

Thermodynamics (Classical) for Biological Systems

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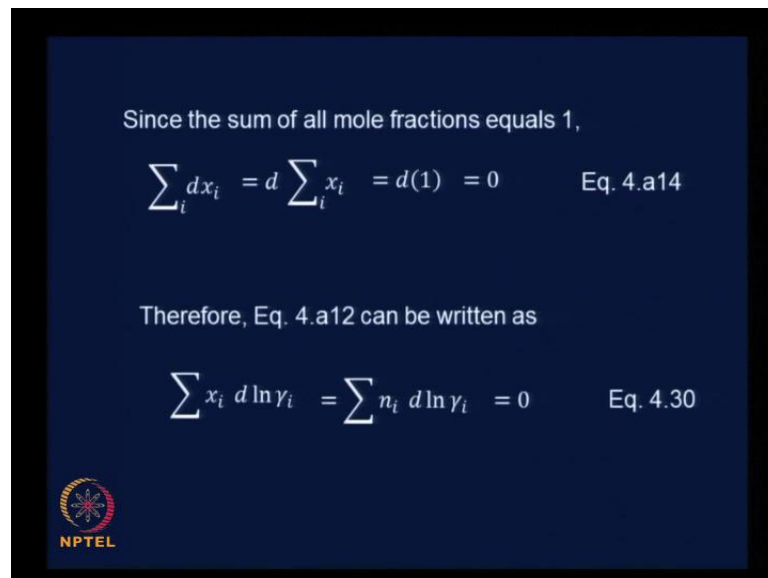
Module No. # 04

Thermodynamics of Solutions

Lecture No. # 25

Activity Coefficient from Excess Property (continued) Models for Activity Coefficient in Binary Systems


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Since the sum of all mole fractions equals 1,

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

Therefore, Eq. 4.a12 can be written as

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


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. 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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The screenshot shows a PowerPoint slide with the following content:

Thus, from Eq. 4.29

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

or, in other words,

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

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

At the bottom of the slide, there is a text box that says "Click to add notes".

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. That was slide number 48 if I remember right.

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The screenshot shows a PowerPoint slide with the following content:

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

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

At constant temperature and pressure, the total differential reduces to

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

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This was the equation 4.29, and this is $dG^{T,E} = RT \sum \ln \gamma_i dn_i$. And we went through an extended duration to show that this term is actually 0. And therefore, $dG^{T,E} = RT \sum \ln \gamma_i dn_i$. And if you transpose this equation, $dG^{T,E} / RT$ becomes $\sum \ln \gamma_i dn_i$ and that is (No audio from 02:31 to 02:37) the next thing that we are going to consider. I think that was in...

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Thus, from Eq. 4.29

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

or, in other words,

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

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

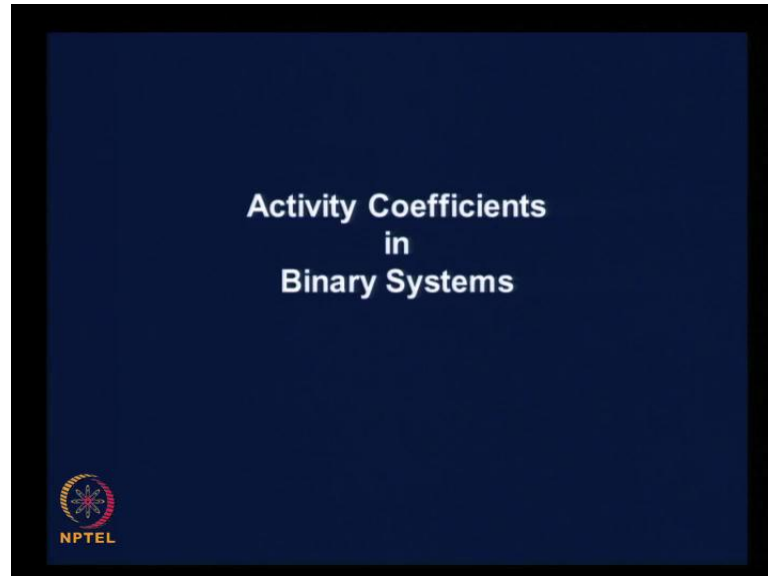


So, $dG^{T,E} / RT$ equals $\sum \ln \gamma_i dn_i$. Now, this is where we are getting to the overall goal of this particular subsection, which is to find means of estimating γ_i s, the activity coefficients. So, this in other words, means that if you take the partial derivative of the left hand side 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 $\ln \gamma_i$. It is easy to see – this is $\ln \gamma_1 dn_1 + \ln \gamma_2 dn_2$ and so on and so forth. Suppose, we take this respect dn_2 . $dG^{T,E} / RT dn_2$ at T, P , and all other n remaining constant. All other terms will drop out except the $\ln \gamma_2$ terms. So, that is what this one gives us, and this is equation 4.31.

Therefore, this is what we were kind of getting at ... if $G^{T,E}$ is known as a function of the composition, then $dG^{T,E} / RT$ is known as a function of composition. Then one can use this relationship between $G^{T,E}$ and γ_i , to get an estimate of γ_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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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. And 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 $G(T, E)$ is known as a function of composition then this equation $4.31 \text{ } d \ln G(T, E) = \sum_i n_i d \ln \gamma_i$ at constant T, P, n_j equals $\ln \gamma_i$ can be used to obtain the activity coefficient γ_i . Essentially we will be looking at models for binary systems of $G(T, E)$ or $G(E)$ as a function of the composition ... x_1 and x_2 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

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

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 $G^{T,E}$; G^E by RT equals A_{21} times x_1 plus A_{12} times x_2 the whole times $x_1 x_2$. 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 RT . This we have already mentioned that the model is written in terms of molar quantities G^E , and not $G^{T,E}$. 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

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

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, x_1 is n_1 by n and x_2 equals n_2 by n , we can write this equation 4.32, which we had seen here, in terms of n $G^{T,E}$ by $R T$ equals $A_{21} \frac{n_1}{n_1 + n_2} + A_{12} \frac{n_2}{n_1 + n_2}$ multiplied by $\frac{n_1 n_2}{(n_1 + n_2)^2}$. We just have to replace x_1 , wherever x_1 occurs, by n_1 by n and wherever x_2 occurs by n_2 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 x_1 equals n_1 by n and x_2 equals n_2 by n in the previous equation, the Margules model, and come up with this please. 5 minutes.

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You would have substituted and reduced the terms, combined the terms, to get $G^{T,E}$ by $R T$ equals $A_{21} \frac{n_1}{n_1 + n_2} + A_{12} \frac{n_2}{n_1 + n_2}$ multiplied by $\frac{n_1 n_2}{(n_1 + n_2)^2}$; equation 4.33. This the same Margules model written in terms of n_1 and n_2 . 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 γ_1 and γ_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, $\ln \gamma_1$ by n_1 ... that is on the left hand side you need differentiate partially with respect to let us say n_1 , in this case, at constant T, P and n_2 .

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, x_1 plus x_2 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 n_1 , 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.

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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 plus x_2 equals 1.

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We get


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

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

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

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 $\ln \gamma_1$ – please check whether you got this – equals x_2 squared times A_{12} plus 2 times A_{21} minus ... A_{21} minus A_{12} , times x_1 . This is how we can get an estimate of γ_1 if we know A_{12} and A_{21} as a function of the mole fractions x_1 and x_2 . Let us call this equation 4.34. ... By following a similar procedure

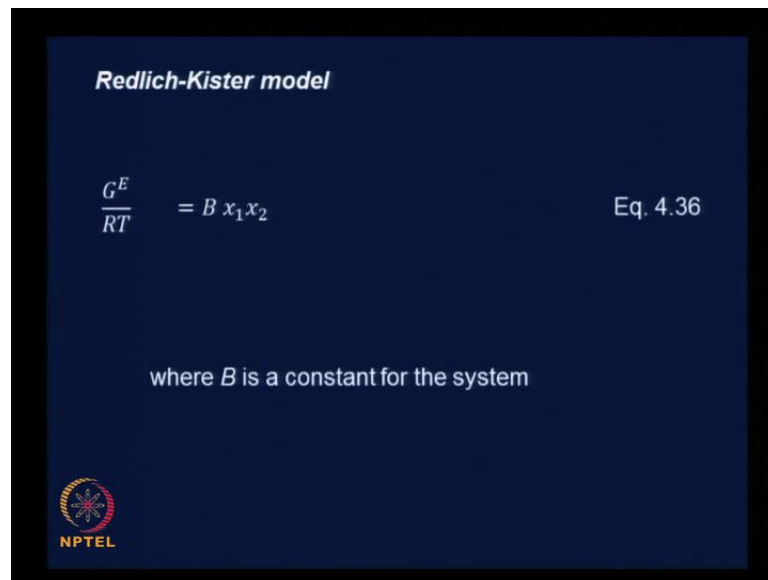
but differentiation with respect to x_2 and similar re-combinations, you would get $\ln \gamma_2 = x_1^2 A_{21} + 2x_1 x_2 A_{12} - x_2^2 A_{11}$; and let us call this equation 4.35.

Therefore, we have obtained a means of finding out γ_1 and γ_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. And, 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 γ_1 and γ_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 x_1 has gone to 0, if you substitute $x_1 = 0$; here $x_2 = 1$. And therefore, $\ln \gamma_1$ is nothing but the constant A_{12} . Therefore, when x_1 tends to 0 or x_2 tends to 1, that is ... one and the same thing, then $\ln \gamma_1$ 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. This is A_{12} and similarly, in the flip case that x_2 goes to 0 or x_1 tends to 1, then if you substitute that here, you can get that $\ln \gamma_2$ at infinite dilution conditions equals A_{21} . These are limiting conditions that we can use to check and get some quick estimates from.

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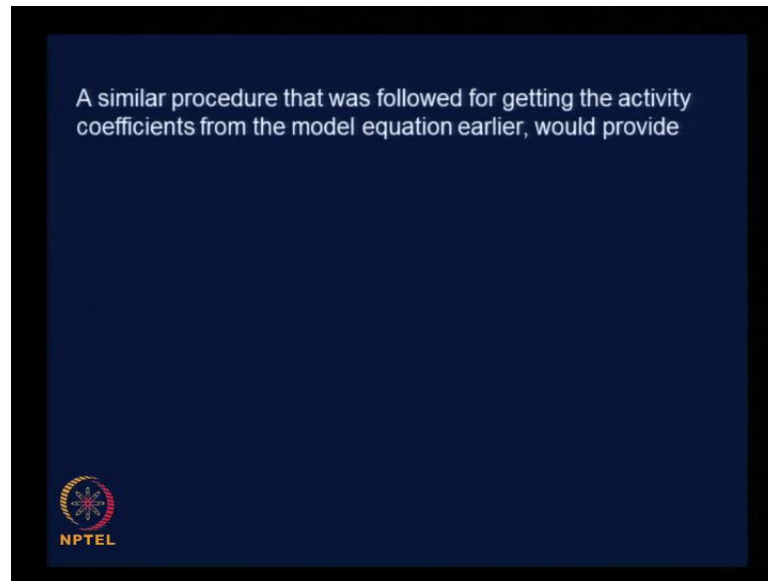


The slide features a dark blue background with a black border. At the top, the text "Redlich-Kister model" is written in white. Below this, the equation $\frac{G^E}{RT} = B x_1 x_2$ is displayed in white, with "Eq. 4.36" to its right. Underneath the equation, the text "where B is a constant for the system" is written in white. In the bottom left corner, there is a circular logo with a red and yellow design, and the text "NPTEL" is written below it.

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 $R T$. 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 G^E by $R T$ is given as equal to B , some constant, times x_1 times 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 γ_1 and estimate for that or an expression for that. And differentiate with respect to n_2 to get an estimate of γ_2 .

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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

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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 γ_1 and γ_2 for the Redlich-Kister model. See you then.