Chemical Engineering Thermodynamics
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Lecture - 46
Two suffix Margules equation

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$$\Rightarrow \frac{\partial (NA x_1 x_2)}{\partial N_1} = A \frac{\partial (N \cdot x_1 x_2)}{\partial N_1}$$

$$= A \frac{\partial}{\partial N_1} \frac{(N_1 N_2)}{(N_1 + N_2)}$$

$$= A \cdot \frac{N_2(N_1 + N_2) - N_1 N_2}{(N_1 + N_2)^2}$$

$$= A \frac{N_2^2}{(N_1 + N_2)^2} \Rightarrow A x_2^2$$

$$\boxed{RT\ln\gamma_1 = A x_2^2} \Rightarrow \bar{G}_1^{ex}$$

Welcome back. So, let us recap what we did in the last lecture. Basically, we were discussing about the models which are relevant for Excess Gibbs Free Energy and the simplest model which we turn out to be the two suffix Margules equation because it satisfies the limiting conditions which is what we described here that if one of the system tends to be a closed system so basically the excess Gibbs free energy should be 0, which essentially means that G can simply be considered as a proportional to X 1 multiplied by X 2, where A is the constant which relates to the interaction strength and is a function of temperature and pressure, not the composition.

So, by considering the basic definition of activity coefficient relations with the partial excess Gibbs free energy one can describe this model or using this model one can come up with an expression of RT ln gamma which is A x2 square that is the basically based on the two suffix model. Now, this turns out to be the simplest model as I said, but it has got some molecular justification.

$$\textit{Molecular justification for two suffix Margule's eqn}:$$

$$g^E = A x_a x_b$$

So, let me; today's class start with the molecular justification of these two suffix Margules equations. So your, the equation is the following. So, what we are going to assume is let us say that all non-ideality is due to the difference in energetics between the a a or a b and so forth. So, if you assume that the non-ideality is due to the difference in energetics between of course a-a, a-b, and b-b, so these are the different combination which essentially also means that Delta S excess is 0.

$$\Delta S^E = 0$$

Now, this assumption valid for roughly same size a and b. So, let us consider the interaction strength and we will be assuming only the two body interaction, so assuming two body interaction that means considering only two body interaction, I can write that energy mix or the energy of the mixture can be simply written by three contribution gamma a a that is interaction strength between a a or the total energy due to a a, gamma a b and gamma b b and they are going to multiply this with the weights.

So, the combination will be xa square 2xa xb and this is xb square. So, this is this contribution of different combination of the groups so in the mixture. You will have a a and then you will have a b and as well as b b and each of them will contribute to the total interaction, but they will have corresponding certain amount of weight that means because that is related to the mole fractions and this is because you can have a gamma a a, a b and gamma b a and if it is just considering gamma a b that would be the weight corresponding to that would be xa and xb.

And since gamma a b is same as gamma b a we got two factors here. So, one can clearly convert this thing into the moles and number of possible combinations and you can write this expression very clearly for the mixtures.

$$\Gamma_{mix} = x_a^2 \Gamma_{aa} + 2x_a x_b \Gamma_{ab} + x_b^2 \Gamma_{bb}$$

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$$\Gamma_{pure,a} = x_a \Gamma_{aa}$$

$$\Gamma_{pure,b} = x_b \Gamma_{bb}$$

Now, in order to find the difference in the energy we need to also find the contribution of the pure species as per the amount present. So, that will be gamma pure a and this would be simply gamma a a multiplied by xa because this is a single component here in this case. And gamma pure b will be simply xb gamma b b. So, if you look into these two terms here, one is gamma mixture, the other one is pure.

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$$\Delta h_{mix} = \{\Gamma_{mix} - (\Gamma_{pure,a} + \Gamma_{pure,b})]$$

$$= x_a^2 \Gamma_{aa} + 2x_a x_b \Gamma_{ab} + x_b^2 \Gamma_{bb} - x_a \Gamma_{aa} - x_b \Gamma_{bb}$$

$$= (x_a^2 - x_a) \Gamma_{aa} + 2x_a x_b \Gamma_{ab} + (x_b^2 - x_b) \Gamma_{bb}$$

$$= -x_a x_b (\Gamma_{aa} + \Gamma_{bb}) + 2x_a x_b \Gamma_{ab}$$

$$= [2\Gamma_{ab} - (\Gamma_{aa} + \Gamma_{bb})] x_a x_b$$

So, the change in energy upon mixing at let us say a given temperature would be your Delta h mix it will be gamma mix minus the pure component gamma pure a plus gamma pure b. So, if you consider this essentially this is the total energy. And now this further can be shown the following

that if you are looking at this, if you replace this expression as xa square gamma a a plus 2 xa xb gamma a b plus xb square gamma b b and then you have this two component minus xa gamma a a minus xb gamma b b.

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So, I can further simplify this by considering the following by taking the common terms here, so xa square minus xa is gamma a a plus 2 xa xb gamma ab plus xb square minus xb gamma b. Now, this will be your xa multiplied by xa minus 1 which would be your minus of xb. Similarly, this would be your xb, so this term remains the same and this term is going to be xb xb minus 1 which will be minus xa. So, you can simplify this further because these two terms are similar in nature. So, we take the minus xa xb and you have this gamma a a plus gamma b b plus 2 xa xb gamma ab.

So, this can be further simplified by considering the fact that this is 2 gamma ab minus gamma a a plus gamma b b and this is xa and xb are common. So, this is the, basically the difference in energy which we are writing this as Delta h mix.

Ideal soln: $\Delta h_{mix} = 0$ or, $\Gamma_{ab} = \dfrac{1}{2}(\Gamma_{aa} + \Gamma_{bb})$

And now one can look at this expression and you can clearly see that if you have this ideal solution you can clearly write as Delta h mix to be 0, if it is ideal solution essentially this has to be 0. So, this is for the ideal solution which essentially means that gamma a b is nothing but half of gamma a a plus gamma bb, it is just a very simple arithmetic mean between the energies here. So, let me also spend a bit of time here.
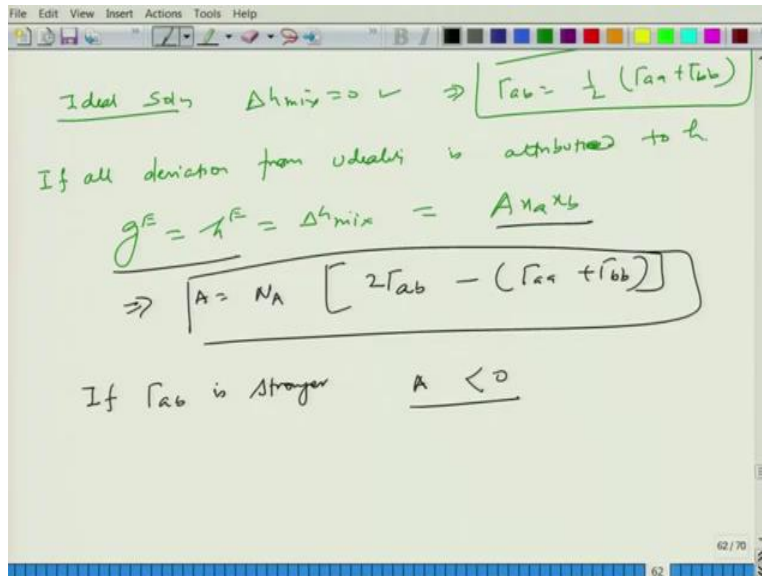
$$g^E = h^E = \Delta h_{mix} = Ax_a x_b$$

$$or, \quad A = N_A[2\Gamma_{ab} - (\Gamma_{aa} + \Gamma_{bb})]$$

$$If \; \Gamma_{ab} \; is \; stronger \; A < 0$$
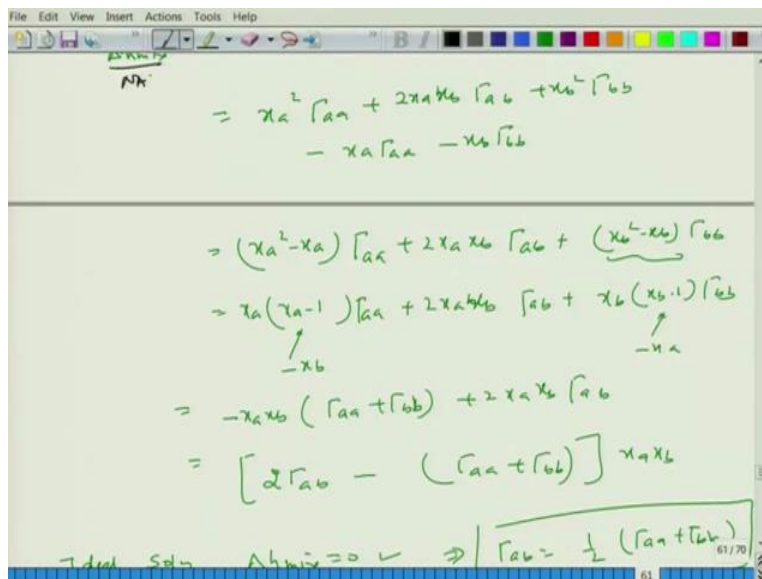
Now, let us assume that if all the deviation, if all deviation from ideality is attributed to basically the energy, attributed to h, then I can write that you know gE is nothing but simply hE which is nothing but simply hE max and in such case I can write this gE, since gE is nothing but A x1 xa and xb, so essentially there now I can relate this because gE is nothing but h minus TS E, since as E is equal to 0 considering that we are considering we are saying that deviation is from idealities all attributed to h.

Then you have this expression and since gE is nothing but this based on the Margules equation and hE can be written as Delta h mix. So, if that is the case, then I can relate this A as the following which means that I can write here A as this term. Now, for the case of normalization we are going to use NA here, so I have missed the Avogadro number, which we have to write here because it is the per mole molecule and hence, I should be writing here this NA.

So, this tells you the following that if gamma a b is stronger than the individual component once, then essentially A has to be less than 0 because stronger means that energy is low and negative, so this is something which we can come up with this expression. So, this gives you an idea of molecular nature of this expression the model which we have come up with. So, let me move forward now. So, clearly, we have now related the A to the interaction behavior between the particles of different type.

$$g^E = \Delta g_{mix} - \Delta g_{mix}^{Ideal}$$

$$or, g = g^E + \sum x_i g_i + RT\sum x_i \ln x_i$$

Now, let me extend this understanding and write the following that you know expression starting from gE. Now, gE by definition we have already discussed this is Delta g mix minus Delta g mix of ideal mixture and we know that Delta g mix is nothing but g minus summation xi gi and this is nothing but your minus RT ln summation xi ln xi. So, that is what we have now. Now, from here I can rewrite this expression, I can of course write this g as gE, I will take this to the left-hand side plus summation xi gi plus RT summation xi ln xi.

So, this is my Molar Gibbs Free Energy which relates to the Excess Gibbs Free Energy plus the component which is nothing but the weighted average of Molar Gibbs Free Energy for individual component plus this RT summation xi ln xi which is mainly due to the entropy expect of that, and of course this is nothing but the Delta g mixture for the ideal solution.

for binary mixture, $g = x_a g_a + x_b g_b + RT(x_a \ln x_a + x_b ln x_b) + g^E$

$$g^E = A x_a x_b$$

So, let me use this expression for the case of binary mixture to understand how does this leads to the changes in the behavior for g or each individual component if we make use of a specific models such as Margules equation here. So, we have 3 components.
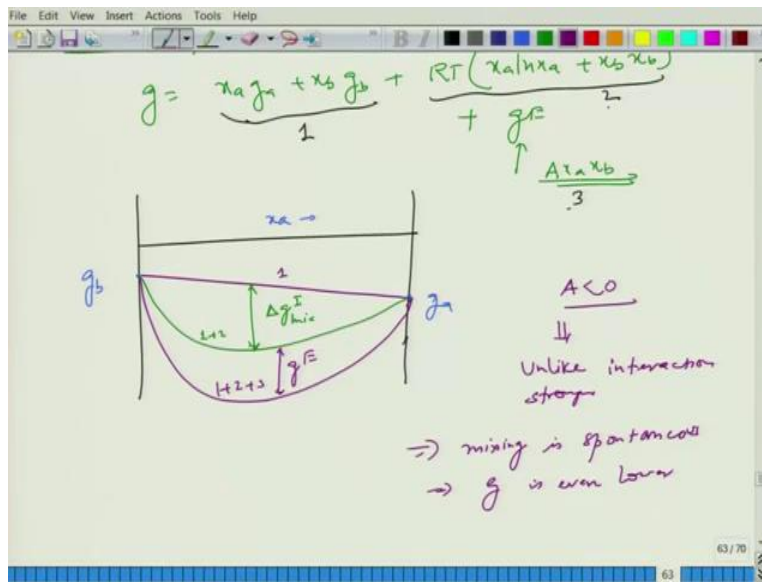
So, let me draw the plot of g and this is let us say 0 here and I am trying to now plot the case where we have g of let us say b here, the pure component g of a. If you look at this one and this is of course the composition. So, if you look at this part 1 or component 1 of this g, then this is nothing but simply a straight line and I can write, I can say that this would be simply like this alright. So, this is nothing but 1.

If I consider the second component together that is the Delta g of ideal mixture this will give us something like this, so this is 1 plus 2 and this is a difference which we see here is due to this mixture. Now, if I add the third component which is A xa xb then essentially, I get say this one this is 1 plus 2 plus 3 and this difference is essentially g of E.

So, this is a case for specifically A less than 0 where you are going to get this kind of curve, this kind of plots for the Molar Free Energies for the case of the binary mixtures where individual component we have described, the first one is a straight line, the second one decreases the Gibbs Free Energy and third one further decreases because A is (less than 1) sorry less than 0.

Now, if is A more than 0 that means if A positive then this becomes a problem. For the case of A less than 0 it means basically the unlike interactions are stronger which essentially means that it is, it prefers to mix which means that mixture or mixing is spontaneous. So, as mixing will be preferred that means g in that case when it is mixed is going to be even lower, (if you have a) if

you have gE term which is non zero that means and considering with A is less than 0 which this means that this will further reduce then mixing will be preferred.

In the case of A greater than 0 which essentially means that if you will go back to the definition of the molecular representation of A, then if A is more than, is positive which means basically this would be more negative compared to this. And that means that interaction between a a and b b is much stronger than a a. So, there are two possible effects which we can consider.

So, this may lead to a two possible or two opposing effect rather, one is that mixing is entropically favored that we know that (intro) you know mixing means that entropy will increase the entropy of mixing, so mixing will lead to increase entropy and hence we call it mixing is entropically favored.

So, if it is a thermal or a non-energetic system essentially which should mean that it would like to mix easily in order to increase the entropy. However, considering that a a and b b interactions together as stronger than a b or unlike interaction this also means that they would like to get separated because of the energetics.

So, separation is energetically favored, so this is something which we can clearly see. Now, what is more dominant in a given system is determined by absolute value of A, so absolute determines the kind of effects. For example, if A absolute is small that means energetic effect is smaller compared to the entropic effect a b will tend to mix in that case. So in such a case, how does your graph may look like?

So, for the case of this essentially now gE which is lower for the case of A is equal to less than 0 will now be little higher for the case of A greater than 0. So, in such case you may see something like this, little bit of here, little bit of up in this which may go. But still we will prefer mixing. So, let me just write it or draw it here.

So, if you are considering this situation so this is gb this is ga and with the ideal part so this is your typical ideal part and with A greater than 0, small a would mean that this slightly above it may go up, but it still prefers to mix because still it is lower, I mean you do not see any specific change in the curvature which would indicate to phase separation.

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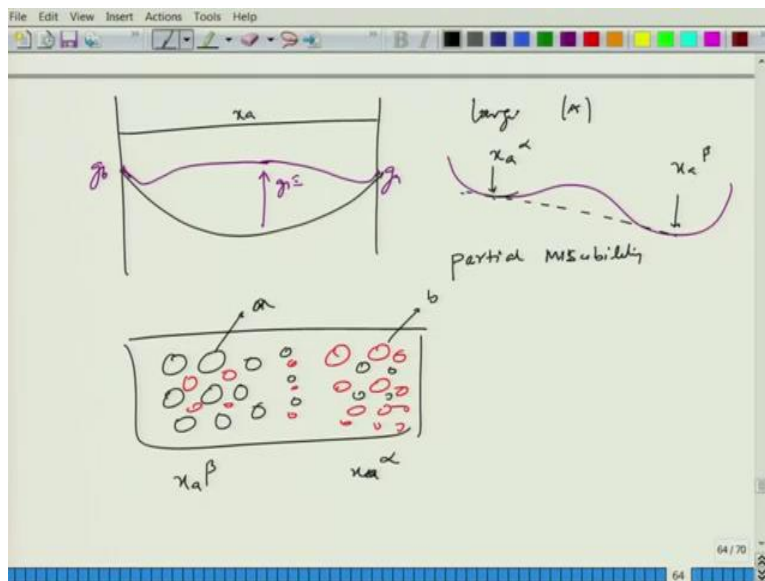
But if it is large, what happens? So, if it is a large you may have a situation like this. So, let me consider the case where it is large and essentially so again we can consider this we have this and here is the one where it was supposed to be like this. Now, this was the case where basically you are considering the one with ideal mixture, so this is the one, the first two component of the g gives you this.

Now, if you considering large, large A then you are going to get something like this where you may have situation where basically you are going to get this. So, it may increase a bit, so it may completely increase in such a way that in certain composition of the mixture the nature of the curve gets completely changed. So, what you had if it is this table part, here you have seen that this would completely change is the nature is like a flipped to the other side.

And this indicates that based on our stability analysis that this part essentially is going to be unstable. So, if you look at a little bit of more carefully this part which I can draw more correctly this may look like this and that is what I wanted to draw. And then if I take a slope here, a tangent here which connects these two minimum, then I obtain a region where basically the intermediate component here, so this is basically from here to here we are changing the composition.

So, the intermediate component will separate in such a way so that it will try to reach a minimum here in one part of the phase and a minimum here in other part of phase. In other word, there will be a phase separation where one phase will be having a composition because it is xa, so let us say this is xa alpha and other one would be your xa beta. So, that would be the composition in a sense. So, this would be a something we call it partial miscibility.

So, you can see from the let us say if you have a container which you are trying to do that then essentially in one part you will have let us say more separated with so this is your composition, the other part will be something like this and there will be some phase separation leading to some kind of a phase separation. So, if you look at this essentially what is that the composition here is with some value xa and this is another phase with value xb, so this could be your xa alpha, this would be your xa beta.

So, these are two completely phase separated in somewhere in this composition leading to a rich let us say in this one, but in this case the rich part would be this, so I will be using separate

connotation this would be your beta and this will be your alpha where this is your a and this is your b. So, this tells you that this is a lean phase and this is a rich phase here.

So, any component when you see such as like this would of course tends to segregate because it will like to have a situation where it is stable based on the nature and the way we do that is we connect or we draw a tangent such that it touches the minimum of it. So, we can move forward now. So, it clearly tells you these examples that the value of a governs the phase stability as well as the composition of the constitute in different phases.

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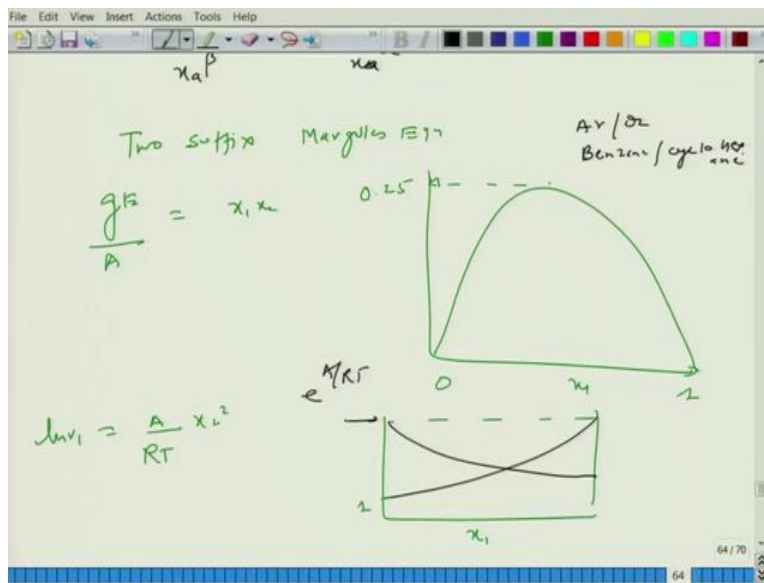
$$\frac{g^E}{A} = x_1 x_2$$

$$\ln \gamma_1 = \frac{A}{RT} x_2^2$$

So, let me look at again the two suffix Margules equation and this particular though is very simple can address some few set of combination of the molecules or mixtures. So, if you look at gE, gE is equal to x1, x2 divided by A. And if you plot this from 0 to 1, what I am going to see is that very interesting that you know this is this will go like this where the maximum is 0.25, so it is quite symmetric.

So, if you get the activity coefficient based on this is going to be like this and it will lead to a symmetric behavior of activity coefficient. So, it is like this that it is from here to here and this somewhere here and this value is nothing but e to power A by RT. So, this kind of expressions of the Margules equation is nothing but it is quite symmetric in behavior. So, if you change x1 to x2 or vice versa the expressions or the behavior does not get affected with that. But still good for couple of systems, the systems for example argon, oxygen, benzene, cyclohexane, so it is simple system of similar size.

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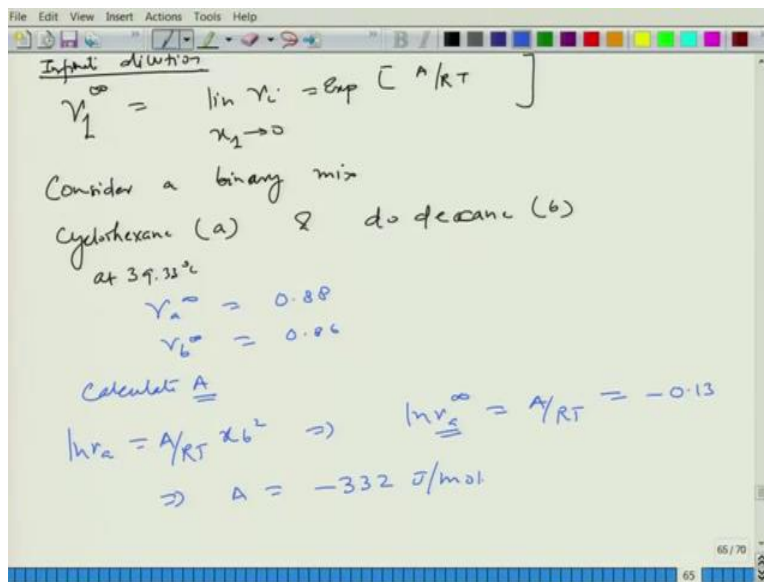
$$Infinite\ dilution:\ \ \gamma_1^\infty = \lim_{x_1 \to 0} \gamma_i = \exp\left[\frac{A}{RT}\right]$$

$$Cyclohexane\ (a)\ and\ dodecane\ (b)\ at\ 39.33\ C,$$

$$\gamma_a^\infty = 0.88\ \ \gamma_b^\infty = 0.86$$

$$Calculate\ A, \quad \ln \gamma_a = \frac{A}{RT}x_b^2\ \ or, \quad \ln \gamma_a^\infty = \frac{A}{RT} = -0.13$$

$$or,\ \ A = -332\frac{J}{mol}$$

So, let me also ask this question that given this how do you effectively calculate A, so we make use of something called infinite dilution conditions when the system is infinitely diluted, the

activity coefficient can be obtained from the experiment. So, in such a case I can define gamma i infinity that is the case of the infinite diluted mixture, where gamma xi goes to 0 and you have this exponential A by RT.

So, given this which is infinite dilution I, so this is something which we can calculate for example so this has to be equal to and this means that this xi goes to 0. So, let me completely write this here, so if it is limit xi gamma i goes to 0 that means it is exponential A by RT x2 square goes to 0, so if it is let us say binary mixture, then essentially I can write this as simply because this other component is going to be 1 and hence I can write this for the case of binary mixture simply like this.

So, this would be true for let us say for component 1 and in that case this will be for the component 1, in that case you are going to get this expression. So, let me try to do an example here, consider a binary mixture with the cyclohexane can be considered let us say a and do decane can be considered as b and they are let us say at 39.33 degree Celsius and what is given to us is gamma a infinity is 0.88 and gamma b infinity is 0.86, so there are two infinite dilution activity coefficients are given to us and we have to calculate based on the data A.

So, if you look at it first, it is straightforward because we are going to apply of course the A when it is referring here is a Margules equation two suffix. So, we are going to simply use ln gamma a as A by RT xb square and for the case of infinity or infinite dilution we have the following A by RT because xb in this case is going to be 1 because XA goes to 0 and this is already given to us so this becomes minus 0.13 and this leads to the value of A which is minus 332 joules per mole.

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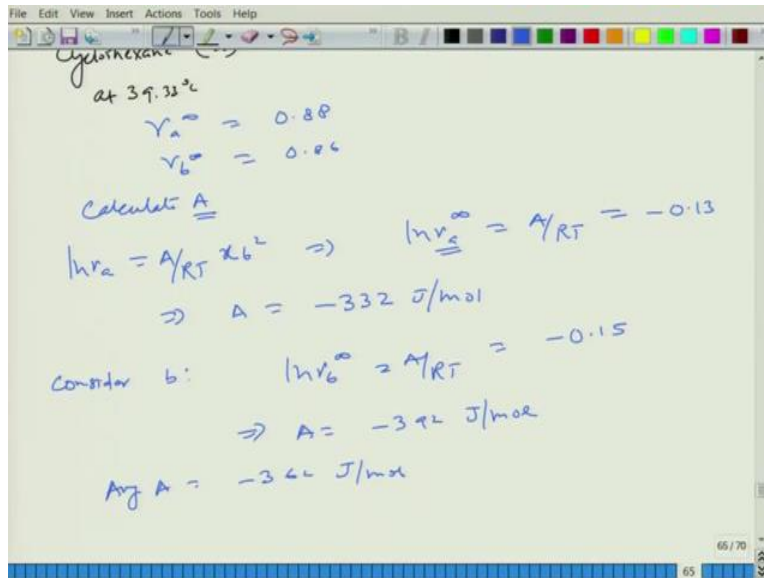
$$\text{Considering } b: \ln \gamma_b^\infty = \frac{A}{RT} = -0.15 \text{ or,} \qquad A = -392 \frac{J}{mol}$$

$$Avg\ A = -366 \frac{J}{mol}$$

Now similarly, we can do that for using this other data which is gamma b infinity 0.86 and let us see how different it is from the one which we just calculated. And if you consider, considering b which means ln gamma b infinity is again A by RT and this is minus 0.15 based on this 0.86 value and this gives us a value of minus 392 joules per mole, very close enough you know but still 20 percent deviation is there.

Considering these variations, we can consider an average value of it, which could be simple arithmetic average which comes out to be minus 362 joules per mole. So, this clearly tells you that based on the experimental data the A can be evaluated, however, it is quite sensitive to what data we have. So, this is what I wanted to cover.

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Basically, there are two things which we have done, one is we have tried to connect the Gibbs Free Energy or the model which was considered in the last class, there are two suffix Margules equations and we connected to the molecular nature of the systems. And the example which we have taken is for the case where basically entropic contributions are negligible and reconnected to the interaction strength of it, which got related to the constant A.

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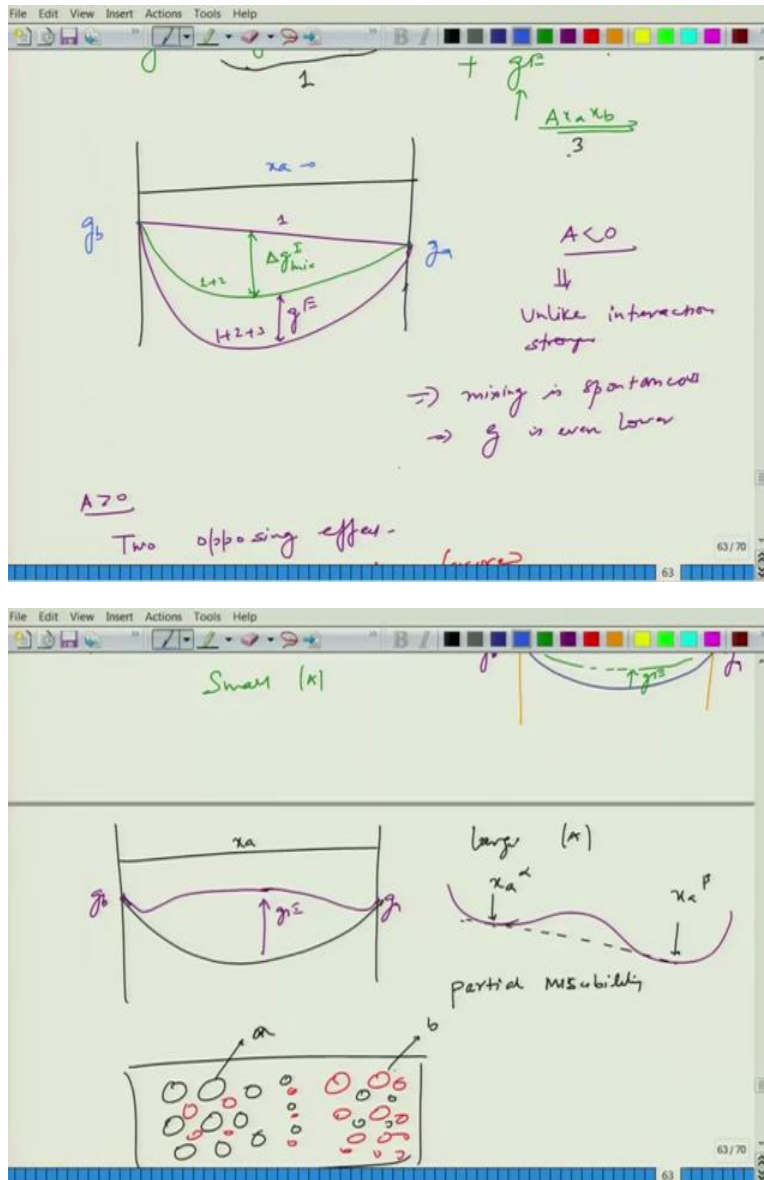
And we consider two cases for the case of A less than 0, it turns out that the mixing is preferred, for the case of A greater than 0, there are two possibilities for a stronger A that means magnitude is much you know higher or the large, you will see a kind of a behavior where basically the curvature gets changed indicating that there is a phase separation a partial miscibility there in the phase leading to two phases in which one is lean in the composition let us say an A and other is in rich.

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And then we finally concluded that you know this constant A can be evaluated from the experiment. However, it is sensitive to the data. So, that would be the end of it, end of today's class. And in the next class we will take it little forward and we consider we will consider different models and try to summarize it and that will be the last class before we move into the phase equilibria calculations, so see you in next class.