Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 13

Maxwell Relations, Properties of Gibbs Energy

Let us discuss today further on the power of thermodynamics. We have earlier developed some equations, some derivatives which can be used to connect one thermodynamic property with another thermodynamic property. Let us develop further on it and discuss Maxwell relations first and after that we will start discussing more about Gibbs free energy.

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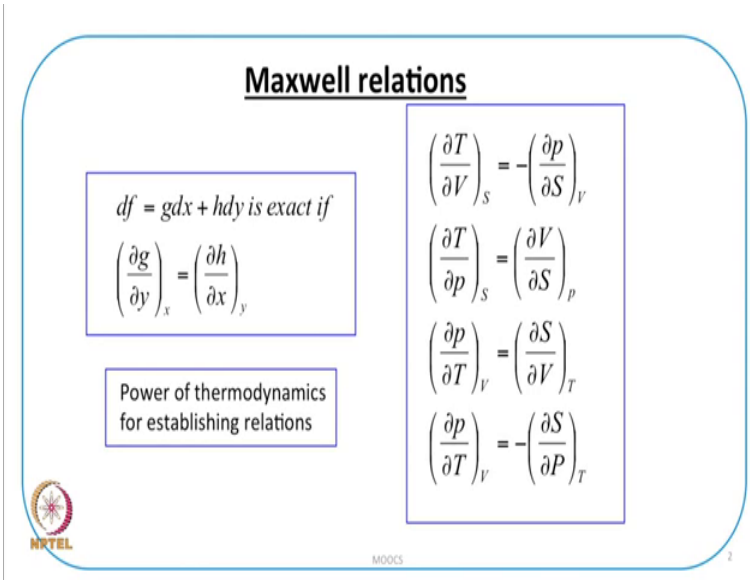

Maxwell relations

$df = gdx + hdy$ is exact if

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

Power of thermodynamics for establishing relations

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

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

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

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

Now, while discussing the Maxwell relations, we will make use of one mathematical fact that is d f if it is expressed like G d x plus h d y is exact; exact means if f is a state property, then d f is exact differential.

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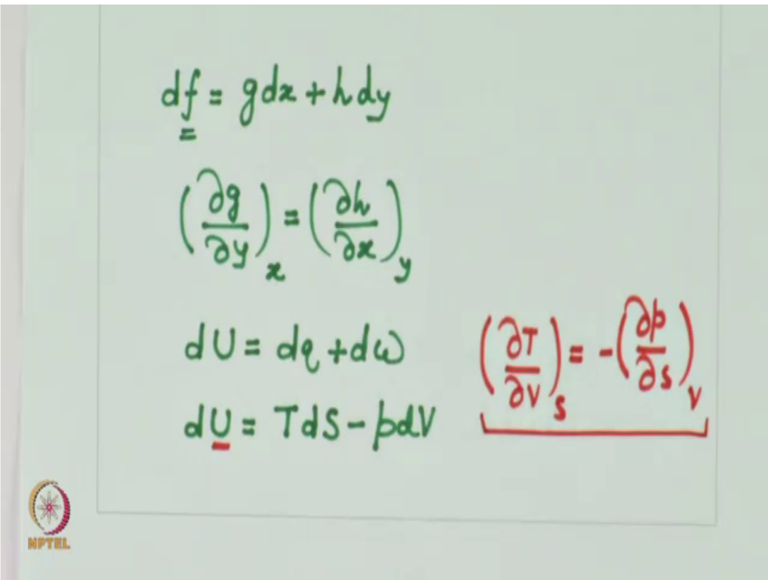

$$d\underline{\underline{f}} = g\,dx + h\,dy$$

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

$$dU = dq + d\omega$$

$$d\underline{U} = TdS - pdV$$

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

So, we say d f is equal to G d x plus h d y is exact if dou G dou y at constant x is equal to dou h dou x at constant y. So, these partial derivatives equality will hold if d f is equal to G d x plus h d y is exact. So, exact differentials once again I am repeating that d f is exact if f is a state property. Now, we will make use of this fact to derive Maxwell relations. Four Maxwell relations which you can see on the screen, the first Maxwell relation is dou T dou V at constant S is equal to minus dou p dou S at constant volume dou T dou p at constant S is equal to dou V dou S at constant pressure. This partial derivative dou p by dou T at constant volume is equal to dou S by dou V at constant temperature, and the final Maxwell relation dou p by dou T at constant V is equal to minus dou S by dou p at constant t. By looking at these four Maxwell relations, you can appreciate that what the power of these mathematical equalities is. These relations, this connects one thermodynamic property with another thermodynamic property without doing experiments.

Let us derive each one of these from the first law of thermodynamics. We had written d u is equal to d q plus d w and for a reversible change, I can write instead of d q, I can write d S minus p d v. So, now, we know that u is a state property. Therefore, d u is exact differential. So, I will make use of this fact that d f is equal to G d x plus h by h d y is exact if such relation holds. So, now by using this result, I will get first Maxwell relation from this because u is a state property and d u is exact differential. Therefore, from this I can write dou T by dou V at constant S is equal to minus dou p by dou S at constant v.

So, what I have done is I have made use of this result and since d u is equal to T d S minus p d V u e u is a state property, d u is exact. It will be exact if dou T by dou V at constant S is equal to minus dou p by dou S at constant v. So, here we derive the first Maxwell relation.

Similarly, we can use some other state properties and derive other Maxwell relations. Now, what are the other state properties? The other state properties we can think of is, one is equal to g, other is equal to other is h and one more state property that we can think of his Helmholtz free energy.

Let us use each one of those state properties. Let me start with since we are going to talk about Gibbs free energy.

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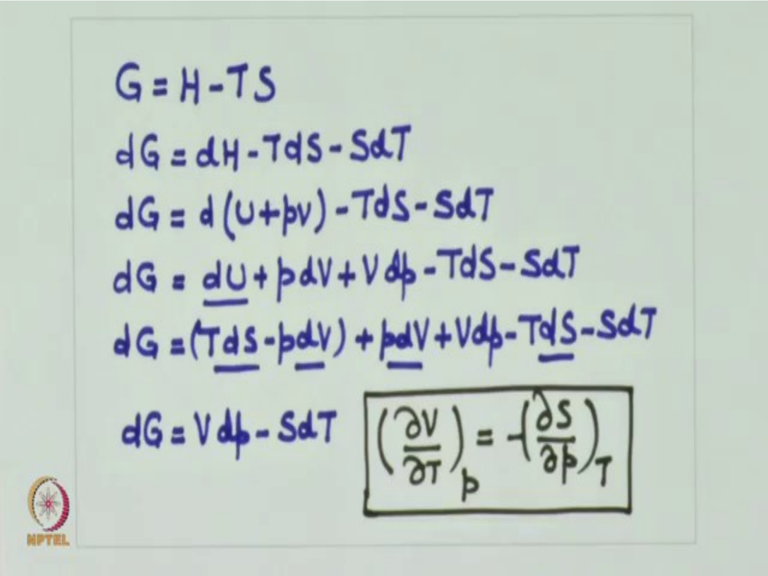

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dG = d(U + pV) - TdS - SdT$$

$$dG = \underline{dU} + pdV + Vdp - TdS - SdT$$

$$dG = (T\underline{dS} - p\underline{dV}) + \underline{pdV} + Vdp - Td\underline{S} - SdT$$

$$dG = Vdp - SdT \qquad \boxed{\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T}$$

Today that we next take up Gibbs function, G is equal to H minus TS. We know that. Therefore, d G is equal to d h minus T d S minus S d t. Let me further work on this. Instead of h, let me use u plus p V minus T d S minus S d t. Further d G is equal to d u plus p d V plus V d p minus T d S minus S d t. Now, let me expand d u. So, d G is equal to d u. We just discussed d u is equal to T d S minus p d v. This is d u and everything else I will write as such plus p d V plus V d p minus T d S minus S d t. So, T d S and T d S will get cancelled minus p d V plus p d V gets cancelled. So, what we have is, d G is equal to V d p minus S d T and keep in mind that so far we have been discussing the closed system, we are not allowing the composition to change. So, this equation that we develop d G is equal to V d p minus S d t, we will make use of this extensively today. Here again d d G is exact differential because G is a state property. So, therefore, by using that the mathematical expression that we discussed in the beginning for d f to be exact will write here. The next Maxwell relation that we can write from this is dou V by dou T at constant p is equal to minus dou S by dou p at constant T dou V by dou T at constant p is equal to minus dou S dou p at constant temperature.

So here we derive another Maxwell relation. Remember that the first Maxwell relation that we derived was based upon this state property internal energy. Now, we have derived based on the state property Gibbs free energy. Let us now next take up enthalpy.

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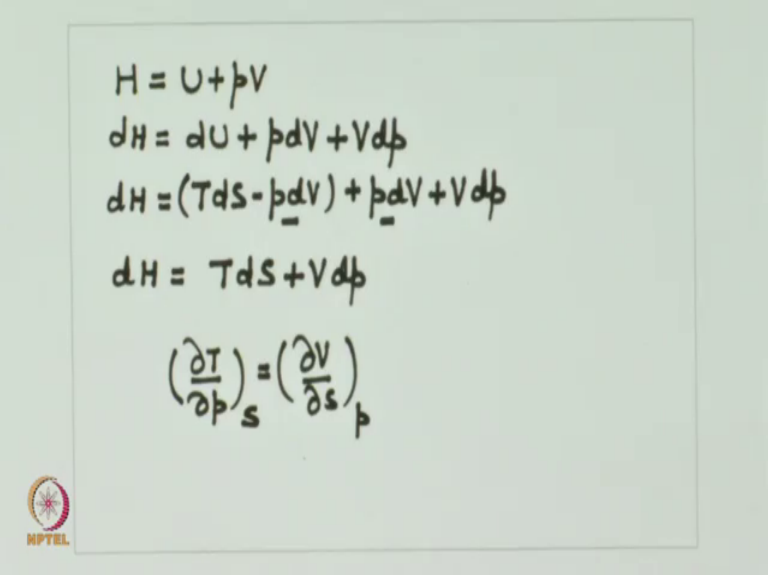

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$dH = (TdS - p\underline{d}V) + p\underline{d}V + Vdp$$

$$dH = TdS + Vdp$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Now, let me take up enthalpy. H is equal to u plus p v. I will just take up this and let see what do we get d h that is for a small change d u plus p d V plus V T p. Let us keep on going. D h is equal to for d u. I will write T d S minus p d v. This is for d u and everything else is same plus p d V plus V d p. Now, here this and this gets cancelled. So, I have d h is equal to T d S plus V d p. So, I can write another Maxwell relation from this, that is dou T by dou p at constant entropy is equal to dou V by dou S at constant pressure. So, here we have third Maxwell relations.

Now, let us derive the 4th Maxwell relation and that we will do by acting on Helmholtz free energy or Helmholtz function, that is let us start with a is equal to u minus T s. This is Helmholtz free energy or Helmholtz function.

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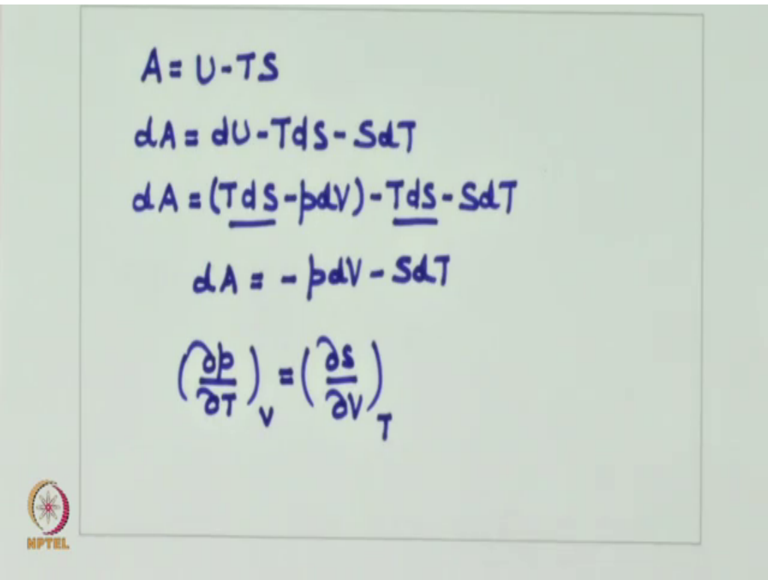

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$dA = (\underline{TdS} - p dV) - \underline{TdS} - SdT$$

$$dA = -p dV - SdT$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial s}{\partial V}\right)_T$$

So, I have d a is equal to d u minus T d S minus S d t. Let us expand for the d a for d u. I will write T d S minus p d V that is for d u minus T d S minus S d t. So, here this and this get cancelled. So, what I have is d A is equal to minus p d V minus S d t.

Now, this leads me to write the expression dou p by dou T at constant volume is equal to dou S by dou V at constant temperature. So, this is the 4th Maxwell relation. So, you see deriving the Maxwell relations is very easy. What we need to do is just pick up a state property and develop an equation in the form of d f is equal to G d x plus h d y and then, write the Maxwell relations. So, let us go back to the slide and take a look at all these four Maxwell relations and conclude that these four Maxwell relations are very important and demonstrate the power of thermodynamics for establishing relations. We will take up some examples during the tutorial sessions later on.

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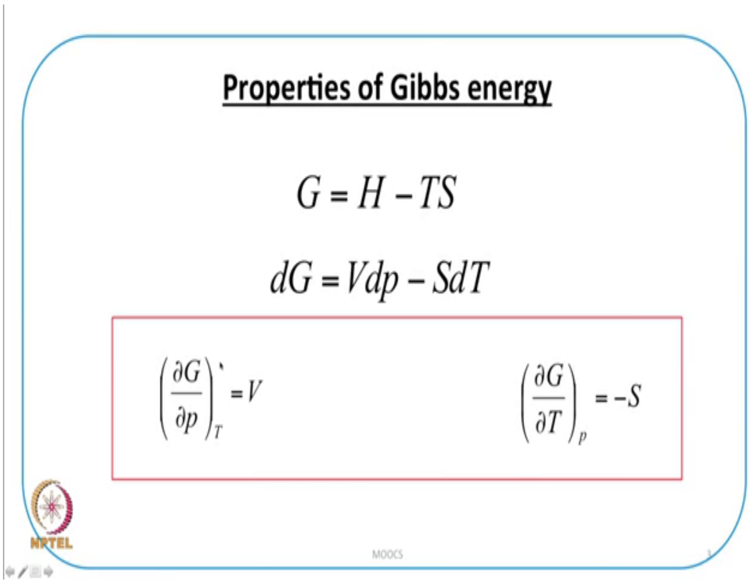

Properties of Gibbs energy

$$G = H - TS$$

$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

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Now, let us start discussing more on Gibbs free energy. Gibbs energy is very important. You remember that we have discussed the criteria of spontaneity d G at constant temperature and pressure less than zero. That is a very important criteria of spontaneity. Again and again I am saying because it is easy to work under constant temperature and pressure conditions. So, under laboratory conditions that is the most widely used criteria of spontaneity, we define Gibbs function of Gibbs free energy by G equal to h minus T S and we have just derived while deriving the Maxwell relations that d G is equal to V d p minus S d t. From this relation, now I can derive two more relations. One when I fix the pressure constant and second, when I fix the temperature constant and let us take a look at those. What are those? If you fix the temperature constant, this term goes away. So, then what you have is dou G by dou p at constant temperature is equal to v. This is what you get dou G by dou p at constant temperature equal to V and if you hold the pressure constant, then this d p term vanishes. You have dou G by dou T at constant pressure equal to minus s.

So, please recognize that what we can obtain from the variation in Gibbs energy with respect to pressure or variation of Gibbs energy with respect to temperature. These can prove to be very important thermodynamic relations because the first of these will give you the volume and second of these will give you the entropy. Both volume and entropy in their own terms can give lot of information. For example, as we will discuss later on the volume itself depends upon intermolecular interactions, the entropy depends on intermolecular interactions. I am only talking about intermolecular interactions at present, but there are many other factors which contribute to volume which contribute to entropy. Therefore, these derivatives can provide very useful information. Second thing let us try to recognize that based on these two relations, we can discuss the temperature dependence of Gibbs free energy, we can discuss the pressure dependence of Gibbs free energy and let us take both one by one.

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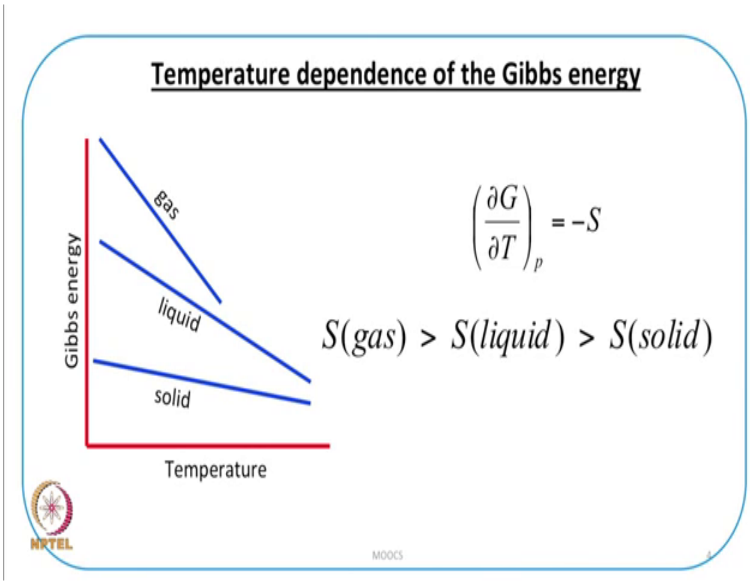

Temperature dependence of the Gibbs energy

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$S(gas) > S(liquid) > S(solid)$$

First let us take the temperature dependence of Gibbs energy. If you plot Gibbs energy versus temperature, this is the kind of variation one may get gas for liquid and for solid. An interesting observation in this figure is that the slope is negative the slope. Obviously because when you take a look at this mathematical expression, the slope of G versus t, the plot is minus S and entropy is always a positive quantity entropy itself cannot be negative. Therefore, minus S will be a negative quantity. So, you expect a negative slope that is what you see here.

However, the slope is most negative for gas followed by liquid and then followed by solid. What could be the reason for this change in slope that is the slope is maximum negative for gas followed by liquid followed by solid. The answer lies in this expression because the slope is dependent on the value of entropy and obviously, the entropy for a substance in the gaseous form will be highest because molecules are free to move around followed by that of liquid and followed by that of solid and this is the reason that you have a maximum negative slope for the gas followed by that for liquid and followed by that for solid.

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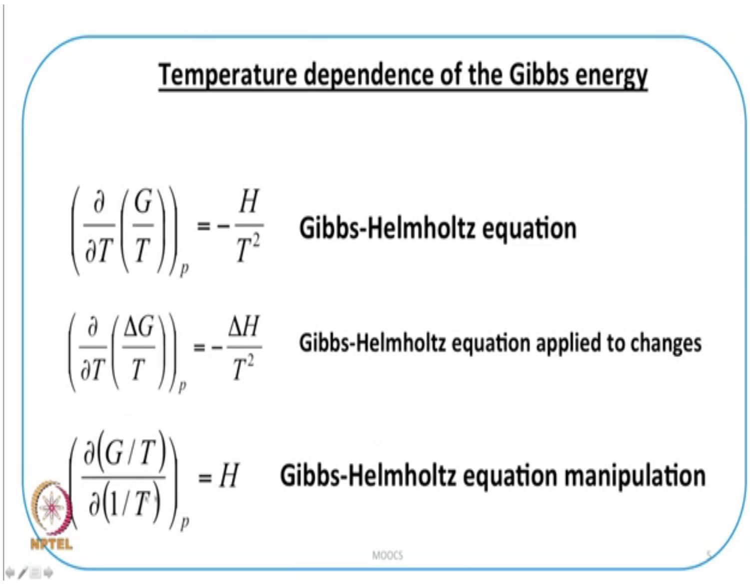

Temperature dependence of the Gibbs energy

$$\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = -\frac{H}{T^2}$$ **Gibbs-Helmholtz equation**

$$\left(\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right)_p = -\frac{\Delta H}{T^2}$$ **Gibbs-Helmholtz equation applied to changes**

$$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_p = H$$ **Gibbs-Helmholtz equation manipulation**

Now, let us discuss a little more on temperature dependence of Gibbs energy temperature. Dependence of Gibbs energy can give rise to very important thermodynamic relations. For example, Gibbs Helmholtz equation which is the temperature derivative of G by T at constant pressure is equal to minus h by T square, where h is enthalpy and if we extend Gibbs Helmholtz equation to changes. I will introduce delta with G and I will introduce delta with H, then it will imply for the changes delta G and delta h are very important thermodynamic quantities because delta G talks about the feasibility of the process and delta h is a content of delta g, but it is also reflecting on many things. For example, intermolecular interactions, it depends on the strength of the bond and many other factors that we can talk about. Let us first derive the first equation. It is very easy to derive.

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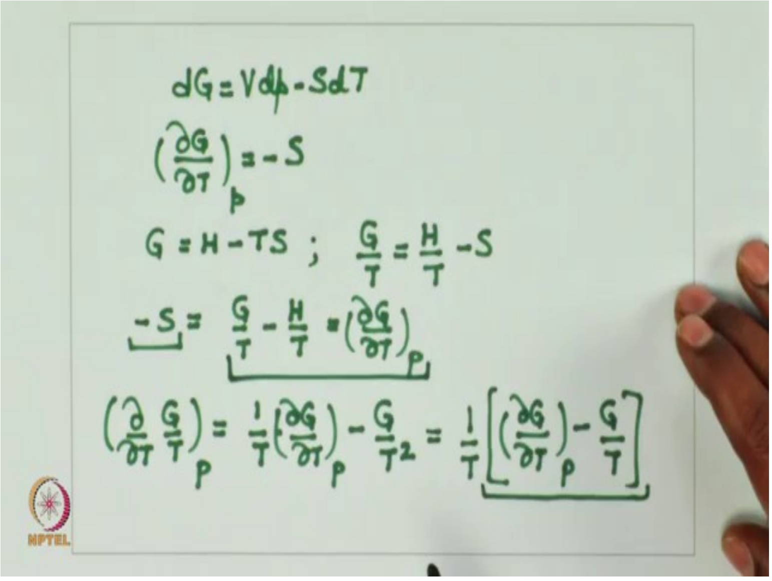

$$dG = V\,dp - S\,dT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$G = H - TS \;; \quad \frac{G}{T} = \frac{H}{T} - S$$

$$\underbrace{-S} = \underbrace{\frac{G}{T} - \frac{H}{T} = \left(\frac{\partial G}{\partial T}\right)_p}$$

$$\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = \frac{1}{T}\underbrace{\left[\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}\right]}$$

We have just derived an equation; the d G is equal to V d p minus S d t. We just derived and from this equation I can write dou G by dou T at constant pressure is equal to minus s.

Now, let me write G is equal to h minus T S and from this equation, I can further write G by T is equal to h by T minus S and further let me write like this minus S is equal to G by T minus h by T and this minus S is nothing, but dou G by dou T at constant pressure. Now, let me consider dou dou T of G by T because this is what I am interested in. Let us differentiate this. This is 1 by T into partial derivative of G with respective T at constant pressure minus G by T square which is equal to 1 by t. What we have now is dou G by dou T at constant pressure minus G by T and this information I can get from here, but we derived and let us now use this information what I have.

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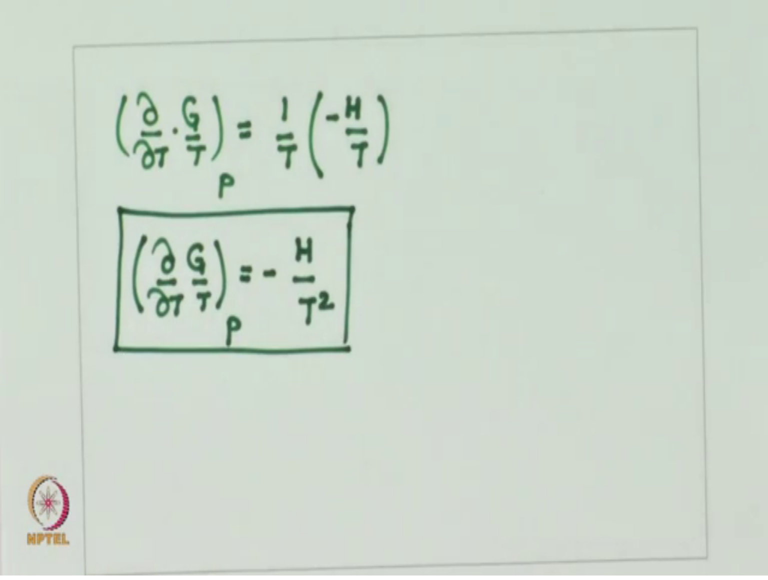

$$\left(\frac{\partial}{\partial T}\cdot\frac{G}{T}\right)_P = \frac{1}{T}\left(-\frac{H}{T}\right)$$

$$\boxed{\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_P = -\frac{H}{T^2}}$$

Now, this dou dou T of G by T at constant pressure is equal to 1 by T into if I use these two, what I get is dou G by dou T at constant pressure minus G by T is equal to minus h by t. So, I have minus h by t. So, now I get this equation dou dou T of G by T at constant pressure is equal to minus h by T square and this is what we wanted to derive. So, let us go back to the slide.

We have derived the dou dou T of G by T at constant pressure is minus h by T square. This is Gibbs Helmholtz equation and when you extend this Gibbs Helmholtz equation to changes, you can introduce delta and later on will let you know to use this equation for deriving very important thermodynamic properties when applied to equilibrium and equilibrium constant. We will discuss this when we talk about the equilibrium constant.

One can manipulate this Gibbs Helmholtz equation to express the derivative exclusively in terms of enthalpy. These are just a mathematical manipulation which you can try yourself, but what is important to note in this discussion is that the temperature dependence of Gibbs free energy gives very useful information. What we have shown here is that the partial derivative of G by T with respect to temperature at constant pressure is connected to a very important thermodynamic property which is enthalpy. So, temperature dependence of Gibbs free energy can be used to get information on the enthalpy of the reaction and the enthalpy of the reaction is a very important thermodynamic quantity because the enthalpy of the reaction not only gives information about the intermolecular interaction, but it is a very important part of the overall value of delta G which decides this continuity of a process. So, therefore, these equations which connect free energy temperature dependence with enthalpy can provide very useful information which we will further discuss while discussing numerical problems.

Thank you very much.