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

Week-10
Lecture-48
Thermodynamic Property Relations

Welcome to part 2 of the Thermodynamic Property Relations Lecture. In this lecture, we will discuss the concept of Thermodynamic Property Relations. In this lecture, we will learn about Maxwell relations which is an important part of thermodynamic relations. And many of the relations that have been made have been made using these Maxwell relations. So, we will learn about how they came out. Let's start. In thermodynamics, one of the most important requirements in thermodynamics is how to evaluate and find out. In the processes we usually have, we don't need exact property or absolute value. Most of the processes we usually do, we need a difference in property. But the problem is that we can't extract all the property through experiments. What we can extract is PVT and Cp minus Cv type of data. As I said, P, V, T, Cp, Cv, we can easily extract these data from experiments. But where we talk about H, U, S, all of these, which is a free energy or total energy, we cannot calculate it directly. For this, we will have to extract some other relations. But Our interest in Thermodynamic means to change these properties. This means that change in H, change in U, change in S is more valuable. We can solve problems with them in thermodynamic relations. As far as S is concerned, since you cannot control S in experiments, we try to replace S with other terms. Since S cannot be replaced directly, we will take out the same relation in Maxwell relation, in which we will connect PVT and S. it will be in the form of partial derivative. As we talked about last time, in the ideal gas, we got delta S. So, you must remember that if we go from P1, V1, T1 to this state, from here, if we go to P2, V2 to this state, then we can get delta S according to this.

$$\Delta s = \ C_p \ln\left(\frac{T_2}{T_1}\right) - Rln(\frac{P_2}{P_1})$$

$$\Delta s = \ C_v \ln\left(\frac{T_2}{T_1}\right) + Rln(\frac{V_2}{V_1})$$

$$\Delta s = \ C_p \ln\left(\frac{V_2}{V_1}\right) + C_v ln(\frac{P_2}{P_1})$$

Now,

$$dU = Tds - PdV$$

$$U = H - PV$$

$$dh = du + pdv + vdp$$

$$dh = TdS + VdP$$

$$\rightarrow dS = \left(\frac{1}{T}\right)dU + PdV; dS = \left(\frac{1}{T}\right)dh - VdP$$

$$dU = C_v dT; dH = C_p dT$$

$$dS = C_v\left(\frac{dT}{T}\right) + PdV; dS = C_p\left(\frac{dT}{T}\right) - VdP$$

if you take out the ideal gas relation then you will get this case in this case, you will get this. And you can also get the third relation from the other side. So, in a way, this relation is easily removed from the ideal gas because you have these expressions. But it is very difficult for real gas. Now, if we talk about S, then your function is like this. Let us say it is in T and P. So, this is what we are interested in. Because, usually, if you see, you can only control the temperature and pressure. If you take an isolated system, then S will not depend on this. Because S will typically depend on things like U and V. Because the first relation is coming out. So, from here, if you see here, is a function of u and v. But if you are interested in s is equal to tp, then if you take out its derivative ds, then you can write it as partial derivative. The exact derivative ds will be written as partial derivative. Similarly, you can write as if you are on TV, you can also draw a relation of this. As if you are on TV, you can also draw a relation of this. Now, if you look carefully, this term here, and if you compare it with the previous term, which we did here, If we compare this with this one, then we will see that the first term is del S by del T by p. So, if we compare this term with this, then this cp by T, this first term, should match with this. del S by del T P, this will come out as cp by T. You can show this if you take it on TV. This is Cp by T. Similarly, we can show that del S by del T which is V is Cv by T. So, this is a generic relation. CPp is normally related to H but you can also relate it to entropy. It comes in this form. So, this is a generic relation. There is no approximation of ideal gas in this. Now let's see. Now we will try to find out how to replace S in the parameters or properties that we can evaluate. For that we will take out the Maxwell relations. To understand that, first you have to understand what the different forms of thermodynamic potentials are. So, let's start with the closed system, in which we have already studied. So, we know that energy is del U is equal to dQ minus, and dU is equal to del Q minus del W. So, this is a closed system.

$$S = S(T,P) \rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T};\ \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$$

So, for closed system,

$$du = dq - dw$$

$$du = Tds - PdV$$

And if we consider it as quasi-equlibrium, static equilibrium, then we can write dQ as Tds and we can write it as PDV. So, this is the heat supplied to the system and what is del W? The work done by the system. So, here, as I said earlier, this means that U is equal to function of Sv. Okay? But as I said, S cannot be controlled. What does it mean? is called home-lord. We can't make a variable in the experiment; we can't control it in the experiment. But what we want is that what we can do is the temperature. So, if we want to replace it with S, V, TV, then what variable will we be able to find? So, let's find out this question, let's try to understand it. How is it? So, and this method we will use is the method of Legendary Transformation So the term is, for example, if we use usv to... We are converting the variable from S to T. So, the function change will be considered as A. Let's assume that A comes. Not U, but A will come. So, we will find out the relation between A and U. And this comes out is that U minus the variable we have to change is S minus, So U minus S multiplied A is equal to U minus S multiplied by the partial derivative of u with respect to which variable we want to change, and the rest is constant. So, the variable we are changing, as we are multiplying it with its partial derivative, its slope with respect to s, which we are keeping constant. And this value del u by del s what does this come out? Note that when we are taking this, we also have this. du is equal to Tds minus pdV in closed system. So, del u by del s at constant V is T. So, this is your T. So, this expression is U minus Sd. Now we will not prove how we can do this expression. How can you do this? I will not present the proof here, but you can see it in any textbook. This is mathematical proof. But it is very simple. You have to multiply the variable you want to change. Along with the slow partial derivative of that function. partial derivative of the function with respect to the variable we are changing. So, this is the function.

$$du = TdS - PdV$$

$$(\frac{\partial u}{\partial s})_V = T$$

$$a = u - s(\frac{\partial u}{\partial s})_V$$

$$a(T,V) = a = u - ST$$

$$a = u - TS$$

$$da = du - TdS - SdT$$

$$da = Tds - PdV - TdS - SdT$$

$$da = -PdV - SdT$$

$$h = h(S, P) \rightarrow g(T, P)$$

$$g = h - s(\frac{\partial h}{\partial s})_p$$

$$dh = TdS + VdP$$

Gibbs free energy,

$$g = h - TS; dg = dh - TdS - SdT$$

$$= TdS + Vdp - TdS - SdT$$

$$dg = Vdp - SdT$$

So,

$$dU = TdS - PdV$$

$$dh = TdS + PdV$$

$$da = -SdT - PdV$$

$$dg = -SdT + VdP$$

$$dZ = Mdx + Ndy$$

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

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

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

So, what happens is that here S and T means that instead of S we are using T. So, A will be the function. A is not changed, so V is constant. So, this is T, which we are seeing. Here, the partial derivative of S. So, this is the T term. So, A is the function of TV. So, this A is called Helmholtz potential. So, a is equal to u minus ST. You have noticed that when I am writing everything in small letters, what does it mean? It means that these specific values are given per unit mass, and we are dividing it. You can also multiply it later if you want, but it won't make any difference. It means that we can write like this also. You can also take it like this. But here I have written A is equal to U minus T s. Which has S small. Now you can also take out from here in its derivative form. So, let's try it. If we write dA is equal to dU minus T dS minus S dT. And what is dU? You take out from here dU. dU is T dS. minus PdV, minus TdS, minus SdT. So, this gets cancelled. So, this comes out. Minus SdT, minus PdV. So, this is your relation. Its differential form is Helmholtz free energy. Now, you can also do this, like we changed U from SV to TV. In the same way, we can write h in SP. Normally, when we talk about h, then your flow will be in the process. Okay? In this case, your h will be in SP. You can also see that if we talk about h, we have already taken out dh is equal to ds plus Vdp. So here you can see that h is close system is function of sp. Like this u as a close system is function of s or v. So, if we want to change this again, we have to change s to T or P. Means in terms of something which we can calculate measure. So again, we will apply the Legendre transformation rule. So, here I will change the color. Here we will get a function g. So, let's assume g is h What do we have to change? We have to change s. So how do we have to multiply s? The partial derivative h with respect to s. What will be the constant? P will be the constant. Now what will this value be? It will come out from here, which is given here. If we remove this now... del h by del s at constant p so what is this? t is the result so what is this? H minus ST so g is your function s minus st so your g is h minus ts and from here we will get dg is your dh minus Tds minus Sdt and dh is dh plus vdp minus ds, so this is cancelled so this is minus sdt plus vdp and what we call this g Gibbs free energy. here gives potential. Take care. give potential or give some potential. It is very important. Now, as we said, the way we did it, now you have two relations. One is A, and one is G. Now, what we can do, we can see the four relations. One is your relation dU dS This is your first clause. Then we introduced H for the definition of IJFLO process. In which we said that H is equal to U plus PV. PV is the workflow. TDS plus VDP came out of here. So, these two relations came out. Now we are talking about the closed system. There is no mass transfer here. If you want to do mass, then this additional term will come here. Which we will ignore now. We will not talk about this. Then we also took out in two terms. One is dA. So, you have 4 relations. This is in your U, H, A and G. This is called Thermodynamic Functions and Thermodynamic Potentials. This is your Helmholtz free energy or potential. This is your Gibbs free energy or potential. And these are all Gibbs relations, and we call these four in combined form Gibbs equations. Now, if we refer to the last lecture, we had defined an exact function. In which we had said that if you have a function like dz is equal to m dx plus n dy. And what is m in this? In this, your del z by del x constant y and this is your del z by del y. constant x. After that I told you to differentiate this. Del n by del y x. So, this will be del square z by del x del y. And this is your del n by del x y. This will be del square z by del y. Since these are continuous functions, the order of the relation will not matter. That's why we can write that del m by del yx by del yx. We did this in the last class. Now, if you apply this relation in all four expressions, what will come out? So, this is where your Maxwell relation will come out. Note that in all four equations, your S is there. So, we will write partial derivative S in the rest of the terms in PVT. We will do this expression. Let's start now. I will write this expression again. del A is equal to minus SdT minus PdV and del G is equal to minus SdT plus PdV. What will come out of this? You have to do partial derivative. del n by del x keeping y constant. So, m is the pre-factor, which is next to dx, m and this is n. So, we have to partial derivative this. So, in this case, if you do, then we start from here. What will come out in the first equation? on the other side is V, so del T by del V keeping X constant, this will be minus del P by del S keeping V constant. Do you understand? I hope you understand this thing. That del M is your first term, so in this case, what happened in the first equation? Mt is done, N is done, P is done, minus P is done. Because there is minus B in this, minus P is done. x is your s and y are your v. So, this is the first relation.

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

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

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

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

So, this is your Maxwell's relation. It is difficult to remember it, but you can easily do it. There are many methods in the book, I have told you some tricks to remember it. I particularly prefer that you can understand these 4 with fundamental equations and you can also do it in a minute. H is U plus PV. A is U minus TS and G is H minus TS. If you understand the relation, you can easily solve this problem. You can call this the first law. This is the first law. In dh, only these changes, the second term. This becomes VdP. In dA, both changes. and in dH, it changes from here. So, if you remember this relation, you can easily solve this. So, these are your four fundamental equations of Maxwell relations. Now we will try to understand this by using some examples. So, we will try to find out whether this expression is valid or not. So, we will write a relation to verify whether it is valid or not. The question is, verify the validity of the max relation for steam at 250 degrees Celsius and 300 kilo Pascal. So, it is asking whether your relation is valid or not. That means, whether the left-hand side is equal to the right-hand side or not. Check this particular data by looking at the table. Let's do it. Now, this relation is given to you specifically in partial derivative and temperature is fixed and pressure is fixed. So, if you, because there is no explicit relation, I mean, there is no equation of state of x or p, then in such a case, what can you do? You can approximate it, that del S by del P at T equal to 250 degrees Celsius. And we can write on the right-hand side that del V by del T at P equal to 300 KPa. If you look at the table, you can also take out the del S on the steam table. Because the temperature is 250 degrees, del S will be variable by pressure. So, the temperature is fixed, we are just changing the pressure. So, if you look at the pressure, 400 KPa. Because the pressure difference will come if we want to give 300 kPa. So, if we are talking about delta P, then it can be 400 minus 200. 300 kPa, which is given on the same table. We have not given 301, 302 or 299. The gap is very big. Still, we will try to use it to see if this relation is maintained or not. Even after such a big change. So, this S is 400 kPa. Let's take it here and this S will be. 200 kPa. And what is on the right-hand side? It is a minus. And delta T is here. Pressure is fixed. So how much delta T we will take? 250 kA. So here is the difference of 50 degrees Celsius. So, this is 300 minus 200 degrees Celsius. And this is your V 300 degrees Celsius. And this is V 200 degrees Celsius. Pressure of course is 300 kPa. So, if you enter this data, you will get 7.3804 minus 7.7100, this is your 200. And this left-hand side will come out as 0.00165-meter cube per kg per Kelvin. And the right-hand side came out as 0.87535 minus 0 71643 meter cube per kg and this is your 100 so this is minus 0.00159 meter cube per kg Kelvin ok so there is only 4% difference between this and this so you can understand that when we have taken such a big change this is a large finite quantity means it is not very small, it is large finite close agreement. So, this helps you understand that these relations are numerically valid. You can use it for table expressions. You can apply these kinds of problems to relations. You will understand it through examples. So, in today's lecture, we will stay here. In next lecture we will discuss about Clipper and other things till then I take your leave See you in next lecture