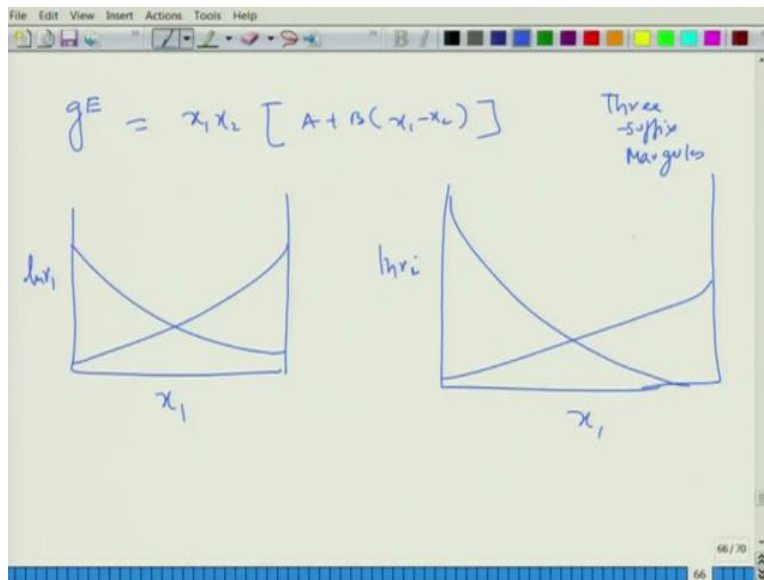


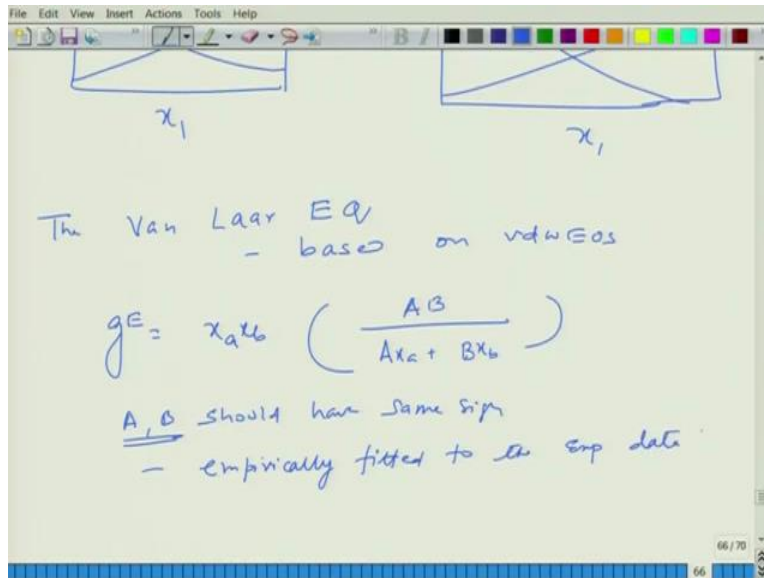
Chemical Engineering Thermodynamics
Professor Jayant K. Singh
Department of Chemical Engineering
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Lecture-47
Excess Gibbs Free Energy Model - II

Welcome back. Last class we talked about 2 suffix Margules equation which is basically used for very similar kind of molecules such as argon, oxygen or cyclohexane and benzene. And the equation if we look at it, it is very symmetrical in nature and does not capture many non-symmetric behavior, which we observe in the real world for most of the cases. Therefore, there are many other models which exist in order to capture the real nature of the mixtures.

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$$g^E = x_1 x_2 [A + B(x_1 - x_2)]$$



One of the simplest ways to consider the asymmetric behavior is to include or rewrite this expression of g^E in the following way. So, it is basically three suffix equation, Margules equation and it is asymmetric in nature. So, in the other word if you look at the $\ln \gamma$ versus x plot. So, the 2 suffix Margules equation gives you the following expression or following plots which essentially is symmetric in nature.

And otherwise if you look at this expression, this will essentially give you asymmetric behavior. Suppose for example we are considering 1, so and this is $\ln \gamma_i$, this will give you the following. So, this is kind of asymmetric behavior for the case of this. But as I said there are many other models which exist, the model for 2 suffix Margules equation is derived from the simply limiting cases so that for the pure component g^E is equal to 0. That means excess molar Gibbs energy has to be 0.

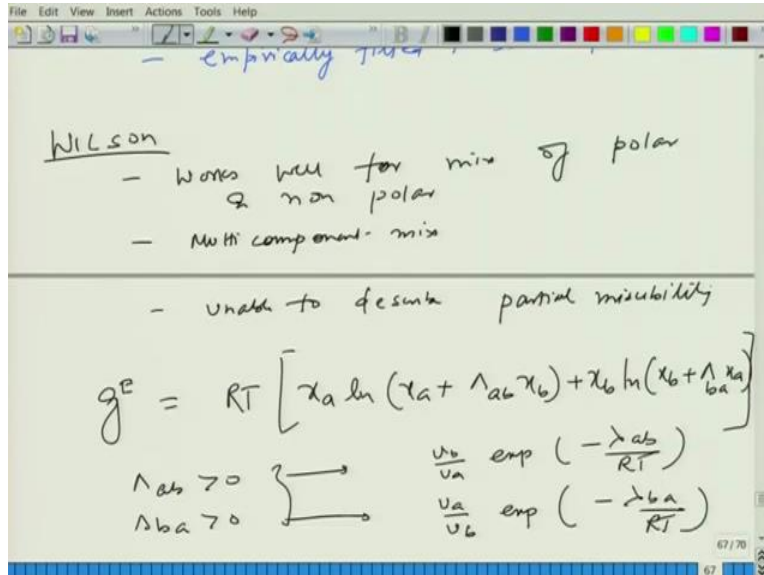
Now, there are the model which more molecular, which has more you know fundamental insight to it. For example, model which is developed based on the Van der Waal equation of state is the Van Laar equation. So, this is based on Van der Waal equation of state and the expression of g^E is $x_a x_b$ again a and b stands for species indices it could be 1 and 2 and this is AB , Ax_a plus Bx_b .

Van Laar Eqn, based on Van der Waal EOS,

$$g^E = x_a x_b \left(\frac{AB}{Ax_a + Bx_b} \right)$$

Now, in this case A and B should have the same sign. And though as I said it is based on Van der Waal equation of state but this usually, in practice these are empirically fitted to the experimental data.

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$$g^E = RT[x_a \ln(x_a + \Lambda_{ab}x_b) + x_b \ln(x_b + \Lambda_{ba}x_a)]$$

$$\Lambda_{ab} > 0 \rightarrow \frac{v_b}{v_a} \exp\left(-\frac{\lambda_{ab}}{RT}\right)$$

$$\Lambda_{ba} > 0 \rightarrow \frac{v_a}{v_b} \exp\left(-\frac{\lambda_{ba}}{RT}\right)$$

$\lambda \rightarrow$ interaction part

- unable to describe partial miscibility

$$g^E = RT \left[x_a \ln(x_a + \Lambda_{ab} x_b) + x_b \ln(x_b + \Lambda_{ba} x_a) \right]$$

$$\Lambda_{ab} > 0 \quad \left\{ \begin{array}{l} \frac{v_b}{v_a} \exp\left(-\frac{\lambda_{ab}}{RT}\right) \\ \frac{v_a}{v_b} \exp\left(-\frac{\lambda_{ba}}{RT}\right) \end{array} \right.$$

$$\Lambda_{ba} > 0$$

$\lambda \rightarrow$ interaction parameter

There is another model which is more commonly used which addresses more set of complex mixtures is Wilson equation. It works well for mixtures of polar and nonpolar components. Example could be alcohol and alkanes which are difficult to model using 2 suffix or 3 suffix models as also extensible for multicomponent mixture. However, this Wilson equation is difficult to describe the partial miscibility, so it is usually unable to describe partial miscibility.

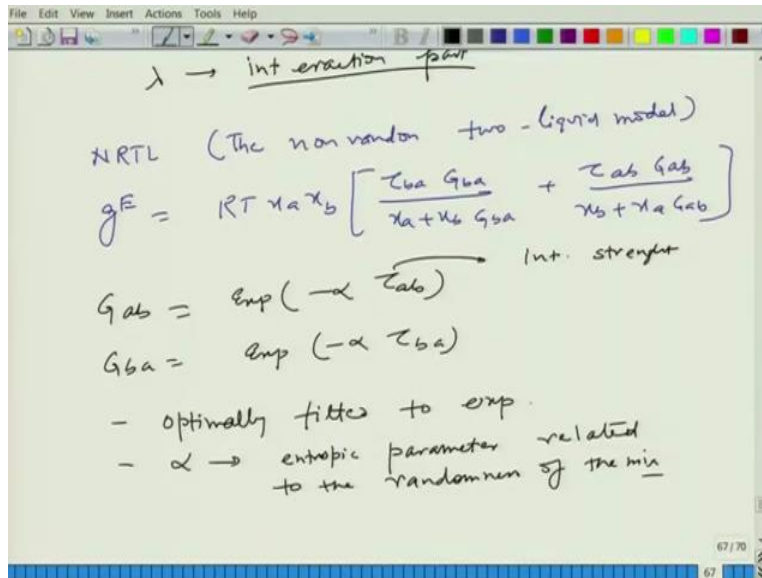
So, let me just write down the expression of the g^E for the case of Wilson equation. It is RT and then you have this $x_a \ln(x_a + \Lambda_{ab} x_b) + x_b \ln(x_b + \Lambda_{ba} x_a)$. So, here if you notice that we have introduced the variable here Λ which of course need to be greater than 0 and these are related to polymetric information, so molar volume of component a and b and exponential minus λ_{ab} by RT where this is related to v_a/v_b exponential minus λ_{ba} by RT , where this λ here is nothing but the interaction parameter.

So, here also this information you can obtain the for example interaction parameter you can obtain and then you for given molar volume one can obtain this information of the Gibbs excess potential. We can extend this, I mean there are many other theories which have been used in order to understand the liquid behavior and obtain using the information.

So, there are many theories which have been used to, which are used to develop the appropriate models for the Gibbs free energy. So, as we said that the Wilson is one thought which has been implemented. Now, the more formal statistical mechanical approach which has been used to obtain

something called NRTL model and there is a group theory also which has been used which I wanted to talk about NRTL model.

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NRTL (the non random two – liquid model)

$$g^E = RTx_a x_b \left[\frac{\tau_{ba} G_{ba}}{x_a + x_b G_{ba}} + \frac{\tau_{ab} G_{ab}}{x_b + x_a G_{ab}} \right]$$

$$G_{ab} = \exp(-\alpha\tau_{ab}) \quad \tau_{ab} = \text{interaction strength}$$

$$G_{ba} = \exp(-\alpha\tau_{ba})$$

So, NRTL is nothing but the nonrandom two liquid model is purely based on (07:30) or statistical mechanics and the expression of the g is the following. So, I am writing this expression just for the sake of the completeness. However, I do not expect that you would be able to remember that. So, the reason for this is to just emphasize the kind of models which are available to address the behavior of the liquid phase. So, here you have g^E which depends on, besides the composition.

So, beside the composition you have this τ and g 's. The g is nothing but the exponential minus alpha tau ab. Here, g_b is exponential minus alpha tau ba. Now, so there are 3 parameters. You have

alpha and you have tau ab and tau ba. There are 3 parameters which essentially one has to use and these parameters you have to fit it into experiments.

So, these are optimally fitted to the experiment. Now, the model NRTL is very valuable if a is large deviation from ideality and hence often used for the cases where you have deviation from ideality. In addition to that, the model is very valuable also to capture the partial immiscibility.

So, here of course this tau's are the interaction strength. Alpha is nothing but entropic parameter which is related to the randomness of the mixture. So, this alpha of course parameter captures entropic nature of the system but it is a short range it also looks into the molecular orientation, so it basically is a composite effect of the randomness in that particular one parameter and that is used or that is obtained using the fitting approach.

Now, one of the thing which this particular model has been as I said is been used for many system by in the addition, Wilson model has been extended to obtain a more complicated model which we call it UNIQUAC model and that is also widely used in very practical systems in the chemical process industries in order to model systems.

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UNIQUAC (The universal quasi-chemical theory)
- Extension of WILSON.

g^E → due to entropy (combinatorial)
 g^E → due to energy (residual)

$g^E = g^E_{\text{combinatorial}} + g^E_{\text{residual}}$

$\ln \gamma_i = \ln \gamma_{i,\text{combinatorial}} + \ln \gamma_{i,\text{residual}}$

$$g^E = g^E_{\text{combinatorial}} + g^E_{\text{residual}}$$

$$\ln \gamma_i = \ln \gamma_{i,\text{combinatorial}} + \ln \gamma_{i,\text{residual}}$$

So, this is called UNIQUAC model where basically it is nothing but extension of Wilson. So, UNIQUAC stands for the Universal Quasi Chemical theory. So, now this particular in this particular approach UNIQUAC which essentially says that well one can segregate this excess Gibbs free energy into 2 parts. 1 due to entropy and other one is due to energy.

The entropy part is often called Combinatorial part of this g^E and energy due to the energy it is nothing but we call it the residual. So, in that case I can write this g^E because it is an extensive property is $g^E_{\text{combinatorial}}$ plus g^E_{residual} and the corresponding $\ln \gamma_i$ can be also written in the same way that is the $\ln \gamma_{i,\text{combinatorial}}$ plus $\ln \gamma_{i,\text{residual}}$.

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UNIQUAC activity model

	Combinatorial	Residual
$\frac{z^E}{RT}$	$x_1 \ln \frac{\Phi_1^c}{x_1} + x_2 \ln \frac{\Phi_2^c}{x_2}$ $+ \frac{z}{2} \left(x_1 q_1 \ln \frac{\theta_1}{\Phi_1^c} + x_2 q_2 \ln \frac{\theta_2}{\Phi_2^c} \right)$	$-x_1 q_1 \ln(\theta_1 + \theta_2 \tau_{12}) - x_2 q_2 \ln(\theta_2 \tau_{12} + \theta_1)$
$\ln \gamma_1$	$\ln \frac{\Phi_1^c}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\Phi_1^c} + \Phi_2^c \left(l_1 - l_2 \frac{r_1}{r_2} \right)$	$-q_1 \ln(\theta_1 + \theta_2 \tau_{12})$ $+ \theta_2 q_1 \left(\frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{12}} - \frac{\tau_{12}}{\theta_2 \tau_{12} + \theta_1} \right)$
$\ln \gamma_2$	$\ln \frac{\Phi_2^c}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\Phi_2^c} + \Phi_1^c \left(l_2 - l_1 \frac{r_2}{r_1} \right)$	$-q_2 \ln(\theta_2 \tau_{12} + \theta_1)$ $+ \theta_1 q_2 \left(\frac{\tau_{12}}{\theta_2 \tau_{12} + \theta_1} - \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{12}} \right)$
where	$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$ $\theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$ $\Phi_1^c = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}$ $\Phi_2^c = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$ $\theta'_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$ $\theta'_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$ $z = 10$	$\tau_{12} = \exp\left(-\frac{\theta_{12}}{T}\right)$ and $\tau_{21} = \exp\left(-\frac{\theta_{21}}{T}\right)$ $\ln \gamma_i = \ln \gamma_{i,combinatorial} + \ln \gamma_{i,residual}$
	$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1)$ $l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1)$	

So, let us look at the bit on this UNIQUAC using some examples or let us emphasize more on this different part of this component. So, as I said UNIQUAC activity model contains 2 part of it, one is the combinatorial and other is residual. Combinatorial is due to the entropic contribution and residual is due to the energy contribution. So, here is the expression for g of E of combinatorial and here is the residual where if you can see there are many components.

So, one is the phi and phi is nothing but basically it relates to or it is written in this way and phi 2 is again in this one. So, we will little bit discuss about that and I will not go into details of it and this appears to be complicated but we will see how this can be used in order to solve a problem.

Now, once you have these expressions you can of course use the same methodology as we have done in order to obtain ln gamma 1 or gamma 2 for the case of the let us say binary mixture. Now, in this case you notice that you have phi, you have q1, you have q2 and then you have these tau's. Tau's are related to the energetic parameter between the components.

So, that is something which has to be provided in some way and then you have this various different definitions which are there. Now, so without going to details of each and every parameters and what does it mean which I will leave it for you to more and explore. Let me just discuss an example which relates how the UNIQUAC parameters in the models can be used in order to solve a problem.

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Example

Prepare a plot of the activity coefficients of a binary mixture of ethanol (1) and n-heptane (2) versus ethanol mole fraction in a binary mixture at 50°C using the UNIQUAC activity coefficient model. The UNIQUAC parameters are reported as follows:

	ethanol	n-heptane		
r	2.11	5.17	and	$q_{12} = -105.23$
q'	1.97	4.40		$a_{21} = -1380.3$
q''	0.92	4.40		

Compare the results to the following set of measured data:

x_1	0.0514	0.118	0.3022	0.4383	0.5862	0.6646	0.7327	0.772	0.823	0.8788	0.9274	0.9769
γ_1	9.837	5.978	2.650	1.876	1.427	1.283	1.184	1.136	1.091	1.143	1.148	1.045
γ_2	0.985	1.069	1.320	1.629	2.158	2.550	3.161	3.561	4.249	4.184	4.540	6.719

UNIQUAC activity model

	Combinatorial	Residual
$\frac{g^E}{RT}$	$x_1 \ln \frac{\Phi_1^c}{x_1} + x_2 \ln \frac{\Phi_2^c}{x_2} + \frac{z}{2} (x_1 q_1 \ln \frac{\theta_1}{\Phi_1^c} + x_2 q_2 \ln \frac{\theta_2}{\Phi_2^c})$	$-x_1 q_1 \ln(\theta_1 + \theta_2 \tau_{21}) - x_2 q_2 \ln(\theta_2 \tau_{12} + \theta_1)$
$\ln \gamma_1$	$\ln \frac{\Phi_1^c}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\Phi_1^c} + \Phi_2^c \left(l_1 - l_2 \frac{r_1}{r_2} \right)$	$-q_1 \ln(\theta_1 + \theta_2 \tau_{21}) + \theta_2 q_1 \left(\frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_1 \tau_{12} + \theta_2} \right)$
$\ln \gamma_2$	$\ln \frac{\Phi_2^c}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\Phi_2^c} + \Phi_1^c \left(l_2 - l_1 \frac{r_2}{r_1} \right)$	$-q_2 \ln(\theta_2 \tau_{12} + \theta_1) + \theta_1 q_2 \left(\frac{\tau_{12}}{\theta_1 \tau_{12} + \theta_2} - \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} \right)$
where	$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$ $\theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$ $\Phi_1^c = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}$ $\Phi_2^c = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$ $l_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$ $l_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$ $z = 10$ $l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1)$ $l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1)$	

$\ln \gamma_i = \ln \gamma_{i,combinatorial} + \ln \gamma_{i,residual}$

$\tau_{12} = \exp\left(\frac{-a_{12}}{T}\right)$ and $\tau_{21} = \exp\left(\frac{-a_{21}}{T}\right)$

So, this is a case of binary mixture of ethanol and heptane. So what is being asked is that prepare a plot of activity coefficient of a binary mixture of ethanol and heptane versus ethanol mole fraction at 50 degree using the UNIQUAC activity coefficient model.

Now, UNIQUAC parameters are reported already. So, r is given. As I said I did not try to unnecessary at this point explain you more about what is r here. So, it looks more like a numerical analysis at this point. So, this is r is given, q is given, q dash is given and the energy parameters

are given to you and then it is being asked that you use this UNIQUAC activity model and compare the results with the measured data which is x is given.

For each x you have γ_1 , γ_2 and so forth. So, essentially you can plot this for x and γ 's and then you compare with this one. So, how do you go about it? So, already r and q and q dash is given. So, for given x so let us say we can consider this. The corresponding ϕ_1 and ϕ_2 can be obtained because r_1 and r_2 are given to you and similarly θ_1 and θ_2 can be obtained because q_1 's are given to you and θ_1 dash is also given to you.

So, essentially in that way you have information of ϕ 's and θ 's and then what about L . Well, z is fixed here. So, L_1 and L_2 is also given to you because the rest of the information is given to you. So, essentially you can now, you have all the information given to you. So, thus you can calculate the combinatorial part of the contribution and similarly you can also do that for this because here the residual part, the energy E_1 and E_2 are given to you and hence you can obtain τ_{12} and τ_{21} and the rest of the parameters you have already calculated for the combinatorial part.

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Procedure

- We need to calculate γ_1 and γ_2 over the range of mole fractions
- We illustrate the calculation procedure using the value of $x_1 = 0.3022$.

	ethanol	n-heptane
$\phi_i = \frac{x_i r_i}{x_1 r_1 + x_2 r_2}$	0.150	0.850
$\theta_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2}$	0.162	0.838
$\theta_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2}$	0.083	0.917
l_i	-0.41	-0.32

Example

Prepare a plot of the activity coefficients of a binary mixture of ethanol (1) and n-heptane (2) versus ethanol mole fraction in a binary mixture at 50°C using the UNIQUAC activity coefficient model. The UNIQUAC parameters are reported as follows:

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Compare the results to the following set of measured data:

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UNIQUAC activity model

	Combinatorial	Residual
$\frac{p_i^s}{RT}$	$x_1 \ln \frac{\Phi_1^s}{x_1} + x_2 \ln \frac{\Phi_2^s}{x_2} + \frac{z}{2} (x_1 q_1 \ln \frac{\theta_1}{\Phi_1^s} + x_2 q_2 \ln \frac{\theta_2}{\Phi_2^s})$	$-x_1 q_1 \ln(\theta_1 + \theta_2 \tau_{21}) - x_2 q_2 \ln(\theta_2 \tau_{12} + \theta_1)$
$\ln \gamma_1$	$\ln \frac{\Phi_1^s}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\Phi_1^s} + \Phi_1^s (l_1 - l_1 \frac{r_1}{r_2})$	$-q_1 \ln(\theta_1 + \theta_2 \tau_{21}) + \theta_2 q_1 (\frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_1 \tau_{12} + \theta_2})$
$\ln \gamma_2$	$\ln \frac{\Phi_2^s}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\Phi_2^s} + \Phi_2^s (l_2 - l_2 \frac{r_2}{r_1})$	$-q_2 \ln(\theta_2 \tau_{12} + \theta_1) + \theta_1 q_2 (\frac{\tau_{12}}{\theta_1 \tau_{12} + \theta_2} - \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}})$
where	$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$ $\theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$ $\Phi_1^s = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}$ $\Phi_2^s = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$ $\theta_1' = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$ $\theta_2' = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$ $z = 10$ $l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1)$ $l_2 = \frac{z}{2} (r_2 - q_2) - (r_2 - 1)$	

So, look at this again. We need to calculate procedure is very straight forward. You need to calculate gamma 1 gamma 2 over the range of mole fractions. We illustrate the calculation procedure using the value of x1 0.3021. So, 0.3021 is this here. So, for that we calculate this phi i stars for this and for both the component and theta i is given to you and theta i dash is also given to you.

In the sense like you have calculated because these parameters are given to you. So, hence you can obtain these i and theta i and Li you have calculated because Li is basically this part. So, r1 and q1 you calculated, z is fixed. So, hence you can calculate Li.

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$$\ln \gamma_{1,combinatorial} = \ln \frac{\Phi_1^*}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\Phi_1^*} + \Phi_2^* \left(l_1 - l_2 \frac{r_1}{r_2} \right) = \underline{-0.17}$$

and,

$$\ln \gamma_{2,combinatorial} = \ln \frac{\Phi_2^*}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\Phi_2^*} + \Phi_1^* \left(l_2 - l_1 \frac{r_2}{r_1} \right) = \underline{-0.0184}$$

For the residual part of the activity coefficients, we calculate the energy parameters:

$$\tau_{12} = \exp\left(-\frac{a_{12}}{T}\right) = 1.39 \quad \text{and} \quad \tau_{21} = \exp\left(-\frac{a_{21}}{T}\right) = 0.014$$

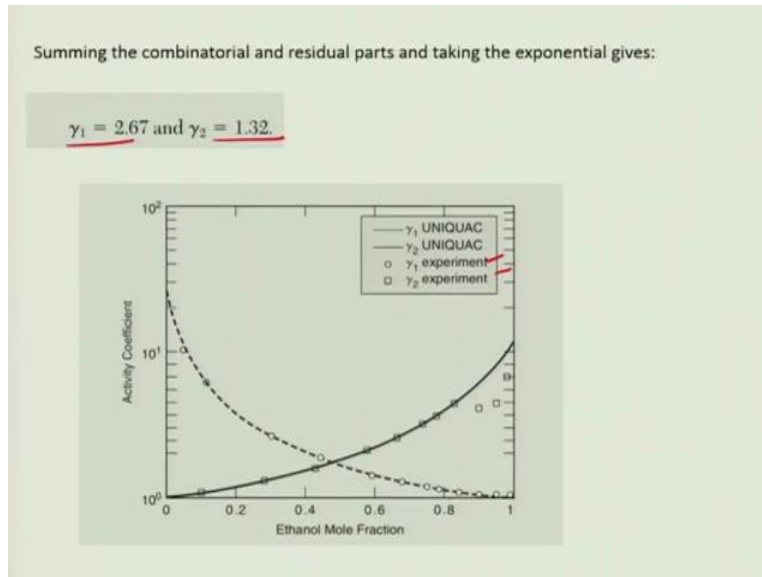
$$\ln \gamma_{1,residual} = -q_1' \ln(\theta_1' + \theta_2' \tau_{21}) + \theta_2' q_1' \left(\frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} - \frac{\tau_{12}}{\theta_1' \tau_{12} + \theta_2'} \right) = \underline{1.148}$$

$$\ln \gamma_{2,residual} = -q_2' \ln(\theta_1' \tau_{12} + \theta_2') + \theta_1' q_2' \left(\frac{\tau_{12}}{\theta_1' \tau_{12} + \theta_2'} - \frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} \right) = \underline{0.299}$$

So, basically you have all the parameters now to plug in into this expression of gamma 1 combinatorial which comes out to be this. Gamma 2 combinatorial which comes out to be this. Similarly, for the residual part of the coefficient a 1 2 is given to you. So, you have tau's are given and then you plug in into the residual part of the expression.

So, you have already calculated this earlier. So, you have calculated this also now. So, you have q1 dash also now and theta dash is also given to you, rather calculated. So, essentially now you have handle to all the parameters and thus you can obtain gamma 1 residual and similarly gamma 2 residual.

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So, with that you can now add it up and there you calculate 2.67 and 1.2 and similarly you can do that for different components. So, when it is done it turns out that the lines in this case is this. So, essentially you can now write a simple code which does this exercise for very small values of the x to large. So, essentially you can easily obtain the curve here and data points are given to you already here. So, it turns out that UNIQUAC model beautifully captures this and look at it, it is not a symmetric behavior.

So, UNIQUAC seems to be very powerful if we have the informations correctly obtained as far as the parameters are concerned. So, I think that would be the end of this lecture where we basically could understand that we have different models which exist for liquid phase for the excess Gibbs free energy and these models are going to be use to obtain the activity coefficients.

Now, so what we are going to do in the next lecture onwards is we will emphasize more on the vapor liquid equilibria calculations, where we are going to use some of these models and try to understand its implications in the predictions of the VLE diagrams. So, that would be the end and I will see you in the next class.