Advanced Thermodynamics
Assistant Prof. Dr. Nanda kishore
Department of Chemical Engineering
Indian Institute of Technology Guwahati, India

Lecture-22
Models for Excess Gibbs Energy-3

Welcome to the MOOCs course advanced thermodynamics the title of this lecture is Models for Excess Gibbs Energy part 3. It is a continuation of our previous lecture, what we have seen in last 2 lecture is that we have written wohl's expansion for a binary mixture, we have written wohl's expansion and from that wohl's expansion by applying certain kind of restrictions, we deduced Van Laar Equations as well as the 2 suffix 3 suffix and 4 suffix modules equation those things we have got.

And also we obtained this Scatchard Hamer equation from the wohl's expansion by applying certain kind of restrictions those things, we have seen and also separately we have derived the van Laar equation to cross check whether the fundamentally developed van laar equation is the same that we got the van Laar equation from wohl's expansion both of them are same or not in order to cross check that we have seen, but all these things we have done kind of for binary nature.

So, we started with the wohl's expansion because of its 2 important factors that it has one is the parameters that it is having A parameters and Q parameters, it has some physical significance or relation to the physical significance of the system, that is one advantage another advantage is that, it can be extended to the multi component mixture. So, based on the second advantage of the wohl's expansion what we do.

Now, in this lecture we will be discussing wohl's expansion for multi component mixture and after that we will be discussing some more models for excess Gibbs energy which cannot be obtained from the wohl's expansion and which are based on some kind of fundamental consideration or based on molecular consideration. So, obviously they are going to be better than the ones that we have discussed, but there are also have certain kind of limitations one of the advantage of the additional and this new excess Gibbs energy model that we are going to study today is that in addition to the composition dependent activity coefficient.

We also get the effect of temperature on the activity coefficients because till now, whatever the activity coefficient that we are getting from the excess Gibbs energy all are giving the kind of information as function of composition only a function of temperature is not brought into the picture either in g^E information or in activity $\ln\Gamma$ information those things we have not done. So, but now, whatever the new models that is Wilson equation, NRTL equation and UNIQUAC equation that we are going to see for both binary and multi component mixture.

So, they are having the advantage of giving the information about the effect of temperature on the activity coefficient in addition to the composition dependent activity coefficient. So, that is what we are going to see in this particular lecture. But let us start with the Wohl's expansion for the multi component mixture before going into the Wilson, NRTL and Uniquac equation. So, excess functions for multi component mixtures.

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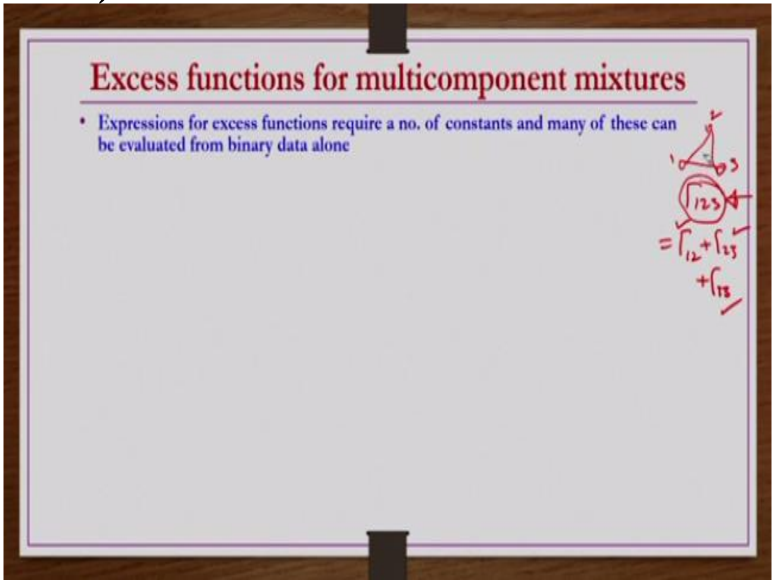

Excess functions for multicomponent mixtures

- Expressions for excess functions require a no. of constants and many of these can be evaluated from binary data alone

Equations for the excess functions require a number of constants and many of these can be evaluated from the binary data alone. That means, you know, let us say as in the case of virial equations of state where we have 3 molecular interactions etc. So, the third virial coefficient, so, there we need to know the effect of interaction the 3 particles. So, we need Γ_{123}.

So, what we have done here, there the assumption was γ_{123} is the summation of $\Gamma_{12} + \Gamma_{23} + \Gamma_{13}$ this is what the assumption we had, right? So, that means, you know though you need a 3 molecular intermolecular potential that you can get directly as a kind of summation of 3 2 body intermolecular interactions, those kinds of assumptions that we have intermolecular in the virial equation of state, especially, when we are talking about the third and higher virial coefficients.

So, these were the assumption that we had that means, it is possible that if you wanted to have an effect of multicomponent interactions or multi molecular interactions, the parameters associated with those multi molecule interaction can be evaluated by the parameters associated with the several number of binary interaction parameters like this. So, similar kind of things are possible in the excess gift energy also that is what we are going to see now.

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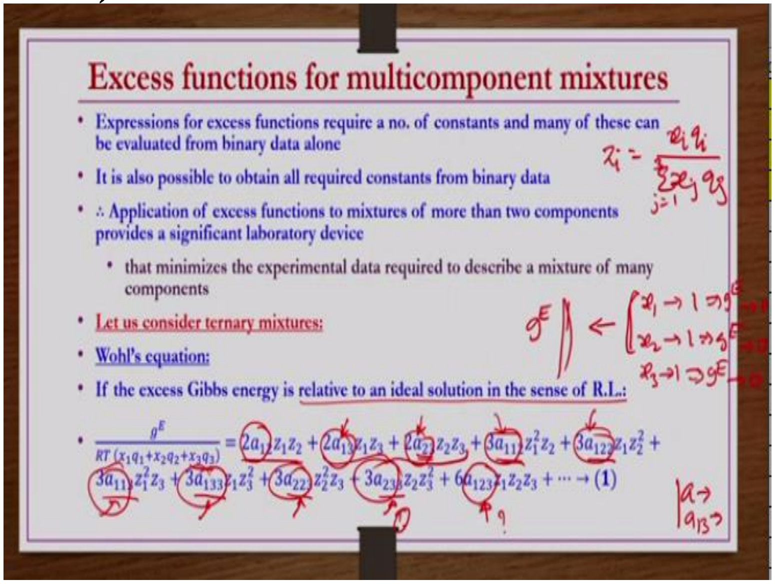

Excess functions for multicomponent mixtures

- Expressions for excess functions require a no. of constants and many of these can be evaluated from binary data alone
- It is also possible to obtain all required constants from binary data
- ∴ Application of excess functions to mixtures of more than two components provides a significant laboratory device
  - that minimizes the experimental data required to describe a mixture of many components
- Let us consider ternary mixtures:
- Wohl's equation:
- If the excess Gibbs energy is relative to an ideal solution in the sense of R.L.:
- $\frac{g^E}{RT\,(x_1q_1+x_2q_2+x_3q_3)} = 2a_{12}z_1z_2 + 2a_{13}z_1z_3 + 2a_{23}z_2z_3 + 3a_{112}z_1^2z_2 + 3a_{122}z_1z_2^2 + 3a_{113}z_1^2z_3 + 3a_{133}z_1z_3^2 + 3a_{223}z_2^2z_3 + 3a_{233}z_2z_3^2 + 6a_{123}z_1z_2z_3 + \cdots \rightarrow (1)$

$z_i = \frac{x_i q_i}{\sum_{j=1} x_j q_j}$

$g^E \leftarrow \begin{cases} x_1 \rightarrow 1 \Rightarrow g^E \\ x_2 \rightarrow 1 \Rightarrow g^E \\ x_3 \rightarrow 1 \Rightarrow g^E \end{cases}$

$a \rightarrow$
$a_{13} \rightarrow$

It is also possible to obtain all required constant from binary data only even though you are doing for multi component mixture. So, how that we are going to see anyway now in the short while. Applications have excess functions to mixtures of more than 2 components provides a significant laboratory device because it reduces or minimizes the experimental data required to describe the mixture of many components, because whatever the multicomponent mixture information is there.

So, if you apply the data that is obtained by the binary mixture, so, that you can obtain for the multi component mixture and then you can get the additional information about the excess functions for the multicomponent mixture. So, obviously, that is working as a kind of device to reduce your experimental dependency, you know dependency are required for obtaining the experimental data required for multi-competent mixture. Because experimentally also when you go for more number of components, getting information experimentally becomes gradually difficult.

As you increase the number of components and the difficulty level gradually increases to get the activity coefficient or any thermodynamic property measurements etc. those kinds of things. So, under such conditions having this kind of advantage of obtaining the parameters associated with multicomponent mixtures by applying the principles or the parameters that are obtained only by binary mixtures. So, obviously it is a huge advantage.

So, for simplicity what we do we start with ternary mixtures, it is a multicomponent mixture anything more than 2 component that we can say as a kind of multicomponent mixture. But simplicity for understanding and writing we start with a ternary mixture and then we generalized them for a number of components. Let us say if you write Wohl's expansion for ternary component related to an ideal solution in the sense of Raoult's law, what does mean by in the sense of Raoult's law.

Let us say if it is in $x_i \rightarrow 1$ or rather x_i. Let us say, if it is a binary component if $x_1 \rightarrow 1$ then $g \rightarrow 0$ or if $x_2 \rightarrow 1$ then also $g^E \rightarrow 0$. And so, if both these are obeyed, then we can say that the excess function whatever the gibbs excess energy is written, that is written related to the ideal solution in the sense for Raoult's law that is what it means. So, now, using the same thing now, here we have the ternary component.

So, when $x_3 \rightarrow 1$ then also this $g^E \rightarrow 0$ that is what it means, in the sense of Raoult's law. Then, if you write this thing, Wohl's expansion for ternary component that are ternary mixture then we have this $\frac{g^E}{RT(x_1q_1+x_2q_2+x_3q_3)}$. This is the additional thing is coming and then that = 2 a_{12} z_1 z_2. So, coming to the 2 molecular interactions, we had only these terms in binary system. Now, because of the ternary system, there are additional to 2 body interact 2 body terms are there that is 2 a_{13} z_1

z_3 + 2 a_{23} z_2 z_3. So, here this is also binary data or the interaction between 2 molecules only this a parameters what they indicate.

If you remember, this a parameters indicate the interactions, interaction amongst molecules if it is a_{12} that means, it gives the interaction between one molecule of component one and another molecule of the component 2. Similarly, a_{13} means it again gives the interaction between 2 molecules one of those 2 molecules is from the component one another molecule is from component 3.

Similarly, a_{23} also it gives the interaction between 2 molecules out of these 2 molecules one molecule is from the component 2 and then another molecule is from component 3 that is a suffix of as whatever are there. They indicate how many suffix are there, how many letters are there 123 like this. So, they indicate those many molecules are involved and then right let us say here now, first 3 terms a_{12} a_{13} a_{23} only 2 or 2 digits are there.

So, these indicate, so, 2 molecule interactions and then one indicate molecule of component one 2 indicates molecule of component 2. So, now, for the ternary component mixture we have additional this you know this additional part, right, in additional 2 binary data is coming into the picture, right, though it is for ternary component 2 additional binary data is coming into the picture.

So, now here this a_{112} a_{122} a_{113} a_{133} a_{223} a_{233} these things only 12345 the 6 is whatever are there. They are also data based on the you know binary system only but only thing that it is interaction between 3 molecules but 3 molecules are from only 2 components, third component is not involved. Let us say here, a_{12} that means its interaction it gives the interaction the significance related to the interaction between 3 molecules out of which 2 molecules from component one, one molecules from component 2.

And then this a_{112} is the same thing 3 body interactions or 3 molecular interaction it signifies but out of these 3 molecules, one is from component one remaining 2 molecules or from component only, here also third component is not coming into the picture like that a_{113} a_{133} a_{223}, a_{2333}. So, that means, here this one what indicates it is again 3 molecule interactions.

But out of those 3 molecular interactions, one molecule is from component 2 remaining 2 molecules from the component 3 that means, the third component that is all component one is now coming into the picture again here. So, these parameters are also based on the, you know on binary data. This information is also related to the binary data and but here now, the 6 a_{123} here it indicates you need information about the interaction between 3 molecules and then each of 3 molecules are from component one, 2 and 3 respectively.

But many cases it may not require to get the required information required activity coefficient that also we see now here in which case it is required in which case it is not required. Let us say van laar equation two suffix Margules equation if you apply for this ternary system, then you do not need this a_{123} information at all. But when you go for 3 suffix margules equation then you need this information.

But however, if you remove this or if you avoid our neglect this one also it is not going to cause a kind of serious error for many cases it has been found those things we are going to see anyway. And then these z_i are similar $z_i = \frac{x_i q_i}{\sum_{j=1}^{3} x_i q_j}$ because we are doing a ternary system. Effective volume fractions of the molecules is given by this z_i that definition is same here.

This is the whol’s expansion for 10 array system that we can take it as a kind of multi component system. So, now here what we do we apply again the limitations to get the binary equation two suffix margules equation 3 suffix margules equation and then we go to the next level.

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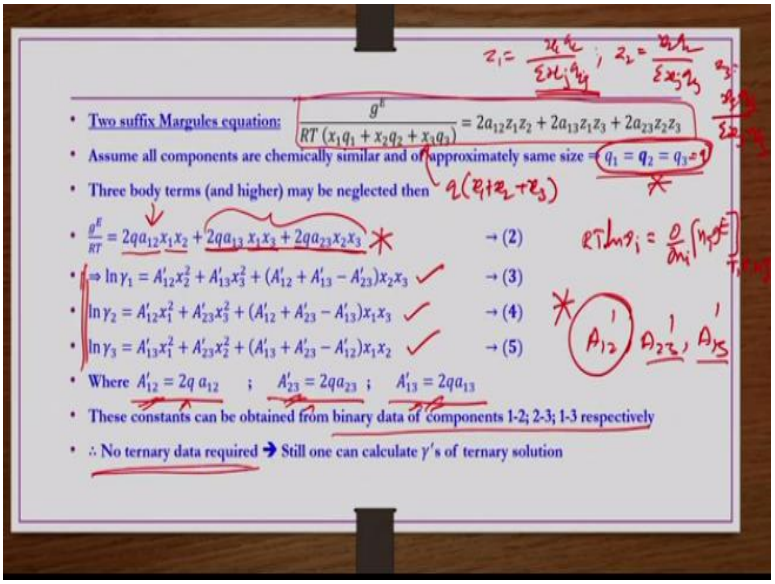

$z_1 = \frac{x_1q_1}{\sum x_jq_j}$; $z_2 = \frac{x_2q_2}{\sum x_jq_j}$

- **Two suffix Margules equation:** $\frac{g^E}{RT\,(x_1q_1 + x_2q_2 + x_3q_3)} = 2a_{12}z_1z_2 + 2a_{13}z_1z_3 + 2a_{23}z_2z_3$
- Assume all components are chemically similar and of approximately same size ⇒ $q_1 = q_2 = q_3 = q$
- Three body terms (and higher) may be neglected then $q(z_1+z_2+z_3)$
- $\frac{g^E}{RT} = 2qa_{12}x_1x_2 + 2qa_{13}x_1x_3 + 2qa_{23}x_2x_3$ → (2)
- ⇒ $\ln\gamma_1 = A'_{12}x_2^2 + A'_{13}x_3^2 + (A'_{12} + A'_{13} - A'_{23})x_2x_3$ → (3)
- $\ln\gamma_2 = A'_{12}x_1^2 + A'_{23}x_3^2 + (A'_{12} + A'_{23} - A'_{13})x_1x_3$ → (4)
- $\ln\gamma_3 = A'_{13}x_1^2 + A'_{23}x_2^2 + (A'_{13} + A'_{23} - A'_{12})x_1x_2$ → (5)
- Where $A'_{12} = 2q\,a_{12}$; $A'_{23} = 2qa_{23}$; $A'_{13} = 2qa_{13}$
- These constants can be obtained from binary data of components 1-2; 2-3; 1-3 respectively
- ∴ No ternary data required ➔ Still one can calculate γ's of ternary solution

$RT\ln\gamma_i = \frac{\partial}{\partial n_i}\left[n_T g^E\right]_{T,P,n_j}$

A'_{12}, A'_{23}, A'_{13}

So, two suffix Margules equations in the margules equations, what is the primary assumption that deep molecular sizes of all i mean the sizes of all molecules are almost same that is q_1 q_2 q_3 are same or equal to each other are closely equal to each other. So, that is the primary assumptions in the 2 suffix margules equations or any suffix margules equation, the difference between 2 for 2 suffix margules equation.

And margules and van Laar equation is that in the 2 suffix margules equation we are saying that $q_1 = q_2 = q_3 = q$ whereas van laar equation, we say $q_1 \neq q_2 \neq q_3$. By size, they are very dissimilar in van laar equation in the suffix equation by size all the molecules are similar that is the assumption, that is the primary difference in these 2. So, to suffix margules equation assume all components are chemically similar and of approximately same size that is $q_1 = q_2 = q_3$.

And then when you include when you say two suffix margules equation, you will have only interaction of 2 molecules only higher third and higher order terms you have to neglect that is you need to have z_1 z_2 z_1 z_3 z_2 z_3 terms are only possible there must be there you cannot have z_1^2 z_2 this power 3 terms are those are the higher power terms should not be there they should be neglected then it is called to suffix margules equation in addition to this assumption.

Then, that if you apply to this equation here, this is actually you know, after discarding the higher order terms higher terms, not higher 3 and then higher body terms if you neglect from the whol's expansion. So, then remaining terms are only these 3 terms in the right hand side. So, now here if you substitute $z_1 = \frac{x_1 q_1}{\sum_{j=1}^{3} x_i q_j}$ and then $z_2 = \frac{x_2 q_2}{\sum_{j=1}^{3} x_i q_j}$and then $z_3 =\frac{x_3 q_3}{\sum_{j=1}^{3} x_i q_j}$.

So, now, this that means, you know this now here q's are same, $q_1 = q_2 = q_3$. So from the denominator if you write x_1 q + x_2 q + x_3 q rather writing q_1 q_2 q_3 because they are same now. You take you when $q_1 = q_2 = q_3 = q$. Then in the denominator you will be having q ($x_1 + x_2 + x_3$). $x_1 + x_2 + x_3 = 1$ for a ternary system and then that q and then in the numerator q if you can cancel out.

So, then z is nothing but simply equal to the mole fraction of the component $z_i = x_i$ here for this condition that is what you can see and then you simplify this one further, then what do you have, you will have here left hand side also $x_1 q_1 + x_2 q_2 + x_3 q_3$ is there. So, if you take q common and then you write $x_1 + x_2 + x_3$ then it is q * 1 is q so, that q if you take to the right hand side.

So, 2 a_{12} q and then z_i is nothing but x_i because of this limitation. So, in place of z_1 z_2 you can write x_1 x_2 and then 2 a_{13} is second term and then *q that we are taking the denominator term of the left hand side to the right hand side. Then q is there and then z_1 z_3 is nothing but x_1 x_3 because of this limitation, $q_1 = q_2 = q_3 = q$ + third term is 2 a_{23} x_2 x_3.

And then q is being multiplied which is coming from the left hand side. So, this is what you have. In the binary system you have only this particular term because of the ternary system. So, additional 2 terms are coming into the picture here for 2 suffix Margules equation. So, now for this one if you apply RT ln $\gamma_i = \left[\frac{\partial}{\partial n_i}(n_T . g^E)\right]_{T,P,n_j}$ and then try to obtain γ_1 γ_2 γ_3 information, then you will get ln γ_1 = this expression, ln γ_2 = this expression.

And then ln γ_3 = this expression. They are simple straightforward it is the first differentiation we have to do for this n_T g^E term with respect to n_1 n_2 n_3 each term to get this ln γ_1 and γ_2 ln γ_3 respectively. And this A'_{12} A'_{13} and then these are the additional terms are there. Actually in the binary system you have only one A, A' because we are having only a_{12} terms only.

Because it was binary system third component was not there because of the third component there are 2 additional constants are there. So, in the case of binary component we know that $A'_{12}=2\, q_1a_{12}$. Now, similarly $A'_{23} = 2\, q_2\, a_{23}$ and then $A'_{13} = 2\, q_1\, a_{13}$. So, though this ln γ_1 ln γ_2 ln γ_3 are for the ternary system all that information you obtained just by you know binary data, this is also a binary data, only thing is that here binary mixture is consisting of component one.

And 2 in the case of first one A'_{12} in the case of A'_{23} the binary mixture is consisting of component 2 and component 3 and then in the case of A'_{13} the binary mixture is consisting of component 1 and component 3. But all of them are binary data so that means with binary data you can get the activity coefficient of ternary system without any difficulty that is one of the advantage. You do not need to have any ternary data in order to get this ln γ_i's for this ternary system.

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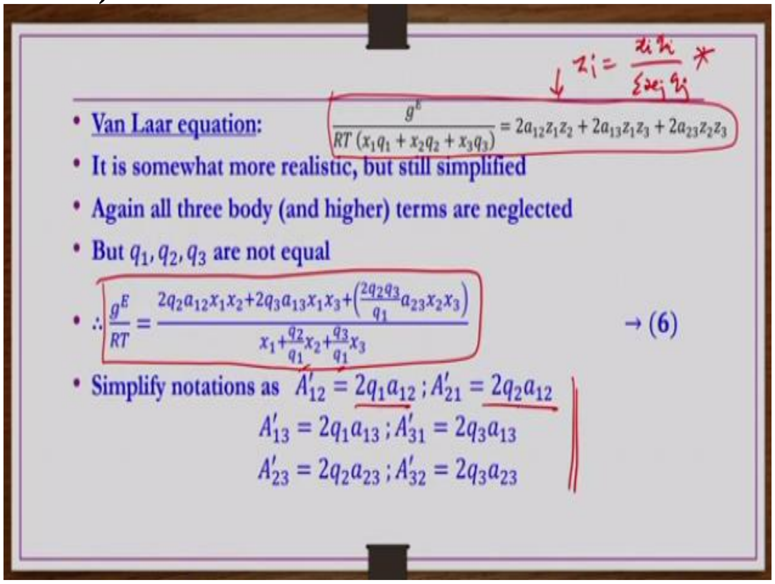

$z_i = \frac{x_i q_i}{\sum x_j q_j}$ *

- Van Laar equation: $\frac{g^E}{RT\,(x_1q_1 + x_2q_2 + x_3q_3)} = 2a_{12}z_1z_2 + 2a_{13}z_1z_3 + 2a_{23}z_2z_3$
- It is somewhat more realistic, but still simplified
- Again all three body (and higher) terms are neglected
- But q_1, q_2, q_3 are not equal
- $\therefore \frac{g^E}{RT} = \frac{2q_2a_{12}x_1x_2 + 2q_3a_{13}x_1x_3 + \left(\frac{2q_2q_3}{q_1}a_{23}x_2x_3\right)}{x_1 + \frac{q_2}{q_1}x_2 + \frac{q_3}{q_1}x_3}$ → (6)
- Simplify notations as $A'_{12} = 2q_1a_{12}\,;A'_{21} = 2q_2a_{12}$
  $A'_{13} = 2q_1a_{13}\,;A'_{31} = 2q_3a_{13}$
  $A'_{23} = 2q_2a_{23}\,;A'_{32} = 2q_3a_{23}$

Now we take a Van Laar equation, which is the same again in terms of the terms we will be having only second order terms only third and higher order terms we are not going to take but in addition to that one we are having the restriction that $q_1 \neq q_2 \neq q_3$ that means q_1 q_2 q_3 are different in the previous case 2 suffix Margules equation we are taking q_i = q for all i component i number of components.

So, that is not there in this case of Van Laar equation that is the only difference, right? So, it is somewhat more realistic but still simplified. Again all 3 body terms are neglected 3 body or higher body terms are neglected but q_1 q_2 q_3 are not equal that is what we have said. So, then again the same equation here we are having after neglecting 3 and 4 body terms or higher body terms if you neglect then we are going to have this equation.

But here we cannot say $z_i = x_i$ because $z_i = \frac{x_i q_i}{\sum_{j=1}^{3} x_i q_j}$ in this case q_i is not equal to $q_j \neq q_k$, or q_1 q_2 q_3 are different. So, you cannot take q common from the denominator to have a q $(x_1 + x_2 + x_3) = q$ that is not possible. So, because of that one the simplified version after substituting this $z_i = \frac{x_i q_i}{\sum_{j=1}^{3} x_i q_j}$in this equation and then simplifying. So, keeping only $\frac{g^E}{RT}$ term in the left hand side the remaining everything if you take to the right hand side so this is what you get.

For example, if you if you take all q's are equal in this equation so, then again it will be same as our 2 suffix margules equation without any difficulties straightforward you can see here because under such condition this will become 1 this will also become 1. So, $x_1 + x_2 + x_3$ that will be 1. So, here also you know out of q_2 q_3 one of the q's would be cancelled out and another only 1 q would be there and then some similarly here also in other terms also.

So, anyway let us not go into those calculations to the back one we go forward. So, now, here in this equation $A'_{12} = 2\ q_1\ a_{12}$ and then $A'_{21} = 2\ q_2\ a_{12}$ here q_1 here q_2 in the previous case. $A'_{12} = A'_{21}$ in the case of 2 suffix margules equation because they are $q_1 = q_2 = q_3$. But here q_1 is not equals to q_2, it is not equals to q_3 so, that is the reason we are having 2 different terms.

So, because of that one rather having 3 A' constants, we are going to have a 6 A' constant here, in the case of 3 suffix margules equation for ternary system, we were having only 3 A' constants. But now here, since these q's are not equal, we are going to have a 6 A' constants given by this.

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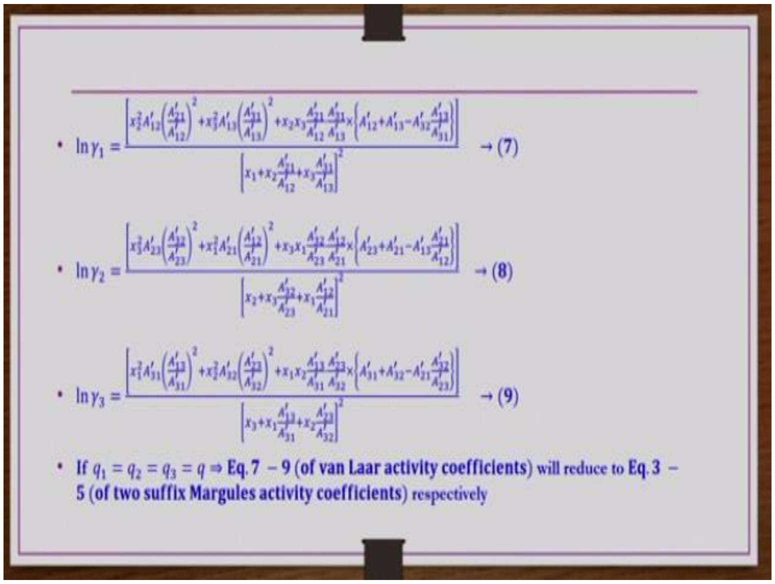

- $$\ln\gamma_1 = \frac{\left[x_2^2 A'_{12}\left(\frac{A'_{21}}{A'_{12}}\right)^2 + x_3^2 A'_{13}\left(\frac{A'_{31}}{A'_{13}}\right)^2 + x_2 x_3 \frac{A'_{21}}{A'_{12}}\frac{A'_{31}}{A'_{13}} \times \left\{A'_{12} + A'_{13} - A'_{32}\frac{A'_{13}}{A'_{31}}\right\}\right]}{\left[x_1 + x_2\frac{A'_{21}}{A'_{12}} + x_3\frac{A'_{31}}{A'_{13}}\right]^2} \rightarrow (7)$$
- $$\ln\gamma_2 = \frac{\left[x_3^2 A'_{23}\left(\frac{A'_{32}}{A'_{23}}\right)^2 + x_1^2 A'_{21}\left(\frac{A'_{12}}{A'_{21}}\right)^2 + x_3 x_1 \frac{A'_{32}}{A'_{23}}\frac{A'_{12}}{A'_{21}} \times \left\{A'_{23} + A'_{21} - A'_{13}\frac{A'_{21}}{A'_{12}}\right\}\right]}{\left[x_2 + x_3\frac{A'_{32}}{A'_{23}} + x_1\frac{A'_{12}}{A'_{21}}\right]^2} \rightarrow (8)$$
- $$\ln\gamma_3 = \frac{\left[x_1^2 A'_{31}\left(\frac{A'_{13}}{A'_{31}}\right)^2 + x_2^2 A'_{32}\left(\frac{A'_{23}}{A'_{32}}\right)^2 + x_1 x_2 \frac{A'_{13}}{A'_{31}}\frac{A'_{23}}{A'_{32}} \times \left\{A'_{31} + A'_{32} - A'_{21}\frac{A'_{32}}{A'_{23}}\right\}\right]}{\left[x_3 + x_1\frac{A'_{13}}{A'_{31}} + x_2\frac{A'_{23}}{A'_{32}}\right]^2} \rightarrow (9)$$
- If $q_1 = q_2 = q_3 = q \Rightarrow$ Eq. 7 – 9 (of van Laar activity coefficients) will reduce to Eq. 3 – 5 (of two suffix Margules activity coefficients) respectively

And then you apply RT ln γ_i = $\left[\frac{\partial}{\partial n_i}(n_T.g^E)\right]_{T,P,n_j}$ and then you find out ln γ_i for this Van Laar equation, for a 3 component system then you have ln γ_1 is this one, ln γ_2 = this one, ln γ_3 this straight forward simple lengthier but straight forward and simple derivation that you can do it. So, now here in place of in these equations wherever you are having q_1 q_2 q_3.

If you replace those q_1 q_2 q_3 by q, then this ln γ_1, ln γ_2, ln γ_3 will be getting back to or you will be getting back your 2 suffix margules equation activity coefficients that we have derived in previous slide. So, this is about 2 suffix margules equations and then van Laar equation for a ternary component.

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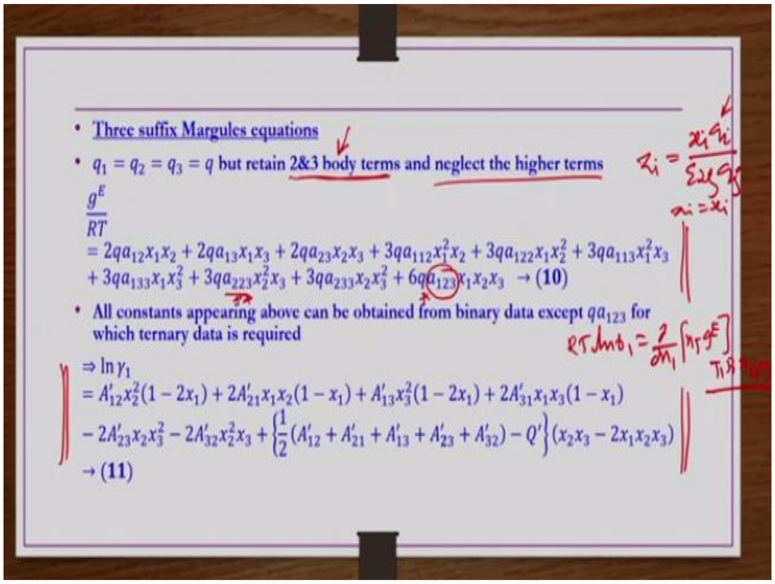

- Three suffix Margules equations
- $q_1 = q_2 = q_3 = q$ but retain 2&3 body terms and neglect the higher terms

$$\frac{g^E}{RT} = 2qa_{12}x_1x_2 + 2qa_{13}x_1x_3 + 2qa_{23}x_2x_3 + 3qa_{112}x_1^2x_2 + 3qa_{122}x_1x_2^2 + 3qa_{113}x_1^2x_3 + 3qa_{133}x_1x_3^2 + 3qa_{223}x_2^2x_3 + 3qa_{233}x_2x_3^2 + 6q\boxed{a_{123}}x_1x_2x_3 \rightarrow (10)$$

- All constants appearing above can be obtained from binary data except qa_{123} for which ternary data is required

$$\Rightarrow \ln\gamma_1 = A'_{12}x_2^2(1-2x_1) + 2A'_{21}x_1x_2(1-x_1) + A'_{13}x_3^2(1-2x_1) + 2A'_{31}x_1x_3(1-x_1) - 2A'_{23}x_2x_3^2 - 2A'_{32}x_2^2x_3 + \left\{\frac{1}{2}(A'_{12} + A'_{21} + A'_{13} + A'_{23} + A'_{32}) - Q'\right\}(x_2x_3 - 2x_1x_2x_3) \rightarrow (11)$$

$z_i = \frac{x_i q_i}{\sum x_j q_j}$

$z_i = x_i$

$RT\ln\gamma_1 = \frac{\partial}{\partial n_1}\left[n_T g^E\right]_{T,P,n_j}$

Now, let us see if you have a 3 suffix margules equation what we will have in the 3 suffix margules equation all the margules equation primary assumption is that all the molecules are chemically similar and then by size wise also they are similar that is $q_1 = q_2 = \ldots = q$ that is the q of each molecule is almost close to each other, and then since it is a 3 suffix margules equation you have to retain up to 3 body terms.

You cannot retain you cannot neglect 3 body terms now, only fourth and higher body terms you have to neglect. So, then the Wohl's expansion for ternary system after or by only retaining 2 and 3 body terms. So, what we will be having we will be having the entire equation whatever we have written in the Wohl's expansion for the ternary system. The same equation will have because that equation itself we are we have written including only up to 3 body terms.

Fourth and higher body terms, we have not written for ternary composition components, because those many number of things are not required here because we are not going up to 4 suffix and then higher suffix margules equation derivation anyway. So, now, this equation we get so here also if you apply $q_1 = q_2 = q_3 = q$, then you have this equation and then here also $z_i = \frac{x_i q_i}{\sum_{j=1}^{3} x_i q_j}$ so, q's are same.

So q if you take common $q \sum x_i$ is there in the denominator that means in the denominator you have only q and then in the numerator, you have 1 q for each z, so q's are same. So those q_i and q_i

would be cancelled, because they are same. So that means here again you have $z_i = x_i$. So, you do the after doing simplification, by replacing $z_i = x_i$'s and then by replacing all q_i's by one single q, you have this equation.

All constants appearing above can be obtained from the binary data except this a_{123} as I was mentioning so if you go for 3 suffix margules equation for it ternary the system then you need data one data point is required from interaction point of view that is a_{123} rest everything can be obtained by the binary data, even this let us say a_{223} it is between 3 molecule interactions it indicates the interaction between 3 molecules.

But those 3 molecules are made up of only 2 components, 2 molecules from the component 2 and then 1 molecule from component 3. So, binary data so, like that all remaining terms you need data from the binary mixtures only or except this particular term. But however, we can see it is not that important for majority of the cases. So, ln γ_1 if you do this one RT ln γ_1 = $\left[\frac{\partial}{\partial n_1}(n_T . g^E)\right]_{T,P,n_2,n_3}$ that you do and then simplify then you have this equation. Simple derivation but lengthier simplification is required to get this one that you can try.

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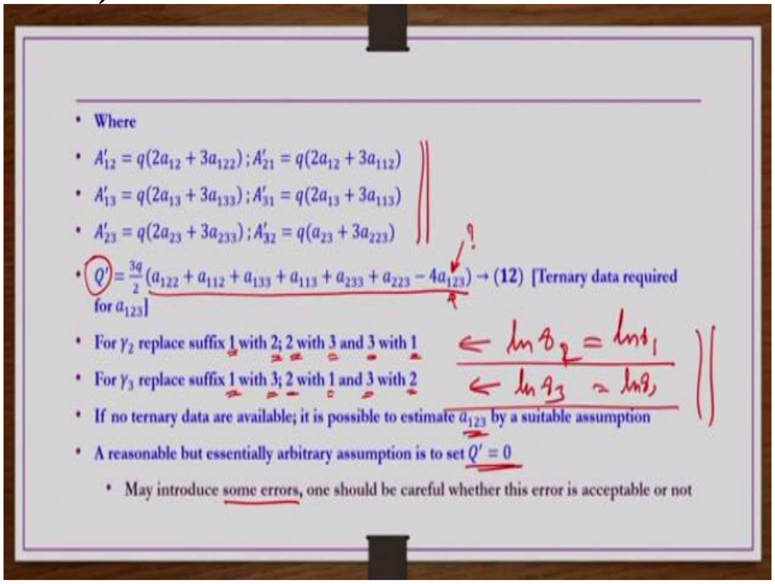

- Where
- $A'_{12} = q(2a_{12} + 3a_{122})\,;A'_{21} = q(2a_{12} + 3a_{112})$
- $A'_{13} = q(2a_{13} + 3a_{133})\,;A'_{31} = q(2a_{13} + 3a_{113})$
- $A'_{23} = q(2a_{23} + 3a_{233})\,;A'_{32} = q(a_{23} + 3a_{223})$
- $\boxed{Q'} = \frac{3q}{2}\underline{(a_{122} + a_{112} + a_{133} + a_{113} + a_{233} + a_{223} - 4a_{123})} \rightarrow$ **(12)** [Ternary data required for a_{123}]
- For γ_2 replace suffix 1 with 2; 2 with 3 and 3 with 1 $\Leftarrow \ln \gamma_2 = \ln \gamma_1$
- For γ_3 replace suffix 1 with 3; 2 with 1 and 3 with 2 $\Leftarrow \ln \gamma_3 = \ln \gamma_1$
- If no ternary data are available; it is possible to estimate a_{123} by a suitable assumption
- A reasonable but essentially arbitrary assumption is to set $\underline{Q' = 0}$
  - May introduce some errors, one should be careful whether this error is acceptable or not

So here A'$_{12}$, A'$_{21}$ and A'$_{23}$, A'$_{32}$ are given A'$_{23}$, A'$_{32}$ are also given 6 parameters are required because it is a 3 suffix margules equation. If it is 2 suffix margules equation only 3 parameters are required and then whatever this $\frac{3q}{2}$ multiplied by this entire term was there in ln γ_1 that we are writing Q'. So, here you need ternary data only for this one.

So, now out of this term, how much it is important magnitude wise how much it is important that is going to affect the Q' and that is further going to show influence in ln γ_a. So, that one has to establish that one has to find out. So, the simplest way is that you take several ternary systems do the calculations or experimentally produce these ln γ_i's and then plot them ln γ_i versus x_i information.

Then the same information you theoretically try to obtain by applying by 3 suffix margules equation for a ternary system without this a_{123} and then see if the error is negligible. So, then you can see that effect of this parameter is very, very small that you can easily realize. For γ_2, if you wanted to get a γ_2 information rather re-deriving everything, replace suffix 1 by 2 and then 2 by 3 and then suffix 3 by 1 then that ln γ_1 information will become ln γ_2 simply if you replace suffix wherever suffixes are there.

In the ln γ_1 information suffix 1 if you replace by 2 and 2 by 3 and 3 by 1 then you will get the final simplified expression or ln γ_2 simply ln γ_3 if you want. So, whatever the ln γ_1 expression that we have written in the previous slides so there suffix 1 if you replace by 3 and then 2 by 1 and 3 by 2 then reduced simplified ln γ_1 is there that is nothing but ln γ_3 so, you can re derive at other re-deriving simply you can see.

Because these parameters in analogously written so it will be easier to replace by this and then get these term ln γ_2 and ln γ_3. You can get this ln γ_2 and ln γ_3 from ln γ_1 information itself. So, here except this a_{123} you do not need to ternary data. A reasonable but essentially arbitrary assumption is set to this entire $Q'_1 = 0$ that if you take off then may introduce some error and one should be careful whether this error is acceptable or not by comparing with experimental data as have just mentioned

So, this is about the Wohl's expansion for binary and the ternary system and then from the Wohl's expansion, discussing the van laar equation and then different suffix equations, different margules equation that is what we have seen for binary and ternary systems. Now, what we will do we will be discussing a few more excess gibbs energy functions which cannot be reduced from Wohl's expansion but are based on the theoretical consideration based on the molecular consideration.

Which also include the effect of temperature in activity coefficient expressions are excess Gibbs energy functions without any difficulty. So, those things we are going to see and there are 3 important or famous models for excess Gibbs energy which are based on the molecular consideration are existing.

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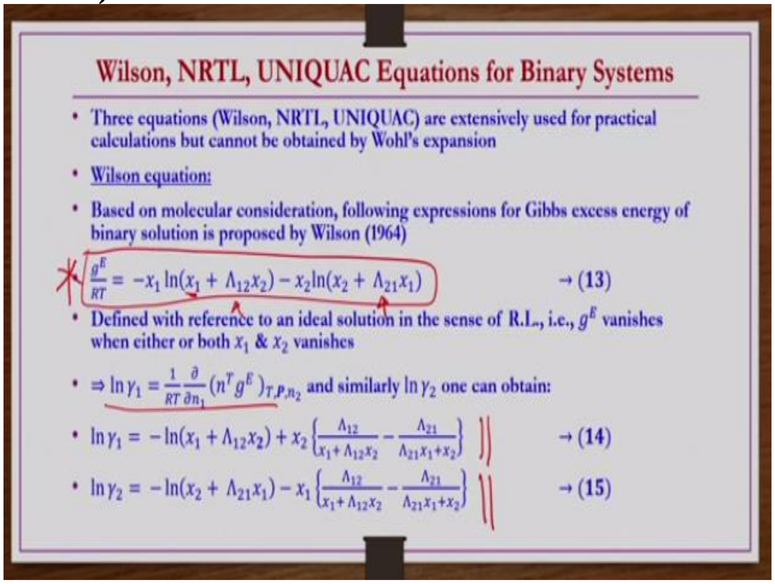

Wilson, NRTL, UNIQUAC Equations for Binary Systems

- Three equations (Wilson, NRTL, UNIQUAC) are extensively used for practical calculations but cannot be obtained by Wohl's expansion
- Wilson equation:
- Based on molecular consideration, following expressions for Gibbs excess energy of binary solution is proposed by Wilson (1964)

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \rightarrow (13)$$

- Defined with reference to an ideal solution in the sense of R.L., i.e., g^E vanishes when either or both x_1 & x_2 vanishes
- $\Rightarrow \ln\gamma_1 = \frac{1}{RT}\frac{\partial}{\partial n_1}(n^T g^E)_{T,P,n_2}$ and similarly $\ln\gamma_2$ one can obtain:
- $\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left\{\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right\} \rightarrow (14)$
- $\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left\{\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right\} \rightarrow (15)$

These are nothing but Wilson equation, NRTL equation and UNIQUAC equation. So, these equations also first we see for the binary system then we discuss for multi component system. So, Wilson equation it is based on molecular consideration and then following expression is given by Wilson for excess gibb's energy of a binary solution that is $\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1)$. This Λ_{12} and then Λ_{21} they are known as the 2 adjustable parameters.

Which are further dependent on the characteristic energy terms characteristics of interaction energy terms. So, which will further give information about the temperature dependence as well. How the temperature is influencing this $\frac{g^E}{RT}$ that information also brought in through these parameters through these 2 adjustable parameters which again depend on the characteristic interaction energy terms as we will see now here.

So, it is defined with reference to an ideal solution in the sense of Raoult's law that is again if you take $x_1 = 1$ then again $\frac{g^E}{RT}$will reduce to 0 if you take $x_2 = 1$ then also $\frac{g^E}{RT}$will reduce to 0. Let us say if $x_1 = 1$. So then ln of 1 + this x_2 is 0, so ln of 1 is nothing but 0. So, though it is x_1 is 1 so, multiplied by 0 and then second term if x_1 is 1, x_2 is 0.

So, anyway what irrespective of the second term is 0 because x_2 is 0. So, same is true for x_2 → you know 1 information if $x_2 \rightarrow 1$ so, then x_1 is 0. So, then first time is anyway 0 x_2 is 1, ln of x_2 is 1 + this x_1 is 0. So this ln of 1 is 0 so in that way also $\frac{g^E}{RT}$ is 0. So, either of the limiting conditions, $\frac{g^E}{RT}$ is vanishing. So, that is ideal solution in the sense of RL, Raoult's law that is what we have defined.

So, here, if you apply this ln γ_i RT ln γ_i = $\left[\frac{\partial}{\partial n_i}(n_T . g^E)\right]_{T,P,n_j}$ and then try to obtain ln γ_1 and ln γ_2 for binary system using this excess gibbs energy function proposed by Wilson then you get this expression after certain simplification for ln γ_1 and then you get this expression after certain simplification for ln γ_2, fine? So now, we see importance of these parameters here.

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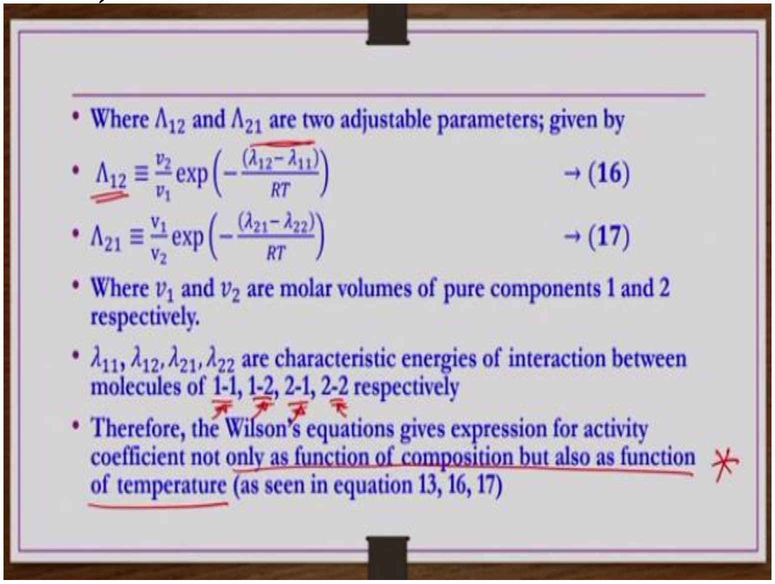

- Where Λ_{12} and Λ_{21} are two adjustable parameters; given by
- $\Lambda_{12} \equiv \frac{v_2}{v_1}\exp\left(-\frac{(\lambda_{12}-\lambda_{11})}{RT}\right)$ → (16)
- $\Lambda_{21} \equiv \frac{v_1}{v_2}\exp\left(-\frac{(\lambda_{21}-\lambda_{22})}{RT}\right)$ → (17)
- Where v_1 and v_2 are molar volumes of pure components 1 and 2 respectively.
- $\lambda_{11}, \lambda_{12}, \lambda_{21}, \lambda_{22}$ are characteristic energies of interaction between molecules of 1-1, 1-2, 2-1, 2-2 respectively
- Therefore, the Wilson's equations gives expression for activity coefficient not only as function of composition but also as function of temperature (as seen in equation 13, 16, 17) *

So, this Λ_{21} and Λ_{12} are 2 adjustable parameters. They are given by $\Lambda_{12} \equiv \frac{v_2}{v_1} exp\left(-\frac{(\lambda_{12}-\lambda_{11})}{RT}\right)$. So, now you can see here this capital delta is a function of T's, so, the effect of T is brought into the picture here and then v_1, v_2 are nothing but the molar volumes of the pure components 1 and 2.

Similarly, this $\Lambda_{21} \equiv \frac{v_1}{v_2} exp\left(-\frac{(\lambda_{21}-\lambda_{22})}{RT}\right)$ here also a function of T is coming into the picture through these parameters. So, v_1, v_2 are molar volumes of pure components 1 and 2 respectively and then this small λ_{11}, λ_{12}, λ_{21}, λ_{22} are characteristic energies of interaction between molecules of 1-1, 1-2, 2-1, 2-2.

What does it mean by 1-1 interaction between 2 molecules of component 1, then 1-2 in the sense interaction between 2 molecules of component 1 and 2, 1 from the component 1 another molecule from the component 2 and then 2-1 is similarly like this and then 2-2 is nothing but interaction between 2 molecules of component 2. So, the Wilson equation gives expression for activity coefficients not only as function of composition but also function of temperature.

This is one of the important advantages compared to the other models that we have discussed till now because other models they give the activity coefficients as function of composition only. But this Wilson equation gives the activity coefficient not only as function of composition but also as function of temperature in terms of these adjustable parameters capital Λ_{12} and then capital Λ_{21} same is true for an NRTL and then UNIQUAC equation as we are going to discuss now.

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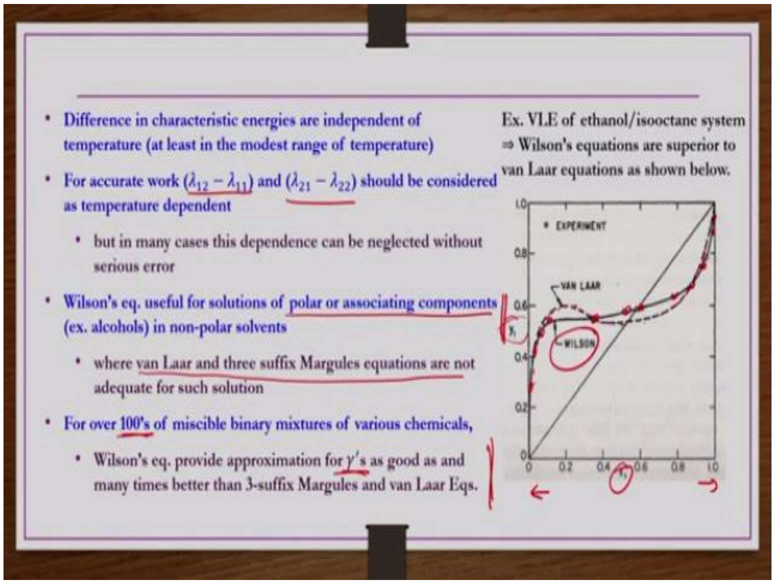

- Difference in characteristic energies are independent of temperature (at least in the modest range of temperature)
- For accurate work $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$ should be considered as temperature dependent
  - but in many cases this dependence can be neglected without serious error
- Wilson's eq. useful for solutions of polar or associating components (ex. alcohols) in non-polar solvents
  - where van Laar and three suffix Margules equations are not adequate for such solution
- For over 100's of miscible binary mixtures of various chemicals,
  - Wilson's eq. provide approximation for γ's as good as and many times better than 3-suffix Margules and van Laar Eqs.

Ex. VLE of ethanol/isooctane system ⇒ Wilson's equations are superior to van Laar equations as shown below.

So, difference in characteristic energies are independent of temperature at least in the modest range of temperature that is what it has been found by many experimental studies. However, for accurate work one has to find out this difference $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$ rather individual interactions the difference between 2 characteristic interaction energies that is more important. So, that should be considered.

These 2 differences should be obtained, as much accurate as possible if you wanted to find out the temperature dependence. But in many cases this dependence can be neglected without any serious error and then Wilson equation useful solutions for polar are associating components in non-polar systems.

Actually, whatever these equations that van Laar 2 suffix margules equations Scatchard's, Hammer equations etc. those things are good for non polar systems mostly, but if you had the polar nature or the associating on components in non-polar solvents then they are not good at all. But, this Wilson equation is found to be very reliable, where this van Laar and 3 suffix margules are not adequate for such solutions.

Though these 2 are also 2 parameter models Wilson equation is also 2 parameter model actually at the beginning of this liquid system we have studied especially for excess gibbs energy if you have more parameters obviously reliability increases. But you know having more than 3 parameters is not going to be useful at all and then further getting such accurate and then large number of data to prove the credentials are important have higher terms are higher parameters is again very difficult experimentally.

So, that is the region 2 parameters is sufficient enough very rarely you need to go for the models which are having 3 parameters. So, that is the region we are mostly we have seen the things especially for binary point of view, you see the parameters 2 suffix Margules equation only 1 parameter is a 3 suffix models equation only 2 parameters are there and then van laar equation only 2 parameters are there.

Here also Wilson equation only 2 parameters are there, capital Λ_{12} capital Λ_{21} so, though all these equations van Laar equation 3 suffix margules equation and Wilson equation though all of them are having 2 parameters. Wilson equation is found to be much better for this polar and associating component in non-polar solvent, which is not possible to trace by this van laar or 3 suffix margules equation at all.

And then for over 100's of miscible binary mixtures of various chemicals Wilson equation provides approximations of activation coefficient as good as 3 suffix margules equation or van laar equation and in many times better than these 2, that is what it has been found. But only thing the more number of information you required in order to use this Wilson equation one example here we take VLE of ethanol and isooctane system.

So whatever the experimentally ln γ_i versus x_i information is there that information is plotted and then again it is plotted or again it is obtained by van Laar equation as well as the Wilson equation to check with the experimental reliability, you can see here experimental data points are given by these circles, right? So, now, these points are properly matching indeed very accurately matching with this Wilson model.

Which is the solid line that we are showing here whereas, the dotted line so, it is van Laar equation it is usually deviating especially at the middle range of x_i that is x_i between 0.2 to 0.9 or 0.8 something like that of course, and then lower limits also it is not matching very accurately as compared to the Wilson equation here, that is what we can see so, what we can see now we can see that Wilson equation is much better than the van Laar equation.

So, however any model you take there will be some kind of advantages but there will also be some kind of disadvantages. One of the main disadvantages of this Wilson equation is that, it is not suitable for partially miscible system. Another disadvantage is that y_i versus x_i information only it is plotted here. So, if you have this ln γ_i versus x_i information in that information if you have a maxima or minima kind of things.

Then Wilson equation is not good, but however van Laar 3 suffix margules equation are also not good for such kind of things. So, though it is a disadvantage for Wilson equation but it is also a disadvantage for van Laar and 3 suffix margules equation. So, they are not having any advantages or Wilson equation even on this point of view also.

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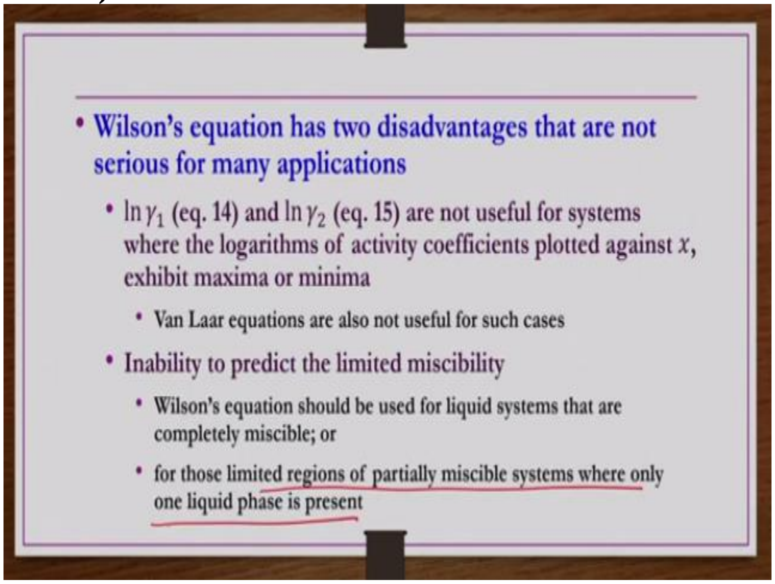

- Wilson's equation has two disadvantages that are not serious for many applications
  - $\ln \gamma_1$ (eq. 14) and $\ln \gamma_2$ (eq. 15) are not useful for systems where the logarithms of activity coefficients plotted against x, exhibit maxima or minima
    - Van Laar equations are also not useful for such cases
  - Inability to predict the limited miscibility
    - Wilson's equation should be used for liquid systems that are completely miscible; or
    - for those limited regions of partially miscible systems where only one liquid phase is present

So, Wilson equation has 2 disadvantages it is ln γ_1 versus x_2 or ln γ_2 versus x_1 plots if you plot if you have ln γ_1 versus x_1 plot and then that plot display some kind of maxima or minima under such conditions you cannot use the Wilson equation that is the one problem. So, but van Laar equation is also not suitable for such cases where ln γ_i versus x_i information is showing some kind of maxima or minima trend.

And then this Wilson's equations inability to predict the limited miscibility it is not suitable for system which are partially miscibility suitable completely miscible systems only even if you are applying for partially miscible system that should be limited for those reasons of partially miscible systems where only one liquid phase is present.

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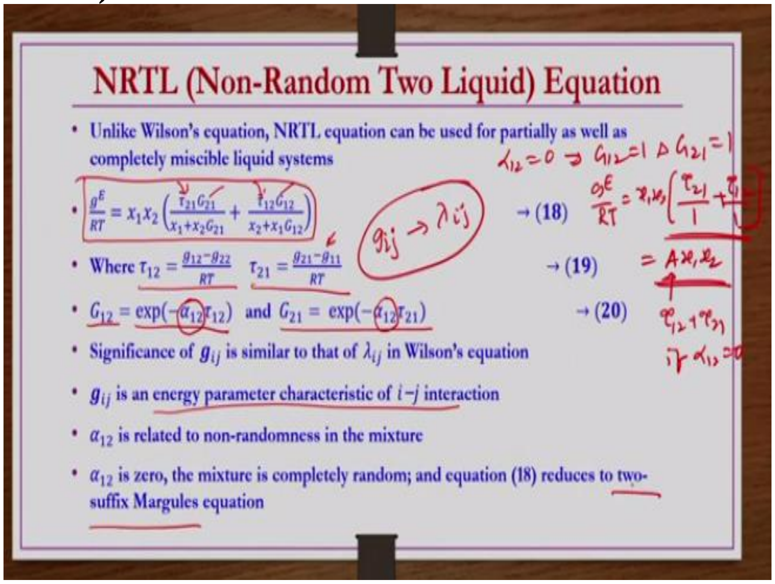

NRTL (Non-Random Two Liquid) Equation

- Unlike Wilson's equation, NRTL equation can be used for partially as well as completely miscible liquid systems
- $\frac{g^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1+x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2+x_1G_{12}}\right)$ → (18)
- Where $\tau_{12} = \frac{g_{12}-g_{22}}{RT}$ $\tau_{21} = \frac{g_{21}-g_{11}}{RT}$ → (19)
- $G_{12} = \exp(-\alpha_{12}\tau_{12})$ and $G_{21} = \exp(-\alpha_{12}\tau_{21})$ → (20)
- Significance of g_{ij} is similar to that of λ_{ij} in Wilson's equation
- g_{ij} is an energy parameter characteristic of $i-j$ interaction
- α_{12} is related to non-randomness in the mixture
- α_{12} is zero, the mixture is completely random; and equation (18) reduces to two-suffix Margules equation

$g_{ij} \to \lambda_{ij}$

$\alpha_{12} = 0 \Rightarrow G_{12} = 1$ & $G_{21} = 1$

$\frac{g^E}{RT} = x_1x_2\left(\frac{\tau_{21}}{1} + \tau\right.$

$= Ax_1x_2$

$\tau_{12} + \tau_{21}$

if $\alpha_{12} = 0$

So, now is the NRTL equation, which is also known as the non-random 2 liquid equation. So, it is having advantage over Wilson equation keeping all other things same as in a qualitatively same as a Wilson equation there is no advantage. But one additional advantage is that this NRTL equation is also suitable for partially miscible system which is not true for the case of Wilson equation so, for the binary system NRTL equation if you write you will get this equation, right?

So, here again we have 2 parameters τ_{21} and τ_{12} there are more other parameters also there that we eventually understand that they are interrelated. So, it is again 2 parameter model only there is an additional parameter third parameter is also there, that also we see, but it is having a limited range of variation so, that can be taken as a constant for many cases. So, here τ_{12} is related to $(g_{12} - g_{22})$ these are the small g's and then here these are the capital G's.

They are different and τ_{21} is nothing but $\frac{g_{21}-g_{11}}{RT}$. So, this g or whatever are there small g_{ij}'s or whatever these things are written here, they are similar to λ_{ij}'s of Wilson equation. They give characteristic energies associated with the interaction amongst these ij molecules. Whereas, the $G_{12} = \exp(-\alpha_{12}\tau_{12})$ and then $G_{21} = \exp(-\alpha_{12}\tau_{21})$.

This α_{12} it indicates that it is a measure of the randomness in the system. It is the measure of randomness in the system it says non random to liquid theory. So, if this α_{12}becomes 0 let us just see, if it is α_{12} is 0. Then G_{12} and then G_{21} both of them are equals to 1. So, that means you how $\frac{\tau_{21}}{x_1+x_2} + \frac{\tau_{12}}{x_1+x_2}$, $x_1 + x_2$ is nothing but, you know, it is same as a binary system $x_1 + x_2 = 1$.

So, that means, if $\alpha_{12} = 0$ that means, this capital $G_{12} = 1$ from equation number 20 and capital G_{21} is also 1 from equation number 20 again. So, that means $\frac{g^E}{RT} = x_1x_2\left(\frac{\tau_{21}}{1} + \frac{\tau_{12}}{1}\right)$. So, this is nothing but some constant A x_1 x_2 if you compare with the 2 suffix margules equation it is same as 2 suffix margules equation if α_{12} is 0. Only thing that are in the 2 suffix margules equation that constant we are writing A.

Now here it is $\tau_{12} + \tau_{21}$. A is nothing but $\tau_{12} + \tau_{21}$ if $\alpha_1 = 0$ and then significance of g_{ij} similar to the λ_{ij} of Wilson equation where it indicates the energy parameter characteristic of ij interactions and then α_{12} is related to non-randomness in the mixture. If it is 0 this will say this NRTL equation reduces to 2 suffix margules equation as shown here.

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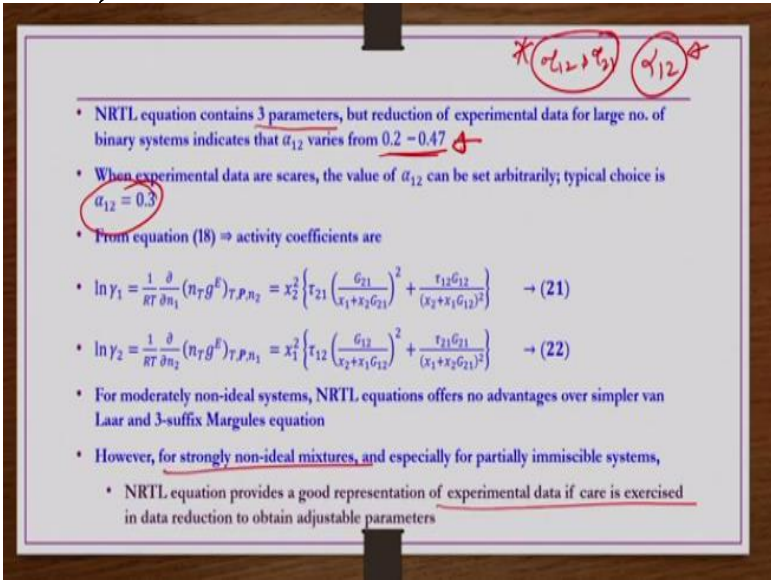

*(α_{12}, τ_{ij}) (α_{12})

- NRTL equation contains 3 parameters, but reduction of experimental data for large no. of binary systems indicates that α_{12} varies from 0.2 – 0.47
- When experimental data are scares, the value of α_{12} can be set arbitrarily; typical choice is $\alpha_{12} = 0.3$
- From equation (18) ⇒ activity coefficients are
- $\ln\gamma_1 = \frac{1}{RT}\frac{\partial}{\partial n_1}(n_T g^E)_{T,P,n_2} = x_2^2\left\{\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right\} \rightarrow (21)$
- $\ln\gamma_2 = \frac{1}{RT}\frac{\partial}{\partial n_2}(n_T g^E)_{T,P,n_1} = x_1^2\left\{\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1+x_2G_{21})^2}\right\} \rightarrow (22)$
- For moderately non-ideal systems, NRTL equations offers no advantages over simpler van Laar and 3-suffix Margules equation
- However, for strongly non-ideal mixtures, and especially for partially immiscible systems,
  - NRTL equation provides a good representation of experimental data if care is exercised in data reduction to obtain adjustable parameters

As I was mentioning there is a third parameter also in this NRTL equation, NRTL equation contains 3 parameters that is τ_{12} and then τ_{21}in addition to this parameter there is α_{12} also but several experimental studies are reduction of experimental data people have found that this α_{12} is having the limited range of variation from 0.2 to 0.47. So, in the case of where you do not have any experimental data about α_{12} then it is safe to take α_{12} = 0.3 without any difficulty.

Because it has already found by several experimental data it changes it varies between 0.2 and 0.47. So, average of 0.31 can take it as a kind of simple approximation which may not lead to any serious errors at all. So, that we also though it looks like a 3 parameter model, you know we can say that it is a 2 parameter model only because third parameter is more or less a kind of constant from the existing literature information.

So, activity coefficients from this NRTL equation for gibb's energy, excess gibb's energy if you try to obtain you will get ln γ_1 = this one, ln γ = this one. For moderately non ideal systems NRTL equations do not offer any kind of advantage or van Laar equations or 3 suffix modules equation if the system is moderately non ideal. But if the system is having high non ideality then it has been found this NRTL equation is much superior to the van Laar or 3 suffix margules equation and the non-idealities moderate.

So, you do not need to worry about going this NRTL or Wilson equation because these equations are based on the molecule consideration. Obviously, they are going to be better one but the thing is that you need more information much more information to get this all the ln γ_1, γ_2 information to be getting final value. So, whereas, you know, getting ln γ_1, ln γ_2 information from van Laar or 3 suffix margules equation is much simpler you need to know only ab constant which you can find out from the experimental things.

So, NRTL equation provides a good representation of experimental data if care is exercised in data reduction to obtain adjustable parameters especially when the system is strongly non-ideal.

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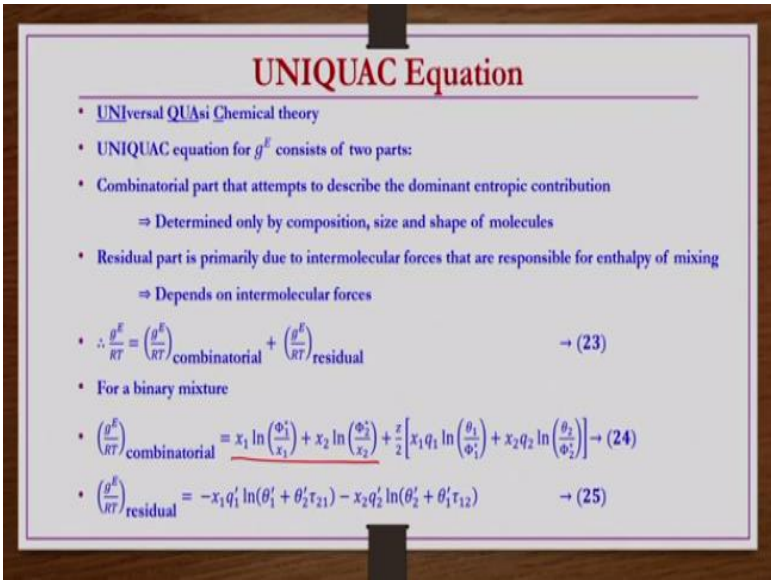

UNIQUAC Equation

- UNIversal QUAsi Chemical theory
- UNIQUAC equation for g^E consists of two parts:
- Combinatorial part that attempts to describe the dominant entropic contribution
  - ⇒ Determined only by composition, size and shape of molecules
- Residual part is primarily due to intermolecular forces that are responsible for enthalpy of mixing
  - ⇒ Depends on intermolecular forces
- $\therefore \frac{g^E}{RT} = \left(\frac{g^E}{RT}\right)_{\text{combinatorial}} + \left(\frac{g^E}{RT}\right)_{\text{residual}} \quad \rightarrow (23)$
- For a binary mixture
- $\left(\frac{g^E}{RT}\right)_{\text{combinatorial}} = \underline{x_1 \ln\left(\frac{\Phi_1^*}{x_1}\right) + x_2 \ln\left(\frac{\Phi_2^*}{x_2}\right)} + \frac{z}{2}\left[x_1 q_1 \ln\left(\frac{\theta_1}{\Phi_1^*}\right) + x_2 q_2 \ln\left(\frac{\theta_2}{\Phi_2^*}\right)\right] \rightarrow (24)$
- $\left(\frac{g^E}{RT}\right)_{\text{residual}} = -x_1 q_1' \ln(\theta_1' + \theta_2' \tau_{21}) - x_2 q_2' \ln(\theta_2' + \theta_1' \tau_{12}) \quad \rightarrow (25)$

So, the Finally, UNIQUAC equation which is also known as the universal quasi chemical theory because of that one you know this universal quasi chemical theory is written in short as a kind of UNIQUAC work it is abbreviated as UNIQUAC. So, it consists of 2 parts, one is the combinatorial part of the g^E another one is the residual part of the g^E each one is having some significance, the combinatorial part of g^E indicates the entropic dominant terms.

Whereas the residual part of the G term indicates, you know because of the enthalpy change or because of the molecular interactions. So, that way on fundamental molecular consideration grounds, this theory has been developed for the g^E has 2 parts and then these 2 parts are added now to get the total excess gibbs energy on the system so combinatorial part that attempts to describe the dominant entropic contribution.

Which is determined by the composition size and shape of the molecules next one is the residual part primarily due to the intermolecular forces that are responsible for enthalpy of mixing. So, it depends on the intermolecular forces, and then total excess Gibbs energy of the system is additional is a summation of these 2 parts.

So, individually for a binary mixture these parts are given like $\frac{g^E}{RT}$ combinatorial part is given by $\left(\frac{g^E}{RT}\right)_{combinatorial} = x_1 ln\left(\frac{\phi_1^*}{x_1}\right) + x_2 ln\left(\frac{\phi_2^*}{x_2}\right) + \frac{z}{2}\left[x_1 q_1 ln\left(\frac{\theta_1}{\phi_1^*}\right) + x_2 q_2 ln\left(\frac{\theta_2}{\phi_2^*}\right)\right]$.

This $\phi_1^*, \phi_2^*$are known as the segment fractions whereas, θ_1 θ_2 are known as the kind of area fractions. So, they are obtained from the relative size of the molecules size and orientation of the molecules. Alright, so, $\left(\frac{g^E}{RT}\right)_{residual} = -x_1 q'_1 \ln(\theta'_1 + \theta'_2 \tau_{21}) - x_2 q'_2 \ln(\theta'_2 + \theta'_1 \tau_{12})$.

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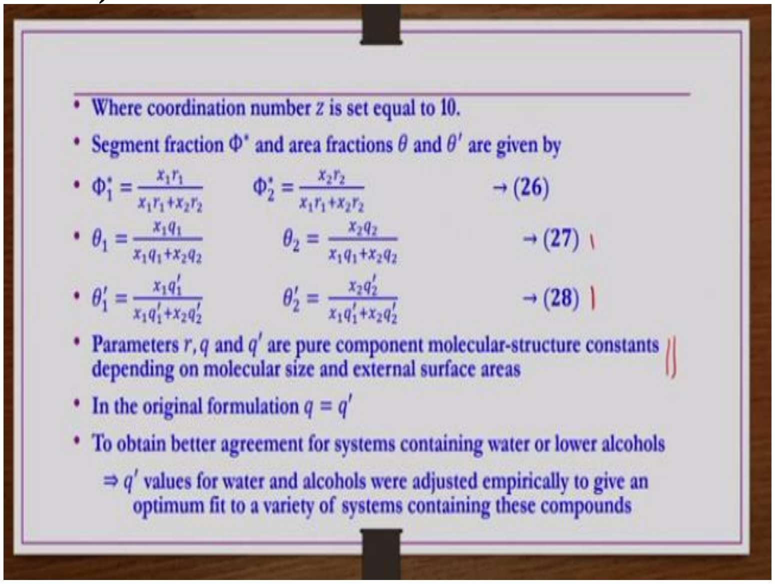

- Where coordination number z is set equal to 10.
- Segment fraction Φ^* and area fractions θ and θ' are given by
- $\Phi_1^* = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}$ $\quad \Phi_2^* = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$ → (26)
- $\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$ $\quad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$ → (27)
- $\theta'_1 = \frac{x_1 q'_1}{x_1 q'_1 + x_2 q'_2}$ $\quad \theta'_2 = \frac{x_2 q'_2}{x_1 q'_1 + x_2 q'_2}$ → (28)
- Parameters r, q and q' are pure component molecular-structure constants depending on molecular size and external surface areas
- In the original formulation $q = q'$
- To obtain better agreement for systems containing water or lower alcohols

  ⇒ q' values for water and alcohols were adjusted empirically to give an optimum fit to a variety of systems containing these compounds

Where z is nothing but the coordination number it is in general taken as a kind of fixed value of 10 segment fraction ϕ^* and area fractions θ and θ' are given us like this. Then here r, q, q' are pure components molecule structure constant which depends on the molecule size and external surface areas of these molecules. So, molecule consideration parts come into the picture here.

In the original formulation actually it has been taken as q = q', but later on it has been found and then segregated the importance and then they have written separately here as we have written in this equation number 28, 27. So, to obtain better agreement for systems containing water or lower alcohols, q prime values for water and alcohols were adjusted empirically to give an optimum fit to a variety of systems containing these components.

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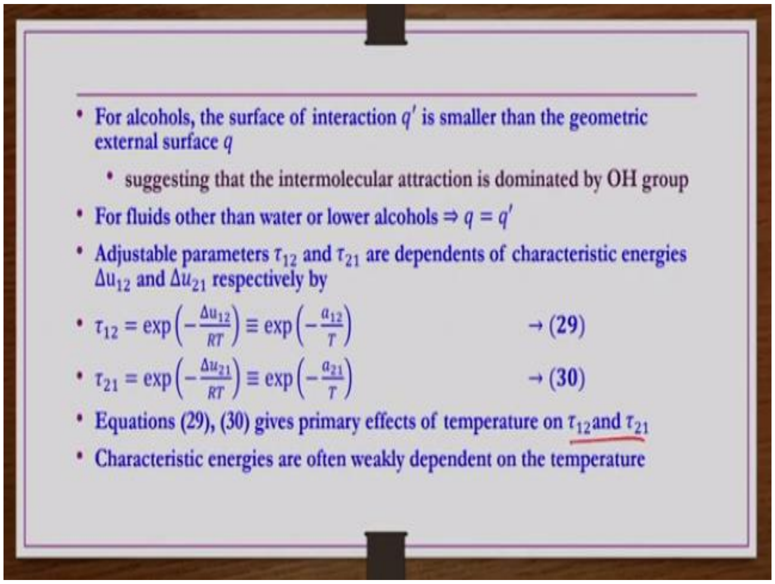

- For alcohols, the surface of interaction q' is smaller than the geometric external surface q
    - suggesting that the intermolecular attraction is dominated by OH group
- For fluids other than water or lower alcohols $\Rightarrow q = q'$
- Adjustable parameters τ_{12} and τ_{21} are dependents of characteristic energies Δu_{12} and Δu_{21} respectively by
- $\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) \equiv \exp\left(-\frac{a_{12}}{T}\right) \quad \rightarrow (29)$
- $\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) \equiv \exp\left(-\frac{a_{21}}{T}\right) \quad \rightarrow (30)$
- Equations (29), (30) gives primary effects of temperature on $\tau_{12}$and τ_{21}
- Characteristic energies are often weakly dependent on the temperature

So, for alcohol the surface of interaction q' is smaller than the geometric external surface q, suggesting that the intermolecular attraction is dominated by the OH group. So, for fluids other than water are lower alcohols you can take q = q' that is the reason primarily, it was taken q = q' in original version where they have excluded water or lower alcohols but if you have those components then in general it has been found.

That q' is smaller than the q, q' is the surface of interaction and then q is nothing but a geometric external surface. Then are adjustable parameter τ_{12} and τ_{21} are again dependent on the characteristic energies of interaction Δu_{12} and Δu_{21} respectively as given by these 2 equations. Basically they are giving the effect of temperature again here on the $\frac{g^E}{RT}$expression so, which was not done in the other models.

Which are not developed based on the molecule concentrations. So, this Wilson's, NRTL UNIQUAC equations are developed based on the molecular conservation. So, the effect of temperature is also brought into the picture of this excess molar Gibbs energy. Equations 29, 22 gives the effect of temperature on tau_{12} and tau_{21} and then characteristic energies are often weakly dependent on the temperature.

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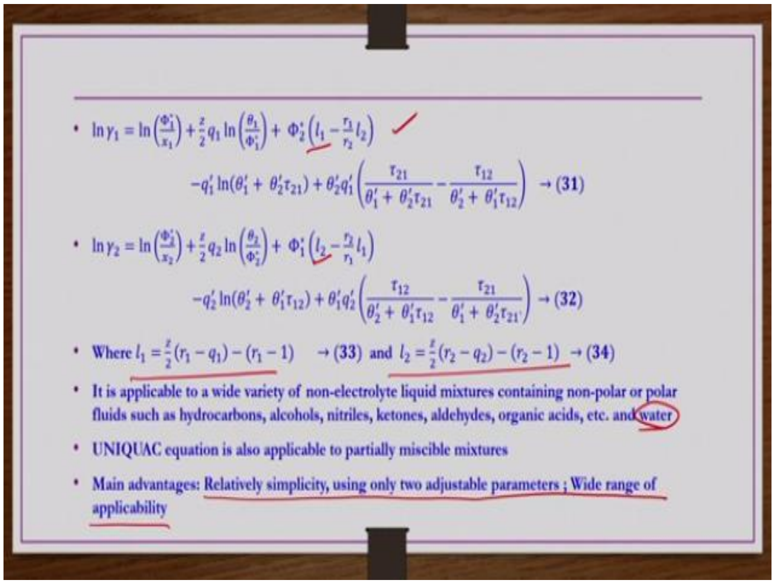

- $$\ln\gamma_1 = \ln\left(\frac{\Phi_1^*}{x_1}\right) + \frac{z}{2}q_1\ln\left(\frac{\theta_1}{\Phi_1^*}\right) + \Phi_2^*\left(l_1 - \frac{r_1}{r_2}l_2\right)$$
  $$-q_1'\ln(\theta_1' + \theta_2'\tau_{21}) + \theta_2'q_1'\left(\frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}} - \frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}}\right) \rightarrow (31)$$
- $$\ln\gamma_2 = \ln\left(\frac{\Phi_2^*}{x_2}\right) + \frac{z}{2}q_2\ln\left(\frac{\theta_2}{\Phi_2^*}\right) + \Phi_1^*\left(l_2 - \frac{r_2}{r_1}l_1\right)$$
  $$-q_2'\ln(\theta_2' + \theta_1'\tau_{12}) + \theta_1'q_2'\left(\frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}} - \frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}}\right) \rightarrow (32)$$
- Where $l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1)$ → (33) and $l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1)$ → (34)
- It is applicable to a wide variety of non-electrolyte liquid mixtures containing non-polar or polar fluids such as hydrocarbons, alcohols, nitriles, ketones, aldehydes, organic acids, etc. and water
- UNIQUAC equation is also applicable to partially miscible mixtures
- Main advantages: Relatively simplicity, using only two adjustable parameters ; Wide range of applicability

If you obtain ln γ_1 for this UNIQUAC equation, by applying RT ln $\gamma_1 = \left[\frac{\partial}{\partial n_1}(n_T . g^E)\right]_{T,P,n_2}$ and then doing certain simplifications then you will get this expression ln γ_2 you will get this expression whereas, in this equation we have this l_1 l_2 terms are there so, l_1 is given by this equation l_2 is given by this equation. It is applicable to a wide variety of non-electrolyte liquid mixtures.

Containing non polar or polar fluids such as hydrocarbons, alcohols nitrites, ketones, aldehydes, organic acids etc and in addition to them water also where you can take q = q' for water. UNIQUAC equation is also applicable to partially miscible mixtures, which is not true for the Wilson equation. So, out of these models which are developed based on the molecular concentration only Wilson equation is the one which is not suitable for a partial immiscible system, but all other NRTL and UNIQUAC equations are suitable.

For partial immiscible systems as well, the major advantage of this UNIQUAC case relatively simplicity using 2 adjustable parameters and then wide range of applicability. So, this is about Wilson NRTL and UNIQUAC equation for a binary system. So, quickly what we do we see this Wilson NRTL and then UNIQUAC equation for multi component system before winding up this you know liquid systems.

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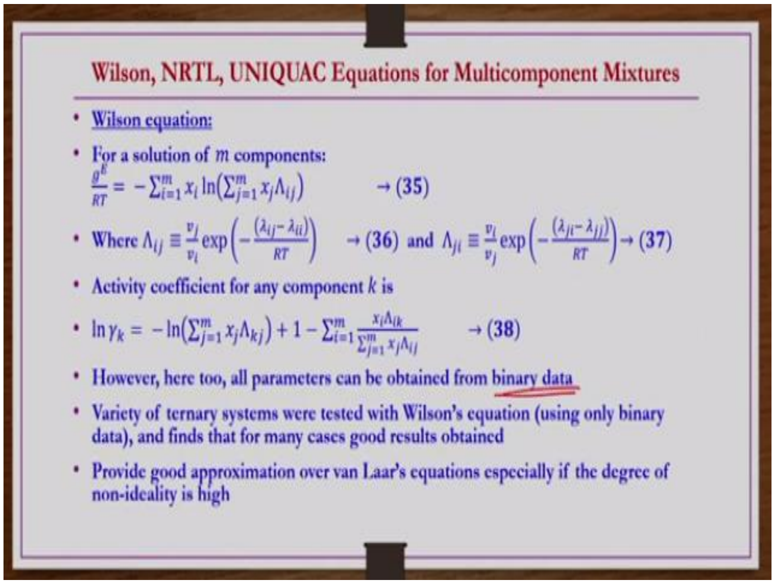

Wilson, NRTL, UNIQUAC Equations for Multicomponent Mixtures

- **Wilson equation:**
- For a solution of m components:
  $\frac{g^E}{RT} = -\sum_{i=1}^{m} x_i \ln\left(\sum_{j=1}^{m} x_j \Lambda_{ij}\right)$ → (35)
- Where $\Lambda_{ij} \equiv \frac{v_j}{v_i} \exp\left(-\frac{(\lambda_{ij}-\lambda_{ii})}{RT}\right)$ → (36) and $\Lambda_{ji} \equiv \frac{v_i}{v_j} \exp\left(-\frac{(\lambda_{ji}-\lambda_{jj})}{RT}\right)$ → (37)
- Activity coefficient for any component k is
- $\ln \gamma_k = -\ln\left(\sum_{j=1}^{m} x_j \Lambda_{kj}\right) + 1 - \sum_{i=1}^{m} \frac{x_i \Lambda_{ik}}{\sum_{j=1}^{m} x_j \Lambda_{ij}}$ → (38)
- However, here too, all parameters can be obtained from binary data
- Variety of ternary systems were tested with Wilson's equation (using only binary data), and finds that for many cases good results obtained
- Provide good approximation over van Laar's equations especially if the degree of non-ideality is high

So, Wilson equation for m number of components $\frac{g^E}{RT}$ is given like this and this adjustable parameters also given here, activity coefficient of any component k is given by this one here to all parameters can be obtained from the binary data, though it is for a multi component mixture you do not need any data for which you need to go beyond the binary system. So, all the parameters associated with this Wilson equation even for multi component mixture.

All those parameters can be obtained from the binary data variety of ternary systems were tested with Wilson's equation using only binary data and finds that for many cases good results obtained provide good approximation over van Laar’s equation especially if the degree of non-ideality is high.

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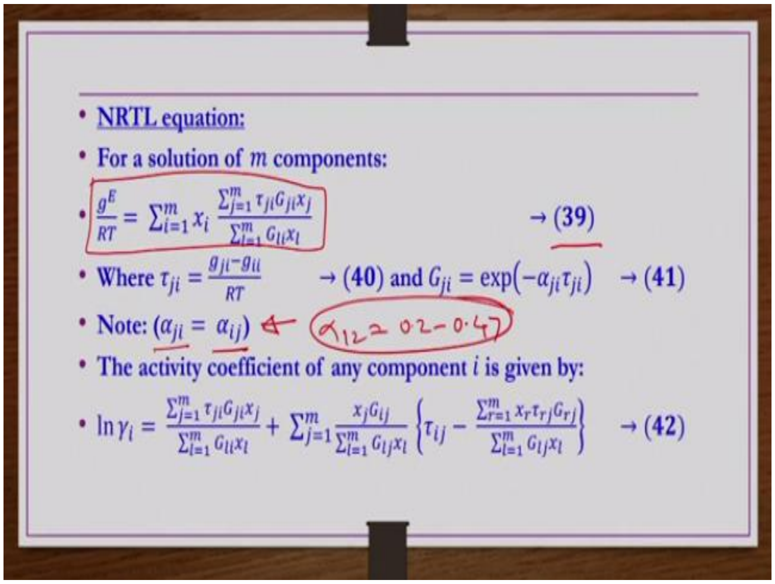

- **NRTL equation:**
- For a solution of m components:
- $\boxed{\frac{g^E}{RT} = \sum_{i=1}^{m} x_i \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l}}$ → $\underline{(39)}$
- Where $\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}$ → (40) and $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$ → (41)
- Note: $(\underline{\alpha_{ji}} = \underline{\alpha_{ij}})$ ← $\boxed{\alpha_{12} = 02-0.47}$
- The activity coefficient of any component i is given by:
- $\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left\{ \tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj} x_l} \right\}$ → (42)

Then NRTL equation for multi component it is written here $\frac{g^E}{RT}$ is given by this equation τ_{ji} and then g_{ji} are given here α_{ij} is nothing but α_{ji} here in the system that α is nothing but one same constant that is α_{12} kind of thing for binary system, which varies between 0.2 to .47. So, this is like you know α_{ji} is nothing but α_{ij} here also it is one parameter it is not 2 parameters. And then activity coefficient of any component i obtained by this $\frac{g^E}{RT}$ expression for multi component system represented by an NRTL equation, you will get this equation.

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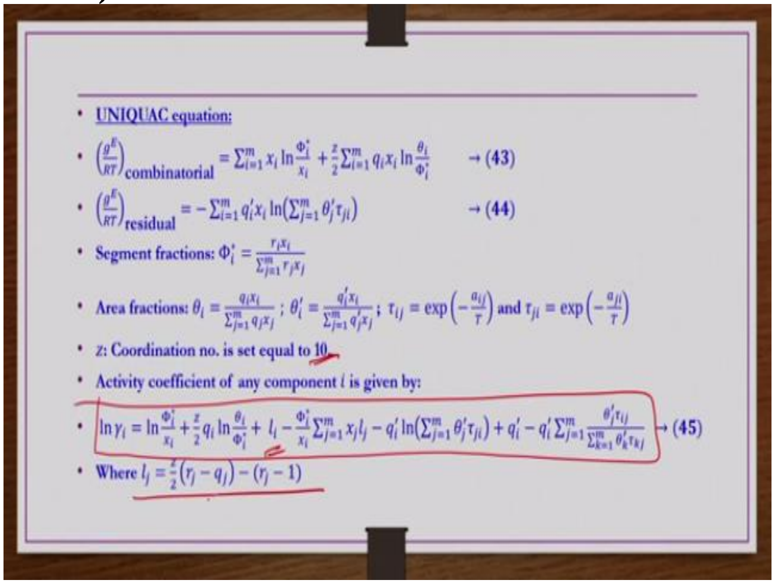

- **UNIQUAC equation:**
- $\left(\frac{g^E}{RT}\right)_{\text{combinatorial}} = \sum_{i=1}^{m} x_i \ln \frac{\Phi_i^*}{x_i} + \frac{z}{2} \sum_{i=1}^{m} q_i x_i \ln \frac{\theta_i}{\Phi_i^*}$ → (43)
- $\left(\frac{g^E}{RT}\right)_{\text{residual}} = -\sum_{i=1}^{m} q_i' x_i \ln\left(\sum_{j=1}^{m} \theta_j' \tau_{ji}\right)$ → (44)
- Segment fractions: $\Phi_i^* = \frac{r_i x_i}{\sum_{j=1}^{m} r_j x_j}$
- Area fractions: $\theta_i = \frac{q_i x_i}{\sum_{j=1}^{m} q_j x_j}$; $\theta_i' = \frac{q_i' x_i}{\sum_{j=1}^{m} q_j' x_j}$; $\tau_{ij} = \exp\left(-\frac{a_{ij}}{T}\right)$ and $\tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right)$
- z: Coordination no. is set equal to $\underline{10}$
- Activity coefficient of any component i is given by:
- $\boxed{\ln \gamma_i = \ln \frac{\Phi_i^*}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i^*} + \underline{l_i} - \frac{\Phi_i^*}{x_i} \sum_{j=1}^{m} x_j l_j - q_i' \ln\left(\sum_{j=1}^{m} \theta_j' \tau_{ji}\right) + q_i' - q_i' \sum_{j=1}^{m} \frac{\theta_j' \tau_{ij}}{\sum_{k=1}^{m} \theta_k' \tau_{kj}}}$ → (45)
- Where $\underline{l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1)}$

Similarly, UNIQUAC like equation if you write for multi component mixture. So, combinatorial real term then the signal terms are given if you add them together you will get total excess gibbs energy for a, you will get the molar excess gibbs energy for a multi component system by adding these 2 here segment fractions capital ϕ^* are given and then area fractions θ_i q_i q' are given here coordination number is taken as 10 even for multi component mixture.

Coordination numbers z is taken as 10 activity coefficient of any component i can be obtained by simple differentiation and then rearrangement of the terms. So, then you will get this particular expression where here you have l_i terms those l_i terms are nothing but or l_j terms are nothing but given here $l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1)$. So, this is about the Wilson NRTL and then UNIQUAC equations for multi component system.

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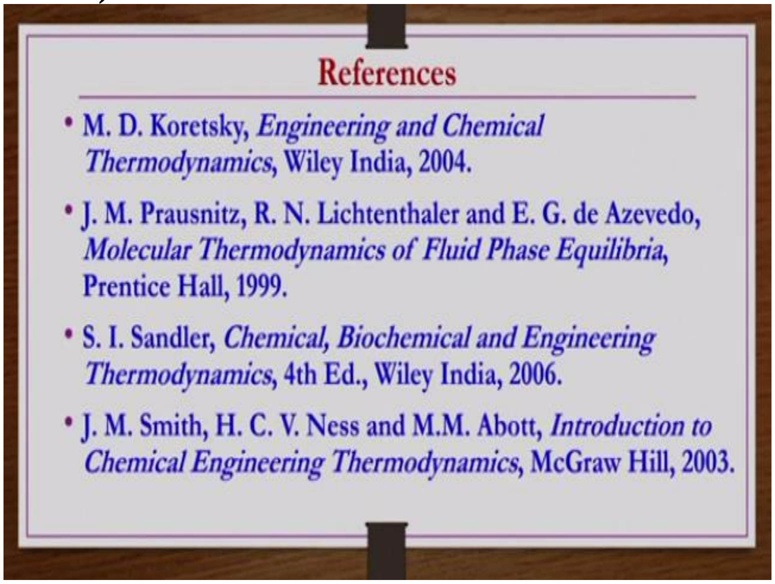

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Now, the references for this lecture are given here, engineering and chemical thermodynamics by Koretsky. Then molecular thermodynamics of fluid phase equilibria then chemical biochemical and engineering thermodynamics by Sandler and then introduction to chemical in thermodynamics by Smith et al, this is the primary reference for this particular lecture. Thank you.