Thermodynamics for Biological Systems: Classical and Statistical Aspects

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Lecture – 36
Review of Module 4

Welcome!

In the last class we had completed whatever we wanted to cover in module 4. What we will do in this class is since we have covered quite a few new concepts, let us look at them one more time, the concepts with some detail not too much detail.

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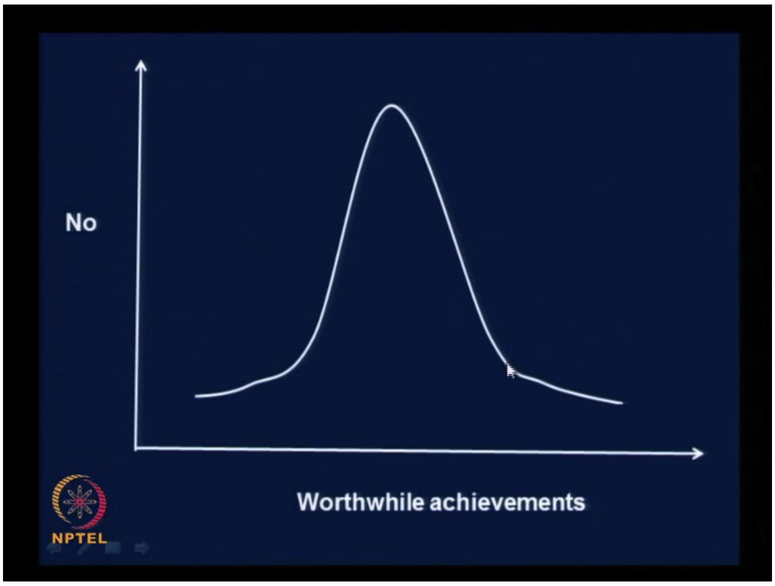

This module, module 4 is on thermodynamics of solutions. Before we got into module 4 we looked at how a typical class is, in terms of worthwhile achievements the number in a class versus worthwhile achievements. Then, I said I typically teach to people here, and the people here will need some help. Probably, they can discuss with me later. The people here are the ones who are expected to contribute a lot more to the area, the course, and so on and so forth.

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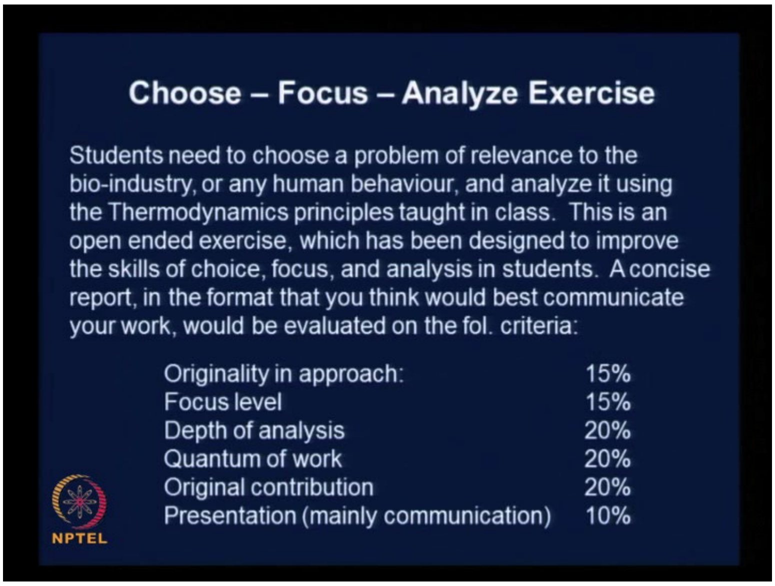

Choose – Focus – Analyze Exercise

Students need to choose a problem of relevance to the bio-industry, or any human behaviour, and analyze it using the Thermodynamics principles taught in class. This is an open ended exercise, which has been designed to improve the skills of choice, focus, and analysis in students. A concise report, in the format that you think would best communicate your work, would be evaluated on the fol. criteria:

Originality in approach:	15%
Focus level	15%
Depth of analysis	20%
Quantum of work	20%
Original contribution	20%
Presentation (mainly communication)	10%

So, for them … let me remind you once again … everybody can do; please try it out. You do not really know where you are in this class till you evaluate yourself, the ease with which you can do this particular exercise. It is actually quite a tough exercise. This is called the choose focus analyze exercise. Students need to choose a problem of relevance to the bio-industry or any human endeavor and analyze it using the thermodynamic principles taught in class.

This is an open ended exercise, which has been designed to improve the skills of choice, focus and analysis in students. A concise report in the format that you think would best communicate your work – this also deliberately done this way – would be evaluated on the following criteria, the criteria are as follows.

Originality in approach would carry 15 percent, focus level 15 percent, depth of analysis 20 percent, quantum of work 20 percent, original contribution 20 percent ,which means this should not exists earlier – that kind of a thing, and presentation, which is mainly communication – communication carries 8 percent and the professional appearance of the report carries 2 percent. So if you can do this for whatever time you want, and you want to get back and discuss – that is also fine.

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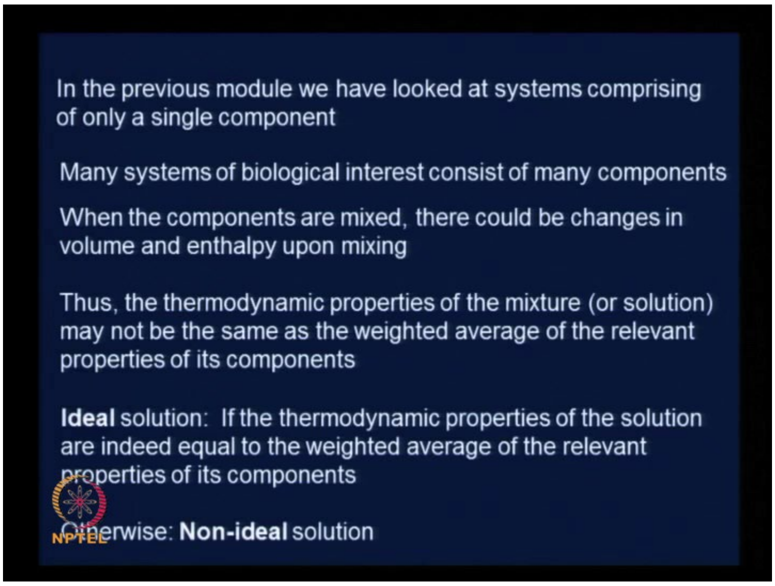

In the previous module we have looked at systems comprising of only a single component

Many systems of biological interest consist of many components

When the components are mixed, there could be changes in volume and enthalpy upon mixing

Thus, the thermodynamic properties of the mixture (or solution) may not be the same as the weighted average of the relevant properties of its components

Ideal solution: If the thermodynamic properties of the solution are indeed equal to the weighted average of the relevant properties of its components

Otherwise: **Non-ideal** solution

Now … we started looking at the thermodynamics of solutions. We said that in the previous module we had looked at pure substances, where as many systems of biological interests consist of many substances. Sometimes we come across, rarely, a pure substance. But, we need to understand the formulations for a pure substance well, before we could appreciate that for solutions. That is the reason why we spent time on the pure substance, first.

Many systems of biological interest consist of many components and when the components are mixed, there could be changes in, for example, volume or enthalpy. What we said was: let us say that there are 2 components; each one has its own volume – volume is easy to imagine – each one has its own volume. When we mix them together in a certain proportion, the final volume may not be the weighted average in terms of the mole fractions of the initial volumes. That is the nature of the substance itself. That we have recognized here. Therefore, we need to treat solutions differently.

Therefore, the thermodynamic properties, not just the volume, all the thermodynamic properties of the mixture or solution may not be the same as the weighted average of the relevant properties of its components.

If that indeed happens, it becomes an ideal solution. If the thermodynamic property of the solution is indeed equal to the weighted average of the components then it is an ideal solution, otherwise it is a non ideal solution. We will predominantly look at non ideal solutions and ways to handle them.

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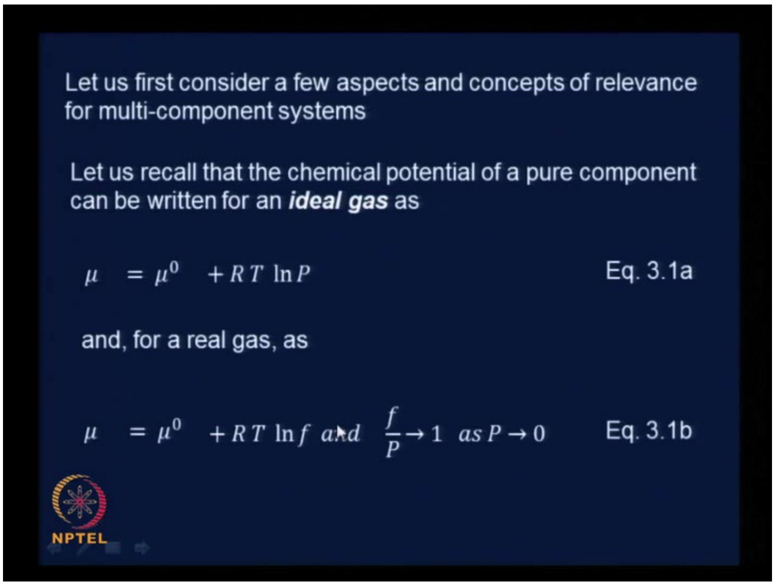

Let us first consider a few aspects and concepts of relevance for multi-component systems

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

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

and, for a real gas, as

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

We said that we will look at some concepts for multi component systems in this particular module, and we recalled what an ideal gas was, in terms of chemical potential, …

$$\mu = \mu^0 + R\,T\ ln\,P$$

For a real gas the P gets replaced with a f;

$$\mu = \mu^0 + R\,T\ ln\,f \quad and \quad \frac{f}{P} \rightarrow 1 \ \ as\,P \rightarrow 0$$

So, this is for ideal gas and this is for real gas pure component. Now, what happens if we mix them together? Before that, we said, we will look at a concept of perfect gas mixtures and imperfect gas mixtures, which are essentially concepts which we will invoke at a later stage. It is just being presented here for completeness; it is nice to have all these formulations at one place.

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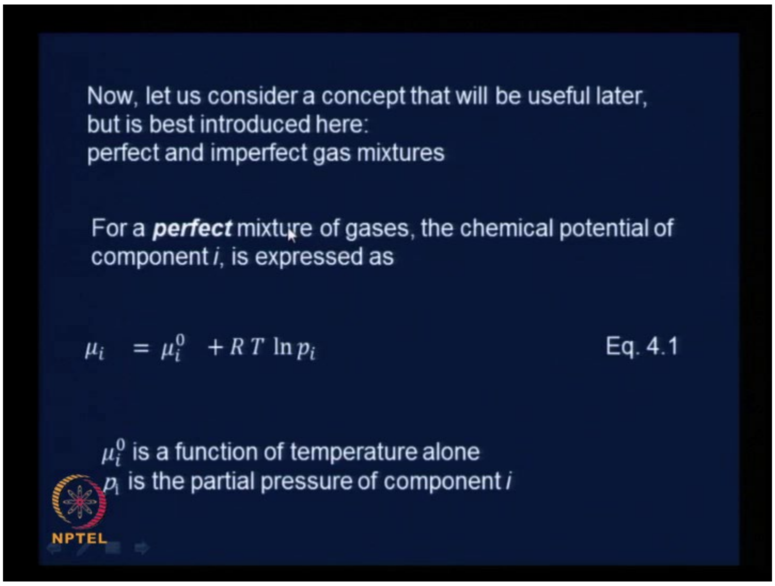

Now, let us consider a concept that will be useful later, but is best introduced here: perfect and imperfect gas mixtures

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*

The perfect gas mixture is one for which the chemical potential of the component i, for each component is expressed as

$$\mu_i = {\mu_i}^0 + R\,T\ \ln p_i$$

${\mu_i}^0$ is a function of temperature alone, as earlier, and pi is the partial pressure as we mentioned … this is a perfect mixture of gases.

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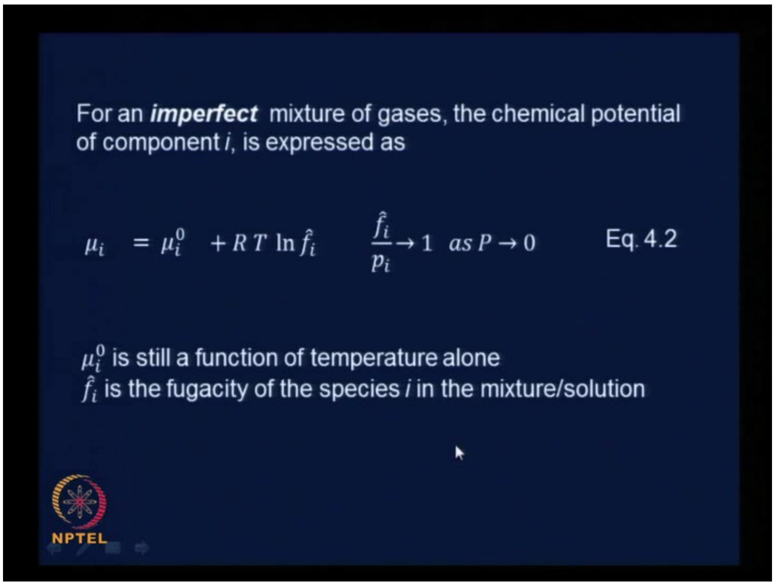

For an ***imperfect*** mixture of gases, the chemical potential of component *i*, is expressed as

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

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

For an imperfect mixture of gases, we said,

$$\mu_i = \mu_i{}^0 + R\,T\;ln\,\hat{f}_i \qquad \frac{\hat{f}_i}{p_i} \rightarrow 1 \;\; as\, P \rightarrow 0$$

mu i naught, is still a function of temperature. These were the two hypothetical substances, perfect gas mixtures and imperfect gas mixtures which are defined this way.

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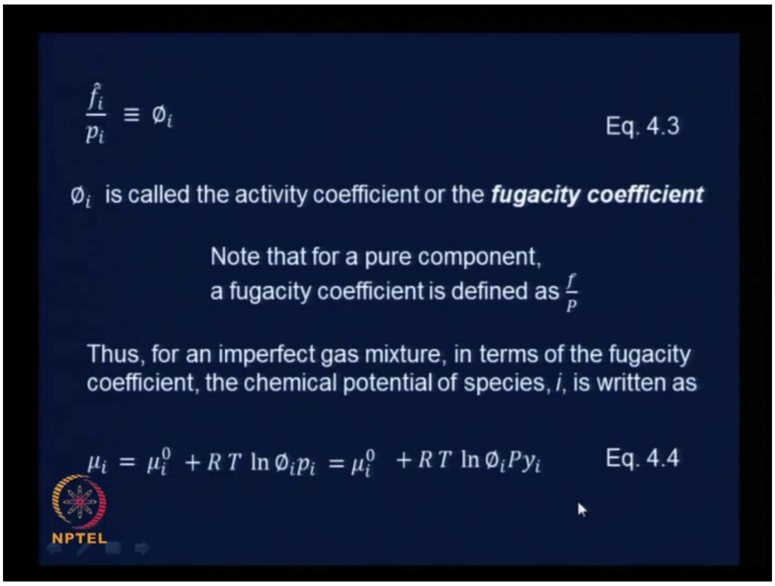

$\frac{\hat{f}_i}{p_i} \equiv \emptyset_i$ Eq. 4.3

$\emptyset_i$ 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

$\mu_i = \mu_i^0 + R\,T\,\ln \emptyset_i p_i = \mu_i^0 + R\,T\,\ln \emptyset_i P y_i$ Eq. 4.4

$\frac{\hat{f}_i}{p_i} \equiv \emptyset_i$ the fugacity coefficient, phi i. Fugacity coefficient of the component in the solution as distinct from the fugacity coefficient of a pure component, which was defined as f by total pressure P.

Therefore, you could write for an imperfect gas mixture, in terms of the fugacity coefficient,

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

This is all for perfect and imperfect gas mixtures.

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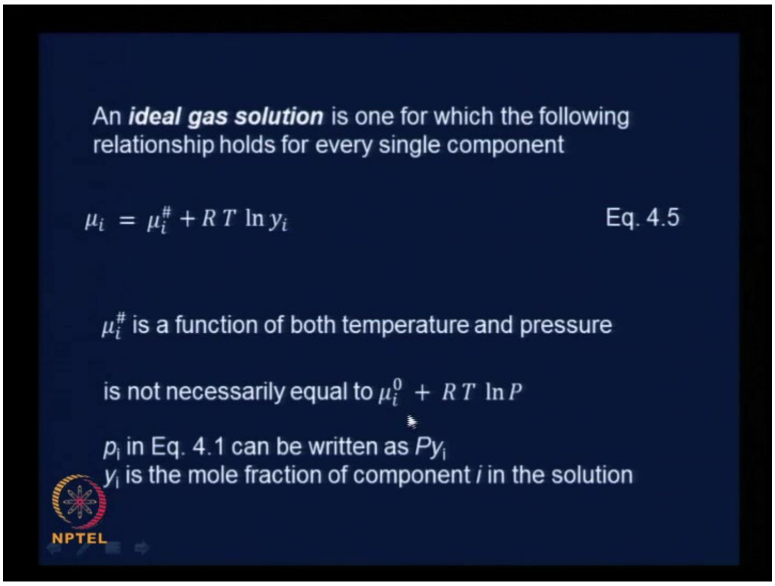

An ***ideal gas solution*** is one for which the following relationship holds for every single component

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

What we would see more of, in this particular module, is an ideal gas solution. We had an ideal gas and non ideal gas. Now, we are looking at an ideal gas solution and a non ideal gas solution. We said with this formulation, it is easy to extend them to either liquid or solid solutions also, mixtures also. Ideal gas solution is one for which the following relationship holds for every single component,

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

yi is the mole fraction of the component in the ideal gas solution. $\mu_i^{\#}$ is a function of both the temperature and pressure. But, not necessarily equal to $\mu_i{}^{0} + R\,T\ \ln P$.

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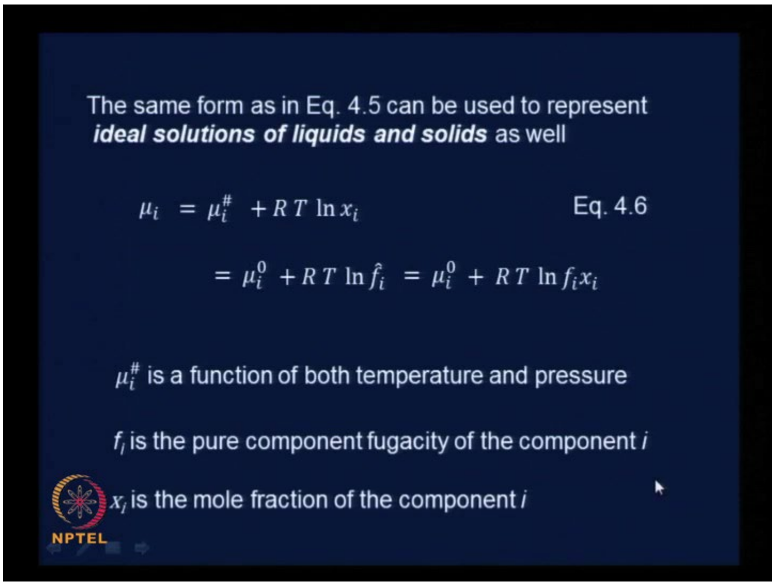

The same form as in Eq. 4.5 can be used to represent ***ideal solutions of liquids and solids*** as well

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

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

$\mu_i^{\#}$ 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*

The ideal solution of liquids and solids can also be expressed in the same way:

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

where x i is a mole fraction of the component i in the ideal solution of a liquid or a solid. The equivalent expressions in terms of the fugacity coefficients were also given. Now, the non ideality is brought about either by a fugacity coefficient for a gas mixture, or an activity coefficient for a liquid or a solid mixture/ solution.

$$\mu_i = {\mu_i}^{\#} + R\,T\;ln\,\hat{f}_i$$

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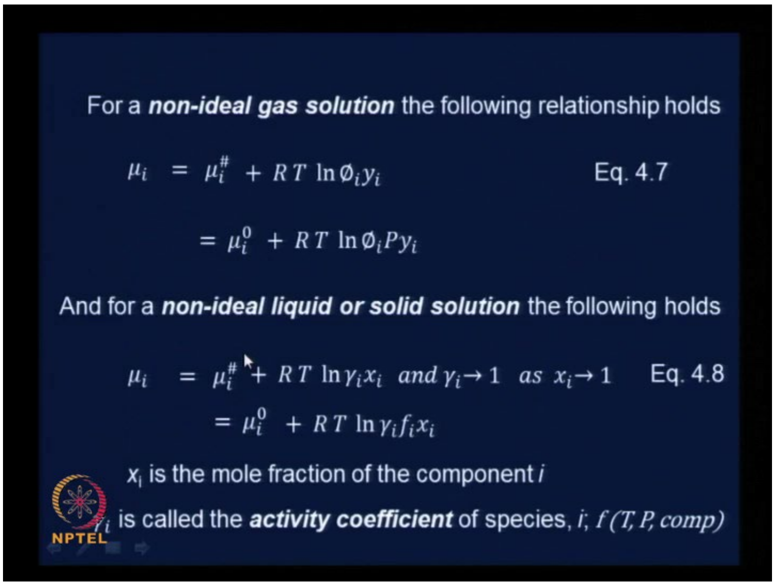

For a ***non-ideal gas solution*** the following relationship holds

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

$$= \mu_i^{0} + RT\ln\emptyset_i P y_i$$

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

$$\mu_i = \mu_i^{\#} + RT\ln\gamma_i x_i \quad and\ \gamma_i \to 1 \quad as\ x_i \to 1 \qquad \text{Eq. 4.8}$$

$$= \mu_i^{0} + RT\ln\gamma_i f_i x_i$$

x_i is the mole fraction of the component *i*

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

So, for a non ideal gas solution

$$\mu_i = \mu_i^{\#} + RT\ ln\,\emptyset_i y_i$$

For a non ideal liquid or solid solution, it was

$$\mu_i = \mu_i^{\#} + RT\ ln\,\gamma_i x_i \quad and\ \gamma_i \to 1\ as\ x_i \to 1$$

This, of course, was expressed in terms of fugacity, and so on for equivalent expressions; gamma i is the activity coefficient. Note that gamma i is a function of temperature, pressure, and composition, whereas mu i hash was only a function of temperature and pressure.

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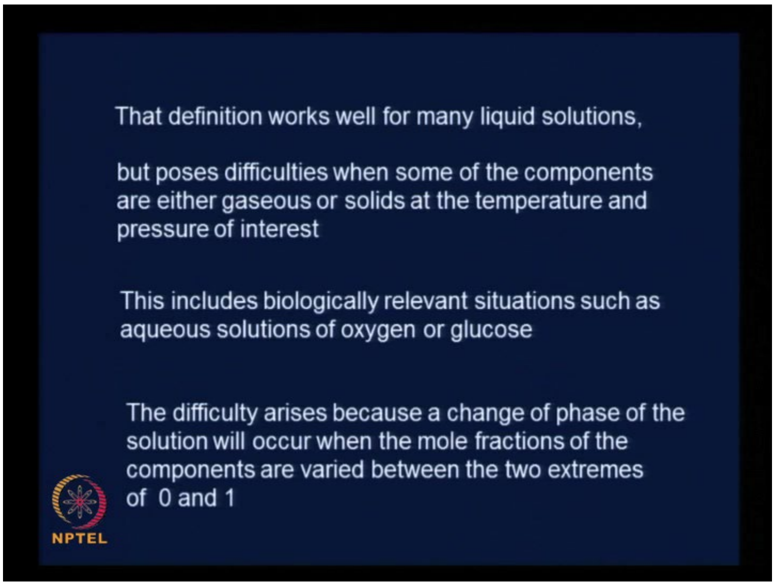

That definition works well for many liquid solutions,

but poses difficulties when some of the components are either gaseous or solids at the temperature and pressure of interest

This includes biologically relevant situations such as aqueous solutions of oxygen or glucose

The difficulty arises because a change of phase of the solution will occur when the mole fractions of the components are varied between the two extremes of 0 and 1

And we said that definition so far for a non ideal liquid or a solid solution works well for many solutions. Let us concentrate on liquid solutions – works well for many liquid solutions. But, it does not work so well when one of the components is either a gas or a solid at the temperature and pressure of interest of the solution. For example, … many solutions of biological interest are of that category.

For example, the solution of glucose, if glucose is in water let us say, then it is going to be a liquid at a certain mole fraction of glucose. But, if you increase the mole fraction of glucose to 1, it is going to be pure glucose, which is going to be a solid at the temperature and pressure of the solution .Therefore, that formulation will not work. A similar example was that of oxygen. Oxygen in water is a liquid at the temperature and pressure of interest for growing cells. Whereas, oxygen itself, is a gas. So, if you increase the mole fraction of oxygen in the solution to 1 then the phase changes, it becomes a gas phase at, let us say at higher mole fractions, definitely at a mole fraction of 1. And therefore, we need to have a different formulation to be able to handle that. The same formulation that we presented will not be able to handle that.

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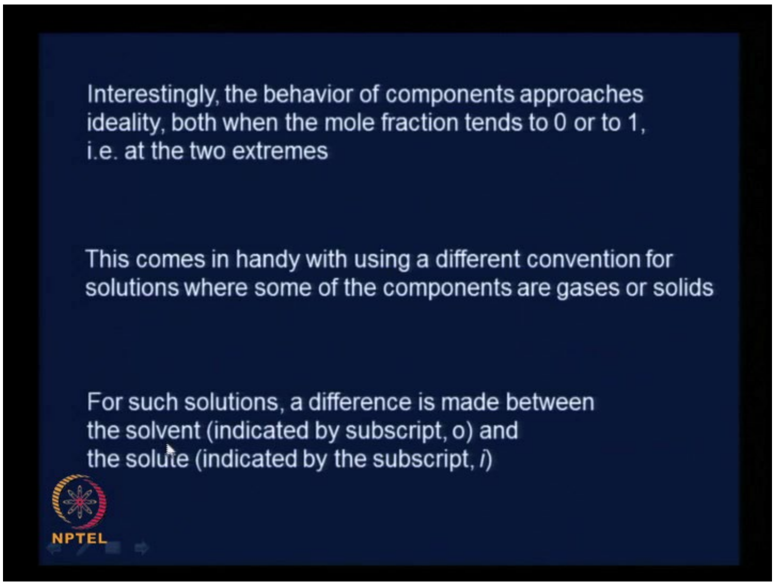

Interestingly, the behavior of components approaches ideality, both when the mole fraction tends to 0 or to 1, i.e. at the two extremes

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*)

And, we did that by noticing that at the extremes, that is when the mole fraction either tends to 0 or 1, the behavior is ideal .We had used that fact, and then we had come up with a separate expression for the solvent and a separate expression for the solute; both need to be used together in the model for chemical potential. The solvent is indicated by the subscript o and the solute is indicated by the subscript i.

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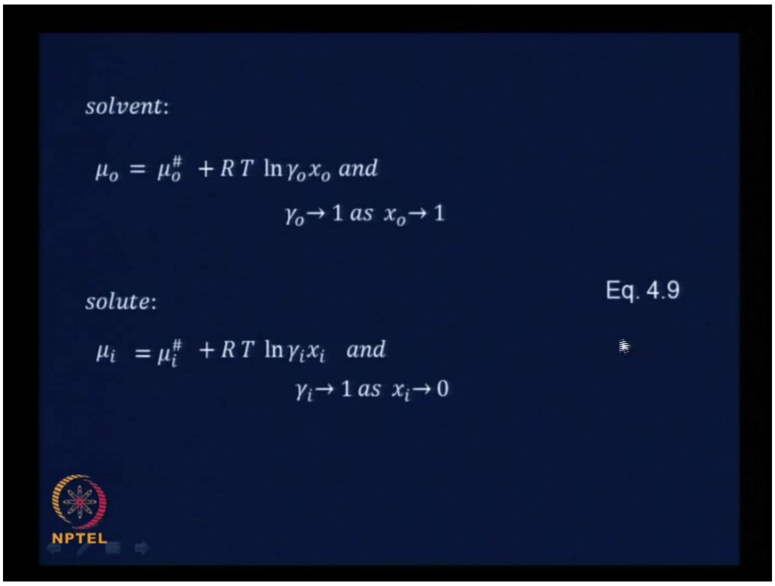

solvent:

$$\mu_o = \mu_o^{\#} + RT \ln \gamma_o x_o \text{ and}$$

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

Eq. 4.9

solute:

$$\mu_i = \mu_i^{\#} + RT \ln \gamma_i x_i \text{ and}$$

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

For example,

$$\mu_o = \mu_o^{\#} + R\,T\ \ln \gamma_o x_o \qquad and\,\gamma_o \rightarrow 1\ as\ \ x_o \rightarrow 1$$

for the solvent. And, for the solute,

$$\mu_i = \mu_i^{\#} + R\,T\ \ln \gamma_i x_i \qquad and\,\gamma_i \rightarrow 1\ as\ \ x_i \rightarrow 0$$

Here this is for the solute. Both these put together as equation 4.9.

So these are the various models for the chemical potential for the various kinds of solutions that we have seen from the ideal to the real; and, we did make a difference between the gas and liquid & solid.

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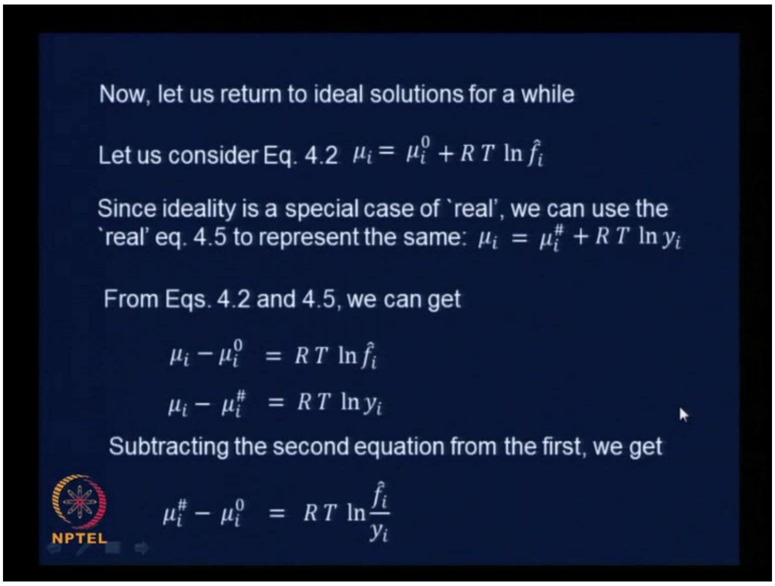

Now, let us return to ideal solutions for a while

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 by considering the ideal solution and manipulating the expression,

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

we came up with the expression:

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

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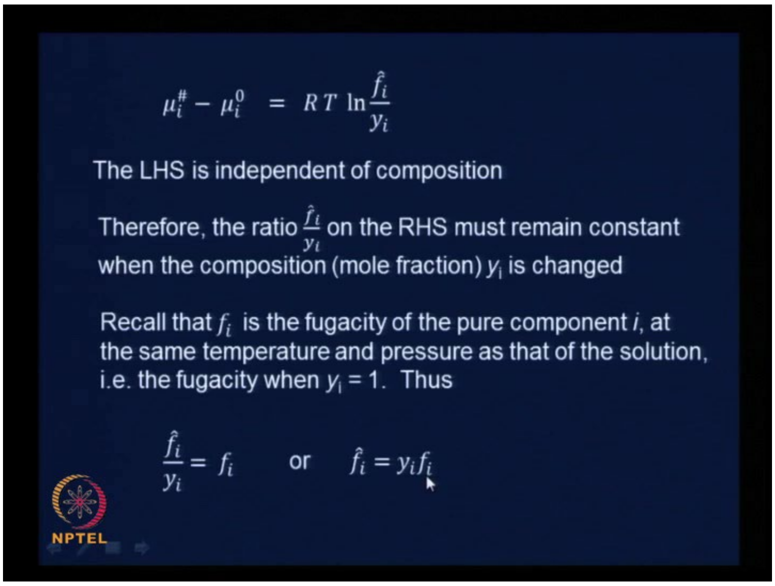

$$\mu_i^{\#} - \mu_i^0 = RT \ln \frac{\hat{f}_i}{y_i}$$

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

$$\frac{\hat{f}_i}{y_i} = f_i \quad \text{or} \quad \hat{f}_i = y_i f_i$$

This argument was important there: In

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

we said that the left hand side is independent of composition. Therefore, the right hand side should also be independent of composition. But, you have a term for the composition yi here. Therefore, the only way by which the right hand side will be independent of composition is if the ratio $\frac{\hat{f}_i}{y_i}$ remains a constant when yi is changed.

We had used that argument to get to this expression: fi hat by y i must be equal to fi by 1. fi hat is the fugacity of the component in the solution, and fi is the fugacity of the pure component when yi equals 1. Therefore, in such a case,

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

It is powerful because we could get an estimate of fi hat – some sort of a hypothetical quantity – well, I should not say hypothetical quantity but, not so easy to determine quantity – as a function of yi, and the fugacity of the pure component. Therefore, there is a way of estimating fi hat by this expression.

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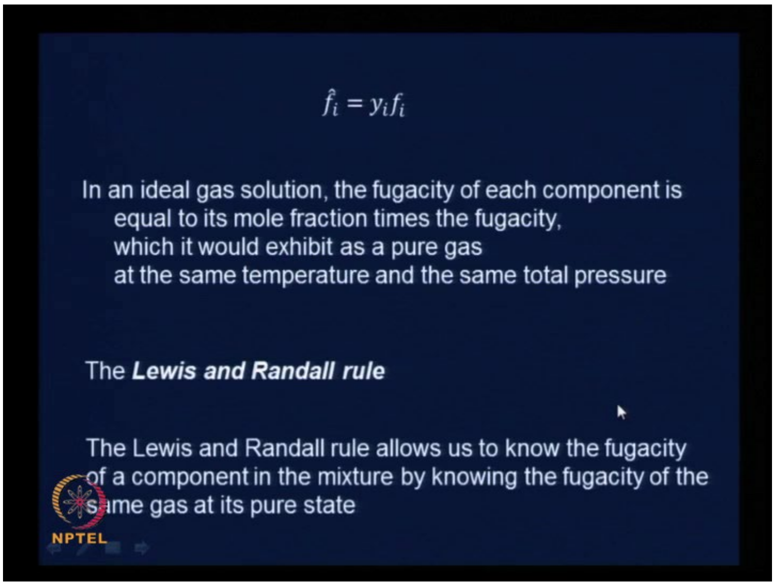

$$\hat{f}_i = y_i f_i$$

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 was actually called the Lewis and Randall rule. This, of course, is valid only for an ideal solution. In an ideal gas solution the fugacity of each component is equal to the mole fraction times the fugacity, which it would exhibit as a pure gas at the same temperature and total pressure. And, this we have already seen.

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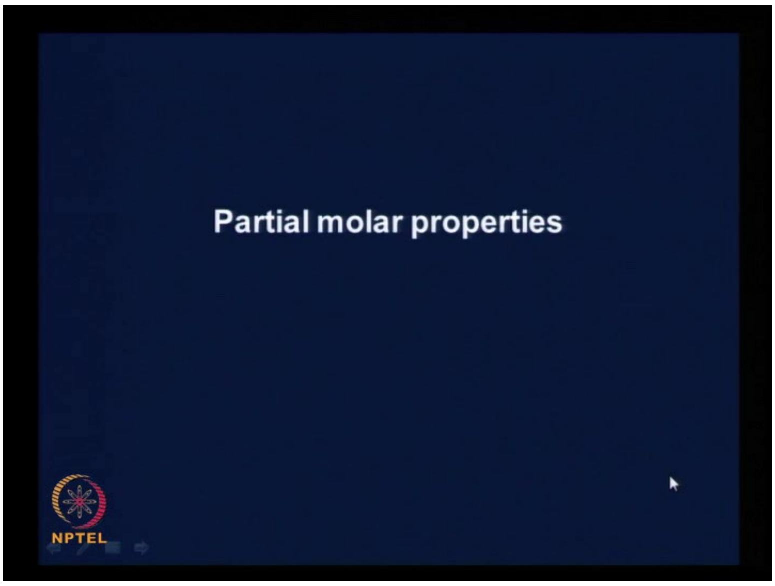

Partial molar properties

Then, we went into something called partial molar properties which would give us a way of handling our initial problem. We said that in terms of volumes – we started in terms of volumes – the volume of the final solution may not be equal to the weighted average of the volumes of the components. If we need a formulation to express it that way, that would be in terms of partial molar properties.

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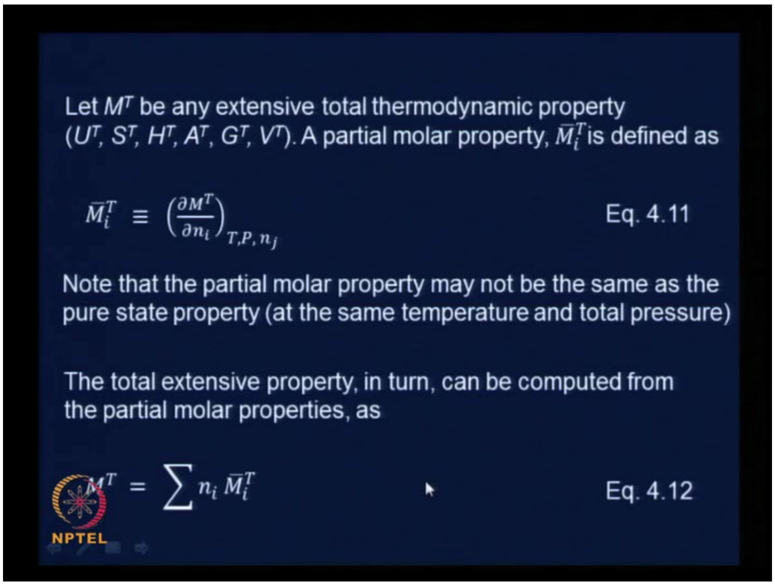

Let M^T be any extensive total thermodynamic property (U^T, S^T, H^T, A^T, G^T, V^T). A partial molar property, $\bar{M}_i^T$ is defined as

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

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

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

And, we had defined the partial molar property for any property as

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

This you could write for any of the extensive properties U^T, S^T, H^T, A^T, G^T, or V^T. And, of course, it is quite obvious that the partial molar property may not be the same as the pure state property at the same temperature and total pressure.

The total property, extensive property, can be computed from the partial molar properties as the sum over n I, the mole numbers, times the partial molar property of that component. You sum them over all the components then you get the total property. To be able to express it this way, was the need to define a partial molar property at all.

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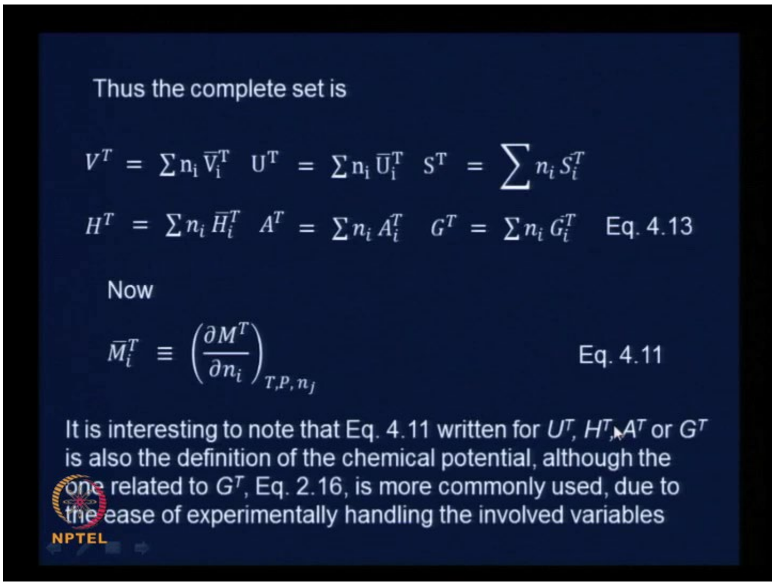

Thus the complete set is

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

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

Now

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

It is interesting to note that Eq. 4.11 written for U^T, H^T, A^T or G^T is also the definition of the chemical potential, although the one related to G^T, Eq. 2.16, is more commonly used, due to the ease of experimentally handling the involved variables

And, then we wrote the complete set of … the expressions for getting the total properties in terms of the partial molar properties. This is total volume, total internal energy, total entropy, total enthalpy, total Helmholtz free energy and total Gibbs free energy. All these in terms of the partial molar properties was written down.

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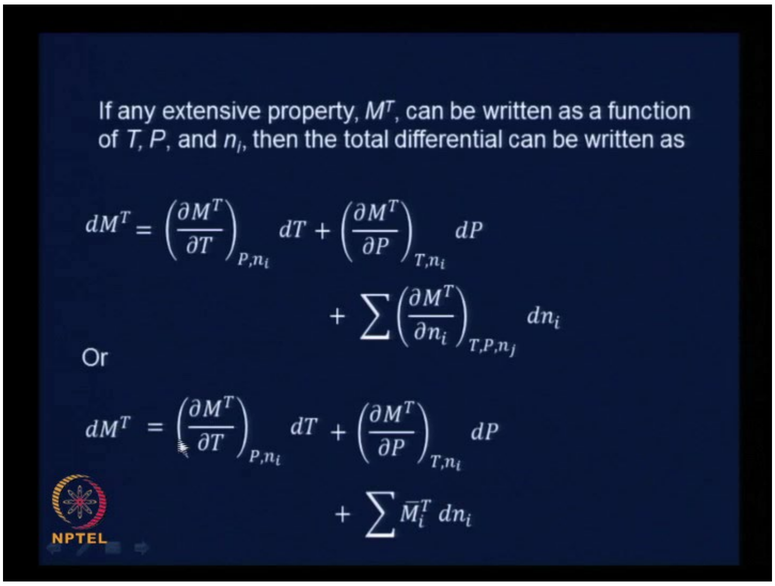

If any extensive property, M^T, can be written as a function of T, P, and n_i, then the total differential can be written as

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

Or

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

And, then we went into arguments … with using the expansion of the total derivative

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

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

Therefore, you get this in terms of temperature, pressure and the number of moles variation.

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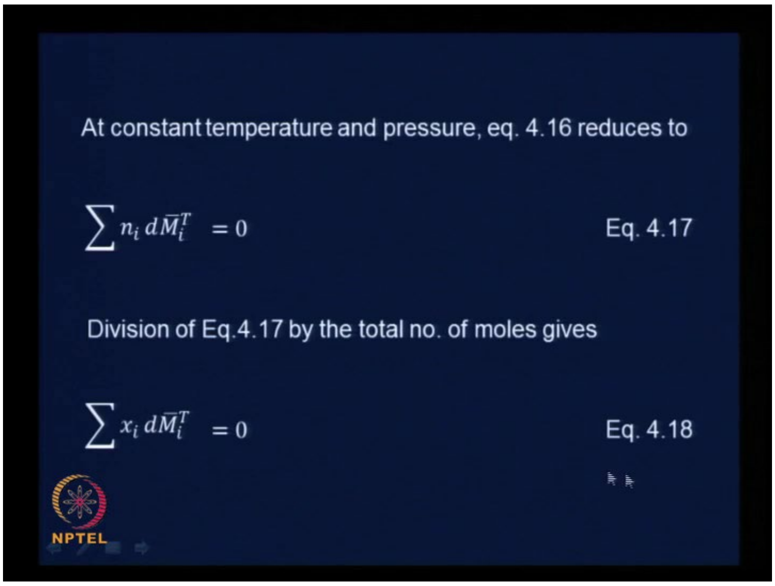

At constant temperature and pressure, eq. 4.16 reduces to

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

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

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

And we got this particular expression, which is an useful expression to have:

$$\sum n_i \, d\bar{M}_i^T = 0$$

If you divide this expression equation 4.17 by the total number of moles we get

$$\sum x_i \, d\bar{M}_i^T = 0$$

sum over x i d M i T hash equals 0. This is a very useful expression to have; this is equation 4.18.

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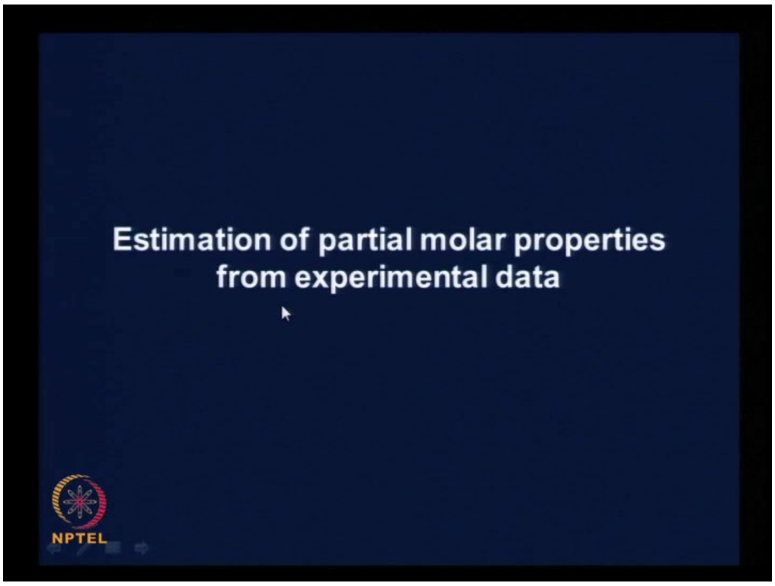

Estimation of partial molar properties from experimental data

And, then we looked at how to estimate the partial molar properties from experimental data. The experiments that we are interested in are called mixing experiments, where the initial values are measured and the total value upon mixing is measured.

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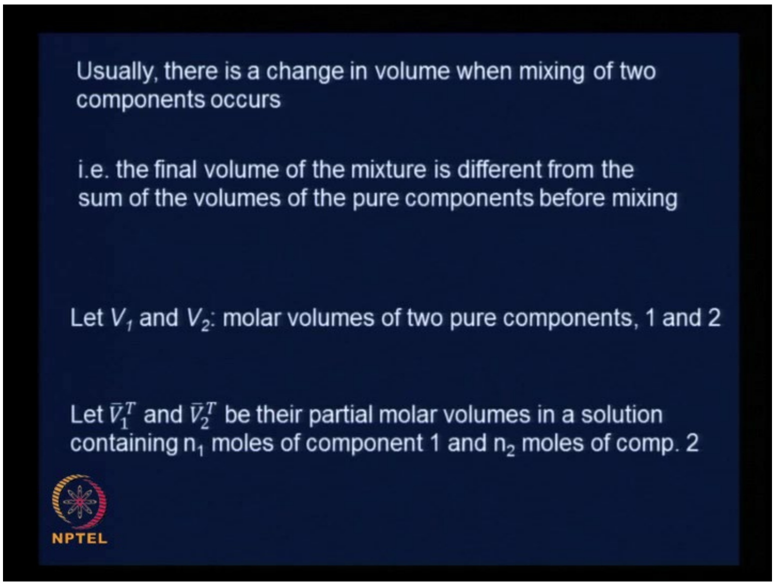

Usually, there is a change in volume when mixing of two components occurs

i.e. the final volume of the mixture is different from the sum of the volumes of the pure components before mixing

Let V_1 and V_2: molar volumes of two pure components, 1 and 2

Let $\bar{V}_1^T$ and $\bar{V}_2^T$ be their partial molar volumes in a solution containing n_1 moles of component 1 and n_2 moles of comp. 2

For example, if we take volume, since it is easy to imagine, if V1 and V2 are the molar volumes of the pure components 1 and 2, and $\bar{V}_1^T$ and $\bar{V}_2^T$ are the partial molar volumes in a solution containing n 1 moles of component 1 and n 2 moles of component 2.

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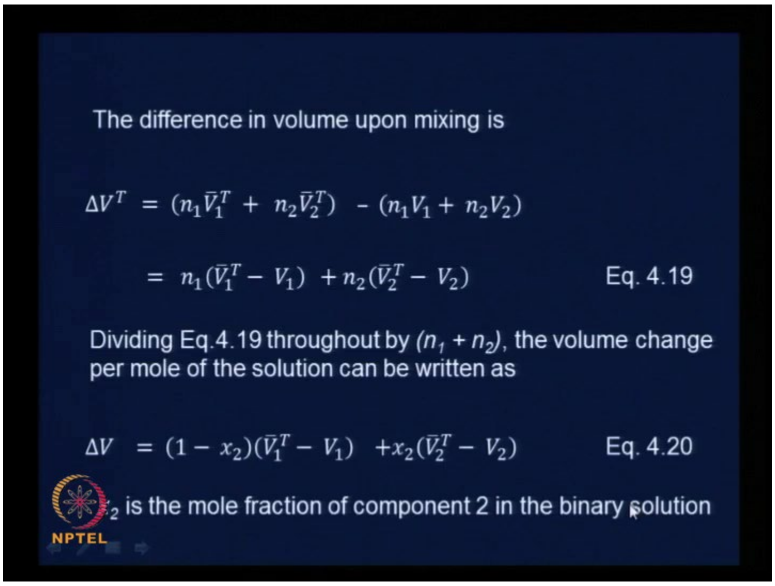

The difference in volume upon mixing is

$$\Delta V^T = (n_1\bar{V}_1^T + n_2\bar{V}_2^T) - (n_1V_1 + n_2V_2)$$

$$= n_1(\bar{V}_1^T - V_1) + n_2(\bar{V}_2^T - V_2) \qquad \text{Eq. 4.19}$$

Dividing Eq.4.19 throughout by $(n_1 + n_2)$, the volume change per mole of the solution can be written as

$$\Delta V = (1 - x_2)(\bar{V}_1^T - V_1) + x_2(\bar{V}_2^T - V_2) \qquad \text{Eq. 4.20}$$

x_2 is the mole fraction of component 2 in the binary solution

Then the difference in volume upon mixing, which is what actually is measured and plotted, is $\left(n_1\bar{V}_1^T + n_2\bar{V}_2^T\right)$ – this is the volume of the solution after, and this is the volume before. That is the volume of the pure components n1 V1 … the volume of the pure component 1, n2 V2 … the volume of the pure component 2. Note these are molar quantities. Therefore, when you multiply it by the mole numbers you get the total quantity. So after mixing volume, minus volume before mixing that is delta V T, which can be transposed into a convenient form to get

$$\Delta V = (1 - x_2)\left(\bar{V}_1^T - V_1\right) + x_2\left(\bar{V}_2^T - V_2\right)$$

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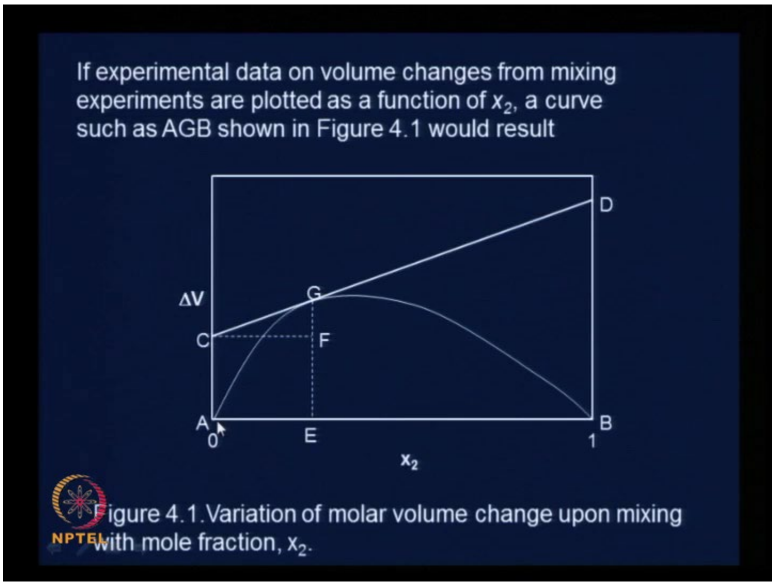
If experimental data on volume changes from mixing experiments are plotted as a function of x_2, a curve such as AGB shown in Figure 4.1 would result

Figure 4.1. Variation of molar volume change upon mixing with mole fraction, x_2.

And, this is what is plotted, delta V, the volume change upon mixing, as a function of the mole fraction x 2, if it is plotted, we get a curve something like A G B here. If we are interested in the partial molar volumes at the point E, we said, we draw a tangent to the curve at the point E. We actually proved this: that the intercept of the tangent on this axis, when x2 equals 0, or the distance AC gives the partial molar volume 1, $(\bar{V}_1^T)$, and the intercept of the tangent on the line on the ordinate of x 2 being equal to 1 or the distance DB gives us the partial molar volume of the second component $(\bar{V}_2^T)$.

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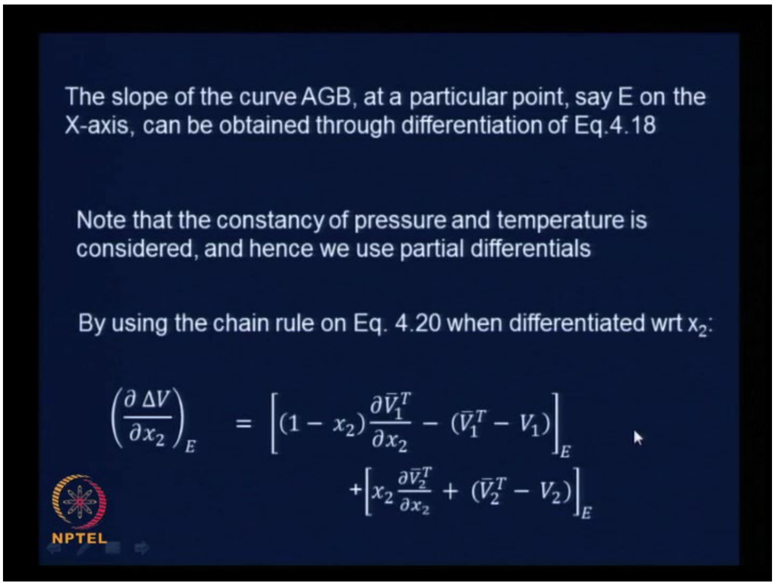
The slope of the curve AGB, at a particular point, say E on the X-axis, can be obtained through differentiation of Eq.4.18

Note that the constancy of pressure and temperature is considered, and hence we use partial differentials

By using the chain rule on Eq. 4.20 when differentiated wrt x_2:

$$\left(\frac{\partial \Delta V}{\partial x_2}\right)_E = \left[(1-x_2)\frac{\partial \bar{V}_1^T}{\partial x_2} - (\bar{V}_1^T - V_1)\right]_E + \left[x_2\frac{\partial \bar{V}_2^T}{\partial x_2} + (\bar{V}_2^T - V_2)\right]_E$$

And we had gone through expressing equation 4.20 in terms of the derivative and so on.

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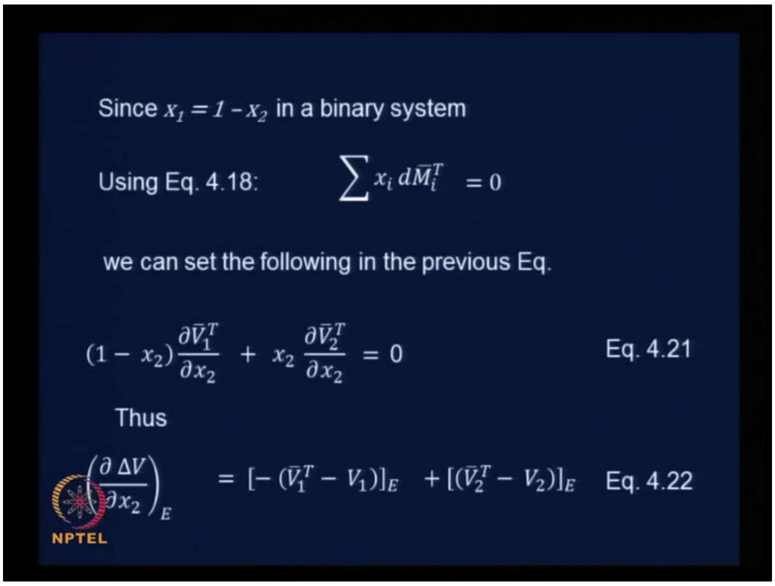

Since $x_1 = 1 - x_2$ in a binary system

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

we can set the following in the previous Eq.

$$(1 - x_2)\frac{\partial \bar{V}_1^T}{\partial x_2} + x_2 \frac{\partial \bar{V}_2^T}{\partial x_2} = 0 \qquad \text{Eq. 4.21}$$

Thus

$$\left(\frac{\partial \Delta V}{\partial x_2}\right)_E = [-(\bar{V}_1^T - V_1)]_E + [(\bar{V}_2^T - V_2)]_E \qquad \text{Eq. 4.22}$$

We had formulated it in such a way that some of the quantities that we are interested in would correspond to distances on the delta V versus x 2 diagram, and therefore, we went about proving that indeed or deriving that you can indeed use the distances on the delta V versus x2 graph to find out $(\bar{V}_1^T)$and $(\bar{V}_2^T)$.

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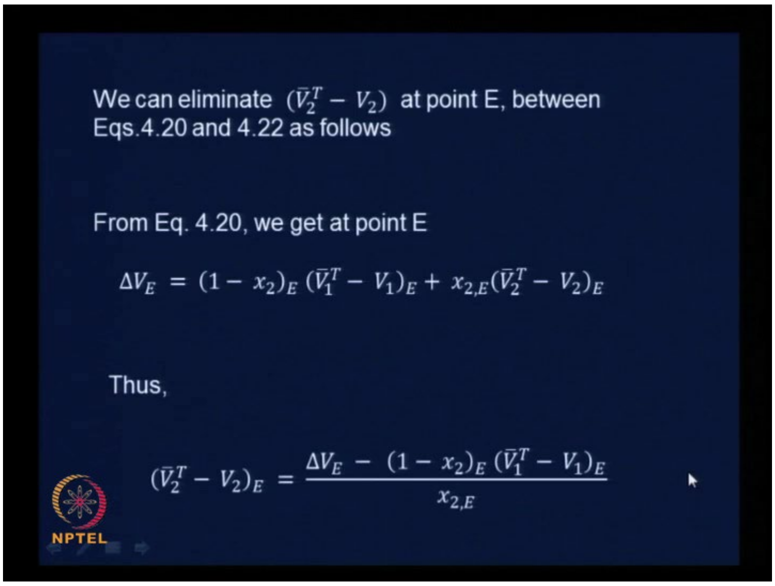

We can eliminate $(\bar{V}_2^T - V_2)$ at point E, between Eqs.4.20 and 4.22 as follows

From Eq. 4.20, we get at point E

$$\Delta V_E = (1 - x_2)_E\,(\bar{V}_1^T - V_1)_E + x_{2,E}(\bar{V}_2^T - V_2)_E$$

Thus,

$$(\bar{V}_2^T - V_2)_E = \frac{\Delta V_E - (1 - x_2)_E\,(\bar{V}_1^T - V_1)_E}{x_{2,E}}$$

Actually what you are finding out is $(\bar{V}_1^T - V_1)$ – that is the intercept, not the $(\bar{V}_1^T)$ itself. You know, this distance AC is actually $(\bar{V}_1^T - V_1)$, and this distance is $(\bar{V}_2^T - V_2)$.

And, since we know the molar volumes of the pure components, $\bar{V}_1^T$ can be computed from this distance, and $\bar{V}_2^T$ can be computed from this distance. Please make that correction. This is the way we went about deriving that particular expression. Please look through the derivation one more time; if you have any difficulties … we can always discuss.

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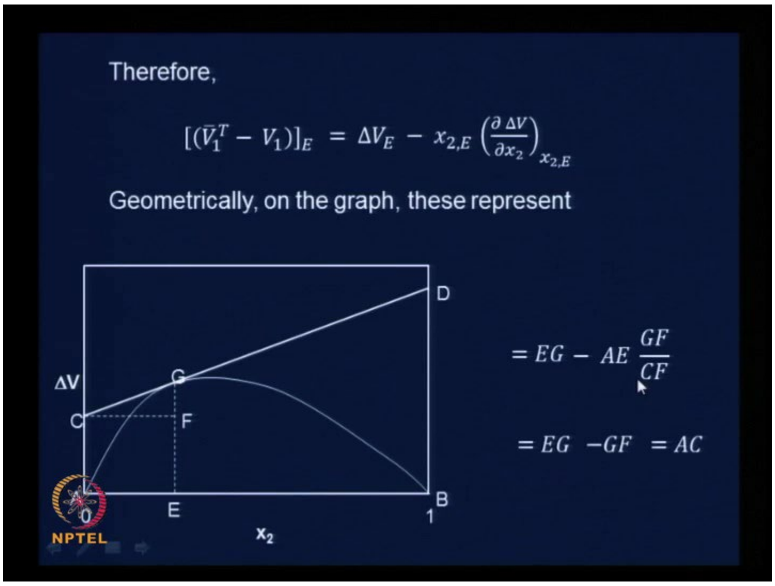

Therefore,

$$[(\bar{V}_1^T - V_1)]_E = \Delta V_E - x_{2,E}\left(\frac{\partial \Delta V}{\partial x_2}\right)_{x_{2,E}}$$

Geometrically, on the graph, these represent

$$= EG - AE\,\frac{GF}{CF}$$

$$= EG - GF = AC$$

This is the way we showed you, know there is some equality of distances AE is the same as CF and therefore, we could cancel the two. Therefore, $(\bar{V}_1^T - V_1)$ at the point E became GE minus GF, … which is FE. FE is nothing but CA, which is the intercept of the tangent on the x2 equals 0 line. Then we worked out an example by which we could find out the partial molar volumes for a case of relevant interest.

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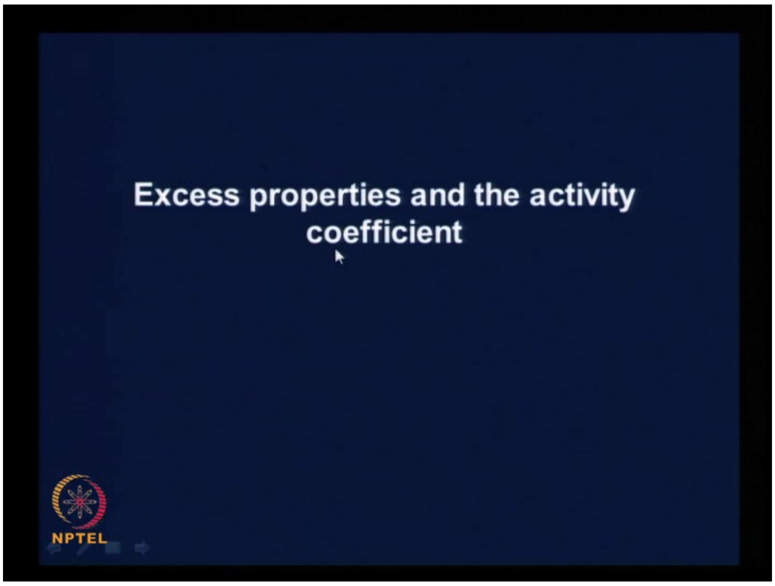

Excess properties and the activity coefficient

Then, we started looking at the relationship between excess properties and activity coefficient. We first saw what an excess property was. Excess property is nothing but, the difference between the actual property and the ideal property, and we said excess properties are defined the same way, and play a pretty much the same role as the residual properties for pure components; residual properties – we had seen in module 3. You can go back and refer to that also. In other words M R the residual property is defined as M the actual property minus M ideal gas.

$$M^R \equiv M - M^{ig}$$

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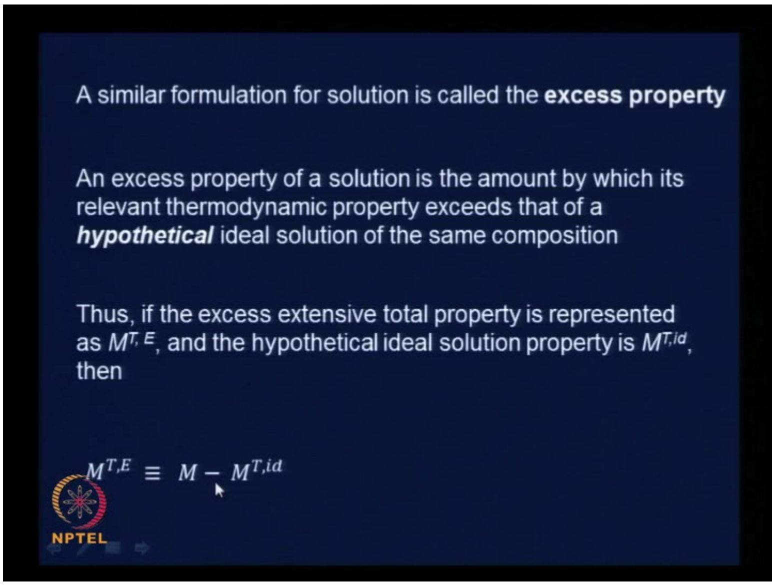

A similar formulation for solution is called the **excess property**

An excess property of a solution is the amount by which its relevant thermodynamic property exceeds that of a ***hypothetical*** ideal solution of the same composition

Thus, if the excess extensive total property is represented as $M^{T,E}$, and the hypothetical ideal solution property is $M^{T,id}$, then

$$M^{T,E} \equiv M - M^{T,id}$$

An excess property of a solution is the amount by which its relevant thermodynamic property exceeds that of the hypothetical ideal solution of the same composition. We had given this

$$M^{T,\,E} \equiv M - M^{T,\,id}$$

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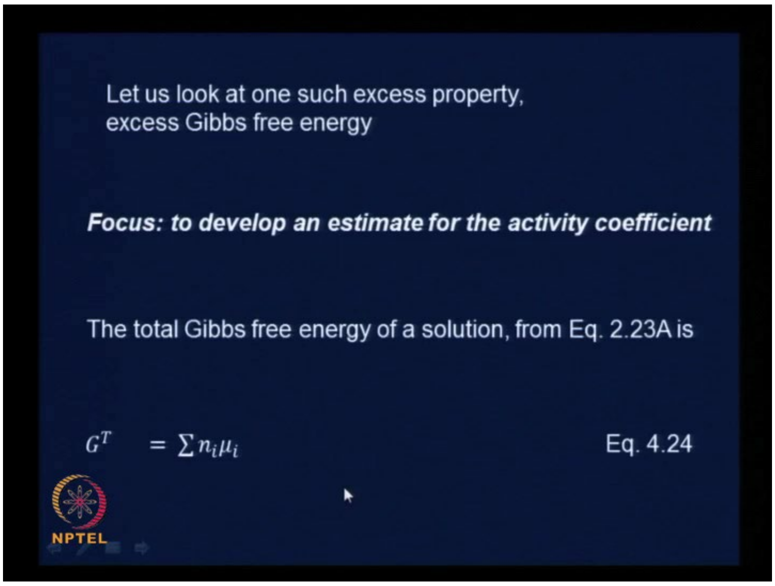

Let us look at one such excess property, excess Gibbs free energy

Focus: to develop an estimate for the activity coefficient

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

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

Then, we started looking at one of the excess properties, which is the excess Gibbs free energy. We had a very specific objective in mind, which was to develop an estimate for the activity coefficient using the excess Gibbs free energy. Then, we said the total Gibbs free energy

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

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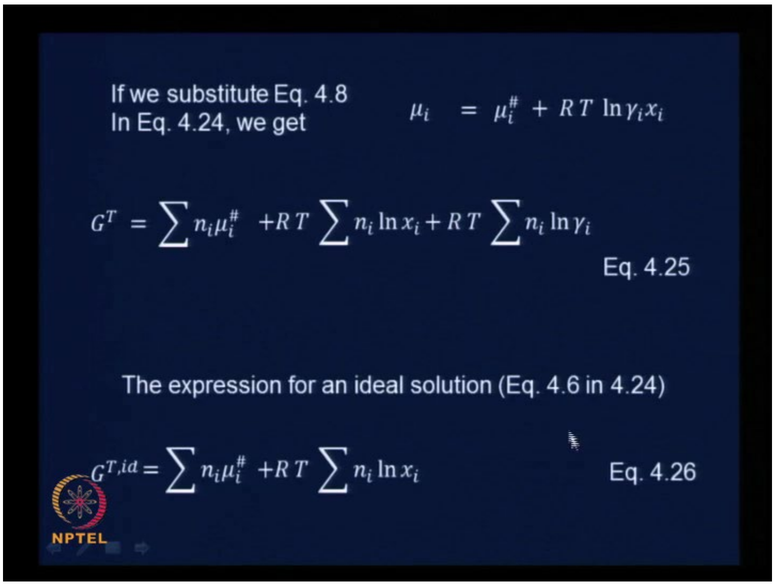

If we substitute Eq. 4.8
In Eq. 4.24, we get

$$\mu_i = \mu_i^{\#} + RT \ln \gamma_i x_i$$

$$G^T = \sum n_i \mu_i^{\#} + RT \sum n_i \ln x_i + RT \sum n_i \ln \gamma_i$$

Eq. 4.25

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

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

Eq. 4.26

And, then we went through the difference between the total and the ideal that gives us the excess, which will turn out to be only this term on the right hand side,

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

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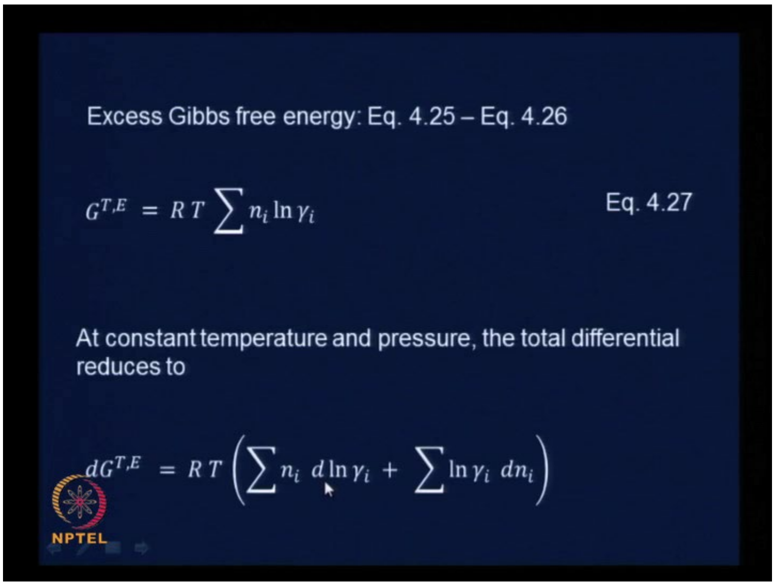

Excess Gibbs free energy: Eq. 4.25 – Eq. 4.26

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

Eq. 4.27

At constant temperature and pressure, the total differential reduces to

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

Therefore, dG^{TE}, the derivative the total a total differential of G^{TE}, d G^{TE}, by chain rule would turn out to be

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

Then, we went through an interesting derivation, or an interesting proof, where we started from a very fundamental Gibbs Duhem equation, and pretty much without any assumptions, we actually showed that for any case sum over n i d ln gamma i goes to 0. We had worked that out …we had worked that out together, so that it will strengthen some of the ideas in you. Therefore, we were left with

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

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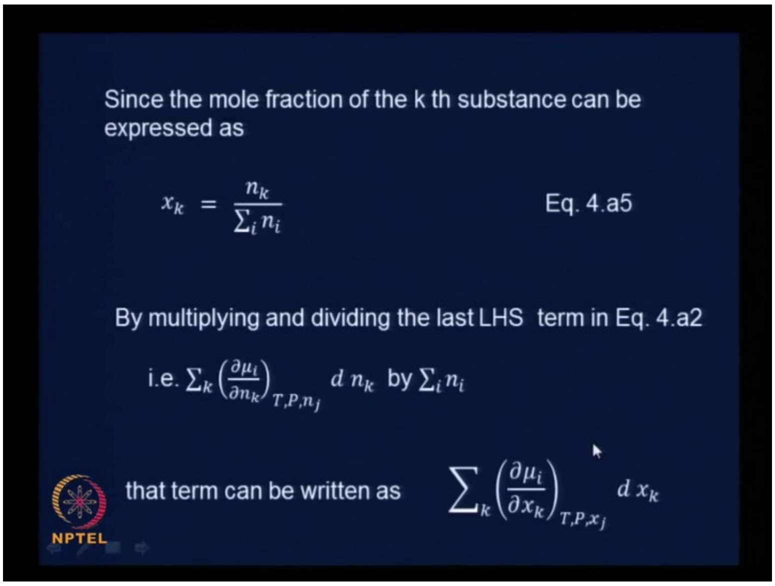

Since the mole fraction of the k th substance can be expressed as

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

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

This is the process that we went through – a very interesting kind of a derivation. You may want to look at it again. It also shows the level of care, or carefulness that one needs to exhibit while doing these kinds of manipulations.

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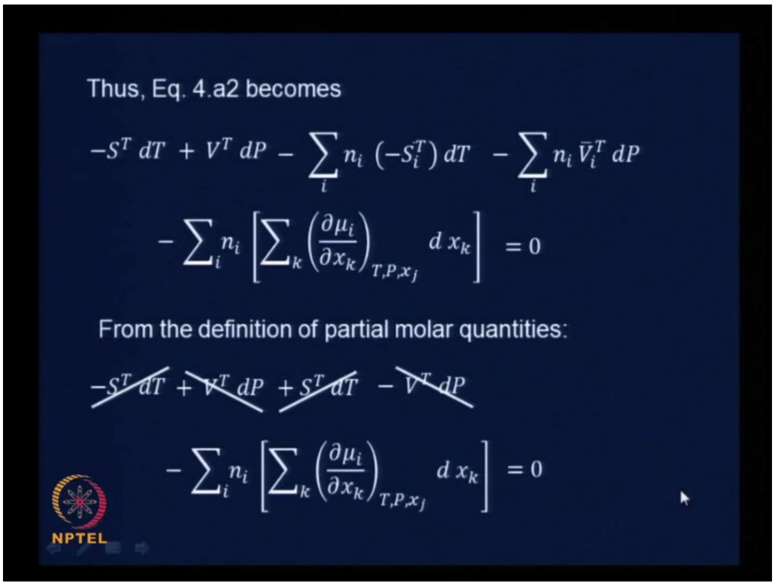

Thus, Eq. 4.a2 becomes

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

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

From the definition of partial molar quantities:

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

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

And, this is where we brought these two terms in terms of … you know, we had used the reciprocity relationships to convert the third and the fourth terms as equivalent to the first and the second terms with the opposite signs and therefore, we could get rid of them.

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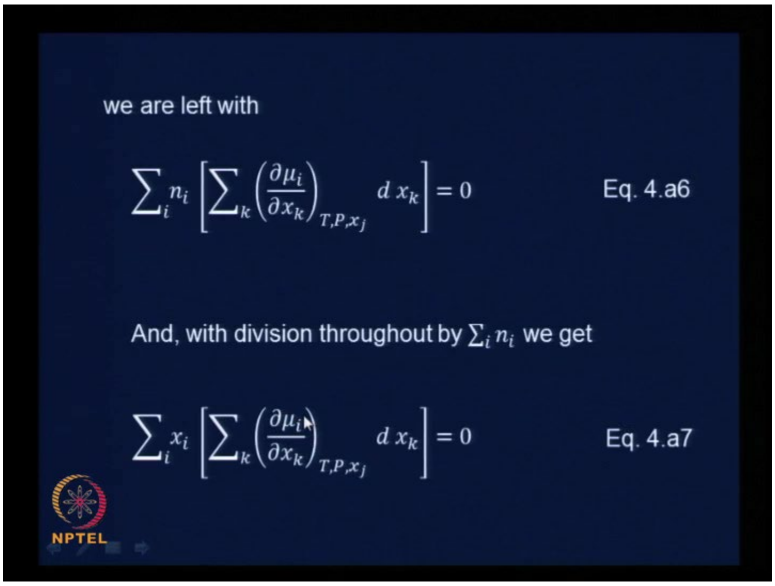

we are left with

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

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

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

And, we were left with just this, which

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

What would be easier is if we divided throughout by sum over n i then this n i by sum over n i would become x i; here it goes to 0 anyway. Therefore, it became

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

From here we had used the expression for mu i as $\mu_i = \mu_i^{\#} + R\,T\ ln\,\gamma_i x_i$

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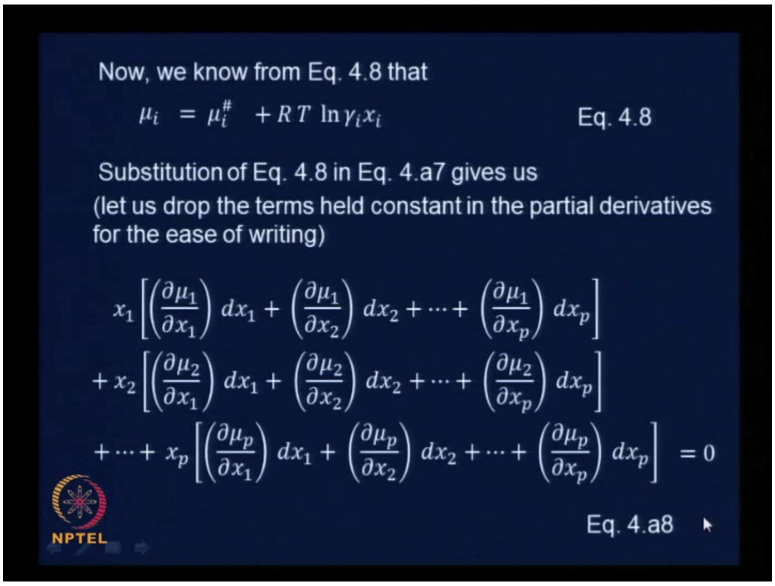

Now, we know from Eq. 4.8 that

$$\mu_i = \mu_i^{\#} + RT \ln \gamma_i x_i \qquad \text{Eq. 4.8}$$

Substitution of Eq. 4.8 in Eq. 4.a7 gives us
(let us drop the terms held constant in the partial derivatives for the ease of writing)

$$\begin{aligned} & x_1\left[\left(\frac{\partial \mu_1}{\partial x_1}\right) dx_1 + \left(\frac{\partial \mu_1}{\partial x_2}\right) dx_2 + \cdots + \left(\frac{\partial \mu_1}{\partial x_p}\right) dx_p\right] \\ & + x_2\left[\left(\frac{\partial \mu_2}{\partial x_1}\right) dx_1 + \left(\frac{\partial \mu_2}{\partial x_2}\right) dx_2 + \cdots + \left(\frac{\partial \mu_2}{\partial x_p}\right) dx_p\right] \\ & + \cdots + x_p\left[\left(\frac{\partial \mu_p}{\partial x_1}\right) dx_1 + \left(\frac{\partial \mu_p}{\partial x_2}\right) dx_2 + \cdots + \left(\frac{\partial \mu_p}{\partial x_p}\right) dx_p\right] = 0 \end{aligned}$$

Eq. 4.a8

And an interesting formulation … beautiful actually … the way it turns out, you know, these are just writing out all the terms. We need to write, all the terms if we need to do it properly.

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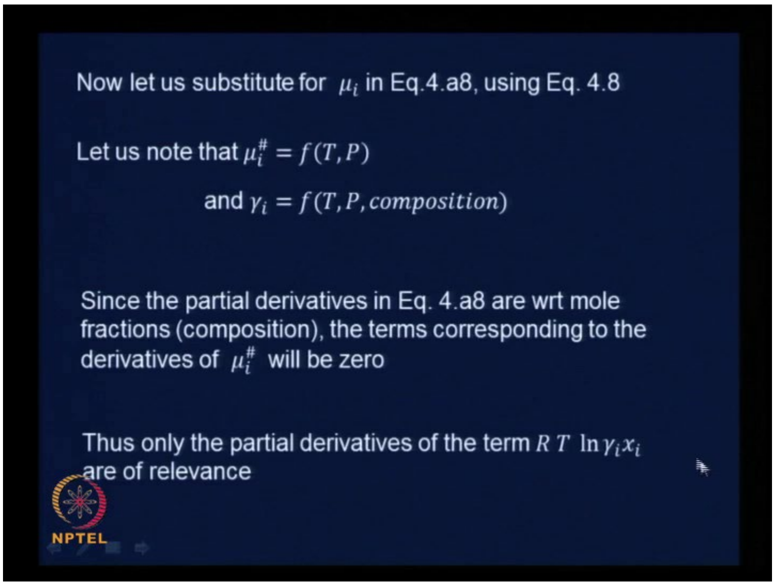

Now let us substitute for μ_i in Eq.4.a8, using Eq. 4.8

Let us note that $\mu_i^{\#} = f(T,P)$

and $\gamma_i = f(T,P,composition)$

Since the partial derivatives in Eq. 4.a8 are wrt mole fractions (composition), the terms corresponding to the derivatives of $\mu_i^{\#}$ will be zero

Thus only the partial derivatives of the term $R\,T\,\ln \gamma_i x_i$ are of relevance

But, for ease we took one term at a time. Also, we had noticed or noted that mu i hash is a function of temperature and pressure alone, and this became handy. When we had taken the derivative with respect to composition, such terms would vanish because this is not a function of composition, whereas gamma i is a function of temperature, pressure and composition. Therefore, all terms would remain there.

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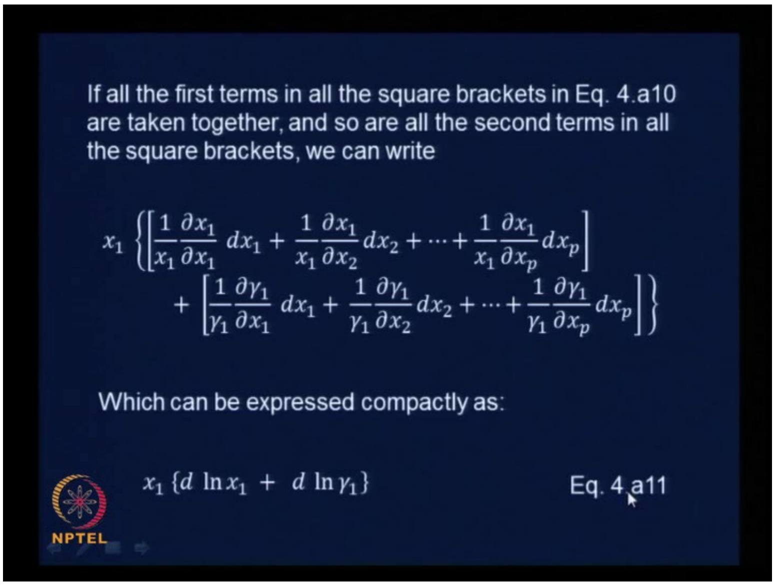

If all the first terms in all the square brackets in Eq. 4.a10 are taken together, and so are all the second terms in all the square brackets, we can write

$$x_1 \left\{ \left[\frac{1}{x_1}\frac{\partial x_1}{\partial x_1} dx_1 + \frac{1}{x_1}\frac{\partial x_1}{\partial x_2} dx_2 + \cdots + \frac{1}{x_1}\frac{\partial x_1}{\partial x_p} dx_p \right] + \left[\frac{1}{\gamma_1}\frac{\partial \gamma_1}{\partial x_1} dx_1 + \frac{1}{\gamma_1}\frac{\partial \gamma_1}{\partial x_2} dx_2 + \cdots + \frac{1}{\gamma_1}\frac{\partial \gamma_1}{\partial x_p} dx_p \right] \right\}$$

Which can be expressed compactly as:

$$x_1 \{d \ln x_1 + d \ln \gamma_1\} \qquad \text{Eq. 4.a11}$$

After going through some more algebra, which we … went through together, we got for the first term alone, $x_1 \{d \ln x_1 + d \ln \gamma_1\}$.

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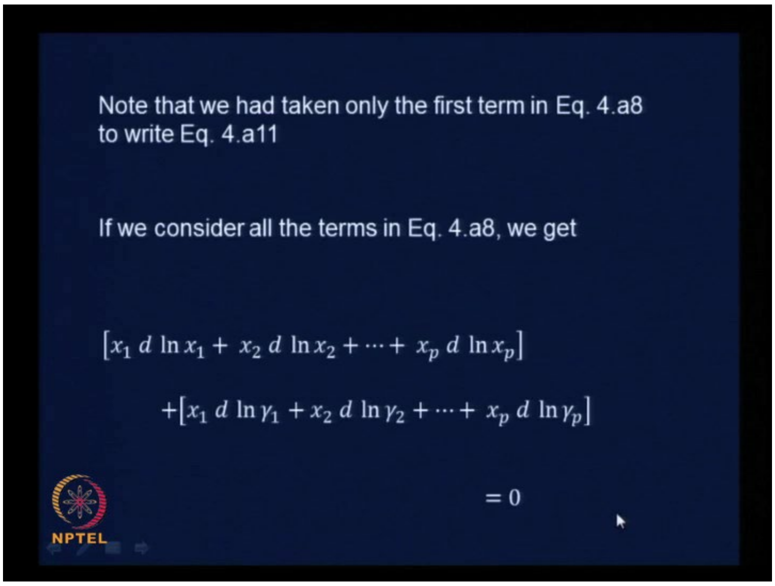

Note that we had taken only the first term in Eq. 4.a8 to write Eq. 4.a11

If we consider all the terms in Eq. 4.a8, we get

$$[x_1\, d\, \ln x_1 + x_2\, d\, \ln x_2 + \cdots + x_p\, d\, \ln x_p]$$

$$+[x_1\, d\, \ln \gamma_1 + x_2\, d\, \ln \gamma_2 + \cdots + x_p\, d\, \ln \gamma_p]$$

$$= 0$$

And, if we considered all the terms and combine them appropriately we got

$$[x_1\, d\, \ln x_1 + x_2\, d\, \ln x_2 + \cdots + x_p\, d\, \ln x_p]$$

$$+[x_1\, d\, \ln \gamma_1 + x_2\, d\, \ln \gamma_2 + \cdots + x_p\, d\, \ln \gamma_p] = 0$$

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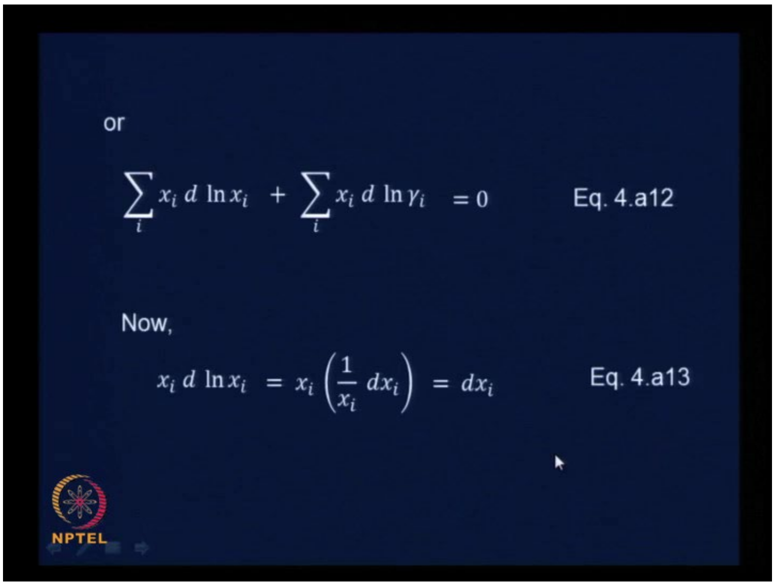

or

$$\sum_i x_i\, d\, \ln x_i + \sum_i x_i\, d\, \ln \gamma_i = 0 \qquad \text{Eq. 4.a12}$$

Now,

$$x_i\, d\, \ln x_i = x_i \left(\frac{1}{x_i}\, dx_i\right) = dx_i \qquad \text{Eq. 4.a13}$$

Which can be written as

$$\sum_i x_i\, d\, \ln x_i \;+\; \sum_i x_i\, d\, ln\, \gamma_i = 0$$

x i d ln x i is nothing but, each one of these terms is nothing but,

$$x_i\, d\, \ln x_i \;=\; x_i \left(\frac{1}{x_i}\, dx_i\right) \;=\; dx_i$$

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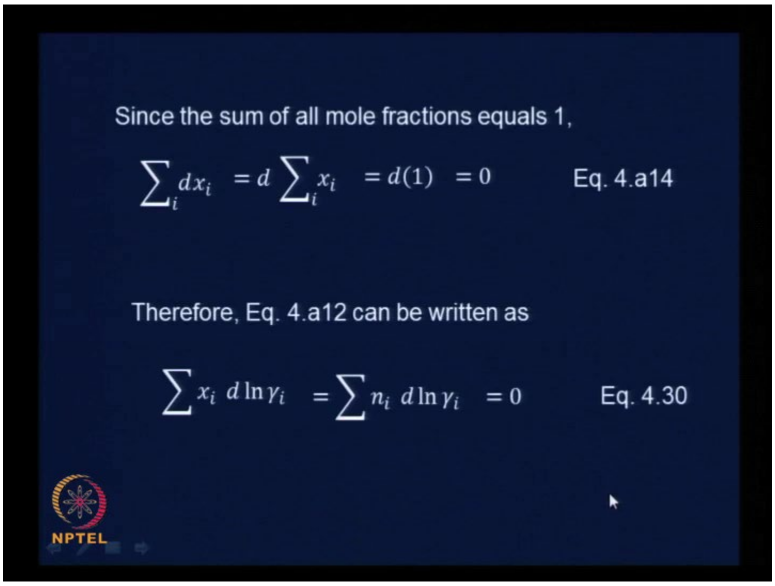

Since the sum of all mole fractions equals 1,

$$\sum_i dx_i = d\sum_i x_i = d(1) = 0 \qquad \text{Eq. 4.a14}$$

Therefore, Eq. 4.a12 can be written as

$$\sum x_i\, d\ln\gamma_i = \sum n_i\, d\ln\gamma_i = 0 \qquad \text{Eq. 4.30}$$

And then the sum over all d x i would be

$$\sum_i dx_i \;= d\, \sum_i x_i \;= d(1) = 0$$

d of the sum over all the x i s, which would be d of a constant, … which is nothing but 0. Therefore, we obtained

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

This was our equation 4.30.

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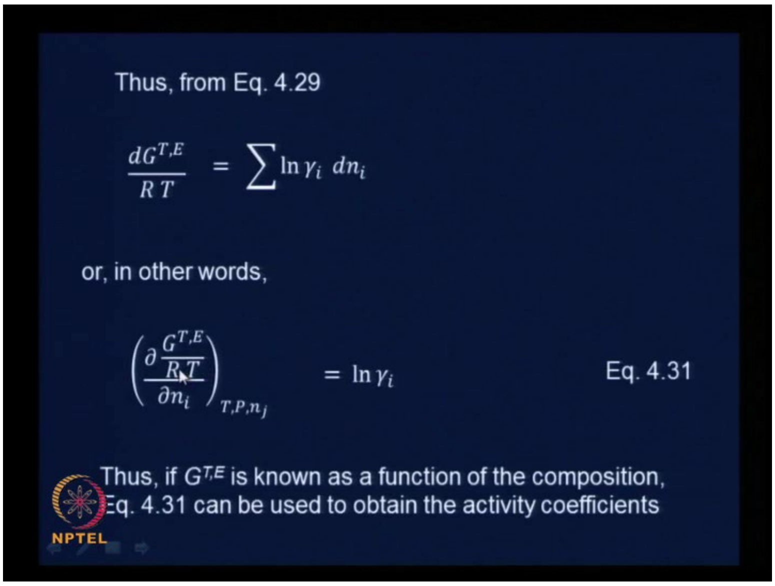

Thus, from Eq. 4.29

$$\frac{dG^{T,E}}{RT} = \sum \ln \gamma_i \, dn_i$$

or, in other words,

$$\left(\frac{\partial \frac{G^{T,E}}{RT}}{\partial n_i}\right)_{T,P,n_j} = \ln \gamma_i \qquad \text{Eq. 4.31}$$

Thus, if $G^{T,E}$ is known as a function of the composition, Eq. 4.31 can be used to obtain the activity coefficients

From here we could … you know, when we went back to the expression for d G E we had those two terms. We got rid of one term. Therefore, only one term remains here,

$$dG^{T,E} = R\,T\left(\sum ln\,\gamma_i \; dn_i\right)$$

This is what we are left with, in a nice way. But, what this also tells us is if you take the derivative, the partial derivative with respect to a certain n i with temperature, pressure and all other n s remaining constant, then that would actually give us ln gamma i.

$$\left(\frac{\partial \frac{G^{T,E}}{R\,T}}{\partial n_i}\right)_{T,\ P,\ n_j} = ln\,\gamma_i$$

We had used this as the basis, to come up with models or at least to see the models for obtaining activity coefficients, if G^{TE} by R T is known as a function of composition.

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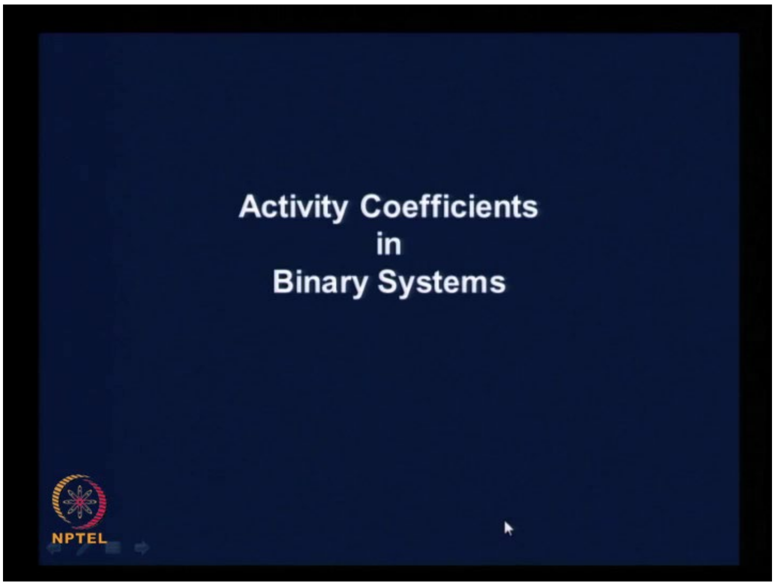

Activity Coefficients
in
Binary Systems

Earlier, we saw some intuitive models. … Before that I should say we started looking only at binary systems, the activity coefficients in binary systems, from then onwards.

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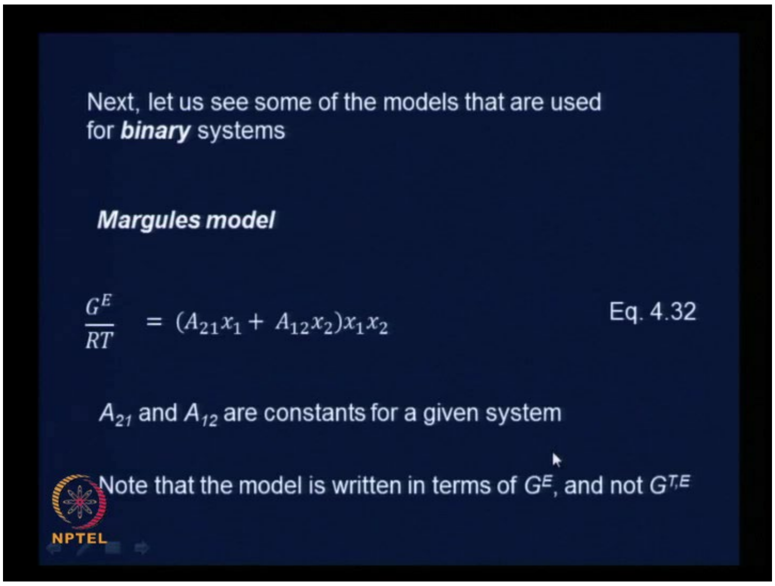

Next, let us see some of the models that are used for ***binary*** systems

Margules model

$$\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1x_2 \qquad \text{Eq. 4.32}$$

A_{21} and A_{12} are constants for a given system

Note that the model is written in terms of G^E, and not $G^{T,E}$

Earlier, we saw some intuitive models by Margules, which gave us

$$\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1x_2$$

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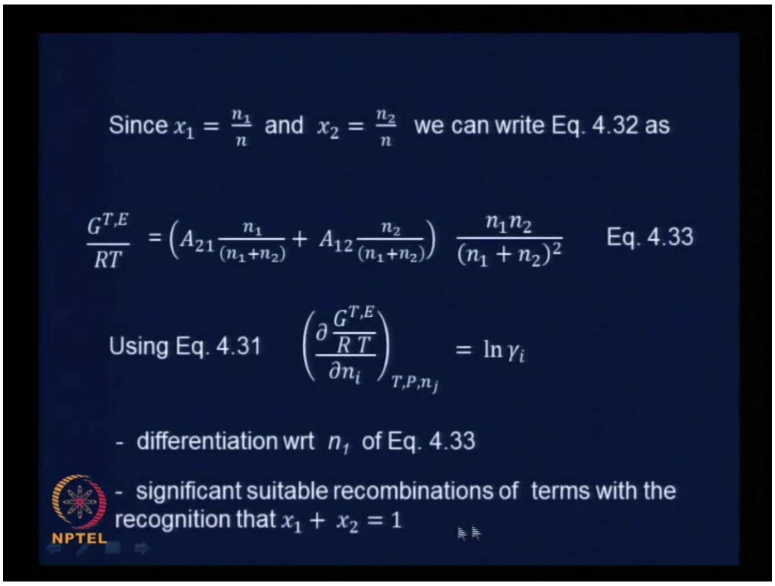

Since $x_1 = \frac{n_1}{n}$ and $x_2 = \frac{n_2}{n}$ we can write Eq. 4.32 as

$$\frac{G^{T,E}}{RT} = \left(A_{21}\frac{n_1}{(n_1+n_2)} + A_{12}\frac{n_2}{(n_1+n_2)}\right)\frac{n_1 n_2}{(n_1+n_2)^2} \qquad \text{Eq. 4.33}$$

Using Eq. 4.31 $\left(\frac{\partial \frac{G^{T,E}}{RT}}{\partial n_i}\right)_{T,P,n_j} = \ln \gamma_i$

- differentiation wrt n_1 of Eq. 4.33
- significant suitable recombinations of terms with the recognition that $x_1 + x_2 = 1$

By following the differentiation with respect to one of the mole numbers and suitable recombination … we could convert it this way or we could do it in terms of x1 x2 also; that is what we did later but, here we did covert it to n1 and so on.

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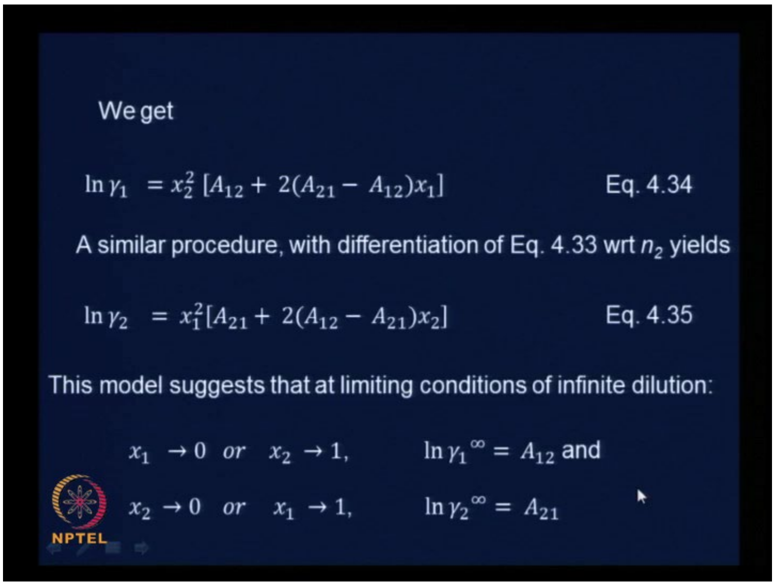

We get

$$\ln \gamma_1 = x_2^2\,[A_{12} + 2(A_{21} - A_{12})x_1] \qquad \text{Eq. 4.34}$$

A similar procedure, with differentiation of Eq. 4.33 wrt n_2 yields

$$\ln \gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2] \qquad \text{Eq. 4.35}$$

This model suggests that at limiting conditions of infinite dilution:

$x_1 \to 0$ *or* $x_2 \to 1$, $\ln \gamma_1{}^{\infty} = A_{12}$ and

$x_2 \to 0$ *or* $x_1 \to 1$, $\ln \gamma_2{}^{\infty} = A_{21}$

We got expressions for gamma 1 and gamma 2. For example, in the case of Margules we got

$$\ln \gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1]$$

$$\ln \gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2]$$

Then we looked at what happens at infinite dilution,

$x_1 \rightarrow 0 \;\; or \;\; x_2 \rightarrow 1, \qquad ln\, \gamma_1{}^{\infty} = A_{12}$

$x_2 \rightarrow 0 \;\; or \;\; x_1 \rightarrow 1, \qquad ln\, \gamma_2{}^{\infty} = A_{21}$

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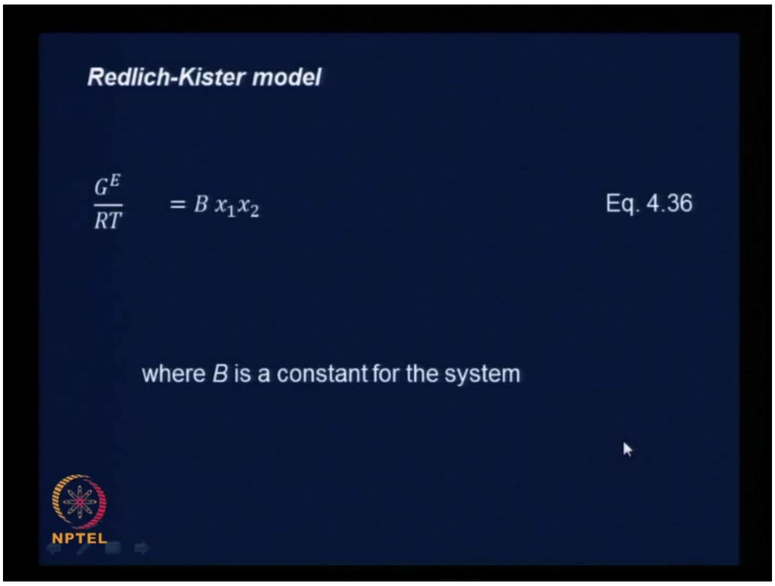

Redlich-Kister model

$$\frac{G^E}{RT} = B\, x_1 x_2 \qquad \text{Eq. 4.36}$$

where B is a constant for the system

We also saw the other models, the Redlich-Kister model which is a very simple

$$\frac{G^E}{RT} = B\, x_1 x_2$$

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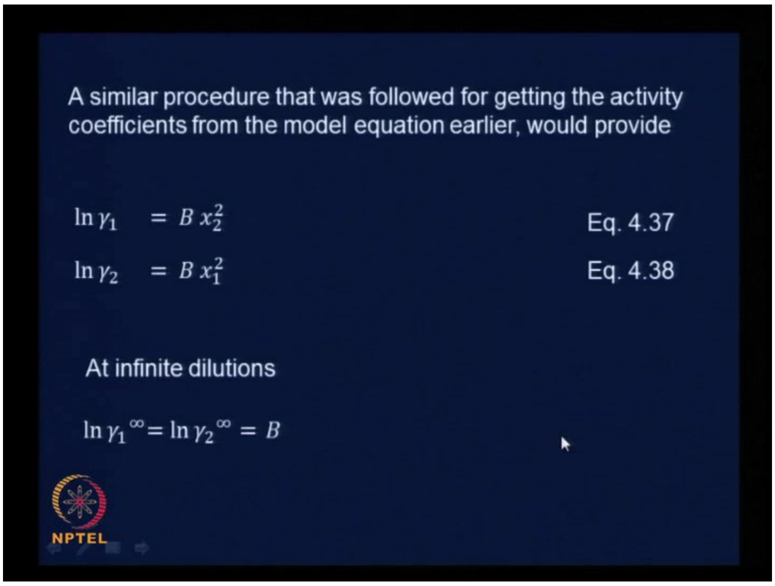

A similar procedure that was followed for getting the activity coefficients from the model equation earlier, would provide

$$\ln \gamma_1 = B x_2^2 \qquad \text{Eq. 4.37}$$

$$\ln \gamma_2 = B x_1^2 \qquad \text{Eq. 4.38}$$

At infinite dilutions

$$\ln \gamma_1{}^{\infty} = \ln \gamma_2{}^{\infty} = B$$

And, we got expressions for ln gamma 1 ln gamma 2.

$$\ln \gamma_1 = B x_2^2$$

$$\ln \gamma_2 = B x_1^2$$

The expressions at infinite dilutions:

$$\ln \gamma_1{}^{\infty} = ln\, \gamma_2{}^{\infty} = B$$

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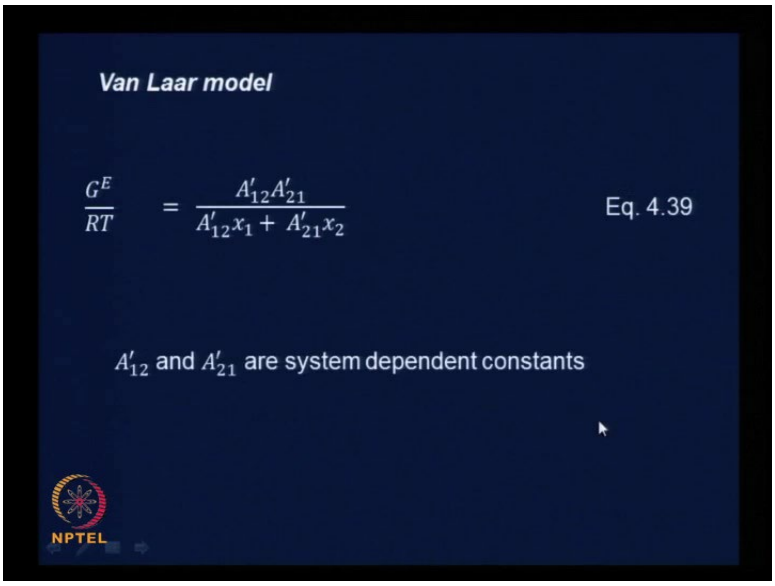

Van Laar model

$$\frac{G^E}{RT} = \frac{A'_{12}A'_{21}}{A'_{12}x_1 + A'_{21}x_2} \qquad \text{Eq. 4.39}$$

A'_{12} and A'_{21} are system dependent constants

Van Laar model which is one of the popular models:

$$\frac{G^E}{RT} = \frac{A'_{12}A'_{21}}{A'_{12}x_1 + A'_{21}x_2}$$

A12 dash and A21 dash are constants for a given system.

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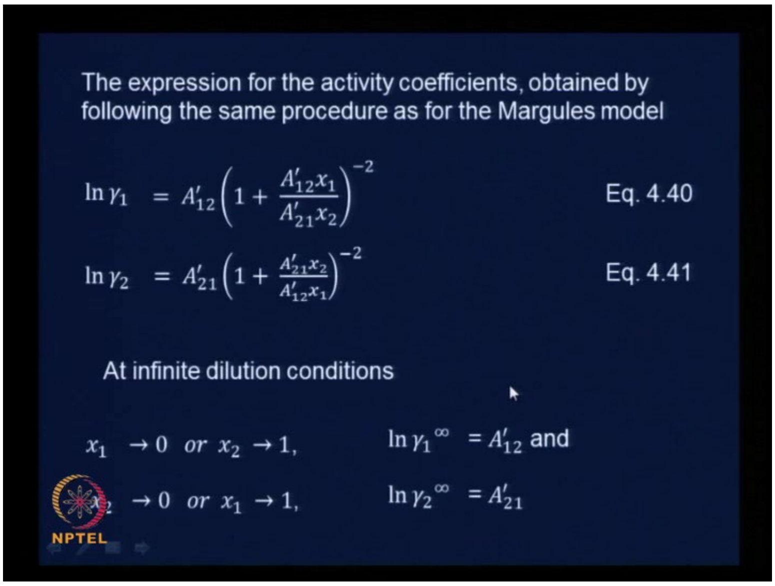

The expression for the activity coefficients, obtained by following the same procedure as for the Margules model

$$\ln \gamma_1 = A'_{12}\left(1 + \frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2} \qquad \text{Eq. 4.40}$$

$$\ln \gamma_2 = A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2} \qquad \text{Eq. 4.41}$$

At infinite dilution conditions

$x_1 \to 0$ *or* $x_2 \to 1$, $\ln \gamma_1^{\infty} = A'_{12}$ and

$x_2 \to 0$ *or* $x_1 \to 1$, $\ln \gamma_2^{\infty} = A'_{21}$

And from that we got the expressions for

$$\ln \gamma_1 = A'_{12}\left(1 + \frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2}$$

$$\ln \gamma_2 = A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2}$$

We also saw the infinite dilution expressions.

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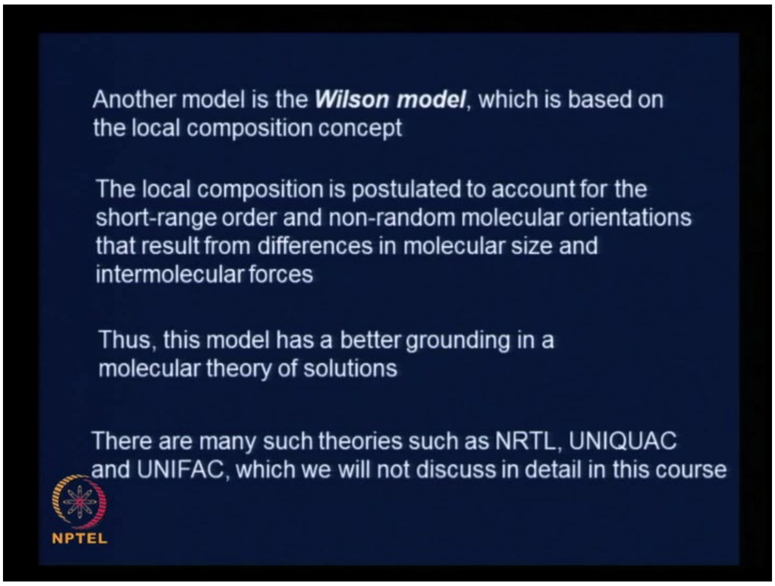

Another model is the ***Wilson model***, which is based on the local composition concept

The local composition is postulated to account for the short-range order and non-random molecular orientations that result from differences in molecular size and intermolecular forces

Thus, this model has a better grounding in a molecular theory of solutions

There are many such theories such as NRTL, UNIQUAC and UNIFAC, which we will not discuss in detail in this course

Then we started considering the Wilson model. Apart from the others which had some sort of an intuitive bases, the Wilson model was based on a theoretical concept – the local composition concept. The local composition concept, just for information, we are not going to look closer at this in this particular course. It is outside the scope of the course.

The local composition is postulated to account for the short range order and non random molecular orientations that result from differences in molecular size and the intermolecular forces. If you get into statistical thermodynamics you would need to worry about all these things.

And therefore, this Wilson model has a better grounding in the molecular theory of solutions. So, are many other models such as NRTL, UNIQUAC, UNIFAC and so on and so forth … that are available in the literature. They were developed ages ago, decades ago and but, which are very useful for finding out activity coefficients, for estimating activity coefficients … from the models.

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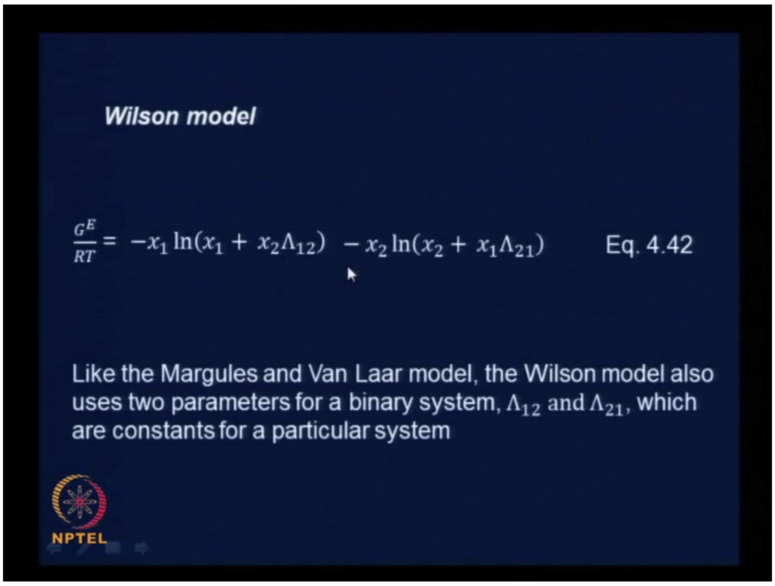

Wilson model

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + x_2\Lambda_{12}) \; - x_2 \ln(x_2 + x_1\Lambda_{21}) \qquad \text{Eq. 4.42}$$

Like the Margules and Van Laar model, the Wilson model also uses two parameters for a binary system, Λ_{12} and Λ_{21}, which are constants for a particular system

Wilson model was

$$\frac{G^E}{RT} = -x_1\, ln(x_1 + x_2\Lambda_{12}) - x_2\, ln(x_2 + x_1\Lambda_{21})$$

Gamma 1 2 and Gamma 2 1 are the Wilson constants for a particular system.

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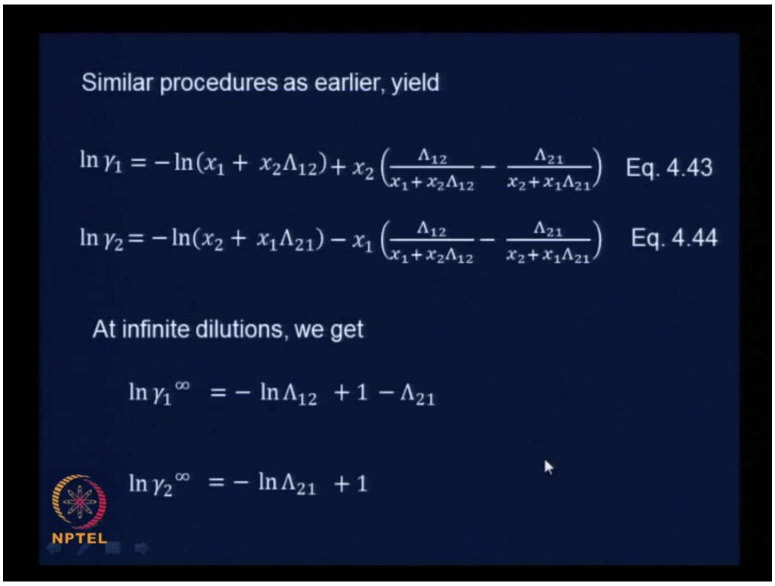

Similar procedures as earlier, yield

$$\ln\gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}\right) \qquad \text{Eq. 4.43}$$

$$\ln\gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}\right) \qquad \text{Eq. 4.44}$$

At infinite dilutions, we get

$$\ln\gamma_1^{\infty} = -\ln\Lambda_{12} + 1 - \Lambda_{21}$$

$$\ln\gamma_2^{\infty} = -\ln\Lambda_{21} + 1$$

And similar procedures as for the other models would yield … this was again left to you as an exercise hopefully you did them; if not please do them, and convince yourself that this is indeed the case …

$$\ln \gamma_1 = -ln(x_1 + x_2\Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)$$

$$\ln \gamma_2 = -ln(x_2 + x_1\Lambda_{21}) - x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)$$

This is actually the same in both these expressions, the second combination term. And we saw the expression for infinite dilutions also.

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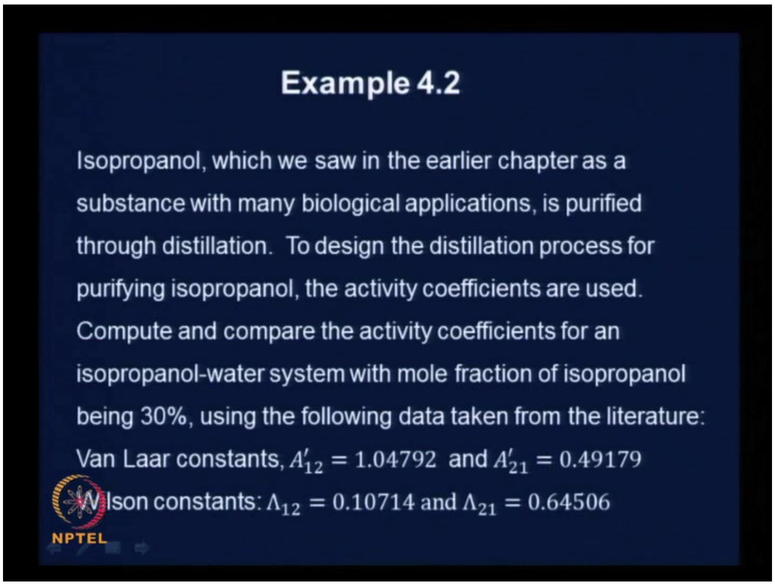

Example 4.2

Isopropanol, which we saw in the earlier chapter as a substance with many biological applications, is purified through distillation. To design the distillation process for purifying isopropanol, the activity coefficients are used. Compute and compare the activity coefficients for an isopropanol-water system with mole fraction of isopropanol being 30%, using the following data taken from the literature:

Van Laar constants, $A'_{12} = 1.04792$ and $A'_{21} = 0.49179$

Wilson constants: $\Lambda_{12} = 0.10714$ and $\Lambda_{21} = 0.64506$

Then we worked out an example. This example was deliberately chosen to tell you something more. The first one is a direct calculation. … The example was with respect to isopropanol. Isopropanol has many biological applications. To design the distillation process for purifying isopropanol, the activity coefficients are required. Compute and compare the activity coefficients for an isopropanol water system with mole fraction of isopropanol being 30 percent, using the following data taken from the literature – the Van Laar constants and the Wilson constants for a particular condition were taken from the literature.

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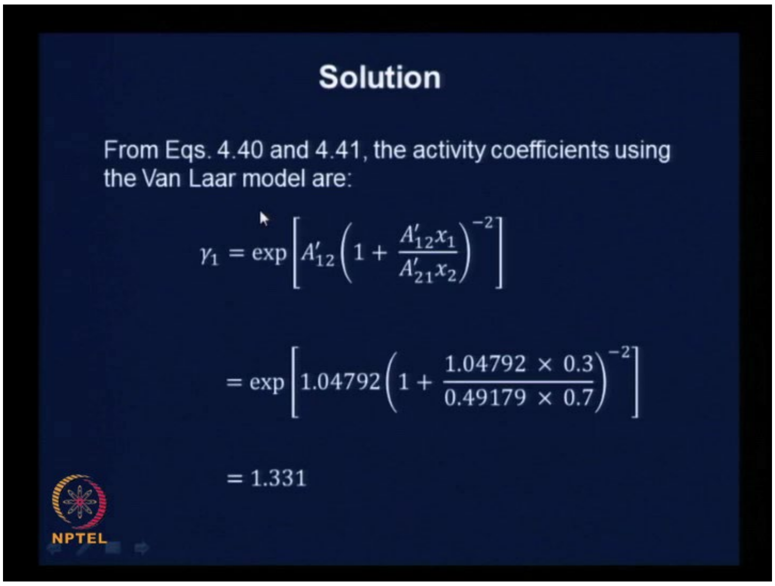

Solution

From Eqs. 4.40 and 4.41, the activity coefficients using the Van Laar model are:

$$\gamma_1 = \exp\left[A'_{12}\left(1 + \frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2}\right]$$

$$= \exp\left[1.04792\left(1 + \frac{1.04792 \times 0.3}{0.49179 \times 0.7}\right)^{-2}\right]$$

$$= 1.331$$

We went through the calculations. You went through it first, then I showed it to you. We found that in the Van Laar model we got gamma 1 was 1.331 and gamma 2 was 1.119, whereas, … using the Wilson model we got a gamma 1 of 1.965.

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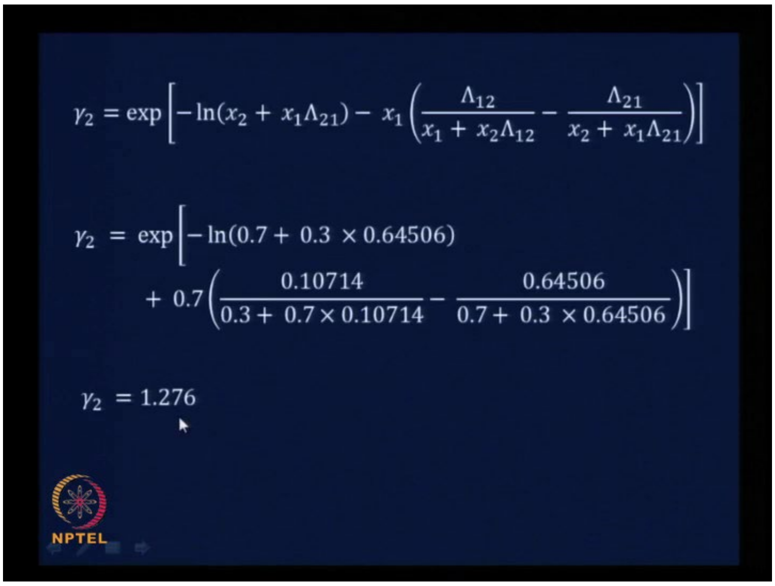

$$\gamma_2 = \exp\left[-\ln(x_2 + x_1\Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)\right]$$

$$\gamma_2 = \exp\left[-\ln(0.7 + 0.3 \times 0.64506) + 0.7\left(\frac{0.10714}{0.3 + 0.7 \times 0.10714} - \frac{0.64506}{0.7 + 0.3 \times 0.64506}\right)\right]$$

$$\gamma_2 = 1.276$$

And, gamma 2 of 1.276. Of course, different models would give different gamma values. … To get better and better estimates, different models were developed, or better and better models were developed. And some of the model names we saw in the earlier part of this particular subsection itself. This is what we did in terms of thermodynamics for solutions or of solutions in this particular module.

There are two more modules that we will look at in this particular course. The first module or the fifth module in the sequence is on phase equilibria and the sixth module is on reaction equilibria.

We will use whatever we have developed so far. This will give you a flavor. After a review, we looked at thermodynamic properties. We defined thermodynamic properties, and presented ways of manipulating them, getting useful information from whatever is available easily and so, on and so forth.

And then we also found that there were ways of expressing the not so easy to measure thermodynamic variables in terms of easy to measure thermodynamic variables, P, V, and T. Then, we looked at the thermodynamic aspects of pure substances, and thermodynamic aspects of solutions. Then we are going to use all of those in predicting phase equilibria, and coming up with relevant useful predictions for reaction equilibria also. That is what will follow. See you in the next class.