7Thermodynamics (Classical) for Biological Systems
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Module No. # 04
Thermodynamics of solutions
Lecture No. # 26
Models for Activity Coefficient in Binary Systems (continued)

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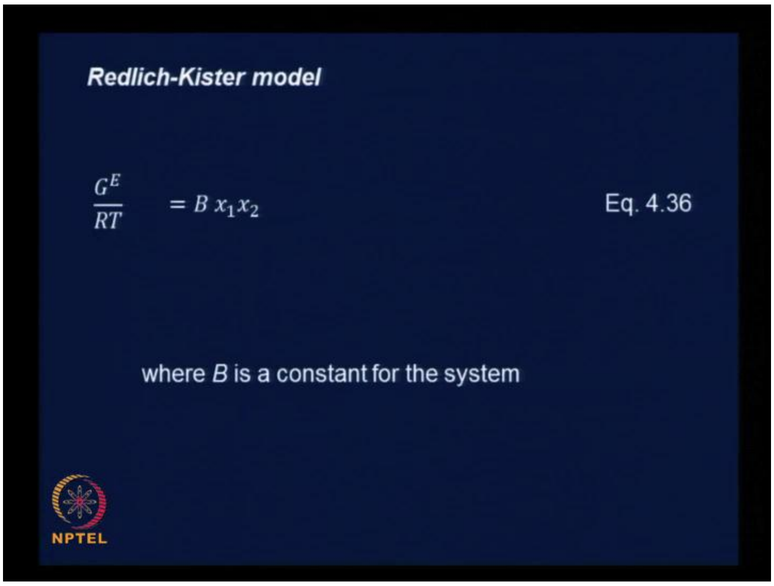

Redlich-Kister model

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

where B is a constant for the system

Welcome!

In the last lecture we started looking at models for activity coefficients for binary systems – consisting of two components. … We said we have to limit ourselves to binary systems in this particular course. We looked at the Margules model, and we found expressions for gamma 1 and gamma 2. We started looking at the Redlich-Kister model which is G E by R T equals B x 1 x 2, where B is a constant for the particular system. And, what was started out in class and left as homework was that to derive the expressions for ln gamma 1 and ln gamma 2 for the Redlich-Kister model, using the same procedure as we did for the Margules model.

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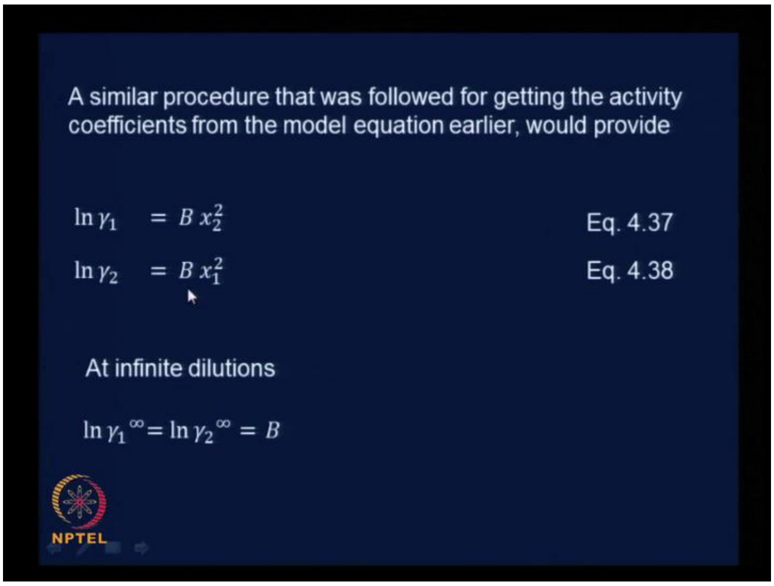

A similar procedure that was followed for getting the activity coefficients from the model equation earlier, would provide

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

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

At infinite dilutions

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

Hopefully you would have obtained these particular expressions. I will start this again (no audio from 01:08 to 01:15) … ln gamma 1 equals a simple, B x 2 squared; equation 4.37. And ln gamma 2 equals B x 1 squared; equation 4.38. Hopefully you would have gotten this. And in the same way that we did by analysis of the Margules model at infinite dilutions, you know that … one of the mole fractions will go to 1. And as a consequence, the other mole fraction will go to 0. ln gamma 1 infinity equals ln gamma 2 infinity. That is B, the constant B, which would be the constant in the Redlich-Kister model.

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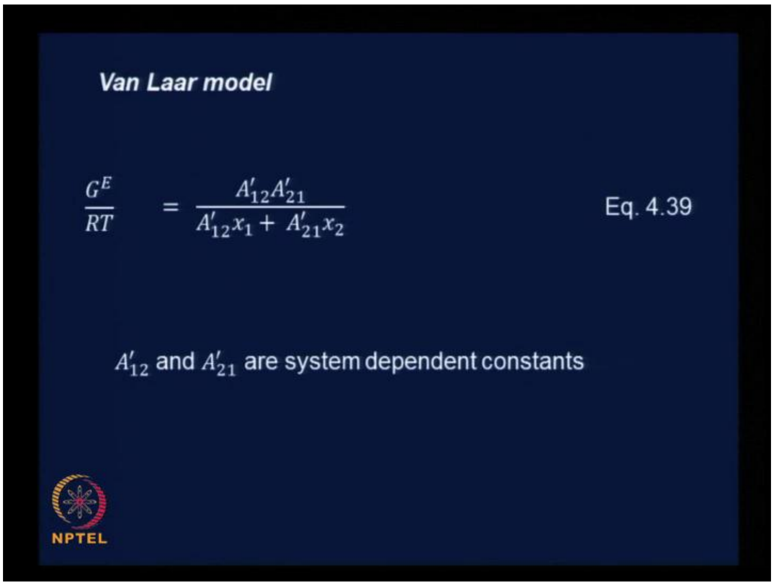

Van Laar model

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

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

There is another model, again for binary systems, to find activity coefficients, which is called the Van Laar model. Of course, the model is for G E by R T. Van Laar model says that G E by R T equals A 1 2 dash A 2 1 dash divided by A 1 2 dash x 1 plus A 2 1 dash times x 2. This is the Van Laar model; equation 4.39, where A 1 2 dash and A 2 1 dash are system dependent constants. They are particular values for a given system. …

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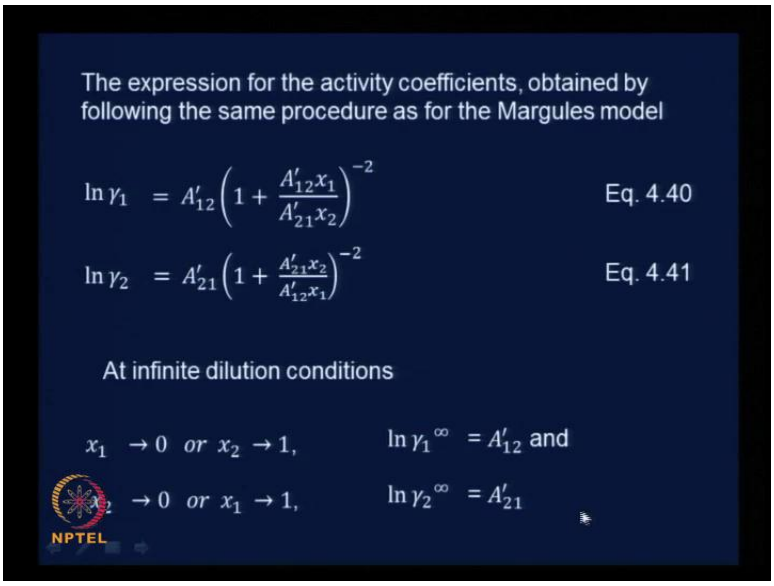

The expression for the activity coefficients, obtained by following the same procedure as for the Margules model

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

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

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

I am not going to give you extra time in class this time please take this as homework and do this may be it will be come back as one of the exercise problems too….By using a similar procedure as we did for the Margules and the Redlich-Kister models, if we find the expressions for activity coefficients they would turn out to be ln gamma 1 equals A 1 2 dash times 1 by the square of … see this is to the power of minus 2 …therefore, 1 by the square of 1 plus A 1 2 dash x 1 divided by A 2 1 dash x 2. Let us call this equation 4.40. And ln gamma 2 would be A 2 1 dash times 1 by square of 1 plus A 2 1 dash x 2 divided by A 1 2 dash x 1. We will call this equation 4.41.

And, at infinite dilutions, as we did earlier, when x 1 tends to 0 or x 2 tends to 1, we have ln gamma 1 infinity equals A 1 2. Quite easy to see; you put in x 1 equals 0. Irrespective of x 2, this term vanishes, and therefore, this term just becomes 1. Therefore, ln of gamma 1 at infinite conditions, we are left with A 1 2 dash constant alone. … Similarly, if you substitute x 2 equals 0 here, this term vanishes completely, and this term reduces to 1. … Therefore, ln gamma 2 infinity is nothing but A 2 1 dash.

So, we have seen three models the Margules model, the Redlich-Kister model and the Van Laar model.

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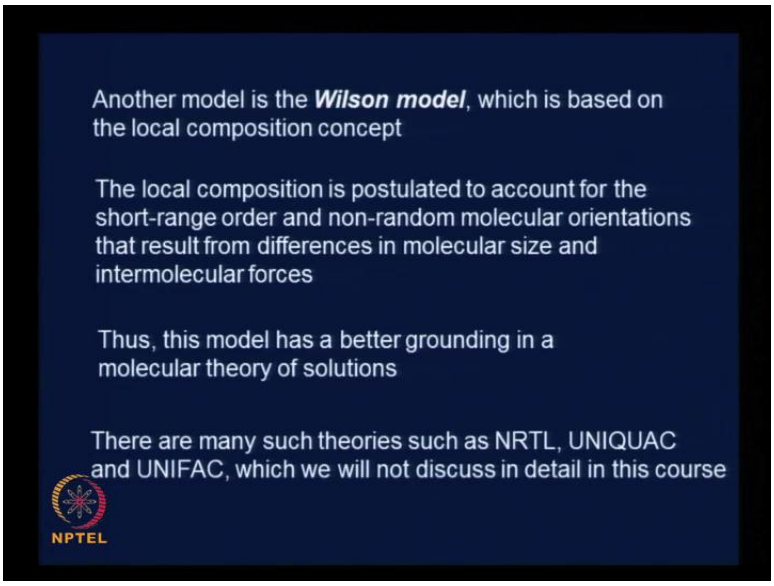

Another model is the ***Wilson model***, which is based on the local composition concept

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

We will look at another model which is Wilson model, which has some backing in theory. It is based on something called a local composition concept. We will not get into the details of what the concept is and so on … slightly beyond the scope of this particular course. But you need to know that this has some grounding in theory. The local composition is postulated to account for the short range order and the non-random molecular orientations … if you can imagine that is fine. if you do not that is also fine … that result from differences in molecular size and intermolecular forces. This is, you know, some … general basis for the Wilson model. You can look at this; if you understand that it is ok. and as we mentioned this model has a better grounding in molecular theory of solutions. …

There are so many different models that are available in the literature. All these were developed a long time back – many decades ago some of them are NRTL, UNIQUAC, UNIFAC and many of these require computer programming to get at solutions. We will not get into the theories. I just wanted to mention the theories, so that you will know the names when you come across them later. … You can easily pick them up once you know the basis … G E by R T and so on and so, forth. You can pick them up and then use them for estimating activity coefficients. As long as you know that there are models called NRTL, UNIQUAC, UNIFAC, and probably others too, which can be used for estimating activity coefficients, that is good enough from this particular course.

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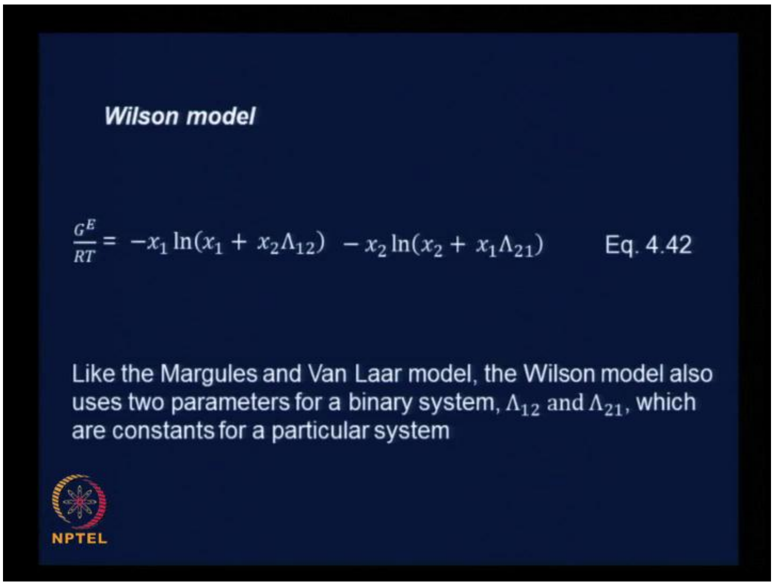

Wilson model

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

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

But for now, let us look at the details of the Wilson model. The Wilson model says that G E by R T – it has to be a model for G E by R T – equals minus x 1 times ln of x 1 plus x 2 times gamma 1 2 minus x 2 times ln of x 2 plus x 1 times gamma 2 1. … We will call this equation 4.42. This is the model. gamma 1 2 and gamma 2 1 are the constants, the Wilson model constants or Wilson constants for a particular system. And you could do the same things that we did with the other models, the Margules, Redlich-Kister, Van Laar and so on, to get at expressions for gamma 1 and gamma 2.

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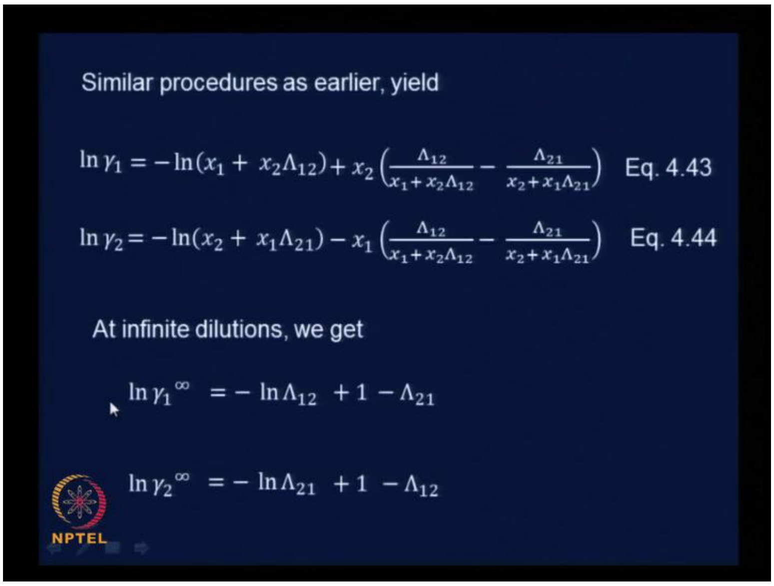

Similar procedures as earlier, yield

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

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

At infinite dilutions, we get

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

$$\ln\gamma_2^{\infty} = -\ln\Lambda_{21} + 1 - \Lambda_{12}$$

If you do that you know, … to recall, you need to differentiate it with respect to n 1 with constant T, P, n 2, and then recombine the terms with the recognition that x 1 plus x 2 equals 1. So, if we do that, ln gamma 1 will turn out to be minus ln of x 1 plus x 2 times gamma 1 2 plus x 2 times gamma 1 2 divided by x 1 plus x 2 times gamma 1 2 minus gamma 2 1 divided by x 2 plus x 1 times gamma 2 1. This is equation 4.43. And, ln gamma 2 is a similar expression. There will be some changes here; there will be no changes here. minus ln of x 2 plus x 1 times gamma 2 1 minus x 1 times gamma 1 2 x 1 plus x 2 times gamma 1 2 minus of gamma 2 1 divided by x 2 plus x 1 times gamma 2 1. We will call this equation 4.44.

At infinite dilutions, we will get ln gamma 1 … you know, the x 1 tending to 1 and x 2 tending to 0. x 2 tends to 0; this whole term will drop out. x 1 is tending to 1; therefore, we will get minus ln of gamma 1 2… I think it is the other way round … plus 1 minus gamma 2 1 and ln of gamma 2 infinity equals minus ln of gamma 2 1 plus 1 minus gamma 1 2. This by substituting 1 or the other. x 1 tends to 1 and x 2 tends to 0 or x 2 tends to 1 and x 1 tends to 0.

I think we have seen enough models for the G E by R T and therefore, for estimating gamma 1 and gamma 2.

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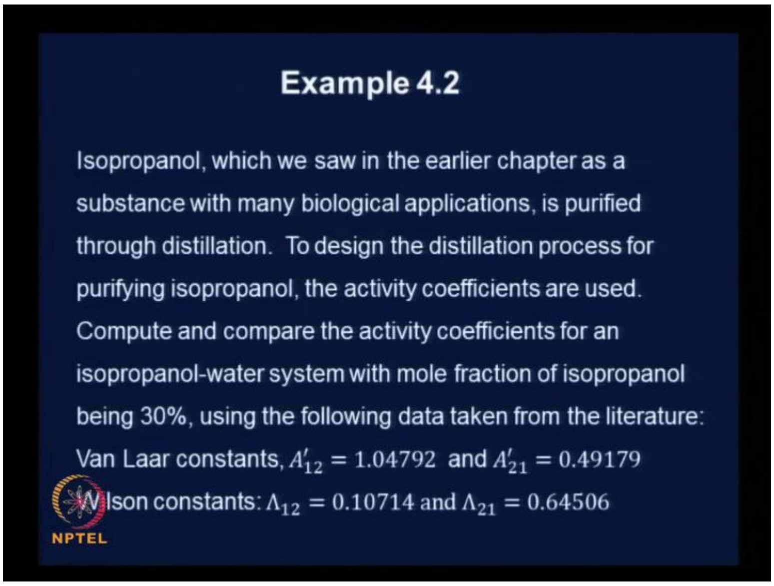

Example 4.2

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 $\Lambda_{21} = 0.64506$

It is time to do an example and we will finish up this module with this example of estimating activity coefficients. And of course, we will review whatever we did in this particular module. The example is as follows. It is a straightforward example. Of course, I am going to give you time to work it out.

Isopropanol which we saw in the earlier chapter as a substance with many biological applications, and our very favourite substance, is purified through distillation. To design the distillation process for purifying isopropanol the activity coefficients need to be used.

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 are given A 1 2 dash equals 1.04792 and A 2 1 dash equals 0.49179; and the Wilson constants gamma 1 2 is 0.10714 and gamma 2 1 equals 0.64506. These have been taken from the literature, the journal of chemical engineering data. If you look at the notes the reference will be there. What I will do is give you some time to think about it. And then should I give you some hints?

I think it is reasonably straightforward thing; it is a mere substitution. So, think about it for 5 minutes, and then take the next about 20 minutes, total of about 25 minutes to work this out because you need to work out numbers and long calculations and so on and so forth. So, take about 5 minutes for thinking getting to how to go about doing it, and then do it actually. Then we will meet after about 25 minutes go ahead please.

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You would have had time to think about this. What we are looking at is isopropanol. What we need to do is compute and compare the activity coefficients using two models that we have covered so far. It is quite evident that we have models for ln gamma 1, ln gamma 2 – the expressions for them, which we derived from the various models, which are expressions for G E by R T. … Therefore, if you substitute the constants that are given here, with the molar fraction of isopropanol being 30 percent – … it is an isopropanol water system; therefore, the mole fraction of water needs to be 70 percent.

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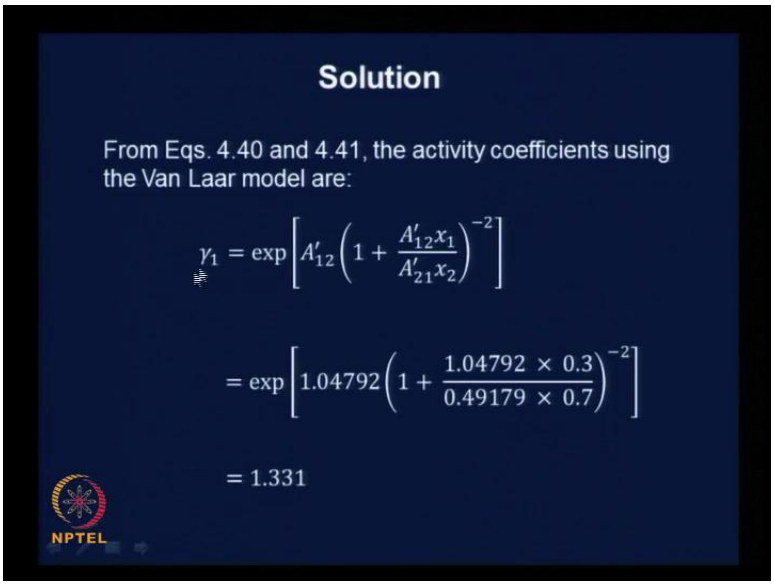

Solution

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

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

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

$$= 1.331$$

If we do that, for the Van Laar model … ln gamma 1 was this. Therefore, gamma 1 would be exponential of A 1 2 dash times 1 plus A 1 2 x 1 by A 2 1 dash x 2, the whole power minus 2. If you substitute the values which have been given, it turns out to be exponential of 1.04792 for A 1 2 dash times 1 plus 1.04792 times 0.3, which is the mole fraction of isopropanol in the binary solution, divided by 0.49179, which is the constant A 2 1 dash in this model, Van Laar model, times the mole fraction of water, 0.7. `1' for isopropanol, `2'for water. If you do the calculations you should get1.331. So, this is gamma 1 for isopropanol in this particular binary system.

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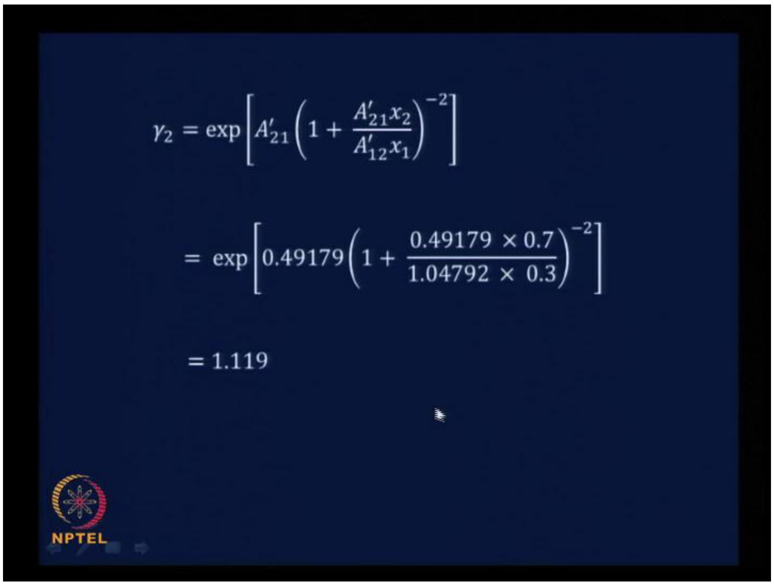

$$\gamma_2 = \exp\left[A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2}\right]$$

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

$$= 1.119$$

And gamma 2 is through a similar expression that we already seen, which becomes exponential of A 2 1 dash times 1 plus A 2 1 dash x 2 divided by A 1 2 dash x 1 the whole power minus 2. And substituting the values, 0.49179 for A 2 1 dash and … 1.04792 for A 1 2 dash; 0.7 for x 2, and 0.3 for x 1. On doing the calculations on a calculator you will get 1.119 for gamma 2. What I would like you to note … we will note that a little later. Now, we were asked to do that for the Wilson model and compare the two.

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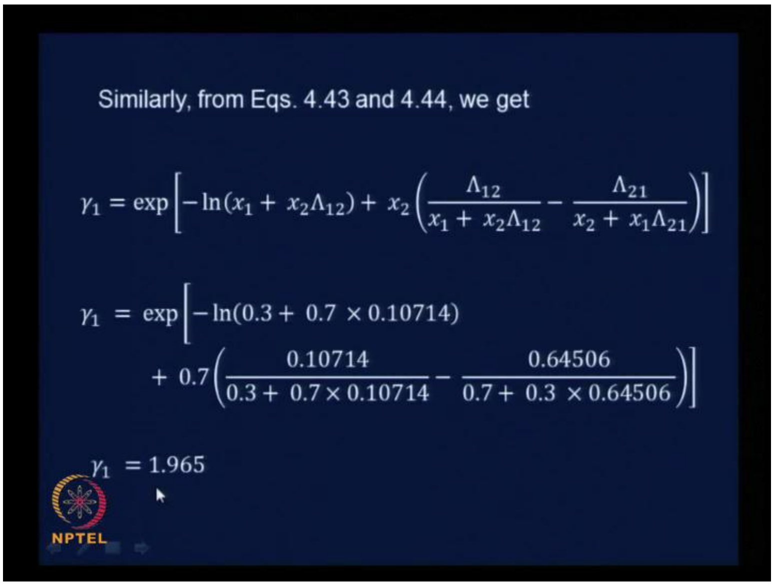

Similarly, from Eqs. 4.43 and 4.44, we get

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

$$\gamma_1 = \exp\left[-\ln(0.3 + 0.7 \times 0.10714) + 0.7\left(\frac{0.10714}{0.3 + 0.7 \times 0.10714} - \frac{0.64506}{0.7 + 0.3 \times 0.64506}\right)\right]$$

$$\gamma_1 = 1.965$$

Therefore, if you look at the Wilson model expression which is a slightly longer expression; gamma 1 equals exponential of minus ln of x 1 plus x 2 times gamma 1 2 plus x 2 times gamma 1 2 divided by x 1 plus x 2 gamma 1 2 minus gamma 2 1 divided by x 2 plus x 1 times gamma 2 1. As we can directly pick from whatever is given in your notes earlier … Substituting the values, in this case, 0.3 and 0.7 remains the same as mole fractions of x 1 and x 2 isopropanol and water respectively; whereas, gamma 1 2 is 0.10714 and gamma 2 1 is 0.64506. That is what was given in the problem statement itself.

If you substitute various the values here, which you would have done in the time that was given, you would get gamma 1 equals 1.965. A similar exercise for gamma 2 would yield gamma 2 equals 1.276. Now, look at this gamma 2 value. From the Wilson model it is 1.276, and from the Van Laar model it is 1.119. There is a variation, and that is the reason for coming up with different models for different systems – this just gives you an idea of the variations that you can expect.

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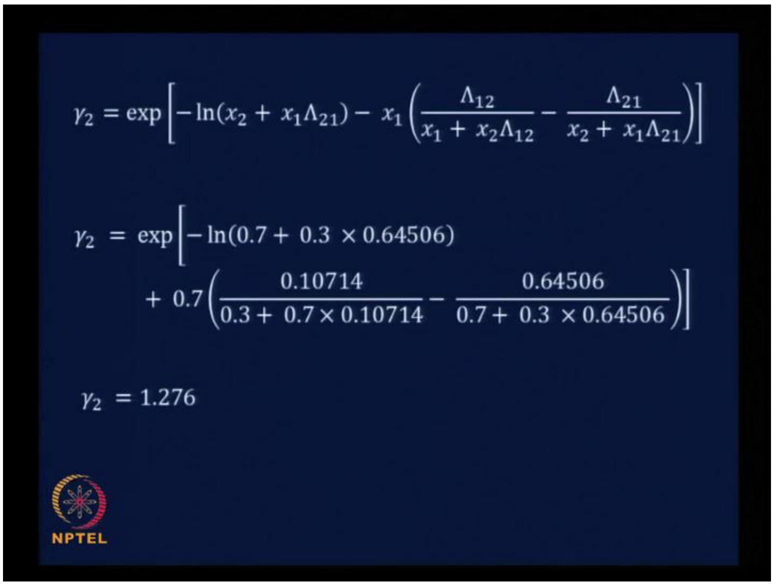

$$\gamma_2 = \exp\left[-\ln(x_2 + x_1\Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)\right]$$

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

$$\gamma_2 = 1.276$$

gamma 1 also has a variation. In the case of Van Laar it is 1.331 that we got, and in the case of Wilson it is 1.965. You need to be aware of this. There is nothing wrong with this – the various constants were taken from experimental data. So, this is the kind of variation that you would expect. And, that was the reason for coming up with better and better models. We already talked about NRTL, UNIQUAC, UNIFAC, and so on. I think we need to stop here, in this class and in the next class, we will summarize whatever we have done in this module, which has been thermodynamics of solutions.