Engineering Thermodynamics
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Week-10
Lecture-49
Thermodynamic Property Relation

Welcome to the Thermodynamic Property Relation part 3. In this lecture, we will learn about the Clapeyron equation and how to extract the enthalpy of vaporization from your PVT experimental data. This diagram is called P and T. You can see three phases in this diagram. This is a single component of the fluid. It has solid, vapor and liquid. The red line is the slope. It is a slope at a temperature T. We will call this slope del P by del T sat. And this is constant. So, let's discuss this. Let's start with Maxwell relations which we studied in the last lecture. I write all the relations here. This is a recall in which we developed all the relations. I am writing that for your reference. So, this is the first relation. This is derived from the thermodynamic relation, the Gibbs equation, which we had discussed earlier. So, this is your relation. We will keep an eye on the third relation in this lecture.

$$(\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V$$

$$(\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P$$

$$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V$$

$$-(\frac{\partial S}{\partial P})_T = (\frac{\partial V}{\partial T})_P$$

Let's pay attention to this relation. And this is your del S by del V at constant T equal to del P by del T at constant V. If you talk about phase change, then in phase change, like in this phase change, what is this phase change? Here is your triple point. And from here, this is your liquid vapor. coexistence curve which is here at the critical point which stops at pcr, t critical, p critical so on this line as soon as you fixed PSat if we if we called it as t set then here your corresponding Tsat is fixed and if this is your t dash set So this is your P' It means that P-Sat is a function of T-sat Once you have fixed T-sat, then fix P-sat This is your during phase change where phase change occurs, this relation will occur. We are talking about single components here. In this way, your del P by del T which we are writing, del P by del T at constant v we can write this as dP by dt sat. So, this is simply your slope. So, I can call this slope m., So this is basically the slope. And this slope is independent of what? Whose will it be? volume of the slope is independent of V. In this case, if you want to integrate the slope in this relation, if you want to integrate the left-hand side del S by del V at constant T, because the slope on the right-hand side is constant, then you can consider M as constant in integration. It is constant. And consider this slope as constant because it is independent of the volume. So, look at the left-hand side. So, this is your del S, which is your M which we had sloped, it became del V. Of course, at constant temperature. You have to keep the temperature fixed. At constant temperature. In this way, if you do it then this is Sg minus Sf delta S is equal to mVg minus Vf. This is isothermal, which is the temperature fixed in liquid vapor phase change. M is your DP by dT at set. And this is your Vg minus Vf, i.e. liquid from gas. We are talking about the phase change between gas and liquid. We can also call this Fg, as we have already used it. And this is your Sfg. What does this mean? by Vfg. You can write this relation. And this thing is on your isothermal. If you note one more thing, then the pressure of isothermal liquid vapor phase change is constant. So, in such a case, if you take out your relation between D and H, because you have to take out S from here. See, the relation that has come out is this. So, this is the relation. So, this Here you have to replace S in some form which you typically H because we want to get enthalpy so we will get H back So here you will specifically take out the same relation which was on dH TdS plus VdP So if you take the relation dH is equal to TdS plus VdP The pressure is also P sat, which can be called as a constant. Where your phase is changing. What will change in phase change? Volumes are changing. So, volume and entropy will change. But the pressure and temperature are fixed. So, when we integrate this part, we can call it zero. So, Tds. Or we can call dh as Tds. What does this mean? When we integrate this, h is equal to t ds which is t constant so this will be s fg and we can write h as h fg because this will be f2g this means that we can write s fg as h fg by t now you can put this relation back here In this one, your dp by dts will be on saturation, this will come hfg by TVfg. So, this relation is called Clapeyron. This is called the Clapeyron equation.

$$(\frac{\partial P}{\partial T})_V = (\frac{\partial P}{\partial T})_{sat} = m$$

Slope is independent of V.

$$\int \partial S = \int m\, \partial V$$

$$S_g - S_f = m(V_g - V_f)$$

$$S_{fg} = \left(\frac{\partial P}{\partial T}\right)_{sat} (V_{fg})$$

$\Rightarrow$ $(\frac{dP}{dT})_{sat} = \frac{S_{fg}}{V_{fg}}$

$$h_{fs} = \int_f^g dh = \int_f^g TdS$$

$$S_{fg} = \frac{h_{fg}}{TV_{fg}}$$

It allows you to extract enthalpy and vaporization if you know the volume of the fluid and gas, if you know the p-v-t diagram and the slope of dp by dt, if you know dP by dT, you can extract Hfg in any T, which is your enthalpy of vaporization. You can experiment with this. You can draw P and T diagrams. You can make a slope on it. You can draw a slope at any temperature. And then you can draw how much enthalpy is there. Because it will be difficult to draw enthalpy. There will be different techniques for enthalpy. You can use this. But this is a very simple method. Which you can draw from the P-T diagram. So, the P-T diagram is your specific volume of the phases. You can draw it at any temperature. This relation is not only for liquid vapor but can be used even if there are any phases. If you are talking about the phase change, then if there is any phase change, if there is a process, So, at constant temperature and pressure, you can use this relation. Constant S, S means saturation, H12 means phase, which is changing between 1 and 2, and TV12, So, you can use this. Let’s do one thing first, let's do a simple problem to understand this. In this, the question is, using the Clapeyron equation, the value of enthalpy of vaporization of refrigerant 134A at 20 degrees Celsius and compare it with the tabulated data. This means that you use the Clapeyron equation, and you extract the enthalpy of vaporization from there. From which? Refrigerant 134A At what temperature? At 20 degrees Celsius. And the enthalpy of vaporization given on the table, i.e. HFG, you check how close you are to it. Let's start. We have to extract dP by dT sat. This is your Hfg by TVf. dP by dT sat is equal to Hfg. We have to extract Hfg. We can extract Hfg from here. This is your TVfg multiplied by dP by dT sat. Now how will we extract dP by dT? We can get delta P by delta T. In which condition? Saturation, 20 degrees Celsius. Now, here you will see that you have to go on the same line. Note that you have to go on the same line. So, we have to get this. We will take this point on this saturation line. Means, this T dash here and this T double dash here. And the corresponding Data will be here. P' and P". So, these data you have to take out from the table. So here we have seen that since we have to see the 20-degree angle, the data given is 24 degrees Celsius minus 16 degrees Celsius. Means we have got a gap of 4 degrees. So, 24 degrees Celsius minus 16 degrees Celsius. And the pressure is P sat at 24-degree Celsius minus P sat at 16 degrees Celsius. Note that there is no difference in the data, even if I write in Kelvin. Because delta T degree Celsius is the same in this. So, there will be no difference in the difference. Now take out this data from the table. And you will get Vfg minus Vf, which is you’re at 20 degrees Celsius. And T, we know it is 20 degrees Celsius. Now this equation, suppose this is 2, this is 3. So, you can plug in 1, 2 and 3 in this equation. So, Hfg will come out from here, which is 182.62 kJ per kg. If you look at the table, then the value of Hfg on the table is 182.33 kJ per kg. Although it is very close. Powerful equation. This is used in many industrial applications.

Because it is very powerful. Approximation is done when you talk about liquid vapor or small temperature difference. So, you can easily find it.

$$V_g \gg V_f$$

$$V_{fg} = V_s - V_f \approx V_g = \frac{RT}{P}$$

$$(\frac{dP}{dT})_s = \frac{h_{fs}}{TV_{fg}} = \frac{h_{fs}}{TV_g} = \frac{h_{fs}P}{TRT} = \frac{h_{fs}P}{RT^2}$$

$$\int \frac{dP}{P} = \int \frac{h_{fs}P}{RT^2} dT$$

$$\ln(\frac{\mathrm{P}_1}{\mathrm{P}_2})_s = \frac{h_{fs}}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

Now let's talk about liquid vapor and solid vapor system. Where we can do some approximations. because the volume of the vapor is very high compared to the specific volume of the fluid so the difference of Vfg can be approximated to Vg which means that if you consider at low pressure Vg is very high compared to the volume of the fluid So if we are talking about liquid vapor and solid vapor, then the volume of the vapor will be much higher than the volume of liquid and solid. So, we can take advantage of this in our approximation. And we can say that the difference Vg-Vf can be approximated from Vg. And the advantage of this is that you can say that the Vg is The volume of the vapor behaves like the ideal gas. If you approximate this also, then you can write Vg as RT by P. So, we considered this as approximation in the form of idle gas. If we treat the vapor as ideal gas. In this case, the dp by dt saturation equation that you wrote, hfg by Tvg Vg vfg you said vfg right so this We can write this hfg by Tvg Because you can directly approximate fg and vg you can write hfg by t rt by Divided by p which will come which you can write hfg p by RT square If you want to integrate this small temperature interval, then the normal heat of vaporization will not change much if the temperature interval is small. So, more or less, you can consider this to be very constant. In such cases, you can write the expression as dF dP by P. And, if you bring it down here, Here you can write Hfg RT square dt and you can integrate it and on integrating it comes ln P2 by P1 Of course, we are talking about saturation and here we considered Hfg constant because the temperature difference is the temperature at which we are integrating if it is less, then it comes 1 by T1 minus 1 by T2 So this relation that we have written here, this relation is the Clapeyron-Clausius equation. What is this relation? Clapeyron-Clausius equation. So, this is your ln P2 by P1 S is equal to Hfg divided by 1 by T1 minus 1 by T2. I will write this again. This is Ln P2 by P1. This is the saturation. We have approximated Hfg. The approximation is that Hfg is constant, and you can calculate this at this interval. This is your Clapeyron. Where you are not liquid vapor, you can change Hfg to Hsg for example. If there is ice, then ice, ice. When we replace this, it is enthalpy of sublimation. We call this enthalpy of sublimation. which is the simple change of enthalpy of solid vapor. This expression is very valuable and used in many places. Whenever we have a very large volume in two phases, like liquid vapor and solid vapor, we apply Clapeyron equation. In general, you can use Clapeyron equation to extract enthalpy. In general, how pressure is changing to pressure difference. You can see how the pressure changes with the temperature. So, you can take it out. You can notice that this relation also says that if you plot lnP from 1xT, then it comes like a straight line from this type. So, this also suggests this. So, you will understand this thing from here too. So, you must have understood how to use the Clapeyron equation. In the next lecture, we will learn about the general relation of Cv, Cp, dU, dH and dS, which are pure substances. We will discuss how relations are formed. So, I will take your leave. See you in the next lecture. Till then, bye-bye.