Thermodynamics (Classical) for Biological Systems

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Module No. # 02
Additional Thermodynamic Functions
Lecture No. # 03
Equations for a Closed System
Chemical Potential Concept
Gibbs-Duhem Equation

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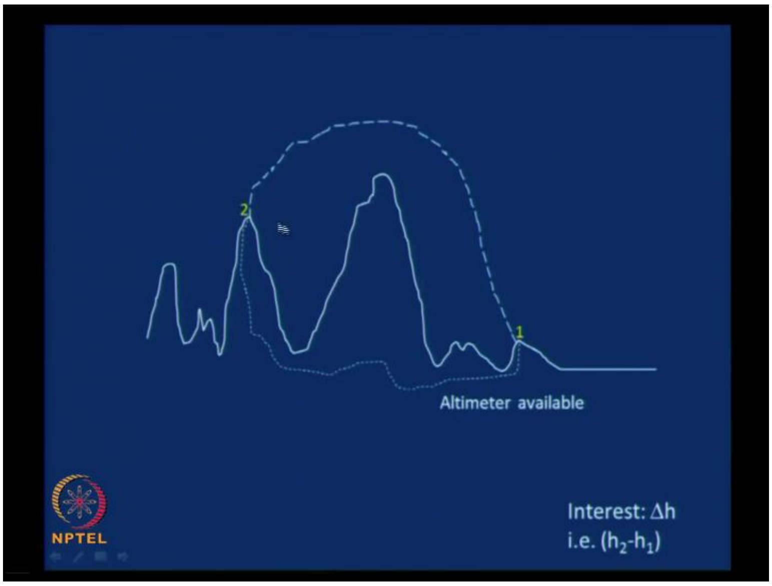

Interest: Δh
i.e. (h_2-h_1)

In the last class, we saw an important aspect or an important concept that we will use repeatedly in Classical Thermodynamics. That is the concept of state variable values not depending on the path taken between the two states. The … To understand that a little better, the example that we had considered was taking multiple routes between two destinations, 1 and 2, in a mountainous region. And, if we are interested in the difference in heights between 1 and 2 let us say, then the … then the height being a state variable, which depends only on the state of the system or the state 1 or the state 2 and not on the path in between them, irrespective of the path that we take, the value of the difference in the state variable or the difference in heights, in this case, will always be the same. This is a very powerful concept or idea that we will repeatedly use. This route, where the altimeter was available – it gave us a means of measuring. Similarly, we would have routes in Thermodynamics between two states, various paths. And, one of those paths would have some easy way of measuring the state variable between … the state variable values at these two points. This was one important aspect.

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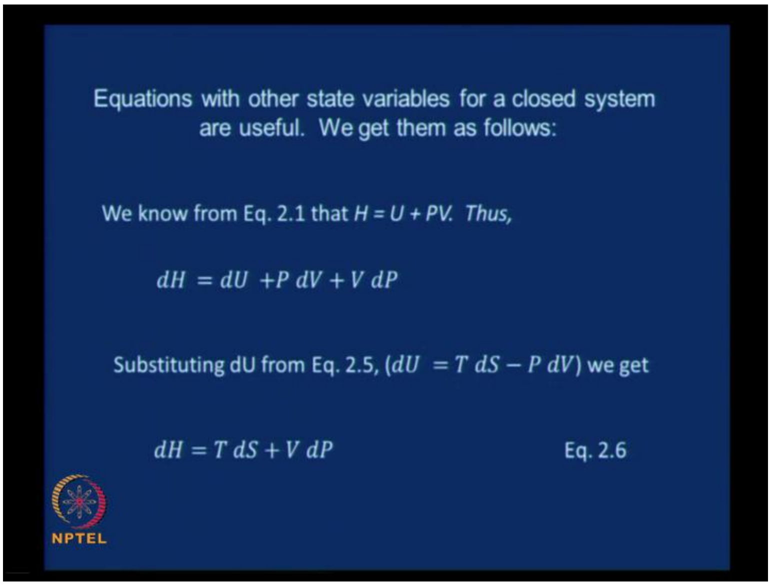

Equations with other state variables for a closed system are useful. We get them as follows:

We know from Eq. 2.1 that $H = U + PV$. Thus,

$$dH = dU + P\,dV + V\,dP$$

Substituting dU from Eq. 2.5, ($dU = T\,dS - P\,dV$) we get

$$dH = T\,dS + V\,dP \qquad \text{Eq. 2.6}$$

Then, we started looking at equations for a closed system, useful thermodynamic equations for a closed system. Let us start with that again for this particular class. We just had done one last time. For a closed system, we have already seen from the definition of enthalpy H from equation 2.1. Enthalpy, it is defined as U plus PV. Therefore, the total differential of enthalpy dH is d of (U plus P V). And, if we use the rules of differentials, it will be d U plus, using chain rule here it will be first function into derivative of the second function plus derivative … plus the second function into derivative of the first function; that is P dV plus V dP. And, we already know dU as T dS minus P dV. That was our equation 2.5 earlier. And, if you substitute this here, we have T dS minus P dV plus P dV. So, these two will cancel out and we have dH equals T dS plus V dP. This is the equation 2.6 that we ended up with the last class.

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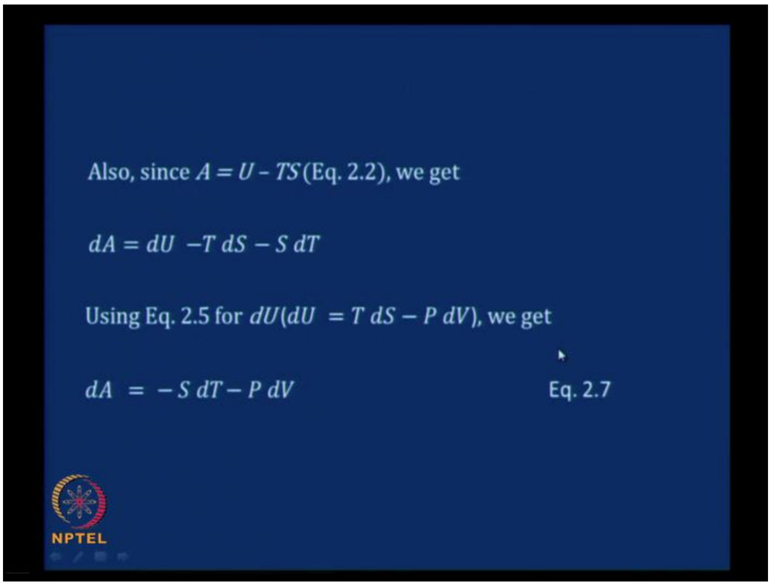

Also, since $A = U - TS$ (Eq. 2.2), we get

$$dA = dU - T\,dS - S\,dT$$

Using Eq. 2.5 for dU ($dU = T\,dS - P\,dV$), we get

$$dA = -S\,dT - P\,dV \qquad \text{Eq. 2.7}$$

There are other useful equations or relationships that we can derive for the other thermodynamic variables. And, let us see some of them here. If you recall the definition of the Helmholtz free energy A, we have defined it as U minus TS. If you want, you can go back and check equation 2.2 in your notes or in the video lectures. A equals U minus TS. Therefore, the total differential of A; following the same scheme earlier, it is nothing but dU minus, by a chain rule, T dS minus S dT. And, we already know that dU equals T dS minus P dV from equation 2.5. And therefore, if we substitute T dS minus P dV here, T dS minus P dV minus T dS minus S dT. T dS minus T dS will get cancelled out. And therefore, we are left with dA equals minus S dT minus P dV. We will call this equation 2.7.

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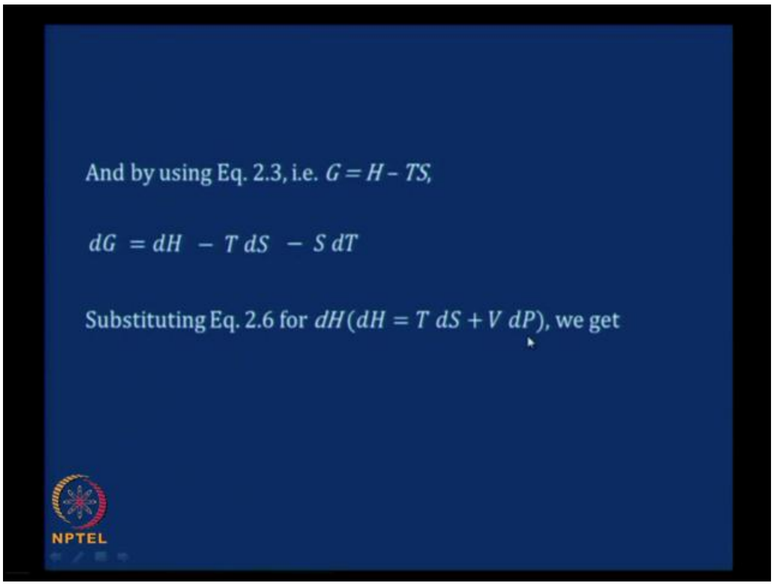

And by using Eq. 2.3, i.e. $G = H - TS$,

$$dG = dH - T\,dS - S\,dT$$

Substituting Eq. 2.6 for dH ($dH = T\,dS + V\,dP$), we get

So, we have looked at internal energy U, enthalpy H, Helmholtz free energy A. And, the only other thermodynamic variable that we have defined so far is the Gibbs free energy G. According to our definition of Gibbs free energy, G equals H minus TS; enthalpy minus the product of temperature and entropy. Same scheme as earlier; dG equals dH minus T dS minus S dT. We know that dH is T dS plus V dP. This we have already seen, when we derived equation 2.6. Now, if you substitute T dS plus V dP for dH, you can see that, this T dS and this minus T dS will get cancelled out. And, what we are left with is dG equals minus S dT plus V dP. Let us call this equation 2.8. Remember, we have derived these equations for a closed system.

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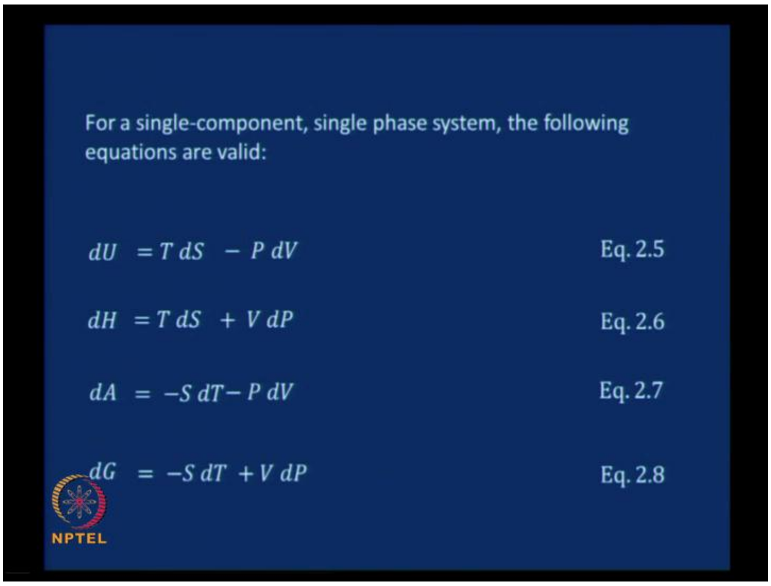

For a single-component, single phase system, the following equations are valid:

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

$$dH = T\,dS + V\,dP \qquad \text{Eq. 2.6}$$

$$dA = -S\,dT - P\,dV \qquad \text{Eq. 2.7}$$

$$dG = -S\,dT + V\,dP \qquad \text{Eq. 2.8}$$

It is useful to see all these equations together. So, let us see that. And it is nice to have it in one place for reference later. Therefore, let us do that now. So, for a single-component, single phase … single phase closed system, the following equations are valid; which we just derived, dU equals T dS minus P dV. This was our equation 2.5. dH equals T dS plus V dP, equation 2.6; dA equals minus S dT minus P dV, equation 2.7; dG equals minus S dT plus V dP, equation 2.8.

Usually, these useful relationships become a part of us because of repeated use. But, for examination purposes, for your university examination purposes, you might want to remember these equations. We can always derive them quite simply from first principles as we have shown.

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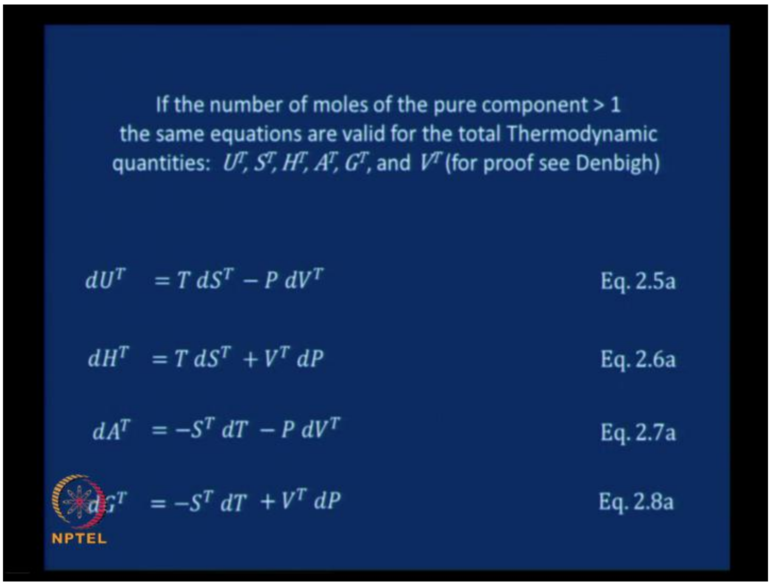

If the number of moles of the pure component > 1 the same equations are valid for the total Thermodynamic quantities: U^T, S^T, H^T, A^T, G^T, and V^T (for proof see Denbigh)

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

$$dH^T = T\,dS^T + V^T\,dP \qquad \text{Eq. 2.6a}$$

$$dA^T = -S^T\,dT - P\,dV^T \qquad \text{Eq. 2.7a}$$

$$dG^T = -S^T\,dT + V^T\,dP \qquad \text{Eq. 2.8a}$$

So far, we had looked at a single-component system, one mole of that system and that being a closed system. Now, let us slightly complicate the system. Let us increase the number of moles of the pure component. Earlier it was one; let it now be more than one. It is still a closed system, it is still a pure component and only the numbers of moles are more than one. If that is a case, remember we had used U, S, H, A, G for one mole of the substance; the thermodynamic quantities for one mole of the substance. Now, since the numbers of moles are greater than one, let us use a slightly different terminology, so that there is no confusion later.

So, the terminology for the thermodynamic variables of a system consisting of, let us say n moles of a pure component is U^{total}; represented as U^T, S^{total} : S^T, H^{total} : H^T, A^{total} : A^T, G^{total} : G^T and V^{total} : V^T. The four equations that we derived for a closed system earlier, for one mole of a closed system, sorry … closed system consisting of one mole of a pure component earlier are valid, even in this case. I am not going to prove that in this particular lecture. If you need proof, you can see one of your reference books which is by Kenneth Denbigh. Let me just state the equations here, d U^T equals T dS^T minus P dV^T; remember that, T is an intensive variable. Its value will not depend on the amount of substance present. It is going to be T, dS^T minus P dV^T; P is also an intensive variable. Let us call this equation 2.5a. dH^T is T dS^T plus V^T dP; equation 2.6a. You can compare these equations with the equations for one mole of a pure substance. d A^T equals minus S^T dT minus P dV^T; equation 2.7a. And, d G^T equals minus S^T dT plus V^T dP, which is equation 2.8a. To reemphasize, these are the equations for a system that consist of n moles of a pure substance, and system is a closed system.

Now, let us look at a slightly higher level of complication. Let us stick ourselves to one phase. Let us say a gas phase or a liquid phase; just one phase there, but now, let us increase the number of components from one earlier. If we had only one component, it was a pure substance. Let us increase the number of components from one to many. Now, we have a multi-component system. But, still let us work in single phase. Therefore, we are looking at a multi-component system, but a homogeneous … a homogeneous system.

For example, it could be a mixture of gases of a different species. It is all going to be in the gas phase, but it is going to consist of many different species. The air is a very good example of a multi-component, homogeneous gas phase system. Air has predominantly nitrogen, oxygen, but you also have carbon dioxide, you also have water vapor and so on and so forth. So, this is an example of a multi-component, homogeneous system.

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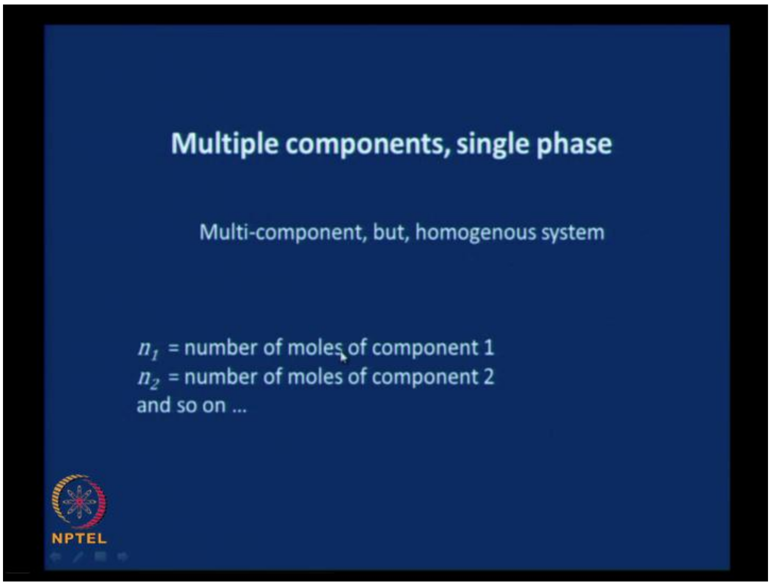

Multiple components, single phase

Multi-component, but, homogenous system

n_1 = number of moles of component 1
n_2 = number of moles of component 2
and so on ...

Let us look at some of the relationships that will … be useful for a multi-component, single phase system. Before we do that, we need to know some terminology that we will use here. Let n_1 be the number of moles of component 1, n_2 be the number of moles of component 2 and so on.

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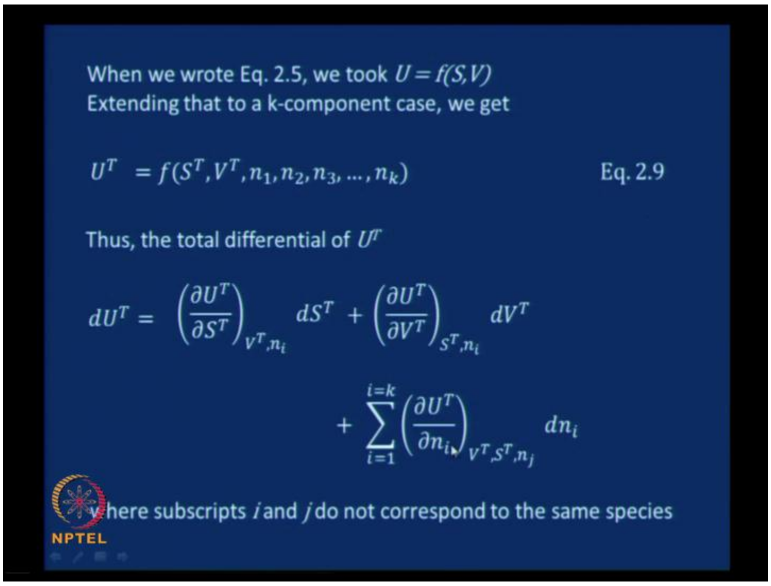

When we wrote Eq. 2.5, we took $U = f(S,V)$
Extending that to a k-component case, we get

$$U^T = f(S^T, V^T, n_1, n_2, n_3, \dots, n_k) \qquad \text{Eq. 2.9}$$

Thus, the total differential of U^T

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

where subscripts i and j do not correspond to the same species

If you recall our equation 2.5, we know dU equals T dS minus P dV; you can recall that we took the internal energy U as a function of S and V. It will become clearer when I say the next thing. And, for saying the next thing, let me extend this to a k-component case. This U as a function of S and V that we took to write for equation 2.5 was limited for a single-component system or a pure substance. Now, we are extending this to a k-component case.

Since it has k components, it has to be indicated by the total internal energy. And, let us say that, this is a function of entropy, total entropy, and total volume. And, since it is a multi-component system, it will definitely depend on the number of moles of each component present. And, we are taking k components to be present. So, n_1 number of moles of the first component, n_2 number of moles of the second component and so on, till n_k; number of moles of the k th component. And, call this equation 2.9. Therefore, the total differential of U^T, if you recall the way the total differentials are written is the partial differential of U^T with respect to S^T at constant other variables are at the conditions, where the other variables are held constant; which is V^T, n_1, n_2, n_3 are all held constant, which is indicated by n i being constant. So, dou U^T by dou S^T times dS^T plus dou U^T by dou V^T the second variable at constant S^T and all n_i times d V^T plus dou U^T by dou n 1 d n 1 plus dou U^T by dou n 2 d n 2 and so on and so forth and which can be indicated in short form as sum of i equals 1 to i equals k because there are k components.

dou U^T by dou n_i at constant V^T, S^T and n_j dn_i. Note that the subscripts i and the subscripts j do not correspond to the same species.

We are taking the partial differential with respect to one of the species, when all the other species are held constant. This is a notation to indicate that and this will be consistent. This will help us in developing a consistent notation for representing this kind of a situation throughout the course. So, summation of i equals 1 to k, dou U T by dou n i V T at constant V T, S T and n j times d n i. This is the total differential. This comes from the theorem in Mathematics, where you can represent the total differential by this particular thing, if it is an exact differential. We will call this equation 2.10.

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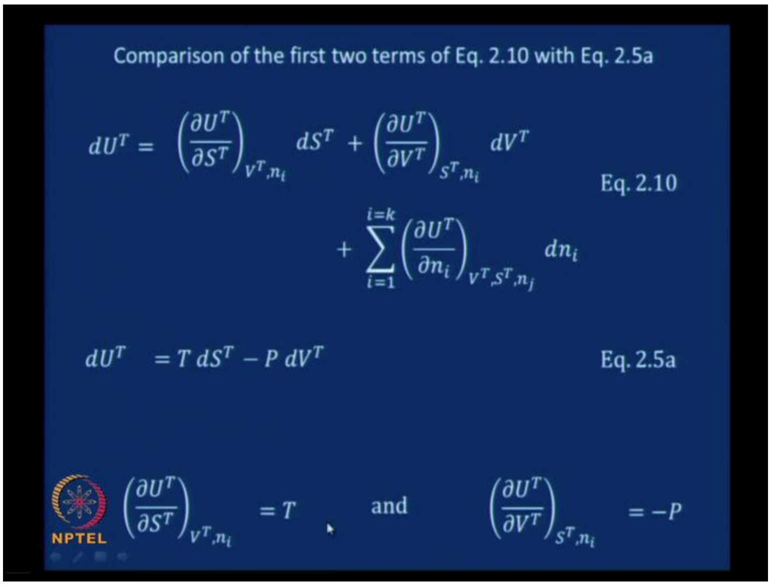

Comparison of the first two terms of Eq. 2.10 with Eq. 2.5a

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

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

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

If we compare the first two terms of equation 2.10 that we just wrote down with equation 2.5a; I am going to give you both these equations now. This is 2.10 that we derived just now and this is 2.5a. Here going by the same scheme, d U T is dou U T by dou S T at constant V d S T minus dou U T by dou V T at constant S T d V T. It is quite easy to see the correspondence between the two. And therefore, it is quite straightforward to write dou U T by dou S T at constant V T, n i equals a temperature and dou U T by dou V T at constant S T and all other components, the number of components being held constant, as minus P. Note that, this is for a multi-component system and we have compared it with single-component system and we are drawing useful relationships.

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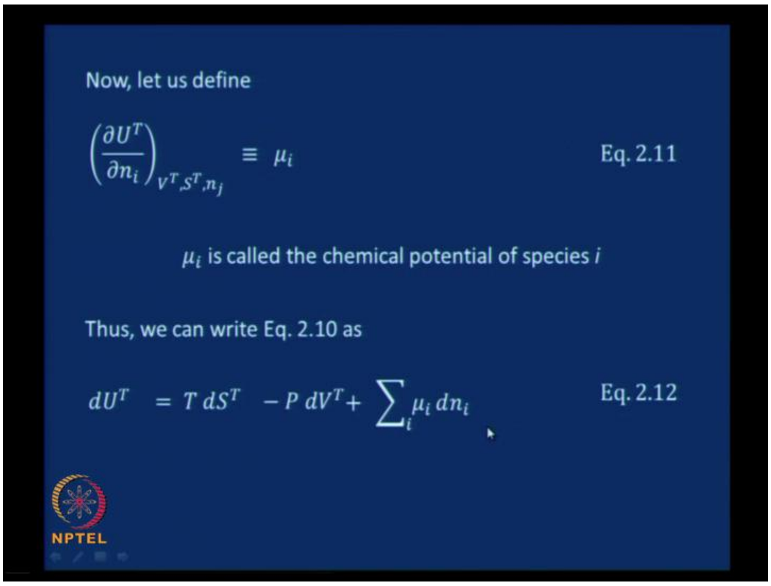

Now, let us define

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

μ_i is called the chemical potential of species *i*

Thus, we can write Eq. 2.10 as

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

Now, let us define … let me go back a little bit. 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. 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 d U T equals T d S T minus P d V T plus summation of, summation over i mu i d n i. We will call this equation 2.12. … excuse me ... So, that was for internal energy.

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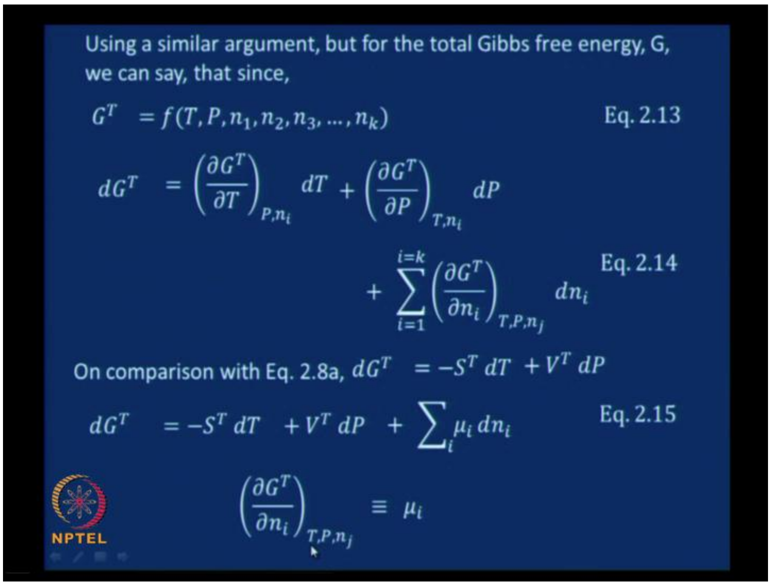

Using a similar argument, but for the total Gibbs free energy, G, we can say, that since,

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

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

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

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

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

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; equation 2.13. Therefore, the total differential G T; d G T can be written as dou G T by dou T at constant P, all other n i or all n i d T plus dou G T by dou P at constant T n i d P plus, as we have seen dou G T by dou n 1 at constant T and P and all other n j’s d n 1; dou G T … plus dou G T by dou n 2 at constant T and P all other n i’s d n 2 and so on; which can be represented in short form as summation of i over 1 to k … summation over i from 1 to k dou G T by dou n i at constant T P n j, where we already saw that i and j won’t be the same … times d n i. And, call this equation 2.14.

If we compare this 2.14 with 2.8a, which for pure component system or a single component system d G T equals minus S T d T plus V T d P. 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 dou G T by dou n i at constant temperature, pressure and n j, which is this quantity, as mu i itself. That is what I have done here, when I wrote this equation. 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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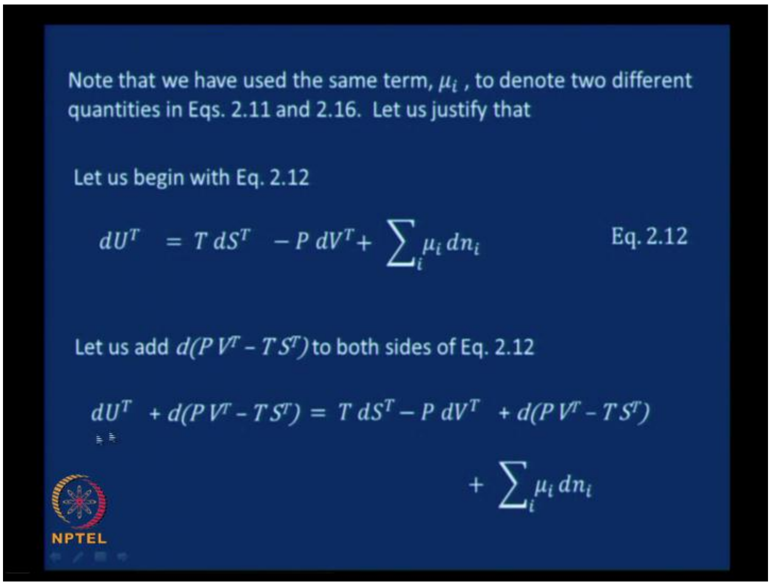

Note that we have used the same term, μ_i , to denote two different quantities in Eqs. 2.11 and 2.16. Let us justify that

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 $d(PV^T - TS^T)$ to both sides of Eq. 2.12

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

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 d U T equals T d S T minus P d V T plus summation of mu i d n i. Let us add d of… the total, the differential of this particular quantity P V T minus T S T to both sides of equation 2.12. If we do that, d U T plus d of P V T minus T S T equals T d S T minus P d V T plus the same quantity on the right hand side plus summation of mu i d n 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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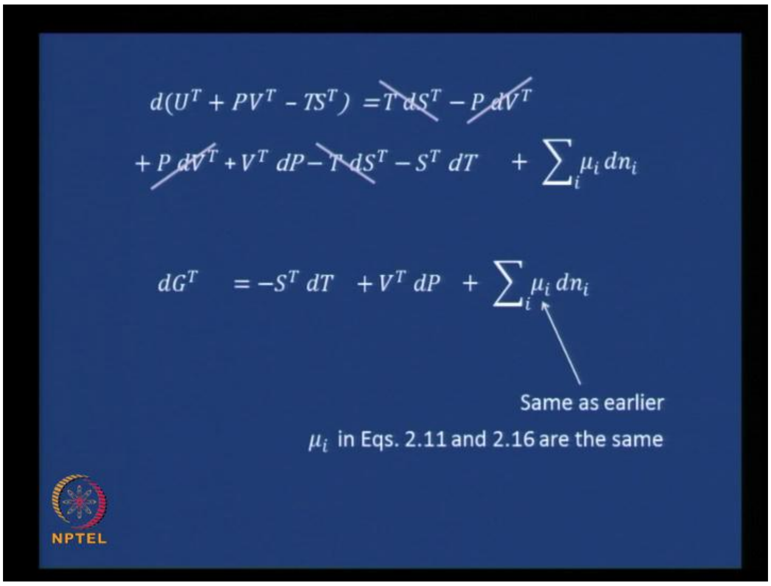

$$d(U^T + PV^T - TS^T) = \cancel{T\,dS^T} - \cancel{P\,dV^T}$$

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

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

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 of U T plus P V T minus T S T equals T d S T minus P d V, we already had. Now, if we expand the term that we added by chain rule, we have P d V T plus V T d P minus T d S T minus S T d T plus whatever remained there, which is summation of mu i d n 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, d G T equals minus S T d T plus V T d T plus summation of mu i d n i. Note that, this term automatically became d G T. And, whatever was left here was only minus S T d T plus V T d P plus summation of mu i d n i. And, this was the same mu i that we started with earlier, we did not do anything to it. And 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. So, … although we had used different ways to define the chemical potential, they all turn out to be the same quantity.

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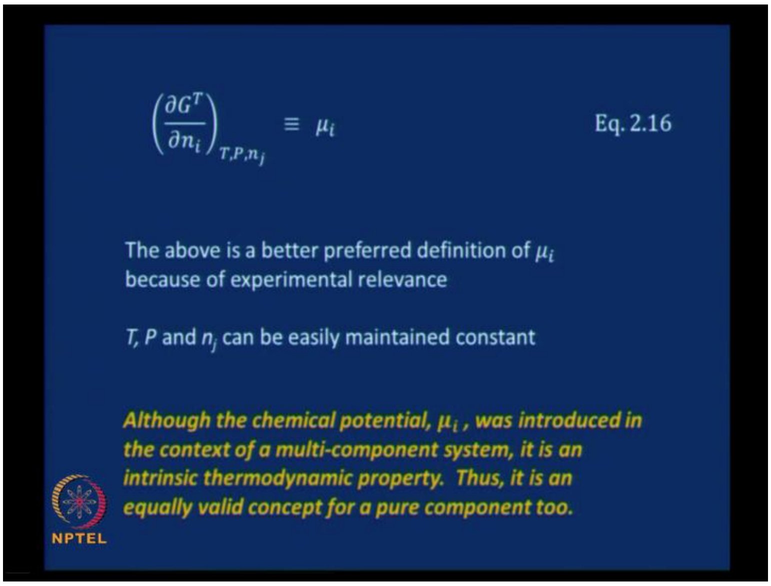

$$\left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} \equiv \mu_i \qquad \text{Eq. 2.16}$$

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. … dou G T by dou n i at constant temperature, pressure and all other mole numbers remaining constant, we had defined as 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. And 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, I have written here, 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. And, 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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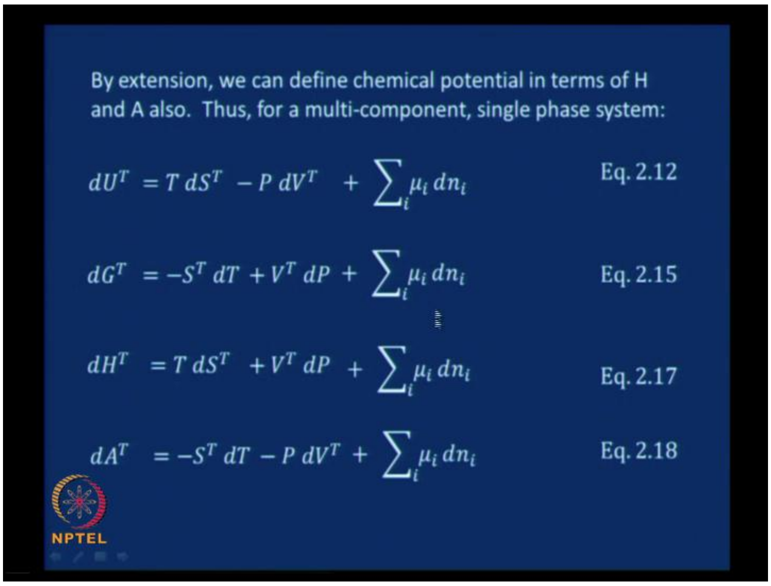

By extension, we can define chemical potential in terms of H and A also. Thus, for a multi-component, single phase system:

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

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

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

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

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. 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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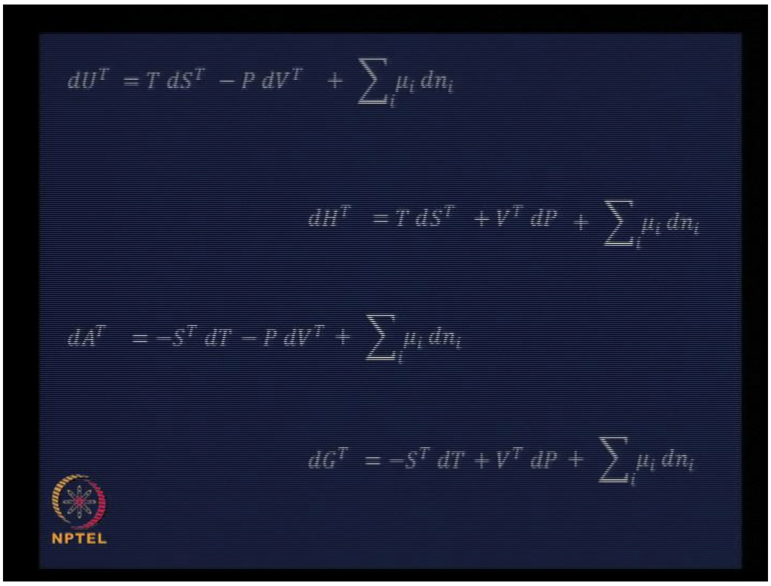

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i$$

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

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

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

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.

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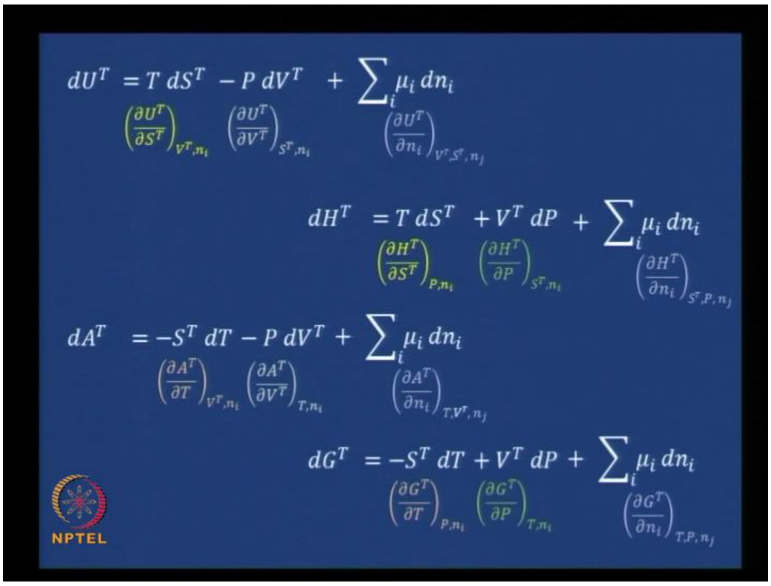

$$dU^T = \underset{\left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i}}{T}\,dS^T - \underset{\left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,n_i}}{P}\,dV^T + \sum_i \underset{\left(\frac{\partial U^T}{\partial n_i}\right)_{V^T,S^T,n_j}}{\mu_i}\,dn_i$$

$$dH^T = \underset{\left(\frac{\partial H^T}{\partial S^T}\right)_{P,n_i}}{T}\,dS^T + \underset{\left(\frac{\partial H^T}{\partial P}\right)_{S^T,n_i}}{V^T}\,dP + \sum_i \underset{\left(\frac{\partial H^T}{\partial n_i}\right)_{S^T,P,n_j}}{\mu_i}\,dn_i$$

$$dA^T = \underset{\left(\frac{\partial A^T}{\partial T}\right)_{V^T,n_i}}{-S^T}\,dT - \underset{\left(\frac{\partial A^T}{\partial V^T}\right)_{T,n_i}}{P}\,dV^T + \sum_i \underset{\left(\frac{\partial A^T}{\partial n_i}\right)_{T,V^T,n_j}}{\mu_i}\,dn_i$$

$$dG^T = \underset{\left(\frac{\partial G^T}{\partial T}\right)_{P,n_i}}{-S^T}\,dT + \underset{\left(\frac{\partial G^T}{\partial P}\right)_{T,n_i}}{V^T}\,dP + \sum_i \underset{\left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j}}{\mu_i}\,dn_i$$

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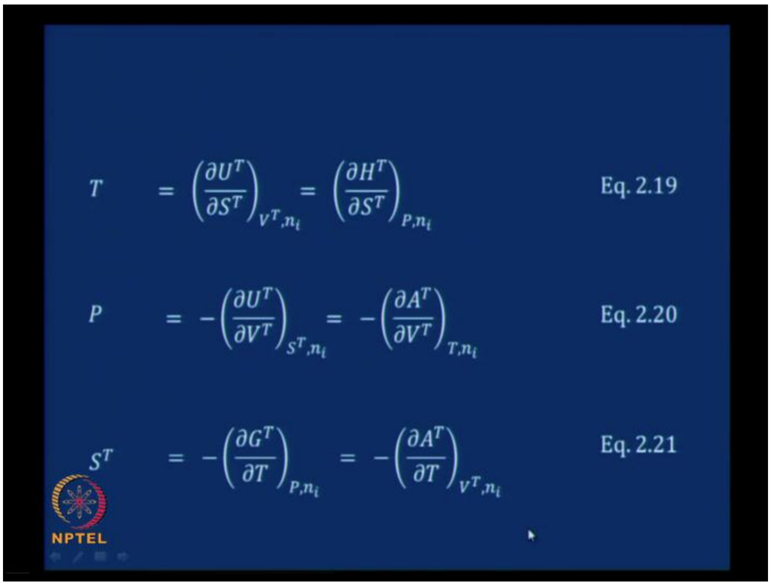

$$T = \left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i} = \left(\frac{\partial H^T}{\partial S^T}\right)_{P,n_i} \qquad \text{Eq. 2.19}$$

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

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

If we put this all together in one place, we can say a temperature can be represented as the partial of U T with respect to S T at constant V T, n i or partial of H T with S T at constant P, n i. We had seen P appearing in two different equations there and which represented, … which we represented as partial derivatives. I am just compiling those here, as equation 2.19, P as minus of dou U T by dou V T at constant S T, n i or minus dou A T by dou V T at constant T, n i; equation 2.20. S T as minus of dou G T by dou T constant P n i or minus of dou A T by dou T at constant V T, n i; equation 2.21.

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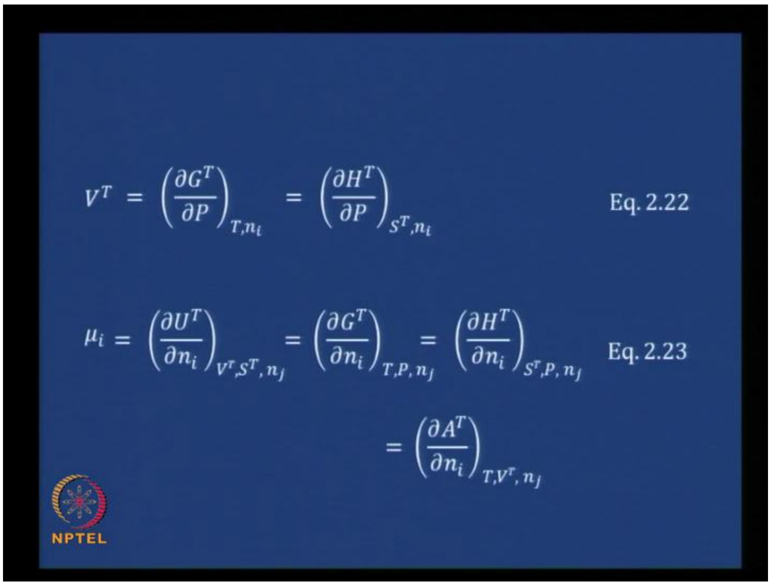

$$V^T = \left(\frac{\partial G^T}{\partial P}\right)_{T,n_i} = \left(\frac{\partial H^T}{\partial P}\right)_{S^T,n_i} \qquad \text{Eq. 2.22}$$

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

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

V T as dou G T by dou P constant T, n i or dou H T by dou P at constant S T, n i; equation 2. 22. And, all the four ways of representing the chemical potential as either dou U T by dou n i at constant V T, S T, n j, dou G T by dou n i at constant T, P, n j, dou H T by dou n i at constant S T, P, n j or dou A T by dou n i at constant T, V T, n j. … Let me call this equation 2.23. These are very useful equations as we will see in a little while. I will give you an example and we will use this again and again in this course.

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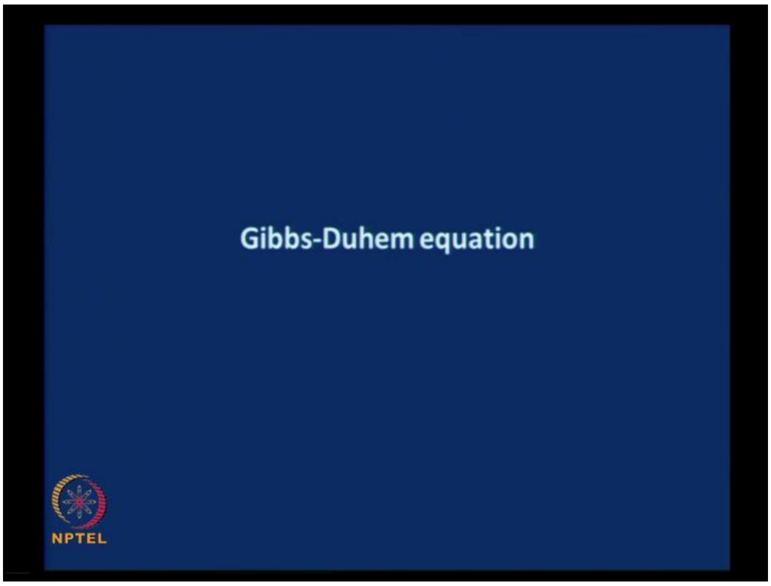

Gibbs-Duhem equation

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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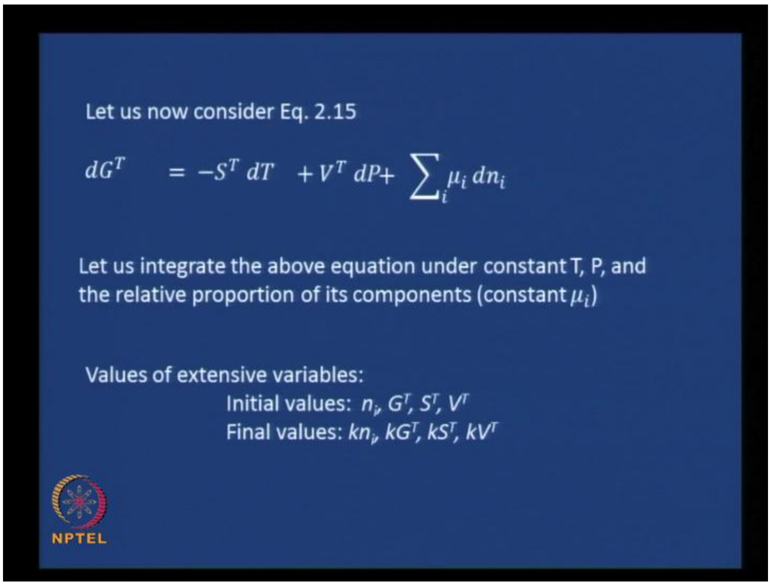

Let us now consider Eq. 2.15

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

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. With this, d G T equals minus S T d T plus V T d P plus summation of mu i d n 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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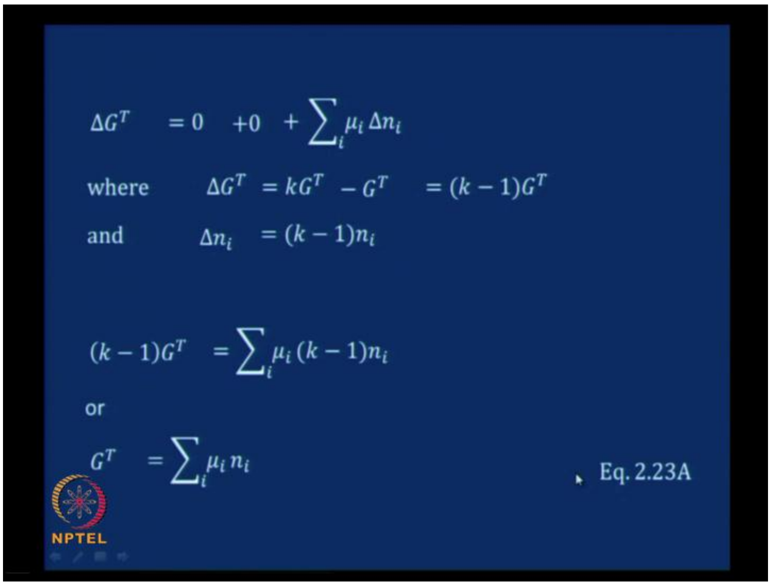

$$\Delta G^T \quad = 0 \quad +0 \quad + \sum_i \mu_i \Delta n_i$$

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

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

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

or

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

Eq. 2.23A

Now, we are integrating … this equation d G T minus S T d T equals S minus S T d T plus V T d P plus summation of mu i d n i. And, 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, where delta G T equals k G T minus 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. Substituting these values back into the integrated expression, k minus 1 times G T equals summation of mu i into k minus 1 times n i. or, this k minus 1, k minus one is a constant. It can be taken out and cancelled. G T equals summation of mu i n i. Let us call this equation 2.23A.

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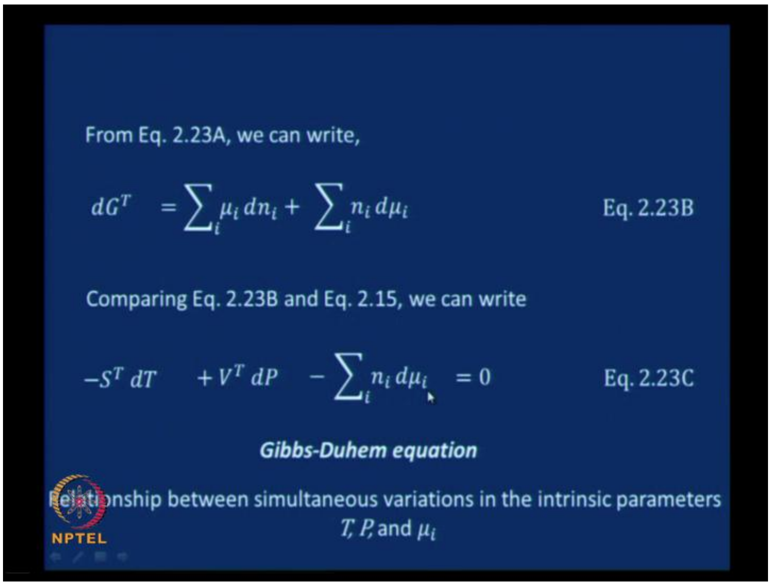

From Eq. 2.23A, we can write,

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

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. 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. Let us call that equation 2.23C. This equation, minus S T d T plus V T d P minus summation of n i d mu i equals 0 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. And 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 a variable of … 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.

When we begin the next class, let us look at Maxwell’s relations, which are very useful relations that we can derive from whatever we have learnt so far and by applying a basic theorem in Calculus to the equations that we have derived so far. That, we will start doing in the next class.