Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture - 7
Chemical Potential

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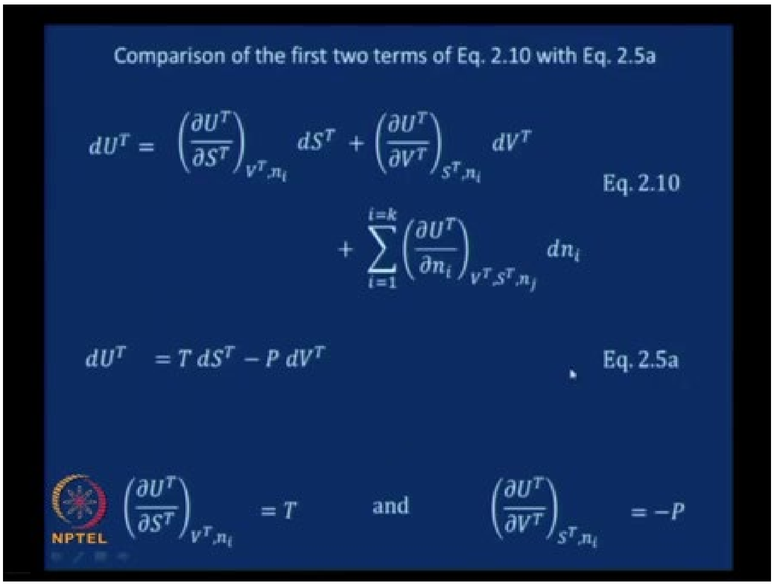

Comparison of the first two terms of Eq. 2.10 with Eq. 2.5a

$$dU^T = \left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i} dS^T + \left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,n_i} dV^T + \sum_{i=1}^{i=k}\left(\frac{\partial U^T}{\partial n_i}\right)_{V^T,S^T,n_j} dn_i \quad \text{Eq. 2.10}$$

$$dU^T = T\,dS^T - P\,dV^T \quad \text{Eq. 2.5a}$$

$$\left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i} = T \quad \text{and} \quad \left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,n_i} = -P$$

Welcome!

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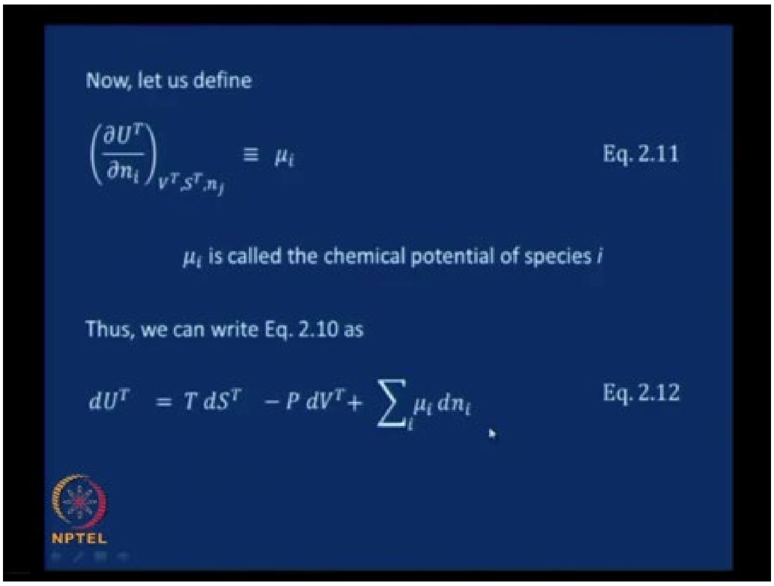

Now, let us define

$$\left(\frac{\partial U^T}{\partial n_i}\right)_{V^T,S^T,n_j} \equiv \mu_i \quad \text{Eq. 2.11}$$

μ_i is called the chemical potential of species i

Thus, we can write Eq. 2.10 as

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i \quad \text{Eq. 2.12}$$

Let us look at this quantity a little more closely. dou U T by dou n i at constant V T, S T, n j. Let us define that quantity dou U T by dou n i at constant V T, S T, n j as something called mu i; where mu i is actually called the chemical potential of species i.

$$\left(\frac{\partial U^T}{\partial n_i}\right)_{V^T,\ S^T,\ n_j} \equiv \mu_i$$

Note this term chemical potential. This is going to be a very important intrinsic variable in this entire course. So, please take a note of this. We will call this equation as 2.11. Therefore, in terms of, whatever we have defined just now, the chemical potential; we can write our equation 2.10 that we saw earlier as

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i$$

We will call this equation 2.12. So, that was for internal energy.

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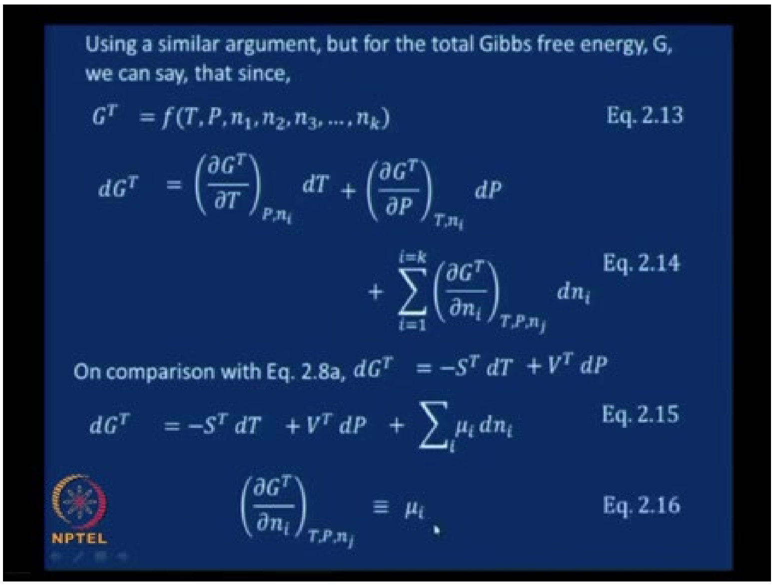

Using a similar argument, but for the total Gibbs free energy, G, we can say, that since,

$$G^T = f(T, P, n_1, n_2, n_3, \ldots, n_k) \qquad \text{Eq. 2.13}$$

$$dG^T = \left(\frac{\partial G^T}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G^T}{\partial P}\right)_{T,n_i} dP + \sum_{i=1}^{i=k} \left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} dn_i \qquad \text{Eq. 2.14}$$

On comparison with Eq. 2.8a, $dG^T = -S^T\,dT + V^T\,dP$

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

$$\left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} \equiv \mu_i \qquad \text{Eq. 2.16}$$

Let us follow a similar argument for the total Gibbs free energy, G. G T, we know … Rather, let us take G T as a function of temperature, pressure and all the number of moles of the components; so, n 1, n 2 till n k;

$$G^T = f(T, P, n_1, n_2, n_3, \ldots, n_k)$$

equation 2.13. Therefore, the total differential G T; d G T can be written as

$$dG^T = \left(\frac{\partial G^T}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G^T}{\partial P}\right)_{T,n_i} dP + \sum_{i=1}^{i=k} \left(\frac{\partial G^T}{\partial n_i}\right)_{T,\ P,\ n_j} dn_i$$

We will call this equation 2.14.

If we compare this 2.14 with 2.8a, which for pure component system or a single component system

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

We can write d G T equals minus S T d T plus V T d P plus the remaining term, which comes in for the multi-component case, since, we have for a multi-component case, G T to be a function of all other components also … the amounts of components also. So, we have this extra term here. Summation of mu i d n i. We will call this equation 2.15. Let us define

$$\left(\frac{\partial G^T}{\partial n_i}\right)_{T,\ P,\ n_j} \equiv \mu_i$$

as mu i itself. Somebody can ask me this question now. You had earlier said that, dou U T by dou n i at certain variables being constant S T, V T, and n_i s being constant, n_j s being constant, you had defined as mu i, whereas now you are defining dou G T by dou n i at constant T, P and n j is mu i. How can you do that?

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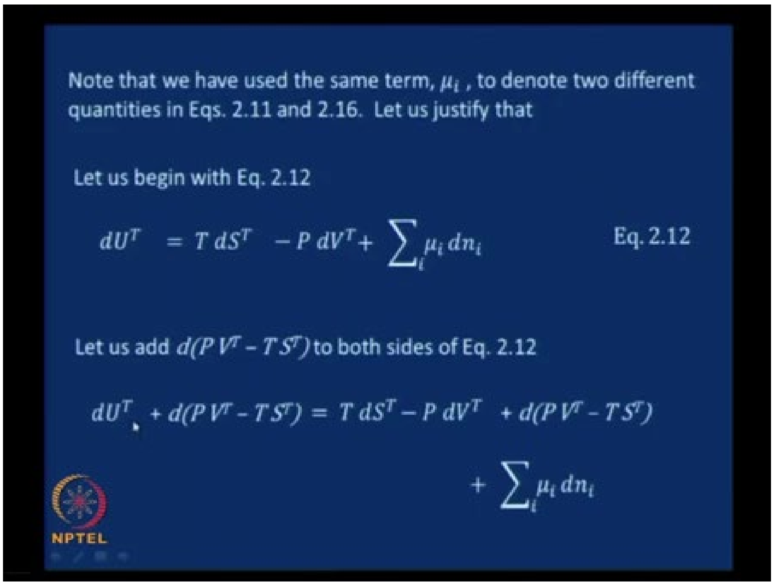

Note that we have used the same term, μ_i, to denote two different quantities in Eqs. 2.11 and 2.16. Let us justify that

Let us begin with Eq. 2.12

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.12}$$

Let us add $d(P\,V^T - T\,S^T)$ to both sides of Eq. 2.12

$$dU^T + d(P\,V^T - T\,S^T) = T\,dS^T - P\,dV^T + d(P\,V^T - T\,S^T) + \sum_i \mu_i\,dn_i$$

Let us now go ahead and show that, these two quantities are actually the same. To justify, let us begin with equation 2.12 where we first defined our mu i. We started with

$$dU^T = T\,dS^T - P\,dV^T + \textstyle\sum_i \mu_i\,dn_i$$

Let us add

$$d(P\,V^T - T\,S^T)$$

to both sides of equation 2.12. If we do that,

$$dU^T + d(P\,V^T - T\,S^T) = T\,dS^T - P\,dV^T + d(P\,V^T - T\,S^T) + \textstyle\sum_i \mu_i\,dn_i$$

Note that, we can combine these together. They are additive. The differentials are additive. You can visualize the differential in a graph or in two dimensional graph or a three dimensional graph. Then, you can understand why this is additive.

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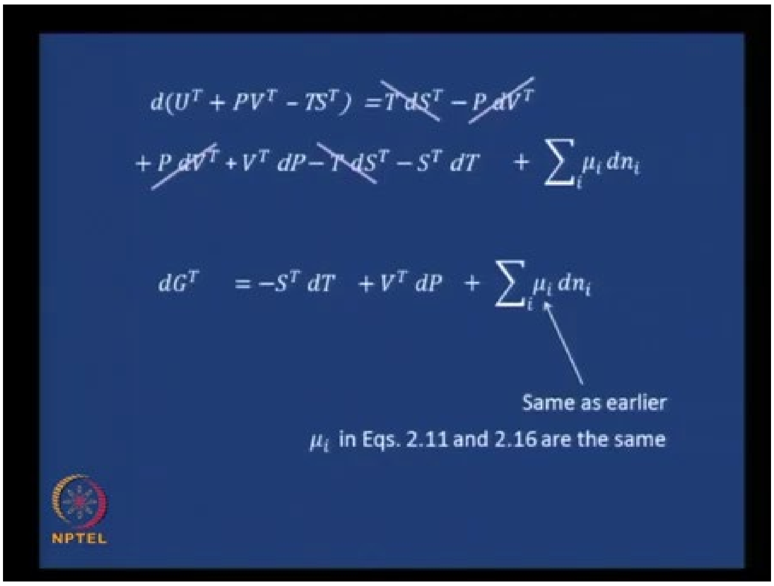

$$d(U^T + PV^T - TS^T) = \cancel{T\,dS^T} - \cancel{P\,dV^T}$$

$$+\cancel{P\,dV^T} + V^T\,dP - \cancel{T\,dS^T} - S^T\,dT \quad + \sum_i \mu_i\,dn_i$$

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

Same as earlier

μ_i in Eqs. 2.11 and 2.16 are the same

So, if we recognize that this is additive and you can expand the term on this side using chain rule. Let us do that; therefore,

$$d(U^T + P\,VT - T\,ST) = T\,dS^T - P\,dV^T + P\,dV^T + V^T\,dP - T\,dS^T - S^T\,dT + \sum_i \mu_i\,dn_i$$

We can cancel T d S T and minus T d S T. We can also cancel plus P d V T and minus P d V T. And therefore,

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

This was the same mu i that we started with earlier, we did not do anything to it. Therefore, the mu i's in equation 2.11, which was for the internal energy d U T and equation 2.16 for the Gibbs free energy d G T are the same. Although we had used different ways to define the chemical potential, they all turn out to be the same quantity.

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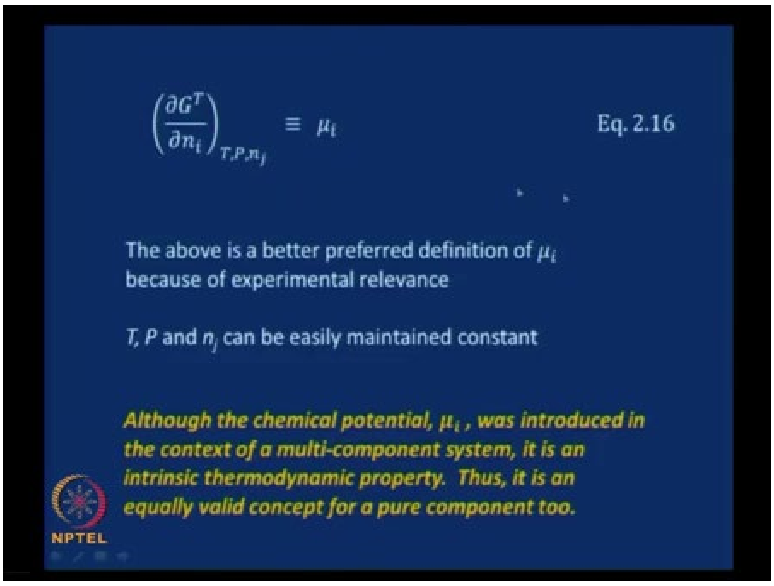

$$\left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} \equiv \mu_i \qquad \text{Eq. 2.16}$$

The above is a better preferred definition of μ_i because of experimental relevance

T, P and n_j can be easily maintained constant

Although the chemical potential, μ_i, was introduced in the context of a multi-component system, it is an intrinsic thermodynamic property. Thus, it is an equally valid concept for a pure component too.

Let us look at this equation 2.16 a little closer. Is a very useful equation.

$$\left(\frac{\partial G^T}{\partial n_i}\right)_{T,\ P,\ n_j} \equiv \mu_i$$

Note that, we had defined we have defined mu i in the context of a multi-component system. That is purely didactic; that is purely to facilitate a certain flow in the development of the subject. The chemical potential itself is an intrinsic quantity for a particular system. Therefore, whether the system is multi-component or whether it is a single component or whatever it is, whatever other combinations you may have, the concept of chemical potential is still valid for any system that you take. To put a little more formally, although the chemical potential mu i was introduced in the context of a multi-component system, it is an intrinsic thermodynamic property. Thus it is an equally valid concept for a pure component also.

Let us look at this a little closer now. Look at the quantities that are being held constant in this definition; dou G T by dou n i at constant temperature, pressure and all other n j's different from n i, which is taken for the differentiation. These are very easy to maintain constant in an experimental situation. Therefore this definition of chemical potential has significant experimental relevance. … Because of that, although you could define chemical potential as dou U T by dou n i at certain variables constant dou a T by dou n i at certain other variables constant and so on and so forth, this definition is most commonly used.

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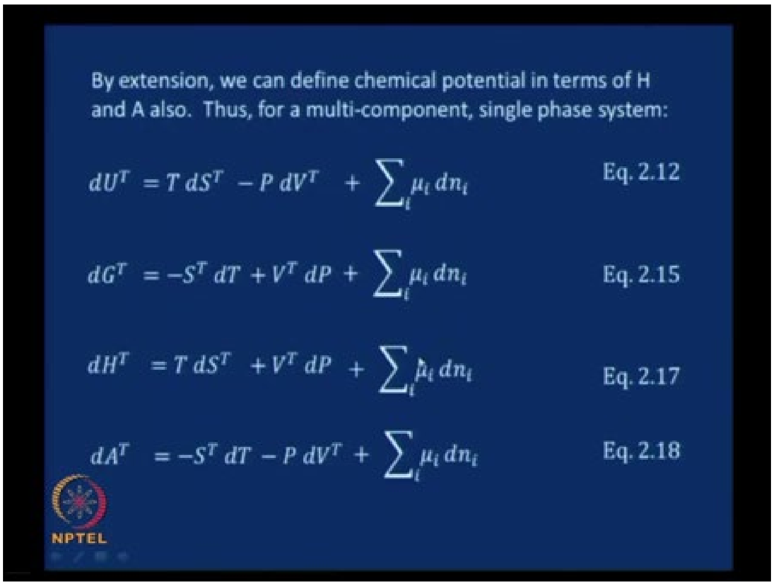

By extension, we can define chemical potential in terms of H and A also. Thus, for a multi-component, single phase system:

$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i$ Eq. 2.12

$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i$ Eq. 2.15

$dH^T = T\,dS^T + V^T\,dP + \sum_i \mu_i\,dn_i$ Eq. 2.17

$dA^T = -S^T\,dT - P\,dV^T + \sum_i \mu_i\,dn_i$ Eq. 2.18

I have already mentioned this, but let me complete the definitions here. So, by extension, as mentioned earlier, we can define chemical potential in terms of enthalpy, H, or the Helmholtz free energy, A. Therefore, for a multi-component, single phase system, d U T equals T d S T minus P d V T plus summation of mu i d n i, equation 2.12. We just compiling all the equations together, we will have it at one place for easier reference later.

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i$$

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

$$dH^T = T\,dS^T + V^T\,dP + \sum_i \mu_i\,dn_i$$

$$dA^T = -S^T\,dT - P\,dV^T + \sum_i \mu_i\,dn_i$$

d G T equals minus S T d T plus V T d P plus summation of mu i d n i over all i, equation 2.15; d H T equals T d S T plus V T d P plus summation of mu i d n i, equation 2.17 and d A T equals minus S T d T minus P d V T plus summation of mu i d n i, we will call this equation 2.18.

What I would like you to do, is to actually sit down and verify the same way that we did, that these two mu i's were the same. It will be good if you verify and convince yourself that these two mu i’s are also the same. And, they are the same as the other mu i’s that are here. That way, there will be no doubts in your mind.

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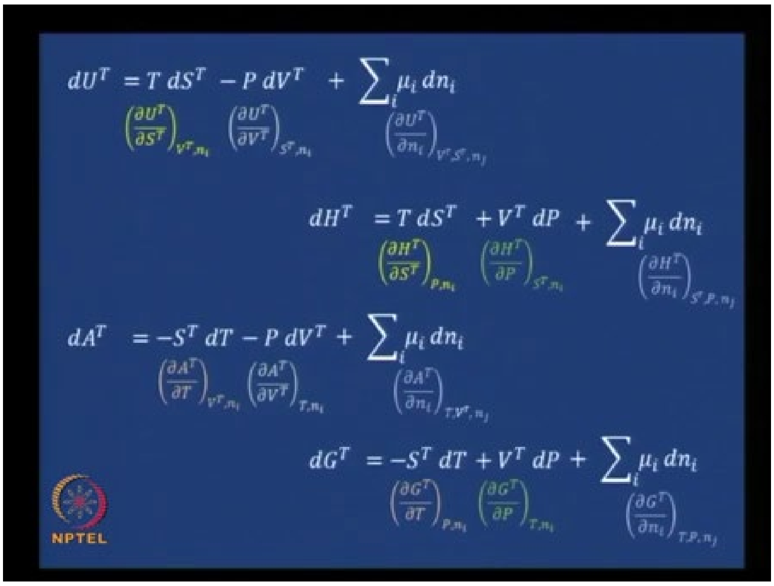

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i$$

$$\left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i} \quad \left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,n_i} \quad \left(\frac{\partial U^T}{\partial n_i}\right)_{V^T,S^T,n_j}$$

$$dH^T = T\,dS^T + V^T\,dP + \sum_i \mu_i\,dn_i$$

$$\left(\frac{\partial H^T}{\partial S^T}\right)_{P,n_i} \quad \left(\frac{\partial H^T}{\partial P}\right)_{S^T,n_i} \quad \left(\frac{\partial H^T}{\partial n_i}\right)_{S^T,P,n_j}$$

$$dA^T = -S^T\,dT - P\,dV^T + \sum_i \mu_i\,dn_i$$

$$\left(\frac{\partial A^T}{\partial T}\right)_{V^T,n_i} \quad \left(\frac{\partial A^T}{\partial V^T}\right)_{T,n_i} \quad \left(\frac{\partial A^T}{\partial n_i}\right)_{T,V^T,n_j}$$

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

$$\left(\frac{\partial G^T}{\partial T}\right)_{P,n_i} \quad \left(\frac{\partial G^T}{\partial P}\right)_{T,n_i} \quad \left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j}$$

These are the four equations that we have just derived. I would like to point out some interesting features here. These four equations d U T equals T d S T minus P d V T plus mu i d n i, d H T equals T d S T plus V T d P plus mu i d n i, d A T equals minus S T d T minus P d V T plus mu i d n i and d G T equals minus S T d T plus V T d P plus mu i d n i … summation.

Let us look at it in terms of writing a total differential, in terms of its partial differentials.

$$dU^T = T\,dS^T - \qquad P\,dV^T + \qquad \textstyle\sum_i \mu_i\,dn_i$$

$$\left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,\ n_i} \quad \left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,\ n_i} \quad \left(\frac{\partial U^T}{\partial n_i}\right)_{VT,ST,\ n_j}$$

This term, as you can recall can be written as dou U T by dou S T at constant V T, n i; both these held constant. And, this term can be written as dou H T by dou S T at constant P and n i. Similarly, this term P can be written as dou U T by dou V T at constant S T and n i.

The same P here, which appears in this other equation can be represented in terms of the Helmholtz free energy as dou A T by dou V T at constant T and n i.

Now, you get the scheme with which we are going to do things. Minus S T is dou A T by dou T at constant V T and n i. Let us look for another S T. It is here; S T … minus S T equals dou G T by dou T at constant P and n i. Similarly, this V T can be written as dou H T by dou P at constant S T and n i. And, V T which appears here can be written as dou G T by dou P at constant T and n i. And, as we have already seen, the chemical potentials can be written in terms of either the partial of U T with n i at constant S T, V T and all other n j's here. In terms of enthalpy, you could write mu i as dou H T by dou n i at constant S T V T and all other n j's. dou A T by dou n i at constant T V and all other n j's. And, d G T at constant … dou G T by dou n i at constant T, P and all other n j's.

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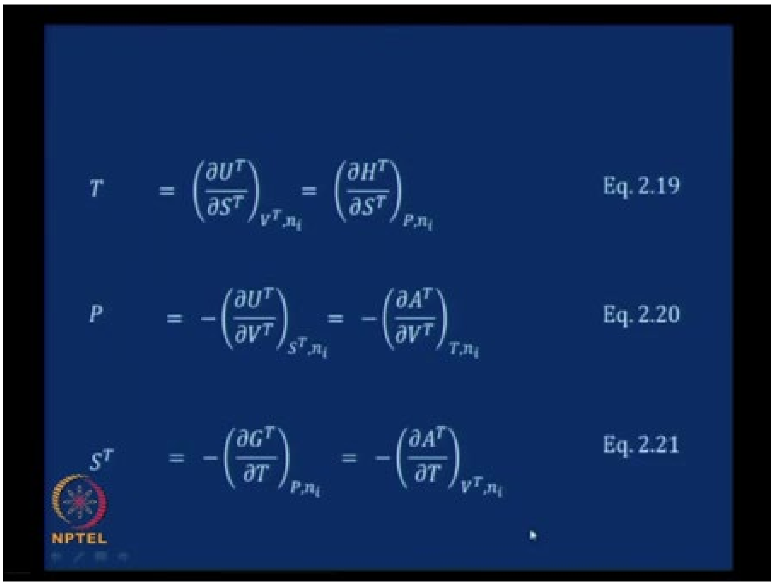

$$T = \left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i} = \left(\frac{\partial H^T}{\partial S^T}\right)_{P,n_i} \qquad \text{Eq. 2.19}$$

$$P = -\left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,n_i} = -\left(\frac{\partial A^T}{\partial V^T}\right)_{T,n_i} \qquad \text{Eq. 2.20}$$

$$S^T = -\left(\frac{\partial G^T}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial A^T}{\partial T}\right)_{V^T,n_i} \qquad \text{Eq. 2.21}$$

If we put this all together in one place,

$$T = \left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,\ n_i} = \left(\frac{\partial H^T}{\partial S^T}\right)_{P,\ n_i}$$

equation 2.19

$$P = -\left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,\ n_i} = -\left(\frac{\partial A^T}{\partial V^T}\right)_{T,\ n_i}$$

equation 2.20

$$S^T = -\left(\frac{\partial G^T}{\partial T}\right)_{P,\ n_i} = -\left(\frac{\partial A^T}{\partial T}\right)_{V^T,\ n_i}$$

equation 2.21

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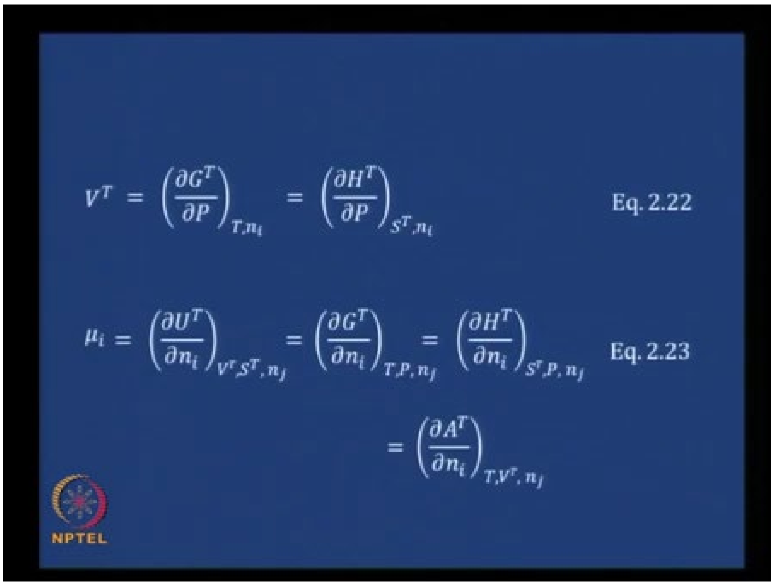

$$V^T = \left(\frac{\partial G^T}{\partial P}\right)_{T,n_i} = \left(\frac{\partial H^T}{\partial P}\right)_{S^T,n_i} \qquad \text{Eq. 2.22}$$

$$\mu_i = \left(\frac{\partial U^T}{\partial n_i}\right)_{V^T,S^T,n_j} = \left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial H^T}{\partial n_i}\right)_{S^T,P,n_j} \qquad \text{Eq. 2.23}$$

$$= \left(\frac{\partial A^T}{\partial n_i}\right)_{T,V^T,n_j}$$

$$V^T = \left(\frac{\partial G^T}{\partial P}\right)_{T,\ n_i} = \left(\frac{\partial H^T}{\partial P}\right)_{S^T,\ n_i}$$

equation 2. 22.

And, all the four ways of representing the chemical potential as

$$\mu_i = \left(\frac{\partial U^T}{\partial n_i}\right)_{VT,S^T,\ n_j} = \left(\frac{\partial G^T}{\partial n_i}\right)_{T,\ P,\ n_j} = \left(\frac{\partial H^T}{\partial n_i}\right)_{ST,\ P,\ n_j} = \left(\frac{\partial A^T}{\partial n_i}\right)_{T,VT,\ n_j}$$

Let me call this equation 2.23.

These are very useful equations as we will see.

See you in the next class.