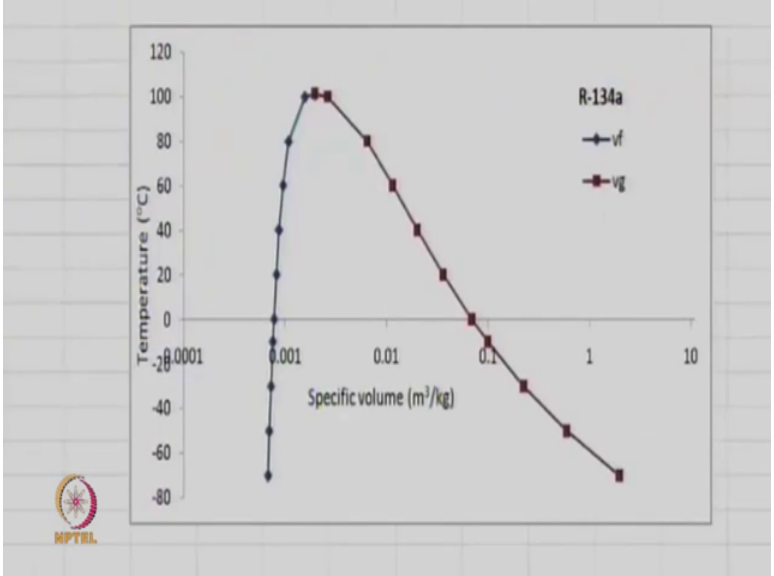

But then we plot this thing in a different scale we just change the y axis the x axis to a logarithmic scale, now you begin to see a for which a looks something like what I have been drawn. So, this side this is the critical point at the top, the parameters are the same temperature in degree Celsius specific volume in metre cube per kg and of this side we see that there is a very steep line which is the saturated liquid states and this side we have the saturated vapour states.

So, this begins to look like the picture that we have been made here. And yesterday we saw that on this side all those lines where the pressure dependencies so, weak that almost all states in the compressed liquid state they all are pretty much close to this line itself its not falling on the same line. So, that that is one thing we get to know that pressure does not have a very big depend effect on specific volume, and later on also has we will see does not have a very strong effect on specific enthalpy or specific internal energy also ok. So, this is a real behaviour and what we have been looking at and now let us see the same thing for different substances ok.

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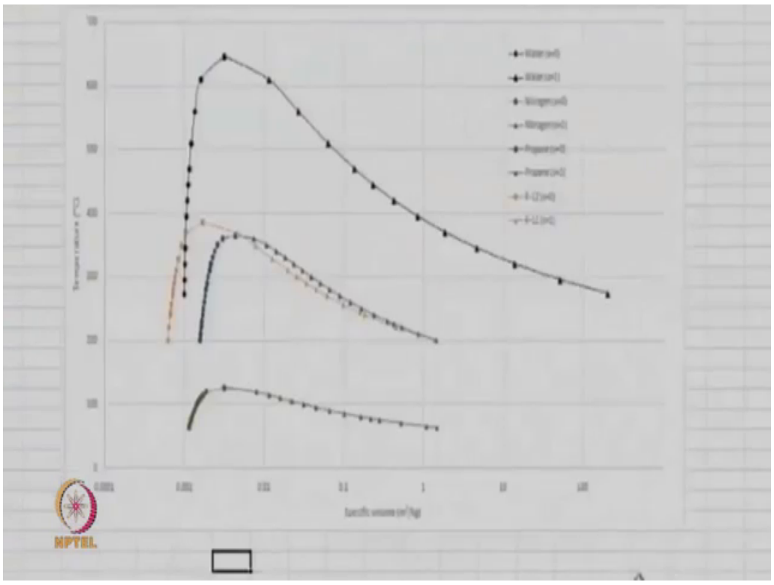

So, here is the picture. So, what I have try to do here is make a similar T v diagram for different substances. We can do that because temperature scale is absolute it is the same temperature scale everywhere and the specific volume is also an absolute scale. So, that is metre cube per kg here ok. There is a small change here I have written here temperature in degree Celsius this is not right this is temperature in Kelvin ok. So, we can make that change here.

This curve at the top is for water. The bottom most curve here this is for nitrogen. So, we can see that it is going to very very lower temperature there something like 126 Kelvin is the critical point, the critical temperature for nitrogen. And between here there are two things I have drawn one is propane which is this curve and this next to that is this curve which is for R 12c c l 2 f 2 which is the refrigerant.

And we can see the range over which these properties varies nitrogen goes everything below 126 Kelvin, oxygen will go below that hydrogen will be even smaller than that. So, it will all be like small dons over there in between we get lot of substances water comes here and all of them have the same behaviour a very weak dependence on pressure on the saturated liquid side and thoroughly strong dependence on the saturated vapour side, but they all have the same general thing that I have been described here. So, that is the important thing about this.

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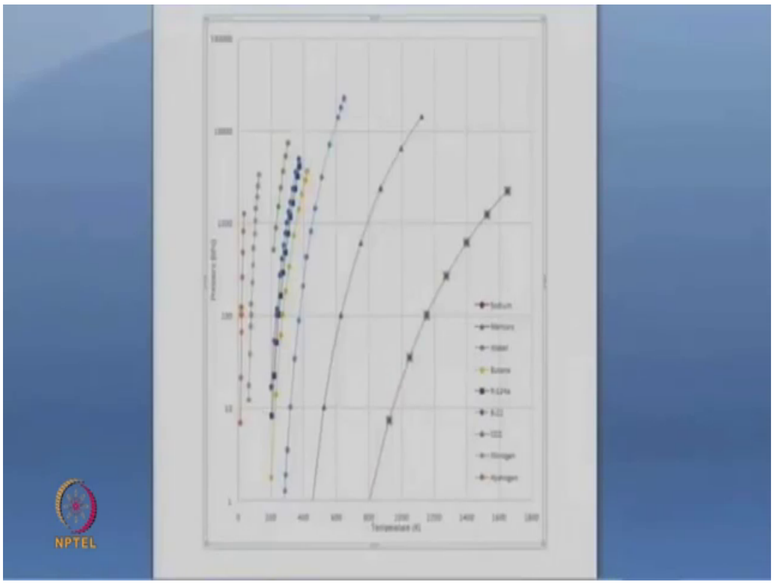

So, we made up separate plot last time where we put on the x axis the temperature and of the y axis we plotted the pressure and the lines that you see on this picture these are lines of saturated states. So, if this is the temperature, question is what is the saturated pressure at that point? If this is the temperature what is the saturation pressure here and all these lines are for different substances on the extreme left is hydrogen. So, we can see that the topmost point is the critical point for each of the substances.

So, hydrogen goes to very higher pressure, but a critical temperature is like you know 10 or 20 Kelvin somewhere about that when you have nitrogen which is there and goes up to about 126 Kelvin, then we start getting here like carbon dioxide and then a lot of curve which are very very similar to one another they are R 22 R 134 8 these are hydro fluoro carbons of different types and then this one which is butane.

The reason for bringing butane and all these substances together is that if you look at the thermodynamic properties of all these they are somewhat comparable and so, one would say that I could have use butane as a refrigerant or better stay substitute that hydrogen in butane or propane or ethane by chlorine or fluorine and start getting all this wonderful chemicals which were the refrigerants.

And of these wonderful chemicals that were responsible for ozone layer depletion and so, this refrigerants R 12 I have not put here, but R 22 R 22 is a little bit still used, but it is later to be banned and we are moving on to R 134 and other refrigerants where chlorine is much less or its not there at all. So, there will huge environmental problem with these materials and so, why they are very popular for a very long time starting about 20 years back, the global community decided that we do not want this they are too bad for the environment we should go for more eco-friendly refrigerants that is what you see happening today ACs and refrigerants.

Then we have this state here this line is for water and to tell you that its not just water and all the substances which behave like this, we have gone little bit further as and here these were the properties of mercury. We have see mercury in the lab which is the liquid what it means is that at that 1 bar pressure mercury has the saturation pressure there is a vapour pressure at that point and some mercury vapour would be getting into the atmosphere, but this is very very small.

But you can see that here now the temperatures are gone very high before we can even start thinking of mercury become your saturated liquid. So, one must thinks that 100 kilo Pascal which is here the saturation temperature of mercury is about 600 something Kelvin surely high temperature before mercury will begin to boil.

And on the right is sodium and here you can see that as 100 kPa, we have to sodium will melt at about something like 1150 Kelvin, surely high temperature when it melts and after that it will it can boil and change phase at constant pressure, but the pressure is increased it does the same thing.

So, all the substances are basically showing us the same thing that, you increase the pressure the saturation temperature increases or vice versa and it ends this behaviour ends at the critical point for all substances. So, we will now look at few more charts to tell you that this is not just the case with proper materials like this and one would say ask you know why are you bothered about sodium because that sodium is the main material which is used in the coolant in your first breeder reactors or a breeder reactors in the nuclear industry.

So, the first reactors that have been build, the core of the nuclear reactor is surrounded by liquid sodium or may be liquid sodium plus liquid potassium and we need to know the thermodynamic properties in the transport properties of those materials in order to work with that.

We will look at one more set of materials and see how their properties are and then we will move forward. So, here is the picture that is here is the plot may not look very clear right.

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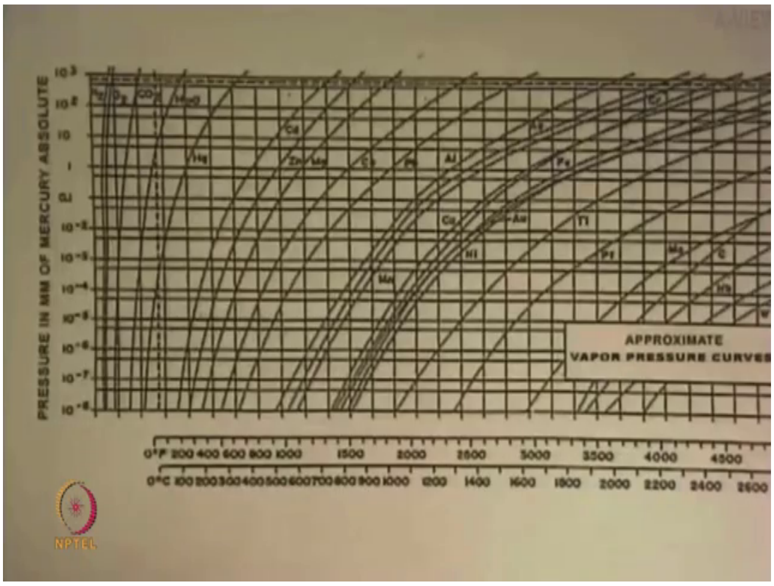

Its not very good, but what it has is that on the x axis its temperature in here in degree Celsius going from 0 degrees to 2800 degree Celsius. It can be higher temperatures and on the y axis its pressure, but now the units of this pressure are very very different what you see here is pressure in millimetres of mercury absolute. So, we know 760 millimeters of mercury is 100 kPa 1 bar. So, that will be something like this is 100. So, this is that dashed line here this is likely to be at atmospheric pressure.

So, here looking at pressures which go below that 1 millimetre of mercury this is 1 micro 1000 of a millimeter 1 micro meter of mercury 1 nanometer of mercury and even smaller than that. So, we are looking at very very low pressures which means that we are looking at very high degree low vacuum, and that is where you have seen all these materials have been plotted here nitrogen oxygen, carbon dioxide and water are at this extreme end followed them.

Mercury which is put at that and then we have all bunch of lines with similar shapes with different magnitude slope starting with cadmium, zinc, magnesium, calcium, led aluminium, copper, gold, iron, titanium, platinum, magnesium, tungsten, tantalum chromium. So, practically every material that we use in engineering is on this chart and it all behaves in exactly the same way.

So, the difference is that for the materials we get saturated states at very very low pressures and very very high pressures, but the behaviour is the same. So, one can ask you know why do I need to look at the vapour pressure curve or say in this case is tungsten w the recalls that earlier we had incandescent bulbs and the original bulb in the olden times the bulb was evacuated because of vacuum.

So, tungsten was heated to high temperature something like 2500 3000 Kelvin and if you saw this a bulb goes fused, it is because that solid tungsten at the temperature kept evaporating, went into the vapour phase the diameter of the wire kept going down it got more hot and at some point the bulb goes fused that is what this is the filament breaks.

So, there are many such cases and many manufacturing courses when we deal with large mass, but that was plasma deposition on a material you get very very different and very desirable properties, where we deal with materials like chromium and nickel and molybdenum and all that, we are looking at very high temperatures and would like to work with very low pressures create a plasma and you do plasma processing of materials, which is a very key technology today in the type of new materials and new processes that we have seen is around us using this.

So, these are that is where these properties become important, but many related to thermodynamics is that, they all behave exactly the same way that what we have learnt about says water that is started with for butanes and pentanes and all of that. So, that was the vapour pressure curve that we have looked at last time.