Chemical Engineering Thermodynamics Professor Jayant K. Singh Department of Chemical Engineering Indian Institute of Technology, Kanpur Lec 7 Basic properties, phase diagram, and thermodynamic table

Welcome back. In today's lecture, we are going to just talk about basic properties, phase diagram and thermodynamic tables. This is just to make sure, that those who have not gone through the earlier engineering thermodynamics course can get an exposure to fundamental aspects of properties and how to extract those from the tables for solving problems.

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So, these are the learning objectives. We will be talking about basic phase diagrams, saturated liquid and vapour states, what are those on the phase diagrams. Similarly, what are the superheated vapour and compressed sub cooled liquid states and eventually for the case of the water and refrigerant and some simple systems or simple fluids will be also demonstrating what are the typical property tables. In case of saturated system, the quality is another term which we are going to show you how to use that.

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So, we all aware of phases of pure substances, we know that pure substances can form different phases, but the common ones are solid, liquid and gas, which are basically differentiated based on density of the system. So, for example, that would be your water which you can easily see. Now, the molecules those interact very closely as in a lattice structure, tends to attain a solid structure, such as this.

Now, if you increase the temperature, for example, it will start melting at certain temperature and you may get the particles, which are moving in random directions, which would be the phase called liquid and if we further expand it or further increase the temperature and leading to expansion, let us say, in a volume and leading to decrease in the density, you may get a gas phase.

Now, you may think that the interactions effectively reducing, as you change the phases, which is true. However, the type of interaction remains the same, as the effective interaction reduces as they are far apart. At a certain point, they will be so far apart from each other, that they will not have any effect, leading to something called ideal gas scenario, okay? So, this the typical structure of the different kind of phases.

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Now, the change in phases are described on a diagram, which we call it as a phase diagram. Now, these are usually demonstrated in intensive 2D kind of a plot. Example would be something like temperature against specific volume; this is something like volume divided by mass. Now, this is just for the sake of illustration, so this is an example for the Tv diagram of water, where what we are doing is heating water at constant pressure.

So, to illustrate this example, you can consider that you have mass-less piston here, right. This is mass less piston and essentially the heat is being provided and the pressure outside is one atmosphere which always remains the same and initial temperature is 20 degree Celsius, at which the liquid, we call it compressed liquid. Now, we will come to that definition of compressed liquid later.

But what happens that, subsequently, once you put more heat to the system, eventually it follows this line, which is a green line. At a certain temperature, of course the temperature increases, at a certain temperature which, we all know is 100 degree Celsius, the first bubble of vapour starts coming in and eventually, now it follows this horizontal line, which essentially means, that at certain point here, you have a state, something like this, where you have a saturated vapour in equilibrium with saturated liquid, okay?

And the vaporization of the liquids keeps happening, until you reach this point, where the last drop of liquid vaporizes and subsequently what you have is nothing but all gas, but in a something called super-heated state. So, at this point, at 4 you have state which is a completely vapour, but it is saturated. This will be your saturated vapour, ok. And this will be you saturated liquid, ok. So, this kind of plot or the diagram is usually also called the phase diagram. But essentially, what you are doing is, looking at the process here, along a certain condition, so you can feel this T-v plot at a different conditions or different pressures.

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For example, and if you do that, essentially what you going to get, for example we had this scenario earlier, ok which is nothing, but the same point 1 mega pascal. Now, if you do it similar kind of operation, you are going to get different pressure based curve, which are nothing, but isobars and, at a certain point, what you are going to see is that, is very interesting here is, this, this inflection point, where there is no horizontal line, which is the region of phase transitions.

So, this phase transition, if you look at very carefully, the length of this ok decreases, at a certain point becomes just a point and this is where, the both the saturated liquid and vapour co-exist and this we call it critical point. For the case of water, the critical point is 373.95 degree Celsius and critical pressure, this is the critical pressure here, is 22.06 mega pascal.

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Now, we can also summarise this in a simple curve here, which is now basically addressing the same thing. So, what we are trying to emphasise again here that this is the TCR and this is the cross pointing specific volume or the molar volume, is going to be VCR, in which CR stands for critical point here. And anything beyond that is the super critical region, where the pressure is greater than PCR at this point, ok. So, at supercritical pressures, that are P greater than PCR, there is no distinct phase change, that means the boiling does not occur at pressure greater than PCR, ok. So, again to summarise here, the critical point is the point at which saturation liquid and vapour states are identical.

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So, now if you try to connect these isobars here, ok. So this is what, this pressure, constant pressure lines. If we just try to connect the point, which cause constant saturated vapour and the liquid, remember that, this region, we are saying this compressed liquid, this the points we are talking, we are saying that, these are the saturated liquids and this is going to be saturated vapour. So, if you connect this point, these dots here, the point of phase transition, so you get a curve here and this curve is called saturated liquid line.

That is what, is written over here, saturated liquid line. Similarly, this one is, saturated vapour line and it connects to the critical point. So what you get is now, is truly the T-v diagram. Earlier you had only the lines here, ok, which are the isobars, but now you have the complete phase diagram. Now, in between, you have saturated vapour liquid region. Here left side is, compressed liquid region and the right side is superheated vapour region. So, this is a typical T v diagram of pure substance.

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Now similarly, you can have a pressure volume diagram, ok. Which is written here P and V, remember that, these are all intensive variable. In this case also, the left-hand side is compressed liquid region, left, this is saturated line and saturated vapour line. So, what we are doing in this case of P-v diagram is, we are getting isothermal lines here, which is nothing but essentially at a given temperature, temperature less than the critical point.

If you start from the compressed region here and if you reduce the pressure, you follow this line here. For example, ok, you can consider this from this perspective here, that you are maintaining the temperature here, for example, and you are trying to reduce the pressure, that means that you have weight on the piston. And if you allow this weight to reduce here, in such a manner that this follows very slowly, the process is extremely slow, then basically there will be expansion in this.

So, essentially when you remove this, the piston is going to move up a little bit and that means it follows the line. At a certain point, when you have a specific pressure on the system, it is going to face change, ok and then subsequently, follow the superheated region. So, this is an isothermal lines, you know similar to the T v diagram, in the P v diagram, you connect these two points, points cross point to the saturated liquid and saturated vapour. And the when you connect, you get a curve and leading to the critical point here, ok. So, this is a typical P v diagram for the pure substance.

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Now, we talked about only 2D plots, but you have the pressure, you have the volume, you have the temperature, so PVT is a normal still variable which essentially, you can club 3 together, you can get this 3D diagram where you can have solid vapour phase transitions, you can have solid liquid regions, you can have only solid, you can have vapour and it usually is very difficult, to remember, to draw, but it is illustrative, that what we are doing is, what we are taking the projection of the systems, which is the 3D here to 2D here.

And you can get this P-T diagram here, as we have said there you can have this P-v diagram, which is this one. So, this is what we have shown on the last slide. So, what you are getting is basically isothermal lines here, alright? But this is in the saturated liquid vapour region, so you can also have solid vapour region in a same way and if you add it all together, if you put it all together on a 1 plot, you are going to get this very complicated plots here.

Simplified version is pressure and temperature plots where essentially you have a 3 specific line for pure substance. 1 is your saturated vapour line which on P-T diagram it will look like a simple curve that means each point here represent something like this, where you have vapour and you have liquid. So, essentially, this point corresponds to the case, where you have this, if you clearly see this, vapour, liquid vapour region, so if you take it and take a projection on this side, you are going to get just one point here.

So, for example in this case this one corresponds, to let us say, this you can consider this to be this 2 phase region. Similarly, this single point corresponds to triple line which you say that ok. So triple line on this P-T Temperature would be simple triple point, this is the point where, basically 3 phases co-exist.

So, again let me go back here and this is what we, I was talking about saturated vapour line, then you have this solid liquid fusion line and then you have solid vapour which we often called sublimation line ok. Now, what you notice is that depending on the substance, which can contact our expand upon freezing, you will have this slope this, this, fusion line to be positive or negative. (Refer Slide Time: 11:46)

So, as I said that in PT diagram here, so here as I have already mention. This is the one, which is the negative this is the substances that expand on freezing example would be water. Now, I assume that the most of the people have seen this thing, so hence I am not trying get into more details at this point. We will discuss this later, when we make use of free energy calculations to explain all these aspects.

> \Box HQQQQ. $\mathcal{Q} \neq T \odot \mathcal{Q} \equiv \mathbb{R} \times \odot \odot \mathcal{Q} \cdot \frac{1}{T} \cdot \mathbb{R} \bullet \blacksquare \blacksquare \blacksquare \blacksquare \blacksquare \square \square \blacksquare \blacksquare \square \square \blacksquare$ Sans Normal 12 VAPOR . At triple-point pressure and temperature, a Critical
point substance exists in three LIQUID Liquid phases in equilibrium. **SOLID** Sublimation line: solid-vapor Vapor
phase \bullet coexistence Fusion line: solid-liquid ٠ coexistence Vaporization line: liquid-vapor coexistence At low pressures (below the Triple point: All the three triple-point value), solids ٠ evaporate without melting phases at equilibrium first (sublimation). Above critical point no \bullet distinction between vapor and 0.01 ^{*} liquid phases 6117 kP

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So, let me also further summarise this from the point of view of phase transition. This is again the pressure and temperature for the pure substance. So, this is your sublimation line that means essentially this solid and vapour coexist which essentially means that let us say that if your system is in solid, it directly goes to the vapour case. Now this would be the case, which essentially you see in a dry ice, CO2 at room temperature immediately from solid CO2 goes to the vapour.

This is the triple point, this is essentially, you have a solid here. If you heat it up at certain point here, you will have 3 phases in co-existence, something like this, ok. And then it immediately goes to the vapour phase. This is the fusion line, where basically, if you go from E to F, imagine that you first have solid followed by liquid followed by vapour. Other than, if you consider, let us say, here A to B, it is like solid to vapour, here solid and then co-existence followed by vapour, ok.

So, there is no specific conversion to the transformation to the liquid completely, ok. So, it gives you an idea of phase transitions, if you have these phase diagrams clearly, ok. For example, let me also complete with this statement here, that from G to H, if there is a transform process leading to this, then essentially, there is no phase transition in this case.

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So, you have this phase transition, it occurs upon, some changes in the state variables, so some changes, just like said we change in temperature, pressure you see this phase transition to occur. In order to change this temperature and pressure and other state variables, you have to apply certain external law sudden, heat or work you have to conduct on the system. So, what we define, as per heat associated with phase transition is called usually latent the heat.

So, for the case of fusion process, the latent heat of fusion would be the amount of energy absorbed or released during the phase transition. Similarly, you will have Latent heat of vaporization that is the heat associated with the vaporization and similarly, that for sublimations, ok. So, the magnitude of the latent heat depends on the temperature and pressure at which the phase transition or phase change occurs.

So, consider this example, where you have the pressure which is 1 atmosphere, the latent heat of fusion water is 333.7 kilo joules per kg, ok, but the corresponding pressure, the latent heat of vaporization, is much-much higher, ok. Now, there is a variation of also the boiling temperature, so if you look at again the phase diagram, you will notice that, as you change the pressure, the line saturated to isobars shifts up. So, essentially what is happening that, the corresponding boiling temperature also changes.

So, something called standard boiling temperature, something called normal boiling temperature, something called saturation temperature corresponding to the pressure. So, that do change, so if you look at the example here, the variation of the standard atmospheric pressure and boiling temperature water, so this would also give an example of, why it takes longer time to cook at higher altitude. So, you take an example of this, at 0 elevation corresponding, with respect to sea level, at normal pressure the boiling temperature we know is basically 100 degree Celsius.

But as you go higher, let us say 1000 meter, the boiling temperature is much lower, ok. So, essentially much of the energy is vaporised or enhanced, you are losing the energy at higher elevation, ok which is the basically, the latent heat vaporization takes away and does need you more time for cooking, because your liquid is vaporizing much earlier, ok. So, this gives you an idea about, process much more effectively and hence you think how to correct it, if you need to do any modifications in the process, ok.

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Now, as I have already mention that, this phase diagram, corresponding changes and in the properties, in the process, is, is something, which you can solve by making use of something called property, so essentially a property table. So, this becomes very useful and usually you will notice that all the thermodynamic textbooks will have this kind of thing, NIST webbook of science also has such such tables.

So, property table is nothing but tabulating information of the property of the pure substances, such as your internal energy, your enthalpy and entropy and so forth, for given temperature or pressure. Now, usually you will see that you have this $U + P$ -v term, which we call enthalpy, we have not introduced it yet, but for the sake of property table illustration, I am just mentioning this over here.

So, this is combinatory property, which is very useful for flow system. So usual property table would be something called saturation properties, under temperature we will be using water as an example and the other would be saturation property of water under pressure.

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So, this is an example of that, this is the saturated water temperature table which essentially mean that, what we are looking at each temperature, there is corresponding saturation pressure and then you have this 2 phases system. So, saturation liquid specific volume is given here, saturated vapour, specific volume is given similarly for internal energy and then this U_{fg} is nothing but the difference between U^g and Uf.

That is U_{fg} and then you have this enthalpy and then entropy. So, these are only for water, there are other fluids, which are also used, but not many because it is something which is tremendous time-consuming operation and since water is used in steams and turbines and so forth it becomes very valuable to have a table. Similarly, for refrigerant you will have it but 1that is about it not much particular individual test book. If you want more information about properties then essentially the web of NIST Webbook of chemistry becomes valuable source for you to consider.

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So, this is again saturation water but now what we are doing is, we are changing the pressure here. So if you look it for a given pressure and corresponding saturation temperature. Then the similar thing, that saturation liquid molar volume, saturated vapour moral volume then have internal energy and for the fluid, for the gas and difference between the fluid and gas. Similarly, for the enthalpy which is $U + Pv$ for the fluid, there is liquid for vapour and then the difference between that.

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Let us look at, if you have saturated vapour liquid system, then how do you define the amount of vapour present in a given system. So, we often use term called quality. So quality is nothing but ratio of the mass of the vapour to the total mass of the mixture.

$$
m_{total} = m_{liquid} + m_{vapor} = m_f + m_g
$$

$$
\zeta = \frac{m_{vapor}}{m_{total}}
$$

And this becomes very valuable in various different calculations and I am going to show some example with that. So effectively, what I am trying to say if you have system such as a saturation vapour and saturation liquid then you can consider this equivalently having a homogenous system with specific volume of V average.

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So, if you want to have this kind of representation then you need to use something called by definition because you already have definition of x so V average would be simply molar volume of liquid plus the quality multiplied by V_{fg} which is nothing but V_g - V_f . That is why you get this kind of expression. Similarly, you can do for internal energy, similarly you can do for enthalpy.

$$
y \rightarrow v, u, or h
$$

$$
y_{avg} = y_f + \zeta y_{fg}
$$

$$
y_f \le y_{avg} \le y_g
$$

Thus, if y is v,

$$
\zeta = \frac{v_{avg} - v_f}{v_{fg}} , \quad v_{avg} = v_f + \zeta v_{fg}
$$

Similarly, $u_{avg} = u_f + \zeta u_{fg}$ and $h_{avg} = h_f + \zeta h_{fg}$

You can also understand the quality from a graphical approach, where if you have this phase diagram given to you, then the point you been asked to find the quality.

Quality would be simply let us say you have point here this is the system when which we are talking about vapour and liquid and you have been asked to find out quality that means ratio of mass of volume divided by total mass then you can consider this simple length with respect to volume here so this will be AB, A and B divided by total length here that means essentially you can use graphical approach also, if you have data and you can plot it also. But if you have the numerical values you can clearly use that. The other thing is that if you see this data specific volume of gases going to be much larger than specific volume of fluid hence any point here, the volume would be in between these 2 points.

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So now let us do an example, so this is an example of a rigid tank containing 10 kg of water at 90 degree Celsius. If 8 kg of the water is in the liquid form and the rest is in vapour form, we have to determine the pressure of the tank and the volume of the tank ok. So, what we do is that we have been given these 90 degrees Celsius and essentially it is being told to us that this is the system which is in saturated condition.

So, we look at the first saturation table, the property table but the temperature 1 so I extract that so essentially, we got the data here this the temperature here at corresponding to 90 degree Celsius we have the saturation pressure and the molar volumes I got it here. So, this corresponds to this kind of situation where you have 90 degree and this is the isobar and this is the pressure and somewhere here the system is with this condition 90 degree Celsius the gas is the vapour mass is 2 kg and the liquid mass is 8 kg.

So, I need to find out pressure in the tank pressure is of course corresponds to directly to this, which is saturation pressure because it is a 2 phases system that is the vapour and liquid in coexistence and the volume of the tank would be simply the total volume of the fluid plus total volume of gas which will be the mass of the fluid multiplied by the specific volume of the liquid plus the mass of the gas or the vapour multiplied by specific volume of fluid.

So, this we know m_f and m_g we know v_f and v_g we know from table and then we can plug it in. So, this is one approach. The other approach is since we know the definition of x is nothing but the m_g by m_{total} , so this is what we are doing here 2kg divided by 10 kg which is 0.2. Now, given this we can find out v of the system specific volume of the system complete system which would be nothing but v_f plus x times v_{fg} .

Now v_f comes directly from table, x we have calculated 0.2 and v_{fg} is nothing but v_g - v_f which again we make use of the table and then from there we can get the same information. So, this is nothing but t your specific volume so with this we have to multiply by total mass then this what is being done here this will give us the total volume of the system. So, both the approaches are same and gives you the same answer as well.

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Now similarly you can do another example but now in this case, you can consider refrigerant. So, without solving this I am just going to read out here so, for example, if you consider, an 80 litre vessel contains 4kg of refrigerant 134 at pressure of 160 Kelvin. Determine the temperature, the quality, the enthalpy of the refrigerant and the volume occupied by the vapour liquid.

So essentially what is given is total volume you can convert this into metre cube is we have been given the mass that means you do have the total specific volume and you have been given that pressure so essentially you are going to take that pressure saturation table of the specific refrigerant 134 from there you will find out what is the corresponding temperature.

That means the saturation temperature that will give you this making use of the fact that v, you know which is the specific volume this is going to be $v_f + x * v_{fg}$ so that means x is v - v_{fg} / v_f . So you know this because you can convert 80 litre into metre cube and then you can divide by 4 kg so you have this information this comes from the table and this comes from the tables so you know the x here.

Once you know the x, h is going to be $h_f + x^*h_{fg}$. Now from here you will also know this you can calculate for this one for the volume particularly volume occupied by the vapour phase you know the x is nothing but m_g by m_{total} . x you have calculated from here m total you know is 4 kg so this gives you m_g. v_g is nothing but V this is small v_g which is the specific volume divided by m_g so from here you can get Vg this from the table. So, this is how you are going to make use of the table to obtain information such as quality, enthalpy, the volume occupied by the vapour phase.

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So that is another example which you can do at home. Last few minutes I am going to just quickly wrap the other cases which is the case of super-heated vapour which is on the right-hand side. So, in this region which is the usually temperature over the critical point, this is going to be superheated vapour ok and usually the temperature and pressure or in this region temperature and pressure are independent properties.

We need 2 intensive variables to define this state here ok. So, for this case also you have specific tables the tables are given in this cases v u h there is no saturation conditions, hence you will have only the specific volume, internal energy and enthalpy. So, note that is the case of superheated vapour you have this h which is greater than enthalpy of gas.

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So, similar to that we will also talk about compressed liquid compressed liquid is on the left hand side of the diagram so this is an example of T and internal energy it could be volume also. So here you note very carefully here that these are the condition where the temperature, let us say is here this temperature is less than corresponding temperature at which this isobar is being sketched.

So, this isobar has so this will be your T_{sat} at 5 mega pascals so this is the isobar for which your saturation temperature is something T here. This T is certainly more than, let us 80 degree Celsius which is being the point of interest for us. So, this state 80 degree Celsius 5 mega pascal would be you compressed liquid but the property would be that T_{sat} corresponding to P is going to be more than the temperature.

The compressed liquid is usually at lower temperature than the saturation temperature of given pressure at given pressure. Similarly, it is at higher pressure P is much greater than P_{sat} at given temperature. So that also you can show, so usually properties of the compressed liquid would be

that your volume would be less than fluid volume at given P or T, u is less than u_f , h is less than hf. So that is property of Compressed liquid.

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Considering that we do lot of approximation one of the common approximations is that we tried to approximate the property let us y which could be volume, internal energy or enthalpy, as a value of a y fluid at a given particular temperature. A more accurate relation let us for particularly for enthalpy is going to be the h is hf t plus the volume of the fluid at t multiplied by the difference of pressure with respect to the P_{sat} value but this is approximation we commonly use.

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Ok so the last slide which I am going to cover in this lecture is, about reference state. Remember that, we cannot calculate absolute value of entropy, enthalpy basic the free energy we cannot, so we always take the reference, we always calculate the difference between the value with respect to some other reference, so reference becomes important. We often choose reference state for water in terms of temperature is 0.01 degree and for the refrigerant is minus 40-degree Celsius.

So, it is important when you look at the table you look at what also reference is being considered. So, I am sure you have looked into you have gone through particular exercises earlier what I wanted in this lecture was to quickly recap the phase diagram and other thermodynamic properties at this point I am going to stop and we will continue in next lecture. Thank you.