**Engineering Thermodynamics**
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**Week-02**
**Lecture-9**
**Properties**

Welcome to the second lecture of this property. In this, as we read last time about pure substance, how thermodynamically the composition should be constant, throughout should be same. The second thing we read is about phase change processes. Today we will move forward with the same and try to understand the property diagram which is a good platform which you can understand about the phase transition. water phase change liquid to vapor we are repeating this is your region sub cooled liquid and different regions this is your sub cooled liquid and this is your discontinuous where slope is changing this point this point is your saturated liquid and where again it is changing, your saturated vapor and in between this line which you can see, it is called tie line, here your phase is transitioning, phase is converting from liquid to vapor. As pressure increases, with less pressure, more pressure is generated, this length, where this phase transition is happening, which represents, it gets smaller. And finally, you get to a point where liquid and vapor are in the same condition, so you won't be able to distinguish it. So that's why it becomes one state. And this point is called a critical point. After that, the line becomes continuous, there is no change in it, you can see. So, this is supercritical, which is above critical. So, this TV diagram represents the property diagram. These are valuable and useful to understand the phase transition. The same type of diagrams will be used in PV and PT diagrams. So, wherever there is a phase transition, these processes are there. We try to understand these through these property diagrams. Now we will move on to other things. Because usually we don't write like this. and we don't always represent like this Because to change this you have to change the pressure. Usually what we do is that these points are connected to this point. Now if we connect it, then you get a diagram like this. T is again your pure substance. We have not said that it is water. This is generic. This is how the T-V diagram will look. You can take water or any other substance. If you change the pressure here, if P is less than Pc, then you get this type of diagram. If you keep the pressure constant and increase the temperature, if you supply heat, then the temperature will increase. So, at one point, the disc will change, the saturated liquid state will come. phase transition and then your saturated vapor state will come and then it will go to superheated region So this is the discontinuance in this pressure line If you keep increasing it like this So as you have seen One point is that this critical point will come here. So, where these saturated liquid points are, if this is joined, then this continuous line can be formed, which we call the saturated liquid line. So, this line is the saturated liquid line. This line that you can see. And the second one where these saturated vapor states are, if this is joined, so this is your saturated vapor. Normally, the standard diagram of the step shown in the TV diagram is shown. So, we show it like this. This curve normally represents the vapor-liquid transition. This is the saturated liquid line. This line is your saturated vapor. This is your critical point. If you want to add vapor to solid liquid, it is also possible. But for that you have to add it in the additional space.

This region in the middle is called the saturated liquid vapor region. This means that both phases, liquid and vapor, exist. On this side is the liquid region, the compressed liquid region, and this is the superheated region. The upper region, which is at a higher temperature, is the supercritical region. So, this is again a TV diagram. There will be no phase transition on this supercritical pressure. There will be no distinct phase transition. There will be no boiling. So, this is supercritical because you will not see any discontinuous change in the flow. If you have the same property diagram as I said earlier, then you can have the T, V, P, type diagrams. So far, we have only represented the phase transition at temperature vs. specific volume. If we do the same thing in P, V instead of T, V, then how will it be? Let's see again. So, if P is V, then it is M. We are representing phase transition as temperature constant. We are trying to maintain constant temperature in any process. Earlier we tried to maintain pressure constant. Now we are trying to maintain constant temperature. There will be constant temperature lines. Let's understand this. Suppose you have fixed a temperature. You have to change the pressure. We have represented the pressure as a piston and the weight is applied to it. If you are reducing weight, then a high pressure will be applied. From here you are coming to this line which is a constant temperature line. When the pressure changes and decreases, you can understand that the pressure is decreasing. The pressure has decreased so much that it has reached the point where it has become saturated liquid. state. This state is supposed to be 1. Yeah, I guess date too. where it is saturated liquid which means that if we try to change the pressure a little bit more This is the state 2 which is saturated liquid. It will be ready to be vaporized. So, when it is vaporized in this process, it will remain at constant temperature. Along with that, the pressure constant is called P-sat. As we discussed earlier, when the pressure is fixed, then there is a corresponding T-sat. It will vaporize at a certain temperature. Similarly, when the temperature is fixed, then there will be a particular P-SAT, which will be vaporized at a certain temperature. So here, as you can see, I came from this line, which is reducing the pressure on it, and at one point, it became a saturated liquid. Now it has vaporized. So, it has vaporized. After that, again, here comes your saturated vapor. It means that all liquid molecules have come into the vapor phase. Now, if you reduce the pressure further, then the volume will increase. Okay? And in this way, superheated vapor region. So, this is the superheated vapor region.

If you look at it schematically, notice that the volume is increasing. The specific volume is increasing. If the mass is fixed, the volume increases, which means the volume is increasing. If you release the pressure, it increases and the volume increases. So, this is a PV diagram that represents you. So, we can take it at different temperatures. And there will be only one temperature where you cannot separate liquid and vapor. We will make it a critical point. There will be no distinct phases above it. This is also your super critical region. So, we will represent this as a PV diagram. in this step. Like this was a TV diagram. Okay, same thing here. Similarly, your PV diagram. The difference is that in the PV diagram, we put pressure, this was P1, this was P2 and here is your critical Pc. And here is yours, this is T1, this is T2, and this is Tc. T2 is greater than T1 and here also T2 is greater than P1. So, this is your representation, this shows your phase diagram. What we have discussed is the PV diagram. independent variable changes. The P-V diagram you saw is and simply it was that this is your T2 vs T1. This is your isotherm; we are fixing the temperature. And T2 is greater than T1. And this is the critical point. And the TV diagram which I have seen before was this, in which we are changing the pressure. P1, P2 and this is your critical point Pc in which P2 is greater than P1 and Pc is greater than P2, Pc is greater than P2 and Pc is greater than P2 so the pressure increases from below here the temperature is increasing from below and Tc is your critical point so this represents phase transition I tried to understand how you can control the pressure or the temperature by heating. The actual realistic thermodynamics surface is three dimensional because of pressure, volume and temperature. But what we represent to a simple system, which is a compressible fluid, means what you are compressing, for that you need two independent intensity variables, You have to define two variables to define the state of the fluid You have to define two independent intensive variables to define the state of any compressible fluid So that is why we say that any equation with two variables is a surface. present with full data. So, this is a kind of a PVT diagram.

You can see that it is very complex. It will be difficult to understand. So that's why we take its projection in two dimensions. Like this is a PET diagram. In which you can see that these are mainly lines. We will discuss this. If we take the projection in the PV diagram, then it will be like this. In which we have kept three states. There is liquid, gas and solid. And this is the liquid that I have discussed so far and wiper. Phase transition is about liquid and wiper region. When we include solid and liquid then you will get a separate line here. And here also. and this line is called the triple line where all three phases are there liquid, vapor, gas so this is liquid plus vapor this is solid plus liquid this is solid we have already mentioned this region we have said this region is all cool liquid this is super-heated vapor this is super critical and this is critical but it will remain the same when you play with volume, temperature or pressure and this region below is your solid plus vapor So this is a complete phase diagram.

When you take the complete phase diagram under all conditions, then this complicated phase diagram will come out. So, PVT surface normally has a lot of information. But it is difficult to read. That's why we use the easy ones in two variables, in two dimensional diagrams, whether it is a PV diagram or a TV diagram. So, if we are taking the PV diagram, then here we will take the substance that contacts on the freezing, means the density of which increases when it freezes. These normal fluids behave like this, only water will expand its volume when the temperature becomes sub-zero. So, it expands on the freezing. So, in this way, its behavior, solid liquid, is different. and other fluids behave differently and their density increases. So, there are different behaviors in these plots. Let's present them first. This PV diagram is liquid vapor, compressed liquid and this is superheated vapor. We have discussed this earlier.

The pressure is low, and the temperature is low. The triple line shows the three phases vapor, liquid and solid. The solid liquid region is below the liquid solid region. This is the boundary. As we have considered this boundary, this is your saturated vapor line, this is your saturated liquid line. Similarly, this is your, at this point, your complete liquid is converted from solid. Similarly, at this point, your complete solid is solidified. And in between this, solid plus liquid is a mixture. And finally, this is your solid region. So, this is the PV diagram which presents all three phases solid, liquid and vapor If you talk about water, then in the case of water this line is not positive, it will remain negative and that is why we are representing it in dash form, the rest Behavioral regions in terms of solid vapor, solid liquid, liquid vapor are same but the slope changes. These cases are the cases where the substance is made hydrogen bonding. And such is your PV diagram. Particularly, in this case, where the solid comes. So, if we do this in the PT diagram, note the PT diagram. This is the projection of the PVT surface. In PT diagram, volume change is not visible. Only temperature and pressure vary. And the regions that you have seen earlier, if we take projection, then these two points, This type of change in the isotherm Right? So, we did it, temperature 1, temperature 2, and this was the critical point Okay? So, If we take this projection, then these two points This saturated liquid and saturated vapor These two will come on top of

each other So because of which In the PV diagram. This is what it looks like in the PV diagram. This line you were seeing. These points merge together and represent the liquid and the vapor in a box. This line goes from the critical point to the triple point. This line is called the vaporization line. Triple point is where all three phases, vapor, liquid and solid, coexist. So, at this point, all three phases, vapor, liquid and solid, coexist and you will see all three phases. It will look like this. If your sub-shaft is solid, then liquid and this vapor. They coexist. How much amount will it vary on the continuous. That's why you have a triple line.
At this point, the volume of all three will be different. Okay, so if you see at this point, it is completely Vapor plus solid will be there. And here, the composition of these three will be different. As we have noticed here, at this point, when this liquid is vapor, then your vapor plus liquid will vary. And at this point, only your vapor remains. Similarly, at the triple point, the composition of the three will vary. As we will go from one point to another. But in the PT diagram, you will represent this only through a point, there is no line, line becomes a point. So, in vaporization, every point is an equilibrium point. And this is vapour liquid vaporization. This part here is the sublimation which comes from below. It represents solid plus vapor equilibrium. After that, this point is the vaporization line. And this point is the melting line. And here is the solid liquid equilibrium. This is the vapor liquid equilibrium. And this is the solid vapor equilibrium. This is the sublimation line, this is the vaporization line, this is the fusion, and this is the melting line. In case of water, this line will not remain as positive slope, it will become like this So the substance that expands, its volume increases Its PET line, solid liquid, will be negative slope from this side Let's try to understand it more clearly. So, this line is the PTU line. Let’s try to understand it more clearly. In this, this is the substitution line that we discussed. This is the solid vapor coexistence line. Fusion line and melting line are the solid liquid coexistence lines. Sublimation line is solid vapor coexistence and fusion line is solid liquid coexistence And at triple point, all three phases coexist in equilibrium All three phases are in equilibrium Vaporization line means liquid vapor coexistence And at critical point, no one can distinguish you We have already discussed this in the previous slide We will detail it more So, if you take a process, A to B is equal to the initial temperature of A. So, the pressure is below triple point. So, what is going to change in the line between A and B? You are in the solid phase and the pressure is below the triple point. Because the pressure is at P triple point, and this is at T triple point. So, at this point, from A to B, the solid will directly vaporize. It won't condense. The solid won't come into the liquid. It will directly go into the vapor. Right? Then you will have a process called CD. So, what will happen in C and D? You will have the solid at the triple point where the liquid, vapor and solid coexist. and then it goes into the vapor then comes the E point if we start this process where the pressure is now at the triple point the pressure is now at the triple point and then it goes above the triple point so any solid will first vaporize after coming here it will go to this point and vaporize at this point the vapor will be made slowly sorry this liquid will be made before the solid After condensing, the liquid will form and you will increase the temperature. After that, the liquid will vaporize and eventually the vapor will come to the F. In this case, from solid to liquid plus vapor came to this point then came directly to the vapor came to the triple point and at this point, came directly from solid to vapor and in the case of G to H, where it is above the critical point, so it is on the liquid so there is no change here, this is supercritical state so there will be no change in the state. There will be no distinction in the faces. So, this is a process of phase transition and transformation. Now when we change the phase, as we are applying energy, notice that if we are coming from this point to this point, then the pressure and temperature are fixed. So, what has changed? We are giving more energy, is going into internal

energy. So eventually the internal energy of the vapor is the change we have given is called Latent Heat is the amount of energy absorbed or released in a phase change process the energy change between two phases is called Latent Heat Sublimation. These are solid, liquid, vapor and solid vapor. These are three types of latent heat. The magnitude of the latent heat depends on the temperature and pressure where this phase occurs This length represents the latent heat. There is no change in the critical point, so you can consider the latent heat as zero. Here it keeps increasing, as we go down, it keeps increasing. And here it will be very high. So, it depends on the temperature and pressure on which you are applying it. So, for example, the latent heat of fusion of water at 1 atmosphere pressure is 33.7. per kg and latent heat of vaporization will be more.

It is normal that the latent heat of the latent vaporization is more than the latent heat of the latent vaporization in the fusion. The internal energy of the gas will be more. It also matters that as we said that the pressure varies on the temperature. If the pressure changes, the water will start boiling at 101.33 kPa. As the elevation increases, the atmospheric pressure will decrease. Now the boiling point will also decrease. So it means that it will start boiling at a low temperature And that's why your food takes a long time to cook If you are cooking in open air because it is getting vaporized quickly All the energy is going out So the energy is not in the container at all So how will it boil So that's why it is necessary to close And that's why making pressure cooker It is more relevant if you are on high elevation We have talked about water phase diagram. Carbon dioxide phase diagram is very interesting. Because you will find interesting phenomena in its phase diagram. It is called dry ice. We will discuss it. This is a typical phase diagram. Pressure vs temperature. As you can see, this is your sublimation. This is the vaporization, and this is the fusion line but notice that this is not straight, it is a little curved and the important thing is that the triple point pressure is much higher than 1 atmosphere So if you keep the solid carbon dioxide at room temperature and pressure, it is easily transformed. Because if you see the room temperature at 300 degrees, it is easily transformed and it becomes a vapor form. If you keep it at room temperature, it will immediately start to form a bubble So it will look like this The reason for this is that the triple point is more than the atmospheric pressure and that is why when we initially bring solid phase but the actual condition is here where T is the room temperature room condition and around 300 Kelvin so it is here and your pressure is 1 atmosphere so immediately if you bring some solid then immediately it will be here This will be converted and changed to sublimation process. This is also known as dry ice. If triple point is above room temperature and pressure, then you will get this type of behavior in any product. Normally we use this you can experiment with this.

We have talked about three phases till now. Solid, liquid and vapor. But if we look at solid, it also has some forms and conditions. We call it allotropes. Like in carbon, you will get graphite, bucky ball, or nanotubes. There are many forms like this. The forms are different in temperature and pressure. These are called allotropes. Like in carbon, you will get diamond and graphite. So, these are different forms of allotropes. But if you look at pure substance, there can be many triple points. Like in this case, if you look at it, Diamond, liquid, graphite, etc. can coexist at one point. But there is only one triple point where vapor, liquid and solid coexist. This means that there can't be two triple points in any substance. There is only one. Of course, the temperature is very high. The temperature is not at normal room temperature pressure. But such forms exist. The water face diagram is very complex and complicated, and the reason is not only that the reason is that hydrogen bonds can make ice in many different ways. This is the unit of pressure. This is the solid-liquid-vapor triple point This is the vaporization line liquid plus solid. But in this solid, how many allotropes are there? There are many forms of ice. Today, 20 allotropes were found in the ice. But in the atmosphere of the Earth, you get ICOIH. And if you change the pressure and temperature, then you get different forms. For example, this one is in the same way, Saturn and the planets have different types of ice. Because the pressure is very high, and the temperature is very low. So, with this different structure, we can also know that such as satellite, X-ray, diffraction. We can find out if the ice is alive or not. So, it is very important to understand different allotropes of water. And that is why research groups across different countries try to understand it. We will not discuss ice structure; we will discuss only two types of ice structure. One is the one which is normally found at room temperature and atmospheric pressure. The other type is the ordinary ice which is found at home. IH has three layers. One is the one which has two layers. So, there are two layers of ordinary ice. ABAB AAB 2nd phase is cubic ice It is seen as ABC It has 3 stacks and its structure is slightly different It is in a proper hexagonal form It is in a cubic form and it repeats 3 types of stacks Normally you will get this in Earth or room temperature 100% you will not get this you will get this in some forms As I told you before, ICE 11 is found in Antarctica. Its age is also mentioned as 10,000 years old. It has many properties like ferroelectric and other important properties. You can read about them if you want to know about Jhankar. In this particular lecture, we will only discuss the property diagram. We will use this phase diagram in the future. You can understand how complicated a simple molecule water can be. How complex can be the phase diagram. And how important it can be to understand its things. Because you can analyze it. and other places where you can discover different types of life So we will stop here and will continue this lecture in the next one till then. Bye see you next time.