Thermodynamics for Biological Systems:
Classical and Statistical Aspects

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Lecture – 39
Clausius Clapeyron Equation

Welcome!

Let us, begin to look at one of the fundamental relationships, when we consider phases in equilibrium, especially, when transitions between phases takes place. That is called the Clausius-Clapeyron equation. We are going to start doing this, and let us see how far we get today.

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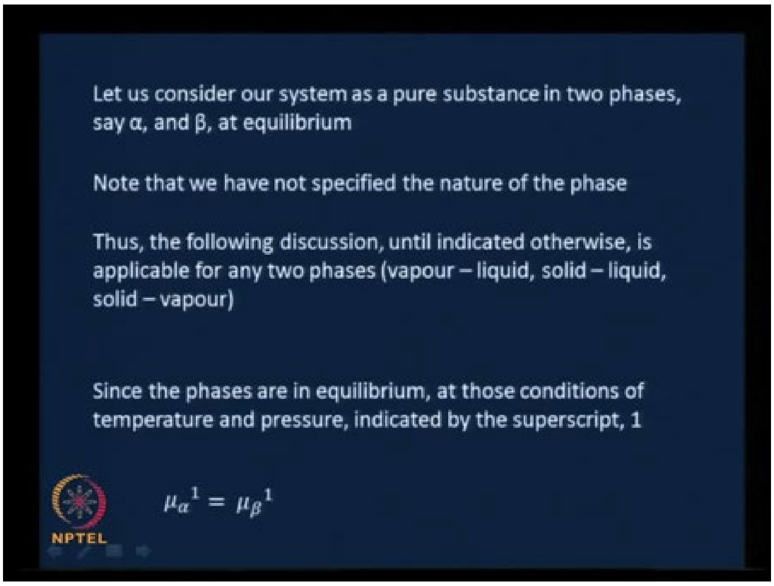

Let us consider our system as a pure substance in two phases, say α, and β, at equilibrium

Note that we have not specified the nature of the phase

Thus, the following discussion, until indicated otherwise, is applicable for any two phases (vapour – liquid, solid – liquid, solid – vapour)

Since the phases are in equilibrium, at those conditions of temperature and pressure, indicated by the superscript, 1

$$\mu_\alpha{}^1 = \mu_\beta{}^1$$

Let us consider our system as a pure substance. We will start with pure substances. That is a good to understand the basis. Let us consider our system as a pure substance in two phases, say alpha and beta at equilibrium. What I would like you to note is, that we have not specified the nature of the phase. These alpha and beta could be any 2 phases. They could be liquid and vapour phase, liquid and solid phase, vapour and solid phase. That is what is given here: The following discussion, unless indicated otherwise, is applicable for any 2 phases … they could be vapour-liquid, solid-liquid, solid-vapour. Since the phases are in equilibrium at those conditions of temperature and pressure, which we will indicate by the superscript, 1, we can certainly write from the condition of equilibrium, you know the first 5 equations, equations 5.1 to 5.5 and so on, mu alpha at the conditions specified by the temperature and pressure – we will indicate that by 1 – must equal mu beta, which is a chemical potential of a pure component in the other phase, in the beta phase. That is, the chemical potential of the pure component in the alpha phase at certain conditions of temperature and pressure must equal the chemical potential of the same component in the beta phase at the same conditions of temperature and pressure. This automatically comes from the condition of equilibrium.

$$\mu_\alpha{}^1 = \mu_\beta{}^1$$

Let us call this equation 5.8.

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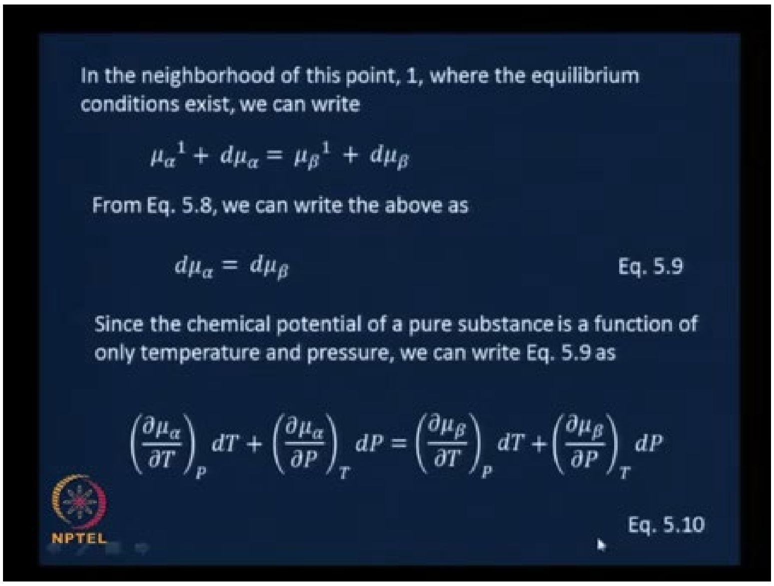

In the neighborhood of this point, 1, where the equilibrium conditions exist, we can write

$$\mu_\alpha{}^1 + d\mu_\alpha = \mu_\beta{}^1 + d\mu_\beta$$

From Eq. 5.8, we can write the above as

$$d\mu_\alpha = d\mu_\beta \qquad \text{Eq. 5.9}$$

Since the chemical potential of a pure substance is a function of only temperature and pressure, we can write Eq. 5.9 as

$$\left(\frac{\partial\mu_\alpha}{\partial T}\right)_P dT + \left(\frac{\partial\mu_\alpha}{\partial P}\right)_T dP = \left(\frac{\partial\mu_\beta}{\partial T}\right)_P dT + \left(\frac{\partial\mu_\beta}{\partial P}\right)_T dP$$

Eq. 5.10

In the neighborhood of this point, which means a very small region around this point, mathematically speaking, where the equilibrium conditions can be considered to exist. You know it is a hypothetical situation here, but, we need the concept of neighborhood to completely develop this particular concept. Therefore, in the neighborhood of this point where the equilibrium conditions can still be considered to exist, we can write mu alpha 1 plus d mu alpha – that is a change from the point 1, in the neighborhood of point 1,

$$\mu_\alpha{}^1 + d\mu_\alpha = \mu_\beta{}^1 + d\mu_\beta$$

Of course, from 5.8 the previous equation, we know that mu alpha 1 equals mu beta 1. Therefore, they can be cancelled. Therefore, the differential of mu alpha equals the differential of mu beta.

$$d\mu_\alpha = d\mu_\beta$$

Let us call that equation 5.9.

Since the chemical potential of a pure substance is a function of only temperature and pressure, we can write equation 5.9 in terms of the expanded functionalities. You know this is the total differential; writing it in terms of partial differentials, from the theorem in mathematics,

$$\left(\frac{\partial \mu_\alpha}{\partial T}\right)_P dT + \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T dP = \left(\frac{\partial \mu_\beta}{\partial T}\right)_P dT + \left(\frac{\partial \mu_\beta}{\partial P}\right)_T dP$$

Let us call this equation 5.10.

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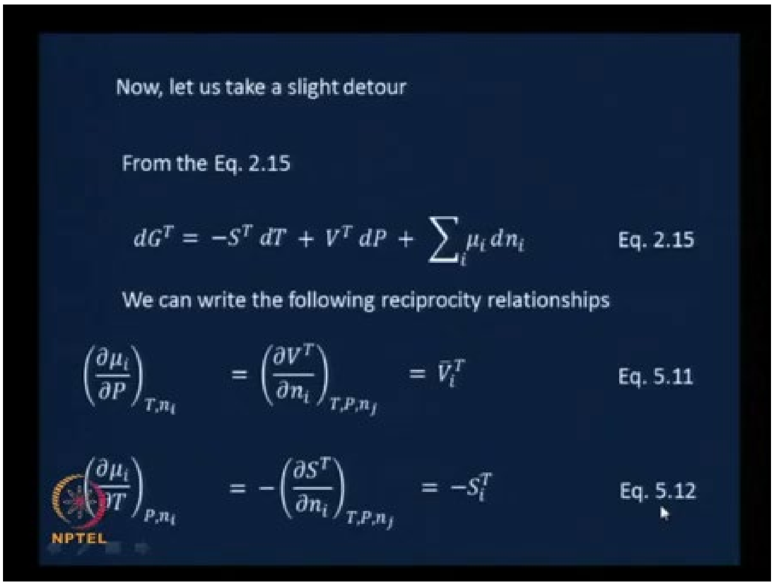

Now, let us take a slight detour

From the Eq. 2.15

$$dG^T = -S^T dT + V^T dP + \sum_i \mu_i dn_i \qquad \text{Eq. 2.15}$$

We can write the following reciprocity relationships

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V^T}{\partial n_i}\right)_{T,P,n_j} = \bar{V}_i^T \qquad \text{Eq. 5.11}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial S^T}{\partial n_i}\right)_{T,P,n_j} = -S_i^T \qquad \text{Eq. 5.12}$$

Now, let us take a slight detour to establish a few things, and then we will come back to our 2 phases and so on. From equation 2.15, 2 15 that we saw earlier, in the module number 2,

$$dG^T = -S^T dT + V^T dP + \sum_i \mu_i dn_i$$

This is the equation 2.15 that we saw earlier.

Recall the reciprocity relationships that we, again, saw in the second module. Following the reciprocity relation … rather doing the reciprocity relationship for equation 2.15, the following relationships can be written.

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,\ n_i} = \left(\frac{\partial V^T}{\partial n_i}\right)_{T,\ P,\ n_j} = \bar{V}_i^T$$

Let us call this equation 5.11.

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,\ n_i} = -\left(\frac{\partial S^T}{\partial n_i}\right)_{T,\ P,\ n_j} = -\bar{S}_i^T$$

We will call this equation 5.12.

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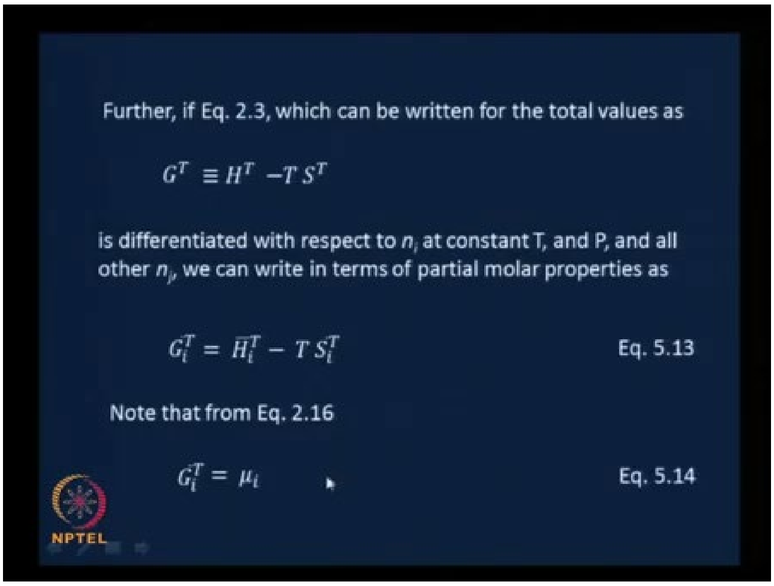

Further, if Eq. 2.3, which can be written for the total values as

$$G^T \equiv H^T - T\,S^T$$

is differentiated with respect to n_i at constant T, and P, and all other n_j, we can write in terms of partial molar properties as

$$\bar{G}_i^T = \bar{H}_i^T - T\,\bar{S}_i^T \qquad \text{Eq. 5.13}$$

Note that from Eq. 2.16

$$\bar{G}_i^T = \mu_i \qquad \text{Eq. 5.14}$$

Further, if equation 2.3, which can be written for the total values as

$$G^T \equiv H^T - T\,S^T$$

This is the definition of Gibbs free energy, and we are writing this for the total values … you know … not for a single mole. If this is differentiated, with respect to n i at constant T and P and all other n j s, we can write in terms of partial molar properties as

$$\bar{G}_i^T = \bar{H}_i^T - T\,\bar{S}_i^T$$

We are differentiating each term with respect to n i at constant T, P, and n j, and by definition that derivative would be G i T hash. By definition, this derivative would be H i T hash, and this one would be minus T S i T hash. We will call this equation 5.13. And, from equation 2.16, we get

$$\bar{G}_i^T = \mu_i$$

partial molar property with respect to the single mole there. Therefore, we get it equal to mu i.

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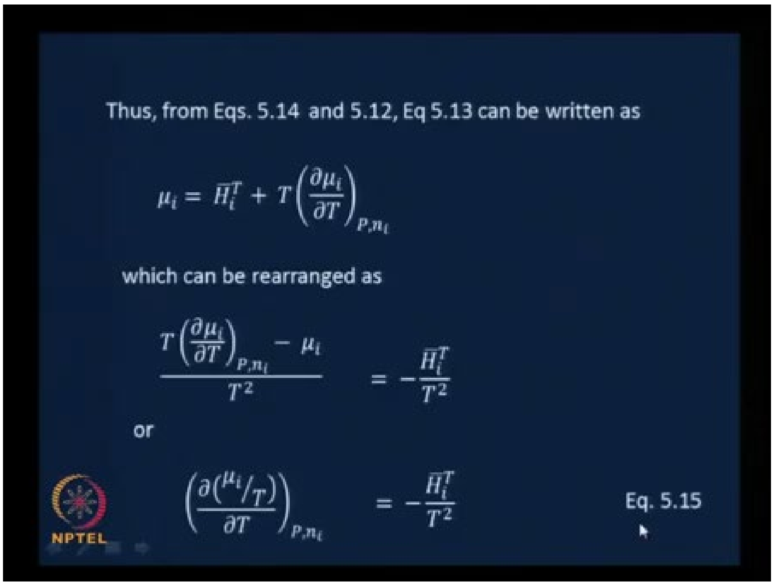

Thus, from Eqs. 5.14 and 5.12, Eq 5.13 can be written as

$$\mu_i = \bar{H}_i^T + T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i}$$

which can be rearranged as

$$\frac{T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} - \mu_i}{T^2} = -\frac{\bar{H}_i^T}{T^2}$$

or

$$\left(\frac{\partial(\mu_i/T)}{\partial T}\right)_{P,n_i} = -\frac{\bar{H}_i^T}{T^2} \qquad \text{Eq. 5.15}$$

Therefore, from equations 5.14 and 5.12, equation 5.13; from 5.14 and 5.12; 5.14 is this: G i T hash equals mu i. and 5.12 was this, which we obtained from the reciprocity relationship. From these two equations, we can write

$$\mu_i = \bar{H}_i^T + T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,\ n_i}$$

Which can be rearranged as … I am just rearranging this by T dou mu i dou T at constant P, n i minus mu i , and I am dividing this by T squared is nothing but, minus H i – now I have taken this to the other side – minus H i T hash by T squared. Just a rearrangement. There is the reason for this rearrangement. …

$$\frac{T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,\, n_i} - \mu_i}{T^2}$$

The reason for this rearrangement is this: This form is nothing but

$$\left(\frac{\partial\left({}^{\mu_i}/_{T}\right)}{\partial T}\right)_{P,\, n_i} = -\frac{\bar{H}_i^T}{T^2}$$

If you are unable to see this, consider this as u by v, or numerator by denominator. Denominator function into derivative of the numerator function minus the numerator function into derivative the denominator function, which is 1 here, divided by the square of the denominator function and that is the derivative. dou mu i by T dou T at constant P, n i equals minus H i T hash by T squared. We will call this equation 5.15.

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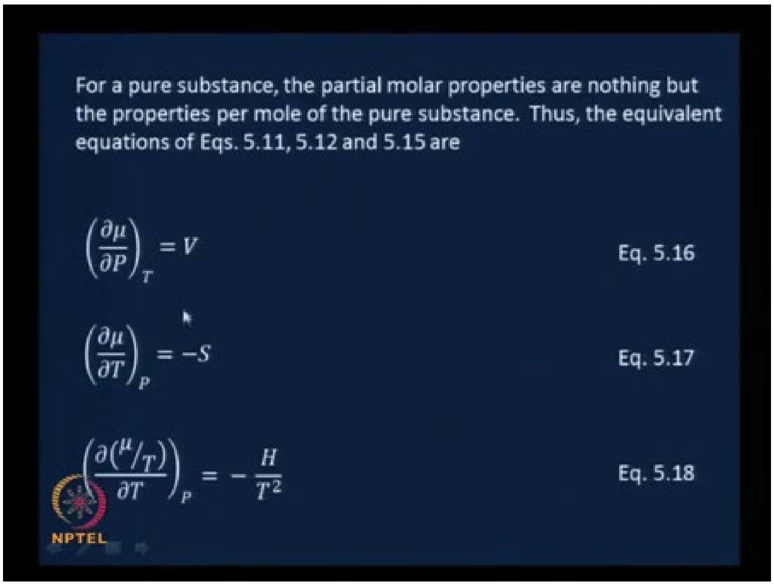

For a pure substance, the partial molar properties are nothing but the properties per mole of the pure substance. Thus, the equivalent equations of Eqs. 5.11, 5.12 and 5.15 are

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V \qquad \text{Eq. 5.16}$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S \qquad \text{Eq. 5.17}$$

$$\left(\frac{\partial\left({}^{\mu}/_{T}\right)}{\partial T}\right)_P = -\frac{H}{T^2} \qquad \text{Eq. 5.18}$$

For a pure substance, the partial molar properties are nothing but the properties per mole of the pure substance. You know the kind of coalesce into each other. Thus the equivalent equations of 5.11, 5.12 and 5.15 … you know, when we write down the equations, you can recall those, or you can go back and check what 5.11 5.12 and 5 15 are

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V$$

equation 5.16.

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S$$

equation 5.17.

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

equation 5.18. Our 5.11 was when you had i here and V i T hash here. 5.12 was you had a i here and S i T hash here. And you had to take other n also as constant. And here, you had i and H i T hash here, and P and other n s to be constant here.

Therefore, since these are written for a single mole of the pure substance, we can drop all these i s, and hashes, and so on because, the partial molar property becomes the property per mole of the pure substance.

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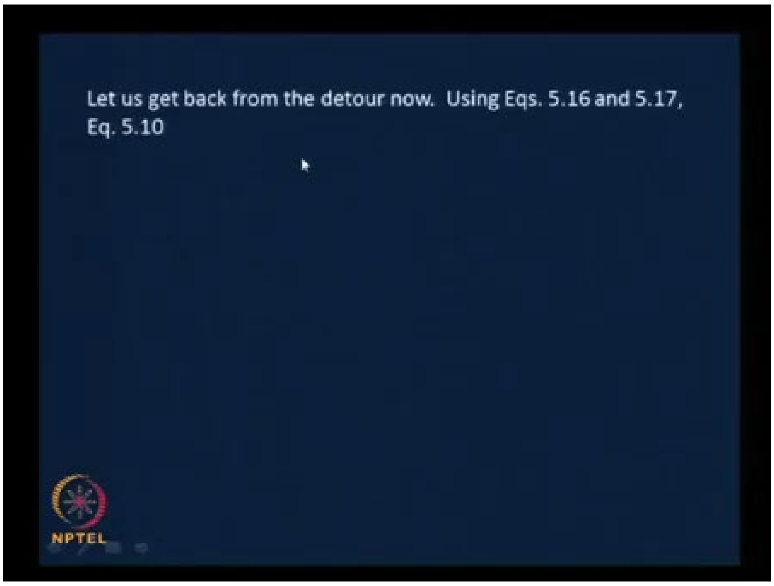

Let us get back from the detour now. Using Eqs. 5.16 and 5.17, Eq. 5.10

What we will do, when we begin the next class is we will get back from this detour. We essentially wanted to come up with these relationships, and that is why we took a detour. When we begin the next class, we will get back to considering the 2 phases in equilibrium and the process of transfer from one phase, or transition from one phase to another, which is the context of the Clausius-Clapeyron equation.

See you in the next class.