

Chemical Engineering Thermodynamics
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Lecture - 36
Equilibrium and Stability

Hello and welcome back to this video lectures on Chemical Engineering Thermodynamics. In the previous lectures we looked at phase equilibrium problem in particular vapour liquid equilibrium and given a set of thermodynamic variables, we looked at how the other set of thermodynamic variables can be calculated for vapour liquid equilibrium. We have started with the simple Raoult's law approach then we have modified it to account for non-idealities of the liquid phase or non-ideal solution as we called it, and then we also looked at how the non-idealities of the gas phase or the vapour phase can be accounted for by using the fugacity coefficients to describe the non ideal gas behaviour.

Then we also looked at using cubic equations of state to achieve this objective. In this lecture today what we look at is how we can extend the ideas and concepts we have developed in phase equilibrium calculations for vapour liquid equilibrium to other types of equilibrium. In particular we are interested in a liquid-liquid equilibrium, LLE and a three phase vapour liquid-liquid equilibrium that is two liquid phases in equilibrium with their vapour. Before we do that what we want to do is, first understand why immiscibility occurs when two liquids are mixed? We will do a little derivation to understand this idea right.

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$$dS_r = \frac{dQ_r}{T_r} = \frac{-dQ}{T_r}$$

If reversible $T_r = T \Rightarrow dS_r = \frac{-dQ}{T}$

$$dS + dS_r \geq 0 \Rightarrow dS - \frac{dQ}{T} \geq 0 \quad \text{--- (1)}$$

$$dU = dQ + dW \Rightarrow dQ = dU - dW \quad \text{--- (2)}$$

$$dS - \frac{(dU - dW)}{T} \geq 0 \Rightarrow TdS - dU + dW \geq 0$$

$$\Rightarrow TdS - dU - PdV \geq 0$$

$dU|_{V,S} \leq 0$

$$\Rightarrow \boxed{dU + PdV - TdS \leq 0}$$

So, first let us take a closed system which is not at equilibrium right, this closed system is not at equilibrium and it is free to exchange energy as well as work with the surroundings. This is the system of interest, it has some arbitrary number of phases, it can be a single phase or it can be more than one phase, but it is not at equilibrium. And, it will reach final equilibrium state by exchanging heat as well as work with the surroundings and we want to use the subscript r for the surroundings.

So, the change in entropy of the surroundings dS_r is going to be dQ_r over T_r and because the amount of heat exchanged with the surroundings is negative of what has been added to the system, it will be negative dQ without a subscript is for the system over T_r . Let us assume that this heat and work exchanges by the system to the surroundings are reversible and if it is reversible then it should occur the system needs to be at equilibrium with the surrounding. So, T will be equal to T_r which implies the change in entropy of the surroundings is going to be negative dQ over T .

Now, in accordance with the second law the change in entropy of the system plus that for the surroundings needs to be greater than or equal to 0, which means dS minus dQ over T is going to be greater than or equal to 0. In addition the first law also requires that dU is dQ plus dW , which means dQ is dU minus dW . So, if I put equation 2 in equation 1 what I end up with is dS minus dU minus dW over T right is greater than or equal to 0

and remember we said that the process is of exchange of heat and work with the surroundings we wanted them to occur reversibly.

So, dW in fact is going to be negative PdV . So, this will be dS or I will simply call it as TdS minus dU plus dW is going to be greater than or equal to 0 right if I multiply it with d all through and then I am going to substitute negative PdV for dW in which case it becomes TdS minus dU minus PdV is greater than or equal to 0. TdS minus dU minus PdV is greater than or equal to 0 or this also means dU plus PdV minus TdS is going to be less than or equal to 0. So, any change that occurs in the system needs to obey this particular inequality right.

And, now all the variables in this inequality are only state variables. So, irrespective of the path we choose whether reversible or not, this particular inequality needs to be satisfied for all changes that are occurring in the system. What this inequality also means is that the change in U at constant V and S is going to be less than or equal to 0 and so on. Of particular interest is the change that occurs at constant temperature and pressure.

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The image shows a blackboard with handwritten mathematical equations. On the left side, the following equations are written:

$$dU + PdV - TdS \leq 0$$

$$dU + d(PV) - d(TS) \leq 0 \quad (\text{at } T, P)$$

$$d(U + PV - TS) \leq 0 \quad (\text{at } T, P)$$

The final result is boxed in blue and labeled with a circled 3:

$$dG|_{T,P} \leq 0 \quad - (3)$$

On the right side of the blackboard, the definition of Gibbs free energy is written:

$$dG = VdP - SdT$$

Below this, the condition for equilibrium at constant temperature and pressure is boxed in blue:

$$dG|_{T,P} = 0$$

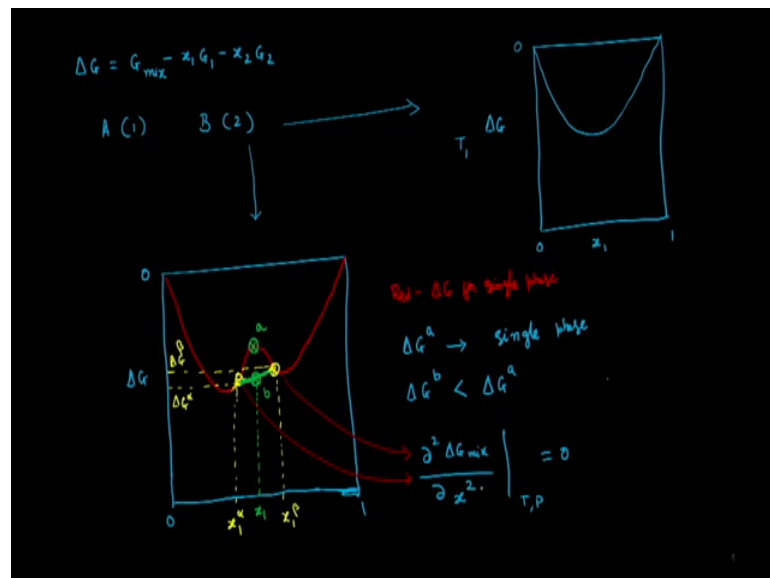
So, let us carry that equation from the previous slide, it is dU plus PdV minus TdS is less than or equal to 0 and if the process occurs at constant temperature and pressure I can also write this as dU plus d of PV , P can go inside the derivative because it's constant the same holds for Td of TS is less than or equal to 0, this is of course, true only at constant T and P . So, if the process occurs at constant temperature and pressure then this

inequality needs to be satisfied. I can also write this as $U + pV$ which is h minus TS is less than or equal to 0.

And since $U + pV - Th$ is the Gibbs free energy I can also write this particular inequality as dG at constant T and P is less than or equal to 0. So, any process needs to obey this particular inequality if it is moving from a non equilibrium state to an equilibrium state. Recall for a closed system dG is $VdP - SdT$ at constant temperature and pressure once the system reaches equilibrium then dG is going to be equal to 0.

So, in a sense the equality in this particular equation three or in this particular expression three is for the equilibrium condition and the inequality is for the change that takes the system from a non equilibrium state to its equilibrium state. So, any movement that occurs needs to satisfy this particular relation or in other words we say that the Gibbs free energy needs to be minimized for an equilibrium state right. So, we can use this idea to understand why immiscibility occurs in a liquid liquid mixture?

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For example let us look at liquid binary liquid liquid mixture, the x axis is for the mole fraction of component 1 and the y axis is for ΔG . Recall the change in Gibbs free energy of mixing ΔG when I mix 2 liquids 1 and 2 the change in Gibbs free energy of the mixing ΔG is defined as G for the mixture minus $x_1 G$ for pure 1 minus $x_2 G$ for pure 2 right.

So, G_1 G_2 are for pure components 1 and 2, G_{mix} is for the molar Gibbs free energy of the mixture, ΔG is the change in Gibbs free energy upon mixing the molar value of course, and because we said if we are doing this process at constant temperature and pressure say room temperature and atmospheric pressure. If I mix 2 liquids then there will be a change in Gibbs free energy of those 2 liquids and that quantity is ΔG , but because we said when the mixing occurs and the system moves from a non-equilibrium state to an equilibrium state, there should be a decrease in the total Gibbs free energy, it automatically means that ΔG always needs to be negative right.

So, this is 0 here and ΔG is always going to be negative at a particular temperature something like that right. At the two pure component ends ΔG of course, is 0 and at intermediate compositions it will have a negative value. Now this particular ΔG curves looks nice and smooth. There is no problem here, but let us take another example, let us say the same mixture of two components A and B right. I am mixing two liquids a denoted by subscript 1 and B denoted by subscript 2. At a particular temperature the change in mixing is given by this figure let us call this as temperature T_1 .

Now, if I mix the same two liquids at a different temperature it might so happen that the change in Gibbs free energy versus the composition might look something like this. Let me use a different colour. Now if this happens first the ΔG is still negative at all points between 0 and 1. The solid red curve here represents the change in the Gibbs free energy if the system remains in a single phase. So, this red curve here denotes ΔG for single phase.

But, notice that between these two points corresponding to this point here and this point here, let us identify those values of the mole fractions x_1^α and let us say the corresponding mole fraction for the second point is x_1^β right. Now, if this particular curve has a different shape between the points x_1^α and x_1^β right. It is concave downward and for example, if I pick a point a then if the mixture stays in a single phase then the Gibbs free energy change upon mixing at point a would be ΔG_a .

On the other hand; however, if the mixture splits into two phases each phase having a composition of x_1^α and x_1^β in different proportions then the overall Gibbs free energy of this two phase mixture would be a linear combination of ΔG at the for the alpha phase and ΔG for the beta phase right, which means it is going to fall on this

line joining ΔG for the alpha phase and ΔG for the beta phase right. So, that would be ΔG for the alpha phase and somewhere there would be ΔG for the beta phase.

And if the mixture splits into two different phases with x_1 alpha and x_1 beta as the compositions for one in those two phases then ΔG would be a linear combination of this which falls on this dotted yellow line or maybe I should change that colour and make it a solid green line and then to maintain the overall composition that value should be at the same value as that of x_1 for a right. Let us call this as point b, and because now the linear combination of Gibbs free energy for phases alpha and beta which is given by ΔG_b is less than ΔG_a .

It turns out that the Gibbs free energy will be lower if the mixture splits into two phases then existing in a single phase. So, the Gibbs free energy of the points on the solid green line are lower than the corresponding points on the solid red curve and because of that reason in between the points x_1 alpha and x_1 beta this particular liquid mixture will exist in two phases. The compositions of the two phases will be x_1 alpha and x_1 beta respectively, they will be existing in different proportions such that the overall composition of the mixture will be such that the overall composition of the mixture can be obtained by the mass balance.

For example in the initial to this requirement it also turns out that mathematically the derivative of ΔG mixing with respect to x at constant T and P will be equal to 0 at these two points. These two points the second derivative of ΔG mixing with respect to x will be equal to 0. So, the condition for immiscibility to occur in a binary system is that ΔG versus x curve needs to be concave downwards or the second derivative of ΔG with respect to x should go to 0.

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$$\begin{aligned}
 & \Delta G, \frac{\partial \Delta G}{\partial x}, \frac{\partial^2 \Delta G}{\partial x^2} \text{ Continuous} \left. \vphantom{\frac{\partial^2 \Delta G}{\partial x^2}} \right\} \text{Complete miscibility} \\
 & \frac{\partial^2 \Delta G}{\partial x^2} > 0 \\
 & \frac{\Delta G}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{G^E}{RT} \\
 & \frac{\partial^2 (\Delta G/RT)}{\partial x_1^2} = \frac{1}{x_1 x_2} + \frac{\partial^2 (G^E/RT)}{\partial x_1^2} \\
 & \frac{\partial^2 (G^E/RT)}{\partial x_1^2} + \frac{1}{x_1 x_2} \geq 0 \quad \text{Stability Criterion}
 \end{aligned}$$

Another way of stating the criteria for stability is that delta G are the first derivative of delta G with respect to the composition or mole fraction. And, the second derivative all of them need to be continuous functions and the second derivative needs to be always if these conditions are satisfied then we will have complete miscibility or stability otherwise instability can set into the system. We talked about excess Gibbs free energies and activity coefficients it is rather convenient to state the condition for miscibility or stability in terms of excess Gibbs free energies and activity coefficients rather than the change in Gibbs free energy of mixing.

So, what we do is try to convert this particular condition for stability in terms of GE and then in terms of activity coefficients. For example, if you recall we said that the Gibbs free energy change upon mixing is related to the excess Gibbs free energy via this equation right. Now, if I take a second derivative of this with respect to x 1 then on the right hand side what I get is one by x 1 x 2 plus the second derivative of GE by RT with respect to x 1 square. So, another way of stating the criteria for stability is derivative of GE over R T by dou x 1 square plus 1 by x 1 x 2 is less than or equal to sorry is greater than or equal to 0.

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$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

$$\Rightarrow \frac{\partial(G^E/RT)}{\partial x_1} = \ln \gamma_1 - \ln \gamma_2 + x_1 \frac{\partial \ln \gamma_1}{\partial x_1} + x_2 \frac{\partial \ln \gamma_2}{\partial x_1} \xrightarrow{\text{Gibbs' Duhem}} = 0 \quad \text{At const. T \& P}$$

$$\left. \frac{\partial(G^E/RT)}{\partial x_1} \right|_{T,P} = \ln \gamma_1 - \ln \gamma_2$$

$$\left. \frac{\partial^2(G^E/RT)}{\partial x_1^2} \right|_{T,P} = \frac{\partial \ln \gamma_1}{\partial x_1} - \frac{\partial \ln \gamma_2}{\partial x_1} = \frac{\partial \ln \gamma_1}{\partial x_1} - \left[\frac{x_1}{x_2} \frac{\partial \ln \gamma_1}{\partial x_1} \right]$$

$$= \frac{\partial \ln \gamma_1}{\partial x_1} \left[1 + \frac{x_1}{x_2} \right] = \frac{1}{x_2} \frac{\partial \ln \gamma_1}{\partial x_1}$$

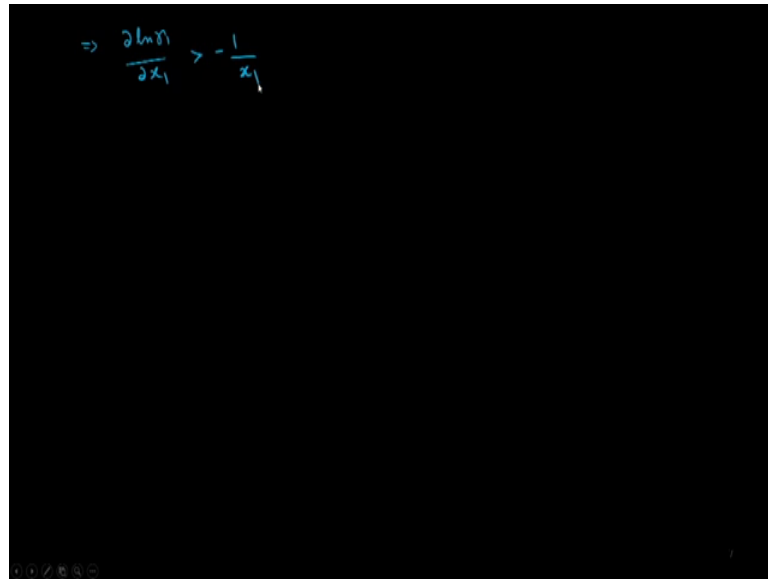
$$\frac{\partial^2(G^E/RT)}{\partial x_1^2} + \frac{1}{x_1 x_2} \geq 0 \Rightarrow \frac{1}{x_2} \frac{\partial \ln \gamma_1}{\partial x_1} + \frac{1}{x_1 x_2} \geq 0$$

Now, one can also express the excess Gibbs free energy in terms of activity coefficients recall that GE by RT is $x_1 \ln \gamma_1 + x_2 \ln \gamma_2$ because $\ln \gamma_1$ is partial molar excess Gibbs free energy. So, what this also means is that the first derivative GE by RT with respect to x_1 is going to be $\ln \gamma_1$ plus well the second one will be negative of $\ln \gamma_2$ because derivative of x_2 with respect to x_1 is minus $1 + x_1/x_2$ now $\ln \gamma_2$ over dx_1 .

Now, remember all these derivations are at constant T and P. So, at constant T and P by Gibbs Duhem equation this particular the sum of these 2 terms will be equal to 0. So, the first derivative then with respect to x_1 at constant T and P will be $\ln \gamma_1 - \ln \gamma_2$. And if I take the second derivative it will be the $2 G^E$ by RT over dx_1 to constant T and P is going to be derivative of $\ln \gamma_1$ over dx_1 minus derivative of $\ln \gamma_2$ over dx_1 .

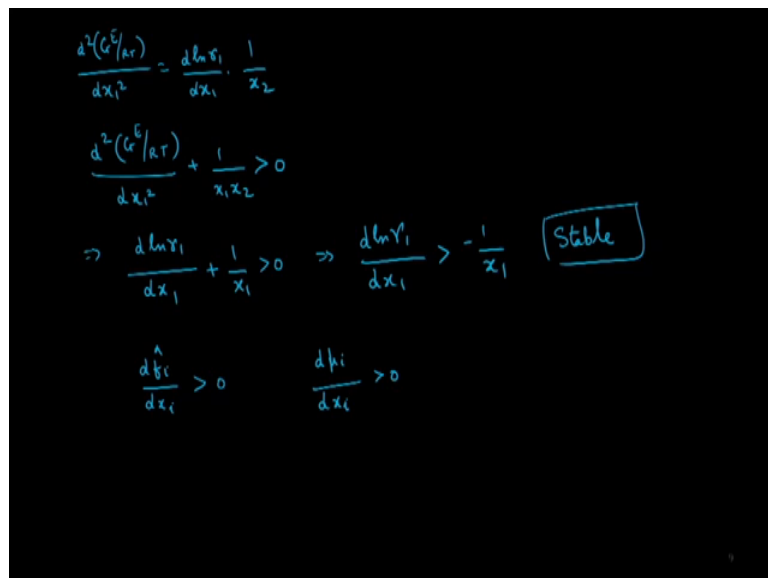
Now, because of Gibbs Duhem equation I can rewrite this as derivative of $\ln \gamma_1$ by dx_1 minus minus x_1/x_2 $\ln \gamma_1$ over dx_1 and that will turn out to be derivative of $\ln \gamma_1$ over dx_1 $1 + x_1/x_2$ which is $1/x_2$ $\ln \gamma_1$ over dx_1 . So, this is the second derivative of GE over RT with respect to x_1 and because of the stability criteria what this means is that derivative of GE over RT by dx_1 squared plus $1/(x_1 x_2)$ was greater than or equal to 0, which implies $1/x_2 \ln \gamma_1$ over dx_1 plus $1/(x_1 x_2)$ is greater than or equal to 0

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$$\Rightarrow \frac{\partial \ln \gamma_1}{\partial x_1} > -\frac{1}{x_1}$$

Or if I were to rewrite this particular equation what this means is, derivative of $\ln \gamma_1$ over x_1 is going to be greater than negative 1 over x_1 .

(Refer Slide Time: 22:57)


$$\frac{d^2(G^E/RT)}{dx_1^2} = \frac{d \ln \gamma_1}{dx_1} \cdot \frac{1}{x_2}$$
$$\frac{d^2(G^E/RT)}{dx_1^2} + \frac{1}{x_1 x_2} > 0$$
$$\Rightarrow \frac{d \ln \gamma_1}{dx_1} + \frac{1}{x_1} > 0 \Rightarrow \frac{d \ln \gamma_1}{dx_1} > -\frac{1}{x_1} \quad \boxed{\text{Stable}}$$
$$\frac{d \hat{f}_i}{dx_i} > 0 \quad \frac{d \hat{\mu}_i}{dx_i} > 0$$

If this happens then the particular liquid mixture is going to be stable there would be no immiscibility otherwise immiscibility will set in, one can also write these criteria in terms of fugacity coefficients and chemical potentials for example, the criteria for stability can also be written as $d \hat{f}_i / dx_i > 0$ or in terms of chemical potential we can show that it will be $d \hat{\mu}_i / dx_i > 0$, etcetera.

So, depending on where we want to use the stability criteria one or more of these equations will come in handy, but of course, all of these are at constant temperature and pressure fine.

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Example

The excess Gibbs' free energy of a liquid mixture is given by $\frac{G^E}{RT} = Ax_1x_2$. For what values of A will the mixture exhibit immiscibility?

$$\frac{d^2(G^E/RT)}{dx_1^2} + \frac{1}{x_1x_2} > 0 \text{ (Stable)} \quad \frac{d^2(G^E/RT)}{dx_1^2} + \frac{1}{x_1x_2} \leq 0 \text{ (immiscible)}$$

$$\frac{G^E}{RT} = Ax_1x_2 \quad \frac{d(G^E/RT)}{dx_1} = A(x_2 - x_1) \quad \frac{d^2(G^E/RT)}{dx_1^2} = A(-1-1) = -2A$$

Immiscible if $-2A + \frac{1}{x_1x_2} \leq 0 \Rightarrow -A \leq -\frac{1}{2x_1x_2} \Rightarrow A \geq \frac{1}{2x_1x_2}$

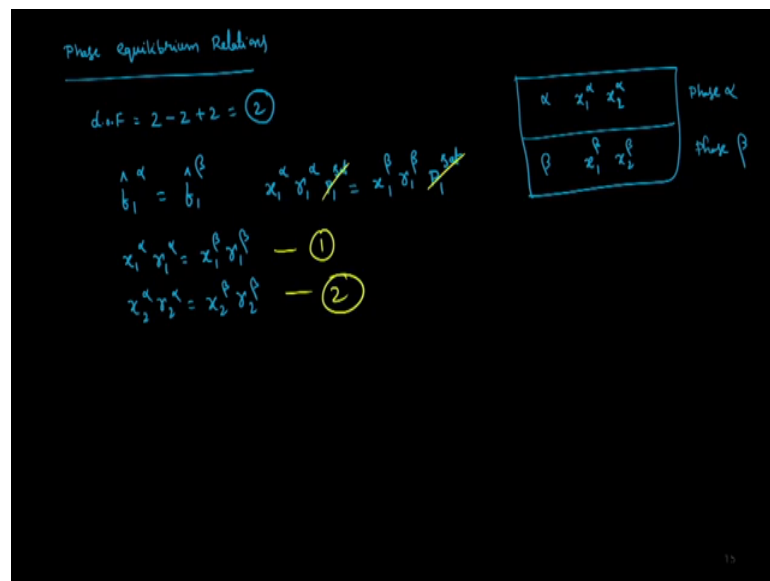
Let us look at an example; the excess Gibbs free energy of a liquid mixture is given by the expression here $x_1 x_2$ that is G^E over RT . So, what values of A will the liquid mixture exhibit immiscibility? We will now solve this problem, the excess Gibbs free energy of a liquid mixture is given by G^E by RT is $x_1 x_2$ and we want to know for what values of A will the liquid mixture exhibit immiscibility.

To solve this particular problem what we will do is actually write the condition for stability, recall that the condition for stability is $\frac{d^2(G^E/RT)}{dx_1^2} + \frac{1}{x_1 x_2}$ is greater than 0 or in other words the condition for immiscibility is $\frac{d^2(G^E/RT)}{dx_1^2} + \frac{1}{x_1 x_2}$ is less than or equal to 0 then there will be immiscibility.

Of course, the inequality is for immiscibility at equal to 0 immiscibility just sets n . Now, so what we will do is we will take the expression for G^E by RT given to us and find its second derivative; so, let us find the first derivative G^E over RT by dx_1 is A derivative of x_1 is 1. So, x_2 minus derivative of x_2 is negative 1 minus x_1 and that implies the second derivative is going to be A minus 1 minus 1 so that is minus 2 A .

So, the second derivative for this particular expression is negative $2A$. So, for immiscibility negative $2A$ plus 1 over $x_1 x_2$ should be less than or equal to 0 or negative A is less than or equal to negative 1 over $2 x_1 x_2$ or A is greater than or equal to 1 over $2 x_1 x_2$ so, the criteria for immiscibility or instability is that the coefficient A needs to be greater than or equal to 1 over $2 x_1 x_2$. Now, that we have seen the criteria for immiscibility let us look at how we can write the phase equilibrium relations for a liquid liquid equilibrium.

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Essentially what we have is, two liquid phases; an alpha phase and a beta phase, each having let us say a binary mixture. So, the composition in the beta phase is x_1^β and x_2^β the composition in the alpha phase is x_1^α and x_2^α .

Notice that I am using the same variable named x for both phases because we are talking about liquid phases here, to distinguish between the phases we're using a superscript alpha and a beta. Now if I were to write the phase equilibrium relations for this, now before writing the phase equilibrium relations let us identify the degrees of freedom for this particular system, I have 2 phases 2 components plus 2 so, degrees of freedom is 2.

What it tells me is that given any two criteria just as in a vapour liquid equilibrium given temperature and mole fraction of one of the phases I should be able to find all the other thermodynamic variables etcetera. And we do that by writing the phase equilibrium relations. Phase equilibrium relations for this particular system are given by equality of

fugacities for component 1 it would be f_1 in the alpha phase needs to be equal to f_1^{hat} in the beta phase and the fugacity coefficient in the liquid mixture can be expressed in terms of activity coefficients x_1^{alpha} the activity coefficient of 1 in the alpha phase γ_1^{alpha} times the vapour pressure of 1 we are ignoring the non idealities of the vapour phase.

So, we are going to assume that the vapour phase is ideal gas like will ignore the Poynting correction factor as we have done earlier for expressing the liquid phase fugacity coefficients and for the beta phase it will be x_1^{beta} γ_1^{beta} times the vapour pressure again for 1 at the saturation conditions. So, notice that I have the vapour pressure for 1 at the saturation condition on both sides, which can be cancelled. So, what I am left with essentially for the phase equilibrium relation is that x_1^{alpha} γ_1^{alpha} is going to be equal to x_1^{beta} γ_1^{beta} .

And I can write a similar expression for two x_2^{alpha} γ_2^{alpha} will be equal to x_2^{beta} γ_2^{beta} . So, these are my two phase equilibrium relations. So, if I have an activity coefficient model then I can use these two phase equilibrium relations along with the activity coefficient models to solve for the unknown variables given sum of the thermodynamic variables of interest. With that let us stop the lecture for today, when we come back we will solve an example on a phase equilibrium relation involving liquid-liquid mixture. And then we will look at what is known as a vapour liquid-liquid equilibrium a three phase equilibrium.

Thank you.