Thermodynamics for Biological Systems:
Classical and Statistical Aspects

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Lecture - 8
Gibbs Duhem Equation

Welcome!

Let us, now look at something called a Gibbs-Duhem equation. This is a fundamental equation in Classical Thermodynamics. And, as we go along, let us see the features of that. But, now let us derive the Gibbs-Duhem equation.

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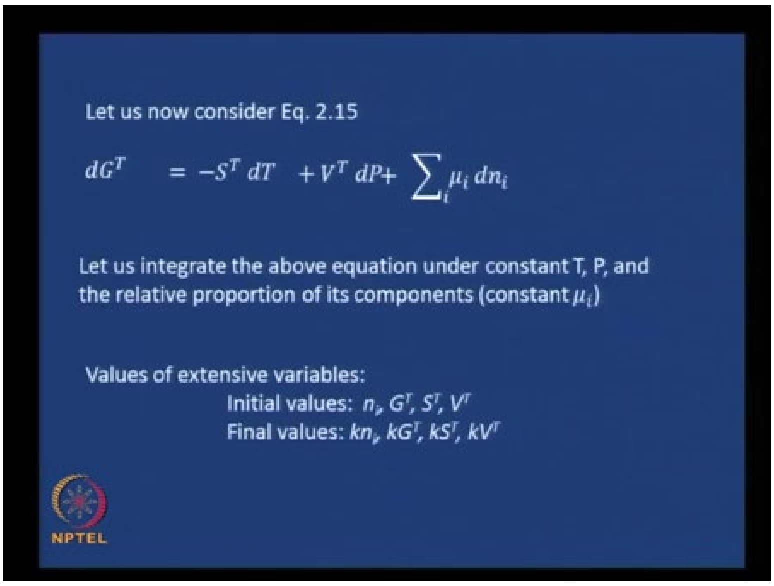

Let us now consider Eq. 2.15

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

Let us integrate the above equation under constant T, P, and the relative proportion of its components (constant μ_i)

Values of extensive variables:

Initial values: n_i, G^T, S^T, V^T

Final values: kn_i, kG^T, kS^T, kV^T

Let us consider equation 2.15.

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

Now, this is a differential. Let us integrate this equation at constant T and constant P. If it is constant T, this term will completely vanish. And, if it is constant P, this term will completely vanish. And, also let us retain the relative proportions of the components in the system, while we are integrating the equation; which means the mu i's are also being held constant. Integration can be viewed as increasing the size … under the same conditions as the small aspect that we initially looked at. Therefore, if the initial values where n i, G T, S T and V T of the system; the final values where it is integrated or it has been made big could be k n i, k G T, k S T and k V T. The values have increased k… It is quite easy to see. These are all extensive quantities. If you have k number of moles, the other variables are going to increase k times and therefore, it is quite valid to write this. And, we are viewing the integration as increasing the size of the system.

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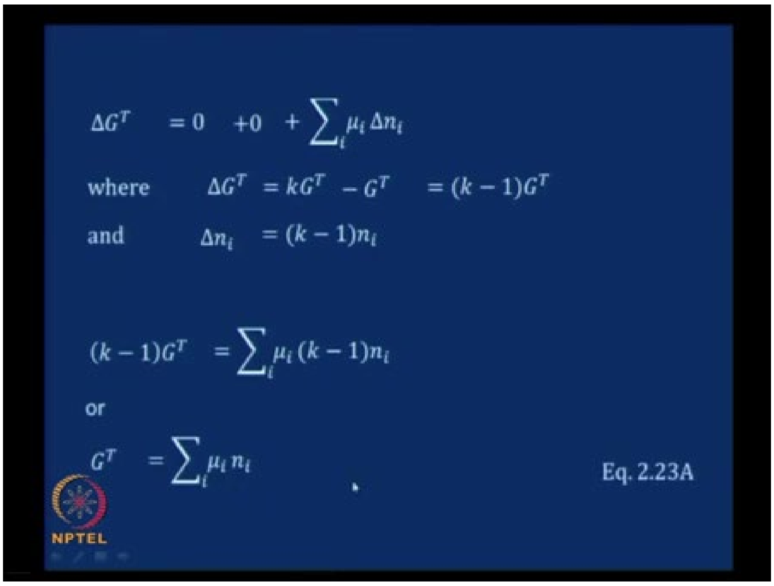

$$\Delta G^T = 0 + 0 + \sum_i \mu_i \Delta n_i$$

where $\Delta G^T = kG^T - G^T = (k-1)G^T$

and $\Delta n_i = (k-1)n_i$

$$(k-1)G^T = \sum_i \mu_i (k-1) n_i$$

or

$$G^T = \sum_i \mu_i n_i$$

Eq. 2.23A

We are looking at this integration as increase in the size of the system. Initially it had, let say one mole and it is now going to k moles. And therefore, the values of the extensive variables, initially, were, let us say n i number of moles, G T the total Gibbs free energy, S T the total entropy and V T the total volume to the final values, which is k times that of the initial values. Now, if we do that, the delta G T, which is the integrated value, the difference between the values of two states, say 1 and 2, delta G T equals; since, we had taken at a constant temperature, the first term turns to 0; at constant pressure, the second term goes to 0. And, the third term, summation of mu i delta n i,

$$\Delta G^T = 0 + 0 + \sum_i \mu_i \Delta n_i$$

where

$$\Delta G^T = kG^T - G^T = (k-1)G^T$$

Remember, I mentioned about the difference between the final value and the initial value. And therefore, which can be, it can be written as k minus 1 times G T. And, our delta n i is nothing but k times n i minus n i, which can be written as k minus 1 times n i.

$$\Delta n_i = (k-1)n_i$$

Substituting these values back into the integrated expression,

$$(k-1)G^T = \sum_i \mu_i \, (k-1)n_i$$

$(k-1)$ can be taken out and cancelled.

$$G^T = \sum_i \mu_i \, n_i$$

Let us call this equation 2.23A.

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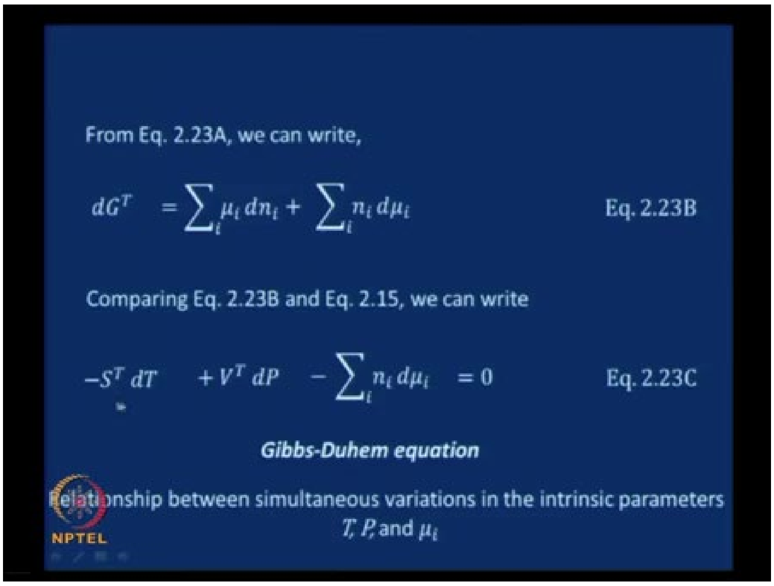

From Eq. 2.23A, we can write,

$$dG^T = \sum_i \mu_i \, dn_i + \sum_i n_i \, d\mu_i \qquad \text{Eq. 2.23B}$$

Comparing Eq. 2.23B and Eq. 2.15, we can write

$$-S^T \, dT + V^T \, dP - \sum_i n_i \, d\mu_i = 0 \qquad \text{Eq. 2.23C}$$

Gibbs-Duhem equation

Relationship between simultaneous variations in the intrinsic parameters T, P, and μ_i

From that equation, G … delta G equals summation of mu i n i. If we take the total differential of that expression, we get d G T equals mu i d n i, the first term; the first function into the derivative of the second function, but at sum over all terms. Therefore, this will just be a sum; plus the other part of the differential in the chain rule, n i times d mu i.

$$dG^T = \sum_i \mu_i \, dn_i + \sum_i n_i \, d\mu_i$$

Let us call that equation 2.23B.

If i compare 2.23B with 2.15 and like you to compare yourself, we can write minus S T d T plus V T d P minus summation of n i d mu i. If you substitute the expression for d G T and cancel the common terms here, we get minus S T d T plus V T d P minus summation of n i d mu i. This mu i d n i will get cancelled with … of mu i d n i, which appears in d G T and that equals 0.

$$-S^T\, dT + V^T\, dP - \sum_i n_i\, d\mu_i = 0$$

Let us call that equation 2.23C. This equation is called the Gibbs-Duhem equation.

Note, although we, while deriving this equation, we had made assumption about constancy of temperature and constancy of pressure, the final equation that we have is in terms of state variables. What is a state variable mean; its value depends only on the state of these systems and not on the path taken to reach the two states. A constant temperature process or constant pressure process are all paths between the same two states. Therefore, whatever had been the path, say a constant temperature and a constant pressure and so on and so forth, this final equation here is valid for all conditions because they are in terms of the state variables. Note the variables… here S T the total entropy, which is a state function, temperature state function; V T, it is a state function; P, a pressure state function; n i, the number of moles depends on the state; mu i, definitely it depends on the state. Therefore, this is an equation of all state variables. Therefore, this is valid in general.

Also, note that, this equation is the relationship between simultaneous variations in the intrinsic parameters. That is what makes this equation special. This is temperature; this is pressure; this is chemical potential; d T, the variation in temperature; d P, the variation in pressure; and d mu i, the variation in chemical potential. And, this equation gives us a nice relationship, when all three are varied simultaneously. That is … another special thing about the Gibbs-Duhem equation.

See you in the next class.