Thermodynamics of Fluid Phase Equilibria
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Lecture - 44
Models for Fugacity of Liquid Mixtures-1

Welcome back. In the last lecture we introduced a simple equation one constant Margules equation which satisfies the boundary condition for g axis to be 0, when excess approaches towards 0 ok.

And we made a comment that such kind of equation works well if you have a binary mixtures like argon, oxygen, benzene, cyclohexane. These are the mixtures or these are the molecules which are similar size shape and chemistry.

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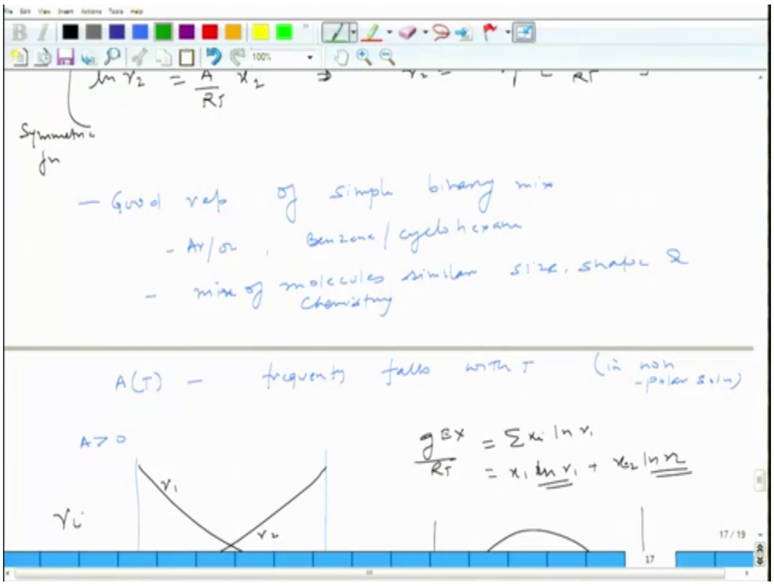

$\ln \gamma_2 = \frac{A}{RT} x_2 \Rightarrow$

Symmetric fn

- Good rep of simple binary mix
  - Ar/O₂ , Benzene/cyclohexane
  - mix of molecules similar size, shape & Chemistry

A(T) – frequently falls with T (in non-polar soln)

A > 0

$$\frac{g^{EX}}{RT} = \sum x_i \ln \gamma_i = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

But you have deviation from this kind of you know characteristic properties or similarity then you may have to consider more complex relations ok. That in other word more complex equations are needed in order to represent g e of a binary solution to represent adequately.

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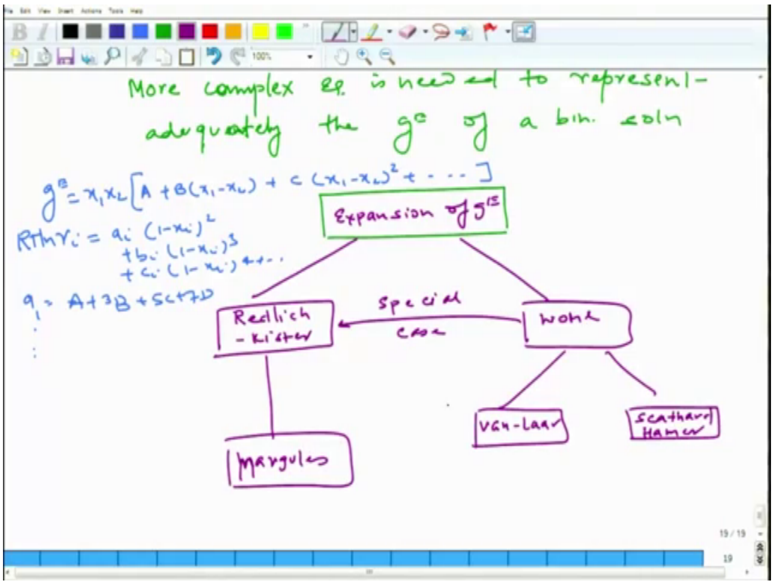

More complex eq. is needed to represent adequately the g^E of a bin. soln

$$g^E = x_1x_2\left[A + B(x_1-x_2) + C(x_1-x_2)^2 + \dots\right]$$

$$RT\ln\gamma_i = a_i(1-x_i)^2 + b_i(1-x_i)^3 + c_i(1-x_i)^4 + \dots$$

$$a_1 = A+3B+5C+7D$$

$\vdots$

So, this is needed if you have you know problems related to let us say you know because what we are talking about is similar chemistry size and shape. So, any small deviation can affect you know large and I will come to this point I will show you that even the small difference in the size you know if they like say not like 3 times 4 times, but if they are very close by, but still is like 1.2, 1.5 times you might see some kind of deviation from where you need more number of terms.

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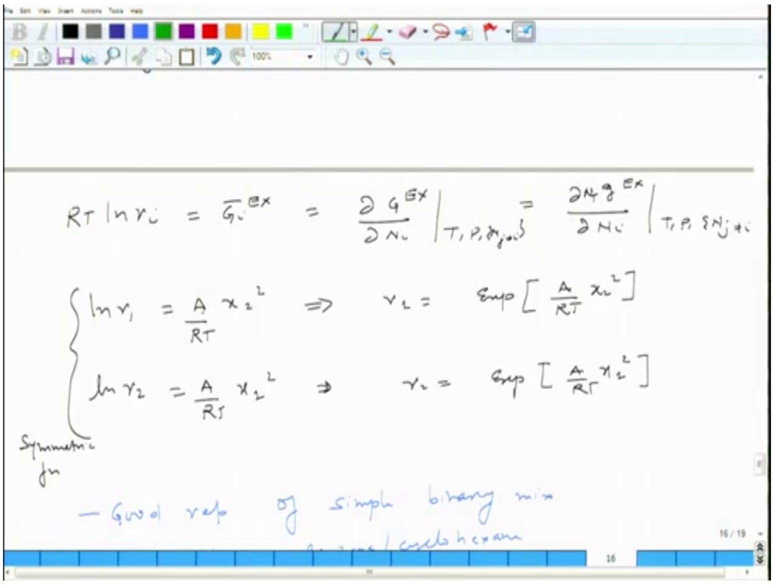

$$RT\ln\gamma_i = \bar{G}_i^{EX} = \left.\frac{\partial G^{EX}}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \left.\frac{\partial N_T g^{EX}}{\partial N_i}\right|_{T,P,\{N_j\}_{j\neq i}}$$

$$\ln\gamma_1 = \frac{A}{RT}x_2^2 \Rightarrow \gamma_1 = \exp\left[\frac{A}{RT}x_2^2\right]$$

$$\ln\gamma_2 = \frac{A}{RT}x_2^2 \Rightarrow \gamma_2 = \exp\left[\frac{A}{RT}x_2^2\right]$$

Symmetric fn

— Good rep of simple binary mix

/cyclohexane

So, remember that for one constant Margules equation you have only one constant term this one. You are trying to characterize all kind of provisions with the sizes chemistries and shape with just one constant.

So, what is the generic equation which we can come up? So, there are many equations which have people have developed and this I can summarize in terms of some kind of flow chart. So, now, one can consider this expansion of g e in terms of moles and various different component ok.

Now, as you correlate all these different equations which people have developed they have a common reason for that or they are they are well connected for example, the generic equation such as g e which I can write in this way I can write g e as x 1, x 2 right if you have one then basically it is a one constant right, but then you can add other plus C and so forth ok, it will still satisfy the boundary conditions.

Now, this will yield your activity coefficient in this way 1 minus x i square plus b i 1 minus x i q plus c i 1 minus x i 4 and so forth ok, where a are related to this abc ok. For example, a 1 is related to A plus 3 B plus 5 C plus 7 d and so forth.

So, this is the generic expression we satisfy the boundary condition and now, what you know using this if you consider different kind of approximation different kind of formalism although the expression comes up ok. So, I will just write down this for example, you can get this Redlich Kister ok, you can also get this Wohl's which is more exhaustive or more it contains physical interpretation of the system and the and a special case is basically this Redlich crystal.

Again it has expansion of some kind of expansion of g its special case. Now, using Wohl's we can get Van Laar and we can get also Scathard Hamer and Redlich special cases basically nothing but Margules Margules equation.

So, let me again come to this generic term which we which we have written here. Now, this A, B and C the number of constants in the generic expression depends on the number of or the kind of a complexity of the system which we are going to consider ok.

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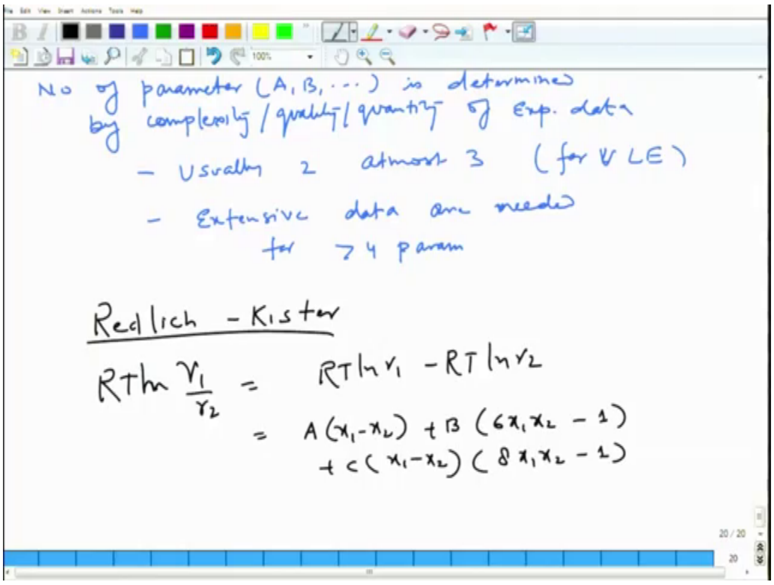

No of parameter (A, B, ...) is determined by complexity / quality / quantity of Exp. data

- Usually 2 atmost 3 (for VLE)
- Extensive data are needed for > 4 param

Redlich - Kister

$$RT\ln\frac{\gamma_1}{\gamma_2} = RT\ln\gamma_1 - RT\ln\gamma_2$$

$$= A(x_1-x_2) + B(6x_1x_2-1) + C(x_1-x_2)(8x_1x_2-1)$$

So, in other word this number of parameters A B C is determined by complexity, quality and quantity of what experimental data. Remember we are trying to fit with the experimental data to get the information between the system so.

Now, what we consider? Usually only two variables or at most 3 for really kind of exercises ok; Anything beyond 4 parameters requires extensive extensive experimental data ok. So, let me first draw for the Redlich-Kister. So, Redlich-Kister expression from here ok, this is the generic expression. So, what I can do is basically instead of writing this without solving the expression I am going to write down the generic expression of Redlich-Kister. So, RT ln gamma 1 by gamma 2 nothing but RT ln gamma 1 minus RT ln gamma 2 and from here you can do the mathematics you know rearrange everything and so that we can avoid here and I can simply write this expression as.

So, point is that these are the expression which are little complicated and thus we do not have to remember this. But having understanding of what was the origin of this at least appreciates little more then simply giving you or using this you know my just like standalone expressions. So, now, you have these expressions is just to give an idea of what this A B C contributes.

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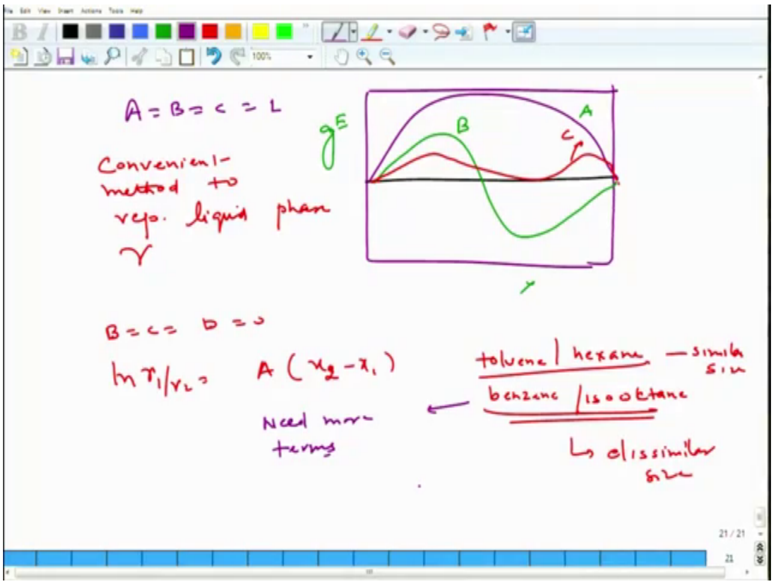

What I am going to do is I am going to draw A is equal to B is equal to C for the case of this where we consider equal values, all right. So, just to give you that how different these different groups or the component of this expression contributes to the g of e, so this is let us say 0 ok, and you have x 1 of the variable x. So, I am just going to draw it that for the case of A B C equal to 1 this is how it is looking like for the case of A.

Student: Sir, with respect to x.

Yeah, with respect to x here and this is the one for b and this is c its not perfect the way the experimental data would be, but just to give you an idea that these contributions are non-trivial ok. Now, as far as this is concerned this Redlich-Kister is concerned it is a convenient method to represent liquid phase gamma ok.

Now, note that if I have to consider B is equal to C is equal to D equal to 0 because there could be other terms also ok, then ln gamma 1 by gamma 2 would be simply k times x 2 minus x 1 and it is straight line. So, for simple system where you have a similar size the way we have used for one constant Margules equation you can also use the same way for similar system such as toluene hexane benzene iso-octane ok, for the case of this is a similar size ok. So, it works well for the case of this is dissimilar size. So, it does not work and thus here in this case you need more terms.

So, in other word one thing which is clear to you should be that if you have the data of the experiment then you should be able to derive or calculate the activity coefficients as a function of composition ok.

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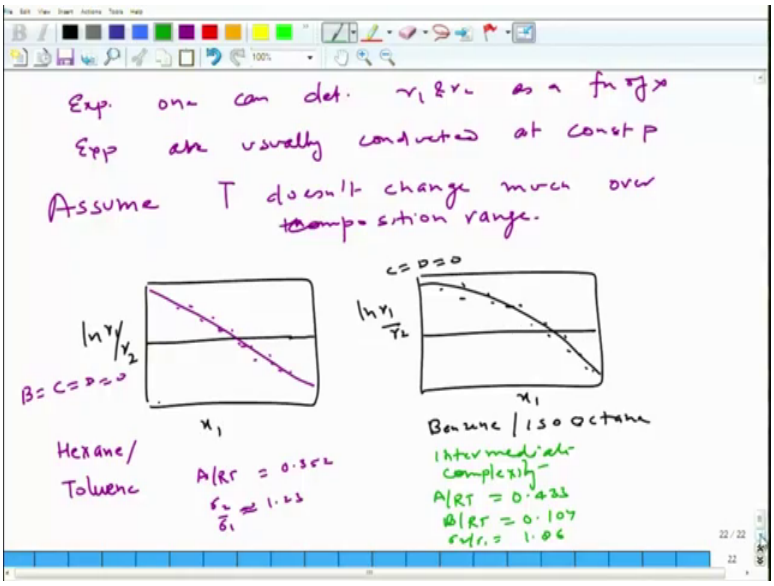

Exp. one can det. γ_1 & γ_2 as a fn of x

Exp are usually conducted at const P

Assume T doesn't change much over ~~t~~composition range.

So, experimentally one can determine gamma 1 and gamma 2 as a function of x ok, usually this expression should be at constant temperature what you have seen here this.

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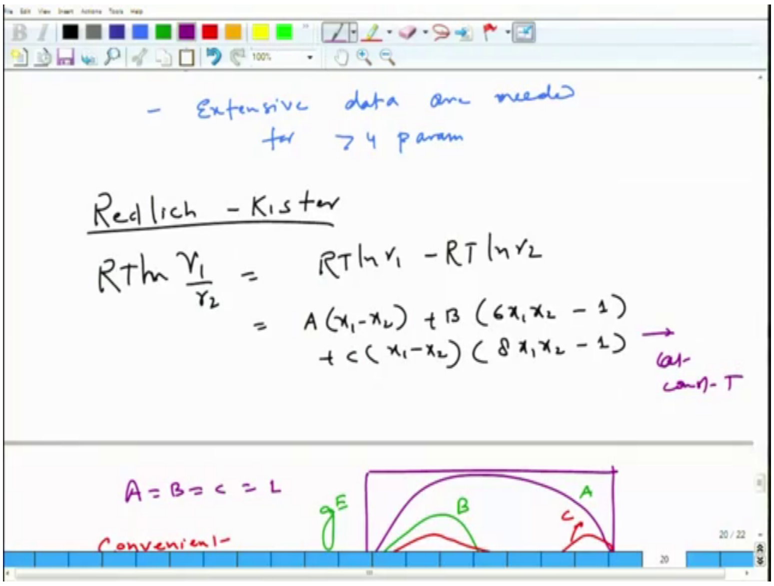

- Extensive data are needed for > 4 param

Redlich - Kister

$$RT \ln \frac{\gamma_1}{\gamma_2} = RT \ln \gamma_1 - RT \ln \gamma_2$$
$$= A(x_1 - x_2) + B(6x_1x_2 - 1) + C(x_1 - x_2)(8x_1x_2 - 1) \rightarrow \text{at const. T}$$

$A = B = C = L$

Convenient

This is supposed to be at constant T, but in practice the temperature is varying and thus we consider that you know it is valid in the other thing is usually the experiments are conducted at an usually conducted at constant pressure.

So, what we assume in this case? Assume that T does not change over the composition much because of course, there will be this much changes in the temperature over composition. Now, let me just give you a flavour of this again A B C for different kind of systems and how does it look like if you plot this ln gamma 1 gamma 2.

So, again this is x 1, gamma 1, gamma 2 ok. Now, this is the case of hexane toluene ok. So, in this case as we said that we can consider B C D is equal to 0 ok, and this log 1, log gamma 1 gamma 2 will be a straight line and its beautifully the data as if whatever the datas in the experiment between falls along it which clearly tells you that you know it is a good approximation because your one data is able to fit where a by RT is 0.352, if we want to understand the sizes if sigma represents the sizes then its approximately 1.23 ok. So, so effectively they almost close to each other.

Now, if you consider as I said the benzene and iso-octant I said these are not good enough because these are dissimilar size all right. Because the ratio of the sigma is around 1.86, so in this case let us look at how the datas looks like ok. So, again here C is equal to D is equal to 0 ok, so I am not I am, so I am going to consider B also in this case the two two parameters. So, it is something like this and the data is pretty good, pretty much well fitted to these things again this is x 1.

So, this is your benzene iso-octane where we have considered two two constants here and so this is in low-complexity this will be intermediate complexity right. Remember these are non-polar still we are not talking about hydrogen bond we are not talking about anything like that right. So, it is a still intermediate complexity where only the size can create such kind of complexity.

So, here if you look at A by RT it turns out to be 0.433, B by RT is equal to 0.104 and this data is some pressure range ok, it is not at constants some pressure is varying here and sigma difference is size this is 1.86 ok. So, if you want to fit this using this of course, you can clearly see that this is not going to be well fitted. So, you need to include second constant here.

Now, let us look at little more complications where you have hydrogen bond also ok.

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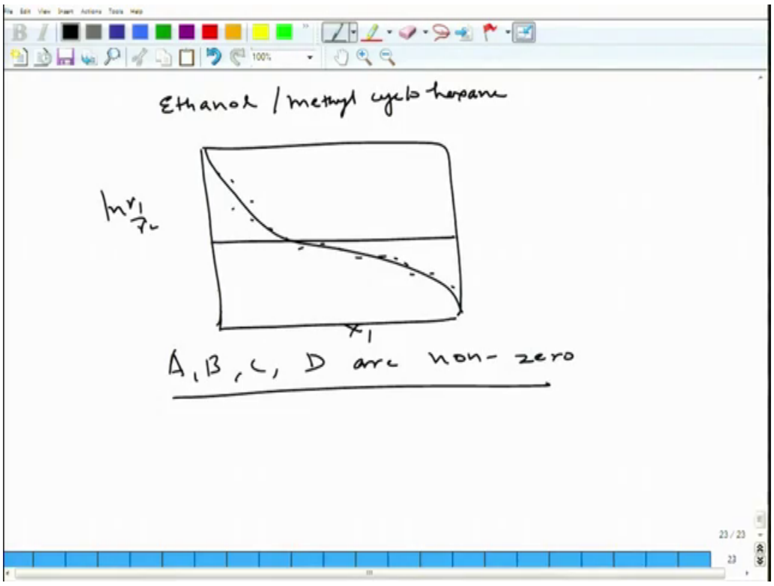

Ethanol / methyl cyclo hexane

A, B, C, D are non-zero

So, I will consider the case of ethanol and methyl cyclohexane ok. So, here you have this and then gamma 1 by gamma 2 x 1 ok. So, it is a complex shape and as well as the hydrogen bond methyl cyclohexane, complex shape and as well as the hydrogen bond, in this case you need 4 parameters and the way the data looks like is this ok. So, there is 4 parameters. So, in this case A B C D non-zero ok.

And of course, degree of hydrogen bond depends on the concentration the values may have more effect on it. More or less the message here was that that the number of terms in the expressions of g x there clearly depends on the molecular nature of the systems ok. So, you cannot randomly just use anything you have to understand the nature also in order to come up with the right kind of terms in the system.

So, now, you can clearly see right here that this kind of expression Redlich-Kister is coming directly from here and from here you can get a yeah Margules kind of equation also. Now, look at Wohl's expression term.

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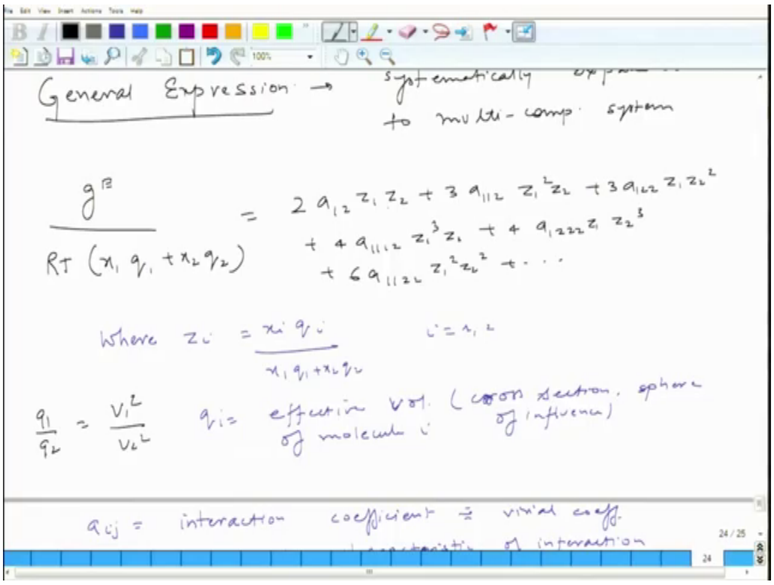

General Expression → systematically exp to multi-comp. system

$$\frac{g^E}{RT\,(x_1 q_1 + x_2 q_2)} = 2 a_{12} z_1 z_2 + 3 a_{112} z_1^2 z_2 + 3 a_{122} z_1 z_2^2 + 4 a_{1112} z_1^3 z_1 + 4 a_{1222} z_1 z_2^3 + 6 a_{1122} z_1^2 z_2^2 + \cdots$$

Where $z_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2}$ $i = 1, 2$

$\frac{q_1}{q_2} = \frac{v_1^L}{v_2^L}$ q_i = effective vol. of molecule i (cross section, sphere of influence)

a_{ij} = interaction coefficient ≑ virial coeff.

characteristic of interaction

So, let us we describe Wohl’s expression yeah. So, this is a general expression again which can be systematically expandable for multiple component system ok.

So, I will first let me just write it down and try to give an idea that why this is a very profound expression. See the expression looks like this, and it may look like to you very arbitrary, but there is a sound reason for all this term and I will just come back come back to that and explain you that and so forth ok.

So, what is Wohl’s did is basically it tried to explain or give a physical significance to model parameter remember this earlier we talked about A B C D. It is a function of temperature no less so, but effectively does not capture the typical sizes of the molecule and we know that the number of parameters which we require depends on the dissimilarity of the size shapes and other chemistry.

So, what Wohl’s tried is basically bring that some kind of physical representation of the system. So, what it did is that it it expressed the Gibbs free energy of binary solution as a power series in z ok, which is the effective volume fraction of each component. So, what is a z? So, we considering only binary component here right where q i; So, this is the effective volume fraction of the component.

What is q i? q i is effective volume or you know or you know, so this would be nothing but cross section of our section of sphere of influence right, the defining exactly the molecular size you know. So, we are trying to make use of that concept. So, this is effective volume of let us say molecule i, ok.

So, what, so if you look at the expression this expression is nothing on the right hand side if you look at it this is effectively as a function of z which is nothing, but the volume fraction of each component. So, this is look at this is a volume fraction it is like a weighted volume fraction right.

Now, let me just spend bit more time here. This is the effective one, and if you are bit concerned that where these terms comes into why there is a 2 here, why there is a 3 here, let us look at it. This is basically you assume that your system is filled with two types of particles one is 1, other is 2.

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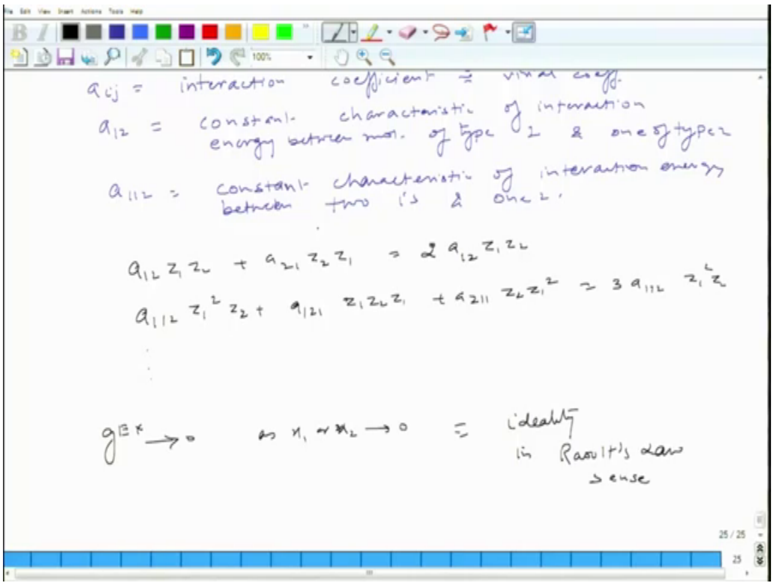

a_{ij} = interaction coefficient ≑ virial coeff.

a_{12} = constant characteristic of interaction energy between mol. of type 1 & one of type 2

a_{112} = constant characteristic of interaction energy between two 1's & one 2.

$$a_{12} z_1 z_2 + a_{21} z_2 z_1 = 2 a_{12} z_1 z_2$$

$$a_{112} z_1^2 z_2 + a_{121} z_1 z_2 z_1 + a_{211} z_2 z_1^2 = 3 a_{112} z_1^2 z_2$$

$$\vdots$$

$g^{EX} \to 0$ as x_1 or $x_2 \to 0$ ≡ ideality in Raoult's law sense

Now, a is basically is a ij is nothing but interaction coefficient which one can model as virial coefficient ok. So, let us ask this question what is a 12 this is going to be a constant ok, constant which is basically nothing, but characteristic of interaction energy between molecule of type 1 and one of type 2 ok; And a 112 would be, so a 12 is basically simply between 1 and 2. Now, a 112 means they were two of type 1 and one of type 2.

So, that is the effective interaction between them. So, this will be a constant characteristic of interaction energy between two 1's and one 2 ok, right.

So, this number the prefix of these two comes from this combinatorial factors. So, for example, if you look at it here a 12 multiplied by z 1 z 2 effective volume fractions. This plus A 21 z 2 z 1 this is considered to be same and that is why you have A 12 z 1 z 2 ok.

Similarly, we can consider a 112 z 1 square there two of type 1, one of type 2 and this is 2 plus a 121 z 1 z 2 z 1 plus a 211 z 2 z 1 square. So, this is basically 3 combination we have for having two of type 1 and one of type 2 and if you come up with different combination this is the way you want to write it and these are going to be all same z 1 square z 2 ok. Similarly, you can come up with the other terms.

So, these numbers which you are getting is basically coming from the combinatorial approach to a 12 z 1, so 3; a 112 z 1 z 2 square. Now, if you consider two of type 2 another type 2 means you will be having the same prefix 3 and it will this means z 1 z 2 square. If you have 4 of type you know 4 particles 3 of type 1 and two of type 1 you can show this to be like this.

So, this is the basic the idea this is how Wohl's have come with the expansion of g in terms of the effective volume fractions of molecules ok, it will continue. So, this is the expansion we considering. That is how the what we are doing is in similar way virial coefficient works well why the virial coefficients are there first if you look at the carefully B stand for two particle, C stand for 3 particle, D stand for 4 particles. So, D present the entire effective virial coefficient of having 4 particle contribution to the equation of state, right.

So, similarly here the similar concept has been used where this different groups of particles of different combination contributes to the excess free energy Gibbs excess free energy right, in the same form. Of course, the question is how far we would like to go and practically we cannot go beyond certain place. So, that is what different possible models we have to consider.

Now, one model suggest that if you can simply consider let us say for binary mixture q 1 q 2 simply is molar volume ratios because q what is q, q is effective volume. So, if we just consider molar volume, but that is one approximation we can consider. So, let me just elaborate more on this.

Now, note that in that expression which have written it goes to 0 as x 1 or x 2 goes to 0 which essentially means that this general expression of Wohl's is basically the considering the ideality in the Raoult's law sense ok. So, now, if you would like to consider g x in terms of the Henry's law and you have to come up with a different expressions ok. So, when you consider the Henry's law then we will be writing something like this.

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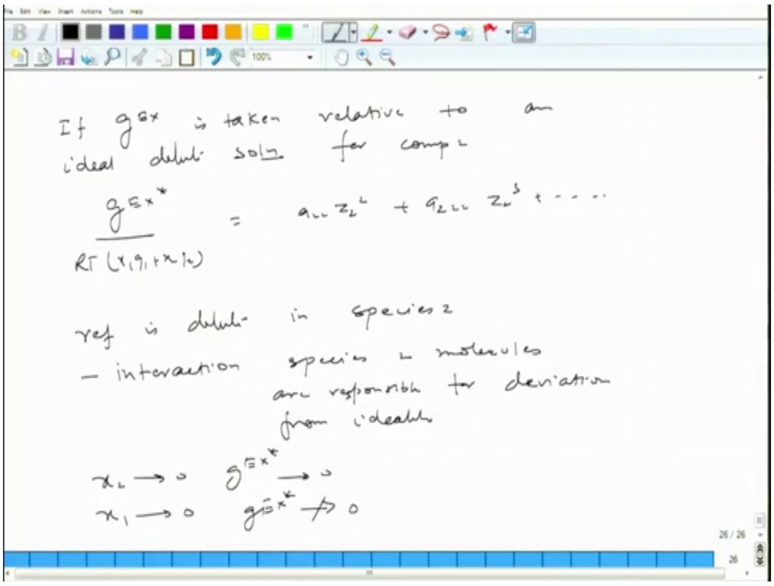

If g^{Ex} is taken relative to an ideal dilute soln for comp 2

$$\frac{g^{Ex^*}}{RT(x_1q_1+x_2q_2)} = a_{22}z_2^2 + a_{222}z_2^3 + \cdots$$

ref is dilute in species 2

– interaction species 2 molecules are responsible for deviation from ideality

$x_2 \rightarrow 0 \quad g^{Ex^*} \rightarrow 0$

$x_1 \rightarrow 0 \quad g^{Ex^*} \not\rightarrow 0$

So, if g x is taken relative to an ideal dilute solution for component 2 then you will going to write like this star RT x 1 q 1 x 2 q 2 and the right hand side is little different. Any idea why this is different? So, any idea why I am not considering other combination; so, g x is right. So, it is already dilute in component 2 ok.

So, it is a dilute solution. So, any deviation is due to the interaction between 22 not between 11 or 12. So, this is why they any because the excess right. So, any deviation is basically due to the due to the interactions between that two particles.

So, when I said reference is dilute in species 2, that means interaction among species 2 molecules are responsible for deviation from ideality ok. So, in this case you are going to consider for x 2 equal to 0, g x putting star is going to 0 and x 1 goes to 0, g x is not equal to 0 because when disappear the other one g x will be 0, but not this one right ok. So that means, the idea behind introducing Wohl's I will take in a next lecture, examples of special consideration for getting Van Laar equations ok, and the other one Scathard Hamer’s equations ok.

So, I will stop here. I will see you in the next lecture.