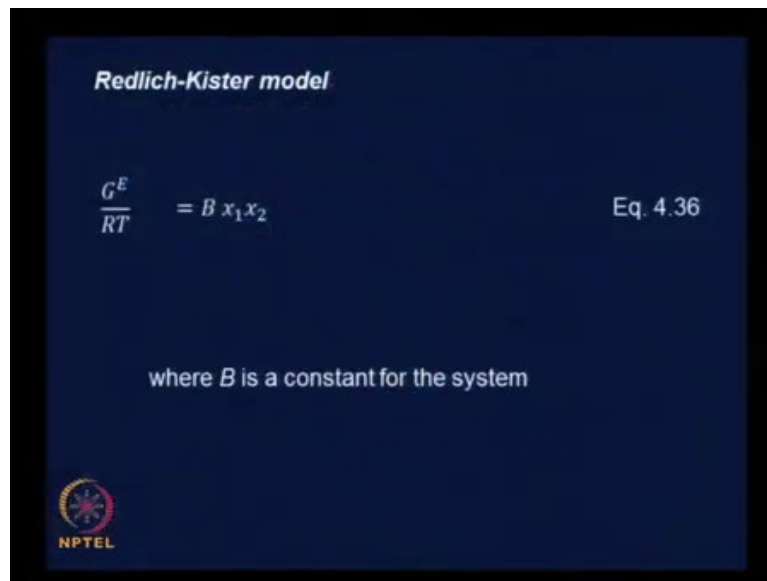


**Thermodynamics for Biological Systems:  
Classical and Statistical Aspects  
Prof. G.K. Suraishkumar  
Department of Biotechnology  
Indian Institute of Technology - Madras**

**Lecture – 35  
Models for Activity Coefficient in a binary System (Contd.,)**

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

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. 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

$$\ln \gamma_1 = B x_2^2 \quad \text{Eq. 4.37}$$
$$\ln \gamma_2 = B x_1^2 \quad \text{Eq. 4.38}$$

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 ...

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

Equation 4.37.

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

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.

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


That is B, the constant B, which would be the constant in the Redlich-Kister model.

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**Van Laar model**

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

$A'_{12}$  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.

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

This is the Van Laar model; equation 4.39, where  $A'_{12}$  and  $A'_{21}$  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


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

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

At infinite dilution conditions

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

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



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

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

Let us call this equation 4.40.

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

We will call this equation 4.41.

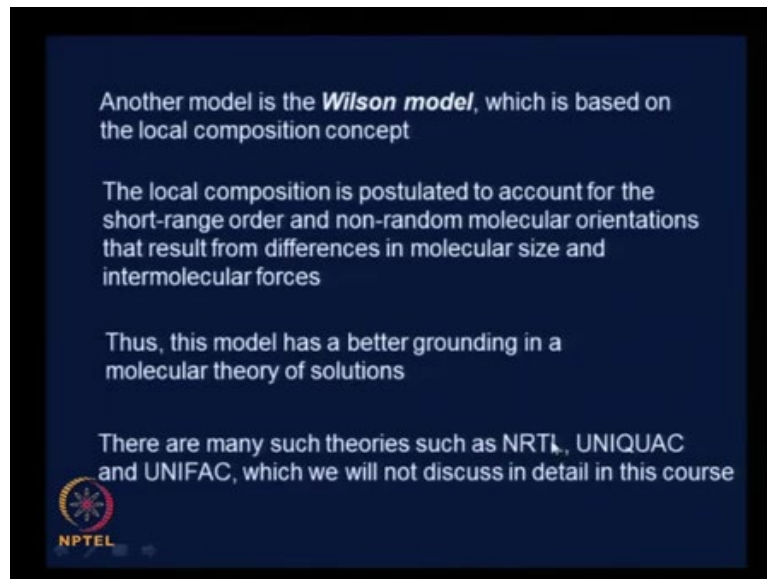
And, at infinite dilutions, as we did earlier,

$$x_1 \rightarrow 0 \text{ or } x_2 \rightarrow 1, \quad \ln \gamma_1^\infty = A'_{12}$$

$$x_2 \rightarrow 0 \text{ or } x_1 \rightarrow 1, \quad \ln \gamma_2^\infty = A'_{21}$$

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  $A'_{12}$  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  $A'_{21}$  dash. So, we have seen three models the Margules model, the Redlich-Kister model and the Van Laar model.

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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 RT 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**

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

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



For now, let us look at the details of the Wilson model. The Wilson model says that

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

We will call this equation 4.42. This is the model.  $\gamma_{12}$  and  $\gamma_{21}$  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,

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

This is equation 4.43. And,

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

We will call this equation 4.44.

At infinite dilutions, we will get

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

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

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. 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  $A_{12} = 1.04792$  and  $A_{21} = 0.49179$ ; and the Wilson constants  $\gamma_{12}$  is 0.10714 and  $\gamma_{21}$  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:

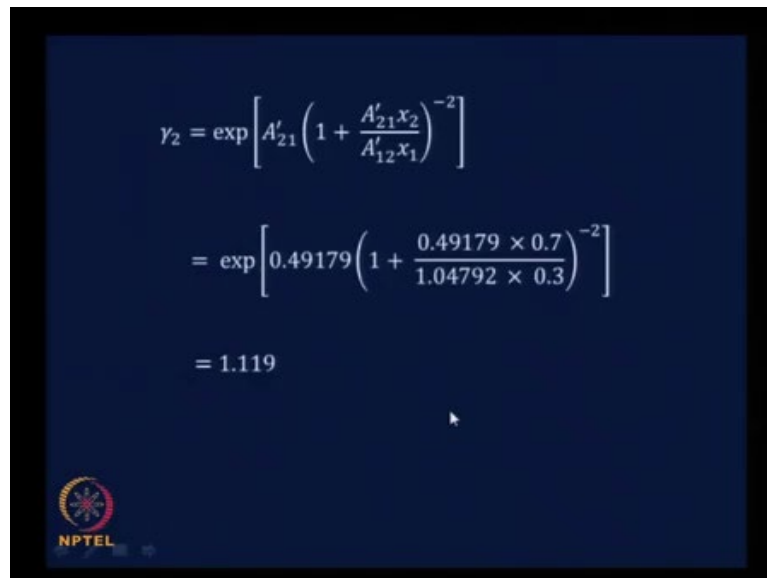
$$\gamma_1 = \exp \left[ A'_{12} \left( 1 + \frac{A'_{12} x_1}{A'_{21} x_2} \right)^{-2} \right]$$
$$= \exp \left[ 1.04792 \left( 1 + \frac{1.04792 \times 0.3}{0.49179 \times 0.7} \right)^{-2} \right]$$
$$= 1.331$$


If we do that, for the Van Laar model ...

$$\begin{aligned}\gamma_1 &= \exp \left[ A'_{12} \left( 1 + \frac{A'_{12}x_1}{A'_{21}x_2} \right)^{-2} \right] \\ &= \exp \left[ 1.04792 \left( 1 + \frac{1.04792 \times 0.3}{0.49179 \times 0.7} \right)^{-2} \right] = 1.331\end{aligned}$$

So, this is gamma 1 for isopropanol in this particular binary system.

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$$\begin{aligned}\gamma_2 &= \exp \left[ A'_{21} \left( 1 + \frac{A'_{21}x_2}{A'_{12}x_1} \right)^{-2} \right] \\ &= \exp \left[ 0.49179 \left( 1 + \frac{0.49179 \times 0.7}{1.04792 \times 0.3} \right)^{-2} \right] \\ &= 1.119\end{aligned}$$

And gamma 2 is through a similar expression

$$\begin{aligned}\gamma_2 &= \exp \left[ A'_{21} \left( 1 + \frac{A'_{21}x_2}{A'_{12}x_1} \right)^{-2} \right] \\ &= \exp \left[ 0.49179 \left( 1 + \frac{0.49179 \times 0.7}{1.04792 \times 0.3} \right)^{-2} \right] = 1.119\end{aligned}$$

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;

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

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,  $\gamma_{12}$  is 0.10714 and  $\gamma_{21}$  is 0.64506. That is what was given in the problem statement itself.


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

$$\gamma_1 = 1.965$$

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

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

$$\gamma_2 = 1.276$$


A similar exercise for gamma 2 would yield gamma 2 equals 1.276.

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

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

$$\gamma_2 = 1.276$$

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.

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. 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. See you in the next class.