Thermodynamics for Biological Systems:
Classical and Statistical Aspects

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Lecture - 6
Equations for a Closed System

Welcome!

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.

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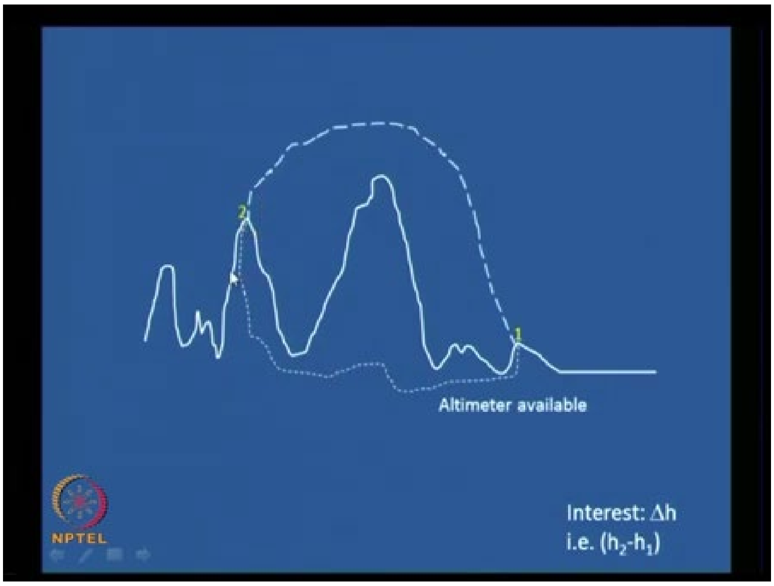

Interest: Δh
i.e. (h_2-h_1)

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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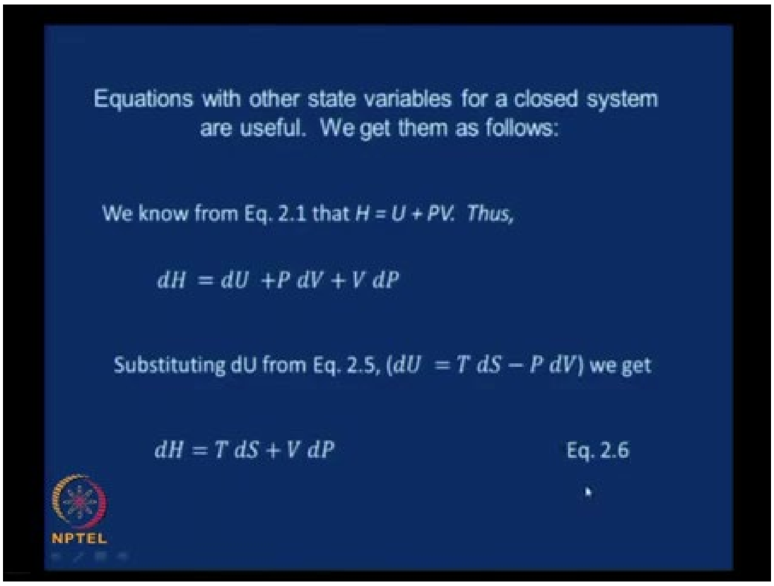

Equations with other state variables for a closed system are useful. We get them as follows:

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.

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

And, we already know dU as T dS minus P dV.

$$dU = T\,dS - P\,dV$$

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.

$$dH = T\,dS + V\,dP$$

This is the equation 2.6.

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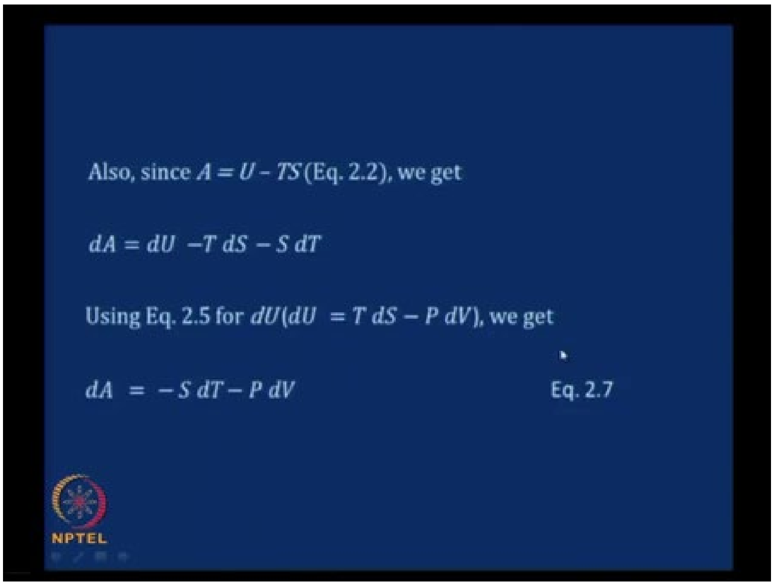

Also, since $A = U - TS$ (Eq. 2.2), we get

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

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.

$$A = U - TS$$

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.

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

And, we already know that dU equals T dS minus P dV from equation 2.5.

$$dU = T\,dS - P\,dV$$

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.

$$dA = -S\,dT - P\,dV$$

We will call this equation 2.7.

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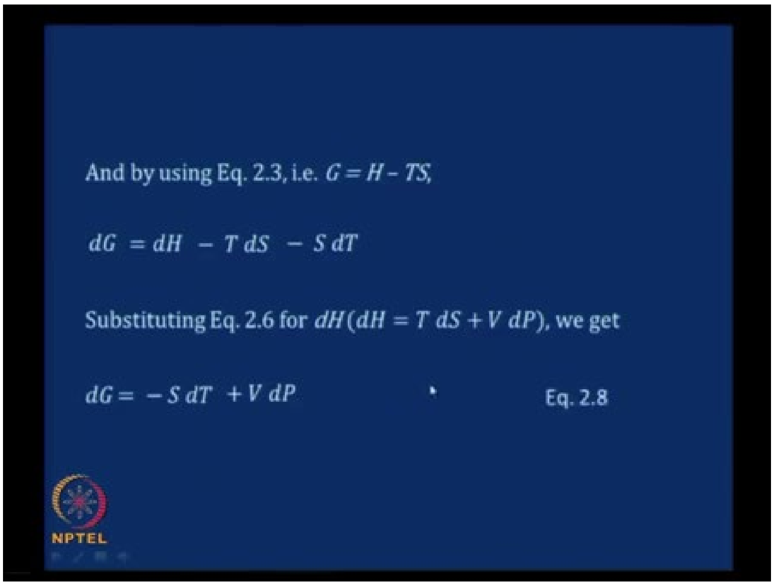

And by using Eq. 2.3, i.e. $G = H - TS$,

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

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

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

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,

$$G = H - TS$$

enthalpy minus the product of temperature and entropy. Same scheme as earlier;

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

We know that

$$dH = T\,dS + V\,dP$$

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

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

Let us call this equation 2.8. Remember, we have derived these equations for a closed system.

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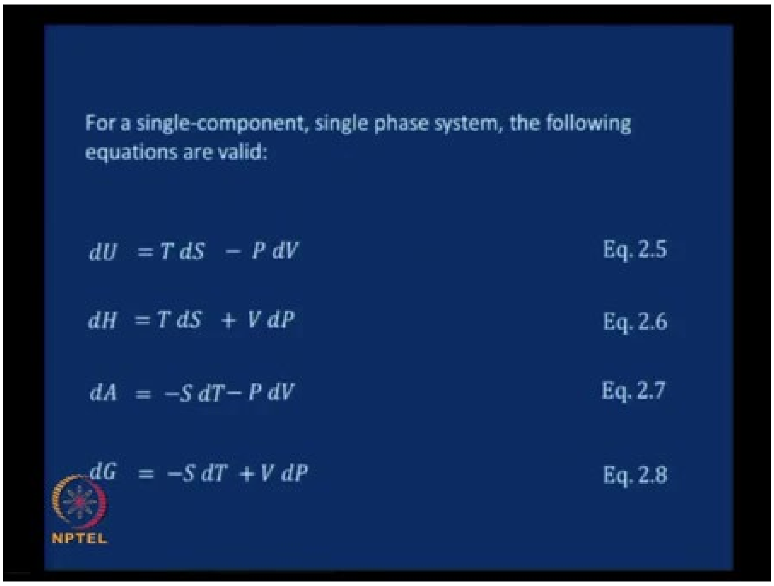

For a single-component, single phase system, the following equations are valid:

$dU = T\,dS - P\,dV$ Eq. 2.5

$dH = T\,dS + V\,dP$ Eq. 2.6

$dA = -S\,dT - P\,dV$ Eq. 2.7

$dG = -S\,dT + V\,dP$ Eq. 2.8

So for a single component single faced single-phase closed system the following equations are valid which we derived dU equals TdS - PdV this was that equation 2.5, dH equals TdS + VdP equation 2.6 dA equals - SdT - PdV equation 2.7 dG equals - SdT + VdP equation 2.8.

$$dU = TdS - PdV$$
$$dH = TdS + VdP$$
$$dA = -SdT - PdV$$
$$dG = -SdT + VdP$$

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 you can always derive them quite simply from first principles as we shown.

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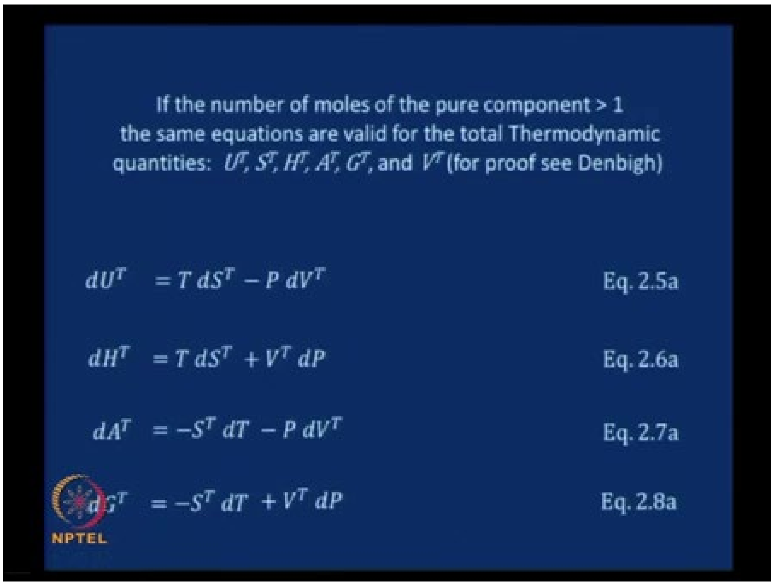

If the number of moles of the pure component > 1
the same equations are valid for the total Thermodynamic
quantities: U^T, S^T, H^T, A^T, G^T, and V^T (for proof see Denbigh)

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

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

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

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

So far we had looked at a single component system 1 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 1 did it now be more than 1. It is still a closed system it is still a pure component and only the number of moles are more than 1. If that is the case remember we had used U S H A G for 1 mole of the substance.

The thermodynamic quantities for 1 mole of the substance. Now since the number of moles are greater than 1 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 as total UT; H total, HT; A total, AT; G total, GT, and V total VT. The 4 equations that we derived for a closed system earlier for 1 mole of a closed system consisting of 1 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 1 of your reference books which is by Kenneth Denbigh. Let me just state the equations here dU T equals T dS T remember that T is an intensive variable its value will not depend on the amount of substance present so it is going to be T dS T - P dV. P is also an intensive variable; let us call this equation 2.5a. dHT is T dS T + VT dP equation 2.6a you can compare these equations with the equations for 1 mole of a pure substance dAt equals – ST dT - P dV T equation 2.7a and dGT equals – S T dT + VT dP which is equation 2.8a.

$$dU^T = TdS^T - PdV^T$$
$$dH^T = TdS^T + V^T dP$$
$$dA^T = -S^T dT - PdV^T$$
$$dG^T = -S^T dT + V^T dP$$

To reemphasize, these are the equations for a system that consists 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 1 phase let us say a gas phase or a liquid phase just 1 phase there. But now let us increase the number of components from 1 earlier if you had only 1 component it was a pure substance. Let us increase the number of components from 1 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 homogenous of a homogenous system for example it could be a mixture of gases of 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 what away and so on and so forth. So, this is a an example of a multi-component homogeneous system. Let us look at some of the relationships that will that will be useful for a multi-component single phase system.

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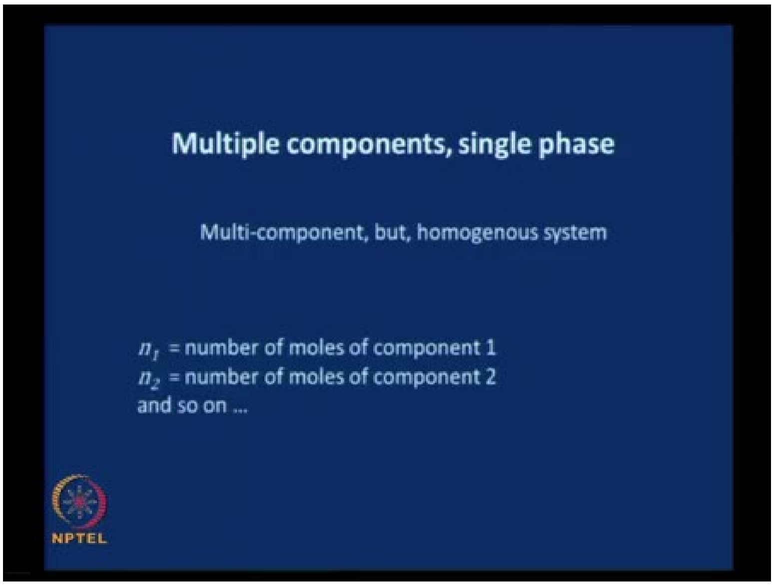

Multiple components, single phase

Multi-component, but, homogenous system

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

Before we do that we need to know some terminology that we use here let n1 be the number of moles of component 1 n to be the number of moles of component 2 and so on.

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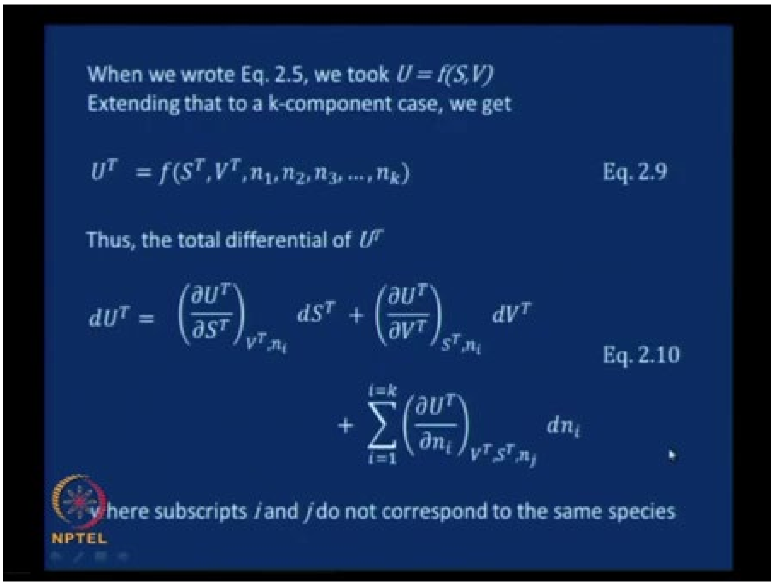

When we wrote Eq. 2.5, we took $U = f(S,V)$
Extending that to a k-component case, we get

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

Thus, the total differential of U^T

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

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

If you recall our equation 2.5

$$dU = TdS - PdV$$

you can recall that we took the internal energy U as a function of S and V.

$$U = f(S, V)$$

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 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 n1 number of moles of the first component and 2 number of moles of the second component and so on till nk number of moles of the kth component.

$$U^T = f(S^T, V^T, n_1, n_2, n_3, \ldots, n_k)$$

I will call this equation 2.9.

Therefore the total differential of UT if you recall the way the total differentials are written is the partial differential of UT with respect to ST at constant other variables or are the conditions where the other variables are held constant which is VT n1 n2 n3 are all held constant which is indicated by ni being constant. So, dou UT by dou ST times dST + dou UT by dou VT the second variable at constant ST and all ni times dVT + dou UT by dou n 1 dn1 + dou UT by dou n 2 dn 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 UT by dou ni at constant VT ST 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 1 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 UT by dou n i VT at constant VT ST and n j times dn i

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

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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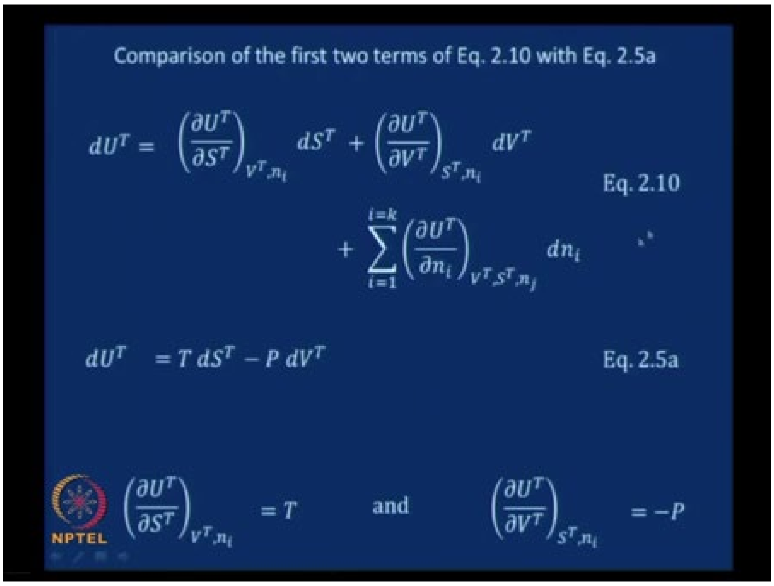

Comparison of the first two terms of Eq. 2.10 with Eq. 2.5a

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

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

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

If we compare the first 2 terms of equation to 10 that we just wrote down with the equation 2.5a I am going to give you both these equations now.

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

This is 2.10 that we derived just now and this is 2.5a.

$$dU^T = TdS^T - PdV^T$$

Here going by the same scheme dUT is dou UT by dou ST at constant V dS T - dou UT by dou VT at constant S T dV T. It is quite easy to see the correspondence between the 2 and therefore quite straightforward to write dou UT by dou S T at constant V T ni equals the temperature and dou UT by dou VT at constant S T and all other components the number of components being held constant.

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

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

Note that this is for a multi-component system and we have compared it with a single component system and we are drawing useful relationships see you in the next class.