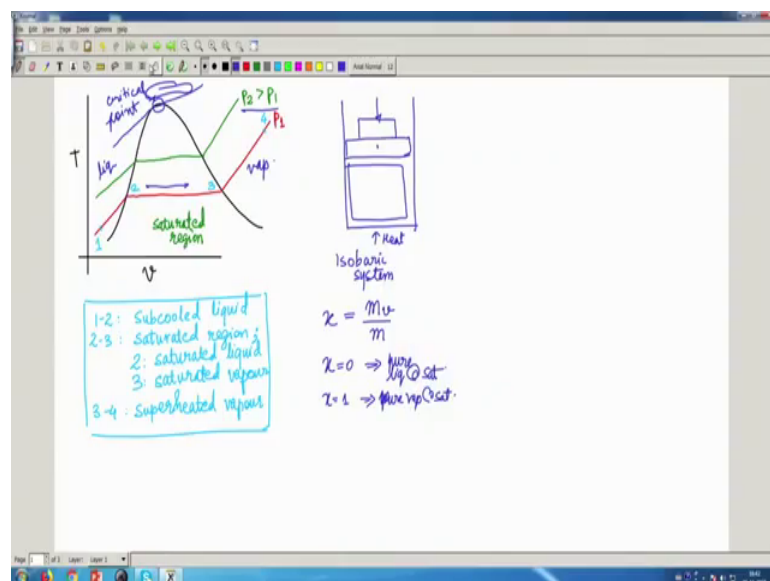


Concepts of Thermodynamics
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Lecture – 03
Properties of Pure Substances (Contd.)

Hello everyone, and welcome to this lecture in which we will continue our journey and consider the Properties of Pure Substances. In the last class we have we had considered.

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A hypothetical experiment in which we had a piston cylinder arrangement and we had loaded the piston with some fixed weight. So, the fixed weight plus the weight of the piston lead to some pressure acting on the inside volume. So, this is the case of a isobaric system. The pressure acting on the system was kept fixed and then we applied some amount of heat from the bottom; as a result of which when we went from liquid which is point 1; when we heated the liquid we went from point 1 to point 2 up end till all the liquid got so, up end till the first vapour started forming.

So, at point 2 vapour just starts to form the liquid starts to boil and we know once the liquid starts to boil it absorbs whatever heat you are supplying as a latent heat. So, temperature does not rise. So, given the fixed pressure despite the change in volume despite there being a change in property the temperature does not change. So, through

the region 2 to 3 the temperature remains fixed and then once all the liquid is converted to vapour there is now then again arise in the temperature.

So, inside the zone between the points 2 and 3 that zone is called as a saturated region. In that region we have a mixture of liquid and vapour where point 2 is purely liquid where point 3 is purely vapour. So, despite there being a difference in the volumes the temperature and pressure are fixed. So, we cannot independently vary temperature and pressure in this region. Outside that; yes, but inside this zone we cannot do an independent variations. So, we had seen that inside the region the quality x was a very important parameter.

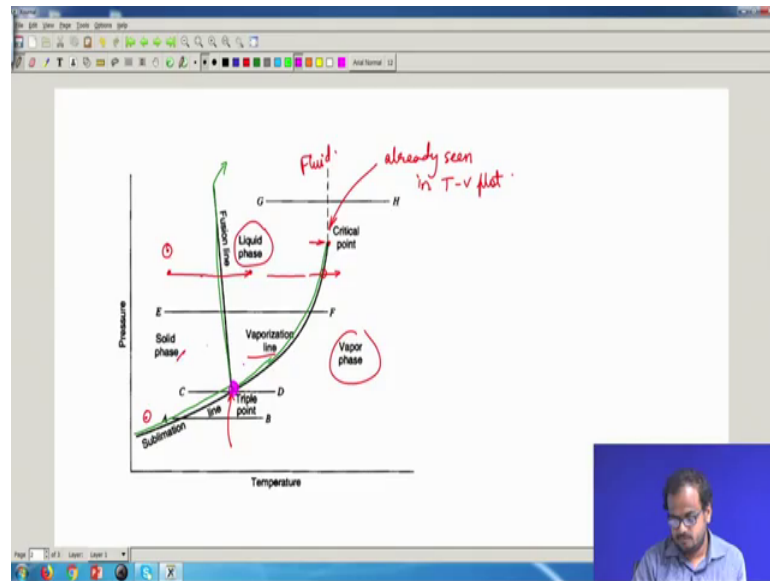
So, x was defined as the mass of vapour by total mass. So, x equal to 0 implied pure liquid at saturation x equal to 1 implies pure vapour at saturation. The temperature is known as the saturation temperature and the corresponding pressure that we have applied is called as a saturation pressure. So, corresponding to the saturation pressure we have the saturation temperature the meaning of saturation in this case refers to boiling because liquid is going from liquid state to vapour state. So, now, we had also seen that if you increase the pressure then the saturation temperature also increases is nothing, but stating the fact that as the pressure applied increases the temperature at which liquid boils increases.

So, for example, we have a pressure cooker we increase the pressure. So, thing start boiling at a higher temperature this is what we infer. So, now, similar to this liquid vapour transition we had seen that at a certain pressure there is no two face region there is a point of inflection over here and then the liquid simply goes to vapour then there is no two face zone. So, this point is called as the critical point. We had also noted at the critical point anything below the critical point only then liquid can exist. So, far pressure below the critical pressure only then there can be a liquid any pressure higher than the critical pressure there is no liquid it's just some continuum business going on where it liquid and vapour has just some phase there is no liquid what we identify as a liquid it's just fluid phase.

So, that is why in order to liquefy helium or in order to liquefy hydrogen and all this one has the tremendous challenge. One has to first increase the pressure to such an extent that you can actually go you have to reduce the pressure to such an extent that you can

actually liquefy something ok. And ordinary pressures are so large that you cannot liquefy helium and hydrogen no matter how much you work on it ok. Thus you have to go below that critical point in order for the liquid to exist ok. So, with these ideas let us see so this kind of diagram we can clearly identify the phases there is a liquid phase there is a vapour phase and in going from a liquid phase to vapour phase we have a two phase.

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Similar to this we can draw this kind of a phase diagram. So, this is a pressure versus temperature plot what we had drawn was a temperature versus volume plot where we had seen that the volume kept on increasing during the heating of the two phase region and the temperature was fixed. But we can obtain some more information if you look at the pressure temperature point we do not refer to the volume in this plot. So, in this phase diagram if we start of at a pressure and temperature over here and given a fixed pressure if you increase the temperature we go from a solid phase to a vapour phase and that process is known as sublimation.

Very famous example of sublimation that occurs at room temperature is that of camphor if you keep camphor in the open it's it said to sublime ok. So, if you keep on increasing the pressure suppose we work in this region we have a relatively higher pressure at a relatively higher pressure the molecules are acted upon by a larger force a larger tendency to compress them. The larger the tendency to compress molecules, the larger the tendency for them to remain as a solid or a liquid because; the pressure here was low.

So, at low pressure and low temperature you do have a solid, but at that low pressure the moment you start increasing the temperature the molecules have enough energy to quickly go into vapour state they do not transact into a liquid state.

However, when the pressure is large then instead of directly going into a vapour state the liquid goes in the solid first melts it undergoes a transition from solid to liquid and it crosses something called as a fusion line ok. So, it goes from solid to liquid. So, the molecules have enough energy because of the increased temperature I have increased the temperature by remaining by keeping the pressure constant. So, essentially the solid molecules have no larger amount of motion and thus they go into a liquid phase the larger pressure makes them not go into a gas phase directly.

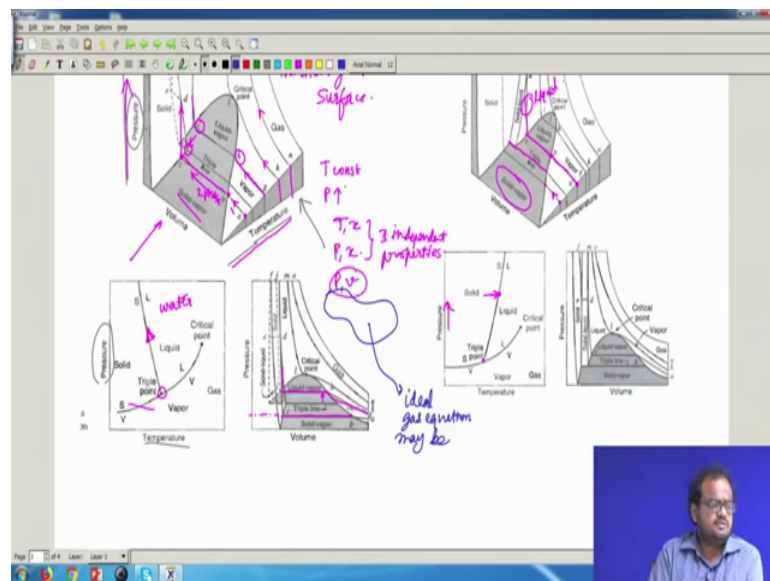
But now over here if I still keep heating it that is to say I keep increasing the temperature then suddenly at a point which is called as the vaporisation point it goes into a vapour stage ok. The volume axis is actually orthogonal to this page what you see here is a pressure temperature we will see in the next plot that the volume is orthogonal to this. And there is a distinct change in volume as we do the process ok. So, this point is called as a vaporization line.

So, this process is the standard process that we observe at atmospheric conditions for water via ice which we when we heat it transits into a liquid which becomes water which then transits into vapour at a certain pressure which is corresponding to this. And, as we increase the temperature there comes a point where there is no distinction between the liquid phase and the vapour phase this point we have already seen in the temperature volume diagram to be the critical point.

So, beyond that pressure there is no existence of a of a liquid gas interface it is simply a fluid it is simply a fluid interface. So, what happens at an intermediate pressure between this pressure where there was sublimation and the higher pressure where there was a gradual transition? There occurs a point where the solid the vapour and the liquid are in equilibrium. So, at this particular point we have an intersection of the three phases along this particular line for example, along that particular line we have an equilibrium of solid and vapour along this particular line we have an equilibrium of liquid and vapour along this particular line we have an equilibrium of solid and vapour.

But all these phases are intersecting at this particular point which I have marked as pink and that point is known as a triple point it is the pressure and temperature at which all the three phases can coexist. So, this is very important in various kinds of applications in physics. In typical thermo dynamics usages we will bother mostly about liquids and vapours because, in typical processing plants and all this that is what we encounter. However, in newer technologies such as adsorption and all this thing when does need to have some kind of information about the solid liquid and all this things also. But we will mostly focus on the liquid and vapour phases.

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Let us see how these plots look in three dimensions. So, what we have just seen was so to say a projection of the pressure and temperature. So, if I view this three dimensional surface from this particular side I will disregard the variations in volume and I will simply observe a pressure versus temperature plot this is what we have just seen above. So, if I start off at this point for example, which is in the vapour zone I keep reducing the I keep increasing the pressure.

So, if I move along with this particular line it simply means I am keeping the temperature to be fixed. So, along this line temperature is fixed because it is a line of constant T, it is parallel it is orthogonal to the temperature axis. So, it means along these lines you keep temperature constant. So, now if you keep the temperature constant and essentially increase the pressure the point because it is quantified by two properties see; yesterday

we have already seen that we need two independent properties to define the state. In this particular state the temperature is fixed. So, temperature becomes one property and in this region we can vary the pressure if the pressure is increased it starts moving along this particular thermodynamic surface this surface is called as a thermodynamic surface.

So, the moment we reach point b the vapour has reached the saturation point. Now we have already seen that now pressure and temperature cannot be independently varying and thus from point b to point c because the temperature is fixed the pressure is also fixed. Because b to c is two phase it is saturated so from b to c it is a straight line which is orthogonal to the pressure axis. So, this line has constant pressure it corresponds to this particular line if I look in the pressure versus volume plot. So, pressure versus volume plot is simply this thermodynamic surface viewed from the front so here the pressure remains constant.

Now as pressure keeps on increasing we suddenly transit from this solid vapour zone this two phase zone into a solid zone. All this is happening because we are working in a temperature zone which is below the triple point. And the moment we are below the triple point there is an equilibrium of solid and vapour this is not the case of liquid and vapour. So, thus we have vapour over here solid plus vapour over here and then solid over here this is what happens. The moment we go above the triple point for example, this particular line we have a transition of vapour to liquid plus vapour where in from point h to point i the pressure will now remain constant after which there will be a transition to liquid.

So, it corresponds to this particular plot ok. So, you have kept that in constant now you are increasing the pressure T constant P increasing. So, during the two phase zone the P does not change only the volume is changing. Thus pressure and temperature are locked in the two phase zone they cannot be independently varied only the volume varies. And thus the quality becomes the only parameter which can help us in this region. The independent property can be temperature and quality T and x or it can be P and x inside or it can be P and V also.

We have already seen how to calculate the specific volume by using the quality for that we just need to know the specific volume of liquid specific volume of the of the two phases rather this all these can be used. So, this was so this particular diagram is the

thermodynamic surface for a surface in which liquid expands on freezing that that is the case for water is a bit of an anomalous entity. So, liquid expands on freezing that is why this slope is negative. So, it means that as the pressure increases the temperature at which the solid liquid transition occurs decreases. But in typical other kinds of fluids other solvents like ethanol and all this things other refrigerants as the pressure increases the temperature at which the solid melts increases ok.

This is the only case where the reverse happens this is the case for water, as the pressure increases the temperature of melting of ice decreases. But for other fluids as the temperature, as the temperature increases or as the pressure increases the temperature of melting increases. So, one can similarly look in this particular diagram that below this triple point you have the solid vapour equilibrium.

So, if you have an isothermal process where you are increasing the pressure you go from vapour to solid plus vapour and then to solid where as if you go above the triple point ok. So, in this diagram; obviously, it is not a point it is a triple line because that pressure is always a line in this two phase zone. So, above the triple line there is vapour as the pressure is increasing it then transits into a two phase region. And then it goes into a vapour it then goes into a liquid zone.

So, this is the liquid zone ok. So, it is not very difficult to understand, but all you have to understand is whether you are operating temperature is below the triple point when you are starting or your operating temperature is above the triple point when it is starting. Below the triple point you do not have a liquid vapour or a liquid solid equilibrium all you have is the solid vapour equilibrium. Above the triple point you can have both the kinds of equilibrium occurring g which is solid liquid and liquid gas ok. All these things are much more clear if we do more examples which will be done in the later classes. So, let us move on something which we may require later on which is Ideal gas relationships.

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ideal gas relationship:

$$PV = n \bar{R} T$$

\bar{R} : universal gas constant
 $8.314 \frac{\text{kJ}}{\text{kmol K}}$

$$n = \frac{w}{M}$$

$$PV = \frac{w}{M} \bar{R} T$$

$$P \frac{V}{w} = \frac{\bar{R}}{M} T \Rightarrow Pv = RT$$

$v = \text{specific volume} = \frac{\text{Vol(Total)}}{\text{mass(Total)}} = \frac{V}{w}$

$R = \frac{\bar{R}}{M}$

$Pv = Z RT$

$Z = 1 \Rightarrow \text{Gas is ideal.}$

$Z < 1, > 1$

van der Waals eq
 virial coefficients

low pressure, high temp } ideal gas.

Compressibility

So, we have we know from our preliminary knowledge that we have picked up in class 11 and all these things; that $P V$ is equal to $n R T$. So, let us call it as R bar it is a molar thing. So, any molar quantity we represent as R bar where R bar is now the universal gas constant. This is 8.314 kilo joule per kilo mole Kelvin. So, given pressure and volume and if you know the number of moles you can then ascertain what the temperature is.

So, given two quantities we can find out the other quantity. So, we can write it in terms of specific quantities that we have learnt. Because we know that the number of moles is the weight taken out the gas or the substance by it is molecular way. So, then we have pressure into volume is equal to weight taken by molecular way into R bar into T . We take the weight taken to the left hand side P into volume by the weight taken is equal to R bar by capital m times T . Now we have already seen that the specific volume is nothing, but the total volume of the total mass.

In this case if you use the symbols that is V by w . And therefore, this implies that P into small v the specific volume is equal to R into T ; where R is now the gas specific universal constant which is the universal gas constant by the molecular weight of the gas ok. And thus we have the relationship $P V$ is equal to $R T$ now this holds true for ideal gases when is the gas ideal. The gas is ideal when see what are the basis what was the basis of the assumption behind the ideal gas. When the pressure is very large and the temperature is very low the molecules have a very strong attraction amongst them when

the pressure keeps on increasing we have already seen that the molecules tend to collide more and that they tend to form a liquid more.

So, when the pressures are small the molecules are almost not interacting with each other there are less collisions going on across molecules. So, each molecule is encountering some other molecule, but they do not have a tendency to coalesce together. And when the temperature is large; when they have large amount of energy so that they are not bogged on by any potential. See every molecule are some potential which tries to absorb molecules or so on.

So, if the temperature is very large and the pressure is very low the molecules are behaving like ideal particles and they are colliding around without really interacting with other molecules they are just colliding with the wall that gives us the notion of a pressure. So, for low pressure and high temperature we go into the zone where the gas behaves like an ideal gas. But a more fundamental measure of the deviation from ideality may be defined by means of the compressibility defined as this.

So, when z equal to 1 the gas is said to be ideal if z is less than 1 or greater than 1 then the gas shows deviations from the ideal gas behaviour. So, this kind of things are then accounted for so we have read this in the past that there was the Van der Waals correction which is the excluded volume and the additional pressure and all these things, but I mean those are not a part of this course. But one should have an idea like these kind of corrections do exist and there are virial coefficients which can account for the deviation from the ideal gas equation.

But in this course when we will do extended cycles and all we will make use of the ideal gas because usually turbines and all are operating at a very high temperature where this ideal gas may be valid. So, in this kind of diagrams so pressure versus volume so in this regions these are sort of the zones where the ideal gas equation may be assumed to be valid without incurring a very strong error on the work done all this things.

See ideal gas is a very strong idealisation there will never be an ideal gas. But as long as it gives you less errors you can make do with it because it simplifies life it gives you a very good relationship a very clean relationship to find out one of the independent properties if, but other two are unknown. So, if pressure and volume are known you find the temperature the pressure and temperature are known you can find the volume ok. So,

ideal gas relationships gives the very very nice and easy way of finding out the other property.

So, with this we wrap up properties of pure substances. In the next class we will see a few examples on how to use the computerised tables. Because one needs to know how to look up the various properties, when to know if the property superheated vapour, when to know the properties, how to find the properties, when the fluid is the super cooled liquid, how to find the properties when it is in saturated region.

So, in the saturated region you can only specify one of the properties temperature or pressure; you cannot satisfy both temperature and pressure. So, then you need to have the quality ok. So, all these things we will first be discussed by means of the tables given in the book. It can be found in any appendix in thermodynamics books and there are entire tables dedicated to this they are known as steam tables ok. And then we will see how to make use of computer aided tables in order to solve such kinds of problems.

So, there is no interference between looking up the value in a table and using a computer to fetch that data. If the concept is there you can very well make use of computer to very well use of a computer to fetch the value of the property that you need and then you can do the calculation ok. So, we will first see how to find out the how to extract the particular values. We will see how a critical the critical temperature can be obtained, how we can find all these things. So, I will see you next time.

Thanks.