Advanced Thermodynamics
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Lecture -26
Liquid - Liquid Equilibrium

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is liquid-liquid equilibrium.

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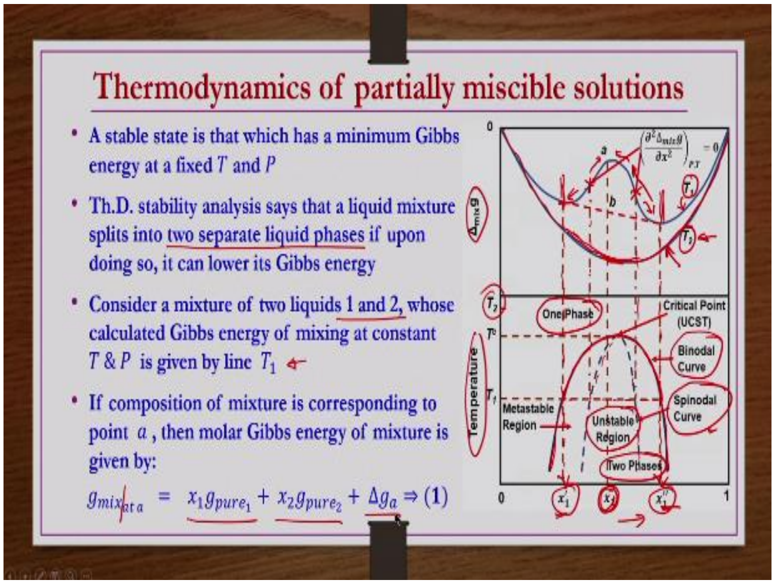

Thermodynamics of partially miscible solutions

- A stable state is that which has a minimum Gibbs energy at a fixed T and P
- Th.D. stability analysis says that a liquid mixture splits into two separate liquid phases if upon doing so, it can lower its Gibbs energy
- Consider a mixture of two liquids 1 and 2, whose calculated Gibbs energy of mixing at constant T & P is given by line T_1
- If composition of mixture is corresponding to point a, then molar Gibbs energy of mixture is given by:

$$g_{mix}\big|_{at\ a} = x_1 g_{pure_1} + x_2 g_{pure_2} + \Delta g_a \Rightarrow (1)$$

Now, we take a thermodynamics of partially miscible solutions where the system trying to lower its energy by separating in two phases. In order to make this system stable, then it has to lower the energy, in the process of lowering the energy it has to split into phases, then only it can become stable. It depends on the temperature pressure and composition and all that. So, but what we do with different temperatures of different compositions?

How this miscibility changes? Or how the behavior like, you know, partially miscible system on their phase diagram. How the Gibbs energy is changing with composition? Or how the temperature is playing in order to form a kind of partially miscible solution or completely miscible solution those things we are going to see now. A stable state is that which has a minimum Gibbs energy at fixed temperature and pressure and then thermodynamic analysis says that a liquid mixture splits in two separate liquid phases if upon doing so, it can lower its Gibbs energy.

So now let us consider a mixture of two liquids, liquid 1 and 2, whose calculated Gibbs energy of mixing it constant temperature and pressure is given by line T_1. So, this is the picture that we see. So, this Gibbs energy, or change in Gibbs energy with respect to the composition is given here. So, you can see when the temperature is T_1 the Gibbs energy versus composition. If you plot it is having this particular shape.

That means the energy is not lowering for certain range of mole fraction, it is having some kind of maximum kind of thing. So, there is a possibility that you know, if you change the composition it may go, towards the lower energy. That is what you can see. So this is a temperature T_1 we are doing. So now clearly we can understand from $\Delta_{mix}g$ versus x_1 plot, it is not having a kind of a lower energy so it is not stable. So what it will do at this composition x_1, if you take $\Delta_{mix}g$ at this point a so it is not the lower energy.

So, it is not stable at this point what it will try to do? In order to lower its energy, it will try to split in 2 phases. And then it forms 2 stable partially miscible liquid phases having this compositions x'_1 and then x''_1. Obviously when we add this liquid component 1 and 2 having x_1 mole fraction. If that x_1 mole fraction, we have seen $\Delta_{mix}g$ versus x_1 if it is having this curve so at x_1 location or at x_1 composition, the point a, it is not the lower the energy it is indeed higher the energy so it will try to split into two phases.

So that it can make the system stable, ultimately it wants the system to be stable. So, then it splits into 2 phases having different composition x'_1 and then x''_1 and then 2 partially miscible phases is taking place. So now this curve whatever $\Delta_{mix}g$ versus x_1 curve. If you see so there is a reason, you know, from this region onwards let us say, this $x'_1$and then x''_1, this region you can say whatever the region that is envelope under which it is there so that region you can call it as a kind of unstable region or the region in which the 2 phases are taking place or the liquid is splitting into 2 phases. So above this envelope whatever the region is there that region we call it as kind of single phase region. So, I am showing temperature versus composition as well the curve also I am showing here.

So, temperature versus this one, we can come to the other case, so a temperature T_1. This whatever the, in respect to x'_1 and x''_1 that region is there envelope, within that region will be having unstable region because we have seen that is the region where in which the energy is going towards the increasing side. So x'_1 to x_1 or x''_1 to x_1 that region, you know.

This term if you go towards this side from x'_1 to x_1 or from x''_1 to x_1 side, either side if you go the system energy is increasing. So that region we call it as a kind of unstable region. And then other regions whatever is there that we call a stable single phase region. So that single phase region with respect to temperature if you see.

Let us say if you obtain the same $\Delta_{mix}g$ versus composition at different temperature T_2 and then for that case, let us say if you have the curve like this shown like this curve here, designated as T_2 curve here, so what happens here this is system is having lower energy at this x_1 are in the vicinity of the x_1, it is having the lower energy. So, it is in a stable position, so obviously it does not require to split into 2 phases rather, it will be forming one single phase.

So, the temperature at T_2 will be having one single phase without, you know, forming partially miscible phases like that, that is there. So that is corresponding to temperature T_2. So, within these two phase regions, whatever this x'_1 and x''_1 region enclosed by this curve that is known as the 2 phase region. Within these 2 phase regions, we may have a two different regions, unstable regions and metastable regions like this.

Unstable region and metastable region, so that you can separate out. So in this $\Delta_{mix}g$ versus x_1, if you plot there would be a kind of point where this second derivative of $\Delta_{mix}g$ = 0. So from this point towards a either side is known as the region completely unstable region and then from this point towards the other side x'_1 and then x''_1 towards this side whatever that region is there that we call it as a kind of metastable region.

And then the temperature whatever the upper limit of the temperature, up to which you know, the 2 phase region is forming, you know, that is known as the critical point. Beyond this critical point of temperature, we can have only single phase only one phase will take place and then below that critical temperature, you know, and then composition is between these x'_1 and then x''_1 in these two regions are there.

Then what happens two phase region will take place within this two phase region, there will be kind of metastable region and then unstable regions are there. So the curve which is you know, distinguishing or separating the two phase region from one phase region is known as the binodal curve. And within the two phase region the curves which this dotted curve which separates the metastable region, unstable region into two is known as the spinodal curve.

And then this binodal curve that means the locations where this $\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} = 0$ that region is designated by this spinodal curve. Now if composition of a mixture is corresponding to point a, then molar Gibbs energy of mixture at this point a is obviously can be given as x_1 g_1 or x_1 $g_{\text{pure }1}$ + x_2 $g_{\text{pure }2}$ + $\Delta g_{a,mix}$. So, that is g_{mix} at point a is nothing but x_1 $g_{\text{pure }1}$ + x_2 $g_{\text{pure }2}$ + Δg_a.

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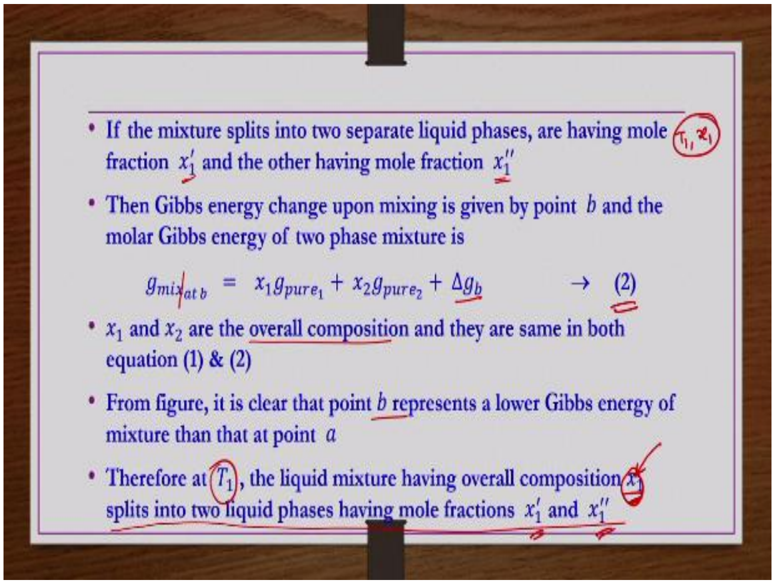

- If the mixture splits into two separate liquid phases, are having mole fraction x_1' and the other having mole fraction x_1''

T_1, x_1

- Then Gibbs energy change upon mixing is given by point b and the molar Gibbs energy of two phase mixture is

$$g_{mix}\big|_{at\ b} = x_1 g_{pure_1} + x_2 g_{pure_2} + \Delta g_b \quad \rightarrow \quad (2)$$

- x_1 and x_2 are the overall composition and they are same in both equation (1) & (2)
- From figure, it is clear that point b represents a lower Gibbs energy of mixture than that at point a
- Therefore at T_1, the liquid mixture having overall composition x_1 splits into two liquid phases having mole fractions x_1' and x_1''

Now if the mixture splits into two separate liquid phases, then having mole fractions x'_1 and then other one is having a mole fraction x''_1 when we add together at temperature T_1 and then composition x_1, if you add these components one and two. So, the energy is higher energy, it is not lower energy. So obviously, it is splitting into two separate phases.

When it is separating into two liquid phases so one phase is having mole fraction x'_1 and then other phase is having mole fraction x''_1. They are not equal to x_1 because partial miscibility is taking, it is not completely immiscible. So partial miscibility is taking place so two phases are forming one phase, may be rich in component one and another phase may be rich in component two. Let us say x'_1 is rich in component two and then the phase with mole fraction x''_1 is say that is rich in component one.

That we can understand from the graph because x''_1 we designated towards mole fraction = one. And then x'_1 we designated towards mole fraction $x_1 = 0$ towards that side pictorially. So, this region this may be pictorially it is not very clear this phase may be rich in component two whichever the phase of being separated by adding these two components if they are splitting in two phases.

Each one having mole fraction x'_1 and x''_1. So x'_1 phase would be rich in component two and then x''_1would be rich in component one. That is what we can see here by pictorially. So now then Gibbs energy change upon mixing is given by point b and the molar Gibbs energy of two, phase mixture is given by g_{mix} at b = $x_1\ g_{\text{pure 1}} + x_2\ g_{\text{pure 2}} + \Delta g_b$.

Now x_1 and x_2 are overall compositions and they are same in both equations 1 and 2. This equation 1 and 2 that is g_{mix} at point a and point b whatever are there. So, they are valid further. I mean the x_1, x_2 required for in those equations are overall compositions x_1 and x_2, they are same in both equations one and two. And from figure it is clear that point B represents a lower Gibbs energy of mixture than that at point a.

Therefore, at T_1 the liquid mixture having overall composition x_1 splits into two liquid phases having mole fractions x'_1 and then x''_1 that is what we have seen pictorially. So, when we add these components one and two at this composition x_1 and then at this temperature T_1 what happens the energy is higher, so it has to lower the energy in order to go towards the stable side.

So, in order to going towards the region stable side what happens? This splits into two phases, two liquid phases having compositions small fraction x'_1 and then x''_1 respectively.

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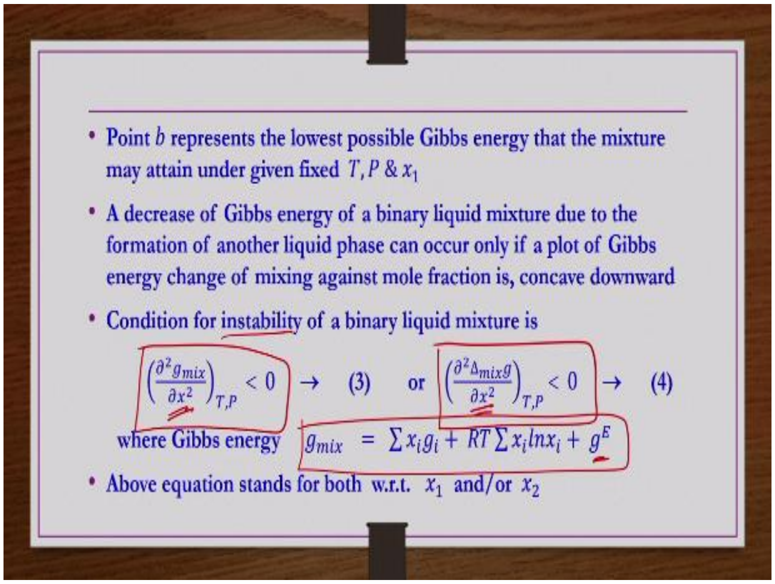

- Point *b* represents the lowest possible Gibbs energy that the mixture may attain under given fixed T, P & x_1
- A decrease of Gibbs energy of a binary liquid mixture due to the formation of another liquid phase can occur only if a plot of Gibbs energy change of mixing against mole fraction is, concave downward
- Condition for instability of a binary liquid mixture is

$$\boxed{\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} < 0} \rightarrow (3) \quad \text{or} \quad \boxed{\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} < 0} \rightarrow (4)$$

where Gibbs energy $\boxed{g_{mix} = \sum x_i g_i + RT\sum x_i ln x_i + g^E}$

- Above equation stands for both w.r.t. x_1 and/or x_2

So, point b represents the lowest possible Gibbs energy that the mixture may attain under given temperature, pressure and then composition. So, a decrease in Gibbs energy of a binary liquid mixture due to the formation of another liquid phase can occur, if a plot of Gibbs energy change of mixing again a small fraction is concave downward as we have seen in the picture. So, condition for instability of a binary liquid mixture should be obviously, what $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} < 0$ or $\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} < 0$.

If this condition is there, then we can say there is splitting in two phases is taking place. So that is the region this condition is known as the instability condition. Where Gibbs energy g_{mix} is nothing but $\sum x_i g_i + RT \sum x_i \ln x_i + g^E$. So, in order to know this, conditions whether the less than or greater than 0 or whether the instability is there or not, we need to know what is this g^E? Once we know this thing then we can simply substitute here and then do the calculation and then these differentiations whatever are there they are true with respect to both x_1 or x_2 or both.

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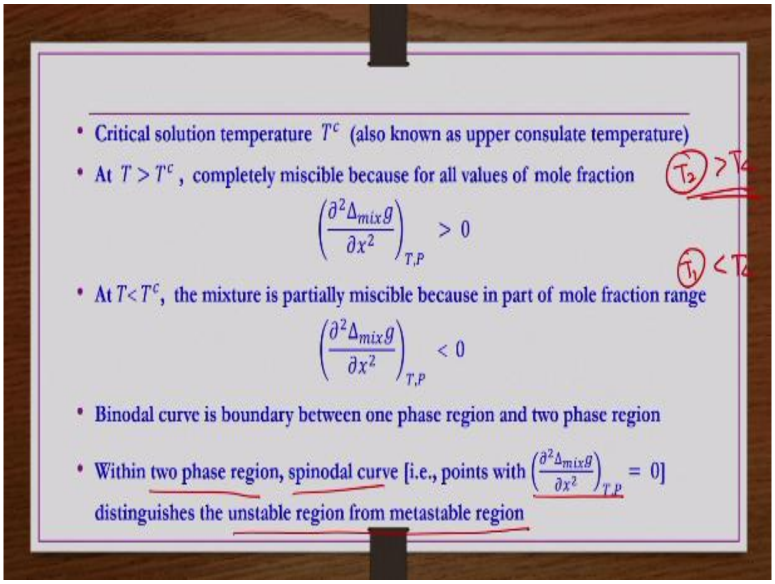

- Critical solution temperature T^c (also known as upper consulate temperature)
- At $T > T^c$, completely miscible because for all values of mole fraction

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

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

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

- Binodal curve is boundary between one phase region and two phase region
- Within two phase region, spinodal curve [i.e., points with $\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} = 0$] distinguishes the unstable region from metastable region

$T_2 > T$

$T_1 < T$

So critical solution temperature T^c that we have seen in the picture, below which the mixture is separating into two phases region and then above which mixture is forming one single phase region by complete miscibility. So that critical solution temperature is also known as the upper consulate temperature. So, if the temperature $T > T^c$ completely miscible solution will take place because for all values of mole fraction we have seen when $T > T^c$.

That is, $T_2 > T^c$ that is what we have seen pictorially. So here what happens we have seen $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} > 0$. And then when temperature $T < T^c$ so in this case $T_1 < T^c$. So, for that case, mixture is partially miscible. Because in some part of mole fraction range what we have seen this $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} < 0$.

So binodal curve is the boundary between one phase region and two phase region and then within the two phase regions spinodal curve that is the points with $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} = 0$ that distinguishes the unstable region from metastable region. Within this two, phase region, there are two unstable regions are there. One is the completely unstable region another one is the metastable region. So, the curve which differentiate between the metastable region and then unstable region is known as the spinodal curve. For this curve whatever this $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} = 0$.

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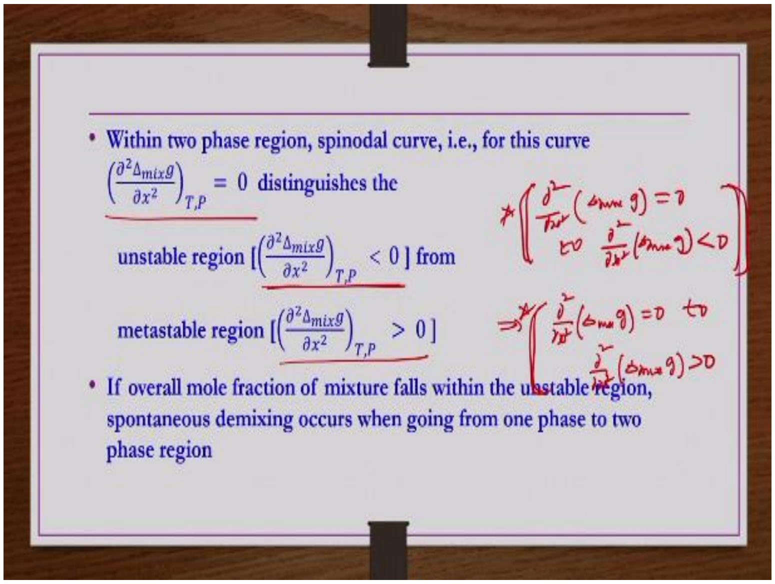

- Within two phase region, spinodal curve, i.e., for this curve $\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} = 0$ distinguishes the

  unstable region [$\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} < 0$] from

  metastable region [$\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} > 0$]
- If overall mole fraction of mixture falls within the unstable region, spontaneous demixing occurs when going from one phase to two phase region

$* \left[\frac{\partial^2}{\partial x^2}(\Delta_{mix} g) = 0 \text{ to } \frac{\partial^2}{\partial x^2}(\Delta_{mix} g) < 0 \right]$

$\Rightarrow * \left[\frac{\partial^2}{\partial x^2}(\Delta_{mix} g) = 0 \text{ to } \frac{\partial^2}{\partial x^2}(\Delta_{mix} g) > 0 \right.$

So, within two phase region, spinodal curve that is for this curve and $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} = 0$, which distinguishes the unstable region. Unstable region further this instability condition is there. Instability conditions whatever $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} < 0$ this is the condition for the instability. So, all that region for which composition this $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} < 0$ is known as the unstable region.

And then for all that composition or the mole fraction region for which $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} > 0$ and between $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} = 0$ between these two region are there whatever the region is that is known as metastable region. It is metastable region that means from the region of, this is the metastable region or the range of composition for which this second derivative of $\Delta_{mix} g$ with respect to the composition is varying between 0 to or greater than 0.

That is metastable region and then unstable region is the region where this second derivative of $\Delta_{mix} g = 0$ to $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} < 0$. So, these range of composition for which these two conditions are there. So that we call it as a kind of a unstable region. This is completely unstable region. This is metastable region.

And then these two, region are separated by a spinodal curve for which we have $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} = 0$. If overall mole fraction of mixture falls within the unstable regions spontaneous de-mixing occurs, when going from one phase to the other phase region, obviously. So now the equation, whatever instability condition that we have seen that is we have written in terms of g or $\Delta_{mix} g$ for that with respect to mole fraction only we have seen.

Now if you wanted to derive similar relation in terms of Gibbs energy, excess smaller Gibbs energy g^E then what should we do? Because for this, liquid solutions in general, the information is available in terms of excess molar Gibbs energy or activity coefficient. So, it is more useful to develop a condition in terms of g^E.

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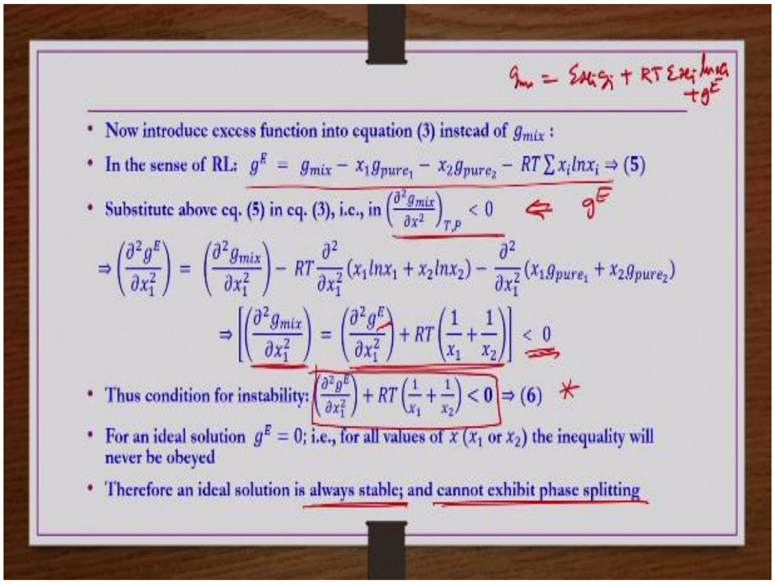

$g_m = \sum x_i g_i + RT \sum x_i \ln x_i + g^E$

- Now introduce excess function into equation (3) instead of g_{mix} :
- In the sense of RL: $g^E = g_{mix} - x_1 g_{pure_1} - x_2 g_{pure_2} - RT \sum x_i \ln x_i \Rightarrow (5)$
- Substitute above eq. (5) in eq. (3), i.e., in $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} < 0$ $\Leftarrow$ g^E

$$\Rightarrow \left(\frac{\partial^2 g^E}{\partial x_1^2}\right) = \left(\frac{\partial^2 g_{mix}}{\partial x_1^2}\right) - RT \frac{\partial^2}{\partial x_1^2}(x_1 \ln x_1 + x_2 \ln x_2) - \frac{\partial^2}{\partial x_1^2}(x_1 g_{pure_1} + x_2 g_{pure_2})$$

$$\Rightarrow \left[\left(\frac{\partial^2 g_{mix}}{\partial x_1^2}\right) = \left(\frac{\partial^2 g^E}{\partial x_1^2}\right) + RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right)\right] < 0$$

- Thus condition for instability: $\boxed{\left(\frac{\partial^2 g^E}{\partial x_1^2}\right) + RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 0} \Rightarrow (6)$ *
- For an ideal solution $g^E = 0$; i.e., for all values of x (x_1 or x_2) the inequality will never be obeyed
- Therefore an ideal solution is always stable; and cannot exhibit phase splitting

So in the sense of RL or Raul's law, we know this $g^E = g_{mix} - \sum x_i g_i - RT \sum x_i \ln x_i$ or g_{mix} is nothing but $\sum x_i g_i + RT \sum x_i \ln x_i + g^E$, this is what we have. So we have written g^E in the left hand side. So now substitute this equation, above equation in equation number three that means here we want partially differentiate this equation with respect to x.

So that we have $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P}$ this equation. So, there will be some condition which will be having g^E terms. Or simply what we do? Now by substituting this equation 5 in equation 3 that is in this equation we can find out what is the instability condition in terms of g^E. What is the instability condition in terms of g^E that is what we get? So for that purpose what we do, this equation 5 that we partially differentiate with x_2 times.

So that left hand side $\left(\frac{\partial^2 g^E}{\partial x_1^2}\right) = \left(\frac{\partial^2 g_{mix}}{\partial x_1^2}\right) - RT\frac{\partial^2}{\partial x_1^2}(x_1 lnx_1 + x_2 lnx_2) - \frac{\partial^2}{\partial x_1^2}(x_1 g_{pure\ 1} + x_2 g_{pure\ 2})$. This if you do the differentiation and simplify then we have we keep now $\left(\frac{\partial^2 g_{mix}}{\partial x_1^2}\right)$ in the left hand side and then right hand, side remaining terms will write after differentiation.

So right hand side will be having $\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)$+ RT$\left(\frac{1}{x_1} + \frac{1}{x_2}\right)$. So now we know for instability this $\left(\frac{\partial^2 g_{mix}}{\partial x_1^2}\right) < 0$. So obviously this should also be less than 0. So in terms of g^E if you wanted to have an instability condition, what is this that is nothing but $\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)$+ RT$\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 0$.

This is the condition for instability in terms of Gibbs energy. Now, but for ideal solutions what we understand g^E is 0. For ideal solutions obviously g^E is 0, if g^E is 0 then for all values of x_1 or x_2, the inequality will never be obeyed that means ideal solutions by default, they are completely miscible solutions they do not form partially miscible solution because ideal solution that means like interactions are same.

Or the like interaction, dislike interactions are almost same. They are completely forming visible solutions that mean an ideal solution is always stable and cannot exhibit phase splitting. Because g^E is 0 for ideal solutions and then for ideal solutions all interactions are similar, whether like interactions are unlike interaction if the solution whether it is pure component or a mixture of solution, if the interactions, all the interactions are same; a-a interaction, b-b interactions or a-b interactions all of them are same.

Then that solution we can say ideal solution. If it is pure component, obviously ideal solution, but mixed solution also it is possible that in the sense of Raoult's law ideal solution may take place or may form in the sense of Raoult's law ideal solution may take place for the binary solution. So, for which you know, all these whatever this like and in unlike interactions are similar or same or equal to each other. So, for ideal solution is always stable and it cannot split in two phases.

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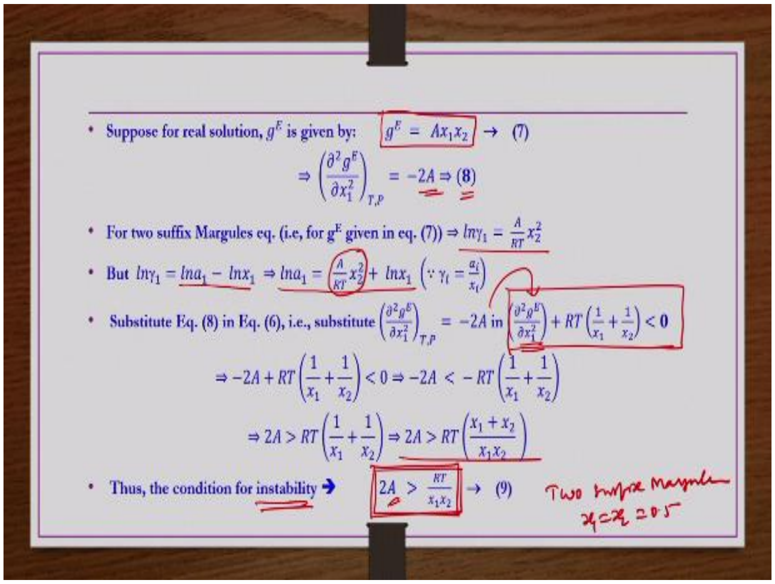

- Suppose for real solution, g^E is given by: $\boxed{g^E = Ax_1x_2} \rightarrow$ (7)

$$\Rightarrow \left(\frac{\partial^2 g^E}{\partial x_1^2}\right)_{T,P} = -2A \Rightarrow (8)$$

- For two suffix Margules eq. (i.e, for g^E given in eq. (7)) $\Rightarrow ln\gamma_1 = \frac{A}{RT}x_2^2$
- But $ln\gamma_1 = lna_1 - lnx_1 \Rightarrow lna_1 = \frac{A}{RT}x_2^2 + lnx_1 \quad \left(\because \gamma_i = \frac{a_i}{x_i}\right)$
- Substitute Eq. (8) in Eq. (6), i.e., substitute $\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)_{T,P} = -2A$ in $\boxed{\left(\frac{\partial^2 g^E}{\partial x_1^2}\right) + RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 0}$

$$\Rightarrow -2A + RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 0 \Rightarrow -2A < -RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right)$$

$$\Rightarrow 2A > RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) \Rightarrow 2A > RT\left(\frac{x_1 + x_2}{x_1x_2}\right)$$

- Thus, the condition for instability ➔ $\boxed{2A > \frac{RT}{x_1x_2}} \rightarrow$ (9)

Two suffix Margules

$x_1 = x_2 = 0.5$

Now, let us say if you have a real solution. So, for that obviously, there will be some expression for g^E and then for simplicity what we take 2-suffix Margules equation. So that real solution if g^E is represented by 2-suffix Margules equation, $g^E = A\ x_1\ x_2$ then $\left(\frac{\partial^2 g^E}{\partial x_1^2}\right) = -2A$. So $\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)_{T,P} = -2A$ for this 2-suffix Margules equation.

For that for 2-suffix Margules equation, we know that ln $\gamma_1 = \frac{A}{RT}x_2^2$ and then $\gamma_1 = \frac{a_1}{x_1}$. So, ln γ_1 = ln a_1 − ln x_1. So that means ln a_1 is nothing but ln γ_1 + ln x_1 and ln $\gamma_1 = \frac{A}{RT}x_2^2$. This we are doing because we wanted to plot a_1 versus x_1 and then see how for how this behavior will change how the a_1 versus x_1 behavior will change for different $\frac{A}{RT}$ values that will see anyway.

Now what we do we substitute this $\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)$ in equation number 6 that is whatever $\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)$+ RT$\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 0$. In this one now we substitute $-2A$ in place of this second derivative of g^E. So there $-2A$ + RT$\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 0$ or $-2A <-$ RT$\left(\frac{1}{x_1} + \frac{1}{x_2}\right)$that means 2 A > RT$\left(\frac{1}{x_1} + \frac{1}{x_2}\right)$.

That means 2 A > RT and then if you do LCM RT$\left(\frac{x_1+x_2}{x_1x_2}\right)$ that means 2 A > $\frac{RT}{x_1x_2}$. This is the condition for instability, and this is true for only 2-suffix Margules equations. If you have Van laar equations or other equations so then accordingly what is $\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)$ that you have to find out. If it is Van Laar equation or any other equations accordingly what is $\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)$.

You have to find out and then substitute here and then find out the condition for those different models of g^E. So then different conditions you may get this condition whatever 2A > $\frac{RT}{x_1x_2}$ is there that is true only for 2-suffix margules equation. Now, what is the lowest possible value of a that satisfies this condition depends on the x_1 and x_2. So, when you have this $x_1 = x_2 = 0.5$.

Then that is the lowest possible value of a that is satisfying this condition. So, if you take $x_1 = x_2 = 0.5$ then what you have? You will be having 2 A > 4 RT that means A > 2 RT.

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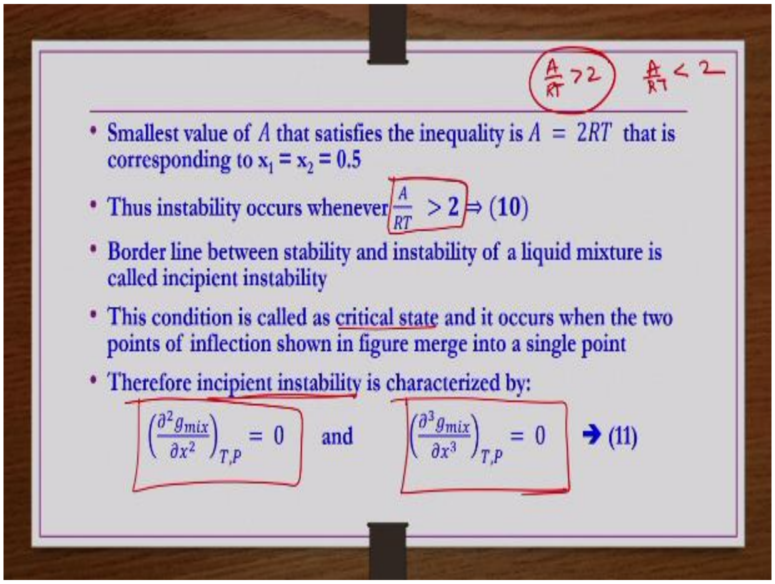

$\boxed{\frac{A}{RT} > 2}$ $\frac{A}{RT} < 2$

- Smallest value of A that satisfies the inequality is $A = 2RT$ that is corresponding to $x_1 = x_2 = 0.5$
- Thus instability occurs whenever $\boxed{\frac{A}{RT} > 2} \Rightarrow (10)$
- Border line between stability and instability of a liquid mixture is called incipient instability
- This condition is called as critical state and it occurs when the two points of inflection shown in figure merge into a single point
- Therefore incipient instability is characterized by:

$$\boxed{\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} = 0} \quad \text{and} \quad \boxed{\left(\frac{\partial^3 g_{mix}}{\partial x^3}\right)_{T,P} = 0} \rightarrow (11)$$

So that means smallest value of A that satisfies, the above inequality is A = 2RT that is corresponding to the case where $x_1 = x_2 = 0.5$. That means if your $\frac{A}{RT} < 2$ then it is going to have a stable single phase solution. It is not going to split into two phases and then if you have $\frac{A}{RT} > 2$ that means there is a condition for instability and then the splitting of system into two phases will take place.

So now for 2-suffix margules equation, if you just know what is this A constant and then what is the temperature operating temperature then from there itself without doing anything you can understand whether that system is going to show a kind of single phase behavior or splitting into two phase behavior that you can understand at that particular temperature or for that given temperature. Thus, instability occurs whenever $\frac{A}{RT} > 2$.

Border line between stability and instability of liquid mixture is called incipient instability. This condition is called a critical state and it occurs when the two points of inflection shown in figure match into a single point will see the picture also. Therefore, incipient instability is characterized by $\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} = 0$ and $\left(\frac{\partial^3 g_{mix}}{\partial x^3}\right)_{T,P} = 0$.

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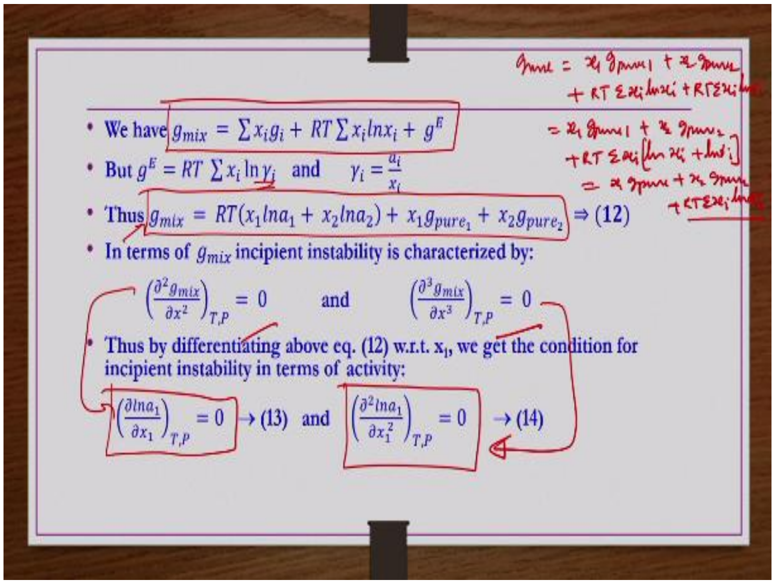

- We have $\boxed{g_{mix} = \sum x_i g_i + RT\sum x_i \ln x_i + g^E}$
- But $g^E = RT\sum x_i \ln \gamma_i$ and $\gamma_i = \frac{a_i}{x_i}$
- Thus $\boxed{g_{mix} = RT(x_1 \ln a_1 + x_2 \ln a_2) + x_1 g_{pure_1} + x_2 g_{pure_2}} \Rightarrow (12)$
- In terms of g_{mix} incipient instability is characterized by:

$$\left(\frac{\partial^2 g_{mix}}{\partial x^2}\right)_{T,P} = 0 \quad \text{and} \quad \left(\frac{\partial^3 g_{mix}}{\partial x^3}\right)_{T,P} = 0$$

- Thus by differentiating above eq. (12) w.r.t. x_1, we get the condition for incipient instability in terms of activity:

$$\boxed{\left(\frac{\partial \ln a_1}{\partial x_1}\right)_{T,P} = 0} \rightarrow (13) \quad \text{and} \quad \boxed{\left(\frac{\partial^2 \ln a_1}{\partial x_1^2}\right)_{T,P} = 0} \rightarrow (14)$$

$g_{mix} = x_1 g_{pure1} + x_2 g_{pure2} + RT\sum x_i \ln x_i + RT\sum x_i \ln$

$= x_1 g_{pure1} + x_2 g_{pure2} + RT\sum x_i[\ln x_i + \ln \gamma_i]$

$= x_1 g_{pure} + x_2 g_{pure} + RT\sum x_i \ln$

Now we have this g_{mix} is nothing but sigma x_i g_i + RT $\sum x_i \ln x_i + g^E$. So now this incipient instability condition whatever we have written in terms of g^E we try to write the same condition in terms of activity. So g^E for this case, we know that $g^E = RT \sum x_i \ln \gamma_i$ and then γ_i is nothing but $\frac{a_i}{x_i}$. If you make use of these two conditions here and then we take it this g_{mix} for a binary case, then we have $g_{mix} = x_1 \ln a_1 + x_2 \ln a_2 + x_1 g_{pure\,1} + x_2 g_{pure\,2}$.

So this g_{mix} for binary component is nothing but $x_1 g_{pure\,1} + x_2 g_{pure\,2}$, that is the first component +

second component, RT sigma x_i ln x_i we keep it as it is and then g^E we can write RT $\sum x_i \ln \gamma_i$ so that means $x_1\, g_{pure\,1} + x_2\, g_{pure\,2}$ + RT if you take common RT $\sum x_i$ln x_i + ln γ_i so that we can write it as x_i ln a_i because $\gamma_i = \frac{a_i}{x_i}$.

So $\gamma_i\, x_i = a_i$, so that is what if you write this RT $\sum x_i$ ln a_i also for binary component then we have RT x_1 ln a_1 + x_2 ln a_2 then + $x_1\, g_{pure\,1} + x_2\, g_{pure\,2}$, these two terms are as it is. So now in terms of g_{mix} incipient instability is characterized by these two conditions. Corresponding conditions, if you try to get by differentiating this equation number 12, you know, second derivative and third derivative of equation number 12 with respect to the composition x.

If you do then you will get $\left(\frac{\partial ln a_1}{\partial x_1}\right)_{T,P}$ = 0 and $\left(\frac{\partial^2 ln a_1}{\partial x_1^2}\right)_{T,P}$ = 0 respectively for these two conditions. Only thing that whatever the incipient instability conditions are there in terms of g^E_{mix} we are representing them in terms of activity. Because exponentially we get either g^E models in activity coefficients. So, in having the conditions in terms of this activity g^E is going to be more useful like this.

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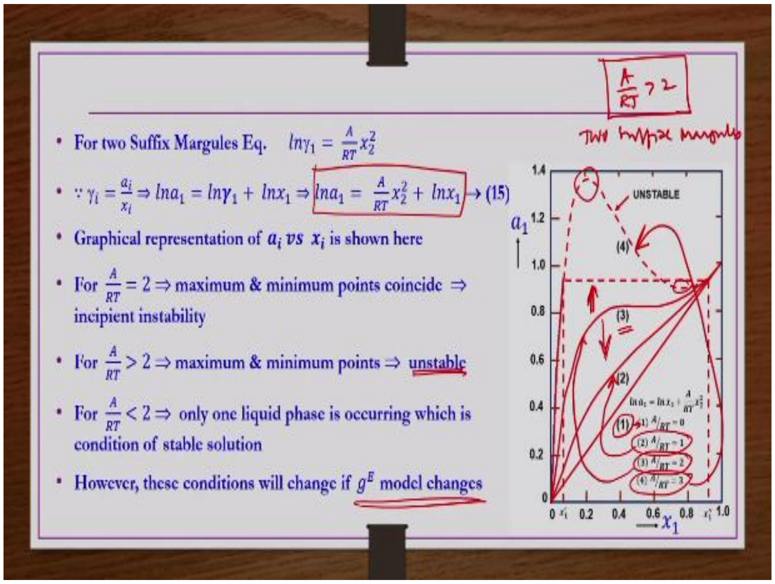

- For two Suffix Margules Eq. $ln\gamma_1 = \frac{A}{RT}x_2^2$
- $\because \gamma_i = \frac{a_i}{x_i} \Rightarrow lna_1 = ln\gamma_1 + lnx_1 \Rightarrow \boxed{lna_1 = \frac{A}{RT}x_2^2 + lnx_1} \rightarrow (15)$
- Graphical representation of a_i *vs* x_i is shown here
- For $\frac{A}{RT} = 2 \Rightarrow$ maximum & minimum points coincide $\Rightarrow$ incipient instability
- For $\frac{A}{RT} > 2 \Rightarrow$ maximum & minimum points $\Rightarrow$ unstable
- For $\frac{A}{RT} < 2 \Rightarrow$ only one liquid phase is occurring which is condition of stable solution
- However, these conditions will change if g^E model changes

$\boxed{\frac{A}{RT} > 2}$

Two suffix margules

So, for 2-suffix margules equation, we have already seen ln $\gamma_1 = \frac{A}{RT}x_2^2$. Now issue rearrange this equation as we have already done. By writing $\gamma_i = \frac{a_i}{x_i}$. So then ln a_i is nothing but ln γ_i + ln x_i so that means for component 1 ln a_1 we can write it as ln γ_1 is nothing but $\frac{A}{RT}x_2^2$ + ln x_1 is as it is. Now we have a graphical representation between a_i versus x_i that is a_1 versus x_1.

Now different values of A by RT we can see here. This first curve we are having for $\frac{A}{RT} = 0$. If $\frac{A}{RT}=0$ in 2-suffix Margules equation that means it representing the ideal solution. So, for ideal solution a_i versus x_i we should have a kind of linear solution. So that is what we getting by taking $\frac{A}{RT}= 0$. If you take $\frac{A}{RT}= 1$ then we have this second curve.

Like this there is no minimum maximum kind of thing, if you take $\frac{A}{RT}= 2$ then we have a condition like this curve given by 3. That is the condition for the instability, so that means below this curve whatever the things are there, you know, you will be having a stable single phase region and then whatever the region above this one is there.

So that is going to have a kind of instability and then splitting into two phases is going to take place. So that we can see by taking $\frac{A}{RT}= 3$, so that curve number 4 then we can see there is a maximum there is a kind of minimum and there splitting it two phases and that if you have such kind of conditions where $\frac{A}{RT}> 2$. Definitely that is going split in two phases that is what we are here.

So for $\frac{A}{RT}= 2$ maximum and minimum points coincides and then incipient instability is taking place for $\frac{A}{RT}$ greater than to maximum and minimum points are there so that means it is unstable. For $\frac{A}{RT} < 2$ only 1 liquid phase is occurring which is condition of stable solution condition. Then obviously this condition will change if your g^E model changes because all these things we have done for 2-suffix Margules equations.

And then where we have found this $\frac{A}{RT} > 2$ as it is the condition of instability. That is what we have seen for 2-suffix Margules equation, so if you take different equations different g^E form will be there and then accordingly different nature would be there. So now we take an example problem.

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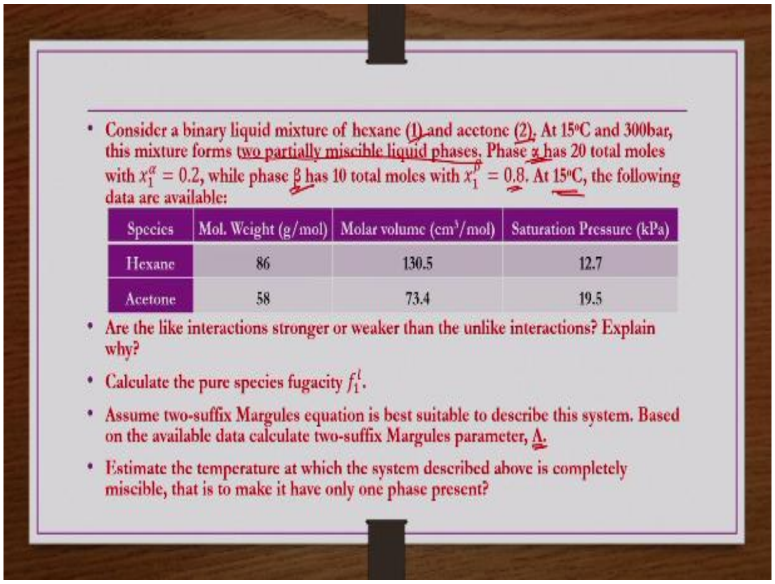

- Consider a binary liquid mixture of hexane (1) and acetone (2). At 15°C and 300bar, this mixture forms two partially miscible liquid phases. Phase α has 20 total moles with $x_1^\alpha = 0.2$, while phase β has 10 total moles with $x_1^\beta = 0.8$. At 15°C, the following data are available:

Species	Mol. Weight (g/mol)	Molar volume (cm³/mol)	Saturation Pressure (kPa)
Hexane	86	130.5	12.7
Acetone	58	73.4	19.5

- Are the like interactions stronger or weaker than the unlike interactions? Explain why?
- Calculate the pure species fugacity f_1^l.
- Assume two-suffix Margules equation is best suitable to describe this system. Based on the available data calculate two-suffix Margules parameter, A.
- Estimate the temperature at which the system described above is completely miscible, that is to make it have only one phase present?

Consider a binary liquid mixture of hexane and acetone at 15 degree centigrade and 300 bar, this mixture forms two partially miscible liquid phases that means what? It means that you know, like interactions are stronger than the unlike interaction. If the like interactions are stronger than the unlike interaction, then only two partially miscible liquid phases will take place. And then out of these two phases.

One phase is designated as α which is having 20 total moles with x_1^α = 0.2 and then another phase is β phase which is having 10 moles with x_1^β = 0.8. That means overall 30 moles are there within the 30 moles 20 moles are going into the α phase and then 10 moles are going into the β phase. A phase is having 20% of component one by mole fraction and then β phase is having 80% of component 1 by mole fraction.

That is what it means by and then at 15 degree centigrade the molecular weight, molar volume and saturation pressure of the system are given here for both the components. So, the first question are the like interactions stronger or weaker than the unlike interaction explain, why? Then calculate the pure species fugacity f_1^l then assume 2-suffix Margules equation is best suitable to describe this system based on the available data calculate 2-suffix Margules parameter A.

And then estimate the temperature at which this system described above is completely miscible.

That is to make it how only one phase present.

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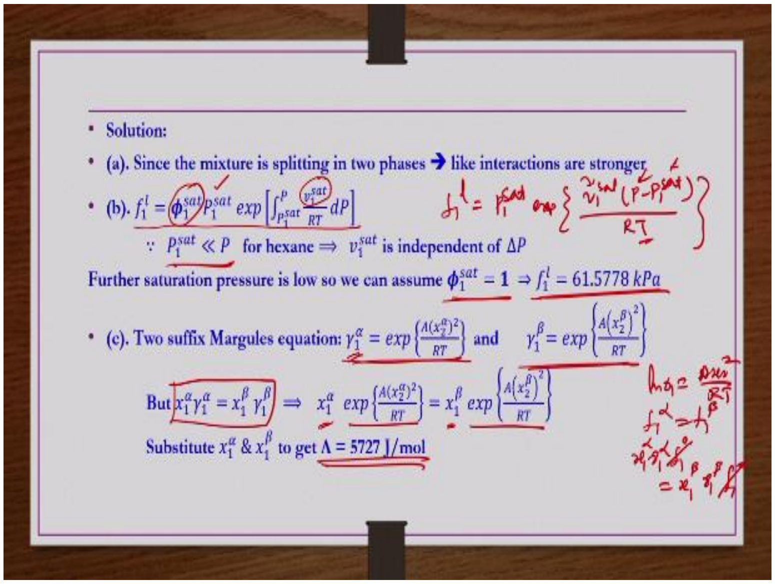

- Solution:
- (a). Since the mixture is splitting in two phases → like interactions are stronger
- (b). $f_1^l = \phi_1^{sat} P_1^{sat} \exp\left[\int_{P_1^{sat}}^{P} \frac{v_1^{sat}}{RT} dP\right]$

$\because$ $P_1^{sat} \ll P$ for hexane $\Rightarrow$ v_1^{sat} is independent of ΔP

Further saturation pressure is low so we can assume $\phi_1^{sat} = 1 \Rightarrow f_1^l = 61.5778\ kPa$

- (c). Two suffix Margules equation: $\gamma_1^\alpha = \exp\left\{\frac{A(x_2^\alpha)^2}{RT}\right\}$ and $\gamma_1^\beta = \exp\left\{\frac{A(x_2^\beta)^2}{RT}\right\}$

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

Substitute x_1^α & x_1^β to get $\Lambda = 5727$ J/mol

$f_1^l = P_1^{sat} \exp\left\{\frac{\tilde{v}_1^{sat}(P-P_1^{sat})}{RT}\right\}$

$\ln\gamma_1 = \frac{Ax_2^2}{RT}$

$f_1^\alpha = f_1^\beta$

$x_1^\alpha \gamma_1^\alpha \cancel{f_1}$
$= x_1^\beta \gamma_1^\beta \cancel{f_1}$

So the first question whether like interactions are stronger or unlike interactions are stronger that is the question obviously the system is splitting into two phases, then that means you know, like interactions are stronger so that is the first question since the mixture is built in two phases, like interactions are stronger second part is that pure component fugacity f_1^l, we have to find out this expression we have already derived.

So now here we need information P_1^{sat} is given, ϕ_1^{sat} is not given, v_1^{sat} is given but whether it is dependent on the pressure or not that is not given. So first we have to make clarity about this, two things first of all what we can say $P_1^{sat} << \text{P}$. For the given problem P_1^{sat} for component one is only 12.7 kilopascal, whereas this system is it 300 bars, so the delta P. So that you know what we have P_1^{sat} is much smaller than the total pressure.

So then we can say that v_1^{sat} is independent of the delta P and then this P_1^{sat} is also low P_1^{sat} is also not very low but still it is low so that what we can say $\phi_1^{sat} = 1$ or system is ideal at the saturation pressure. So now you take v_1^{sat} is independent of pressure, so then we have $f_1^l = P_1^{sat} \exp\left[\frac{v_1^{sat}(P-P_1^{sat})}{RT}\right]$ this is what we have.

So P_1^{sat} is given, temperature is given, pressure is given, P_1^{sat} is given, v_1^{sat} is given, everything is given so even you substitute then you will find out f_1^l is nothing but approximately 61.6 kilopascals. That is the second part of the question, now third part of the question, assume 2-suffix Margules equation and then for 2-suffix Margules equation ln $\gamma_1 = \frac{A}{RT}x_2^2$.

So that ln $\gamma_1 = \frac{A}{RT}x_2^2$, if you apply for two phases; α phase, $\gamma_1^\alpha = \exp\left\{\frac{A(x_2^\alpha)^2}{RT}x_2^2\right\}$ and then $\gamma_1^\beta = \exp\left\{\frac{A\left(x_2^\beta\right)^2}{RT}x_2^2\right\}$. And then for a system where liquid-liquid equilibrium is there. So $x_1^\alpha\ \gamma_1^\alpha$should be equal to $x_1^\beta\ \gamma_1^\beta$ because $f_1^\alpha = f_1^\beta$.

So f_1^α is $x_1^\alpha\gamma_1^\alpha\ f_1^0 = x_1^\beta\ \gamma_1^\beta f_1^0$ and then you cannot have two different states for two different phases of one same system so f_1^0 same for both the phases. So then $x_1^\alpha\gamma_1^\alpha = x_1^\beta\ \gamma_1^\beta$we are having. So γ_1^αyou write $\exp\left\{\frac{A(x_2^\alpha)^2}{RT}x_2^2\right\}$and then for γ_1^β you write $\exp\left\{\frac{A\left(x_2^\beta\right)^2}{RT}x_2^2\right\}$. x_1^α and then x_2^α, x_1^β, $x_2^\beta$are given, temperature is given so you substitute all of them. Then you get A = 5727 joule per mole, so that is the third part of the question.

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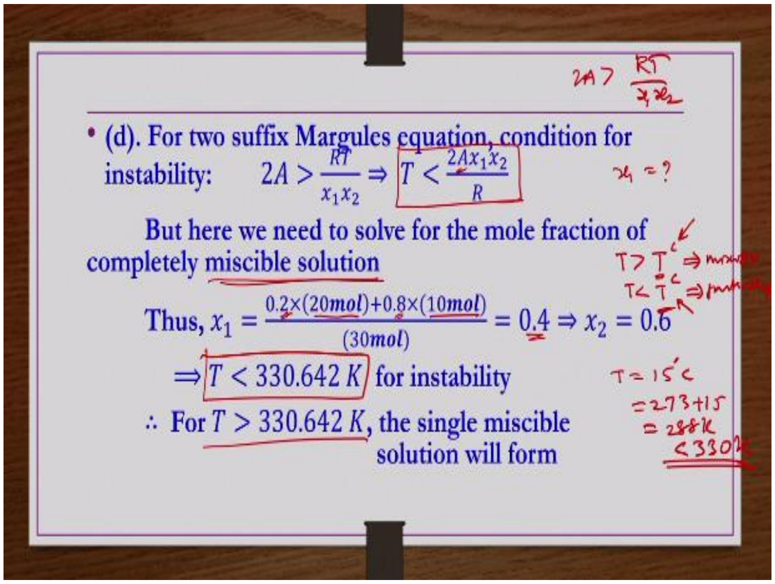

- (d). For two suffix Margules equation, condition for instability: $2A > \frac{RT}{x_1x_2} \Rightarrow \boxed{T < \frac{2Ax_1x_2}{R}}$

But here we need to solve for the mole fraction of completely miscible solution

Thus, $x_1 = \frac{0.2\times(20mol)+0.8\times(10mol)}{(30mol)} = 0.4 \Rightarrow x_2 = 0.6$

$\Rightarrow \boxed{T < 330.642\ K}$ for instability

∴ For $T > 330.642\ K$, the single miscible solution will form

Last part of the question is 2-suffix Margules equation for condition of instability, we found it as 2A > $\frac{RT}{x_1x_2}$. This is what we have found. So that means T has to be less than $\frac{2Ax_1x_2}{R}$. Then it will give the temperature above which the system is going to be stable and then below which system is going to be unstable and then splitting in two phases will take place.

So for this we need A R x_1 x_2, A is we just now obtain 5727 joule per mole, x_1 x_2 we do not know, why we do not know? x_1^{α}, $x_1^{\beta}$are given in two phases, α β phase is when they are splitting, it gives two different α β phases. So, the composition of α phase is x_1^{α} is given and then composition of β phase x_1^{β} is given but what is overall x_1 x_2 with respect to the complete miscible state?

We do not know, so here we need to have solved for the mole fraction of completely miscible solution. Because with respect to the temperature there is a critical temperature, this is the critical temperature let us say. Above the critical temperature, temperature greater than the critical temperature, then miscibility are single phase is taken place. If the temperature is less than this T^c then partial miscibility is taking place or instability is taking or instability is there. So splitting in two phases are there.

So this T we how to find out and this T is now a kind of border line between this single phase and two phase region. So that is corresponding to the case where you know border line on that one, you know complete miscibility is there. So, this x_1 x_2, we have to find out for the case where the complete miscibility is there, so then x_1 we have to find out. What is the overall solution mixture completely, for the overall solution, what is the x_1?

There are 2 phases, each one having 20 and 10 mol. In the phase where 20 moles are there component 1 is 20 % is there x_1^{α} so that is 0.2 and then in the phase component 1 is 80% is there or $x_1^{\beta}$is 0.8. So that is 1, so 0.2 into 20 + 0.8 into 10 divided by 30 that comes out to be 0.4. So, this 0.4 is x_1, so x_2 is 0.6 this if you substitute then you will get temperature less than 330 kelvin will be having instability.

And then indeed we can cross check the solution from the problem statement itself. In the problem statement it said that at 15 degrees centigrade the system splits into two phases, partial miscibility is there that means 273 + 15 is nothing but 288 kelvin so which is less than 330 kelvin so that is the reason this system is splitting into two phases. So, for temperature greater than 330 Kelvin this single miscible solution will form.

What is the critical temperature for this system? Is 330 Kelvin is the critical temperature, above which single one phase solution is taking place below which the system is splitting into two phases. So, this is about the thermodynamics of partial immiscible solutions. Next lecture will be discussing how to obtain the equilibrium composition of liquid-liquid equilibrium cases. References for this lecture are given here.

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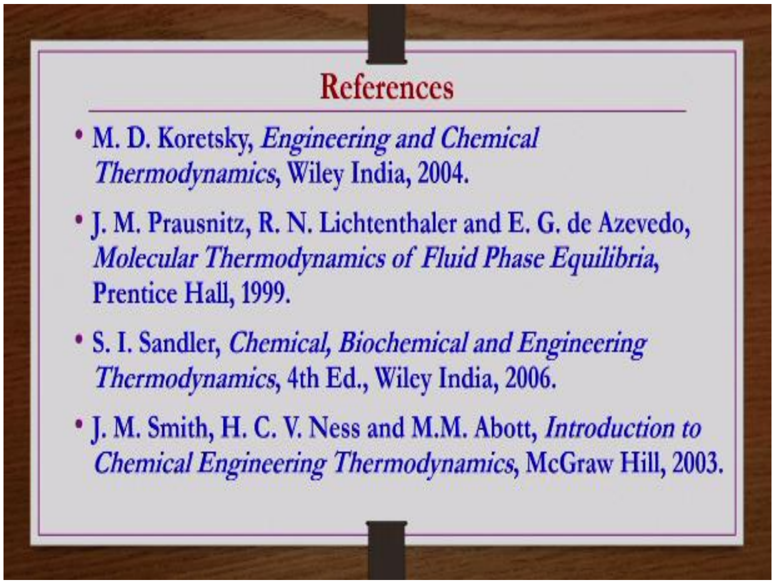

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Engineering and chemical thermodynamics by Koretsky. Molecular thermodynamics of fluid phase equilibria by prausnitz et. al, Chemical biochemical and engineering thermodynamics by Sandler and introduction to chemical engineering thermodynamics by Smith et al. Thank you.