

Chemical Engineering Thermodynamics
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Lecture 54
Liquid-Liquid-Equilibria - 1

Welcome back, in the last few lectures we have been looking at vapor-liquid equilibria and particularly in the last lecture we worked on the isotropic mixtures and we looked at the minimum and the maximum boiling point conditions.

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Liquid-Liquid Equilibria

Oil & water do not mix

Using the μ of eq. between phases α & β

$$\mu_i^\alpha = \mu_i^\beta$$

$$\Rightarrow f_i^\alpha = f_i^\beta$$

$$\gamma_i^\alpha x_i^\alpha f_i^\alpha(pure) = \gamma_i^\beta x_i^\beta f_i^\beta(pure)$$

water \leftarrow

oil β

19/31

In today's lecture we will look at liquid- liquid equilibria and basically beyond the vapor range, so essentially, we will be looking at VLLE and as well as the vapor liquid- liquid equilibria. Now, one of the classic examples for liquid -liquid equilibria is oil and water, we know that oil and water do not mix and there is phase separate, and they are both in the liquid phase. And thus, one can apply such a kind of understanding of the equilibrium conditions to such a system such as oil and water.

So, for the sake of illustration we can simply consider instead of just oil and water we can consider any specific two phases such as alpha and beta which are basically liquid, but stay separate, which essentially means for example in the case of oil and if it is a heavier oil so this could be oil and this could be water. And there would be certain amount of oil present in this mainly due to the limited solubility of oil in this contain and vice versa, but mostly they will reside near the interface.

Now, if you want to find out the phase equilibria of such a thing then how do you go about it? You start with the same fundamental question that what are the conditions of equilibrium, so for a given temperature pressure of course you would like to have a temperature of alpha, it should be same as temperature of beta and similarly the pressure equality would be there due to the mechanical here comes stability.

But, what we are interested in this point is this given conditions is basically chemical equilibria. So, we will look at the chemical equilibrium here. So using the condition of equilibrium between a phase alpha, phases alpha and beta we can consider any component, it need not be just water and oil, for any component i in alpha should be same as i in beta. Now this also means that the fugacity of i in alpha phase should be same as fugacity i in beta.

Now we can write this fugacity in terms of the coefficient activity, coefficient because it is a liquid. So, now I am going to express this liquid in the, with respect to the activity coefficient. So I can write it in this way, for case of alpha is like i alpha \times of i in alpha and fugacity of i . Now i is a pure as a reference we are going to consider that and then this is of course Rendell Lewis reference here.

And same would be that for in the beta phase except that we are going to write it here beta and x_i beta and then this is the same reference which is pure and of course this will cancel all because of the fact that this is the same component.

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Using the cond of Eq. between
phases α & β

$$\mu_i^\alpha = \mu_i^\beta$$
$$\Rightarrow f_i^\alpha = f_i^\beta$$
$$\gamma_i^\alpha x_i^\alpha f_i(\text{pure}) = \gamma_i^\beta x_i^\beta f_i(\text{pure})$$

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta$$

Free energy model is needed to express
the γ as a fun of composition in order
to solve for x at coexistence

$$\mu_i^\alpha = \mu_i^\beta$$

$$\text{or, } f_i^\alpha = f_i^\beta$$

$$\gamma_i^\alpha x_i^\alpha f_i(\text{pure}) = \gamma_i^\beta x_i^\beta f_i(\text{pure})$$

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta$$

So, what you have now is an expression which relates activity coefficient of component i in alpha phase composition of component i in alpha phase with activity coefficient of i in beta phase and composition of i in beta phase. Now, in order to you know solve little more than this we need free energy model, is needed to express the gamma as a function of composition. So, this is needed to, gamma as a function of composition in order to solve, to solve for x at coexistence.

So, we need some representation of gamma in terms of rather than free energy in terms of compositions, in order to express that back in this equation and solve it. So, how do you illustrate this? So, we can do that by taking an example.

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to solve for x at coexistence

Example water - cyclohexane L-L Equilibrium

At 313 K, P_{atm} . mutual solubilities in cyclohexane (1) - water (2) binary system were measured to be 1.56×10^{-5} (mole fraction of cyclohexane in water) & 1.13×10^{-3} (mole fraction of water in cyclohexane)

Calculate the activity coefficients of cyclohexane in water & water in cyclohexane.

20/31

$$\gamma_i^{\alpha} x_i^{\alpha} f_i^{\alpha}(P_{atm}) = \gamma_i^{\beta} x_i^{\beta} f_i^{\beta}(P_{atm})$$

$$\gamma_i^{\alpha} x_i^{\alpha} = \gamma_i^{\beta} x_i^{\beta}$$

Free energy model is needed to express the γ as a fun of composition in order to solve for x at coexistence

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19/31

So, let us consider an example to illustrate this particular liquid-liquid equilibria, we can consider the case of water, cyclohexane, liquid-liquid equilibria. And this is a problem at 313 Kelvin atmospheric pressure and it is being said that mutual solubilities in cyclohexane. Let us say this we represent as 1 and water is represented as 2, so mutual solubility in this binary mixture. So it was let us say measured and it was found that is to be to be 1.56 into 10 to power minus 5 mole fraction of cyclohexane in water.

And 1.13 into 10 to power minus 3 this is was the mole fraction of water in cyclohexane, so these are the two things which are given to us, one is the solubility of at given 313 kelvin atmospheric

pressure. The solubility of cyclohexane in water, at equilibrium and similarly the solubility of water in cyclohexane, which is nothing but the mole fraction of water in the cyclohexane at this condition. So these are the two things which are given to us at these conditions.

Now, the question is to calculate the activity coefficient of basically both the case which means water in cyclohexane and cyclohexane in water. So, this is given to us. Now, how do you go about it? We can start, we can start considering the same thing here, because here you have two equations which you can, because it is a binary mixture so we can use this alpha and beta phases for both the components that is for water and in cyclohexane.

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of cyclohexane in water) & 1.13×10^{-3} (mole fraction of water in cyclohexane)

Calculate the activity coefficients of cyclohexane in water & water in cyclohexane.

Phase α : Mostly cyclohexane (1)
 Phase β : Mostly water (2)

Since the phases are almost pure
 $\gamma_1^\alpha = 1$
 $\gamma_2^\beta = 1$

$x_2^\beta = 1.56 \times 10^{-5}$
 $x_2^\alpha = 1.13 \times 10^{-3}$

$\therefore \frac{\gamma_2^\alpha x_2^\alpha}{\gamma_2^\beta x_2^\beta} = \gamma_2^\beta x_2^\beta \Rightarrow \gamma_2^\beta =$

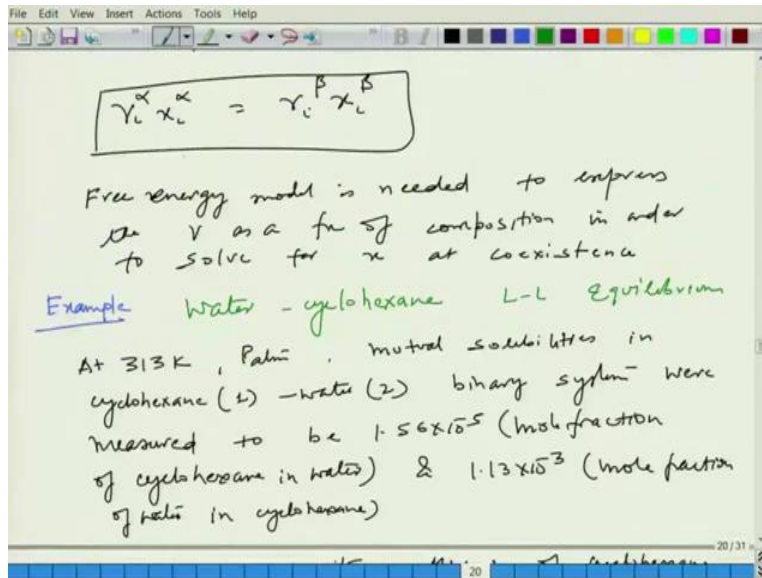
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$\therefore \frac{\gamma_2^\alpha x_2^\alpha}{\gamma_2^\beta x_2^\beta} = \gamma_2^\beta x_2^\beta \Rightarrow \gamma_2^\beta = \frac{x_1^\alpha}{x_1^\beta} = \frac{1-x_2^\alpha}{x_1^\beta} = 6.4 \times 10^4$

$\gamma_2^\alpha x_2^\alpha = \gamma_2^\beta x_2^\beta \Rightarrow \gamma_2^\alpha = \frac{x_2^\beta}{x_2^\alpha} = \frac{1-1.56 \times 10^{-5}}{1.13 \times 10^{-3}} = 885$



So, let us consider the following that phase alpha is mostly cyclohexane and phase beta is mostly water. So, because of the phase separation we can consider that the phase separated or something which is pure or if we consider the specific component. For example, here if we see this is the mostly cyclohexane alpha, so gamma alpha for 1 we can consider to be pure since the phases are almost pure, which means that gamma alpha because the alpha is which contains component 1, so that we can consider 1.

And similarly, beta contains 2, then we can consider it 1. So, the activity coefficient of these phases for these components can be considered 1 because of the pure phase, pure say because of the separation here. Now, we can use this information, now we can plug this let me just expand this with this one. And we can write this expression now. So, what we have here is gamma 1 alpha x 1 alpha is gamma 1 beta x 1 beta.

And similarly, I can write gamma 2 alpha x 2 alpha is equal to gamma 2 beta x 2 beta. So these are the two equations which will come because of the conditions of equilibria. Now, this we can consider to be 1, similarly, this one we can consider it to be 1, this will give us gamma 1 beta, this would be. Now, what is given to us let us also look at it. It is being given is this mole fraction of cyclohexane in water.

So essentially, we have been given mole fraction of cyclohexane in water is something like this x of 1 in beta this is given to us as 1.56 into 10 to the power minus 5. And similarly, mole fraction of water in cyclohexane which is alpha 2 is given to us 1.13 into 10 to power minus 3. So, coming

back to this expression, so we can, we need to find gamma 1 beta, which is nothing but x 1 alpha by x 1 beta.

And similarly, here we can find gamma 2 alpha which is x 2 beta by x 2 alpha and x 1 alpha, x 1 of alpha is nothing but 1 minus x 1 of x 2 of alpha and this is x 1 beta. So essentially, we can now place this so this turns out to be 6.4 into 10 to power 4 and here itself x 2 of beta is 1 minus 1.6 into 10 to power minus 5 divided by x 2 of alpha which is 1.13 10 to power minus 3 and this turns out to be 885.

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Since the phases are almost pure

$$\gamma_1^\alpha = 1$$

$$\gamma_2^\beta = 1$$

$$\therefore \frac{\gamma_1^\alpha x_1^\alpha}{\gamma_2^\alpha x_2^\alpha} = \frac{\gamma_1^\beta x_1^\beta}{\gamma_2^\beta x_2^\beta} \Rightarrow \gamma_2^\beta = \frac{x_1^\alpha}{x_1^\beta} = \frac{1-x_2^\alpha}{x_1^\beta} = 6.4 \times 10^4$$

$$\gamma_2^\alpha = \frac{x_2^\beta}{x_2^\alpha} = \frac{1-1.5 \times 10^{-5}}{1.13 \times 10^{-3}} = 885$$

$\gamma_1^\beta = 6.4 \times 10^4$
 $\gamma_2^\alpha = 885$

Extremely non-ideal system

to solve for x at coexistence

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$$\gamma_1^\beta = \frac{x_1^\alpha}{x_1^\beta} = \frac{1-x_2^\alpha}{x_1^\beta} \quad \gamma_2^\alpha = \frac{x_2^\beta}{x_2^\alpha}$$

$$\gamma_1 = 6.4 \times 10^4 \quad \gamma_2 = 885 \quad (\text{extremely non-ideal system})$$

So, we have gamma 1 so this gives you answers like gamma 1 beta is 6.4 into 10 to power 4 extremely large and gamma 2 alpha is 885 so it clearly tells you and of course because of the phase separation of this nature and non-mixing behavior of the system and this numbers clearly tells us that the system is highly non-ideal, ok extremely non-ideal system, which is indicated by this values which are extremely large.

So, this is something which we can look at it as far as the liquid-liquid equilibria is concerned. Let me little bit more expand it and because see what we have done is we have not used here we not try to use the gamma in terms of the Gibbs free energy models because the problem was here given to us such that we could use these compositions. So, if they that was not the case and if you have to find something in order to be based on the models and then based on the constraints to optimized values or some parameters in order to obtain the phase diagram those condition can be solved using iteratively. So, let me try to little bit add on to this concept so that you can do it on your own.

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ge bar on the suffix Margules Eq

LLE

$$x_1^\alpha \gamma_1^\alpha = x_1^\beta \gamma_1^\beta \rightarrow \exp \left[\frac{A}{RT} (x_2^\beta)^2 \right]$$

$$\downarrow$$

$$\exp \left[\frac{A}{RT} (x_2^\alpha)^2 \right] \quad - \text{Eq 1}$$

Similarly for 2

$$x_2^\alpha \exp \left[\frac{A}{RT} (x_1^\alpha)^2 \right] = x_2^\beta \exp \left[\frac{A}{RT} (x_1^\beta)^2 \right] \quad - \text{Eq 2}$$

21/31

Exp $\left[\frac{A}{RT} (x_2^\alpha)^2 \right]$ - Eq 1

Similarly for 2

$$x_2^\alpha \exp \left[\frac{A}{RT} (x_1^\alpha)^2 \right] = x_2^\beta \exp \left[\frac{A}{RT} (x_1^\beta)^2 \right] \quad - \text{Eq 2}$$

Additionally

$$x_1^\alpha + x_2^\alpha = 1$$

$$x_1^\beta + x_2^\beta = 1$$

Four coupled eq to be solved for four variables.

21/31

$$\text{LLE: } x_1^\alpha \gamma_1^\alpha = x_1^\beta \gamma_1^\beta$$

$$x_1^\alpha \exp \left[\frac{A}{RT} (x_2^\alpha)^2 \right] = x_1^\beta \exp \left[\frac{A}{RT} (x_2^\beta)^2 \right]$$

$$\text{Similarly for 2, } x_2^\alpha \exp \left[\frac{A}{RT} (x_1^\alpha)^2 \right] = x_2^\beta \exp \left[\frac{A}{RT} (x_1^\beta)^2 \right]$$

$$\text{Additionally, } x_1^\alpha + x_2^\alpha = 1 \quad x_1^\beta + x_2^\beta = 1$$

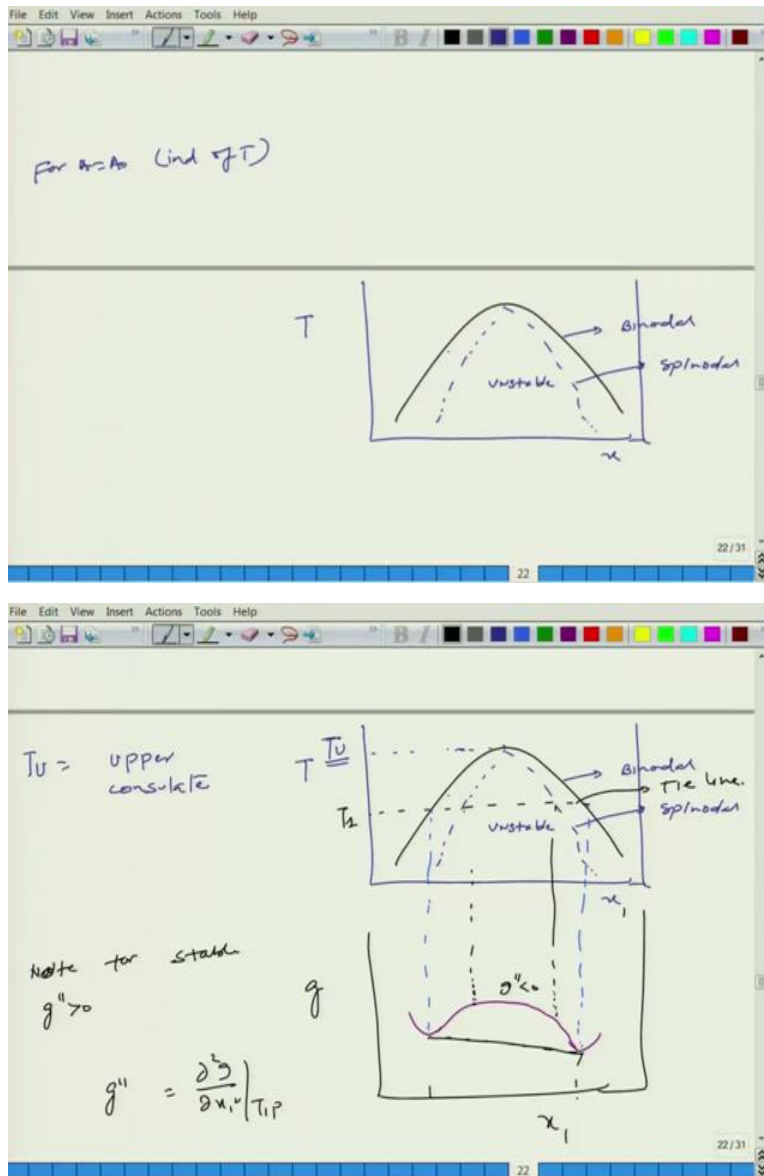
So, let us consider the case that again you have scenario where Gibbs models are given to you. For example, if you use g^E for based on two suffix Margules equation, then the same expression of liquid-liquid equilibria can be written as in this way that $x_1 \alpha_1$ and you have this $\gamma_1 \alpha_1$ is equal to $x_1 \beta_1 \gamma_1 \beta_1$, right so this is our condition of equality. So the question now is that if the models can be used, then how do we solve it?

So, if you are using a two suffix Margules equation we can write γ_1 in terms of exponential A by $RT x_2 \alpha_1^2$. And similarly, here also I can write exponential A by $RT x_2 \beta_1^2$ square this, so this is what you have to do in order to fit, in order to you know express this γ_1 in terms of the composition and temperature. Similarly, if it is a binary component for 2, component 2 I can write $x_2 \alpha_2$ exponential A by $RT x_1 \alpha_2^2$ is equal to $x_2 \beta_2$ exponential A by $RT x_1 \beta_2^2$ square this.

So, you have this let us say equation 2, so this is equation 1, this is equation 2. And then for both the component there are some constraints both the because there are two phases here which we are considering so $x_1 \alpha_1 + x_2 \alpha_1$ is equal to 1, $x_1 \beta_1 + x_2 \beta_1$ is equal to 1, so there are 4 coupled equation which you can solve in order to find 4 variables here which is $x_1 \alpha_1$, $x_2 \alpha_1$, $x_1 \beta_1$, $x_2 \beta_1$. So, this is something which we can solve iteratively, so this is basically the liquid-liquid equilibria.

Now as far as the phase diagrams are concerned one can get a very rich information of in phase equilibria for liquid-liquid. So, let me just provide you an idea about what kind of phase phases or kind of nature we obtain. Because, because of the nature of the molecules, things can be completely different also.

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$$g'' > 0 \quad g' = \left. \frac{\partial^2 g}{\partial x_1^2} \right|_{T,P}$$

So, let us just simply look at one simple case where we have considered let us say A is a constant and let us say for A is equal to independent of temperature you may have a scenario where you have this temperature versus composition, so this is again a binary mixture and you have let us say this is your, the phase diagram here and this is the typical so again this is liquid-liquid equilibria, so this would be more like a rich in one phase or rather it is a pure in one phase this is a pure in

another phase and then you can have this again region where you have unstable region right where it is bound to phase separate and then you have this metastable region which is in this range, right.

So this is often we called earlier also this is a binodal, this is a spinodal and this essentially means that at around this, on this curve the second derivative of Gibbs free energy would be 0 which is the kind of a separation between the metastable and an unstable region. So this point, which is a maximum point is not called critical temperature as you would see in the case of vapor liquid equilibria, so in order to segregate the concept of the maximum temperature at which the phase equilibria can coexist or the vapor liquid can coexist that from the concept to liquid-liquid equilibria we use not TC, but here we use TU here because it is a maximum here and hence we say this as a upper consolute temperature.

Do not get confused with vapor equilibria, there we usually say this as critical temperature, but here since these are liquid-liquid both the phases and hence we use this as your consolute temperature. So, when you go beyond temperature greater than this to consolute temperature of course there will be no phase separation and there is a mixing which completely occurs.

Now, as I said this particular dashed line which I have drawn this is a spinodal and this essentially is also locus of, locus point where basically each one represents double derivative of G to be 0. So, if you plot this corresponding let us say molar G as a function of x again this we can consider one of the components. Then at a given temperature that is a T_1 , you may have a scenario where this is the equilibrium point right and this is where the curvature is going to, the inflection will come, right and basically where the double derivative would be 0.

So, if I have to draw this I would be getting something like this, something like this, so may not be perfect, but so let me try again so this is where I am expecting to be minimum and similarly I am expecting this to be minimum here right and then at this point I am expecting to change the curvature both here. So, this is something where we are expecting that this be something like this, where essentially there this would lead to some curvature change here.

And this point is of course the equilibrium point, this point is where the double derivative is less than 0, so, if you think about this point what if to find out the coexisting condition we often draw if you have the handle to the molar free energy that means if you know the molar free energy we simply draw this tangent line and essentially we obtain these compositions.

So, for the stable region which is the case here the other double derivative is going to be 0. Note for stable phases your double derivative is 0, so essentially this region here which you have here the g double prime is less than 0, alright. So, when I say g double prime actually it means of course double square by $d \times 1$ square at a constant temperature and pressure. So, this is a typical behavior which we can also use in liquid-liquid equilibria, the same way we have tried to explain it, vapor-liquid equilibria so essentially there is no difference as far as the concepts are concerned. Now these concepts are much, not much different also as far as that we use this in the straight line which we have drawn for T_1 is also called tie line.

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$g'' = \left. \frac{\partial g}{\partial x_i} \right|_{T,P}$

$G_{\text{mix}} = RT (x_1 \ln x_1 + x_2 \ln x_2) + g^{EX}$

$G = N \bar{G} = N_1 \bar{G}_1 + N_2 \bar{G}_2 + RT () + g^{EX}$

Gibb's FE of mixing:

$$\Delta G_{\text{mix}} = RT(x_1 \ln x_1 + x_2 \ln x_2) + g^{EX}$$

$g'' = \left. \frac{\partial g}{\partial x_i} \right|_{T,P}$

$G_{\text{mix}} = RT (x_1 \ln x_1 + x_2 \ln x_2) + g^{EX}$

$G = x_1 G_1 + x_2 G_2 + RT () + g^{EX}$

\downarrow
 $A x_1 x_2$

So, now given that it is a mixing which is occurring we can also represent this in terms of Gibbs free energy. Now, we know that Gibbs free energy of mixing can be written as the following, ΔG_{mix} in terms of molar, so molar is of course, if we can use underline here is going to be written by two terms, one is the ideal term once again I am using the binary mixture plus g^{EX} system.

So I can write the total G as $N \bar{G}$ is equal to $N_1 \bar{G}_1$ plus $N_2 \bar{G}_2$ that is the term from the component and then you have this mixing term, which is the same as this plus your g^{EX} ,

multiplied by of course N here. So this will be multiplied by N, so you can multiply by N or I can write actually this further can be written much better by considering this as G molar and this I can represent this as $x_1 g_1 + x_2 g_2$ so this is nothing but the G_1 , capital G 1 underscore.

So, I have this model which I can now, I have this expression which I can now exploit. Now G this I can use this Margules equation we can consider $x_1 + x_2$. Now given this we know from the definition what would be the condition for stability, we need a double g prime greater than 0.

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Gibb FC of mixing

$$\Delta G_{mix} = RT (x_1 \ln x_1 + x_2 \ln x_2) + g^{EX}$$

$$g = x_1 g_1 + x_2 g_2 + RT \left(\dots \right) + g^{EX}$$

↓
A x₁ x₂

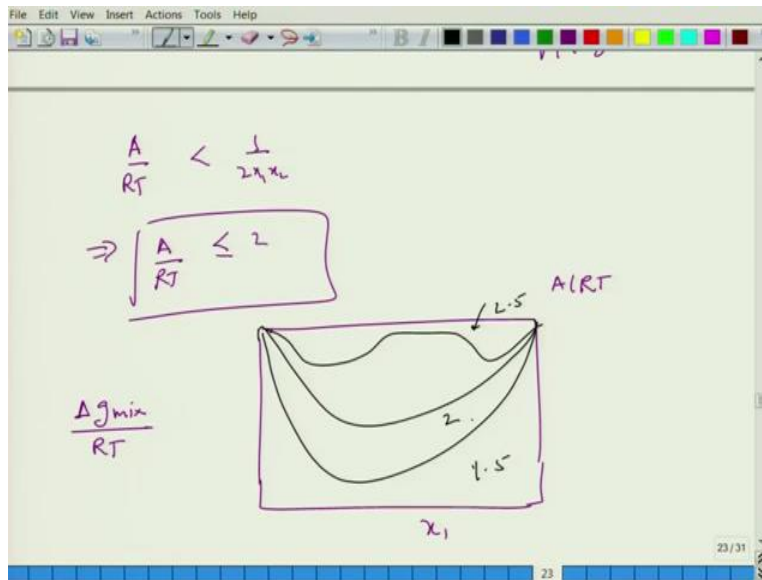
$$\left(\frac{\partial^2 g}{\partial x_1^2} \right)_{T,P} = RT \left(\frac{1}{x_1} + \frac{1}{x_2} \right) - 2A > 0$$

for two suffix Margules eq

$$\left(\frac{\partial^2 g}{\partial x_1^2} \right)_{T,P} = RT \left(\frac{1}{x_1} + \frac{1}{x_2} \right) - 2A > 0$$

So, if I use this double g prime greater than T 1 and P, I am going to get RT 1 by x 1 plus 1 by x 2 minus 2 A for this two-suffix Margules equation. So, if you use, if you use for two suffix Margules equation you have this particular condition. Now for stability we can clearly come up with an expression for the (con) or rather condition for A or which we should have it in order to have the stable phase.

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$$\frac{A}{RT} < \frac{1}{2x_1x_2}$$

$$\text{or, } \frac{A}{RT} \leq 2$$

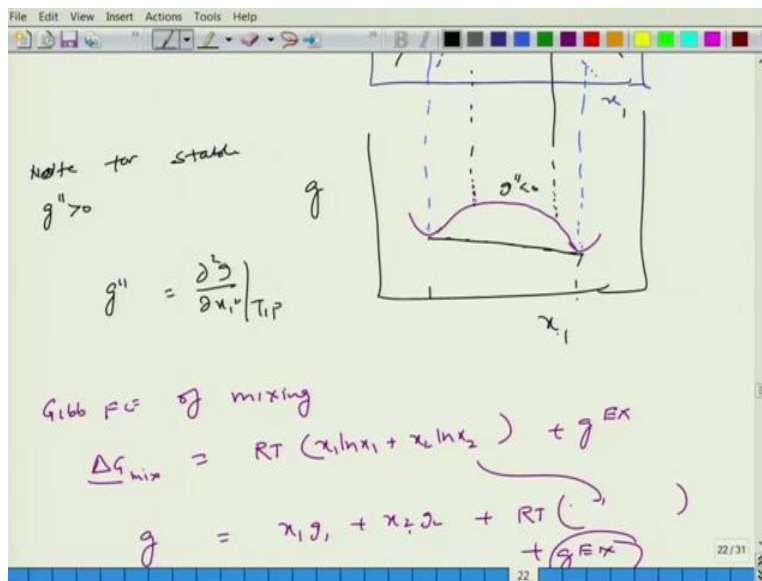
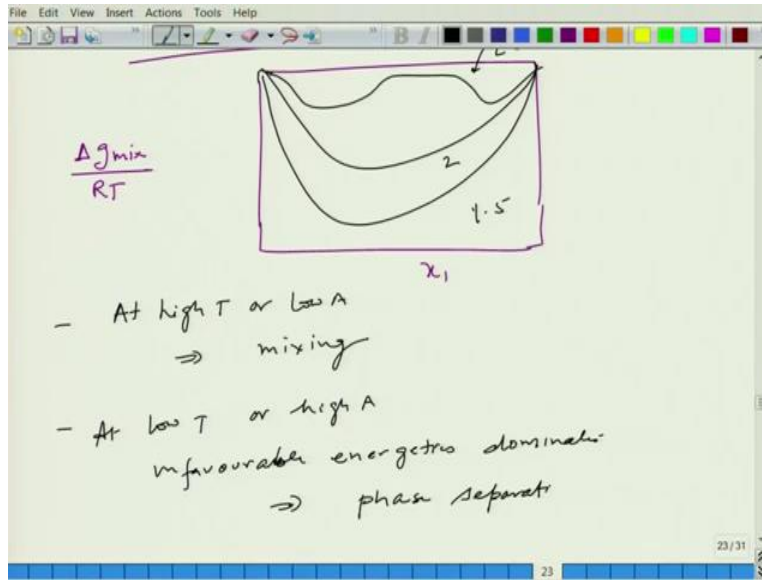
So, if we can simplify this I would get A by RT less than 1 by 2 x 1 x 2. Now, the largest amount so you can optimize this part a bit so because you have to find out the largest amount which would be this one as a limit for that. Now this will be the case when you have x 1 is 0.5 and x 2 is 0.5 which essentially means that this condition can be now written as A by RT less than equal to 2, which will be the case when you have x 1 is equal to 0.5 and x 2 is 0.5.

So this will be the case for your mixing of binary mixtures where you have considered two suffix the Margules equation and you obtain a condition of this constant which we should have it. So, now I can actually draw this this particular delta G mix. So, if I draw Delta G mix so this means it is per mole by RT and I am going to draw this behavior for this binary mixture for the case of more two suffix Margules equation and with a composition of x 1. So here I am going to vary A by RT.

Now, it clearly tells you that A by RT if it is less than 2 or equal to 2 it is going to be stable, so the behavior would be something like this, so this would be something for 1.5 A by RT, this will be the case for 2 and this will be the case and this should be the case for something like this for 2.5

clearly indicating the phase separation. So this is not drawn on scale, but it gives you an idea about that.

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$$g = x_1 g_1 + x_2 g_2 + RT \ln(x_1 x_2) + g^E$$

$$\left(\frac{\partial g}{\partial x_1} \right)_{T,P} = RT \left(\frac{1}{x_1} + \frac{1}{x_2} \right) - 2A > 0$$
 for two suffix Margules eq

$$\frac{A}{RT} < \frac{1}{2x_1 x_2}$$

$$\Rightarrow \boxed{\frac{A}{RT} \leq 2}$$

So, what it can, what you can see that how this number can be achieved is in two ways that at high T which means or low A the values are going to be lower this means it will promote mixing, which we understand that at high T it will try to allow a particle to or molecules to mix, at low T or high A is unfavorable energetics, which dominates, which means that A by RT is going to be larger and this will promote phase separation.

Now this particular expect which we have learned here is also similar analogy or exercise you can do for other phase diagram cases, so you can analyze the parameters which basically can affect the phase separation in the same way. But, what we have done is we have taken a very simple model which is your Margules equation, you can extend this analysis for other models also and try to look at the dependency or the kind of constraints on the parameters on those models.

So I hope that with this you got an idea about liquid-liquid equilibria and particularly how to make use of the activity models in order to obtain the phase diagram, of course if they are constraints as we have discussed that need to be solved iteratively and there is something which you have to try on your own we will not be doing examples to illustrate those things.

But this just to illustrate that what you have done in the case of VLE, the similar kind of exercises have to be in the case of LLE except that we are not going to use Phi or sorry we are not going to use fugacity coefficients, we are going to use activity coefficient of both the phases and similar kind of models for each phases have to be used and the iteratively we have to solve those

constraints. So with that I will stop here and I will see you next time and we will extend this exercise in the next class, so see you later.