Advanced Thermodynamics
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Lecture -27
Liquid - Liquid Equilibrium - 2

Welcome to the MOOCs course advanced Thermodynamics, the title of this lecture is liquid-liquid equilibrium part 2. Before going into the details of today's lecture we will be having a kind of recapitulation of what we have discussed in the previous lecture. In the previous lecture, we have discussed several aspects of thermodynamics of partially miscible systems and then what are the conditions for the instability? Instability in the sense when we add two individual liquid solutions to make a kind of a binary liquid mixture solution.

Is that mixture is going to form a kind of single phase solution or is it going to split into two phases that is what we have discussed and then conditions we have developed for those kind of partially miscible systems, what should be the condition if the system has to form partial miscible system those things we have seen and then this lecture will be discussing how to estimate the equilibrium composition of a liquid-liquid equilibrium problems.

So before going into the details of composition calculations of a liquid-liquid equilibrium problem will have a kind of recapitulation of thermodynamics of partial miscible systems that we have discussed in the previous lecture.

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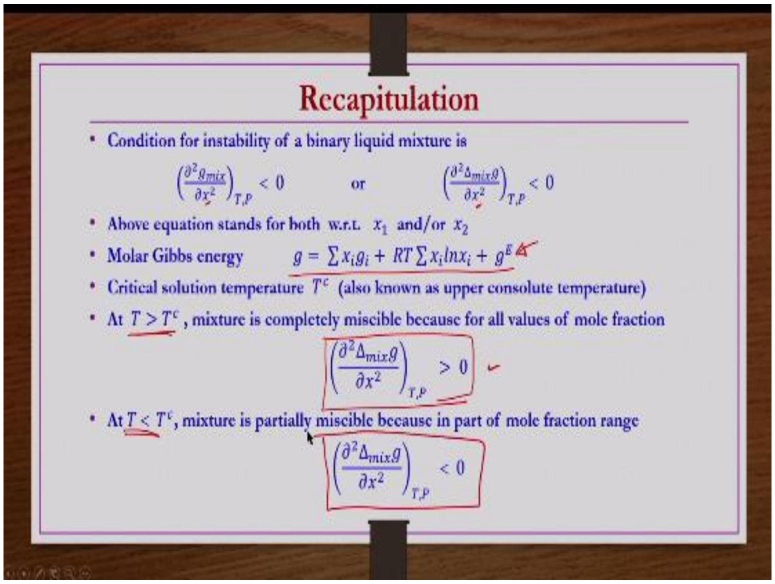

Recapitulation

- Condition for instability of a binary liquid mixture is

$$\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} < 0 \quad \text{or} \quad \left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} < 0$$

- Above equation stands for both w.r.t. x_1 and/or x_2
- Molar Gibbs energy $g = \sum x_i g_i + RT\sum x_i \ln x_i + g^E$
- Critical solution temperature T^c (also known as upper consolute temperature)
- At $T > T^c$, mixture is completely miscible because for all values of mole fraction

$$\boxed{\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} > 0}$$

- At $T < T^c$, mixture is partially miscible because in part of mole fraction range

$$\boxed{\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} < 0}$$

So condition for instability of a binary liquid mixture, we have developed as a $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} < 0$ if you obtain that one that should be less than 0, or $\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} < 0$ this is what we have seen and then this equation whether the differentiation you will do with respect to x_1 or x_2, it is same it is whole square both of them.

And then this condition we obtained by taking you know, Raul's law as a kind of reference state then whatever the g^E expression is therefore for those kind of expressions only we have developed this condition. That is this Gibbs energy of liquid binary liquid solution is defined with respect to the Raoult's law under such conditions then condition for instabilities $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} < 0$ or $\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} < 0$.

Then what is this g of the system that we have seen in nothing but $g = \sum x_i g_i + RT \sum x_i \ln x_i + g^E$. g^E is nothing but Molar Gibbs energy. And then if you take critical solution temperature or upper consolute temperature as T^c then if temperature T is greater than T^c are the system temperature or liquid binary liquid solution temperature is greater than this upper consolute temperature T^c then mixture is completely miscible.

Because for all values of mole fractions if T is maintained greater than T^c we will be getting always this $\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} > 0$. This is what we are going to get provided this temperature is greater than upper consolute temperature. So if it is less than then instability will be there again that will be forming a kind of partially miscible two phases.

So obviously in other words if the temperature is less than T^c less than the if the temperature if the system temperature is less than the upper consonant temperature then may make sure this partially miscible because for some part of mole fraction range what will be getting will be getting those $\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} < 0$ which is the condition for the instability.

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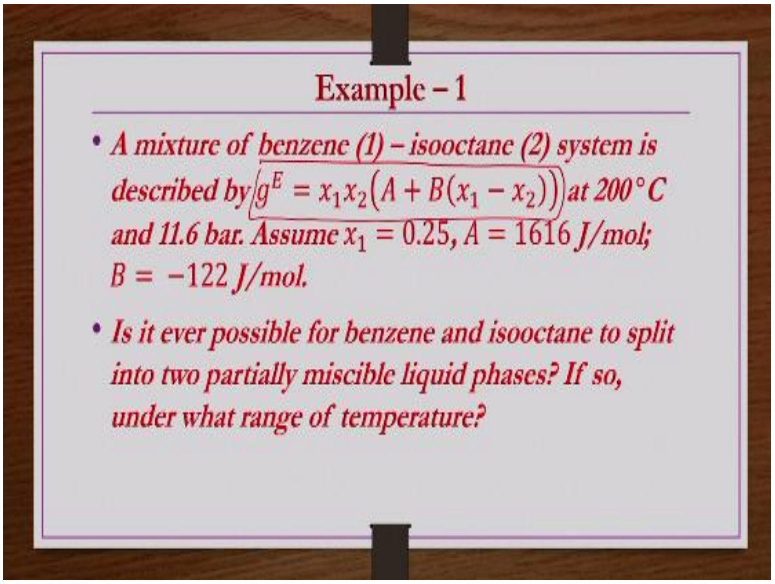

Example – 1

- *A mixture of benzene (1) – isooctane (2) system is described by* $\boxed{g^E = x_1 x_2 (A + B(x_1 - x_2))}$ *at 200°C and 11.6 bar. Assume* $x_1 = 0.25, A = 1616$ *J/mol;* $B = -122$ *J/mol.*
- *Is it ever possible for benzene and isooctane to split into two partially miscible liquid phases? If so, under what range of temperature?*

Example one a mixture of benzene and isooctane system is described by $g^E = x_1 x_2 (A + B (x_1 - x_2))$ at 200 degree centigrade and 11.6 bar. Assume $x_1 = 0.25$, A = 1616, B = - 122 joules per mole. Then question is, is it ever possible for benzene and isooctane to split into two partially miscible liquid phases, if so underwater range of temperature? That is the question.

So g is given by this equation, which is nothing but 3-suffix Margules equation, if the g^E is g^E of this particular system is described by 3-suffix Margules equation under what range of temperature are we going to get 2 partially miscible liquid phases.

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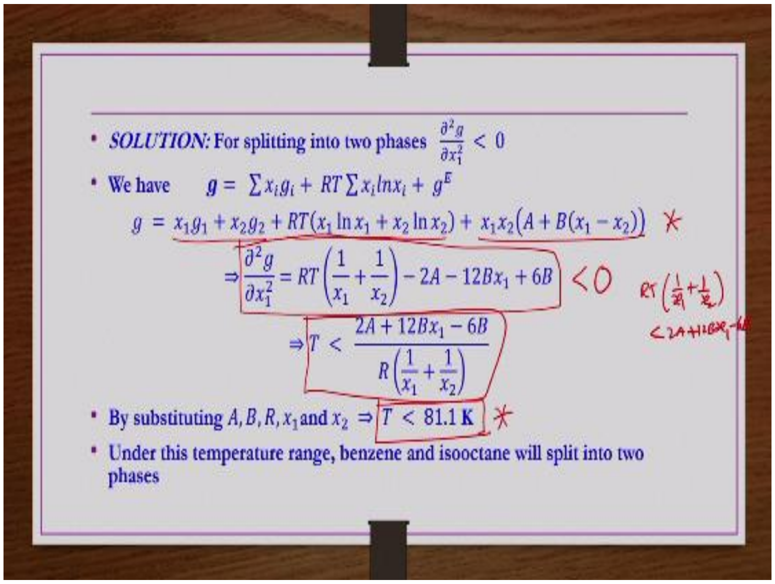

- ***SOLUTION:*** For splitting into two phases $\frac{\partial^2 g}{\partial x_1^2} < 0$
- We have $g = \sum x_i g_i + RT \sum x_i ln x_i + g^E$

$$g = \underline{x_1 g_1 + x_2 g_2 + RT(x_1 \ln x_1 + x_2 \ln x_2)} + \underline{x_1 x_2 (A + B(x_1 - x_2))} \quad *$$

$$\Rightarrow \boxed{\frac{\partial^2 g}{\partial x_1^2} = RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) - 2A - 12Bx_1 + 6B} < 0 \qquad RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 2A + 12Bx_1 - 6B$$

$$\Rightarrow \boxed{T < \frac{2A + 12Bx_1 - 6B}{R\left(\frac{1}{x_1} + \frac{1}{x_2}\right)}}$$

- By substituting A, B, R, x_1 and $x_2 \Rightarrow \boxed{T < 81.1\ \mathrm{K}}$ $*$
- Under this temperature range, benzene and isooctane will split into two phases

That is the question so first what we have to find out? We have to find out$\left(\frac{\partial^2 g}{\partial x^2}\right)_{T,P}$ and then we have to find out the condition for T if it is less than what then it is going to form a kind of partial immiscible system that we have to find out state simple and straightforward. So first splitting into two phases, we know that $\frac{\partial^2 g}{\partial x_1^2} < 0$ or $\frac{\partial^2 g}{\partial x_2^2} < 0$ then we can say that that will and that solution will split in 2 phases.

Two partially visible phases and then g we have defined as $\sum x_i g_i$ + RT $\sum x_i \ln x_i$ + g^E. This is with reference to the Raoult's law. Then this for a binary system of component 1 and 2 $\sum x_i g_i$ we can write x_1 g_1 + x_2 g_2 + RT $\sum x_i \ln x_i$ is nothing but RT $x_1 \ln x_1$ + $x_2 \ln x_2$ for a binary system and g^E is given by 3 suffix Margules equation that is $x_1 x_2$ (A + B (x_1 - x_2)).

Now what we have to do, this equation we have to partially differentiate with respect to x_1 two times. Then to $\frac{\partial^2 g}{\partial x_1^2}$you get as RT$\left(\frac{1}{x_1} + \frac{1}{x_2}\right)$- 2 A - 12 B x_1 + 6B. This is what we get $\frac{\partial^2 g}{\partial x_1^2}$. Now if the solution to split into phases are for instability what we should have we should have this one should be less than 0 that means whatever this RT$\left(\frac{1}{x_1} + \frac{1}{x_2}\right)$ <2 A + 12 B x_1 - 6 B or T < $\frac{2\text{ A} + 12\text{ B } x_1 - 6\text{ B}}{\text{R}\left(\frac{1}{x_1} + \frac{1}{x_2}\right)}$, this is what we get. So, if the system temperature T is less than the value whatever this value is there that is $\frac{2\text{ A} + 12\text{ B } x_1 - 6\text{ B}}{\text{R}\left(\frac{1}{x_1} + \frac{1}{x_2}\right)}$ this if you substitute the values of A B $x_1 x_2$ and R here and then see what is the value of this right hand side is coming of this inequality.

Then if the temperature is less than that number then we can say that under such range of temperature the solution is going to form a kind of partially miscible two phases. So if you substitute A B, R, x_1x_2 in this f of equation then you will get. T is less than 80.1 K. If the temperature of the system or mixing of this benzene and isooctane if you do at a temperature less than 81.1 Kelvin.

Then you are going to have a two partially miscible phases, they will not be completely miscible that is what it is. So under this temperature range benzene and isooctane will split into two phases.

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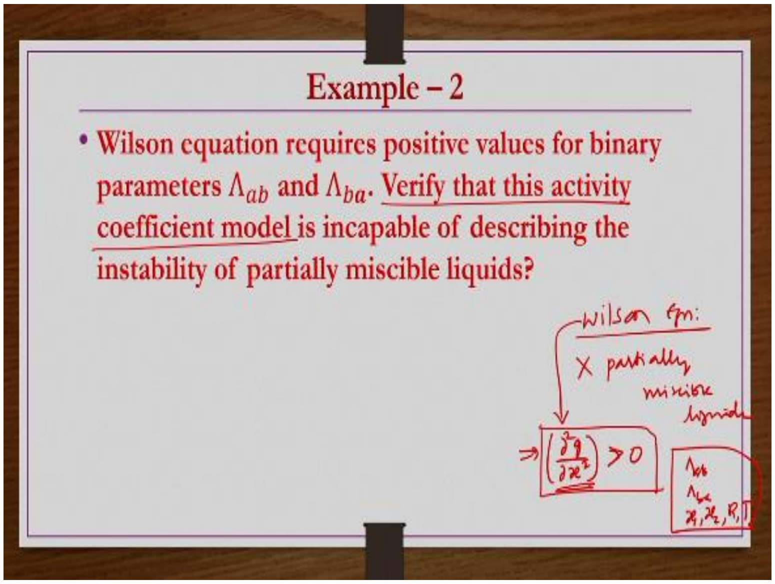

Example – 2

- Wilson equation requires positive values for binary parameters Λ_{ab} and Λ_{ba}. Verify that this activity coefficient model is incapable of describing the instability of partially miscible liquids?

Wilson Eqn:

X partially miscible liquids

$\Rightarrow \boxed{\left(\frac{\partial^2 g}{\partial x^2}\right) > 0}$

Λ_{ab}

Λ_{ba}

x_1, x_2, R, T

Then another example 2 Wilson equation requires positive values for binary parameters Λ_{ab} and Λ_{ba} verify that this activity coefficient model is incapable of describing the instability of partially miscible liquids. We have seen, when we were discussing when we were discussing models for excess Gibbs energy for a binary and multi component system, then we have seen this Wilson equation is not suitable for partially miscible liquids.

This is what we have seen, so that we can prove or using this thermodynamic partially miscible system whatever the conditions that we have derived. So, $\left(\frac{\partial^2 g}{\partial x^2}\right)$if you do for this Wilson equation, then you will always get greater than 0. That is what means by, if you are saying that it is not suitable for partially miscible liquids that means you are not going to get the second derivative of g with respect to mole fraction less than 0 at any cost.

Whatever may be the combination of Λ_{ab} Λ_{ba} x_1 x_2 R T and then whatever the combination of these parameters you take you are not going to have this second derivative of g with respect to mole fraction as less than 0 if it is less than 0 then only that liquid solution is going to form partially miscible two phases or splitting into two phases. If it is greater than 0 it is always going to form a kind of completely miscible solution.

So that means when you used Wilson equation and then do this derivation then you will always find that this is going to be greater than 0 so that is what we have to verify. So for the Wilson equation whatever g^E expression is still that we have to write in place of $g = \sum x_i g_i + RT \sum x_i \ln x_i + g^E$ and in place of g^E, you write Wilson equation and then do the second derivation of this g with respect to the mole fraction.

Then you will find out for any combination of these parameters this second derivative is going to be positive, it is always going to be positive that is what you find out then it is correct otherwise something is wrong. Because it is known that Wilson Equation is not suitable for partial immiscible system, so obviously the second derivative should always you greater than 0 for any combination of these parameters x_1 x_2 RT and then Λ_{ab} Λ_{ba} etc.

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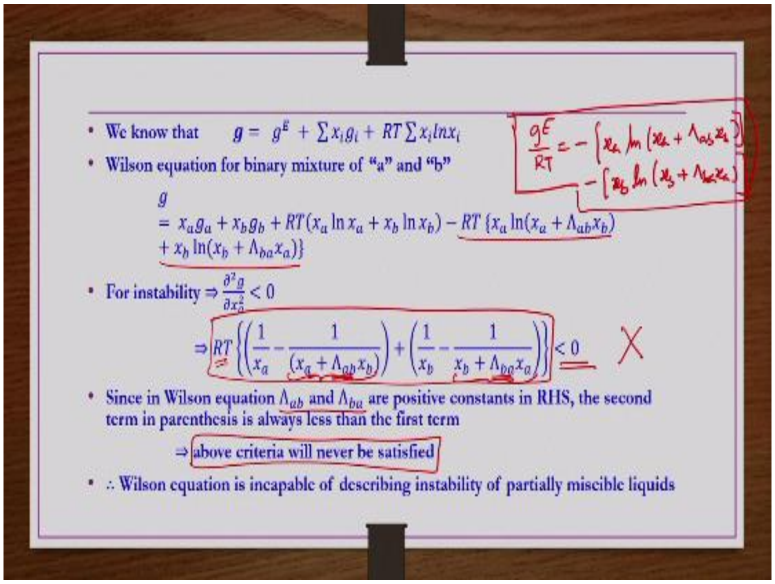

- We know that $g = g^E + \sum x_i g_i + RT \sum x_i ln x_i$
- Wilson equation for binary mixture of "a" and "b"

$$g = x_a g_a + x_b g_b + RT(x_a \ln x_a + x_b \ln x_b) - \underline{RT\,\{x_a \ln(x_a + \Lambda_{ab} x_b)} \underline{+ x_b \ln(x_b + \Lambda_{ba} x_a)\}}$$

$$\boxed{\frac{g^E}{RT} = -\{x_a \ln(x_a + \Lambda_{ab} x_b)\} - \{x_b \ln(x_b + \Lambda_{ba} x_a)\}}$$

- For instability $\Rightarrow \frac{\partial^2 g}{\partial x_a^2} < 0$

$$\Rightarrow \boxed{RT\left\{\left(\frac{1}{x_a} - \frac{1}{(x_a + \Lambda_{ab} x_b)}\right) + \left(\frac{1}{x_b} - \frac{1}{x_b + \Lambda_{ba} x_a}\right)\right\}} \underline{\underline{< 0}} \quad X$$

- Since in Wilson equation Λ_{ab} and Λ_{ba} are positive constants in RHS, the second term in parenthesis is always less than the first term

$\Rightarrow$ above criteria will never be satisfied

- $\therefore$ Wilson equation is incapable of describing instability of partially miscible liquids

Those parameters that we do. So we know that $g^E = g^E + \sum x_i g_i + RT \sum x_i \ln x_i$. So for a binary mixture of components a and b, $g = x_a g_a + x_b g_b + RT x_a \ln x_a + x_b \ln x_b$. And g^E for the Wilson equation is nothing but or $\frac{g^E}{RT}$for Wilson equation is nothing but - x_a ln of $x_a + \Lambda_{ab} x_b$ And then - x_b ln of $x_b + \Lambda_{ba} x_a$ this is what we have seen Wilson equation for a binary system.

So in place of g^E we can write - RT of these two terms so that is what we are having here - RT $(x_a \ln (x_a + \Lambda_{ab} x_b) + x_b \ln (x_b + \Lambda_{ba} x_a)$ then we have this term when you substitute g^E for Wilson equation then we have this additional third term. Now this equation if you partially differentiate two times so that we get $\frac{\partial^2 g^E}{\partial x_a^2} < 0$.

Then we can say that it is suitable for partially miscible system that we have to check. So first what we do when we do this $\frac{\partial^2 g}{\partial x_a^2}$then you will get, RT$\left\{\left(\frac{1}{x_a} - \frac{1}{x_a+\Lambda_{ab}x_b}\right) + \left(\frac{1}{x_b} - \frac{1}{x_b+\Lambda_{ba}x_a}\right)\right\}$. Now we know these two parameters to adjustable parameters of Wilson equation that is Λ_{ab} Λ_{ba} these parameters are always positive.

So now what you see the numbers in these whatever the combinations of x_a x_b Λ_{ab} Λ_{ba} if you take whatever is the combination of these numbers including this R and T you will never get this number as less than 0, you will never get this number as a negative one because this parameters are positive x_a and x_b are also positive at the max they can be 0 and temperature also cannot be negative.

And then the R is also always, you know, positive constant that we know so for whatever combination of these parameters you take this is not going to be negative, so this condition is not going to be satisfied so that means it is not suitable for partially miscible system. Since in Wilson equation this parameters are positive constants in RHS, the second term in parenthesis is always less than the first term.

So because of that one, you know this inequality whatever the inequality criteria that we have shown here that will never be satisfied. Thus Wilson equation is incapable of describing instability of partially miscible liquids or Wilson equation is not suitable for partially miscible liquid systems that is what the conclusion. So, now using the principles of thermodynamics of partially miscible systems.

You can check any model, any model you can check whether that model is suitable for the partially miscible system or not that is one you can check another one you can do for the if it is a suitable for partially miscible systems as well so under what conditions it is going to be suitable those kind of things you can estimate using the principles of thermodynamics of partially miscible system as we have done as two example problems. So now what we do we take up the next problem in LLE that is estimation of composition of liquid liquid equilibrium.

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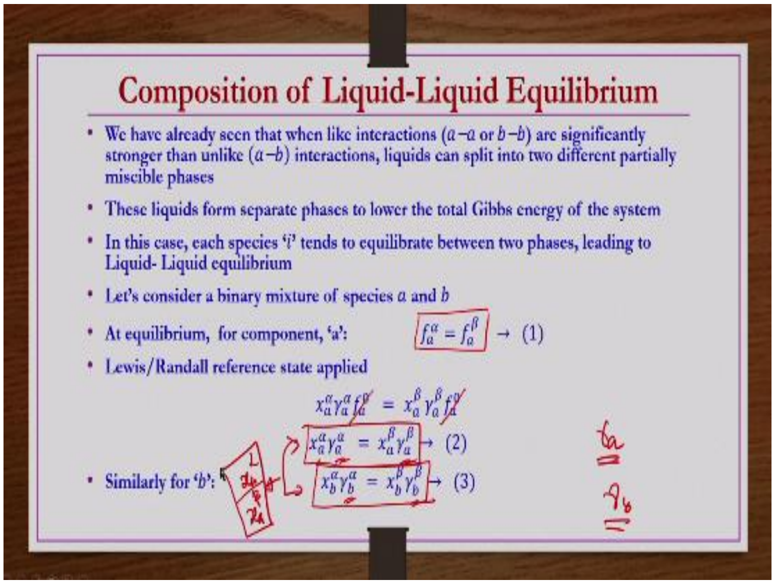

Composition of Liquid-Liquid Equilibrium

- We have already seen that when like interactions ($a-a$ or $b-b$) are significantly stronger than unlike ($a-b$) interactions, liquids can split into two different partially miscible phases
- These liquids form separate phases to lower the total Gibbs energy of the system
- In this case, each species 'i' tends to equilibrate between two phases, leading to Liquid- Liquid equilibrium
- Let's consider a binary mixture of species a and b
- At equilibrium, for component, 'a': $\boxed{f_a^\alpha = f_a^\beta} \rightarrow (1)$
- Lewis/Randall reference state applied

$$x_a^\alpha \gamma_a^\alpha \cancel{f_a^0} = x_a^\beta \gamma_a^\beta \cancel{f_a^0}$$

$$\boxed{x_a^\alpha \gamma_a^\alpha = x_a^\beta \gamma_a^\beta} \rightarrow (2)$$

- Similarly for 'b': $\boxed{x_b^\alpha \gamma_b^\alpha = x_b^\beta \gamma_b^\beta} \rightarrow (3)$

We have already seen that when like interaction whether a- a interactions or b-b interactions, like interactions in the sense the same interaction or interaction between the same molecules if they are very, very strong compared to the unlike interactions. Then liquids can split into two different partially miscible phases that is what we have seen. Obviously if a-a interactions are very strong similarly b-b interactions are very strong compared to the a-b interactions.

So what will happen rather they form as a kind of a completely miscible solution, they prefer to have a kind of pure a-a solution a as a once phase and then pure solution b-b as a kind of another phase, but obviously pure will not be possible so there will be some amount of miscibility will be there, but complete miscibility will not be taking place as long as these like interaction that is a-a and b-b interactions are going to be much stronger than this unlike interactions a-b interactions.

So if the like interactions are much stronger than the unlike interaction then it is possible that this liquids are going to split into two different partially miscible phases that we have already understood by this thermodynamics of partially miscible systems. Then these liquids form separate phases to lower the total Gibbs energy of the system, this is also we have seen. Why these you know two of liquids when we are adding together, they are forming two different separate phases as partially immiscible phases?

Why? because any system that will try to go towards the lower energy system so that it can become stable so they will try to go towards the position where the system total Gibbs energy is getting lower if the Gibbs energy is getting lower, so then system is going to be stable so in order to have a kind of stable whether it is miscible solution or immiscible solution this system wants to be it lower energy level.

So that is the reason the liquids forms 2 separate the phases to lower the total gives energy of the system that is also we have seen. In this case each species i → equilibrate between two phases leading to liquid liquid equilibrium. So when we are these components so component i → equilibrate between two phases. So let us consider a binary mixture of species a and b. Then at equilibrium for component a we know that fugacity of that component a in α phase should be equal to fugacity of component same a in β phase. This is standard condition at equilibrium.

Now applying Lewis Randall reference state then this f_a^{α} for a liquid phase α is what is nothing but $x_a \gamma_a f_a^0$ for α phase similarly f_a^{β} for β phase is what $x_a \gamma_a f_a^0$ but for β phase so that is $x_a^{\alpha}\gamma_a^{\alpha}f_a^0 = x_a^{\beta}\gamma_a^{\beta} f_a^0$this reference state is same for either of the phase.

We cannot take two different reference states for two different phases, which are co-existing. If they are individually existing then then fine we can take different reference state but if these two phases are co-existing and they are ready equilibrium. Then you cannot take two different reference states, for the either of the phases so this f_a^0 for α and then $f_a^0$for β are going to be same so if you cancel out this is what we have, that is $x_a^{\alpha}\gamma_a^{\alpha} = x_a^{\beta}\gamma_a^{\beta}$.

This is for component a, similarly for component b if you write. Then you will get $x_b^{\alpha} \gamma_b^{\alpha} = x_b^{\beta}\gamma_b^{\beta}$. So now if you have this information about the activity coefficient in either of the phases you can solve these two equations to get what is $x_a^{\alpha}$and then x_a^{β}. If $x_a^{\alpha}$is known then x_b^{α} is also known because 1 - $x_a^{\alpha}$is nothing but x_b^{α} similarly if $x_a^{\beta}$is known then x_b^{β} is also known because x_b^{β} is nothing but 1 - x_a^{β}.

So these two equations if you have this information about γ_a^{α} $\gamma_b^{\alpha}\gamma_a^{\beta}$ γ_b^{β} then you can solve to get this equilibrium composition. But it is not as straight forward as easy as this equation looks like, why?

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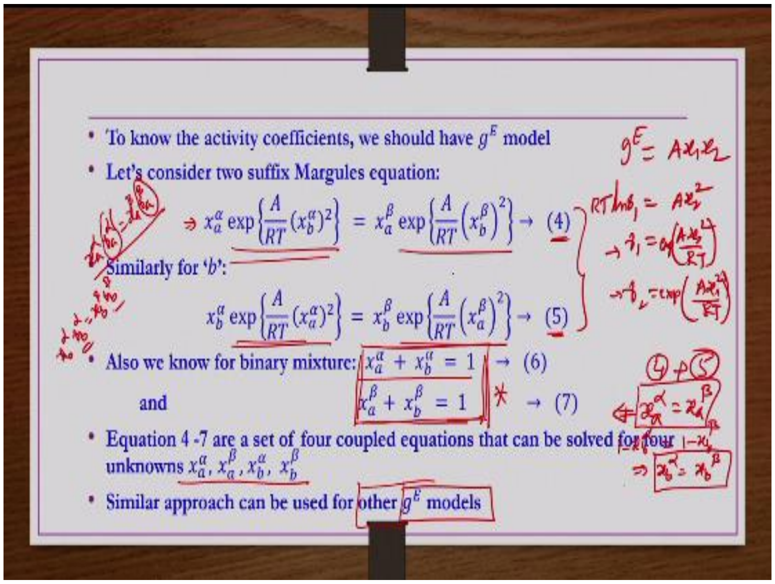

- To know the activity coefficients, we should have g^E model
- Let's consider two suffix Margules equation:

$$\Rightarrow x_a^\alpha \exp\left\{\frac{A}{RT}(x_b^\alpha)^2\right\} = x_a^\beta \exp\left\{\frac{A}{RT}\left(x_b^\beta\right)^2\right\} \to (4)$$

Similarly for '*b*':

$$x_b^\alpha \exp\left\{\frac{A}{RT}(x_a^\alpha)^2\right\} = x_b^\beta \exp\left\{\frac{A}{RT}\left(x_a^\beta\right)^2\right\} \to (5)$$

- Also we know for binary mixture: $x_a^\alpha + x_b^\alpha = 1 \to (6)$

  and $x_a^\beta + x_b^\beta = 1 \to (7)$
- Equation 4 -7 are a set of four coupled equations that can be solved for four unknowns $x_a^\alpha, x_a^\beta, x_b^\alpha, x_b^\beta$
- Similar approach can be used for other g^E models

$g^E = Ax_1x_2$

$RT\ln\gamma_1 = Ax_2^2$

$\to \gamma_1 = \exp\left(\frac{Ax_2^2}{RT}\right)$

$\to \gamma_2 = \exp\left(\frac{Ax_1^2}{RT}\right)$

④ + ⑤

$\Leftarrow \boxed{x_a^\alpha = x_a^\beta}$

$1-x_a$

$\Rightarrow \boxed{x_b^\alpha = x_b^\beta}$

We will see with example problems. To know the activity coefficients, obviously we should have a g^E model let us say if this system a-b binary system whatever we have taken, the activity coefficient are described by two suffix models equations, then g^E we have, A x_1 x_2 and then we have seen for this equations ln γ_1 or RT ln γ_1 is nothing but A x_2^2. That means γ_1 = $\frac{Ax_2^2}{RT}$ under exponential. And then γ_2 is exponential of $\frac{Ax_1^2}{RT}$ this is what we have.

So now that if you write for 2 phases, α and β phases and then component a and b then for this equation is what this is nothing but $x_a^\alpha \gamma_a^\alpha$= same x_a but in β phase and then γ_a but in β phase. So that previous slide we have written that equation for γ_a^α and then γ_a^β we are writing this exponential of $\frac{A(x_b^\alpha)^2}{RT}$ and then exponential of $\frac{A\left(x_b^\beta\right)^2}{RT}$.

And then $x_a^\alpha$and x_a^β is as it is. Similarly for the component b also we have seen that x_b^α γ_b^α= $x_b^\beta \gamma_b^\beta$and then in place of γ_b^αyou can write exponential of $\frac{A(x_b^\alpha)^2}{RT}$ and in place of γ_b^βyou can write exponential of $\frac{A\left(x_b^\beta\right)^2}{RT}$ this is what you can write where as x_b^α and an x_b^βas it is.

These are the two important equations now another two important equations are x_a^α+ x_b^α = 1. Though it is straight forward it is very important equation and in addition to this one another equation x_a^β+ x_b^β= 1 though it is a state forward this one also. These equations are going to be very essential why they are essential because whatever the solution on that you get by solving these two nonlinear equations this equation number 4 and 5 are highly non-linear.

You need to have a kind of trial and error approach or you know, some kind of a numerical methods you apply to get this solutions but when you try to find the solution for this equation if the solution is not satisfying this equations, that means that solution is not reliable. That means that solution is not reliable. Now this equation number 4 and 5 are non-linear equations and then this equations can be solved by trial and error approach or some kind of numerical methods, but if you see this equation if you take $x_a^\alpha = x_a^\beta$.

Any value of x_a^α you take and then that you equate it to x_a^β then this equation would be satisfied now x_a^α= x_a^β so then these are same so exponential of whatever this x_b^α if x_a^α= x_b^α x_a^β then what does it mean it means so 1 - x_b^α = 1 - x_b^β that means x_b^α = x_b^β. So if x_a^α and then x_a^β if you take equals to each other then whatever this x_b^α is there = x_b^β also then this obviously this will also be equals to each other then the equation is satisfied.

Any combination of x_a values you take but provided if you take x_a^α= x_a^β. Now, again, if x_a^α= x_a^β then x_b^α = x_b^β that we have seen here. And then x_a^α you are saying that equals to x_a^β, that means any combination of x_a values you take for two different phases are equal to each other let us say that is x_a^α if you take equals to x_a^β that that is in both α and β phases the mole fraction of component a is equal.

It is 0.1 or 0.9, 0.5, 0.44 whatever the number if you take if you take equals to each other that is mole fraction of component a is equal in both the phases, then these two equations are always being satisfied. So that means there is there could be n number of solutions are possible but they are not reliable because whatever the solution that you take that solution should also satisfy these two equations.

And then this two solution these two equations can be solved and there will be only one solution which would be satisfying these two equations as well. so that is the some kind of trivial solution is possible that is if you take $x_a^\alpha = x_a^\beta$ then you know, any combination of this x_a that you take in either of the phases you get the solution but that is not correct so that is the reason we have to do a trial and error solution.

And then find out some values of x_a^α. And then x_a^β. Which also satisfy this equation number 6 and 7 not only just 4 and 5 they should also satisfy this equation numbers, 6 and 7? Let us say we are going to see a few example problems as well, how to solve this equations? So now equations 4 to 7 are set of 4 coupled equation that can be solved for four unknowns $x_a^\alpha x_a^\beta x_b^\alpha$ x_b^β.

Though there are two unknowns only because two unknowns remaining two unknown unknowns are not independent for a binary system, so what however we have 4 equations for unknowns, we can obtain. So similar approach can be used for g^E models other g^E models also only thing that you know, this equation g^E in place of γ_a γ_b what are we writing that expression will change but the procedure is exactly same but the procedure how to solve this equation is going to be same.

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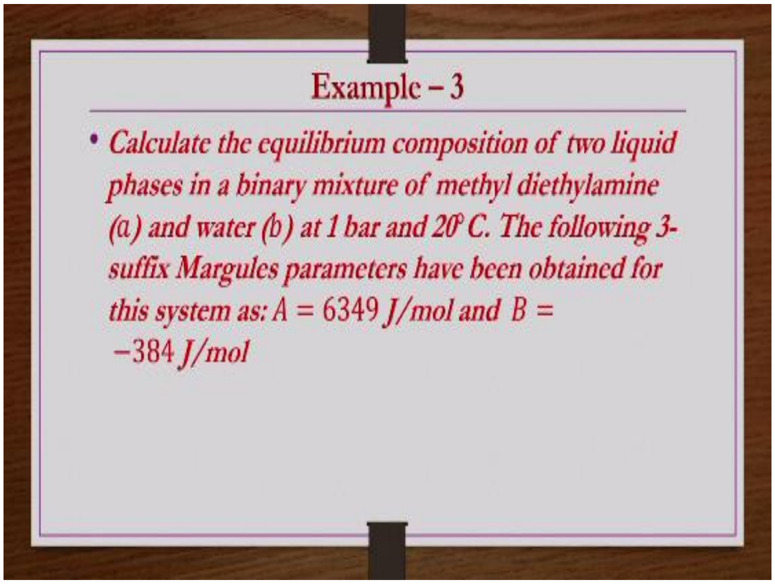

Example – 3

- *Calculate the equilibrium composition of two liquid phases in a binary mixture of methyl diethylamine (a) and water (b) at 1 bar and 20° C. The following 3-suffix Margules parameters have been obtained for this system as:* $A = 6349$ *J/mol and* $B = -384$ *J/mol*

So let us take an example and then solve this equilibrium composition problem equation. Calculate the equilibrium composition of two liquid phases in a binary mixture of methyl diethylamine of water at 1 bar and 20 degree centigrade. The following 3 suffix Margules parameters have been obtained for this system a and b are given. So what we have to find out?

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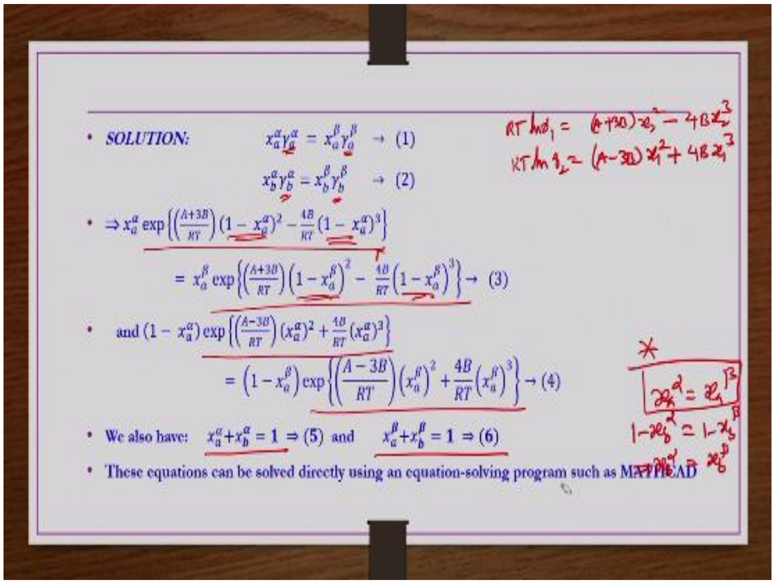

- *SOLUTION:* $x_a^\alpha \gamma_a^\alpha = x_a^\beta \gamma_a^\beta \rightarrow (1)$

  $x_b^\alpha \gamma_b^\alpha = x_b^\beta \gamma_b^\beta \rightarrow (2)$

- $\Rightarrow x_a^\alpha \exp\left\{\left(\frac{A+3B}{RT}\right)(1-x_a^\alpha)^2 - \frac{4B}{RT}(1-x_a^\alpha)^3\right\}$

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

- and $(1-x_a^\alpha)\exp\left\{\left(\frac{A-3B}{RT}\right)(x_a^\alpha)^2 + \frac{4B}{RT}(x_a^\alpha)^3\right\}$

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

- We also have: $x_a^\alpha + x_b^\alpha = 1 \Rightarrow (5)$ and $x_a^\beta + x_b^\beta = 1 \Rightarrow (6)$
- These equations can be solved directly using an equation-solving program such as MATHCAD

$RT \ln \gamma_1 = (A+3B)x_2^2 - 4Bx_2^3$

$RT \ln \gamma_2 = (A-3B)x_1^2 + 4Bx_1^3$

*

$\boxed{x_a^\alpha = x_a^\beta}$

$1 - x_b^\alpha = 1 - x_b^\beta$

$x_b^\alpha \Rightarrow x_b^\beta$

We have to find out what is x_a^α, x_a^β and then x_b^α x_b^β you have to find out equilibrium composition you have to find out. So at equilibrium we know for binary system a and b we know that $x_a^\alpha \gamma_a^\alpha$ = $x_a^\beta \gamma_a^\beta$ and then for second component b also we know that $x_b^\alpha \gamma_b^\alpha$= $x_b^\beta \gamma_b^\beta$ this also we know.

Now if it is a 3-suffix Margules equation then we have this RT ln γ_1 = (A - 3B) x_2^2 - 4B x_2^3 and then for component 2 RT ln γ_2 we have (A - 3B) x_1^2+ 4 B x_1^3 this is what we have seen for 3 -suffix Margules equation, so similarly for γ_a γ_b in we can write for both the phases α and β phases then let us say for the first equation, for component A.

If you write this is exponential of $\left(\frac{A + 3B}{RT}\right)$ $(1 - x_a^\alpha)^2$ - $\frac{4B}{RT}(1 - x_a^\alpha)^3$ = x_a^β as it is exponential of $\left(\frac{A + 3B}{RT}\right)$ $\left(1 - x_a^\beta\right)^2$ - $\frac{4B}{RT}\left(1 - x_a^\beta\right)^3$ then similarly for components B if you will have this equation. This is for γ_b^α and this is for γ_b^β. This is γ_a^α, This is γ_a^β, this is γ_b^α, this is γ_b^β by applying 3-suffix Margules equation.

So now further we have this x_a^α+ x_b^α= 1, and then x_a^β+ x_b^β= 1. Now here also if you take x_a^α=

x_a^β then we have 1 - x_b^α= 1 - x_b^β. So that means this equation if x_a^α= x_a^β is you take whatever this parenthesis 1 - x_a^α is nothing but x_b^α so x_b^α = x_b^β that is what we get by taking this one.

So the first term is also same with the exponential the second term is also same in the exponential because x_b^α = nothing but x_b^β same is true for the second equation also that means any combination of x_a^α= x_a^β if you take these equations are going to satisfy this equation 3 and 4, but this 5 and 6 might not be satisfied. So that means what you have to do?

You have to find out the kind of solution, which is not trivial like this, which is reliable kind of solution. So for that we have to do a kind of appropriate trial and error approach has to be followed. Or some kind of tools like MATHCAD etc. one can use and then obtain the solution of this equations.

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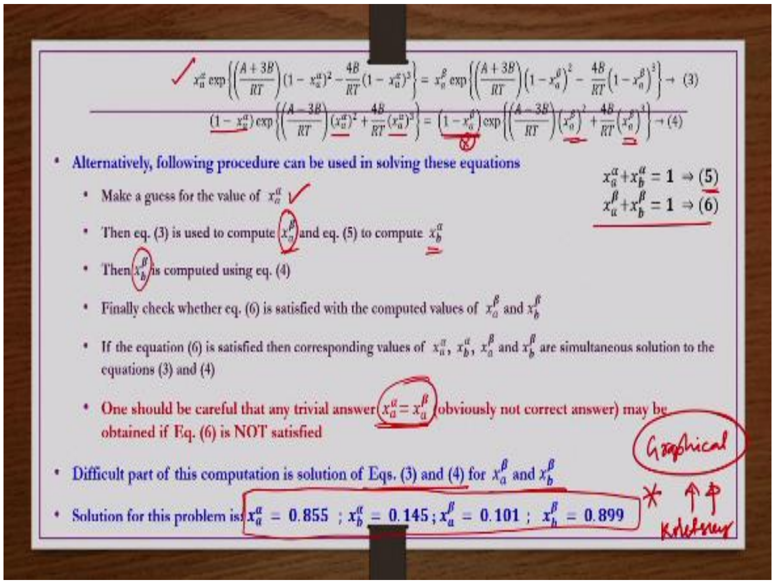

$$x_a^\alpha \exp\left\{\left(\frac{A+3B}{RT}\right)(1-x_a^\alpha)^2 - \frac{4B}{RT}(1-x_a^\alpha)^3\right\} = x_a^\beta \exp\left\{\left(\frac{A+3B}{RT}\right)(1-x_a^\beta)^2 - \frac{4B}{RT}(1-x_a^\beta)^3\right\} \to (3)$$

$$(1-x_a^\alpha)\exp\left\{\left(\frac{A-3B}{RT}\right)(x_a^\alpha)^2 + \frac{4B}{RT}(x_a^\alpha)^3\right\} = (1-x_a^\beta)\exp\left\{\left(\frac{A-3B}{RT}\right)(x_a^\beta)^2 + \frac{4B}{RT}(x_a^\beta)^3\right\} \to (4)$$

- Alternatively, following procedure can be used in solving these equations
  - Make a guess for the value of x_a^α ✓
  - Then eq. (3) is used to compute x_a^β and eq. (5) to compute x_b^α
  - Then x_b^β is computed using eq. (4)
  - Finally check whether eq. (6) is satisfied with the computed values of x_a^β and x_b^β
  - If the equation (6) is satisfied then corresponding values of x_a^α, x_b^α, x_a^β and x_b^β are simultaneous solution to the equations (3) and (4)
  - One should be careful that any trivial answer ($x_a^\alpha = x_a^\beta$ obviously not correct answer) may be obtained if Eq. (6) is NOT satisfied
- Difficult part of this computation is solution of Eqs. (3) and (4) for x_a^β and x_b^β
- Solution for this problem is: x_a^α = 0.855 ; x_b^α = 0.145 ; x_a^β = 0.101 ; x_b^β = 0.899

$x_a^\alpha + x_b^\alpha = 1 \Rightarrow (5)$

$x_a^\beta + x_b^\beta = 1 \Rightarrow (6)$

Graphical

Kretsney

So alternatively following procedure can be followed for solving this equations make a guess first the value of x_a^α first then solve equation 3 to get x_a^β that is this equation you solve to get the x_a^β because now A, B, T etc are given only x_a^α and then x_a^β are not known so we are making assumption of x_a^α and then finding out what is x_a^β. Once x_a^β is known.

Then you find out x_b^α using equation number 5, x_b^α= nothing but 1 - x_a^α then you compute the equation 4 for getting the x_b^β, this is equation number 4, this is one - $x_a^\alpha$is known, $x_a^\alpha$is also known., $x_a^\alpha$is known 1 - $x_a^\beta$is nothing but x_b^β this is the unknown one. This you calculate from equation number 4 now this x_a^βalso you already calculated from this equation number 3, this is also known.

So only thing is not known this x_b^βso that x_b^βyou find out using this equation number 4. Then check whether this x_a^βwhatever x_a^βyou found out and then x_b^βyou found out by solving this equation 3 and 4 are there satisfying this equation number 6 that $x_a^\beta + x_b^\beta = 1$ or not. If it is satisfied then I will assume the case of $x_a^\alpha$is correct and then obtain values of $x_a^\beta x_b^\beta$correct.

Otherwise you have to assume make an assumption of another x_a^α and then continue this solution until this equation number 6 is satisfied, so if the equation is satisfied then the corresponding values of $x_a^\alpha x_b^\alpha x_a^\beta x_b^\beta$are simultaneous solution to the equation 3 and 4 including the 5 and 6 and one should be careful that any trivial answer that $x_a^\alpha = x_a^\beta$.

May be obtained if equation 6 is not satisfied but obviously it is not the correct answer. Difficult part of this computation is the solution of equations 3 and 4 for $x_a^\beta$and then x_b^βbecause these equations are having some nonlinear terms so now when you follow this solution step and then do this on trial and error calculations then. You will find out answer to this question as x_a^α = 0.855 x_b^α= 0.145. And then x_a^β= 0.101 x_b^β= 0.899.

There are other graphical approaches are also available for solving this equation, first those our graphical approaches, you know, first what they give they give the range of mole fraction within which this solution is going to be there the range of this x_a^α and then x_a^βthat range. First obtained by this approach then once defining the range there is a kind of another graphical approach is there by which you can find out exact solution of this $x_a^\alpha$and then x_a^β.

So those graphical methods I am not describing anyway one can go through the books by Koretsky or Sandler etcetera those books one can refer for this graphical methods

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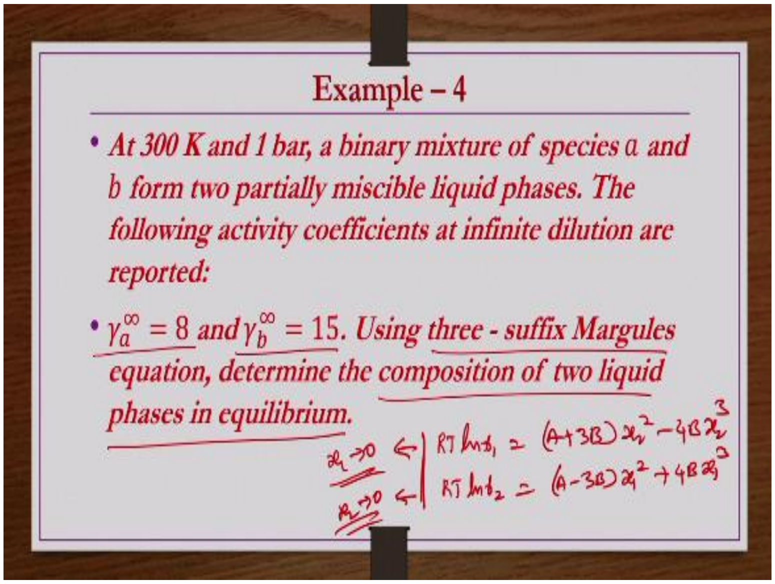

Example – 4

- *At 300 K and 1 bar, a binary mixture of species a and b form two partially miscible liquid phases. The following activity coefficients at infinite dilution are reported:*
- $\gamma_a^\infty = 8$ *and* $\gamma_b^\infty = 15$. *Using three - suffix Margules equation, determine the composition of two liquid phases in equilibrium.*

$x_1 \to 0 \Leftarrow$ | $RT \ln \gamma_1 = (A+3B) x_2^2 - 4B x_2^3$

$x_2 \to 0 \Leftarrow$ | $RT \ln \gamma_2 = (A-3B) x_1^2 + 4B x_1^3$

Now we take another example problem at 300 Kelvin at 1 bar, a binary mixture of species a and b formed two partially miscible liquid phases. The following activity coefficients at infinite dilutions are reported that is $\gamma_a^\infty$and γ_b^∞ are provided using 3-suffix Margules equation, determine the composition of two liquid phases in equilibrium. The problem is exactly same as the previous problem.

But here this 3-suffix Margules parameters a and b are not given in the previous problem this a and b parameters are given and then γ_a γ_b for either of the phases you have to find out by trial and error approach until the solution satisfies that. The equation number six, that is x_a^β + x_b^β= 1. But now here this parameters are not given but this $\gamma_a^\infty \gamma_b^\infty$ are given.

So here what we know that RT ln γ_1 = A + 3B x_2^2 - 4B x_2^3 and then RT ln γ_2 = A - 3B x_1^2 + 4B $x_1^3$for the 3 suffix Margules equation we know so now first equation you substitute $x_1 \to 0$ then that will be γ_1^∞in the second equation if you substitute $x_2 \to 0$ then that would be giving γ_2^∞.

So $\gamma_1^\infty \gamma_2^\infty$ are given so you substitute those values here under this limiting conditions in both the equations, then you will be having two equations in terms of two unknowns A and B if you solve those two equations you find out this a and b required for obtaining the equilibrium composition.

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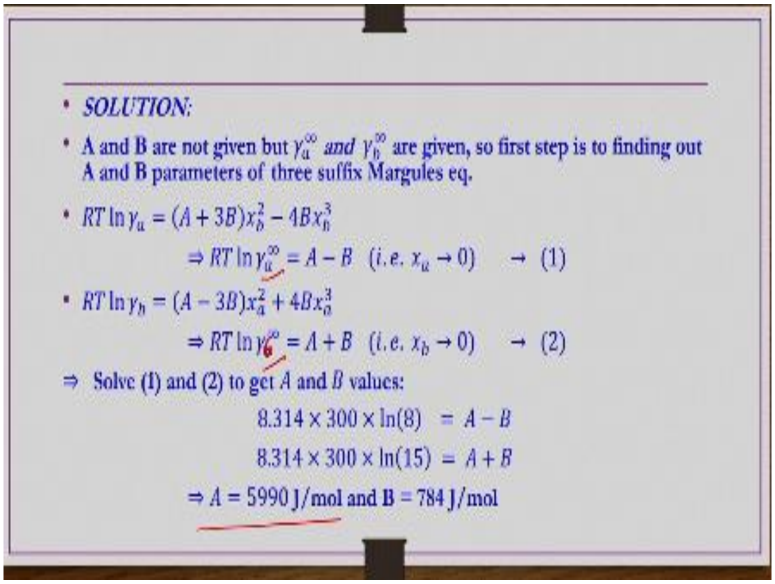

- SOLUTION:
- A and B are not given but γ_a^∞ and γ_b^∞ are given, so first step is to finding out A and B parameters of three suffix Margules eq.
- $RT\ln\gamma_a = (A+3B)x_b^2 - 4Bx_b^3$

$$\Rightarrow RT\ln\gamma_a^\infty = A - B \quad (i.e.\ x_a \to 0) \quad \to (1)$$

- $RT\ln\gamma_b = (A-3B)x_a^2 + 4Bx_a^3$

$$\Rightarrow RT\ln\gamma_b^\infty = A + B \quad (i.e.\ x_b \to 0) \quad \to (2)$$

⇒ Solve (1) and (2) to get A and B values:

$$8.314 \times 300 \times \ln(8) = A - B$$

$$8.314 \times 300 \times \ln(15) = A + B$$

$$\Rightarrow A = 5990\ \text{J/mol and B} = 784\ \text{J/mol}$$

A and B are not given but $\gamma_a^\infty$and γ_b^∞ are given, so first step is to finding out A and B parameters of three suffix Margules equation. For this three suffix Margules equation we know that RT ln γ_a = (A + 3B) x_b^2- 4B x_b^3, so when $x_a \to 0$ that is if you take $x_a = 0$ in this a by equation, then you get RT ln γ_a^∞ = A - B and a similarly RT ln γ_b we have for three suffix Margules equation as.

(A - 3B) x_a^2 + 4B x_a^3 now if $x_b \to 0$ then RT ln γ_b^∞, you will get it as A + B now this γ_a^∞ and $\gamma_b^\infty$are given temperature is also given so if you solve these two equations. Then you will have this A and B as 5990 joule per mole and 784 joule per mole respectively.

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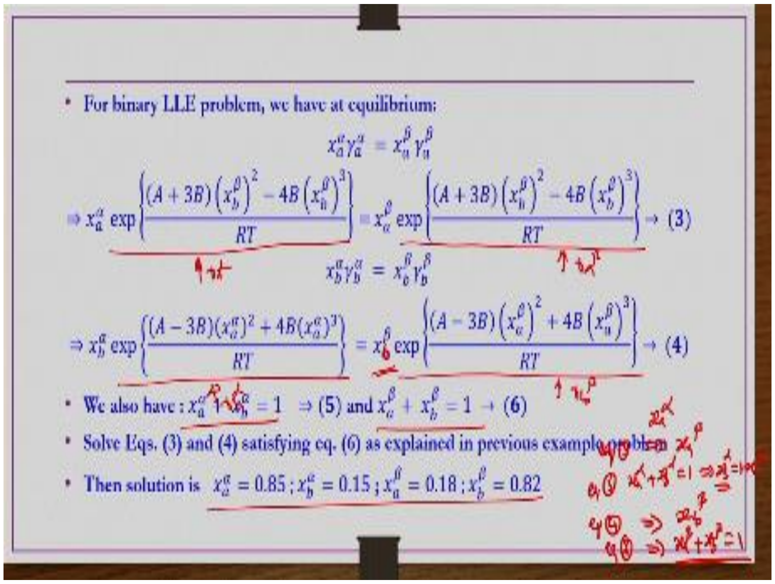

- For binary LLE problem, we have at equilibrium:

$$x_a^\alpha \gamma_a^\alpha = x_a^\beta \gamma_a^\beta$$

$$\Rightarrow x_a^\alpha \exp\left\{\frac{(A+3B)\left(x_b^\alpha\right)^2 - 4B\left(x_b^\alpha\right)^3}{RT}\right\} = x_a^\beta \exp\left\{\frac{(A+3B)\left(x_b^\beta\right)^2 - 4B\left(x_b^\beta\right)^3}{RT}\right\} \to (3)$$

↑ x_a^α ↑ x_a^β

$$x_b^\alpha \gamma_b^\alpha = x_b^\beta \gamma_b^\beta$$

$$\Rightarrow x_b^\alpha \exp\left\{\frac{(A-3B)(x_a^\alpha)^2 + 4B(x_a^\alpha)^3}{RT}\right\} = x_b^\beta \exp\left\{\frac{(A-3B)\left(x_a^\beta\right)^2 + 4B\left(x_a^\beta\right)^3}{RT}\right\} \to (4)$$

↑ x_b^β

- We also have : $x_a^\alpha + x_b^\alpha = 1 \Rightarrow (5)$ and $x_a^\beta + x_b^\beta = 1 \to (6)$
- Solve Eqs. (3) and (4) satisfying eq. (6) as explained in previous example problem
- Then solution is $x_a^\alpha = 0.85 ; x_b^\alpha = 0.15 ; x_a^\beta = 0.18 ; x_b^\beta = 0.82$

x_a^α
eq ③ ⇒ x_a^β
eq ⑤ $x_a^\alpha + x_b^\alpha = 1 \Rightarrow x_b^\alpha = 1-x_a^\alpha$
eq ④ ⇒ x_b^β
eq ⑥ ⇒ $x_a^\beta + x_b^\beta = 1$

So now A and B have been formed so then now you can find out the equilibrium composition by solving these two equation $x_a^\alpha \gamma_a^\alpha = x_a^\beta \gamma_a^\beta$ and then $x_b^\alpha\ \gamma_b^\alpha = x_b^\beta \gamma_b^\beta$ for three suffix Margules equation, this is nothing but γ_a^α and this exponential of term is nothing but γ_a^β here this exponential term is nothing but γ_b^α and this exponential term is nothing but γ_b^β.

In addition to this we also have these two equation $x_a^\alpha + x_b^\alpha = 1$ and an $x_a^\beta + x_b^\beta = 1$, so now this equation 3 to 6 if you solve exactly similar way as we have done in a previous case that is first you assume x_a^α then solve equation number 3 to get x_a^β. Once x_a^β is found then equation number 5, you can find it out. You have $x_a^\alpha + x_b^\alpha = 1$, then you have $x_b^\alpha = 1 - x_a^\alpha$.

So now here x_b^α you are having so now you solve equation number 4 in order to get your x_b^β here, this is nothing but x_b^β. So once you have this x_b^β by solving this equation number 4, then you take this equation number 6 for cross checking whether this $x_a^\beta + x_b^\beta$, are you getting one or not. If summation is coming close to 1 then this assumes x_a^α is correct and then obtained x_a^β and then x_b^β also correct they are the solution.

Otherwise you have to make another assumption of x_a^α and then continue this series of calculations, until you satisfy this condition of equation number 6. So when you do several trial and kind of solutions, then you will find it out x_a^α is 0.85, x_b^α is 0.15, $x_a^\beta = 0.18$, $x_b^\beta = 0.82$.

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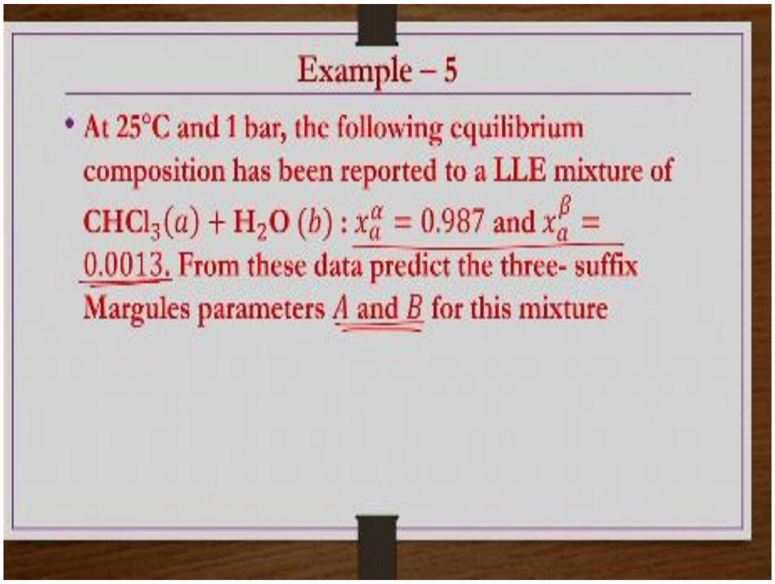

Example – 5

- At 25°C and 1 bar, the following equilibrium composition has been reported to a LLE mixture of $CHCl_3(a) + H_2O\ (b) : x_a^\alpha = 0.987$ and $x_a^\beta = 0.0013.$ From these data predict the three- suffix Margules parameters A and B for this mixture

Now we take one more last example problem to wind up this lecture. At 25 degree centigrade and 1 bar the following equilibrium composition has been reported to a LLE mixture of $CHCl_3$ and water with x_a^α= 0.987 and x_a^β= 0.0013. So here equilibrium composition is given. Now from these data what you have to find out you have to find out this parameters A and B. Three-suffix Margules parameters A and B have to find out.

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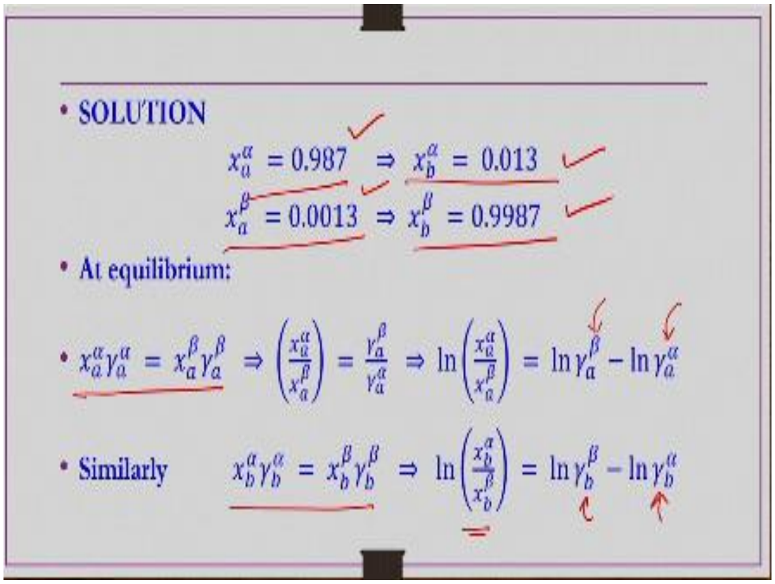

- SOLUTION

$$x_a^\alpha = 0.987 \Rightarrow x_b^\alpha = 0.013$$
$$x_a^\beta = 0.0013 \Rightarrow x_b^\beta = 0.9987$$

- At equilibrium:
- $x_a^\alpha \gamma_a^\alpha = x_a^\beta \gamma_a^\beta \Rightarrow \left(\dfrac{x_a^\alpha}{x_a^\beta}\right) = \dfrac{\gamma_a^\beta}{\gamma_a^\alpha} \Rightarrow \ln\left(\dfrac{x_a^\alpha}{x_a^\beta}\right) = \ln \gamma_a^\beta - \ln \gamma_a^\alpha$
- Similarly $x_b^\alpha \gamma_b^\alpha = x_b^\beta \gamma_b^\beta \Rightarrow \ln\left(\dfrac{x_b^\alpha}{x_b^\beta}\right) = \ln \gamma_b^\beta - \ln \gamma_b^\alpha$

So solution these two are given $x_a^\alpha$is given so x_b^α is also known 1 - $x_a^\alpha$is x_b^α then x_b^β is also given so that means $x_b^\beta$is nothing but 1-x_a^β so that is 0.9987. This 4 equilibrium composition values are given and that equilibrium we know that $x_a^\alpha \gamma_a^\alpha = x_a^\beta \gamma_a^\beta$ so this one since $x_a^\alpha$the compositions are given so what we do compositions, we take one side that is $\frac{x_a^\alpha}{x_a^\beta}$ we take one side another side we take$\frac{\gamma_a^\beta}{\gamma_a^\alpha}$.

Then either side we take ln, so ln of $\frac{x_a^\alpha}{x_a^\beta}$= ln of γ_a^β - ln of γ_a^αthis is why we are writing because three-suffix Margules equation, what is this γ_a γ_b we know, which are having this ab parameters. We can substitute here so they are the only unknown whereas the left hand side $x_a^\alpha x_a^\beta$are given, so left hand side is known.

So that this equation of the substituting is numbers of the substituting this γ expression for three-suffix Margules equation, we can solve this equation we need one more equation because we have to we need to solve two unknowns A and B. So similarly for b equation for b component if you write $x_b^\alpha \gamma_b^\alpha$= x_b^β γ_b^β, here also we take mole fraction terms one side so $\frac{x_a^\alpha}{x_a^\beta}$we take one side another side.

We take $\frac{\gamma_a^\beta}{\gamma_a^\alpha}$and then both sides we take ln so that we have ln of $\frac{x_a^\alpha}{x_a^\beta}$ = ln of γ_b^β - γ_b^αhere also left hand side mole fraction terms are known so right hand side if you substitute 3 suffix Margules equation, whatever activity coefficient expressions are there for either of the phases if you substitute and then you get another equation so that is what we do.

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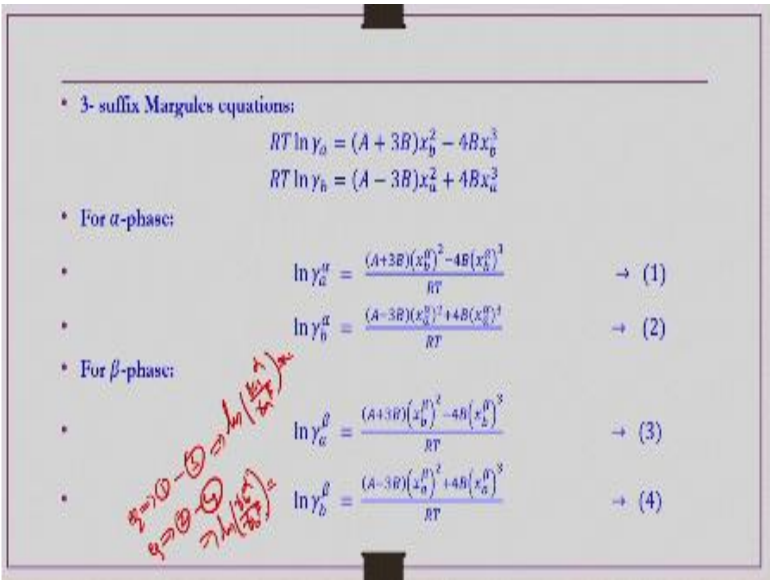

- 3- suffix Margules equations:

$$RT \ln \gamma_a = (A + 3B)x_b^2 - 4Bx_b^3$$
$$RT \ln \gamma_b = (A - 3B)x_a^2 + 4Bx_a^3$$

- For α-phase:

- $$\ln \gamma_a^\alpha = \frac{(A+3B)(x_b^\alpha)^2 - 4B(x_b^\alpha)^3}{RT} \rightarrow (1)$$
- $$\ln \gamma_b^\alpha = \frac{(A-3B)(x_a^\alpha)^2 + 4B(x_a^\alpha)^3}{RT} \rightarrow (2)$$

- For β-phase:

- $$\ln \gamma_a^\beta = \frac{(A+3B)\left(x_b^\beta\right)^2 - 4B\left(x_b^\beta\right)^3}{RT} \rightarrow (3)$$
- $$\ln \gamma_b^\beta = \frac{(A-3B)\left(x_a^\beta\right)^2 + 4B\left(x_a^\beta\right)^3}{RT} \rightarrow (4)$$

$\Rightarrow$ ① − ③ $\Rightarrow \ln\left(\frac{\gamma_a^\alpha}{\gamma_a^\beta}\right)$

$\Rightarrow$ ② − ④ $\Rightarrow \ln\left(\frac{\gamma_b^\alpha}{\gamma_b^\beta}\right)$

So for this suffix Margules equation, we know RT ln γ_a = (A + 3B) x_b^2 - 4B $x_b^3$and then RT ln γ_b = (A - 3B) x_a^2 + 4B x_a^3. So for α phase you write ln γ_a^α= $\frac{(A + 3B)\left(x_b^\alpha\right)^2 - 4B\left(x_b^\alpha\right)^3}{RT}$. Similarly ln γ_b^α is nothing but $\frac{(A - 3B)(x_a^\alpha)^2 - 4B(x_a^\alpha)^3}{RT}$, this is for the all α phase.

Now for the β phase ln of γ_a^β= $\frac{(A + 3B)\left(x_b^\beta\right)^2 - 4B\left(x_b^\beta\right)^3}{RT}$ and then ln of γ_b^β= $\frac{(A - 3B)\left(x_a^\beta\right)^2 - 4B\left(x_a^\beta\right)^3}{RT}$, now if you do with this equation number 1-3 and then the equation number 2-4, then you will be having ln of $\frac{\gamma_a^\alpha}{\gamma_a^\beta}$ and then here ln of $\frac{\gamma_b^\alpha}{\gamma_b^\beta}$. So these values are related to the mole fractions. So they are equal to corresponding mole fractions.

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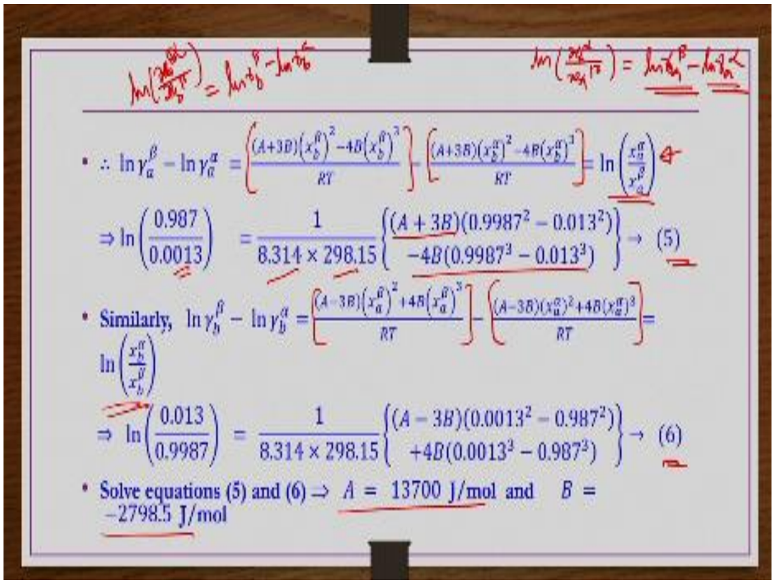

$\ln\left(\frac{x_b^\alpha}{x_b^\beta}\right) = \ln\gamma_b^\beta - \ln\gamma_b^\alpha$ $\ln\left(\frac{x_a^\alpha}{x_a^\beta}\right) = \ln\gamma_a^\beta - \ln\gamma_a^\alpha$

- $\therefore \ln\gamma_a^\beta - \ln\gamma_a^\alpha = \left\{\frac{(A+3B)(x_b^\beta)^2 - 4B(x_b^\beta)^3}{RT}\right\} - \left\{\frac{(A+3B)(x_b^\alpha)^2 - 4B(x_b^\alpha)^3}{RT}\right\} = \ln\left(\frac{x_a^\alpha}{x_a^\beta}\right)$ 4

$\Rightarrow \ln\left(\frac{0.987}{0.0013}\right) = \frac{1}{8.314 \times 298.15}\begin{Bmatrix}(A+3B)(0.9987^2 - 0.013^2) \\ -4B(0.9987^3 - 0.013^3)\end{Bmatrix} \rightarrow (5)$

- Similarly, $\ln\gamma_b^\beta - \ln\gamma_b^\alpha = \left\{\frac{(A-3B)(x_a^\beta)^2 + 4B(x_a^\beta)^3}{RT}\right\} - \left\{\frac{(A-3B)(x_a^\alpha)^2 + 4B(x_a^\alpha)^3}{RT}\right\} = \ln\left(\frac{x_b^\alpha}{x_b^\beta}\right)$

$\Rightarrow \ln\left(\frac{0.013}{0.9987}\right) = \frac{1}{8.314 \times 298.15}\begin{Bmatrix}(A-3B)(0.0013^2 - 0.987^2) \\ +4B(0.0013^3 - 0.987^3)\end{Bmatrix} \rightarrow (6)$

- **Solve equations (5) and (6) $\Rightarrow$ A = 13700 J/mol and B = −2798.5 J/mol**

So that if you have ln of γ_a^β - ln of γ_a^α = this term which is nothing but ln of $\frac{x_a^\alpha}{x_a^\beta}$ we have already done previously simplification so here this $x_a^\alpha x_a^\beta$ given. So RT are known and then here $x_b^\alpha x_b^\beta$ are also known so except A, B everything is known as the parameters. Similarly we have ln of γ_b^β - ln of γ_b^α then we have this expression.

That is nothing but ln of you know, $x_b^\alpha x_b^\beta$. What we have seen in the first slide we have seen of this problem ln of $\frac{x_a^\alpha}{x_a^\beta}$ is nothing but ln of γ_a^β - ln of γ_a^α, this is what we have seen so what we have ln γ_a^β so this term. And then ln of γ_a^α this term. So that this = ln of $\frac{x_a^\alpha}{x_a^\beta}$ this is known so that we are substituted.

Similarly other case what we have, we had this expression ln of $\frac{x_a^\alpha}{x_a^\beta}$ is nothing but ln of γ_b^β - ln of γ_b^α. So this is nothing but ln of γ_b^β and this is nothing but ln of γ_b^α = ln of $\frac{x_a^\alpha}{x_a^\beta}$ these are known so this now you substitute except A and B everything is known in this equation also. So, now equation 5 and 6 are two equations into unknowns A and B.

So if you solve this two equations 5 and 6, then you will get A = 13700 joule per mole and B = 2798.5 joule per mole. So this is how the equations associated with the liquid-liquid equilibrium can be utilized to find out not only the equilibrium composition, but also to find out the parameters associated with the you know, different g^E models applied are used for describing the non-ideality of the liquid phases.

So with this we complete the discussion on liquid-liquid equilibrium as well. The references for this lecture are given here.

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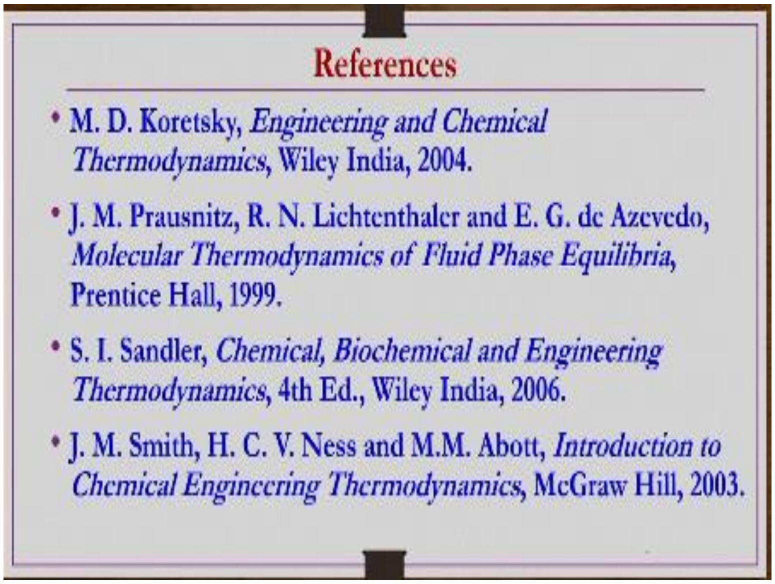

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Engineering and Chemical Thermodynamics by Koretsky. Then Molecular Thermodynamics of Fluid Phase Equilibria by Prausnitz et al and then Chemical Biochemical and Engineering Thermodynamics by Sandler et al and Introduction to Chemical Engineering Thermodynamics by Smith et al. Thank you.