Engineering Thermodynamics
Dr. Jayant Kumar Singh
Department of Chemical Engineering
Indian Institute of Technology Kanpur

Week-11
Lecture-47
Thermodynamics Property Relation

Hello and welcome to Thermodynamics Property Relation part 1. In this lecture, we will try to understand the fundamental relations that we know or encounter or that we get between thermodynamics property. how to measure it directly but how to use the measurable quantity like PVT diagram, PVT data pressure, volume, temperature, all these data to measure all those properties like change in entropy or change in enthalpy and all these things. So, for this, first of all, we have to understand how to relate properties to each other. and a common thing is that differential form is always going to be used because whatever property is usually dependent on one variable it is on 2, 3 or minimum because as you know that any property which is related to two intensive properties that is why we define it as a state so to understand such things we will have to understand the basic partial derivatives first and then we will discuss a little more about what relations are there and how do you calculate the basic things in table or differential form when you don't have functions and tables so let's understand about this and this will be a little more mathematical so it has derivations too, so pay attention to this So the first thing is that we talk about the state postulate, which we call in thermodynamics. If there is a simple compressible substance, then we can completely specify what its state is. And for that you need two independents, which is Intensive property. So independent and intensive, we have already discussed this. Intensive means that it is not mass dependent or volume dependent. like temperature, pressure or specific properties of this stuff. So, if you can express this, then it will be a kind of simple compressible substance which will be completely expressed. and all the other properties are related to that property so after that we will discuss how to connect so let's talk about normal, like this property is z so if z depends on two intensive properties then how we will define the differential of z for that first of all we will talk about if we take any function f equal to fx So what will be the differential of this? What will be the derivative of this? So, the derivative is supposed we want to take it out here. So, this is your slope. If we want to take it out from here, then this is basically the slope. What will be the slope? It will be the derivative. So, this is your df by dx. And because they are talking about this, there is only one variable in this which depends on x. Now for this you can do that If you take a small difference between delta x and x, and take out fx plus delta x correspondingly, then you can assume that this is the right-angle triangle to draw the slope. So, your slope can be drawn in such a way that it is delta f by delta x. Now, if this slope is less, then this point will come here. So, if we say that delta x is the limit goes to 0, then delta f by delta x, which we said is the slope, will point to df by dx. So, we are writing this as df by dx which is the slope, the derivative of function f with respect to x. What does this represent? It represents the change off with x. Meaning the way your change is happening with f with x. And this is the limit of its delta x goes to 0. This ratio is del f by del x. We have called del f by del x. We can write it like this as well. fx plus delta x minus fx, which is the distance divided by the gap value minus fx. So, this is x plus delta x minus x. So, this slope depends on delta x goes to 0 If you want to approximate this by using the example So this is the example in which the Cp value at any temperature is derivative of h divided by dt H is the function in the case of idle gas and the function of temperature. Temperature is the only thing that depends on idle gas. So, Cp of ideal gas depends on temperature, and we can write it like this. Remember that we have also said that dH is Cp dt.

$$Z=z(x,y)$$

$$F=f(x)$$

$$\frac{df}{dx} = \lim_{\Delta x \to 0} \frac{\Delta f}{\Delta x} = \lim_{\Delta x \to 0} \frac{f(x+\Delta x) - f(x)}{\Delta x}$$

So, we are saying this. And normally Cp is also the function of temperature. So, if you change the temperature, then it means that your term is also going to change. The question is that you have to take out the Cp of AL, 300 K using the enthalpy data from the table. And you have to compare this with the value of Cp given in this condition. So, the value of CP is given at 300 K, 1.0. And in the textbook A2B is given. And you can take out the table again. you have the table in the book so now to remove it we have written the values of this table here 300 if you want because we don't have a function this function h as a function of t is not available so this is available no not available means no So what we have to do is, we have to take out Cp is equal to dH by dT. So, we have to take out this Cp is equal to dH by dT. We have to take this out at 300 Kelvin. Now what we are going to do is, we will approximate this as we did earlier. We did it here. So, we will approximate this. And this value will come out as. We are approximating del H on T and del T on 300. You take out delta H and divide it by delta T. Now, as we said that if we take delta T very small, then we can approximate it. that should be almost zero. So, let's say that if we take the difference of 5 K, it means that here we take 350 for 300, because we don't know how much of this we have to take out, but what we do is that we take one here for 295 and one for 305. Why do we take this? Because these values are given on the table. So, we took this one and this one. Now what is this? We have these values of enthalpy. which we have taken out of the table and presented here. We have shown that this enthalpy is at 305 and this is at 295. So, we can write it as H at 305K minus H at 295K divided by 305K minus 295K. And this value that you will plug in, so this is the value of the unit. You put the unit in it. Kilojoules per kg. And you put 10 Kelvin in it. So, this value is 1.005 exactly what we have given here. It means that the differential quantities that you have here, we can write it in the form of a difference. delta t will be taken very small. And if you see, this is the principle which is the final difference which is used in CFD, computational fluid dynamics, or anywhere where you talk about comsol, fluid mechanics, normally we talk about continuum medium, there is a common way to take differential in the form of difference which you can simulate numerically. So, this becomes the basis for This common thing is called the finite difference in numerical simulation. Take care. Let's move ahead.

Now let's talk about partial differentiation. The reason why we want to study partial differentiation is that in many systems, if there is a function or variable x, z which depends on x and y, then sometimes y is constant, and z is the change of x. So, in such a case, what will be the change in z with respect to x? The changes in this step are only one variable change. Rest are constant. We call it partial differentiation. We use the symbol delta. It is called del. Normally I will call it del.

$$z = z(x, y) \qquad\qquad x, y \text{ are independent}$$

$$dz = (\partial z)_x \ + (\partial z)_y$$
$$(\partial z)_y = dx, (\partial x)_y = dx$$

$$\Delta z = z(x + \Delta x, y + \Delta y) - z(x, y)$$

$$\Delta z = \frac{z(x + \Delta x, y + \Delta y) - z(x, y)}{\Delta x} + \frac{z(x, y + \Delta y) - z(x, y)}{\Delta y}$$

$$\lim \Delta x \to 0 \text{ and } \Delta y \to 0$$

$$\Delta z = (\frac{\partial z}{\partial x})_y dx + (\frac{\partial z}{\partial y})_x dy$$

Now we will talk about an example of this. Consider air is 300 Kelvin and 0.83-meter cube per kg. The state of the air changes from 300 K to 302 K. Its density changes from 0.86 to 0.87. per kg. If we consider this as a reference, that your mass is 1 kg, then your volume is changing from 0.86 to 0.87 or you can also say that this is not your specific volume. You can also say that. So, your specific volume is changing from 0.86 to 0.87. Now you have to tell me how much pressure you are under under. To remove this, you have to say that air is idle gas. And then you can write PV as RT. And we can write PV as equal to RT by V. V is your specific volume. Note that r is constant So we can say that p is a function of t and v Now we have to get dp out of here Because we have to get the change And we have to get the changes of dt and dv So what we have done now is del P by del V constant temperature dV from this equation you have seen here from this you will get del P by del T which is R by V what will come out? R by V dT because you will do differentiation so this will come out R by V and this will come out minus RT by V square dV. So, we will approximate dT as delta T because we are saying that it is very small. Changes are very small. And we will approximate dV as delta V. So, this is your 2 Kelvin. 302 minus 300. And this specific volume of del V is 0.87 to 0.8 0.6 to 0.87 meter cube per kg so this is your 0.01 meter cube per kg ok now you can plug it in ok and you know the value of R, gas constant you can take it out of the table so this comes out and then the first term of dp this term this comes out 0.66 0.491 kPa and the second one is 1.155 kPa this one comes out so finally your change is 0.491 kPa this is the dp this means the pressure is reduced this is the minus pressure is reduced how much is it reduced? 0.491 kPa is reduced due to its disturbance. Now you can see that if the temperature was constant, then the changes would have been 0.6. If the temperature was constant, then the first part would have been 0. The other part contributes. If the specific volume increases from 0.01, the pressure decreases to 1.155 kPa. If T was constant, So, what is del P? Del P is your minus 1.15 kilopascal If your volume was constant So, dp is 0.664 kPa. This increases. So, basically, this is your del P by T. This is your del P by V. And we are writing this as del P T plus del P V, as we have already shown. So now you understand how to use the total differential on the left-hand side and partial differential on the right-hand side.

$$z = z(x, y)$$

$$dz = (\frac{\partial z}{\partial x})_y dx + \ (\frac{\partial z}{\partial y})_x dy = Mdx + Ndy$$

$$(\frac{\partial M}{\partial y})_x = \frac{\partial^2 z}{\partial x \partial y} \ , (\frac{\partial M}{\partial x})_y = \frac{\partial^2 z}{\partial y \partial x}$$

For Exact differential equations,

$$(\frac{\partial M}{\partial y})_x = (\frac{\partial M}{\partial x})_y$$

Now let's talk about partial differential relations. So, we can write the total differential of z, x and y in partial differential form. If we consider this as m and this is n, we can write it as m dx plus n dy. And if we take this m as partial derivative, then it comes out as, suppose we take it from y, keeping x constant, then it comes out as del square z by del x del y. Because m is del z by del x It is given here and if you take this del m by del x keeping y constant Then it comes out as del z square del y del x So this is your second derivative, So this is your partial derivative of the first derivative This is a very important relation. If you see, this term and this term are equivalent if you can exchange it. If you exchange the order of differentiation, then it is the same. Then it will be equivalent. And this is what becomes important that the exact differentials in the properties, like the property of you depends on the intensity variable. So, these properties are in general exact. Its differentiation is normally exact. The total differentiation. And since it is a continuous point, in such cases, the order differential becomes immaterial. It doesn't matter. We can write it in any order. So, this exact differential has a definition. If we want to find out that the dZ is exact, the differential, we can write d. So, both the conditions should be satisfied. So, if you want to know that dz is exact then this condition will be there. So, this means that del m by del y x should be equal to del n by del x y. This is the condition. of differentiation. differential becomes immaterial it doesn't matter to us which we normally talk about the property in the thumbnail property because it is the exact differential. This is the basis of our study. Later we will study the Maxwell reduction. So, this is the basis, this is the basis, on this basis, we will try to find the maxwell equation.

$$z = z(x, y)$$

$$x = x(y, z)$$

$$dx = (\frac{\partial x}{\partial y})_z dy + (\frac{\partial x}{\partial z})_y dz$$

$$dz = (\frac{\partial z}{\partial x})_y dx + (\frac{\partial z}{\partial y})_x dy$$

$$dz = \left[\left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz\right]\left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$dz = \left[\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x\right] dy + \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z dz$$

Rearranging,

$$\left[1-\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_z\right]dz=\left[\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_z+\left(\frac{\partial z}{\partial y}\right)_x\right]dy$$

$$1-\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial z}\right)_y=0\rightarrow\left(\frac{\partial x}{\partial z}\right)_y=\frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

$$\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial z}\right)_y+\left(\frac{\partial z}{\partial y}\right)_x=0$$

$$\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial z}\right)_y=-\left(\frac{\partial z}{\partial y}\right)_x$$

$$\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial z}\right)_y=\frac{-1}{\left(\frac{\partial y}{\partial z}\right)_x}$$

$$\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x=-1$$

we call it cyclic relation Notice the reason behind this.

Verification of cyclic and reciprocity relation,

$$PV=RT\rightarrow P=\left(\frac{RT}{V}\right)$$

$$\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V=-1$$

$$V=V(P,T),V=\frac{RT}{P}\rightarrow(\frac{\partial V}{\partial T})_P=\frac{R}{P}$$

$$T=T(P,V),T=\frac{PV}{R}\rightarrow(\frac{\partial T}{\partial P})_V=\frac{V}{R}$$

$$\left(-\frac{RT}{V^2}\right)\left(\frac{R}{P}\right)\left(\frac{V}{R}\right)=-\frac{RT}{PV}=-1$$

So, your left-hand side is equal to right hand side. So, this is also proved. So, this cyclic relation and minus 1 relation are both. or inverse relation, which is called reciprocity relation. Both are very valuable in thermodynamic relations. And we can usually remember it easily. It's not difficult, it's just a normal mathematical function. So, you understood how to use total and partial differential to calculate the change in the properties. In the next lecture, we will talk about the Maxwell relation and move forward with this topic. See you in the next lecture. Till then, bye.