Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 34
Models for Activity Coefficient in a binary System

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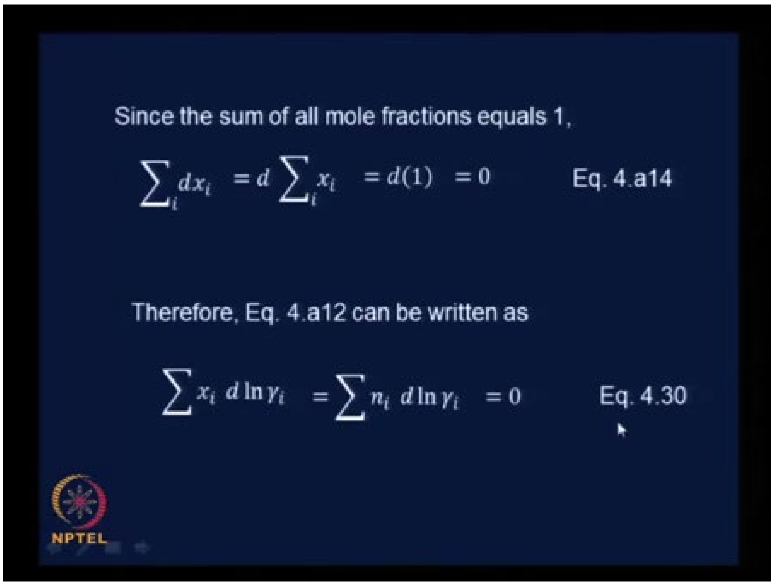

Since the sum of all mole fractions equals 1,

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

Therefore, Eq. 4.a12 can be written as

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

Welcome!

In the last lecture, after an extended derivation starting from the Gibbs-Duhem equation, which is a fundamental equation, we arrived at the fact that summation over x i d ln gamma i, which can of course, can be written as summation over n i d ln gamma i – you know, x i is nothing but n i divided by the sum over all mole numbers n i and therefore, if you multiply both sides of this equation by sum over all n i this one would become sum over n i d ln gamma i – equals 0. This is what we had started out to show.

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

We will call this equation 4.30.

Now, let us take this further. We did this for a purpose. If you remember, we started looking at excess quantities. Again, to recall, excess quantities are defined the same way and play similar roles as the residual properties for pure substances.

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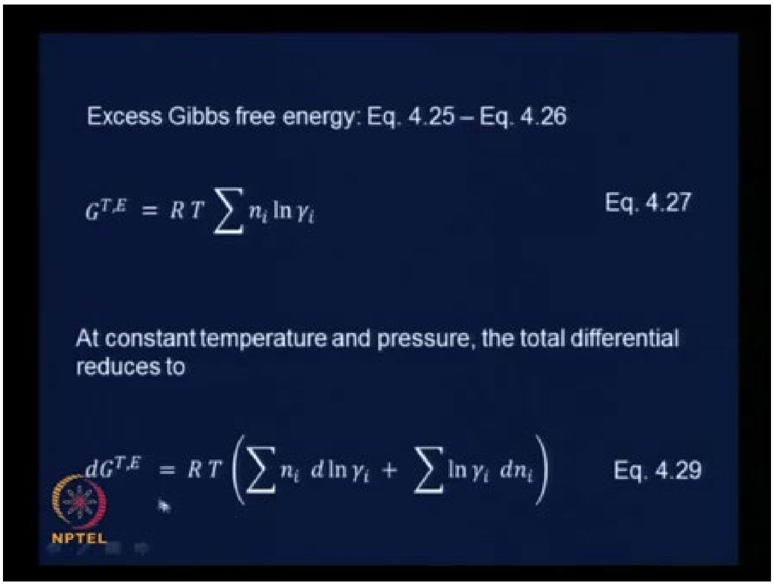

Excess Gibbs free energy: Eq. 4.25 – Eq. 4.26

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

At constant temperature and pressure, the total differential reduces to

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

Let us go forward. From equation 4.29 – let us go back to equation 4.29 to refresh our memories; it has been a couple of classes before which we saw this. So, let us go back to equation 4.29.

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

This was the equation 4.29. We went through an extended derivation to show that this term is actually 0. Therefore,

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

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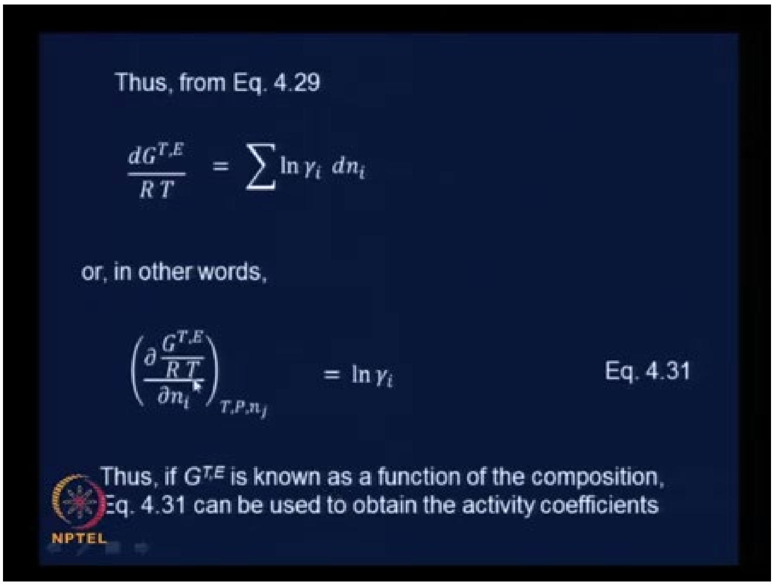

Thus, from Eq. 4.29

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

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

So,

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

Now, this is where we are getting to the overall goal of this particular subsection, which is to find means of estimating gamma i s, the activity coefficients. So, this in other words, means that if you take the partial derivative of the left hand side with respect to a particular n i with all other n s remaining constant and at constant T and P, of course, that was brought from before. This will be equal to ln of gamma i. It is easy to see – this is ln gamma 1 d 1 plus ln gamma 2 d n 2 and so on and so forth. Suppose, we take this respect d n 2, all other terms will drop out except the ln gamma 2 terms.

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

This is equation 4.31.

Therefore, this is what we were kind of getting at … if G^{TE} is known as a function of the composition, then G^{TE} by R T is known as a function of composition. Then one can use this relationship between G^{TE} and gamma i, to get an estimate of gamma i. Now, equation 4.31 can be used to obtain the activity coefficients. So, this gives us one means of estimating the activity coefficient of a component i in a particular solution.

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Activity Coefficients
in
Binary Systems

The remaining part of our module is going to be limited to binary systems, because there is so much of work that is available in binary systems. … Probably, that is good enough for an undergraduate level of understanding. Therefore, let us look at means of estimating activity coefficients in binary systems, and the basis for this is going to be the previous statement that we made. If G^{TE} is known as a function of composition then this equation 4.31 dou G^{TE} by R T dou n i at constant T, P, n j equals ln gamma i can be used to obtain the activity coefficient gamma i. Essentially we will be looking at models for binary systems of G^{TE} or G^{E} as a function of the composition … x1 and x2 in this case – it is a binary system.

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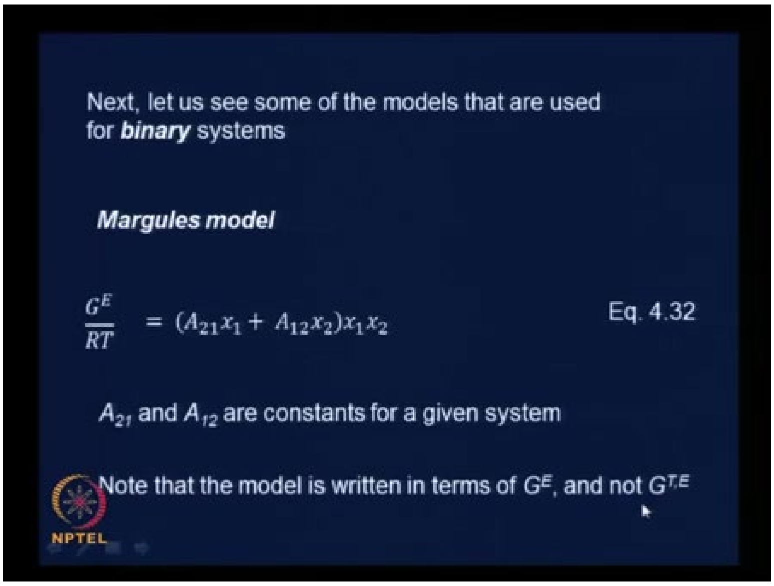

Next, let us see some of the models that are used for ***binary*** systems

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 $G^{T,E}$

So, let us look at some of the models that are available in the literature and somewhat commonly used. The first model that we are going to look at is called the Margules model. … That model is given as G^E by RT. This is given in molar terms, not G^{TE};

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

Let us call this equation 4.32. … A_{21} and A_{12} are the constants for a particular given system. For a particular solution you have particular values of A_{21} and A_{12}.

Therefore, if you know these constants, then you could estimate G^E by RT. Or, this is one of the models that would give us G^E by R T. This we have already mentioned that the model is written in terms of molar quantities G^E, and not G^{TE}. We need to note this because this will come in handy, in terms of certain derivations and so on, one of which is coming up very soon.

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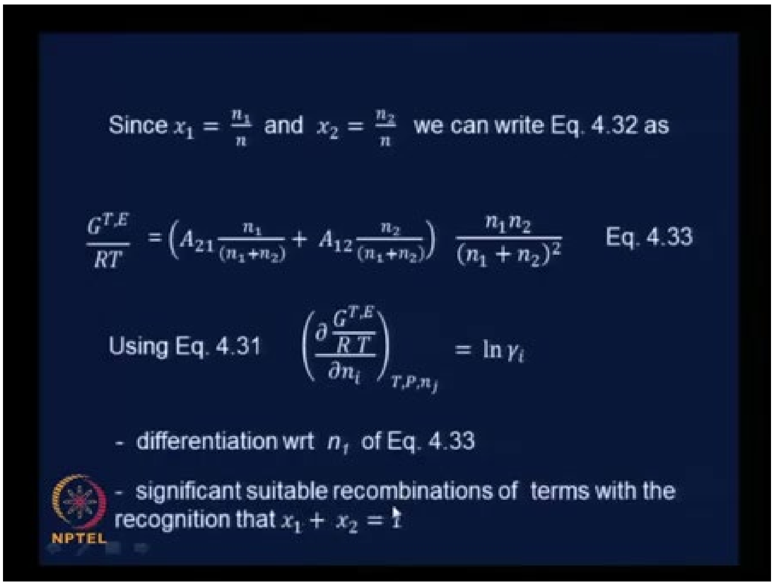

Since $x_1 = \frac{n_1}{n}$ and $x_2 = \frac{n_2}{n}$ we can write Eq. 4.32 as

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

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

Now, … the definition of mole fraction is nothing but the number of moles divided by the total number of moles. Therefore, x1 is n1 by n and x2 equals n2 by n, we can write this equation 4.32, which we had seen here, in terms of

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

We just have to replace x1, wherever x1 occurs, by n1 by n and wherever x2 occurs by n2 by n. In fact, why don't I give you about 5 minutes to just do this algebra, and convince yourself that this is indeed the expression that you get, when you substitute.

The complete expression is given here equation 4.33. Take about 5 minutes. Essentially, substitute x1 equals n1 by n and x2 equals n2 by n in the previous equation, the Margules model, and come up with this please. 5 minutes.

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Please pause the video here. You can pause it as long as you want. The time mentioned is only a guideline

You would have substituted and reduced the terms, combined the terms, to get

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

equation 4.33. This the same Margules model written in terms of n1 and n2. Now, using this equation 4.31 that we wrote down earlier, which is

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

Using this, what I would like you to come up with – using this expression – is an expression for gamma 1 and gamma 2 for this particular system.

Let me start you out a little bit. These steps are very straight forward. You need to differentiate this expression, you know, $\left(\frac{\partial \frac{G^{T,E}}{RT}}{\partial n_i}\right)_{T,\ P,\ n_j}$ … that is on the left hand side you need differentiate partially with respect to let us say n1, in this case, at constant T, P and n2.

And, you will have to do re-combinations – they may be significant – of the terms with the recognition that the sum of the mole fractions in the system, sum of the mole fractions in any system, equals 1. This is a binary system therefore, x1 plus x2 equals 1. Make you use of these 2 hints, and please come up with an expression for ln gamma 1 first, through the differentiation with respect n1, and also ln gamma 2. I am going to give you about 20 minutes to do this, and come up the expressions. Go ahead, please.

By now, you may be comfortable with the math and probably the algebra will take some time. And hopefully you would have obtained by doing the differentiation with respect to n 1 and … recombining significantly, with the recognition that $x_1 + x_2 = 1$.

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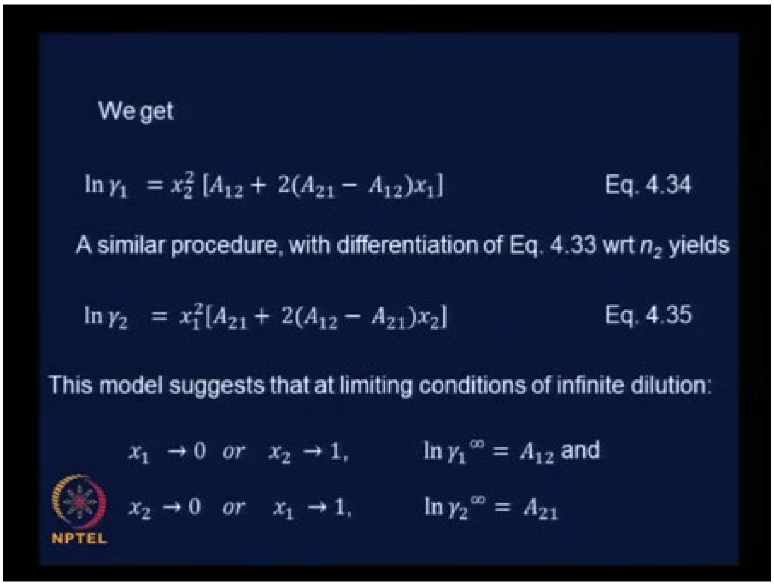

We get

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

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

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

This model suggests that at limiting conditions of infinite dilution:

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

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

You would get

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

This is how we can get an estimate of gamma 1 if we know A 1 2 and A 2 1 as a function of the mole fractions x 1 and x 2. Let us call this equation 4.34. … By following a similar procedure but differentiation with respect to n 2 and similar re-combinations, you would get

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

Let us call this equation 4.35.

Therefore, we have obtained a means of finding out gamma 1 and gamma 2 using the Margules model. This is one of the early models … which helps us find the activity coefficients here. There are many such models, and some models work well for certain systems, some models work well for the systems. That is the reason for having so many different models. Some models have better basis in theory than the other models, and so on. We will see about 3 or 4 such models in this particular module.

Before we do that it is nice to do some small analysis here, you know the model for gamma 1 and gamma 2 – this suggests that at the limiting conditions of infinite dilutions. What does infinite dilution mean? It means that one of the components has gone to 0, and the other component is what is there, completely. If x1 has gone to 0, if you substitute x1 equal 0; here x2 is 1. Therefore, ln gamma 1 is nothing but the constant A_{12}. Therefore, when x1 tends to 0 or x 2 tends to 1, that is … one and the same thing, then ln of gamma 1 infinity. This is infinite dilution when the mole fraction 1 of the components has gone to 1.

And of course, by consequence, the other mole fraction has gone to 0.

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

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

These are limiting conditions that we can use to check and get some quick estimates from.

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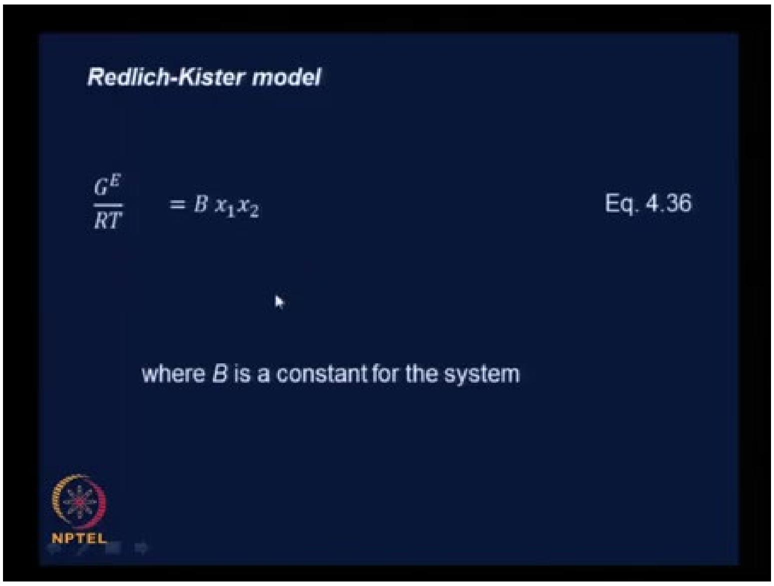

Redlich-Kister model

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

where B is a constant for the system

Now, let us look at another model, that can be used to estimate activity coefficients and that is called the Redlich-Kister model. … Essentially, all these models are expressions of G^E by RT. The basis is equation 4.31, where you have this expression, and you know this as a function of composition. Then, you can find the activity coefficients by taking the partial derivative.

So, here it is a very simple model

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

We will call this equation 4.36. What I would like you to do is go through the same exercise that we did for the Margules model, and come up with expressions for activity coefficients, using this particular model. To recall, you write this in terms of n 1, n 2, if need be. Then you differentiate one with respect to the first with respect to n 1 to get gamma 1 and estimate for that or an expression for that. And differentiate with respective to n 2 to get an estimate of gamma 2.

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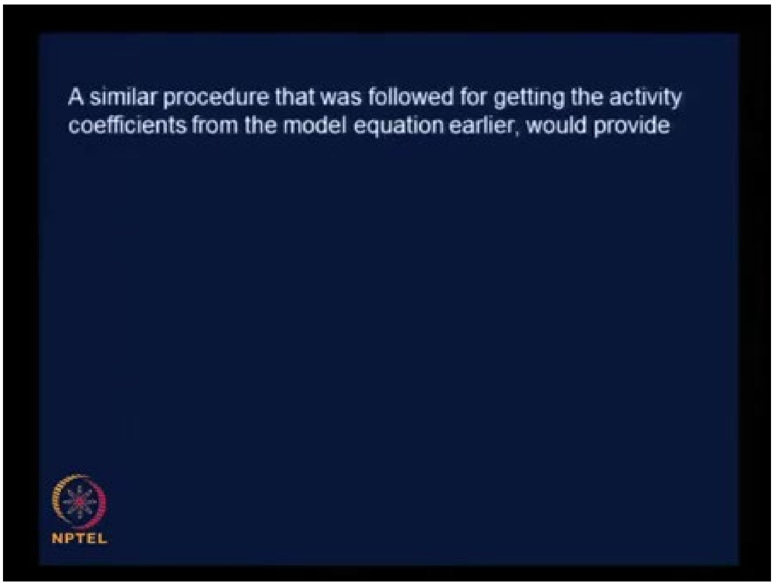

A similar procedure that was followed for getting the activity coefficients from the model equation earlier, would provide

Why don't you go ahead. Take about 10 minutes. This is a simple enough model we have seen this earlier … may be there are quite a few steps. So, take about 15 minutes to do this, and then I will tell you what equations you would get if you do that procedure. Go ahead please. 15 minutes

I think, you need to take that as homework, and when you come back in the next class … we are out of time here … when you come back in the next class, we will start out with the expressions for gamma 1 and gamma 2 for the Redlich-Kister model. See you then.