Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 32
Activity Coefficient from Excess Property

Welcome!

We are looking at the thermodynamics of solutions now. In the last class, we got introduced to a property known as the excess property. We said that excess property, say M^{TE}, plays the same role for solutions as the residual property M^{TR} or M^R played for the pure substance.

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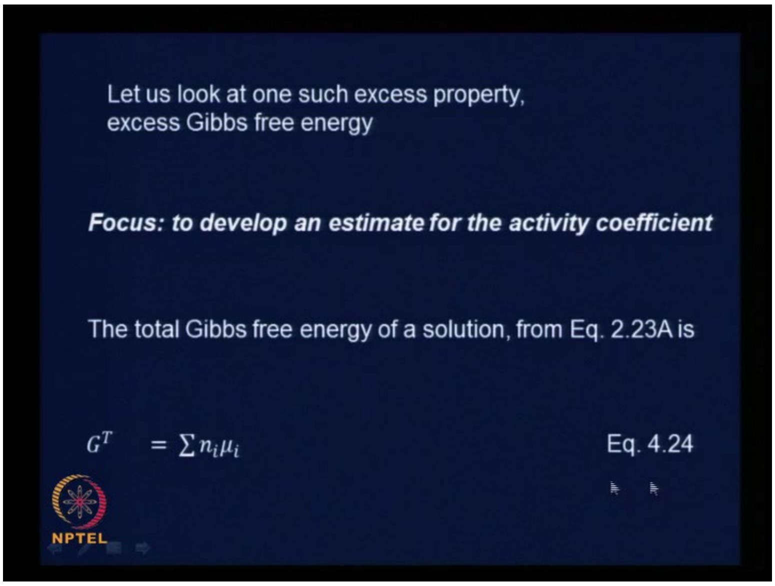

Let us look at one such excess property, excess Gibbs free energy

Focus: to develop an estimate for the activity coefficient

The total Gibbs free energy of a solution, from Eq. 2.23A is

$$G^T = \sum n_i\mu_i \quad \text{Eq. 4.24}$$

Then towards the end of the class, we said let us look at, one such excess property, the excess Gibbs free energy. We are going to look at this with a very specific objective in mind. The focus here is to develop an estimate for the activity coefficient. Remember the activity coefficient is the one that brings about the non-ideality of a liquid or a solid phase. Now, the total Gibbs free energy of a solution, and if you flip back to your second module, … from equation 2.23 A, was

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

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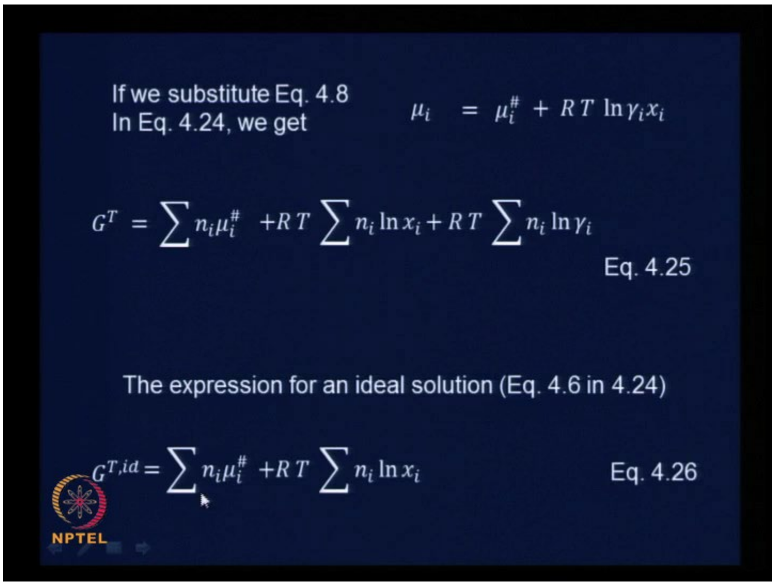

If we substitute Eq. 4.8
In Eq. 4.24, we get

$$\mu_i = \mu_i^\# + R\,T \ln \gamma_i x_i$$

$$G^T = \sum n_i \mu_i^\# + R\,T \sum n_i \ln x_i + R\,T \sum n_i \ln \gamma_i$$

Eq. 4.25

The expression for an ideal solution (Eq. 4.6 in 4.24)

$$G^{T,id} = \sum n_i \mu_i^\# + R\,T \sum n_i \ln x_i$$

Eq. 4.26

We will get from there, and let us call this equation 4.24. We will need to refer to this time to time. So, we will give it a new equation number 4.24. Now if we substitute equation 4.8, which is

$$\mu_i = \mu_i^\# + R\,T\; ln\, \gamma_i x_i$$

If you recall, this is the expression for a non-ideal solution of either liquids or solids. And if you substitute this into this equation 4.24, G T equals summation over n i mu i, then we get G T is summation over … before I do that, I will tell you that how this goes about. We are going to substitute mu i with mu i hash plus R T ln gamma i x i. R T ln gamma i x i could be written as R T ln gamma i plus R T ln x i. You know that ln of (a b) is ln of a plus ln of b.

Therefore, if you multiply each term by n i, and sum at over all i, we get sum over n i mu i hash, which corresponds to this term, plus R T times sum over n i ln x i which corresponds to this term. We will take that first. It will be actually sum over R T n i ln x i. R T is common, so R T comes out, plus … in a similar fashion R T comes out here … sum over n i ln gamma i.

$$G^T = \sum n_i \mu_i^\# + R\,T \sum n_i\, ln\, x_i + R\,T \sum n_i\, ln\, \gamma_i$$

Let us call this equation 4.25. At the same time, the expression for an ideal solution, we all know. You know if you look at this mu i equals mu i hash plus R T ln gamma i x I; we know that gamma i brings in the non-ideality. So, the expression for an ideal equation is actually 4.6 that we presented earlier, would be mu i equals mu i hash plus R T ln x i. Now if you substitute this into 4.24, we would get

$$G^{T,\,id} = \sum n_i \mu_i^{\#} + R\,T \sum n_i \, ln\, x_i$$

Now you know, where we are getting at, you know that the excess property is going to be actual minus the ideal.

So, the expression for the excess property, in terms of mu i hash gamma i x i and so on and so forth, would be obtained if you subtract this equation, which is equation 4.26, from 4.25. As you can see, this term is going to cancel with this term, this term is going to cancel with this term, and so only this term is going to remain.

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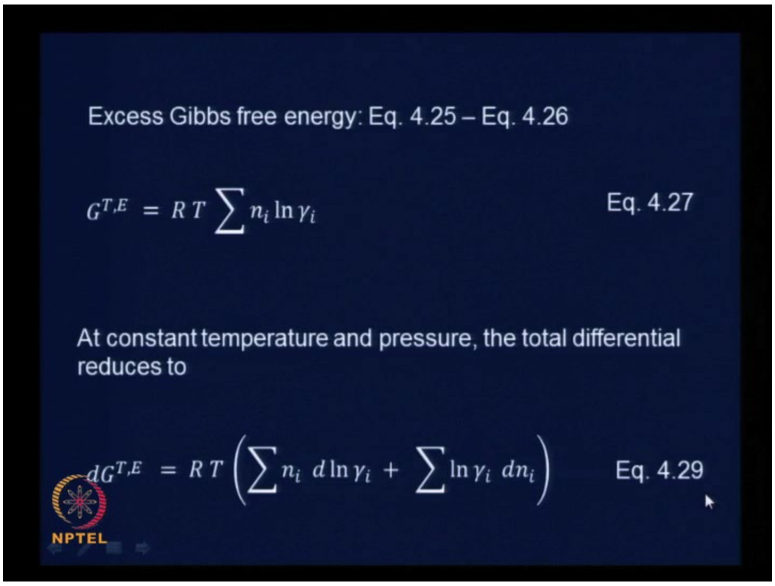

Excess Gibbs free energy: Eq. 4.25 – Eq. 4.26

$$G^{T,E} = R\,T \sum n_i \ln \gamma_i \qquad \text{Eq. 4.27}$$

At constant temperature and pressure, the total differential reduces to

$$dG^{T,E} = R\,T \left(\sum n_i \, d \ln \gamma_i + \sum \ln \gamma_i \, dn_i \right) \qquad \text{Eq. 4.29}$$

For the excess Gibbs free energy

$$G^{T,E} = \; R\,T \sum n_i \, ln\, \gamma_i$$

Let us call this equation 4.27. Now, if we assume constant temperature and pressure, the total differential that is d of G T E. d of G T E would become … R T is common, temperature is a constant; therefore, you can take R T out … and then by chain rule it is sum over n i d ln gamma i plus ln gamma i times d n i. First function into derivative of the second function plus second function into derivative of first function; you do that for each and therefore, you need sum it over all i terms;

$$dG^{T,E} = RT\left(\sum n_i \, d\ln\gamma_i + \sum \ln\gamma_i \, dn_i\right)$$

let us call that equation 4.29.

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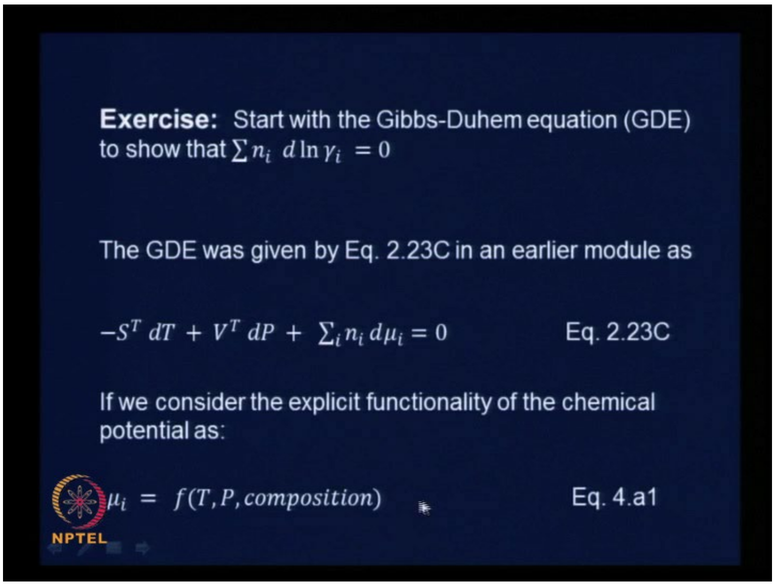

Exercise: Start with the Gibbs-Duhem equation (GDE) to show that $\sum n_i \, d\ln\gamma_i = 0$

The GDE was given by Eq. 2.23C in an earlier module as

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

If we consider the explicit functionality of the chemical potential as:

$$\mu_i = f(T, P, composition) \qquad \text{Eq. 4.a1}$$

Now, let us do an exercise; it is very interesting exercise. It establishes one of the very useful relationships but, it is an involved derivation. It is involved at this stage … the under graduate stage. Therefore, what we are going to do to improve your learning, to get comfortable with what the various terms mean, we are going to do this derivation together. What is required is very simple. Start with the Gibbs-Duhem equation, which I will abbreviate as GDE, to show that

$$\sum n_i \, d\ln\gamma_i = 0$$

How is it relevant here? Remember the previous equation? Here, n i d ln gamma … i sum over – we are going to show that this term goes to 0.

What I am going to do is, start you out. Then leave you alone for about 20 minutes or so to help you think about how to go about doing it, and then goes step by step. We know that the Gibbs-Duhem equation was given us to 2.23 C in an earlier module – second module – was

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

This is simultaneous variation of temperature, pressure and the chemical potential, if you recall that is special aspect about this equation.

Now, the first hint is to get to this from the Gibbs-Duhem equation, the first hint is consider the explicit functionality of the chemical potential as the chemical potential of the species i is a function of temperature, pressure and composition.

$$\mu_i = f(T,\ P,\ composition)$$

This is the hint that I am going to leave you out with. For this special derivation, I am going to use a slightly different equation numbering scheme, I am going to use it something like this 4.a1, all this a would correspond mostly to the details of the derivation. So, this is the equation 4.a1. And, this is your hint: starting with this, try to get at this, which is long way away but, this is the starting point, here. Let us see how far you get. 20 minutes from now. Go ahead please.

Ok, hopefully you would have gotten to some stage. You would have started out with this and substituted it into equation 2.23. minus S T dT plus V T dP plus sum over n i d mu i equals 0. If you need some more help I will present a few more steps and then give you some time to work things out in a directed fashion. What we could do is, we say composition here. This composition essentially is given in terms of the either the number of moles or the mole fractions.

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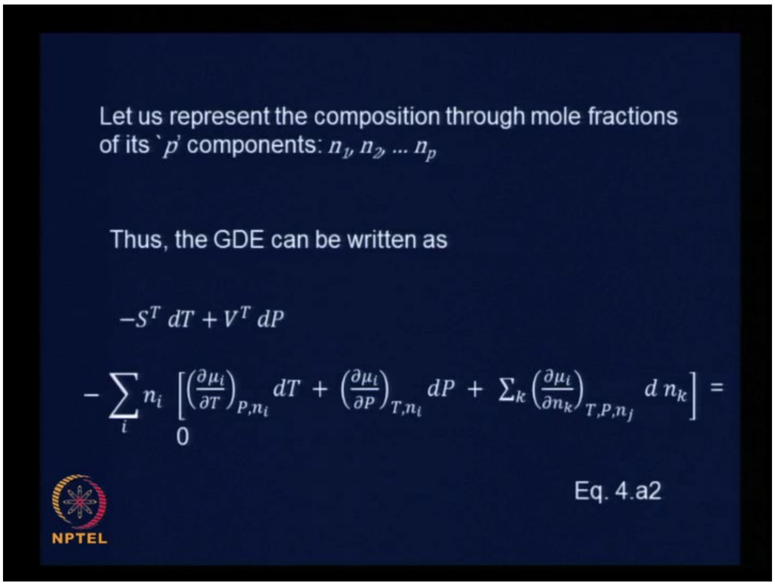

Let us represent the composition through mole fractions of its `p' components: $n_1, n_2, \ldots n_p$

Thus, the GDE can be written as

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

$$-\sum_i n_i \left[\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} dP + \textstyle\sum_k \left(\frac{\partial \mu_i}{\partial n_k}\right)_{T,P,n_j} d\, n_k\right] =$$

0

Eq. 4.a2

Therefore, let us represent the composition through mole fractions here, to begin with, and let us say that there are p components, n1, n2, and so on till np. Therefore, you could write the Gibbs-Duhem equation as

$$-S^T\, dT \;+\; V^T\, dP \;-\; \sum_i n_i \left[\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} dT \;+\; \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} dP \;+\; \sum_k \left(\frac{\partial \mu_i}{\partial n_k}\right)_{T,P,n_j} d\, n_k \right] = 0$$

The total number of components is p. This k is used just as an index for the sum of this term. This equals 0. This is the first term, minus S T dT plus V T dP minus sum of n i d mu i … is written in by considering mu i as a function of temperature, pressure and the composition of all the species.

Since you have species here n1, n2, represented by the mole numbers … or this is actually the number of moles, this is not mole fractions … number of moles n1, n2, np, and so on. You will have to sum over each one of them and that equals 0 here. Let us call this equation 4.a 2. Let me probably give you one more step or may be a few more steps … here, this, probably, I should let you figure out.

Now, let us use the reciprocity relationships from the Gibbs-Duhem equation itself. Remember the reciprocity relationship? You could, if you have an exact differential and you write the expanded form of the total differential in terms of the partial differentials, then you could have a certain relationship between the various terms of the partial derivatives, the partial differentials. That is what we had seen earlier.

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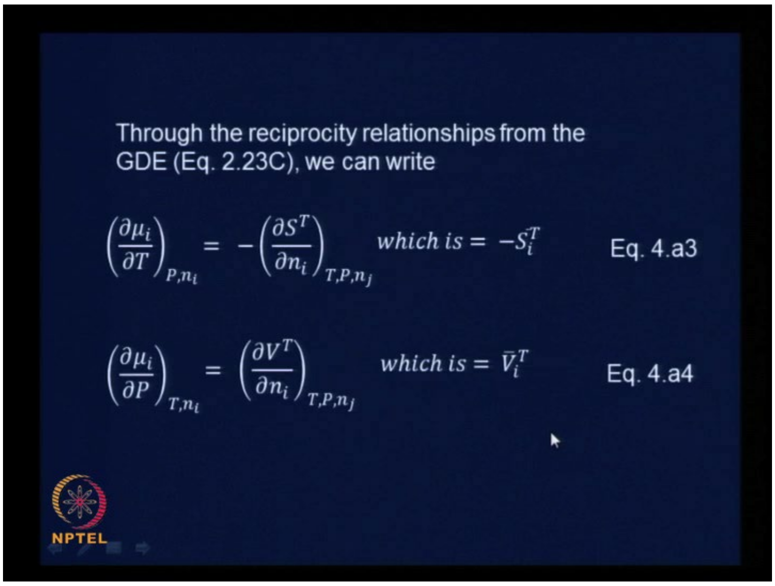

Through the reciprocity relationships from the GDE (Eq. 2.23C), we can write

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial S^T}{\partial n_i}\right)_{T,P,n_j} \quad which\ is = -\bar{S}_i^T \qquad \text{Eq. 4.a3}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V^T}{\partial n_i}\right)_{T,P,n_j} \quad which\ is = \bar{V}_i^T \qquad \text{Eq. 4.a4}$$

And try to figure this out from this equation here or even the previous one. The compact GDE,

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

This is the partial molar entropy, and this relationship is by applying the reciprocity relationship to the Gibbs-Duhem equation. Another reciprocity relationship would give us

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

This is equation 4.a4.

What I would like you to do is, use this and see what 4.a2 becomes. You would be very surprised. Use this, use these reciprocity relationships, and see what 4.a2 becomes. I am going to give you some more time, so that you will get into the feel of the whole thing. Let me give you about 10 minutes to do that. Go ahead please.

Hopefully, you would have realized, that the partial molar volumes here, when multiplied by the number of moles actually give you the total quantity such as this.

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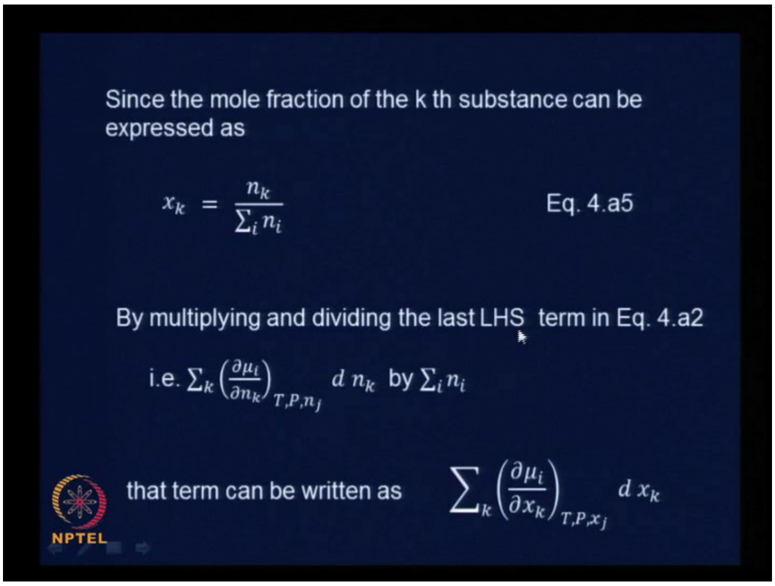

Since the mole fraction of the k th substance can be expressed as

$$x_k = \frac{n_k}{\sum_i n_i} \qquad \text{Eq. 4.a5}$$

By multiplying and dividing the last LHS term in Eq. 4.a2

i.e. $\sum_k \left(\frac{\partial \mu_i}{\partial n_k}\right)_{T,P,n_j} d\,n_k$ by $\sum_i n_i$

that term can be written as $\sum_k \left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_j} d\,x_k$

Before that, let us also see that, the mole fraction – the definition of mole fraction: it is number of moles by the total number of moles.

$$x_k = \frac{n_k}{\sum_i n_i}$$

This is required to express the equation in a convenient form. We will call this equation 4.a5. By multiplying and dividing the last term, one of the things is gone missing I think … it is coming next. … This are a few extra steps before we get to the point of interpreting the partial molar quantities. By multiplying and dividing the last term on the left hand side of equation 4.a 2 by summation over ni.

You know this was the last term,

$$\sum_k \left(\frac{\partial \mu_i}{\partial n_k}\right)_{T,P,n_j} d\,n_k \quad \text{by} \quad \sum_i n_i$$

Therefore, this would become d n k sum over n i. Here you would have dou n k by sum over n i. Therefore, this can be replaced by xk and this can also be replaced by xk. And therefore, the last term on the left hand side – the right hand side was 0 – the last term on the left hand side can be reduced to

$$\sum_k \left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_j} d\,x_k$$

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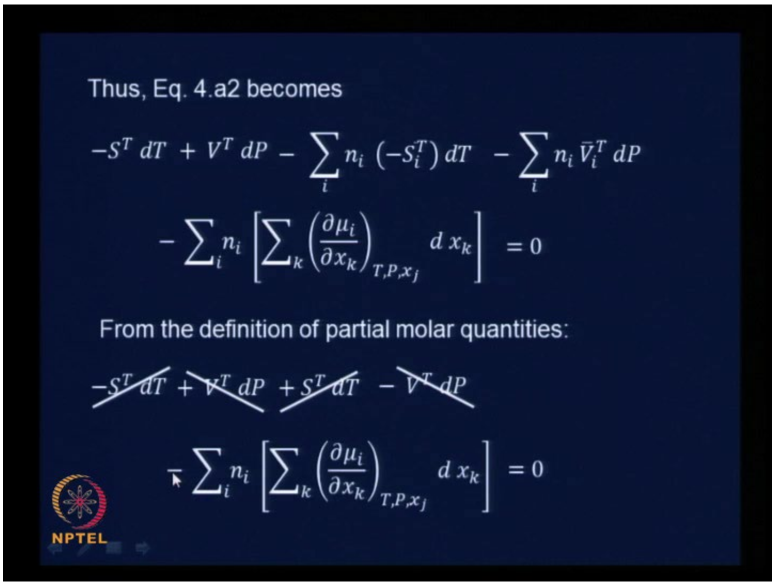

Thus, Eq. 4.a2 becomes

$$-S^T\,dT + V^T\,dP - \sum_i n_i\,(-S_i^T)\,dT - \sum_i n_i\,\bar{V}_i^T\,dP$$

$$-\sum_i n_i \left[\sum_k \left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_j} d\,x_k\right] = 0$$

From the definition of partial molar quantities:

$$\cancel{-S^T\,dT} + \cancel{V^T\,dP} + \cancel{S^T\,dT} - \cancel{V^T\,dP}$$

$$-\sum_i n_i \left[\sum_k \left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_j} d\,x_k\right] = 0$$

If we do this … if we write in terms of mole fractions, and substitute into 4.a2, that would become minus S T dT plus V T dP. Now, this is where we are substituting the relationship that we obtained from the reciprocity relationship as operated on the Gibbs-Duhem equation. Remember we got the partial molar entropy and the partial molar volume. So, the third term was minus of sum over n i of minus S i T, this is what we got from the reciprocity relationship dT. And the fourth term again from the other reciprocity relationship minus sum over n i V i T hash dP, Minus – we are writing this in terms of compact mole fractions – minus sum over i n i, this was there earlier, this we have replaced in terms of sum over k dou mu i dou x k constant T P all other x js d x k, of course equals to 0.

$$-S^T\,dT + V^T\,dP - \sum_i n_i\left(-\bar{S}_i^T\right) dT - \sum_i n_i \bar{V}_i^T\,dP - \sum_i n_i\left[\sum_k \left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_j} d\,x_k\right] = 0$$

And from the definition of partial molar quantities, this is nothing but … sum over n i times minus s i T is nothing but, the minus of the total entropy of the system itself. This minus S T dT will remain here plus V T dP will remain here and there is a minus here, there is a minus here. So this becomes plus. And we said that this is total entropy of the system. So, S T dT this becomes minus … By the same argument, this is nothing but, V T, the total molar volume of the system, V T dP and this term as the same, minus sum over n i times sum over dou mu i dou x k constant T P x j d x k.

Note that this is the double sum, which means for each of this term you need to sum over all the p terms and then take the next. For example, if you take n 1, you need to run through x 1 to x p, and then n 2 … run this through x 1 to x p, and so on and so forth. That is the meaning of this; this equals 0. It is quite obvious that these terms are going to cancel; minus S^T dT will cancel with plus S^T dT plus V^T dP will cancel with minus V^T dP. Therefore, we have this of a nice form here; minus is inconsequential.

$$-\sum_i n_i \left[\sum_k \left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_j} d\,x_k\right] = 0$$

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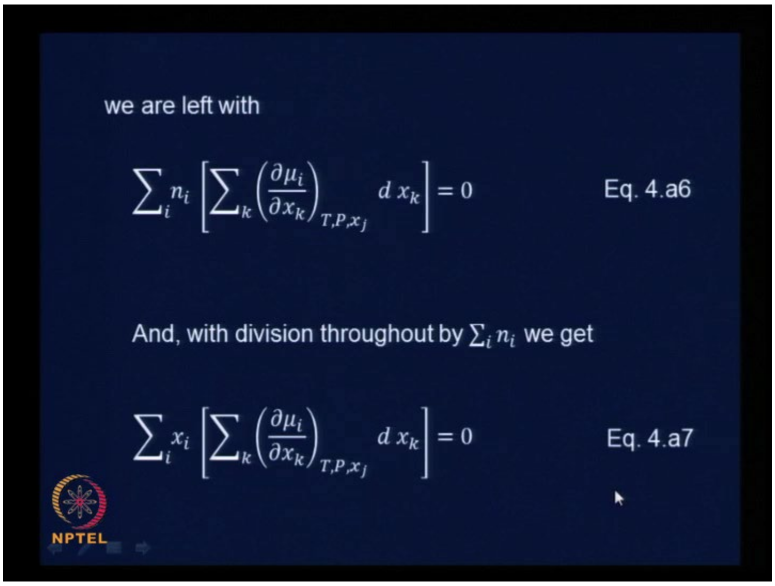

we are left with

$$\sum_i n_i \left[\sum_k \left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_j} d\,x_k\right] = 0 \qquad \text{Eq. 4.a6}$$

And, with division throughout by $\sum_i n_i$ we get

$$\sum_i x_i \left[\sum_k \left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_j} d\,x_k\right] = 0 \qquad \text{Eq. 4.a7}$$

We are left with

$$\sum_i n_i \left[\sum_k \left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_j} d\,x_k\right] = 0$$

We will call this equation 4.a6. And with division throughout by sum over n i, in other words, we are going to divide the left hand side by sum over n i and right hand side also by sum over n I, … here it does not matter. We will get

$$\sum_i x_i \left[\sum_k \left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_j} d\,x_k\right] = 0$$

Equation 4.a 7.

I think we need to stop here, we are out of time. What we are going to do in the next class is substitute mu i in terms of mu i hash gamma i x i and so on, and see where we go. Remember the whole idea is … this is an exercise starting from the Gibbs-Duhem equation; we are going to show a specific relationship, that is why we are doing all this. See you in the next class.