Advanced Thermodynamics
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Lecture-21
Models for Excess Gibbs Energy – 2

Welcome to the MOOCs course advanced thermodynamics, the title of this lecture is models for excess Gibbs energy part 2 since it is a continuation of previous lecture, and we will be having a kind of recapitulation of what we have seen in previous lecture. In the previous lecture, we were discussing Wohl's expansion and then by applying some kind of limiting conditions or restrictions, we reduced Wohl's expansion to the Van Laar equation.

Or otherwise we derived Van Laar equation by making some kind of simplification to this Wohl's expansion that is what we have seen and then for those Van Laar equation we have also developed in our activity coefficients etc., those things we have seen and those things we have seen for binary system. Then not only from the Wohl's expansion part of you, but also individually also we have derived.

The Van Laar equation and then cross check that we were getting the same Van Laar equation from the Wohl's expansion as well. So now what we do in this lecture, we will be obtaining Margules equations and then sketch out models equations etc. for excess Gibbs energy from this same Wohl's expansion that we have written for a binary mixture. So, let us start with Margules equation.

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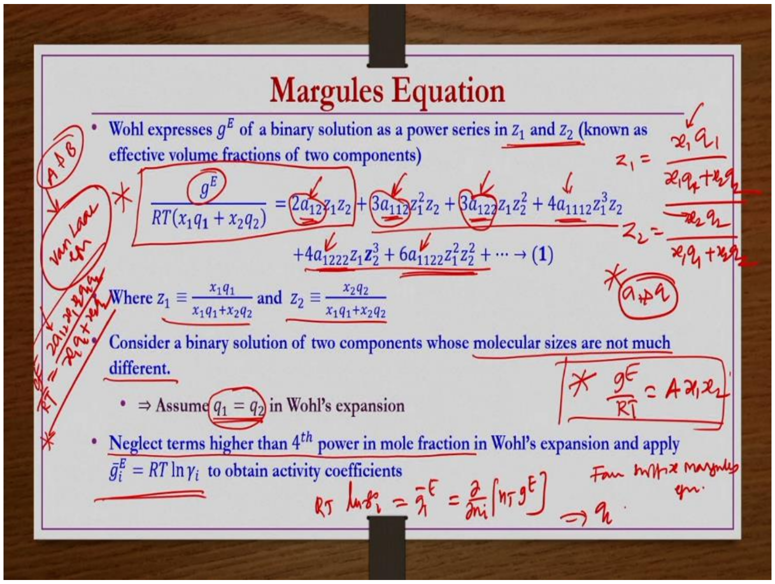

Margules Equation

- Wohl expresses g^E of a binary solution as a power series in z_1 and z_2 (known as effective volume fractions of two components)

$$\frac{g^E}{RT(x_1q_1 + x_2q_2)} = 2a_{12}z_1z_2 + 3a_{112}z_1^2z_2 + 3a_{122}z_1z_2^2 + 4a_{1112}z_1^3z_2 + 4a_{1222}z_1z_2^3 + 6a_{1122}z_1^2z_2^2 + \cdots \rightarrow (1)$$

Where $z_1 \equiv \frac{x_1q_1}{x_1q_1+x_2q_2}$ and $z_2 \equiv \frac{x_2q_2}{x_1q_1+x_2q_2}$

- Consider a binary solution of two components whose molecular sizes are not much different.
  - ⇒ Assume $q_1 = q_2$ in Wohl's expansion
- Neglect terms higher than 4th power in mole fraction in Wohl's expansion and apply $\bar{g}_i^E = RT\ln\gamma_i$ to obtain activity coefficients

A→B

Van Laar eqn

$z_1 = \frac{x_1q_1}{x_1q_1+x_2q_2}$

$z_2 = \frac{x_2q_2}{x_1q_1+x_2q_2}$

$q_1 \neq q_2$

$\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2}$

$\frac{g^E}{RT} = Ax_1x_2$

$RT\ln\gamma_i = \bar{g}_i^E = \frac{\partial}{\partial n_i}[n_T g^E]$

From here Margules eqn.

$\Rightarrow q_1$

Before directly going into the Margules equation, what we do we will have a kind of recapitulation of what is this Wohl's expansion because from this Wohl's expansion only, we are trying to get all the details. Wohl express this excess Gibbs energy of a binary solution as a power series of z_1 and z_2. This z_1, z_2 are known as nothing but our effective volume fractions of 2 component notice also we have seen.

And then this g^E for binary solution they have written as a kind of power series of z_1 and z_2 and then $z_1 = \frac{x_1q_1}{x_1q_1+x_2q_2}$ this is what we have seen and $z_2 = \frac{x_2q_2}{x_1q_1+x_2q_2}$. q_1, q_2 are nothing the but the size of the molecules that are present trendy species 1 species 2 respectively x_1 and x_2 are nothing but the mole fraction of that particular component 1 and 2 that are present in the liquid solution.

This is what we have seen. So, then what is this expansion that we have seen the $\frac{g^E}{RT(x_1q_1+x_2q_2)} =$ this one we have written only up to 4th power terms only we have written. And then this series continuous actually where that z_1 is given by this one and z_2 is given by this one. They indicate the effective volume fraction of 2 components further this a_{12} and then a_{112} a_{122} a_{1112} etc.

Whatever these a parameters are there they indicate the interaction they indicate the kind of interaction between those molecules. Let us say a_{12} indicate the interaction between 1 molecule of species 1 and then another molecule of species 2 similarly, a_{112} indicates the interaction between

2 molecules of component 1 and then 1 molecule of component 2 like that, all these a parameters are indicating.

So, primarily this is having 2 constants a and then q types of constant it is having these are the kind of some kind of significance it is having from the interactions point of view. So that is the reason it is one of the you know, better expansion though it is not having a kind of strong theoretical background to derive it unless we make some kind of drastic assumptions and it is having 2 constants a and then q types of constants.

Constant q indicates the size of the molecules. And constant a indicate some kind of interaction amongst the molecule, if you consider binary solution of 2 components whose molecular sizes are not much different that is when you take a $q_1 = q_2$ in Wohl's expansion then when we neglect terms higher than the 4th power in mole fractions. So, actually we are having terms in this expansion we are not having any terms more than 4th power.

So, we are having only up to 4th power terms if you include all these terms and then you write $q_1 = q_2$ because we are taking for molecular sizes are not much different then whatever this expansion is still that is nothing but 4 suffix Margules equations and then once we have this one you apply this when RT ln $\gamma_i = \bar{g}_i{}^E$ then simplify this $\bar{g}_i{}^E = \left[\frac{\partial}{\partial n_i}(n_T . g^E)\right]$.

So, this g^E is nothing but the right hand side multiplied by $RT(x_1q_1 + x_2q_2)$ that if you substitute here differentiate and simplify. Then you will get and then you equate that one part to the RT lnγ_i. So, then you will get expression for ln γ_i for 4 suffix Margules equation.

Remember in previous lecture what we have done we have taken only up to this part that is we have taken, only you know terms which are having you know z_1^1 and z_2^1 only that is we have not taken any 3rd power or higher power terms we have not taken that is what we have done 1 simplification another simplification we have done you know $q_1 \neq q_2$ then whatever this expression simplified expression that we got. You know we call it as a kind of Van Laar equation.

Which was also having 2 constants A and B are A' B' constants only we were having like those constants again written in terms of this a_1 to q_1, q_2 etc. in those only we have written this A B constant. So, from this point of view, if you take only this part of equation $\frac{g^E}{RT(x_1q_1+x_2q_2)} = 2a_{12}\, z_1z_2$ and then z_1 z_2 also if you substitute with these things and then simplify then you will get $\frac{g^E}{RT}=\frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2}$ that is what you get.

You should write $\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2}$ this is what you get when you take only up to 2nd power terms and then not taking higher power terms then substituting z_1 z_2 then $\frac{g^E}{RT}$you get this 1 this is nothing but Van Laar's equation. And then here you see it is kind of to this a_{12} q_1 q_2 3 parameters are there but you know activity coefficient when you derived you got only 2 parameters A and B.

Because they are you know, this ratio of q_1 and q_2 we have taken rather taking individually q_1 q_2, because in general we have also same the ratio of this molecular sizes molar volume of this component is much more important compared to the individual size of this molecule. So, that is the reason we are having this term. So, this was the Van Laar equation that we have seen in the previous lecture.

And then corresponding ln γ_1 and ln γ_2 also we have derived we have seen some examples as well. Then, not only from all the expansion individually from the physics of the problem point of view also when to pure liquid solutions are mixed at temperature pressure T and pressure P and forming is solution non ideal solution it same temperature and pressure same temperature T and pressure P then whatever the process that you have done.

You have taken in 3 step processes and then derive that same Van Laar equation again. So, then you got the same equation, so, that we also we have seen. So, now, in this equation we are starting with Margules equation. So, rather starting with 2 suffix Margules equation which we have already seen previously 2 suffix Margules equation is nothing but $\frac{g^E}{RT}= A\, x_1\, x_2$ this is what 2 suffix Margules equation.

This we have seen in one of the previous lecture, but we rather going with the simplest 1 what we are doing we are taking Trafford 1 that is up to 4th power in mole fraction those terms will be including and then we what we do gradually, we come back to the smaller level that is 3 suffix and then 2 suffix Margules equation by making some alternative you know by making some kind of adjustment or simplifications.

Adjustment simplification instance let us say you are taking up 4th power series than it is 4 suffix Margules equation you should take only up to 3rd power in mole fraction then it will be 3 suffix Margules equation. So, those kinds of things would be there here that is the only difference. If you take only up to 2 power series in mole fraction then further taking $q_1 = q_2$ then you will get the 2 suffix Margules equation.

Which would be same as $\frac{g^E}{RT}$ = A x_1 x_2 a would be function of a_{12} q_1 q_2 etc. Now, in the Margules equation what we have the all q_i q_j is are same that is $q_1 = q_2$. So, we are taking same sized molecules so, when you do the thing.

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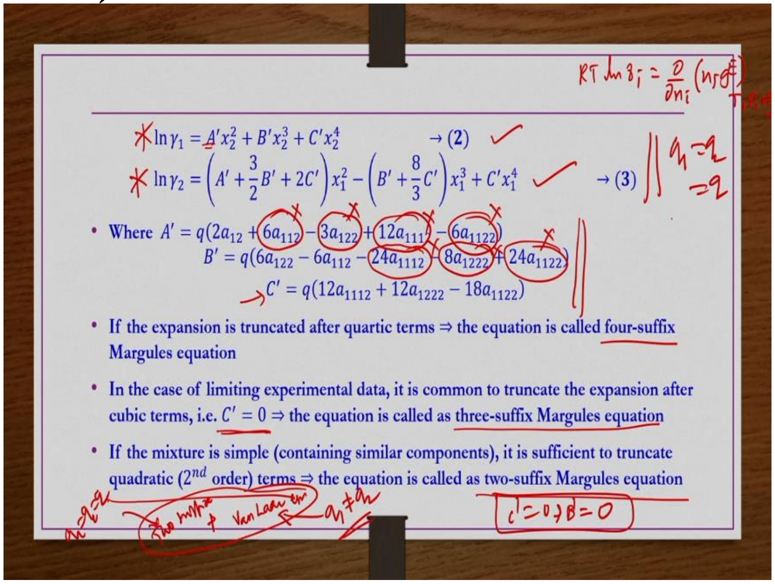

$RT \ln \gamma_i = \frac{\partial}{\partial n_i}(n_T g^E)_{T,P,n_j}$

$$\ln \gamma_1 = A' x_2^2 + B' x_2^3 + C' x_2^4 \rightarrow (2)$$

$$\ln \gamma_2 = \left(A' + \frac{3}{2}B' + 2C'\right)x_1^2 - \left(B' + \frac{8}{3}C'\right)x_1^3 + C' x_1^4 \rightarrow (3)$$

$q_1 = q_2 = q$

- Where $A' = q(2a_{12} + 6a_{112} - 3a_{122} + 12a_{1112} - 6a_{1122})$
  $B' = q(6a_{122} - 6a_{112} - 24a_{1112} - 8a_{1222} + 24a_{1122})$
  $C' = q(12a_{1112} + 12a_{1222} - 18a_{1122})$
- If the expansion is truncated after quartic terms ⇒ the equation is called four-suffix Margules equation
- In the case of limiting experimental data, it is common to truncate the expansion after cubic terms, i.e. $C' = 0$ ⇒ the equation is called as three-suffix Margules equation
- If the mixture is simple (containing similar components), it is sufficient to truncate quadratic (2nd order) terms ⇒ the equation is called as two-suffix Margules equation

$q_1 = q_2$

Two suffix Van Laar eqn

$q_1 \neq q_2$

$C' = 0, B' = 0$

And then you try to obtain the ln γ_1 and then ln γ_2 for that expression whatever that we have written Wohl's expansion in power series by retaining the 4th power terms of small fraction as well. And then by applying this RT ln γ_i = $\left[\frac{\partial}{\partial n_i}(n_T . g^E)\right]_{T,P,n_j}$ this when you apply and then you do for binary mission come having component 1 into, then you will get ln γ_1 this one ln γ_2 as this one.

I am not doing it you can take it as a kind of practice because such a simple differentiation and then rearrangement of the components then here rather writing these parameters constants as you know, a_{12} a_{122} a_{112} etc. those kind of parameters. We are writing A' B' C' because this A' B' C' are again related to this A parameters and then q parameters. Remember in this case what we are taking $q_1 = q_2 = q$.

So, A' is nothing but $q\ (2\ a_{12} + 6\ a_{112} - 3\ a_{122} + 12\ a_{1112} - 6\ a_{1122})$ and then B' is nothing but $q\ (6\ a_{122} - 6\ a_{112} - 24\ a_{1112} - 8\ a_{1222} + 24\ a_{1122})$ this is what you get and then C' is simply $q\ (12\ a_{1112} + 12\ a_{1222} - 18\ a_{1122})$. Now, this A point of view also the suffix of A, we can understand this a_{1112} that means it is including the interaction between 4 molecules and then 4 nearest molecules being 3 from the molecule 1, 3 from component 1 and then 1 molecule from component 2 that is what it means.

And then this indicates an interaction between 4 nearest molecules out of which 3 are from component 2 and 1 is from component 1. And then this indicates you know, interaction amongst 4 molecules out of which 2 molecules are from component 2 and 2 molecules are from component 1. So this is what we understand same is like this. So that means if you do not include this C and then include only this A' and B'.

So then it will become 3 suffix Margules equation. And then if you include only A' and then you do not include any of the other things then it will become 2 suffix Margules equation. And then also when you say including only A'. So, 2 suffix Margules equation that means only this whatever these terms will also be disappearing they will not be present because 2 suffix Margules equation takes interaction only between 2 molecules only.

The 3 suffix Margules equation, then interaction because of you know, because of interaction between 3 molecules will also come into the picture. So, under such conditions what happens you know, let us say 3 suffix Margules equation if you take then this term would be there in here and this one would also be there. This one would also be there, but these 2 will not be there because for 4th power we are not including terms.

And then B also this term would be there, this term would be there, these 2 terms would not be there. Even these 3, 3rd term will also not be there. And then this will not be there at all this whatever this cross now. I am showing those terms would be there, if you are including or if you are expanding if you are having the Wohl's series up to 4th power of mole fractions, then only this cross terms will also be there.

Otherwise only the tick terms would be there. So, that will become 3 suffix Margules equation, if you include the cross term also then that will become this 4 suffix Margules equation. Let us say if you have a 2 suffix Margules equation, so, these terms further they will reduce now, this will also be number all the a parameters with having 3 suffix will not be there ijk. So, if these things are not there.

So then that is 2 suffix Margules equation ijkl also but if only in addition to ijkl if you have a_{xyz} these things also if you do not have then that is a kind of 2 suffix Margules equation, if you have a_{xyz} and then a_{pq} this kind of comes from just indicating the suffix differently. So, that to understand then it is known as the 3 suffix Margules equation. If you have only a suffix pq kind of term then it is 2 suffix Margules equation.

If you have all these a_{pq} kind of interactions a_{xyz} kind of interaction and then a_{ijkl} kind of interaction then that is known as 4 suffix equation. So, that means that is including all these terms. So, this just to explain how this from 4th suffix Margules equation we can get back to the 3 suffix Margules equation and 2 suffix Margules equation that is the point of this description. If the expansion is truncated after quadratic terms.

The equation is called 4 suffix equation or 4 suffix Margules equation that is having all these A' B' C' terms. In the case of limiting experimental data is there and it is common to truncate the expansion after cubic terms, so, that means C' etc. those terms would be 0 if the C' is 0. So, then whatever the equation is did that is known as 3 suffix Margules equation not only C' as I mentioned.

All these parameters which are having the interaction these the 4^{th} power kind of thing these things will also be not there. Then in addition to this C', if you exclude in A'B' also whatever this cross term where the interaction amongst 4 molecules are shown, then that equation would become 3 suffix Margules equation. So, if the mixture is simple containing similar components it is sufficient to truncate quadratic terms.

That is second order terms, then the equation is called 2 suffix Margules equation that means, in under such conditions in addition to C' = 0, B' would also be 0 then we call it as a kind of 2 suffix Margules equation. In addition to this 1 in the A' will not be having these terms which are having, you know, interaction between 3 molecules. So in the 2 suffix Margules equation.

If you do not take $q_1 = q_2$ then we will be having kind of a Van Laar equation. So, what is the relation between Van Laar equation and then 2 suffix Margules equation rather relation what are the difference that point of view if you see 2 suffix equation we are taking $q_1 = q_2 = q$ whereas, in the Van Laar equation we are taking $q_1 \neq q_2$. So, that is the one primary difference between these 2 suffix Margules equation and Van Laar equation respectively.

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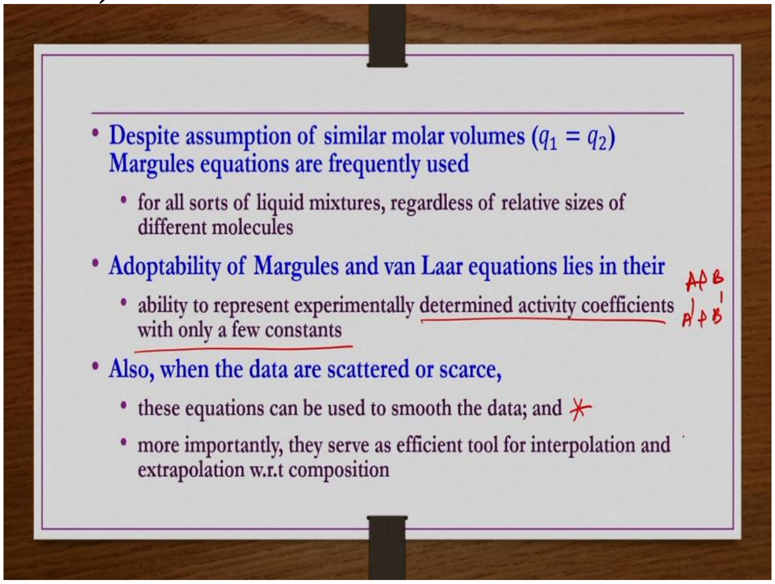

- Despite assumption of similar molar volumes ($q_1 = q_2$) Margules equations are frequently used
  - for all sorts of liquid mixtures, regardless of relative sizes of different molecules
- Adoptability of Margules and van Laar equations lies in their
  - ability to represent experimentally determined activity coefficients with only a few constants
- Also, when the data are scattered or scarce,
  - these equations can be used to smooth the data; and *
  - more importantly, they serve as efficient tool for interpolation and extrapolation w.r.t composition

$A \neq B$

$A' \neq B'$

Despite assumption of similar molar volumes that is $q_1 = q_2$ Margules equations are frequently used for all sorts of liquid mixtures regardless of relative sizes of different molecules and adaptability of Margules and Van Laar equation lies in their simplicity that ability to represent experimentally determined activity coefficient with only a few constants Van Laar equation also we are having only 2 constants A and B.

And then 3 suffix if you take only 3 suffix Margules equation then also we have only A' and B' 2 constants are sufficient to represent successfully the experimentally determined activity coefficient with respect to the mole fraction of the component. Also when the data is scattered scarce then this models whatever the 3 suffix Margules equation and then Van Laar equations are there.

So, they are used for smoothing of the data as well as for some kind of interpolation or extrapolation you know, so, that to get the data additional data which is not obtained by the experimental results. So such as T advantage of these 2 equations 3 suffix Margules equation and then Van Laar equation.

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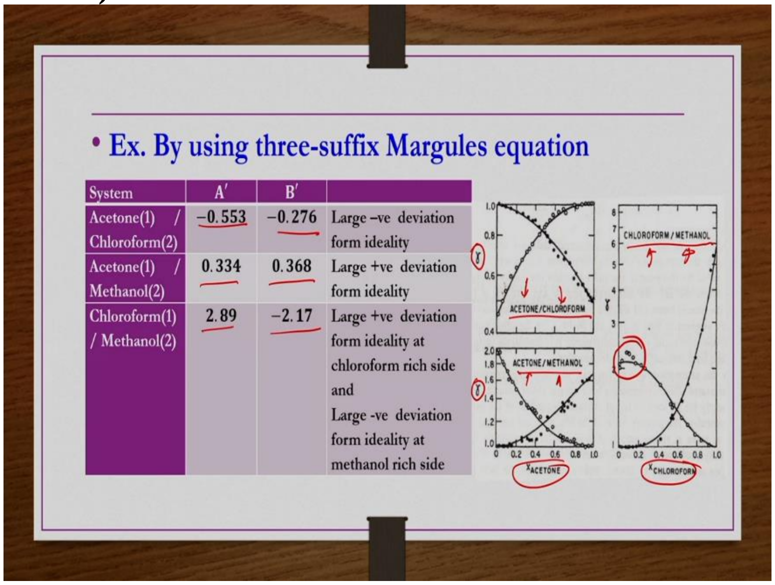

- Ex. By using three-suffix Margules equation

System	A'	B'	
Acetone(1) / Chloroform(2)	-0.553	-0.276	Large –ve deviation form ideality
Acetone(1) / Methanol(2)	0.334	0.368	Large +ve deviation form ideality
Chloroform(1) / Methanol(2)	2.89	-2.17	Large +ve deviation form ideality at chloroform rich side and Large -ve deviation form ideality at methanol rich side

Now by using 3 suffix Margules equation, we take 3 examples acetone, chloroform mixture and then acetone methanol mixture and then chloroform methanol mixture at 50 degrees centigrade. Then whatever this activity coefficient of acetone and then chloroform here in this case and then in this case acetone methanol and then in this case chloroform methanol versus mole fraction of one of the component is presented.

So, then you can see these circles or whatever this unfilled circular symbols are there. They indicate the experimental results and then the solid lines indicate the theoretical results or the 3 suffix

Margules results whatever we have. So that if you see you can see the excellent matching between these 3 suffix Margules equation and then experimental results of the entire range of a mole fraction from 0 to 1, except in this case of chloroform methanol.

Where there is a kind of some amount of discrepancy at x mole fraction of chloroform is very small. So, that is the advantage of these 3 suffix Margules equation and in previous lecture we have seen advantage of Van Laar equation where we have only 2 constants associated with this with the activity coefficient of these equations, but still we are able to represent experimental data with much better accuracy.

And remember all these 3 solutions show kind of azeotropic at certain temperature, you know, especially at 50 degrees centigrade close to that 1. Despite of that 1, you know, the ln γ_i versus x_i or x_i information has been successfully represented with 3 suffix Margules equation. Here we can see this A' B' parameters in the case of acetone, chloroform both are having negative that means large negative deviation from ideality.

And then acetone methanol mixture we can see both of them are positive A' B' values are there. So, that means large positive deviation from ideality is observed. So, in the case of chloroform and methanol, we see A' is positive and then B' is negative. What does it mean by towards the chloroform rich site we have a kind of positive deviation whereas towards the methanol rich site we have a kind of a negative deviation from the ideality. So, this is about you know 3 suffix Margules equation and there applicability comparative with the experimental results.

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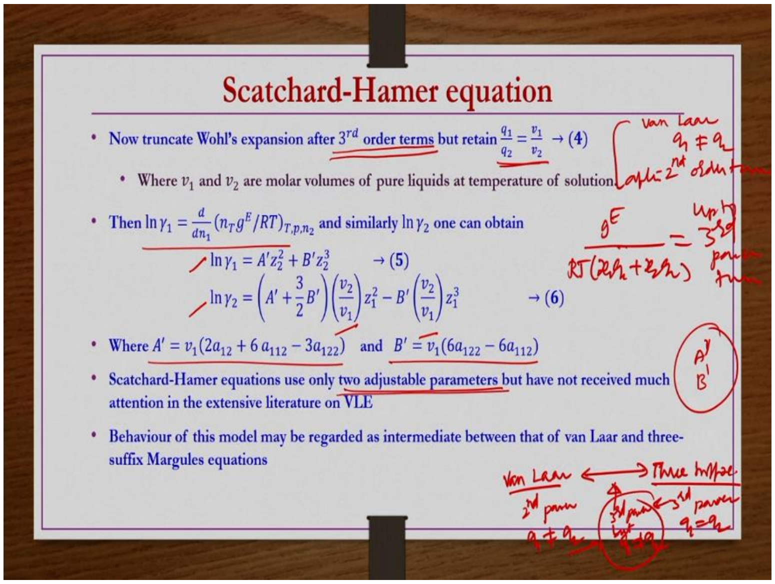

Scatchard-Hamer equation

- Now truncate Wohl's expansion after 3^{rd} order terms but retain $\frac{q_1}{q_2} = \frac{v_1}{v_2} \rightarrow (4)$
  - Where v_1 and v_2 are molar volumes of pure liquids at temperature of solution
- Then $\ln\gamma_1 = \frac{d}{dn_1}(n_T g^E/RT)_{T,p,n_2}$ and similarly $\ln\gamma_2$ one can obtain

$$\ln\gamma_1 = A'z_2^2 + B'z_2^3 \rightarrow (5)$$

$$\ln\gamma_2 = \left(A' + \frac{3}{2}B'\right)\left(\frac{v_2}{v_1}\right)z_1^2 - B'\left(\frac{v_2}{v_1}\right)z_1^3 \rightarrow (6)$$

- Where $A' = v_1(2a_{12} + 6\,a_{112} - 3a_{122})$ and $B' = v_1(6a_{122} - 6a_{112})$
- Scatchard-Hamer equations use only two adjustable parameters but have not received much attention in the extensive literature on VLE
- Behaviour of this model may be regarded as intermediate between that of van Laar and three-suffix Margules equations

Now, we take Scatchard-Hamer equation. Now the Wohl's expansion what we do we truncate expansion after 3rd order terms but will not be taking $q_1 = q_2$ rather we take $\frac{q_1}{q_2} = \frac{v_1}{v_2}$. That is if you compare with the Van Laar equation what we have taken we have taken $q_1 \neq q_2$ same thing we are doing here and then we have taken the terms are discarded terms after the 2nd order terms.

But now here we are taking the same $q_1 \neq q_2$ and then not only 2nd order terms, we are also including the 3rd order terms but truncating the terms after the 3rd order term. So, it is a kind of improvement over the Van Laar equation if you consider in terms of the interactions because higher terms are included compared to the Van Laar equation rest all assumptions are same $q_1 \neq q_2$ and all that.

In the Van Laar equation we have taken only up to 2nd order term, but now we are taking up to 3rd order term also. So, in that way if you see it is a kind of improvement over Van Laar equation but gradually if you see you know. It has it has not been found a better adaptability, especially with the experimental results unfortunately. Though it is a kind of improvement over Van Laar equation especially from Wohl's expansion point of view where we are taking up to 3rd order term as well in this Scatchard Hamer equation.

Despite Van Laar equation, we are taking only up to 2nd order term it is matching very well with the experimental results but here Scatchard Hamer equation though we are taking up to the 3rd order term the experimental matching is not so good. Where v_1 and v_2 are molar volumes of pure liquid at the temperature of the solution. Then if you apply this RT ln $\gamma_i = \left[\frac{\partial}{\partial n_i}\left(\bar{g}_i{}^E\right)\right]_{T,P,n_j}$ and then apply this.

Wohl's expansion whatever $\frac{g^E}{RT(x_1q_1+x_2q_2)}$ = up to 3rd order term or 3rd power terms, if you include those terms, if you simplify, you get the g^E and then you differentiate g^E with respect to n_1 and then the equate it to the RT ln γ_1 then you will get ln γ_1 this one. Similarly, if you do you get ln γ_2 this one, here we have A' B' terms. This A', B' terms and then in addition to that one.

We are also having v_1 by v_2 terms or v_2 by v_1 terms also there where this A', B' are nothing but given by these 2 equations $A' = v_1 (2\ a_{12} + 6\ a_{112} - 3\ a_{122})$ and $B' = v_1 (6\ a_{122} - 6\ a_{112})$. So this is what we get. And then this equation uses only 2 adjustable parameters like Van Laar equation and then 3 suffix Margules equation. Here also we have only 2 parameters.

But have not received much attention in the extensive literature on VLE. Unfortunately and then this can be seen as a kind of intermediate between Van Laar equation and then 3 suffix Margules equation because Van Laar it is including only 2nd power term only it is including 3 suffix Margules equation it is including 3rd power or, 3rd order terms also it is including. And then Van Laar equation we are not taking $q_1 = q_2$.

But in the 3 suffix Margules equation we are taking $q_1 = q_2$. So, this Scatchard Hamer equation is a kind of intermediate where we are taking up to 3rd order or 3rd power terms but $q_1 \neq q_2$. 1 part from here and then 1 part from here. So, that is the reason it is the kind of intermediate of this 1. Despite of that 1, it does not receive much attention in the literature. So, all these 3 equations are having 2 adjustable parameters A' and B'.

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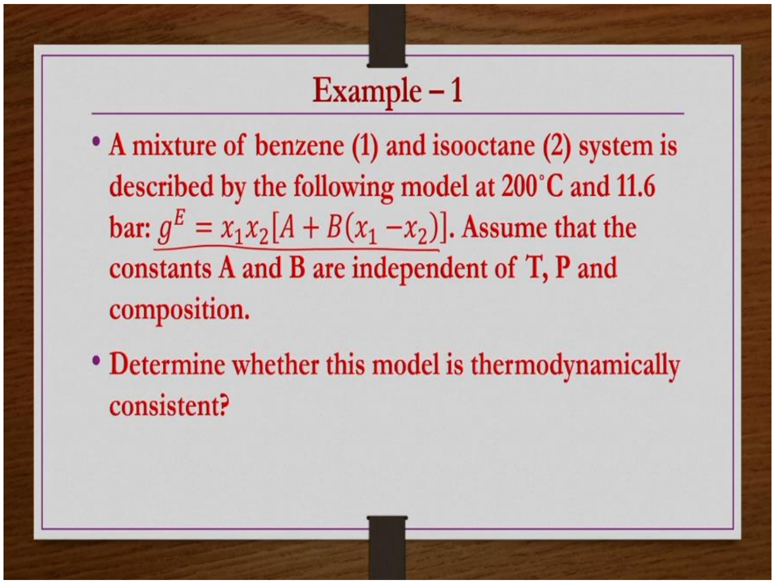

Example – 1

- A mixture of benzene (1) and isooctane (2) system is described by the following model at 200°C and 11.6 bar: $g^E = x_1x_2[A + B(x_1 - x_2)]$. Assume that the constants A and B are independent of T, P and composition.
- Determine whether this model is thermodynamically consistent?

So, that is about the Scatchard Hamer equation now, quickly we see a few example problems. So, a mixture of benzene and iso-octane system is described by this excess Gibbs energy function at 200 degrees centigrade and 11.6 bar. So, assume these constants A and B are independent of temperature, pressure and composition. So, describe whether that this model is thermodynamically consistent or not. So, though we have seen such kind of problems.

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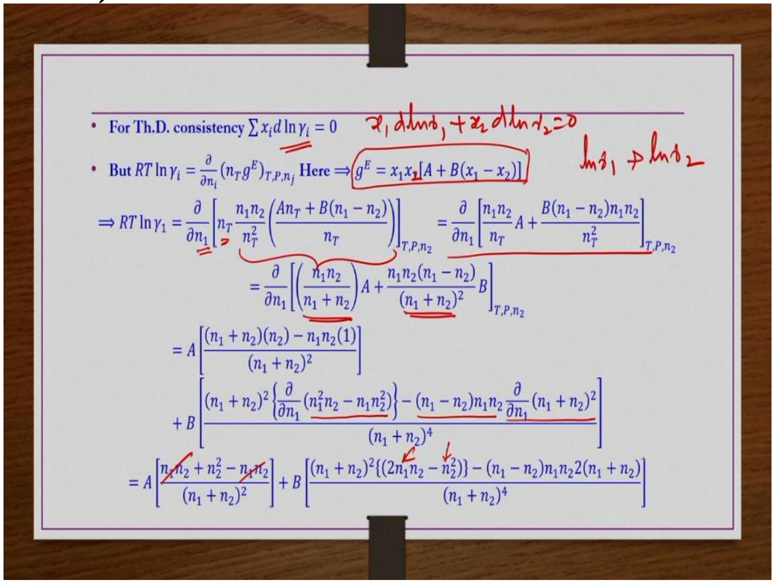

- For Th.D. consistency $\sum x_i d\ln\gamma_i = 0$ $x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0$
- But $RT\ln\gamma_i = \frac{\partial}{\partial n_i}(n_T g^E)_{T,P,n_j}$ Here $\Rightarrow \boxed{g^E = x_1x_2[A + B(x_1 - x_2)]}$ $\ln\gamma_1$ & $\ln\gamma_2$

$$\Rightarrow RT\ln\gamma_1 = \frac{\partial}{\partial n_1}\left[n_T\frac{n_1n_2}{n_T^2}\left(\frac{An_T + B(n_1 - n_2)}{n_T}\right)\right]_{T,P,n_2} = \frac{\partial}{\partial n_1}\left[\frac{n_1n_2}{n_T}A + \frac{B(n_1 - n_2)n_1n_2}{n_T^2}\right]_{T,P,n_2}$$

$$= \frac{\partial}{\partial n_1}\left[\left(\frac{n_1n_2}{n_1 + n_2}\right)A + \frac{n_1n_2(n_1 - n_2)}{(n_1 + n_2)^2}B\right]_{T,P,n_2}$$

$$= A\left[\frac{(n_1 + n_2)(n_2) - n_1n_2(1)}{(n_1 + n_2)^2}\right] + B\left[\frac{(n_1 + n_2)^2\left\{\frac{\partial}{\partial n_1}(n_1^2n_2 - n_1n_2^2)\right\} - (n_1 - n_2)n_1n_2\frac{\partial}{\partial n_1}(n_1 + n_2)^2}{(n_1 + n_2)^4}\right]$$

$$= A\left[\frac{\cancel{n_1n_2} + n_2^2 - \cancel{n_1n_2}}{(n_1 + n_2)^2}\right] + B\left[\frac{(n_1 + n_2)^2\{(2n_1n_2 - n_2^2)\} - (n_1 - n_2)n_1n_2 2(n_1 + n_2)}{(n_1 + n_2)^4}\right]$$

So we have them once again. So, thermodynamic consistency we know that sigma x_i d ln γ_i should be 0. So, here we are having 2 components. So, for the 2 components $g^E = x_1 x_2 [A + B(x_1 - x_2)]$. So, this is the g^E is given we need to know ln γ_1 and ln γ_2 because for these 2 components we have to see whether this x_1 d ln γ_1 + x_2 d ln γ_2 is becoming 0 or not that we have to check if it is becoming 0 then this model is thermodynamically consistent that is what we can see.

So, RT ln γ_i =$\left[\frac{\partial}{\partial n_i}(n_T.g^E)\right]_{T,P,n_j}$ or $\frac{\partial}{\partial n_i}(n_T.g^E)$is nothing but $\bar{g}_i{}^E$, $\bar{g}_i{}^E$is not given. So, that is the reason we are writing $\frac{\partial}{\partial n_i}(n_T.g^E)$. So, this $\frac{\partial}{\partial n_i}$now we are writing for component 1. So RT ln γ_1 = $\left[\frac{\partial}{\partial n_1}(n_T.g^E)\right]$is as it is this part is nothing but g^E and then g^E we are having x_1 x_2 terms that we are writing you know a kind of n_1 by n_T and then n_2 by n_T that is what we are having.

So, this parenthesis system A + B $\left[\frac{n_1}{n_T} - \frac{n_2}{n_T}\right]$. So, LCM when we do we have $\frac{An_T+B(n_1-n_2)}{n_T}$ and then in place of x_1 x_2 we have $\frac{n_1}{n_T}\frac{n_2}{n_T}$. So that is $\frac{n_1n_2}{n_T^2}$. So, now, further if you simplify we have $\left[\frac{\partial}{\partial n_1}\left(\frac{n_1n_2}{n_1+n_2}\right)A + \frac{n_1n_2(n_1-n_2)}{(n_1+n_2)^2}B\right]_{T,P,n_2}$ now differentiation of a, this term we have to do.

So, further n_T you can write n_1 + n_2 it will be easy to differentiate then we have wherever n_T. We are having we are writing n_1 + n_2 because we are differentiating with respect to n_1 and then n_T is nothing but n_1 + n_2. Then we have the differentiation of first term is you know n_1 + n_2 (1)$(n_2 - n_1)$ (1 + 0) / $(n_1 + n_2)^2$. Similarly, differentiation of this term is this denominator $(n_1 + n_2)^2$.

So, that is $(n_1 + n_2)^4$ and then in the numerator $(n_1 + n_2)^2$ and then differentiation of the numerator term $-$ numerator term as it is and then differentiation of denominator that is what we are having here. So, when we do this 1. So then what we have from the first term $\frac{n_1n_2+n_2^2-n_1n_2}{(n_1+n_2)^2}$. So, this is cancelled out and then here.

$(n_1 + n_2)^2$ is as it is differentiation of this 1 is 2 n_1 n_2 and then differentiation of this 1 is simply n_2^2 here $(n_1 - n_2)$ n_1n_2 is as it is differentiation of this term is 2 (n_1 + n_2)(1). So, 2 (n_1 + n_2). So, this is what we are having.

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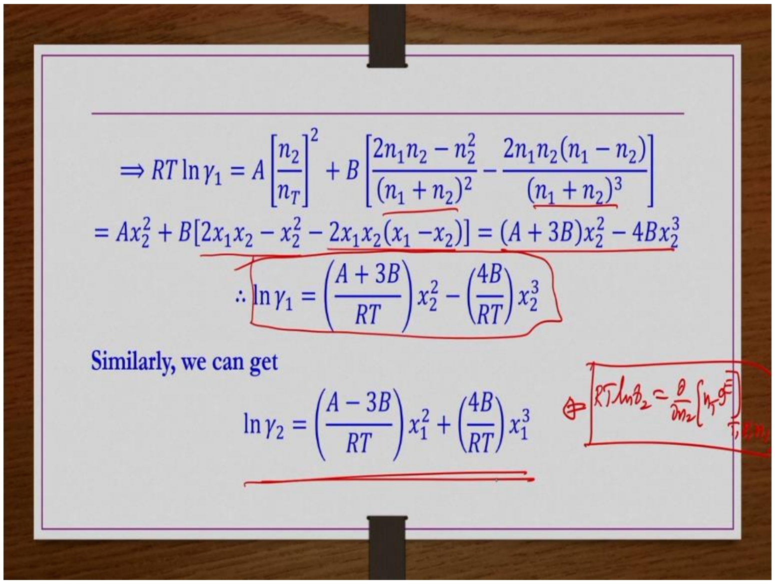

$$\Rightarrow RT\ln\gamma_1 = A\left[\frac{n_2}{n_T}\right]^2 + B\left[\frac{2n_1n_2 - n_2^2}{(n_1+n_2)^2} - \frac{2n_1n_2(n_1-n_2)}{(n_1+n_2)^3}\right]$$

$$= Ax_2^2 + B[2x_1x_2 - x_2^2 - 2x_1x_2(x_1-x_2)] = (A+3B)x_2^2 - 4Bx_2^3$$

$$\therefore \boxed{\ln\gamma_1 = \left(\frac{A+3B}{RT}\right)x_2^2 - \left(\frac{4B}{RT}\right)x_2^3}$$

Similarly, we can get

$$\ln\gamma_2 = \left(\frac{A-3B}{RT}\right)x_1^2 + \left(\frac{4B}{RT}\right)x_1^3$$

$$\boxed{RT\ln\gamma_2 = \frac{\partial}{\partial n_2}\left[n_T g^E\right]_{T,P,n_1}}$$

So, those terms we segregate like this. So, A$\left[\frac{n_2}{n_T}\right]^2$ + B $\left[\frac{2n_1n_2-n_2^2}{(n_1+n_2)^2} - \frac{2n_1n_2(n_1-n_2)}{(n_1+n_2)^3}\right]$ this is we are writing simply. So, that wherever it is n_T^2terms are there. So, n$_1$.n_T^2 you can write x$_1$ x$_2$ similarly $\left[\frac{n_2}{n_T}\right]^2$you can write x_2^2like that. So, for that purpose we have written like this.

So, then we have A x_2^2 + B [2 x$_1$ x$_2$ − x_2^2 − 2 x$_1$ x$_2$ (x$_1$ − x$_2$)] that is what we get when you simplify you will get $\left(\frac{A+3B}{RT}\right)x_2^2 - \left(\frac{4B}{RT}\right)x_2^3$. This is what you get. So, that means, ln γ$_1$=$\left(\frac{A+3B}{RT}\right)x_2^2 - \left(\frac{4B}{RT}\right)x_2^3$. So, ln γ$_2$ also similarly, we can obtain but analogously from here also we can write that ln γ$_2$ =$\left(\frac{A-3B}{RT}\right)x_1^2 + \left(\frac{4B}{RT}\right)x_1^3$. So, that is what you will get for ln γ$_2$.

Similarly, you can do other ways you know RT ln γ$_2$ = $\left[\frac{\partial}{\partial n_2}(n_T.g^E)\right]_{T,P,n_1}$ if you do and then simplify and then we will get our analogously if you how to the level that you can analogously then you can write this.

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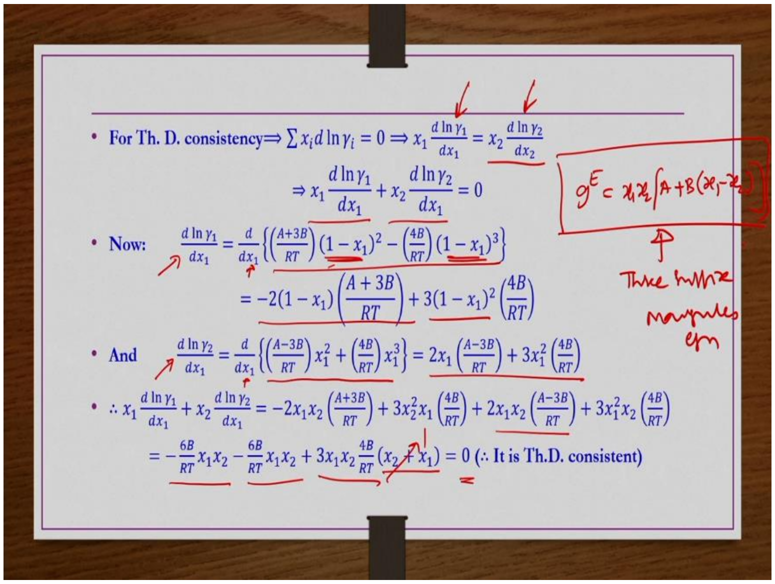

- For Th. D. consistency$\Rightarrow \sum x_i d\ln\gamma_i = 0 \Rightarrow x_1\frac{d\ln\gamma_1}{dx_1} = x_2\frac{d\ln\gamma_2}{dx_2}$

$$\Rightarrow x_1\frac{d\ln\gamma_1}{dx_1} + x_2\frac{d\ln\gamma_2}{dx_1} = 0$$

$g^E = x_1x_2[A+B(x_1-x_2)]$

Three suffix Margules eqn

- Now: $\frac{d\ln\gamma_1}{dx_1} = \frac{d}{dx_1}\left\{\left(\frac{A+3B}{RT}\right)(1-x_1)^2 - \left(\frac{4B}{RT}\right)(1-x_1)^3\right\}$

$$= -2(1-x_1)\left(\frac{A+3B}{RT}\right) + 3(1-x_1)^2\left(\frac{4B}{RT}\right)$$

- And $\frac{d\ln\gamma_2}{dx_1} = \frac{d}{dx_1}\left\{\left(\frac{A-3B}{RT}\right)x_1^2 + \left(\frac{4B}{RT}\right)x_1^3\right\} = 2x_1\left(\frac{A-3B}{RT}\right) + 3x_1^2\left(\frac{4B}{RT}\right)$
- $\therefore x_1\frac{d\ln\gamma_1}{dx_1} + x_2\frac{d\ln\gamma_2}{dx_1} = -2x_1x_2\left(\frac{A+3B}{RT}\right) + 3x_2^2x_1\left(\frac{4B}{RT}\right) + 2x_1x_2\left(\frac{A-3B}{RT}\right) + 3x_1^2x_2\left(\frac{4B}{RT}\right)$

$$= -\frac{6B}{RT}x_1x_2 - \frac{6B}{RT}x_1x_2 + 3x_1x_2\frac{4B}{RT}(x_2 + x_1) = 0 \ (\therefore \text{It is Th.D. consistent})$$

So, then for thermodynamic consistency, we have to see $x_1 \frac{\mathrm{dln}\gamma_1}{dx_1}$ + $x_2 \frac{\mathrm{dln}\gamma_2}{dx_2}$ should be 0. So, if you write in place of dx_1 − dx_2 because it is a binary system. So, $dx_1 + dx_2 = 0$ that means $dx_1 = -d\,x_2$. So then the term − $x_2 \frac{\mathrm{dln}\gamma_2}{dx_2}$ if you take to the right hand side, you will have $x_2 \frac{\mathrm{dln}\gamma_2}{dx_2}$. So, either way you can check you can do this 1.

And then you can do this 1 add them together to see whether it is 0 or not or otherwise individually you find out this 1 and this 1 you check if both of them are equal or not. So, $\frac{\mathrm{dln}\gamma_1}{\mathrm{d}x_1}$ is nothing but $\frac{\mathrm{dln}\gamma_1}{\mathrm{d}x_1} = \left(\frac{A+3B}{RT}\right)x_2^2 - \left(\frac{4B}{RT}\right)x_2^3$. In place of x_2 I am writing $1 - x_1$ because this differentiation I have to do with respect to x_1.

So, then you get this expression similar $\frac{\mathrm{dln}\gamma_2}{\mathrm{d}x_1}$ is nothing but $\frac{\mathrm{d}}{\mathrm{d}x_1}$ $\left\{\left(\frac{A+3B}{RT}\right)(1-x_1)^2 - \left(\frac{4B}{RT}\right)(1-x_1)^3\right\}$. So, here I have to differentiate with respect to x_1. So, what I am doing I am not writing this x_1 as 1 minus x_2 that is not required. So, we have this term. So, now, if you have $x_1 \frac{\mathrm{dln}\gamma_1}{\mathrm{d}x_1}$ + $x_2 \frac{\mathrm{dln}\gamma_2}{\mathrm{d}x_1}$. That means, if you multiply by this one x_1.

And then this one you multiply by x_2 and then simplify then you have these terms. So, when you simplify these terms you have you know from these 2 terms we have $-\frac{6B}{RT}$ x_1 x_2 remaining from this term you have a $-\frac{6B}{RT}$ and then from these 2 terms what you have if you take 3 x_1 x_2 as a common then 3 x_1 x_2 (x_1 + x_2) $\frac{4B}{RT}$. So, x_1 + x_2 is 1. So this is nothing but $\frac{12B}{RT}$ x_1 x_2 so this is$-\frac{12B}{RT}$ x_1 x_2 cancelled out. So, we have 0.

So, that means, we get since we get $x_1 \frac{d\ln\gamma_1}{dx_1} + x_2 \frac{d\ln\gamma_2}{dx_1} = 0$. We can say whatever the Gibbs function that is given $g^E = x_1 x_2 [A + B (x_1 - x_2)]$ is thermodynamically consist. And then this equation, if you recollect is nothing but is also known as 3 suffix Margules equation and then this activity coefficients are known as the corresponding activity coefficients of 3 suffix Margules equations.

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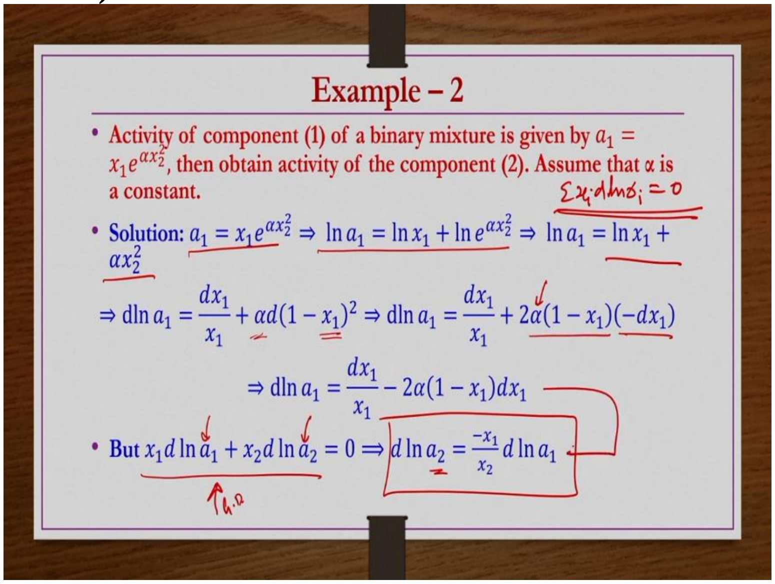

Example – 2

- Activity of component (1) of a binary mixture is given by $a_1 = x_1 e^{\alpha x_2^2}$, then obtain activity of the component (2). Assume that α is a constant.

$\Sigma x_i d\ln\gamma_i = 0$

- Solution: $a_1 = x_1 e^{\alpha x_2^2} \Rightarrow \ln a_1 = \ln x_1 + \ln e^{\alpha x_2^2} \Rightarrow \ln a_1 = \ln x_1 + \alpha x_2^2$

$$\Rightarrow d\ln a_1 = \frac{dx_1}{x_1} + \alpha d(1-x_1)^2 \Rightarrow d\ln a_1 = \frac{dx_1}{x_1} + 2\alpha(1-x_1)(-dx_1)$$

$$\Rightarrow d\ln a_1 = \frac{dx_1}{x_1} - 2\alpha(1-x_1)dx_1$$

- But $x_1 d\ln a_1 + x_2 d\ln a_2 = 0 \Rightarrow \boxed{d\ln a_2 = \frac{-x_1}{x_2} d\ln a_1}$

G.D

So, quickly we take another example in similar lines activity of component 1 of a binary mixture is given by $a_1 = x_1 e^{\alpha x_2^2}$ then obtain the activity of the component 2. So, what we have again we will be using $\sum x_i d\ln \gamma_i = 0$. This expression we use and then we try to obtain the activity of the 2nd component. So this, a_1 is given like this. So, what we are doing we are taking ln either side or then right hand side we are expanding. So, we have $\ln a_1 = \ln x_1 + \alpha x_2^2$.

Now, we need d ln a_1 in order to substitute here so ln a_i or ln γ_i also you can use this Gibbs Duhem equation is the same anyway. We need the ln a_1. So what we are doing the right hand side also we are doing differentiation. So, d ln x_1 is nothing but $\frac{dx_1}{x_1}$ + α is constant and then d x_2^2 is nothing but

2 multiply these x_2 what I am doing I am writing $1 - x_1$. So that we have $2\ (1 - x_1 - dx_1)$ will be having an α is constant as it is.

So that means d ln $a_1 = \frac{dx_1}{x_1} - 2\ \alpha\ (1 - x_1)\ d\ x_1$ this is what we can write. So actually $1 - x_1$ we can write x_2 that will write the next step. So but we have x_1 d ln a_1 + x_2 d ln $a_2 = 0$. This is also Gibbs Duhem equation. You can have in terms of activity coefficient or in terms of activity the same, so we need a_2. So, what we have what how we rearrange this equation we rearrange it has d ln a_2 = minus x_1 by x_2 d ln a_1. So, this equation, if you substitute here in place of d ln a_1.

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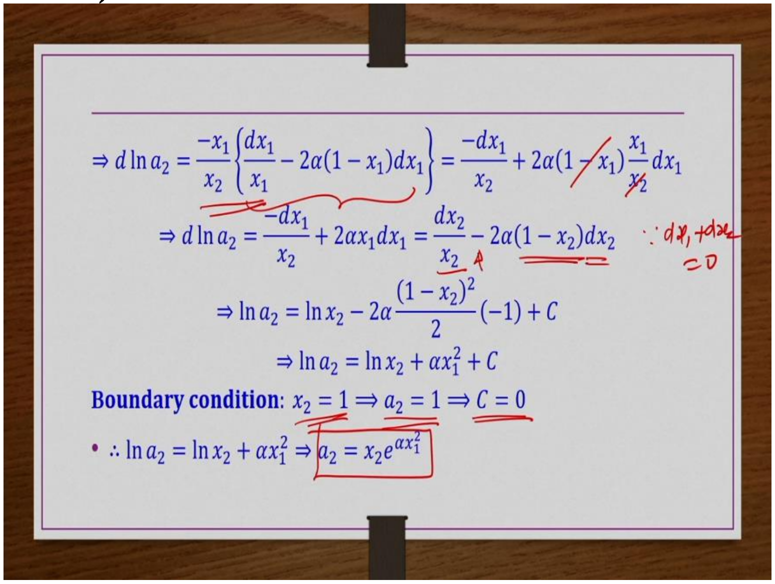

$$\Rightarrow d\ln a_2 = \frac{-x_1}{x_2}\underbrace{\left\{\frac{dx_1}{x_1} - 2\alpha(1-x_1)dx_1\right\}}_{} = \frac{-dx_1}{x_2} + 2\alpha\cancel{(1-x_1)}\frac{x_1}{\cancel{x_2}}dx_1$$

$$\Rightarrow d\ln a_2 = \frac{-dx_1}{x_2} + 2\alpha x_1 dx_1 = \frac{dx_2}{x_2} - 2\alpha(1-x_2)dx_2 \qquad \because dx_1 + dx_2 = 0$$

$$\Rightarrow \ln a_2 = \ln x_2 - 2\alpha\frac{(1-x_2)^2}{2}(-1) + C$$

$$\Rightarrow \ln a_2 = \ln x_2 + \alpha x_1^2 + C$$

Boundary condition: $x_2 = 1 \Rightarrow a_2 = 1 \Rightarrow C = 0$

- $\therefore \ln a_2 = \ln x_2 + \alpha x_1^2 \Rightarrow \boxed{a_2 = x_2 e^{\alpha x_1^2}}$

We have this expression $-\frac{dx_1}{x_2}$ d ln $a_2 = -\frac{x_1}{x_2}$ d ln a_1. This is d ln a_1 so first 2 terms when you joined together you have $-\frac{dx_1}{x_2}$ because x_1 and x_1 cancels out and then $-$ of – is + $2\ \alpha\ (1 - x_1)\frac{x_1}{x_2}$ d x_1 so this $1 - x_1$ and then is x_2 are same. So we have this expression, d ln $a_2 = -\frac{dx_1}{x_2} + 2\ \alpha\ x_1$ d x_1 so this one I am writing minus d x_1 when I am writing as d x_2. So $\frac{dx_2}{x_2} - 2\ \alpha\ (1 - x_2)$.

I am writing for x_1 and then in place of a d x_1 I am writing d x_2 $-$ dx. So that is the reason here minus we are getting because for binary system d x_1 + d x_2 = 0. So that it can easily be integrated that is the purpose we are writing in terms of any one. So that is in terms of x_2 we are writing so ln a_2 if you integrate above equation you get ln a_2 = ln $x_2 - 2\,\alpha\,\frac{(1-x_2)^{\,2}}{2}\,(-\,1)+ C$ that means ln a_2 = ln $x_2 + \alpha\, x_1^2$ + C.

And then when $x_2 = 1$, then activity should be 1 or activity should be equals to the mole fraction. So, mole fraction = 1 now, because when $x_2 = 1$ it is a pure solution. So, for pure solution is always ideal solution and then for ideal solution activities equals the mole fraction. So, that means a_2 = mole fraction and mole fraction here is nothing but 1. So, that you substitute here you get C = 0. So, that means, $a_2 = x_2\, e^{\alpha x_1^2}$ this is what you get. So, now, quickly we take another simple example problem before winding up this lecture,

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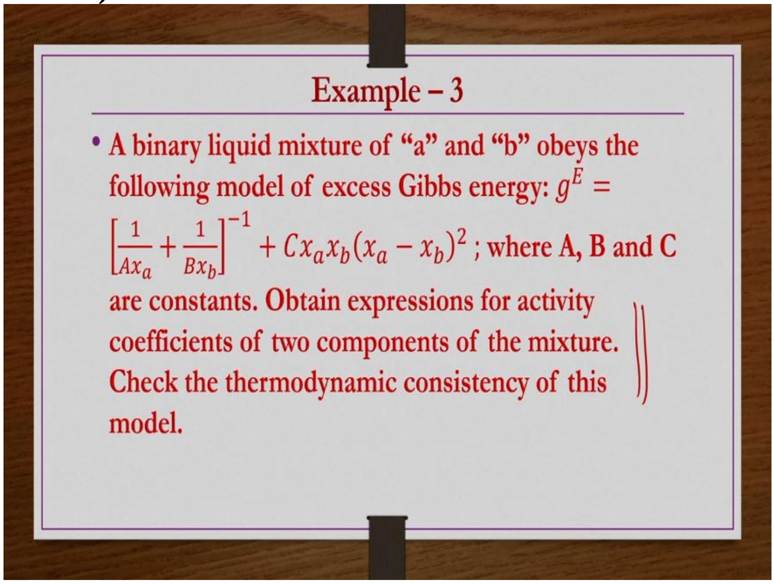

Example – 3

- A binary liquid mixture of "a" and "b" obeys the following model of excess Gibbs energy: $g^E = \left[\frac{1}{Ax_a} + \frac{1}{Bx_b}\right]^{-1} + Cx_ax_b(x_a - x_b)^2$; where A, B and C are constants. Obtain expressions for activity coefficients of two components of the mixture. Check the thermodynamic consistency of this model.

A binary liquid mixture of component a and b obeys the following model of excess Gibbs energy $g^E = \left[\frac{1}{Ax_a} + \frac{1}{Bx_b}\right]^{-1} + C\, x_a\, x_b\, (x_a\, -\, x_b)^{\,2}$, where A, B and C are constants. So, this question is again similar to example 1. So, first obtain the ln γ_a and then ln γ_b then check thermodynamic consistency is existing or not.

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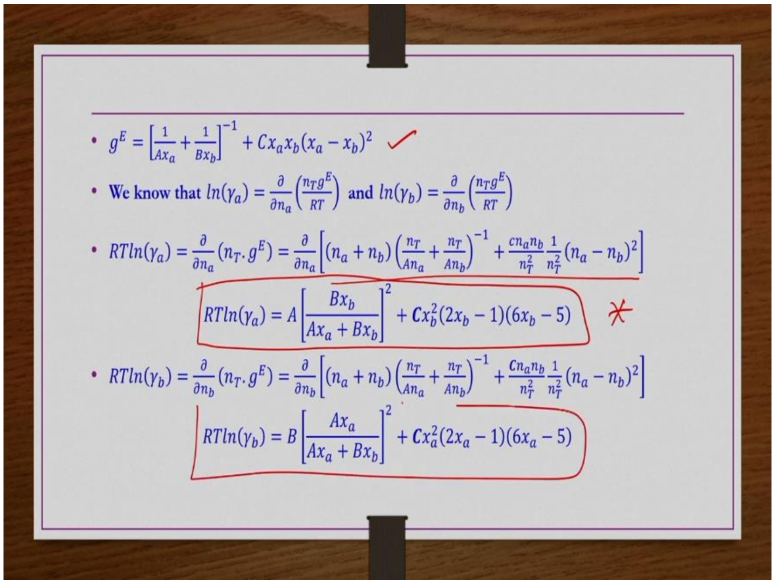

- $g^E = \left[\frac{1}{Ax_a} + \frac{1}{Bx_b}\right]^{-1} + Cx_a x_b (x_a - x_b)^2$ ✓
- We know that $ln(\gamma_a) = \frac{\partial}{\partial n_a}\left(\frac{n_T g^E}{RT}\right)$ and $ln(\gamma_b) = \frac{\partial}{\partial n_b}\left(\frac{n_T g^E}{RT}\right)$
- $RTln(\gamma_a) = \frac{\partial}{\partial n_a}(n_T . g^E) = \frac{\partial}{\partial n_a}\left[(n_a + n_b)\left(\frac{n_T}{An_a} + \frac{n_T}{An_b}\right)^{-1} + \frac{cn_a n_b}{n_T^2}\frac{1}{n_T^2}(n_a - n_b)^2\right]$

$$\boxed{RTln(\gamma_a) = A\left[\frac{Bx_b}{Ax_a + Bx_b}\right]^2 + Cx_b^2(2x_b - 1)(6x_b - 5)} \quad \ast$$

- $RTln(\gamma_b) = \frac{\partial}{\partial n_b}(n_T . g^E) = \frac{\partial}{\partial n_b}\left[(n_a + n_b)\left(\frac{n_T}{An_a} + \frac{n_T}{An_b}\right)^{-1} + \frac{Cn_a n_b}{n_T^2}\frac{1}{n_T^2}(n_a - n_b)^2\right]$

$$\boxed{RTln(\gamma_b) = B\left[\frac{Ax_a}{Ax_a + Bx_b}\right]^2 + Cx_a^2(2x_a - 1)(6x_a - 5)}$$

So, it is quite similar problem that we have already done. So, g^E is given by this one and then we know RT ln γ_a is nothing but $\frac{\partial}{\partial n_a}(n_T . g^E)$ and then RT ln γ_b is nothing but $\frac{\partial}{\partial n_b}(n_T . g^E)$ that is what we know. So, this g^E if you differentiate that is RT ln γ_a = $\frac{\partial}{\partial n_a}(g^E)$is this 1. So, this g^E we are differentiating with respect to n_a for ln γ_a purpose.

So, this enter equation rather writing in x_a x_b we are writing $x_a = \frac{n_a}{n_T}$ and then $x_b = \frac{n_b}{n_T}$ and n_T is total number of moles and n_a and n_b are nothing but the number of moles of A and B components present in the solution. Whereas x_a and x_b are nothing but the mole fraction of component A and B that are presented the solution. So, when you differentiate and then simplify.

We get this equation, I am not doing it because so, many of them we have already done so, you can take up and then try to do yourself. Similarly, RT ln γ_b = $\frac{\partial}{\partial n_b}(n_T . g^E)$if you do then you will get RT ln γ_b is this one simply differentiation and then rearrangement so straightforward one can get.

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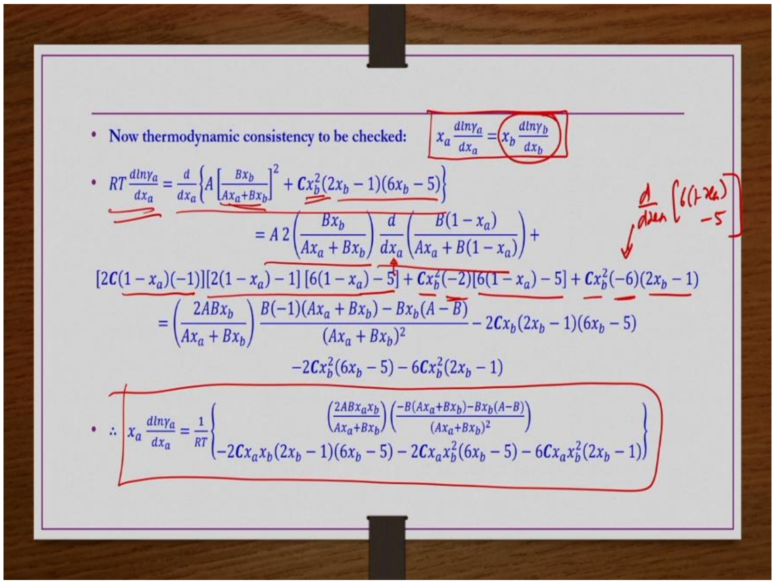

- Now thermodynamic consistency to be checked: $\boxed{x_a \frac{d\ln\gamma_a}{dx_a} = x_b \frac{d\ln\gamma_b}{dx_b}}$
- $RT \frac{d\ln\gamma_a}{dx_a} = \frac{d}{dx_a}\left\{A\left[\frac{Bx_b}{Ax_a+Bx_b}\right]^2 + Cx_b^2(2x_b-1)(6x_b-5)\right\}$

$$= A\,2\left(\frac{Bx_b}{Ax_a+Bx_b}\right)\frac{d}{dx_a}\left(\frac{B(1-x_a)}{Ax_a+B(1-x_a)}\right) +$$

$$[2C(1-x_a)(-1)][2(1-x_a)-1]\,[6(1-x_a)-5] + Cx_b^2(-2)[6(1-x_a)-5] + Cx_b^2(-6)(2x_b-1)$$

$$= \left(\frac{2ABx_b}{Ax_a+Bx_b}\right)\frac{B(-1)(Ax_a+Bx_b) - Bx_b(A-B)}{(Ax_a+Bx_b)^2} - 2Cx_b(2x_b-1)(6x_b-5)$$

$$-2Cx_b^2(6x_b-5) - 6Cx_b^2(2x_b-1)$$

- $\therefore\ \boxed{x_a \frac{d\ln\gamma_a}{dx_a} = \frac{1}{RT}\left\{\begin{matrix}\left(\frac{2ABx_ax_b}{Ax_a+Bx_b}\right)\left(\frac{-B(Ax_a+Bx_b)-Bx_b(A-B)}{(Ax_a+Bx_b)^2}\right)\\ -2Cx_ax_b(2x_b-1)(6x_b-5) - 2Cx_ax_b^2(6x_b-5) - 6Cx_ax_b^2(2x_b-1)\end{matrix}\right\}}$

$\frac{d}{dx_a}\left[6(1-x_a) - 5\right]$

So, now we can be how to do thermodynamic consistency check for that purpose. What we do we check sigma x_i d ln γ_i is 0 or not. So, that means $x_a \frac{d\ln\gamma_a}{dx_a}$ it should be $x_b \frac{d\ln\gamma_b}{dx_b}$. So, first term RT ln γ_a whatever we derived, so that one we are differentiating with respect to x_a. So $\frac{d}{dx_a}$, of right hand side RT ln γ_a term expression that previously we derived this 1. So, differentiation of this first term is nothing but 2 A $\left(\frac{Bx_b}{Ax_a+Bx_b}\right)\frac{d}{dx_a}$ of this particular term.

So, that is this one multiplied by $\frac{d}{dx}\frac{Bx_b}{Ax_a+Bx_b}$. I am differentiating with respect to x_a. So that is the reason all the x_b term I am writing $1 - x_a$ + C and then differentiation of this x_b^2 is nothing but 2 x_b (-1). So, x_b I am writing $1 - x_a$. So, $2(1 - x_a) - 1$ and then remaining 2 terms are as it is, but I am writing in place of x_b $(1 - x_a)$, I am writing.

Then C x_b^2 is remaining as it is differentiation of 2 multiplied by 2 $(x_b - 1)$ is nothing but 2 multiply $\frac{d}{dx}$ of $\frac{d}{dx_a}$ of $2(1 - x_a)$ that is -2 we are having that is $2(-1)$ and then 3rd term is as it is. Similarly, C x_b^2 and then 2 $(x_b - 1)$ term same and then differentiation of 3rd term that is $\frac{d}{dx_a}$by then differentiation of 3rd term that is $\frac{d}{dx_a}$of $6(1 - x_a) - 5$ is nothing but -6. So, that is what we are having.

Now, if you rearrange this equation, then you will get simply this term, quite ln in the term you do not need to further simplify any way, only thing that we have to see the other term $x_b \frac{d\ln\gamma_b}{dx_b}$ is also same or not and that is what we have to find out.

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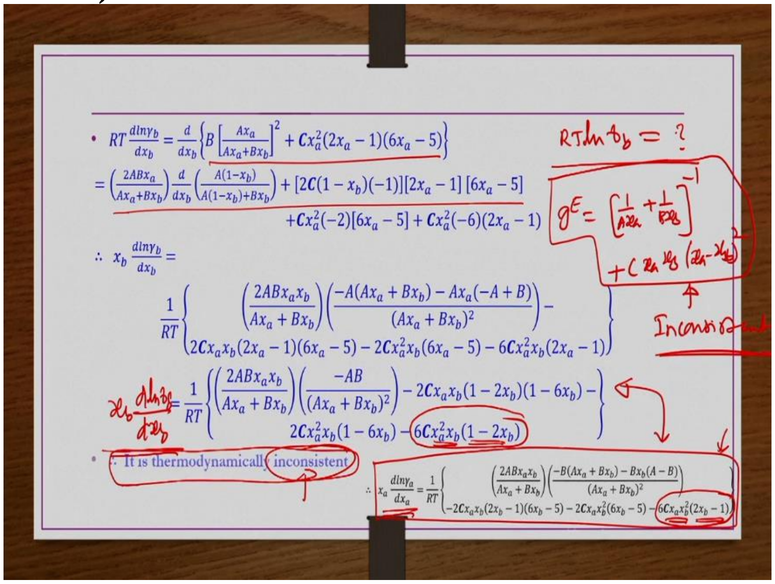

- $RT\frac{d\ln\gamma_b}{dx_b} = \frac{d}{dx_b}\left\{B\left[\frac{Ax_a}{Ax_a+Bx_b}\right]^2 + Cx_a^2(2x_a-1)(6x_a-5)\right\}$

$= \left(\frac{2ABx_a}{Ax_a+Bx_b}\right)\frac{d}{dx_b}\left(\frac{A(1-x_b)}{A(1-x_b)+Bx_b}\right) + [2C(1-x_b)(-1)][2x_a-1]\,[6x_a-5]$

$+Cx_a^2(-2)[6x_a-5] + Cx_a^2(-6)(2x_a-1)$

$\therefore\ x_b\frac{d\ln\gamma_b}{dx_b} =$

$$\frac{1}{RT}\left\{\begin{matrix}\left(\frac{2ABx_ax_b}{Ax_a+Bx_b}\right)\left(\frac{-A(Ax_a+Bx_b)-Ax_a(-A+B)}{(Ax_a+Bx_b)^2}\right)- \\ 2Cx_ax_b(2x_a-1)(6x_a-5)-2Cx_a^2x_b(6x_a-5)-6Cx_a^2x_b(2x_a-1)\end{matrix}\right\}$$

$$x_b\frac{d\ln\gamma_b}{dx_b} = \frac{1}{RT}\left\{\begin{matrix}\left(\frac{2ABx_ax_b}{Ax_a+Bx_b}\right)\left(\frac{-AB}{(Ax_a+Bx_b)^2}\right)-2Cx_ax_b(1-2x_b)(1-6x_b)- \\ 2Cx_a^2x_b(1-6x_b)-6Cx_a^2x_b(1-2x_b)\end{matrix}\right\}$$

- $\therefore$ It is thermodynamically inconsistent

$$\therefore\ x_a\frac{d\ln\gamma_a}{dx_a} = \frac{1}{RT}\left\{\begin{matrix}\left(\frac{2ABx_ax_b}{Ax_a+Bx_b}\right)\left(\frac{-B(Ax_a+Bx_b)-Bx_b(A-B)}{(Ax_a+Bx_b)^2}\right) \\ -2Cx_ax_b(2x_b-1)(6x_b-5)-2Cx_ax_b^2(6x_b-5)-6Cx_ax_b^2(2x_b-1)\end{matrix}\right\}$$

$RT\ln\gamma_b = ?$

$g^E = \left[\frac{1}{Ax_a}+\frac{1}{Bx_b}\right]^{-1} + C x_a x_b (x_a - x_b)$

Inconsistent

So, that we know so, whatever $x_a \frac{d\ln\gamma_a}{dx_a}$ we got I am rewriting here just because we need it for comparison for the next step. So, $\frac{d\ln\gamma_b}{dx_b}$. So, RT $\frac{d\ln\gamma_b}{dx_b}$ that we are doing so whatever the RT ln γ_b expression that we had previously derived that expression both sides we are differentiating with respect to x_b. So, right hand side this is what we have on $\frac{d}{dx_b}$of this term.

So, now, similar differentiation you do as we have done in the case of $\frac{d\ln\gamma_a}{dx_a}$. So, here we are doing this 2nd term we are doing differentiation with respect to x_b. So, we want to have all the terms in terms of x_b. So, wherever x_a is there that you can write $1 - x_b$ and then do the differentiation and then simplify. So, then you have this term this is nothing but x_b d ln x_b $\frac{d\ln\gamma_b}{dx_b}$.

Now, by comparing these 2 equations, this is $x_b \frac{d\ln\gamma_b}{dx_b}$and this is $x_a \frac{d\ln\gamma_a}{dx_a}$. This we derived previous slide we can see they are looking similar but they are not same, we can compare one term if one term is not matching that means you do not need to compare rest of the term take the simplest 1 last term here is 6 C $x_a^2 x_b$ $(1 - 2\ x_b)$.

Whereas here the last term is 6 C x_a x_b^2. So, here it is x_a x_b^2 here is it is $x_a^2 x_b$ and then here it is 2 $x_b - 1$ here it is $1 - 2$ x_b. So they are not same. So, they are not equal to each other. So, that means, we say it is thermodynamically inconsistent. You can say whatever the g^E expression is given that is $\left[\frac{1}{Ax_a} + \frac{1}{Bx_b}\right]^{-1}$ + C x_a x_b . And then what is that they have given. C x_a $x_b(x_a - x_b)^2$. So, whatever this given g^E form is thermodynamically inconsistent.

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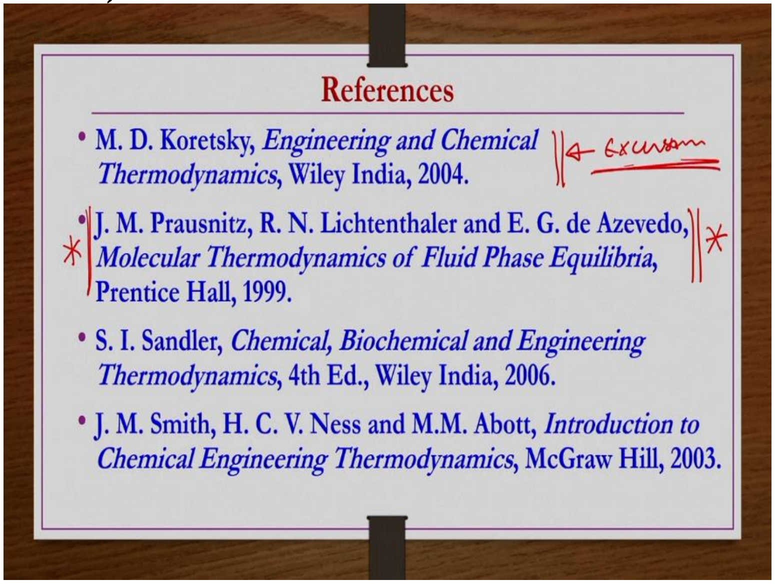

References

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References for this lecture are provided here engineering and chemical thermodynamics by Koretsky molecular thermodynamics of fluid phase Equilibria prentice hall and then chemical biochemical and engineering thermodynamics by Sandler an introduction to chemical engineering thermodynamics by Smith et al. This entire lecture is available in this reference book. Some of the problems that we have solved are exercise problems of this book Koretsky. Thank you.