Thermodynamics (Classical) for Biological Systems

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Module No. # 04

Thermodynamics of solutions

Lecture No. # 20

Lewis and Randall rule Partial Molar Properties

Yesterday, we started looking at multi-component systems. We initially started out with the ideal gas, and since we are doing everything in terms of the chemical potential, we had written down the chemical potential expressions for an ideal gas, which we had already seen in the earlier module, the third module.

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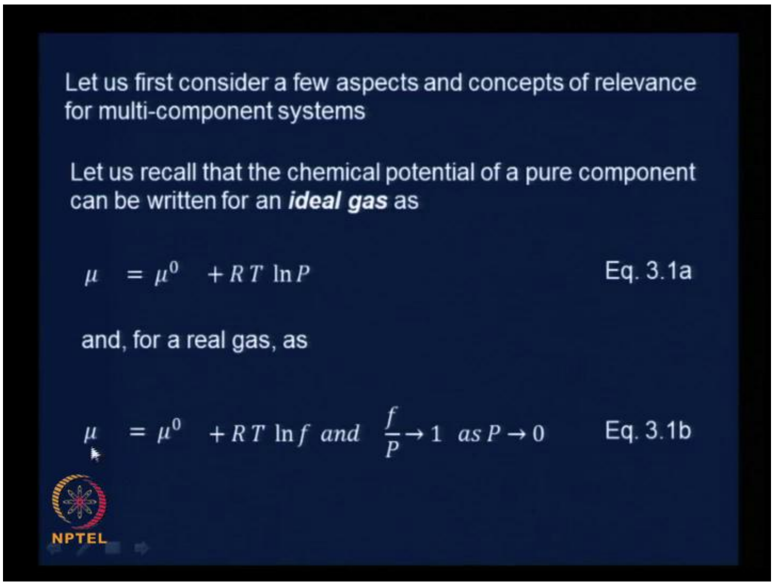

Let us first consider a few aspects and concepts of relevance for multi-component systems

Let us recall that the chemical potential of a pure component can be written for an ***ideal gas*** as

$$\mu = \mu^0 + RT \ln P \qquad \text{Eq. 3.1a}$$

and, for a real gas, as

$$\mu = \mu^0 + RT \ln f \;\; and \;\; \frac{f}{P} \rightarrow 1 \;\; as\, P \rightarrow 0 \qquad \text{Eq. 3.1b}$$

And then we said that the real gas … in the expression for the real gas, you replace the pressure here, mu equals mu naught plus R T ln P, where mu naught is a function of temperature alone. This was for an ideal gas, and when you write it for the real gas, it becomes mu equals mu naught plus R T ln f … and f by P tends to one as P tends to 0. And then we looked at something called perfect gas mixtures and imperfect gas mixtures. And then we looked at something called ideal gas mixtures and non-ideal gas mixtures. And with that formulation we saw that we could expand them or extend that to ideal mixtures of liquids and solids as well as non-ideal mixtures of liquids and solids.

So, essentially, ideal gas, real gas that was initial formulation where we went from P to f and then we used the perfect and imperfect gas mixtures. That is only a concept which we will kind of borrow on from time to time. So, let us keep it aside for the time being. We will go through it and see how we defined it in a little bit. And then we went into … ideal gas mixtures and real gas mixtures. And then we saw that we could extend that formulation to ideal mixtures of liquids and solids as well as non-ideal mixtures of liquids and solids.

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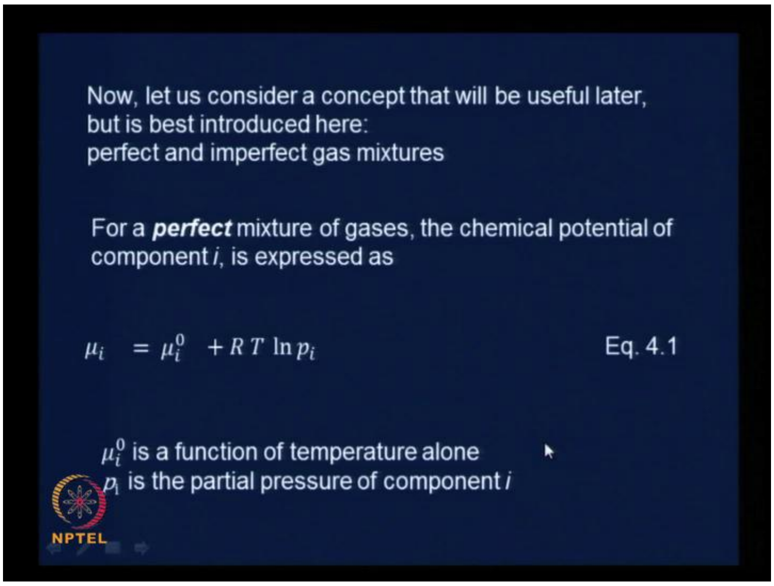

Now, let us consider a concept that will be useful later, but is best introduced here:
perfect and imperfect gas mixtures

For a ***perfect*** mixture of gases, the chemical potential of component *i*, is expressed as

$$\mu_i = \mu_i^0 + R\,T\,\ln p_i \qquad \text{Eq. 4.1}$$

μ_i^0 is a function of temperature alone
p_i is the partial pressure of component *i*

So, we have already seen this. The ideal gas is mu equals mu naught plus R T ln P. For the real gas it was mu equals mu naught plus R T ln f. And, concept-wise, the perfect mixture of gases is something for which the following can be used … as the chemical potential. For every component i mu equals mu i naught plus R T ln p i – this is the partial pressure of the component i in the gas mixture.

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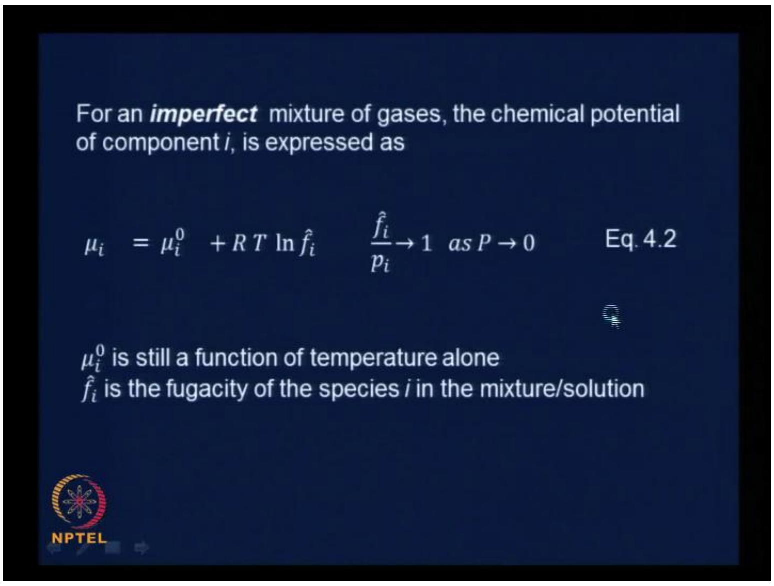

For an ***imperfect*** mixture of gases, the chemical potential of component *i*, is expressed as

$$\mu_i = \mu_i^0 + RT \ln \hat{f}_i \qquad \frac{\hat{f}_i}{p_i} \to 1 \;\; as\, P \to 0 \qquad \text{Eq. 4.2}$$

μ_i^0 is still a function of temperature alone
$\hat{f}_i$ is the fugacity of the species *i* in the mixture/solution

And then for the imperfect gas mixture … we said we should replace this partial pressure with f i hat, the fugacity of the species i in the mixture. Mu i equals mu i naught plus R T ln f i hat; and to complete the definition f i hat divided by p i tends to one as p tends to 0.

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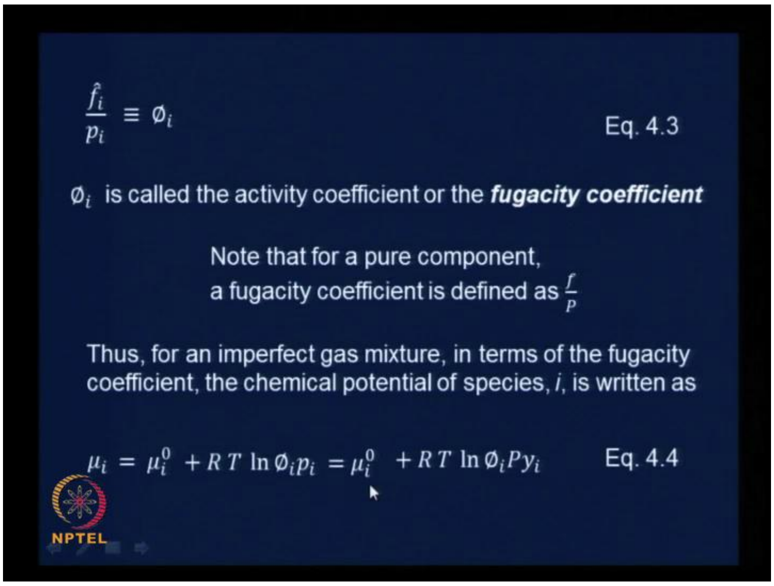

$$\frac{\hat{f}_i}{p_i} \equiv \emptyset_i \qquad \text{Eq. 4.3}$$

$\emptyset_i$ is called the activity coefficient or the ***fugacity coefficient***

Note that for a pure component,
a fugacity coefficient is defined as $\frac{f}{P}$

Thus, for an imperfect gas mixture, in terms of the fugacity coefficient, the chemical potential of species, *i*, is written as

$$\mu_i = \mu_i^0 + RT \ln \emptyset_i p_i = \mu_i^0 + RT \ln \emptyset_i P y_i \qquad \text{Eq. 4.4}$$

The fugacity coefficient for the species i in the mixture becomes f i hat by p i equals phi i. The earlier one the pure gas fugacity coefficient we had defined as f by total pressure P has been equal to phi.

Therefore, we could write mu equals mu i naught plus R T ln phi i p i for an imperfect gas mixture. And if we expand p i into P y i – total pressure into the mole fraction – we get mu i naught plus R T ln phi i P y i as the expression for mu i.

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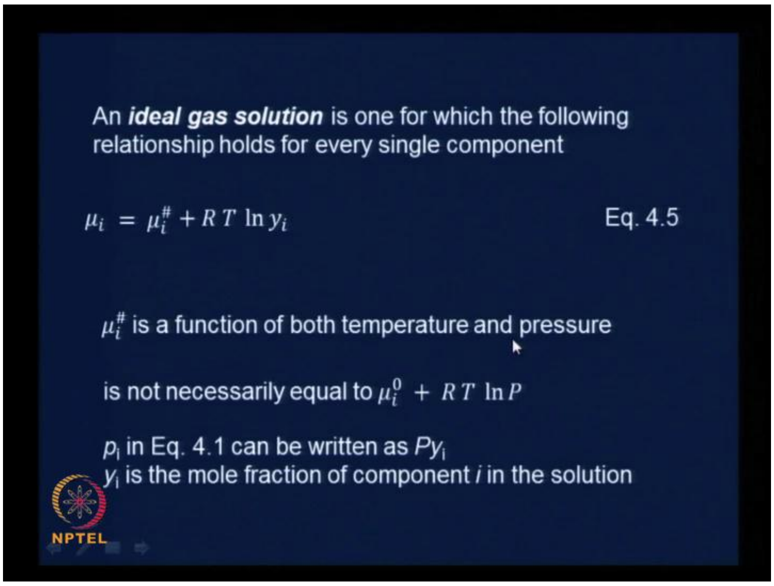

An ***ideal gas solution*** is one for which the following relationship holds for every single component

$$\mu_i = \mu_i^{\#} + R\,T\,\ln y_i \qquad \text{Eq. 4.5}$$

$\mu_i^{\#}$ is a function of both temperature and pressure

is not necessarily equal to $\mu_i^0 + R\,T\,\ln P$

p_i in Eq. 4.1 can be written as Py_i
y_i is the mole fraction of component *i* in the solution

Then this one is what we need to focus on, the ideal gas solution. The formulation that we had used is mu i equals mu i hash plus R T ln y i. The important thing being that mu i hash is a function of both temperature and pressure. And here we have a convenient formulation in terms of the mole fraction. Mu i equals mu i hash plus R T ln y i; … this is for an ideal gas solution.

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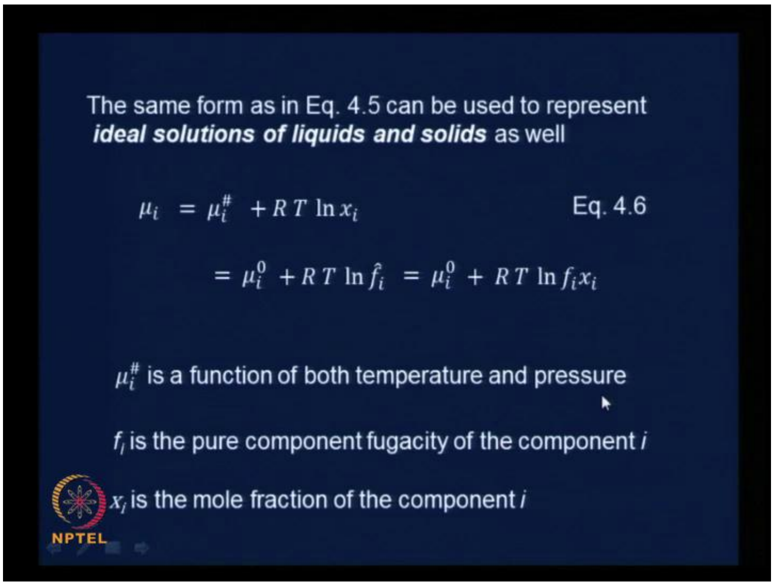

The same form as in Eq. 4.5 can be used to represent ***ideal solutions of liquids and solids*** as well

$$\mu_i = \mu_i^\# + R\,T\,\ln x_i \qquad \text{Eq. 4.6}$$

$$= \mu_i^0 + R\,T\,\ln \hat{f}_i = \mu_i^0 + R\,T\,\ln f_i x_i$$

$\mu_i^\#$ is a function of both temperature and pressure

f_i is the pure component fugacity of the component *i*

x_i is the mole fraction of the component *i*

For the ideal solutions of liquids and solids, we use x i as the mole fraction of the component i in the liquid or the solid solution.

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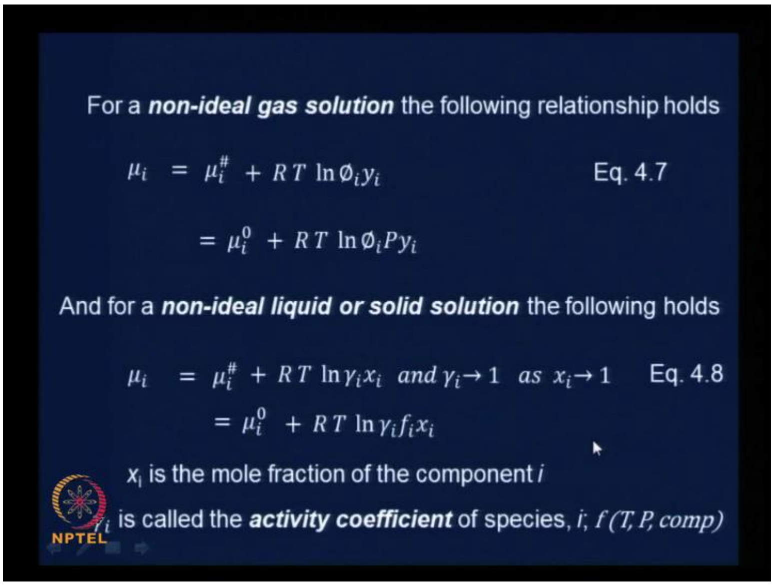

For a ***non-ideal gas solution*** the following relationship holds

$$\mu_i = \mu_i^\# + R\,T\,\ln \emptyset_i y_i \qquad \text{Eq. 4.7}$$

$$= \mu_i^0 + R\,T\,\ln \emptyset_i P y_i$$

And for a ***non-ideal liquid or solid solution*** the following holds

$$\mu_i = \mu_i^\# + R\,T\,\ln \gamma_i x_i \quad and\ \gamma_i \rightarrow 1 \quad as\ x_i \rightarrow 1 \qquad \text{Eq. 4.8}$$

$$= \mu_i^0 + R\,T\,\ln \gamma_i f_i x_i$$

x_i is the mole fraction of the component *i*

γ_i is called the ***activity coefficient*** of species, *i*; *f (T, P, comp)*

Then, for the non-ideal gas solution … I had earlier said real gas solution, make it non-ideal gas solution. We write mu i equals mu i hash plus R T ln phi i y i. This phi i brings in the non-ideality of the component in the gas solution. And for the non-ideal liquid or solid solution we could write mu i equals mu i hash plus R T ln gamma i x i; gamma i tends to 1 as the mole fraction of the component i tends to 1. So, this is what we had essentially seen yesterday and reinforced and again reinforced this morning in this class.

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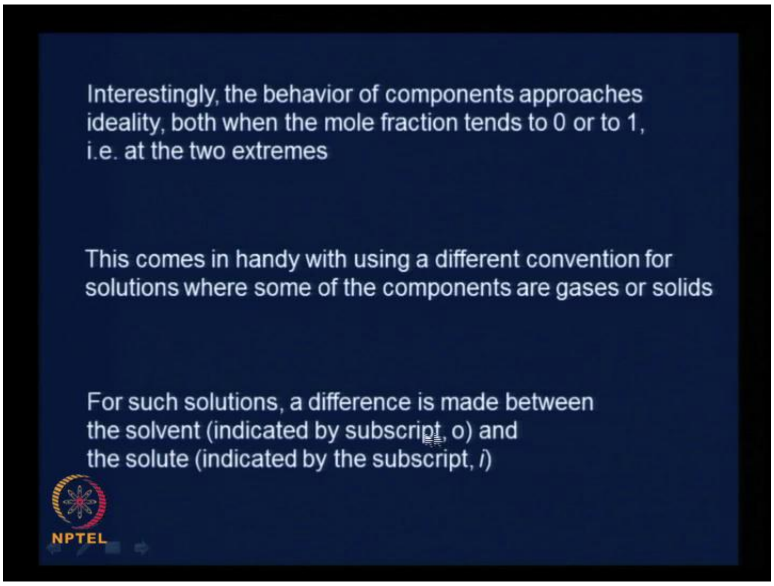

Interestingly, the behavior of components approaches ideality, both when the mole fraction tends to 0 or to 1, i.e. at the two extremes

This comes in handy with using a different convention for solutions where some of the components are gases or solids

For such solutions, a difference is made between the solvent (indicated by subscript, o) and the solute (indicated by the subscript, *i*)

Then we found that that definition especially for the non-ideal liquid and solid solutions work well in most … liquid solution cases. Whereas, when the when the component happens to be either a gas or a solid at the temperature and pressure of the solution in question, then we may run into some difficulties, because as we change the mole fraction of the component in the solution, the phase could change. Therefore, we have to come up with a different formulation. We had used two equation formulation for that. For the solvent we had used a subscript o and the solute we had used the subscript i.

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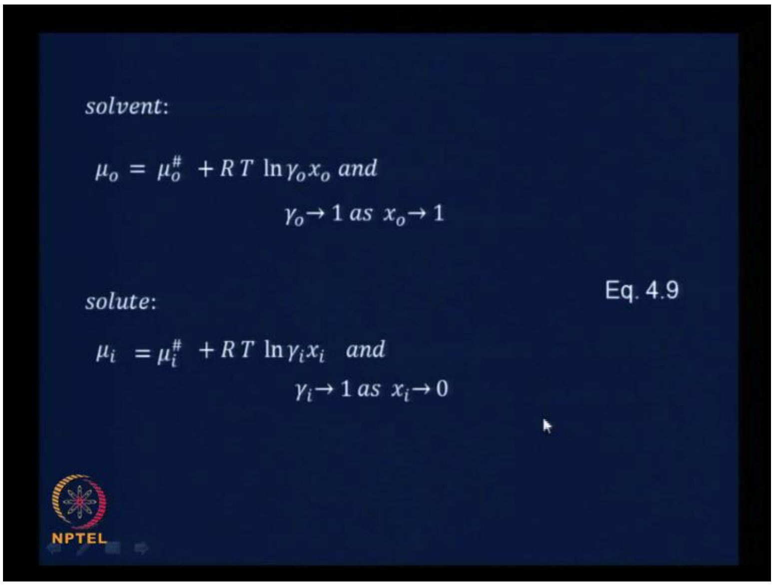

solvent:

$$\mu_o = \mu_o^{\#} + R\,T\,\ln \gamma_o x_o \text{ and}$$

$$\gamma_o \to 1 \text{ as } x_o \to 1$$

Eq. 4.9

solute:

$$\mu_i = \mu_i^{\#} + R\,T\,\ln \gamma_i x_i \text{ and}$$

$$\gamma_i \to 1 \text{ as } x_i \to 0$$

And therefore, we could write for the solvent mu o equals mu o hash plus R T ln gamma o x o along with the completeness of this gamma, activity coefficient. gamma o tends to 1 as x o tends to 1. This is for the solvent and for the solute mu i equals mu i hash plus R T ln gamma i x I, and gamma i tends to 1 as x i tends to 0. This was equation 4.9 and this is where we had finished up yesterday.

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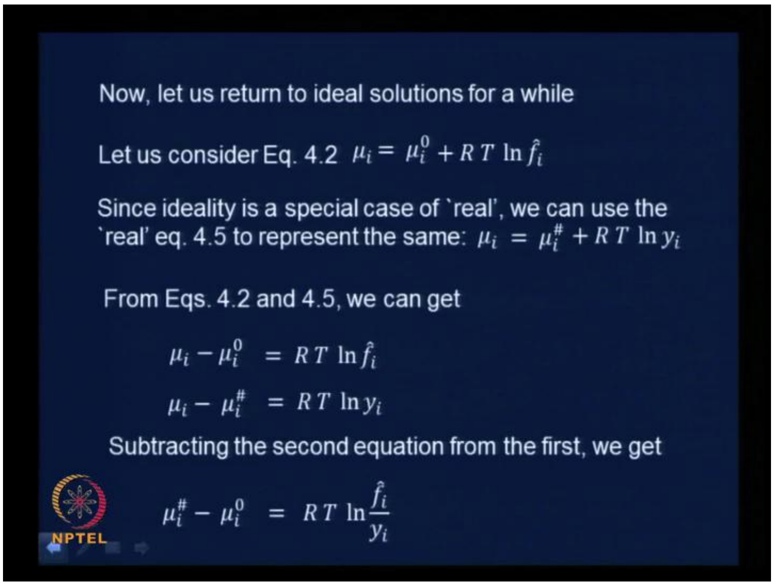

Now, let us return to ideal solutions for a while

Let us consider Eq. 4.2 $\mu_i = \mu_i^0 + R\,T\,\ln \hat{f}_i$

Since ideality is a special case of `real', we can use the `real' eq. 4.5 to represent the same: $\mu_i = \mu_i^{\#} + R\,T\,\ln y_i$

From Eqs. 4.2 and 4.5, we can get

$$\mu_i - \mu_i^0 = R\,T\,\ln \hat{f}_i$$

$$\mu_i - \mu_i^{\#} = R\,T\,\ln y_i$$

Subtracting the second equation from the first, we get

$$\mu_i^{\#} - \mu_i^0 = R\,T\,\ln \frac{\hat{f}_i}{y_i}$$

Now, let us return or look back at ideal solutions for a little bit. We are going to develop something important here. So, let us concentrate on ideal solutions. You know that equation 4.2, you can go back to your notes; it is already given here, mu i equals mu i naught plus R T ln f i hat. This works for the ideal solution case where mu i naught is the function of temperature alone. Now, we know that ideality is nothing but the special case of reality. Therefore, the expression for the real case must also be valid here.

If we write it for the real case it should be valid for the ideal case also. It always the `super' thing should include the special case also. Therefore, this 4.5 equation, mu i equals mu i hash plus R T ln y I; mu i hash is a function of temperature and pressure. This equation should also be valid. Now, from equation 4.2, you know, just by transposing this equation, mu i or in other words, subtracting mu i naught from both sides, we get mu i naught equals R T ln f i hat. And doing the same thing to equation 4.5 we could write … mu i minus mu i hash equals R T ln y i.

Now, what I would like you to do is just subtract the second equation from the first equation and tell me what you get. Take about five minutes – good to juggle, little bit, your brain and your hands and so on so forth. So, just work this out subtract equation two from equation one and tell me what you get. 5 minutes please.

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If you subtract equation two from equation one, you would get mu i hash; this is a minus mu i hash here. Therefore, mu i hash minus mu i naught equals R T ln y i minus R T ln f i hat. … ln a minus ln b equals ln of a by b. Therefore, this becomes R T ln f i hat by y i. Same equation here.

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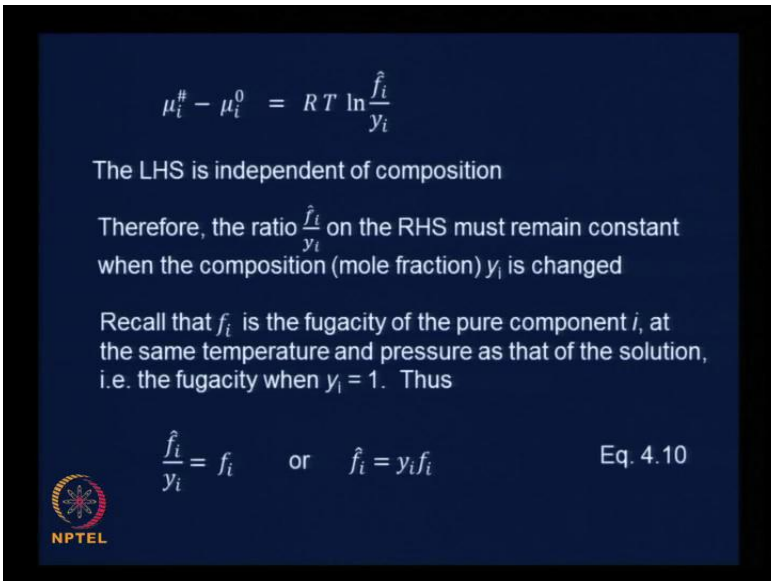

$$\mu_i^\# - \mu_i^0 = RT \ln \frac{\hat{f}_i}{y_i}$$

The LHS is independent of composition

Therefore, the ratio $\frac{\hat{f}_i}{y_i}$ on the RHS must remain constant when the composition (mole fraction) y_i is changed

Recall that f_i is the fugacity of the pure component *i*, at the same temperature and pressure as that of the solution, i.e. the fugacity when $y_i = 1$. Thus

$$\frac{\hat{f}_i}{y_i} = f_i \qquad \text{or} \qquad \hat{f}_i = y_i f_i \qquad \text{Eq. 4.10}$$

Now, note this argument a little carefully. We will be using this argument a few more times in this particular course. You see here – mu i hash mu i naught – this is the left hand side of the equation. You know that in any equation whatever applies to the left hand side must apply to the right hand side. So, we will look at dependencies here. Mu i hash is a function of temperature and pressure. Mu i naught is a function of temperature alone, and … the left hand side, therefore, is definitely independent of composition.

So, that is clear here. Therefore, the right hand side must also be independent of composition. Let us let us look at that point alone. It has to be independent of composition. Therefore, see this is R what is on the right hand side R and T here. There is no problem here. If at all we need to worry about composition it has to be in this term. This ratio f i hat by y i on the right hand side must remain constant when the composition is changed, because you have a left hand side which is independent of composition. Therefore, when you change y i here the only way that this remains independent of composition is that this ratio becomes independent of composition.

Therefore, … f i hat by y i must remain constant when the composition is changed, or when y i, which represents the mole fraction, is changed. I hope this is clear. f i is the fugacity of the pure component i at the same temperature and pressure as that of the solution – that we know. Or, in other words, f i is f i hat when y i equals 1. f i is pure component f i hat is the fugacity of that component in solution. Now, f i can be considered as f i hat when y i becomes 1. Now, you know where I am getting it. Therefore, f i hat by y i is nothing but f i by 1 which i have written as f i. Or, f i hat equals y i into f i directly by transposing this equation.

We will call this equation 4.10. This is something powerful. Before I go forward, let me go through this argument once again, because we will be … using this argument a few times. We have a quantity here on the left hand side, which is independent of composition. Therefore, the right hand side must also be independent of composition. The only term that changes with composition is this. Therefore, this has to remain constant when y i is changed between the ranges that it can take. If we look at one particular value there, which is when y i equals 1 f i hat by y i must equal f i by 1, … because when y i becomes 1 f i hat becomes f i, and therefore, f i hat equals y i into f i.

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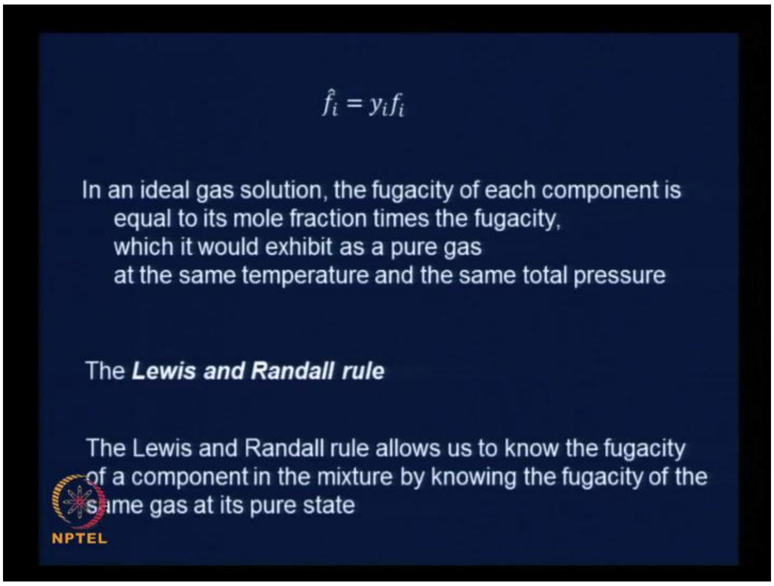

$$\hat{f}_i = y_i f_i$$

In an ideal gas solution, the fugacity of each component is
equal to its mole fraction times the fugacity,
which it would exhibit as a pure gas
at the same temperature and the same total pressure

The ***Lewis and Randall rule***

The Lewis and Randall rule allows us to know the fugacity of a component in the mixture by knowing the fugacity of the same gas at its pure state

This says something powerful. It says in an ideal gas solution – we are looking only at ideal gas solution; remember, that is what we decided to focus on earlier – the fugacity of each component which is represented as f i hat here is equal to its mole fraction, y i, times the fugacity, f i, which is what it would exhibit as a pure gas at the same temperature and pressure as that of the solution. To repeat, in an ideal gas solution, the fugacity of each component, f i hat, is equal to its mole fraction times of fugacity which it would exhibit as a pure gas at the same temperature and the same total pressure.

This is something powerful. What has it given us? It has given us a way of estimating f i hat if f i is known. This is called the Lewis and Randall rule. This name you may have heard it is called the Lewis and Randall rule, which essentially says that f i hat equals y i times f i. And as mentioned, the Lewis and Randall rule allows us to know the fugacity of a component in the mixture by knowing the fugacity of the same gas at its pure state, which is quite powerful.

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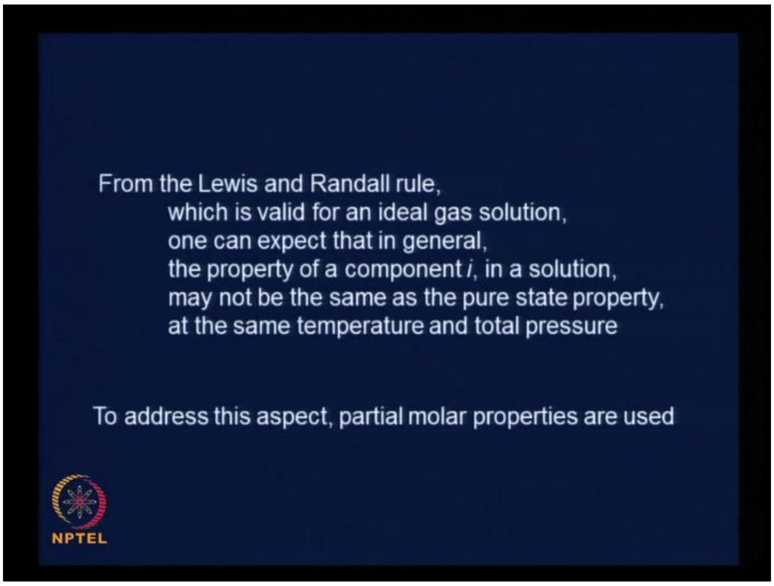

From the Lewis and Randall rule,
which is valid for an ideal gas solution,
one can expect that in general,
the property of a component *i*, in a solution,
may not be the same as the pure state property,
at the same temperature and total pressure

To address this aspect, partial molar properties are used

Now, we will look at something called partial molar properties, which are essential whenever you consider any mixtures or solutions. Let us start with the Lewis and Randall rule itself. From the Lewis and Randall rule, which is valid for an ideal gas equation, we can expect that in general, the property of a component i in a solution may not be the same as the pure state property … at the same temperature and the same total pressure. And therefore, we cannot use a weighted average. What we did in the case of the ideal gas solution is that we use the weighted average: f i hat equals y i times f i; y i was the waiting factor there. Here, … if it is a non-ideal solution we cannot do that. We can do that only for an ideal gas solution.

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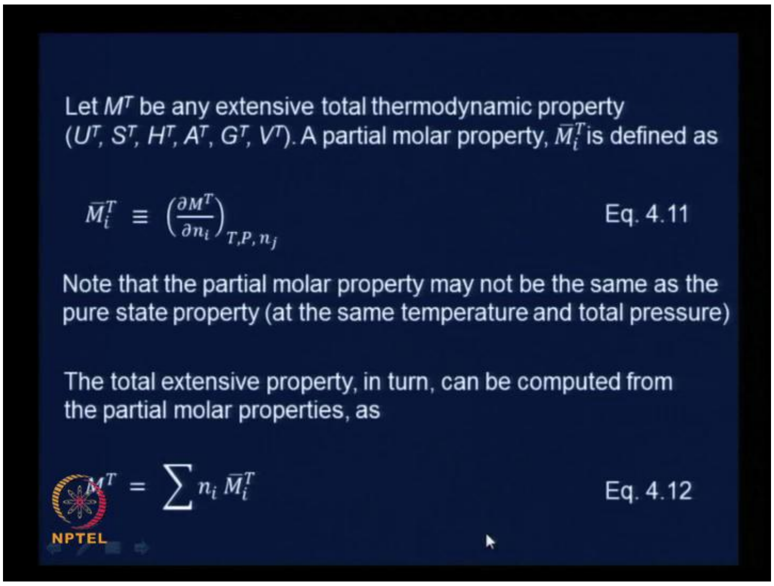

Let M^T be any extensive total thermodynamic property (U^T, S^T, H^T, A^T, G^T, V^T). A partial molar property, $\bar{M}_i^T$ is defined as

$$\bar{M}_i^T \equiv \left(\frac{\partial M^T}{\partial n_i}\right)_{T,P,n_j} \qquad \text{Eq. 4.11}$$

Note that the partial molar property may not be the same as the pure state property (at the same temperature and total pressure)

The total extensive property, in turn, can be computed from the partial molar properties, as

$$M^T = \sum n_i \bar{M}_i^T \qquad \text{Eq. 4.12}$$

Therefore, we use something called partial molar properties to know what partial molar properties are, let us take M superscript T, M T, to be any extensive total thermodynamic property – we have seen this already. For example, it could be U T, which stands for the total internal energy, S T, total entropy, H T, total enthalpy, A T, total Helmholtz free energy, G T, total Gibbs free energy or V T, total volume. If this is the case, then the partial molar property which I am going to represent as M i T with the hash over it, M i T is the total property – I mean, is the property of the component i in the total solution. With the hat it becomes a partial molar property.

It is defined as equal to dou dou n i of M T at constant temperature, pressure and all other mole fractions remaining the same. Again, M i T hash the partial molar property is defined as dou dou n i of M T taken at constant temperature, pressure and all other mole fractions remaining the same. We will call this equation 4.11. This will become clearer as we go along. And, as we have said earlier, the partial molar property may not be the same as the pure state property at the same temperature and total pressure. That is a reason for defining something different as the partial molar property.

It is the property that it seems to exhibit when it is present in solution. In other words it is some sort of hypothetical measure. Why are we using this measure? It gives us an easy means of calculating the total property or estimating the total property. The total extensive property, in turn, can be computed from the partial molar properties as M T is nothing but sum over mole fraction n i times the corresponding partial molar property M i T hat. So, this is a simplistic formulation. To be able to do this, we go in for some sort of a conceptual partial molar property.

What I would like you to do is take a few minutes and write down this expression for each one of these partial molar properties that you have seen so far. There are about six here. Please write them down for each of those properties, this expression. Go ahead, and I will present them in the next 5 minutes or so … after 5 minutes. Go ahead please.

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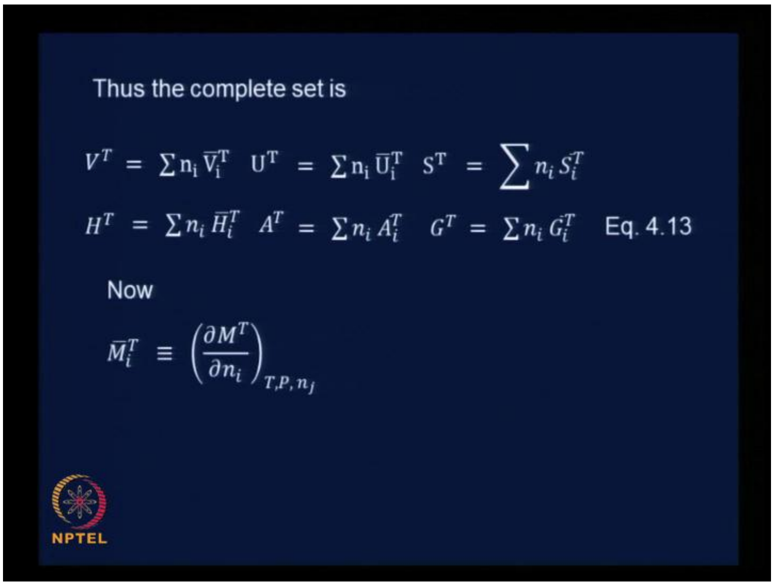

Thus the complete set is

$$V^T = \sum n_i \bar{V}_i^T \quad U^T = \sum n_i \bar{U}_i^T \quad S^T = \sum n_i S_i^T$$

$$H^T = \sum n_i \bar{H}_i^T \quad A^T = \sum n_i A_i^T \quad G^T = \sum n_i G_i^T \quad \text{Eq. 4.13}$$

Now

$$\bar{M}_i^T \equiv \left(\frac{\partial M^T}{\partial n_i}\right)_{T,P,n_j}$$

You would have found it reasonably simple to write this down. V T, total volume, is nothing but summation of n i times partial molar volumes. U T is nothing but summation over n i times partial molar internal energies of each component. S T is nothing but summation over n i S i t hat. H T is nothing but summation over n i H i t hat, the partial molar enthalpies times the mole fraction of each enthalpy summed over all i s gives you the total enthalpy. A T is nothing but sum over n i A T hat, and G T is nothing but sum over n i G i T hat. It is nice to have this here. You can refer to this from time to time equation 4.13.

The dashes are somehow not visible in some cases. Please make sure that these dashes are present in all your quantities. Now, you have already seen this that the partial molar property is defined as dou dou n i of M T at constant T, P, n j. Does this remind you of something that we have seen earlier in the earlier module? Think about it.

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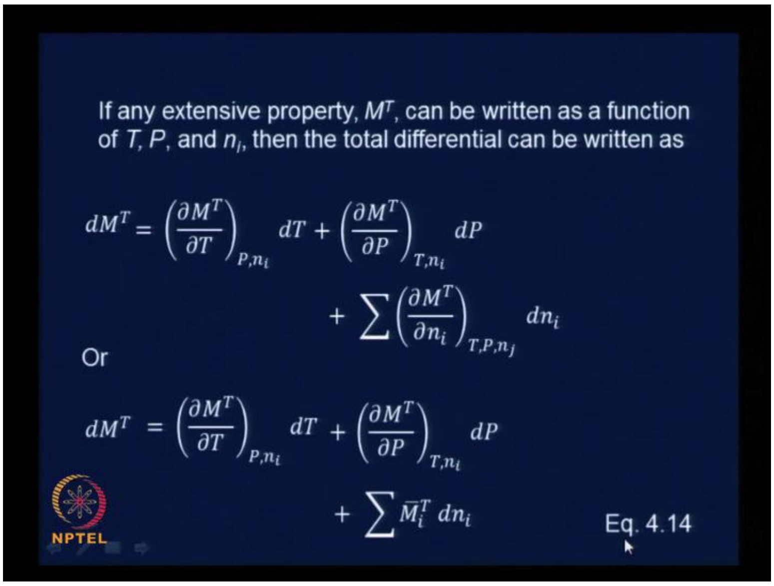

If any extensive property, M^T, can be written as a function of T, P, and n_i, then the total differential can be written as

$$dM^T = \left(\frac{\partial M^T}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial M^T}{\partial P}\right)_{T,n_i} dP + \sum \left(\frac{\partial M^T}{\partial n_i}\right)_{T,P,n_j} dn_i$$

Or

$$dM^T = \left(\frac{\partial M^T}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial M^T}{\partial P}\right)_{T,n_i} dP + \sum \bar{M}_i^T \, dn_i$$

Eq. 4.14

If any extensive property can be written as a function of T, P, and n i then the total differential can be written as … you know this is again an exact differential; therefore, you could write the total differential d M T. Or, this is a state function. Therefore, you could write the total differential as d M T equals dou dou t M T at constant P n i d T plus dou dou P M T at constant T n i d P plus summation over dou dou n i of M T at constant T, P, n j. Here we have taken M T as a function of T, P and n i. Or what is this? This is nothing but the partial molar property.

Therefore, dou M T dou T at constant P, n i, d T dou M T dou P at constant T, n i, d P plus the partial molar property the sum of the partial molar properties times d n i for each species. That is the total differential here. We will call this equation 4.14.

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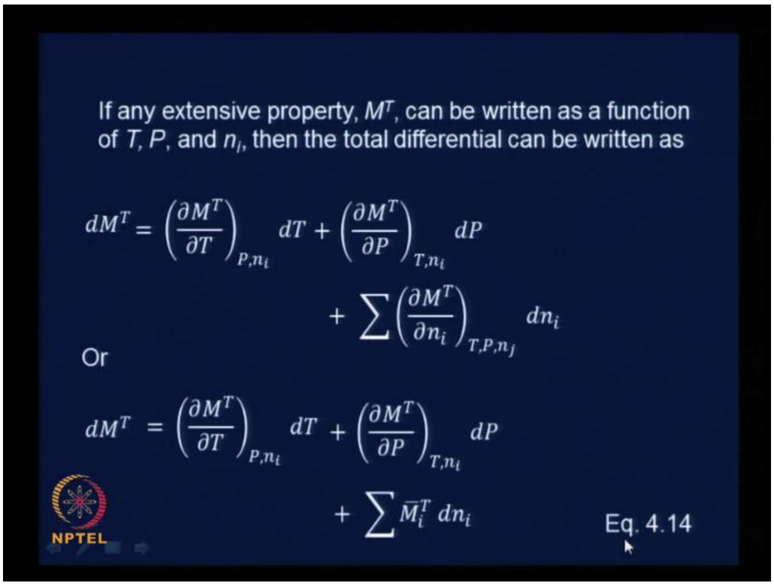


If any extensive property, M^T, can be written as a function of T, P, and n_i, then the total differential can be written as

$$dM^T = \left(\frac{\partial M^T}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial M^T}{\partial P}\right)_{T,n_i} dP + \sum \left(\frac{\partial M^T}{\partial n_i}\right)_{T,P,n_j} dn_i$$

Or

$$dM^T = \left(\frac{\partial M^T}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial M^T}{\partial P}\right)_{T,n_i} dP + \sum \bar{M}_i^T \, dn_i$$

Eq. 4.14

The total differential from equation 4.12, which is this, M T equals summation of n i times the partial molar property of i. Take the product of each and sum them over. That will be equal to the total value, the total extensive property value. This is equation 4.12. If we differentiate this we get the total differential d M T equals summation of n i times the partial molar property of i plus the partial molar property times d n i. This essentially comes from using the chain rule here. Sum over each one of these terms you could do the chain rule for each of these terms. And then separate the terms, group them appropriately to sum them over n i d M i T plus summation of M i T dash d n i – essentially chain rule application.

So, we have the total differential from this expression 4.14 as this on the right hand side and the total differential here. What I would like you to do is equate the right hand sides of 4.14 and this particular expression which is equation 4.15 and tell me what you get. See whether you get something interesting. Take the next 10 minutes to do that. Go ahead please.

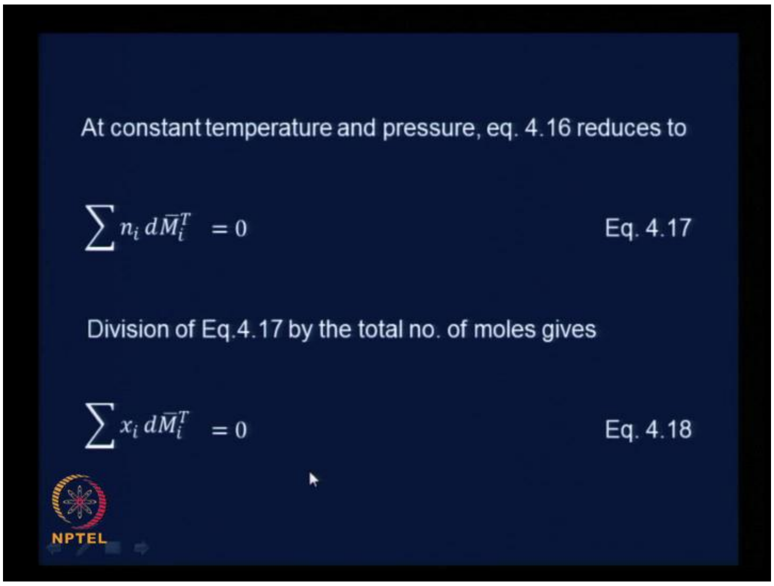
(No audio from 35:17 to 45:23)

I had asked you to equate dou dou T of M T at constant P n i d T dou M T dou P at constant T n i d P plus summation of M i T hat d n i with summation of n i times the partial molar of i plus the summation of the partial molar property times d n i. If we do this you can see that one of these terms is going to cancel out. Then … you should have gotten d M T d t at constant P n i d T. This is the same term as earlier plus d M T d P constant T n i d P. Again same term as earlier. What does not cancel and gets transpose to give you minus summation of n i d M i T is this term.

So, this term essentially gets cancelled with the same term as on the other on the right hand side of equation 4.14. Therefore, dou M T dou T at constant P n i d T dou M T dou P at constant T n i d P plus summation of n i d M i T this equals 0. Are you able to see some nice thing here? We will call this equation 4.16. So, this is if you write it in terms of G, you will see that G is a function of T, P, and mu. Therefore, you can probably make the connection with something that you have already done earlier.

Now, at constant temperature and pressure this equation 4.16 that we saw. This we are writing it writing for all partial molar properties.

(Refer Slide Time: 47:37)



At constant temperature and pressure, eq. 4.16 reduces to

$$\sum n_i \, d\bar{M}_i^T = 0 \qquad \text{Eq. 4.17}$$

Division of Eq.4.17 by the total no. of moles gives

$$\sum x_i \, d\bar{M}_i^T = 0 \qquad \text{Eq. 4.18}$$

So, … instead of concentrating on G alone which we had done somewhat earlier in the earlier module, we will do it for any total property. If we do that at constant temperature and pressure these two terms are going to get to 0, because d T is 0, d P is 0. Therefore, what remains is summation of n i d M i T hash equals 0. We will call this equation 4.17. If we divide summation of n i d M i T hash equals 0 by the total number of moles. You know each term in the sum get divided by n. And therefore, each of these n i s can be replaced by the mole fraction.

That is the definition of mole fraction. n i by n is the mole fraction. Therefore, when you divide it by total number of moles you get sum over x i d M i T hash equals 0. This is equation 4.18. This is quite a powerful equation as we will see later. I think we are almost out of time for this particular … lecture. Let us stop here and continue from here in the next class.