Advanced Thermodynamics
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Lecture- 25
Vapour – Liquid Equilibrium - 3

Welcome to the MOOCs course advanced thermodynamics, the title of this lecture is vapor liquid equilibrium part 3 it is a continuation of our previous lecture, last 2 lectures we have discussed different aspects of vapour liquid equilibrium problems when both phases display ideal behavior, when one of the phase displayed non ideal behavior when both phases display non ideal behavior under such conditions, how to find out the equilibrium composition when 2 phases are coexistent for a binary as well as multi component system those things we have seen.

We have also seen the corresponding phase diagrams, details associated with this vapour liquid equilibrium problems under both ideal and non ideal circumstances those things we have already seen in last 2 lectures. In this lecture, we are going to discuss some more details of vapour liquid equilibrium where azeotropes are also formed, what does mean by azeotropes. Azeotrops means in Greek language azeotropes means boiling without change, what it means it boils, but it does not change that is composition does not change that is what it means.

Those details we are going to see in this particular lecture. And then, subsequently we will be discussing solubility of a liquids and gases and then how to apply the concept of a vapour liquid equilibrium for such conditions. Those things also we are going to discuss at the end of this lecture.

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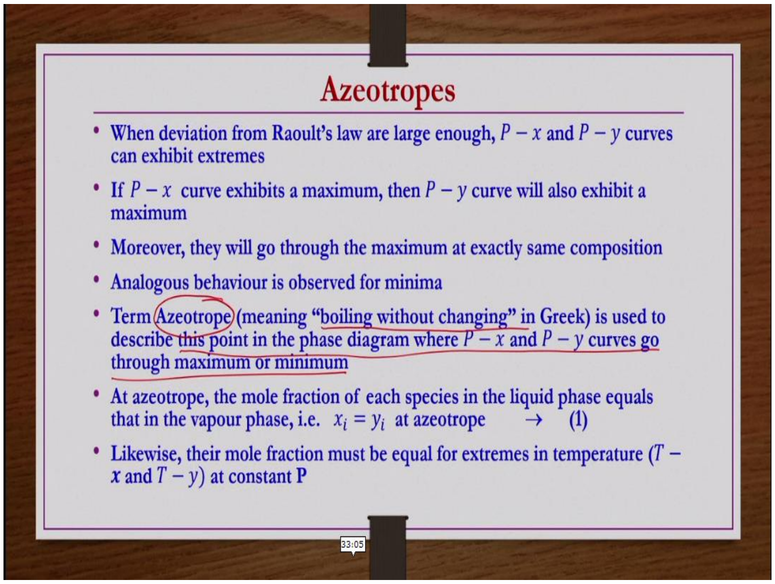

Azeotropes

- When deviation from Raoult's law are large enough, $P - x$ and $P - y$ curves can exhibit extremes
- If $P - x$ curve exhibits a maximum, then $P - y$ curve will also exhibit a maximum
- Moreover, they will go through the maximum at exactly same composition
- Analogous behaviour is observed for minima
- Term Azeotrope (meaning "boiling without changing" in Greek) is used to describe this point in the phase diagram where $P - x$ and $P - y$ curves go through maximum or minimum
- At azeotrope, the mole fraction of each species in the liquid phase equals that in the vapour phase, i.e. $x_i = y_i$ at azeotrope → (1)
- Likewise, their mole fraction must be equal for extremes in temperature ($T - x$ and $T - y$) at constant P

So, this azeotropes when deviation from Raoult's are large enough, then P-x P-y curves can exhibit extremes, extremes in the sense in the P-x-y or T-x-y diagrams that we have seen you know there is a kind of a enclosed between P-x and P-y curve or T-x and T-y curve. That behavior we have seen a kind of enclosed area we have seen in that enclosed area we have a kind of a vapour and liquid phases coexisting and there is one single enclosed areas.

But now, when there is an azeotrope what happens this P-x P-y curves or T-x T-y curves you know, they show a kind of extreme, extreme in the sense they may be a kind of maximum or there may be a kind of minimum is existing and then because of that 1, the envelope, the enclosed area that is forming which is having which is consisting of both vapour and liquid phases. There will be 2 enclosed areas or more than one enclosed areas would be there.

So, why does it occur because when the deviation from Raoult's law becomes very large actually when there is a deviation from Raoult's law then obviously the liquid phase is also showing a kind of non-linearity we have seen but that deviation is very large then it is possible that there could be a kind of some extremes in P-x P-y curves or T-x T-y curves because of that extremes the corresponding pressure system pressure may be higher or lower than the saturation pressure both the combination of the binary system, so, those things are possible.

So, if P-x curve exhibits a maximum then P-y curve will also exhibit a maximum and then moreover, they exhibit the maximum at the exactly same composition. Let us say P-x curve exhibit a kind of a maximum at $x_a = 0.6$ then P-y curve will also exhibit a maximum at the same composition that is $y_a = 0.6$. And then analogous behavior is observed for minima also. If the P-x curve is showing a kind of minima then P-y curve will also show a kind of minima that is also possible and this term azeotrope is used to describe this point in the phase diagram.

Where P-x P-y curves go through maximum or minimum is, you know, described by the term azeotrope. Azeotrope means boiling without changing, without changing in the sense when you boil, obviously composition change then that is indirectly know more volatile component will go into the vapour phase so, obviously composition is going to change. But at this point you know, that boils but there will not be any change in the composition that is not boiling without changing is the meaning in Greek.

The Greek word azeotrope means boiling without the change that is the reason. Since in this case also at that particular point the composition does not change though this mixture is boiling even by boiling the mixture the composition is not changing that is the reason we have used this azeotrope mix on the term azeotrope describing this kind of phenomena. At azeotrope the mole fraction of each species in the liquid phase equals to that in the vapour phase that is $x_i = y_i$ at azeotrope.

Likewise, their mole fraction must be equal for the extremes in temperature curves that is T-x P-y curves also at constant pressure. So, it is not necessary that you know this so, that means, you know these extremes whatever the maxima or minima, they are also possible in T-x T-y curves as well and under such conditions also at azeotrope $x_i = y_i$. We take some examples also.

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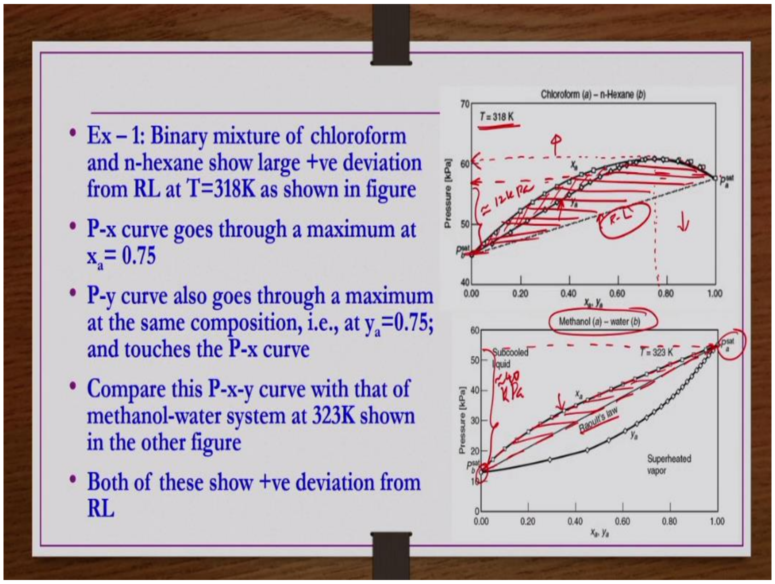

- Ex – 1: Binary mixture of chloroform and n-hexane show large +ve deviation from RL at T=318K as shown in figure
- P-x curve goes through a maximum at $x_a = 0.75$
- P-y curve also goes through a maximum at the same composition, i.e., at $y_a = 0.75$; and touches the P-x curve
- Compare this P-x-y curve with that of methanol-water system at 323K shown in the other figure
- Both of these show +ve deviation from RL

Let us take binary mixture of chloroform and n-hexane show large positive deviation from Raoult's law at 318 Kelvin as shown in the picture. So, actually, this dotted line is for the Raoult's law if the liquid phase is showing a kind of ideal behavior with reference to Raoult's law and we have a dotted lines and this curve is nothing but P-y_a curve. Then now, what happens here at this temperature this chloroform and hexane mixture.

You know, it shows a large deviation from the Raoult's law you can see the deviation is very large and then this is having the P-x curve like this and then it intersects with the P-y curve at something around 0.75 or something like that. And this there is a kind of hysteresis, this is one hysteresis there is a kind of 1 enclosed area and this one where both phases are coexisting and there is also a small enclosed area other side of the azeotrope also there also P both the phases are coexisting.

And then above this P-x_a curve what we have so called liquid below this P-y_a curve we have a superheated vapour those kinds of things are same here also other thing that you can see at the azeotrope whatever the corresponding system pressure is there that is much higher than the saturation pressure of both these components. You can see from here this saturation pressure of component a is roughly around 57 or something like that, whereas the saturation pressure of component b is around 45 or something like that.

The difference is very small and then system pressure is higher than either of the saturation pressures at the extreme point. So, these are the same characteristics of azeotropes that around 0.75

it goes through a maximum P-y curve also goes through a maximum at the same composition that is at $y_a = 0.75$ and touches the P-x curve. Now, if you compare this one with the water methanol system or methanol water system that we have previously seen. So, now here this methanol water system just for comparison I am showing here.

So, this we have already seen in our previous lecture. So, here now, you can see this is the case when you know when the liquid phase are, basically ideal behavior with reference to the Raoult's law and then this it is having some non ideality so, now here this methanol water it is having some non ideal behavior like this. So, that is about this P a curve and you can see the difference between these 2 curves at Raoult's law and P-x curve is very small though not very small it is not very large in like in the previous case, in this case if you see where the azeotrope is forming now.

Here in this case you can see the difference between these 2 curves that you know RL line straight line and then P-x curve you can have RL line and the straight line this RL line Raoult's law curves are when the liquid phase Raoult's law then whatever the straight line instead that 1 and then P-x_a curve when there is a non ideality you can see the gap is more compared to the case here in this case where there is no azeotrope formation, that means you know when the deviation is low to moderate, when the deviation from Raoult's law is low to moderate.

There is no possibility of you know azeotrope formation if the deviation from RL is very large then there is a possibility that there may be azeotrope formation and then further you can see here saturation pressure of the methanol here in this case is approximately 52 kilo Pascal or something like that and then saturation pressure of water that component b is around 12 kilo Pascal's you can see the difference here almost like you know 40 kilo Pascal's that means, if the saturation pressures are far away from each other, then also it is not possible or less possible.

That you know azeotrope may form, but here in this case where the azeotrope is 1, the difference is, you know hardly 10 to 12 kilo Pascal's. If you compare this P^{sat} and then P_a^{sat} and P_b^{sat} roughly it is 12 kilo Pascal only that is the difference. Whereas, here if you see in the case where there is no azeotrope formation, the difference between these 2 is approximately 40 kilo Pascal's. So, that means, more flatter and horizontal this RL line becomes the chance of formation of azeotrope is more.

Because under such conditions saturation pressures are going to be very close to each other and then under such conditions unlike interactions may be very much different from the like interactions that is what we can understand from these 2 images. So, but however both the cases it is showing possible positive deviation from RL. But here in the case of methanol water system, there is no azeotrope formation because the P-x_a curve is slightly away from RL line.

Whereas here; in the case of chloroform and n-hexane the gap between RL line and P-x_a curve is very large. That means in the case of methanol water system, the deviation positive deviation is there but it is moderate whereas in the case of chloroform and n-hexane deviation is there, but that positivity deviation is very large from RL. These are the few characteristics that you can see. So, what you can understand when there would be a kind of possibility.

That azeotrope will form if the saturation pressures of the 2 components are close to each other are the difference between saturation pressures is not very high. If it is very small, then we can say that there is a possibility of azeotrope formation. So, what does it mean by saturation pressure are close to each other. So, these RL line whatever is still that slope would be very less it will not be very steep slope kind of.

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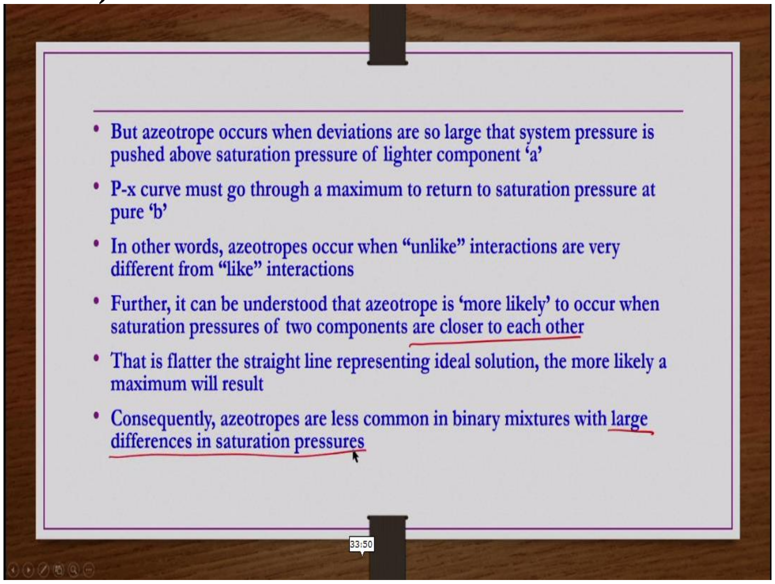

- But azeotrope occurs when deviations are so large that system pressure is pushed above saturation pressure of lighter component 'a'
- P-x curve must go through a maximum to return to saturation pressure at pure 'b'
- In other words, azeotropes occur when "unlike" interactions are very different from "like" interactions
- Further, it can be understood that azeotrope is 'more likely' to occur when saturation pressures of two components are closer to each other
- That is flatter the straight line representing ideal solution, the more likely a maximum will result
- Consequently, azeotropes are less common in binary mixtures with large differences in saturation pressures

But azeotrope across when deviations are so large that system pressure is pushed above the saturation pressure of lighter component a, as we have seen. P-x curve must go through a maximum to return to saturation pressure at pure b, that is P_b saturation point. In other words azeotrope occur when unlike interactions are very different from like interactions, obviously, they are different from like interaction.

Then only there is a kind of a deviation from RL but that difference between this like and an unlike interaction is very high then there is a possibility that azeotrope will form. It can be understood that azeotrope is more likely to occur when saturation pressures have 2 component are close to each other as we have seen in the previous picture. That is flatter this straight line representing the ideal solution by RL, the more likely the maximum will result in P-x P-y curve.

And then consequently azoetrope's are less common in a binary mixtures with large differences in saturation pressures, if the difference between saturation pressures is large then it is less likely that the mixture is going to exhibit any kind of azeotrope.

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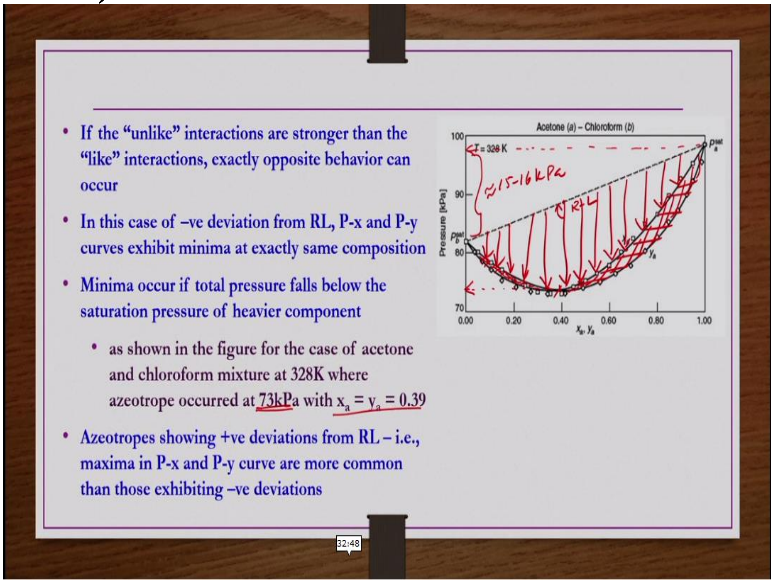

- If the "unlike" interactions are stronger than the "like" interactions, exactly opposite behavior can occur
- In this case of –ve deviation from RL, P-x and P-y curves exhibit minima at exactly same composition
- Minima occur if total pressure falls below the saturation pressure of heavier component
  - as shown in the figure for the case of acetone and chloroform mixture at 328K where azeotrope occurred at 73kPa with $x_a = y_a = 0.39$
- Azeotropes showing +ve deviations from RL – i.e., maxima in P-x and P-y curve are more common than those exhibiting –ve deviations

If the unlike interactions are stronger than the like interactions then exactly opposite behavior will occur. What does mean by unlike interactions are stronger that means negative deviation. The previous example of chloroform and hexane we have seen the positive deviation from RL we have seen, so, but there is a negative deviation then also it is possible that azeotrope may form, negative deviation in the sense the unlike interactions are much stronger than like interactions.

Then negative deviation from RL will take place and then if there is a kind of negative deviation under such conditions also there is a possibility of azeotrope may form again provided the reason is that you know the saturation pressure for those cases also if the difference between saturation pressures is not very less then under the case of negative deviation from ideal behavior also it is there is a possibility that azeotropes would form though, we have seen that negative deviation from RL is a kind of very rare case very few examples we find.

In this case of negative deviation from RL P-x P-y curves exhibit minima at exactly same composition. So, if it is a positive deviation from RL and there is azeotrope then there will be a kind of maxima as we have seen in the previous slide in the image, but if there is a negative deviation from RL and there is also possibility of azeotrope then azeotrope will occurred because of exhibiting or kind of minima that is P-x P-y curves exhibiting minima at same composition in the case of negative deviation.

We will be seeing an example also, minima occur if total pressure falls below the saturation pressure of heavier component in the previous example, where the positive deviation from Raoult's law was there and then there was also azeotrope formation was there under such condition what we have seen, the system pressure goes at the azeotrope higher than the saturation pressure of the both components, but in this case of negative deviation from Raoult's law and there exist azeotrope also.

Then the system pressure at the azeotrope goes below the, or lower than the, you know saturation pressure of either of the components. Especially total pressure falls below the saturation pressure of heavier component that we see pictorially as well here. So, if you take example of acetone and chloroform at 328 Kelvin then we can see azeotrope maybe forming it when $x_a = y_a = 0.39$ at 73 kilo Pascal's pictorially if you see, so, now you can see here.

So, now you can see azeotrope is forming at around 0.39, $x_a = 0.39$ and then system pressure you can see here system pressure is around you know 73 kilo Pascal at azeotrope. So, the saturation pressure of component b that is P_b^{sat} is around 82 kilo Pascal's whereas, the saturation pressure of lighter component is around 98 kilo Pascal's. Roughly 98 kilo Pascal let us say here it is 82 kilo Pascal's here also the difference is you can see 15 to 16 kilo Pascal's only.

And then system pressure you can see the azeotrope it is much lower than either of the saturation pressures it is around roughly 72 kilo Pascal's or something like that whereas, the saturation pressure of these 2 components are respectively you know 97 and then 82 kilo Pascal's respectively for component a and b. So, here when there is a negative deviation you can see there is a minima kind of thing is forming and P-x and P-y curve and then further you can see obviously, there is a deviation from RL line.

This is the RL line and then this is your P-x_a curve now, you can see the difference between these P-x_a curve and then RL line is very high first of all negative deviation is there and this negative deviation is also very large. As we have seen, if the unlike and like interactions are very much different from each other then there is a possibility of an azeotrope formation and when the like and unlike interactions are very different from each other.

The gap between RL line and P-x_a curve is going to be larger like this we have seen. And then you can see the enclosed area where both vapour and liquid phases are coexisting. So this is one area in this area, we have 1 enclosed area where both the phases are coexisting. And then there is another enclosed area here where again, both the, you know, both the phases are coexisting and equilibrium. If there is no azeotrope formation then we have seen that there is only 1 enclosed area between P-x_a P-y_a curve. If there is an azeotrope formation.

Then it is possible that more than 1 enclosed area between P-x_a and P-y_a curve representing the coexistence of vapour and liquid phases take place like this. One is before the azeotrope point and another one is the after the azeotrope point azeotrope showing positive deviation from RL that is maxima in P-x_a and P-y_a curves are more common than those exhibiting negative deviations. So, this is a very common observation that negative deviation from ideal behavior represented by RL are very few cases are there.

So, obviously, corresponding azeotropes coexisting along with the negative deviation from RL are also going to be very few compared to the cases of you know, positive deviation coexisting with the azeotropic behavior.

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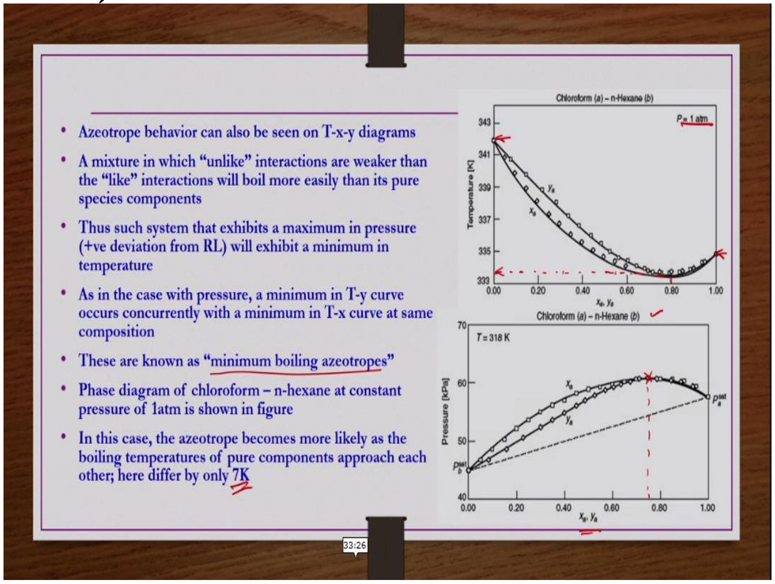

- Azeotrope behavior can also be seen on T-x-y diagrams
- A mixture in which “unlike” interactions are weaker than the “like” interactions will boil more easily than its pure species components
- Thus such system that exhibits a maximum in pressure (+ve deviation from RL) will exhibit a minimum in temperature
- As in the case with pressure, a minimum in T-y curve occurs concurrently with a minimum in T-x curve at same composition
- These are known as “minimum boiling azeotropes”
- Phase diagram of chloroform – n-hexane at constant pressure of 1atm is shown in figure
- In this case, the azeotrope becomes more likely as the boiling temperatures of pure components approach each other; here differ by only 7K

So, azeotrope behavior can also be seen on T-x-y diagrams also. A mixture in which unlike interactions are weaker than the like interactions will boil more easily than its pure species components. That means, what unlike interactions are weaker that means, like interactions are stronger if the like interactions are stronger that means, positive deviation is there. So, if the positive deviation from the RL is there, so then P-x P-y curves are showing a kind of maxima if at all there is a kind of you know azeotrope is there.

So, could the corresponding T-x or T-x T-y curve will be showing a kind of minima, it will be showing you a kind of minimum point so then because T-x T-y curves having a kind of minimum point then it is also called as a kind of minimum boiling mixture. Thus such system that exhibits a maximum in pressure that is positive deviation from RL will exhibit a minimum in temperature like this. So, the same chloroform n-hexane system that P-x-y curve will take it positive deviation and then around at 7.75 we are having a kind of azeotrope point.

So, if you draw the T-x-y curve for the same system but at 1 atmosphere, then you will have this kind of system where here you can see the azeotrope phase formed around at 0.79 or 0.8 and then it is having a kind of a minimum here. In the P-x-y diagram there is a maxima for a positive deviation curve. So, in the T-x-y curve there is a minima for the same system showing a positive deviation from the ideal behavior? As in the case with pressure a minimum in T-y curve occurs concurrently with minimum in T-x curve at the same composition.

And these are known as the minimum boiling azeotropes because here the mixture boiling point here we can see what we can understand from here we can understand at azeotrope, system is boiling a temperature much lower than the boiling point of component b and then boiling point of component a. So, in the minimum boiling azeotrope pressure system pressure is going to be more than the saturation pressure of either of the components, whereas the system temperature is going to be lower than the boiling point of either of the components a and b.

So, if you wanted to find out whether the system that is exhibiting azeotrope is a minimum boiling azeotrope or maximum boiling azeotrope, then you have to find out the pressure of the system at the azeotrope composition. At the azeotropic point if you find out the system pressure and then if you compare that pressure with the saturation pressure of the both the components a and b, if it is more than the saturation pressure then that is a minimum boiling mixture or minimum boiling azeotrope.

If the pressure is less than the saturation pressure of either of the components then we can say that system is the kind of maximum boiling azeotrope as we are going to see that example as well phase diagram of chloroform n-hexane constant pressure of an atmosphere is shown here. And then we can see the azeotrope becomes more likely as the boiling temperature of pure components approach each other and they differ by only 7 K approximately 7 Kelvin.

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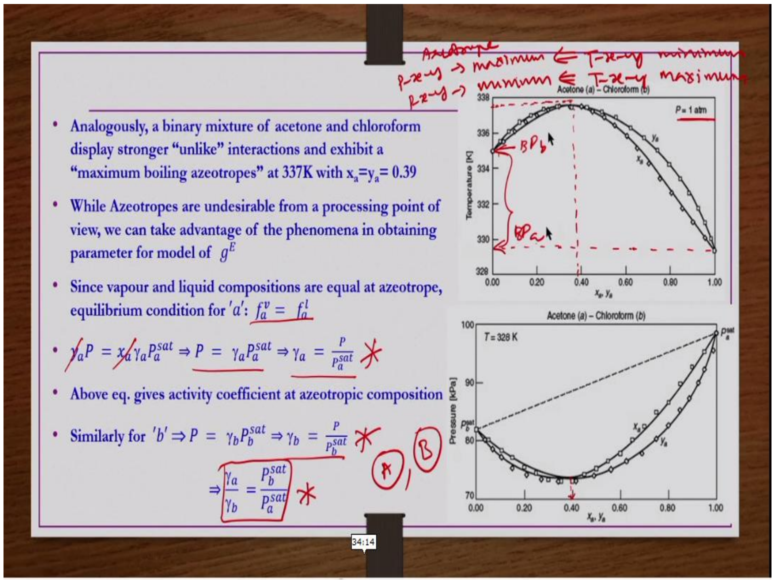

Azeotrope
P-x-y → maximum ⇐ T-x-y minimum
P-x-y → minimum ⇐ T-x-y maximum

- Analogously, a binary mixture of acetone and chloroform display stronger "unlike" interactions and exhibit a "maximum boiling azeotropes" at 337K with $x_a = y_a = 0.39$
- While Azeotropes are undesirable from a processing point of view, we can take advantage of the phenomena in obtaining parameter for model of g^E
- Since vapour and liquid compositions are equal at azeotrope, equilibrium condition for 'a': $\underline{f_a^v = f_a^l}$
- $\cancel{y_a} P = \cancel{x_a} \gamma_a P_a^{sat} \Rightarrow \underline{P = \gamma_a P_a^{sat}} \Rightarrow \underline{\gamma_a = \frac{P}{P_a^{sat}}}$ *
- Above eq. gives activity coefficient at azeotropic composition
- Similarly for 'b' $\Rightarrow P = \gamma_b P_b^{sat} \Rightarrow \gamma_b = \frac{P}{P_b^{sat}}$ *

$$\Rightarrow \boxed{\frac{\gamma_a}{\gamma_b} = \frac{P_b^{sat}}{P_a^{sat}}} \; *$$

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So analogously a binary mixture of acetone and chloroform display a stronger unlike interactions and exhibit a maximum boiling azeotropes at 337 Kelvin with $x_a = y_a = 0.39$. If unlike interactions are stronger, then what we call, we call a negative deviation from RL, if the negative deviation from RL is there, then P-x P-y curve are going to be, you know below the RL line.

So, if there is an azeotrope along with this negative deviation, both the behavior are there then P-x P-y curve is going to display a kind of minimum. So the corresponding behavior in T-x-y diagram is going to be depicted by the maximum point in T-x T-y curves and then if in T-x T-y curves there is a maximum that means at azeotrope composition system is boiling at a temperature much higher than the boiling temperatures or boiling points of either of the components.

So, that is what we can see here, T-x-y curve of acetone chloroform and then P-x P-x-y curve of the same acetone chloroform system this is what we have already seen. We have seen that this P-x-y curve there is an azeotrope formation at around 0.39 composition at around 0.39 of mole fraction for both you know liquid and vapour phase. So, there is an azeotrope formation but the corresponding T-x-y diagram if you plot at 1 atmosphere, then you can find the azeotrope is forming approximately at the same composition of 0.39.

But in the T-x-y curve we are having a kind of maximum, we are having a kind of maximum whereas the P-x-y curve for the same system is showing a kind of minimum because it is a negative deviation. And now this is the boiling point of component b. And then this is the boiling point of component a. And now as azeotropic composition at 0.39 the system temperature is much higher or much higher than this either 2 boiling points have 2 components a and b respectively.

So, the system is boiling at higher temperature than the boiling point of either of the 2 components at the azeotropic composition. That is the reason these kinds of azeotropes are known as the maximum boiling azeotropes. Then here also you can see the difference between boiling point of these 2 components is approximately 7 Kelvin as we have seen previously it is the same system. So, this is what we can understand.

So, that means, if there is an azeotrope then if the P-x-y curve we showing you a kind of minimum then T-x-y curve is going to show you a kind of maximum and then if there is an azeotrope and then system P-x-y diagrams showing a kind of maximum then corresponding T-x-y curve is going to show a kind of minimum opposite trend we see. So, that is to recapitulate, let us say if you have the azeotropes then P-x-y curve if there is a kind of maximum is existing.

So, there will be kind of minimum in corresponding T-x-y phase diagram and then such mixtures are known as the not mixtures, the mixture that azeotropic point is known as the minimum boiling azeotropes and then if P-x-y curve is having a kind of minimum in its P-x-y, phase diagram, then corresponding T-x-y curve is going to have a kind of a display a kind of maximum then that means see azeotropic mixture is boiling it maximum boiling point are known as the maximum boiling azeotropes.

So, this is about a few characteristics about the azeotrope. So, what we understand obviously azeotropes are undesirable, because we know when this y_i and then x_i the difference between y_i and x_i is small, then this operation is going to be difficult that we already understand now, in the case of azeotrope what happens this y_i is becoming equal to the x_i that means, separation is not possible, separation is not at all possible, while azeotropes are undesirable from a processing point of view.

We can take advantage of the phenomena in obtaining parameters for model of g^E, let us say, two suffix parameter a is there at three suffix parameters a b are there. So, if you know there is azeotrope formation for a given system. So, then that information may be used to find out these parameters. Because, vapour and liquid compositions are equal at azeotrope. At equilibrium for component a we can write $f_a^v = f_a^l$.

That means if the system is let us say is having a kind of non ideality only in the liquid phase the vapour side is a kind of ideal 1 then we can write it as $y_a P = x_a \gamma_a P_a^{sat}$and now, azeotrope this y_a and x_a both are equal to each other, then we can write $P = \gamma_a P_a^{sat}$ or $\gamma_a = \frac{P}{P_a^{sat}}$ that means, that azeotropic composition if you know if you wanted to know the activity coefficient of a given component you need to know only this system, total pressure and then saturation pressure of that particular component.

Because the ratio of the system total pressure to saturation pressure of that component gives the activity coefficient of that component that azeotropic composition. Now, similarly, for component b also if you write you get $\gamma_b = \frac{P}{P_a^{sat}}$. That means $\frac{\gamma_a}{\gamma_b}$ is nothing but $\frac{P_b^{sat}}{P_a^{sat}}$. This is one additional information you get this is another additional information you get. And now using these equations you can find out what is this constant associated with the g^E model etc. those things you can find out.

So, this is the advantage, mathematical advantage only, but operational wise azeotrope is always going to be undesirable. Now, this is all about the characteristics of azeotropes, but can we prove it thermodynamically that is what we are going to see now.

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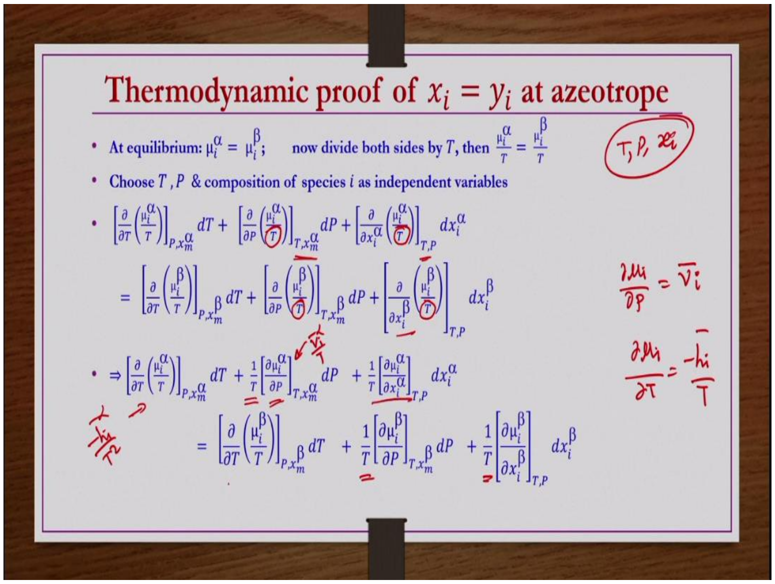

Thermodynamic proof of $x_i = y_i$ at azeotrope

- At equilibrium: $\mu_i^\alpha = \mu_i^\beta$; now divide both sides by T, then $\frac{\mu_i^\alpha}{T} = \frac{\mu_i^\beta}{T}$
- Choose T, P & composition of species i as independent variables
- $\left[\frac{\partial}{\partial T}\left(\frac{\mu_i^\alpha}{T}\right)\right]_{P,x_m^\alpha} dT + \left[\frac{\partial}{\partial P}\left(\frac{\mu_i^\alpha}{T}\right)\right]_{T,x_m^\alpha} dP + \left[\frac{\partial}{\partial x_i^\alpha}\left(\frac{\mu_i^\alpha}{T}\right)\right]_{T,P} dx_i^\alpha$

$$= \left[\frac{\partial}{\partial T}\left(\frac{\mu_i^\beta}{T}\right)\right]_{P,x_m^\beta} dT + \left[\frac{\partial}{\partial P}\left(\frac{\mu_i^\beta}{T}\right)\right]_{T,x_m^\beta} dP + \left[\frac{\partial}{\partial x_i^\beta}\left(\frac{\mu_i^\beta}{T}\right)\right]_{T,P} dx_i^\beta$$

- $\Rightarrow \left[\frac{\partial}{\partial T}\left(\frac{\mu_i^\alpha}{T}\right)\right]_{P,x_m^\alpha} dT + \frac{1}{T}\left[\frac{\partial \mu_i^\alpha}{\partial P}\right]_{T,x_m^\alpha} dP + \frac{1}{T}\left[\frac{\partial \mu_i^\alpha}{\partial x_i^\alpha}\right]_{T,P} dx_i^\alpha$

$$= \left[\frac{\partial}{\partial T}\left(\frac{\mu_i^\beta}{T}\right)\right]_{P,x_m^\beta} dT + \frac{1}{T}\left[\frac{\partial \mu_i^\beta}{\partial P}\right]_{T,x_m^\beta} dP + \frac{1}{T}\left[\frac{\partial \mu_i^\beta}{\partial x_i^\beta}\right]_{T,P} dx_i^\beta$$

T, P, x_i

$\frac{\bar{v}_i}{T}$

$-\frac{\bar{h}_i}{T^2}$

$\frac{\partial \mu_i}{\partial P} = \bar{v}_i$

$\frac{\partial \mu_i}{\partial T} = -\frac{\bar{h}_i}{T}$

Thermodynamic proof of $x_i = y_i$ at azeotrope. So, we start with equal chemical potential that is $\mu_i^\alpha = \mu_i^\beta$. If you have α and β phase then for ith component this what we can write now, what do you do? You divide this equations by temperature T that is $\frac{\mu_i^\alpha}{T} = \frac{\mu_i^\beta}{T}$. Now, what do you do? You take this temperature pressure and then composition as a kind of independent variables and then try to obtain differentiation of this particular equation.

Then what you have $\left[\frac{\partial}{\partial T}\left(\frac{\mu_i^\alpha}{T}\right)\right] dT + \left[\frac{\partial}{\partial P}\left(\frac{\mu_i^\alpha}{T}\right)\right] dP + \left[\frac{\partial}{\partial x_i^\alpha}\left(\frac{\mu_i^\alpha}{T}\right)\right] dx_i^\alpha = \left[\frac{\partial}{\partial T}\left(\frac{\mu_i^\beta}{T}\right)\right] dT + \left[\frac{\partial}{\partial P}\left(\frac{\mu_i^\beta}{T}\right)\right] dP + \left[\frac{\partial}{\partial x_i^\beta}\left(\frac{\mu_i^\beta}{T}\right)\right] dx_i^\beta$. This is what you get. Now, in the next step what you do this T you can take it out of partial differentiation because it is it constant T, x_m same is here also, this T you can also take out of the partial differentiation because it is at constant T and P.

Likewise, same is true for the β phase also, when you do this thing, so, here $\frac{1}{T}\left[\frac{\partial \mu_i^\alpha}{\partial P}\right]$ you will get and then here $\frac{1}{T}\left[\frac{\partial \mu_i^\alpha}{\partial x_i^\alpha}\right]$ you will get same is true in the right hand side also. Now, at the beginning of this particular course, when we are discussing about the chemical potential, what we understood, we understood that $\frac{\partial \mu_i}{\partial P} = \bar{v}_i$ and also, we understand that $\frac{\partial \mu_i}{\partial T} = -\frac{\bar{h}_i}{T}$ that is what we understand.

So, here you will get $-\frac{\bar{h}_i^\alpha}{T^2}$ and then for this part you will get $\frac{\bar{v}_i^\alpha}{T}$ is as it is this will remain same and then same is true for the β phase terms also.

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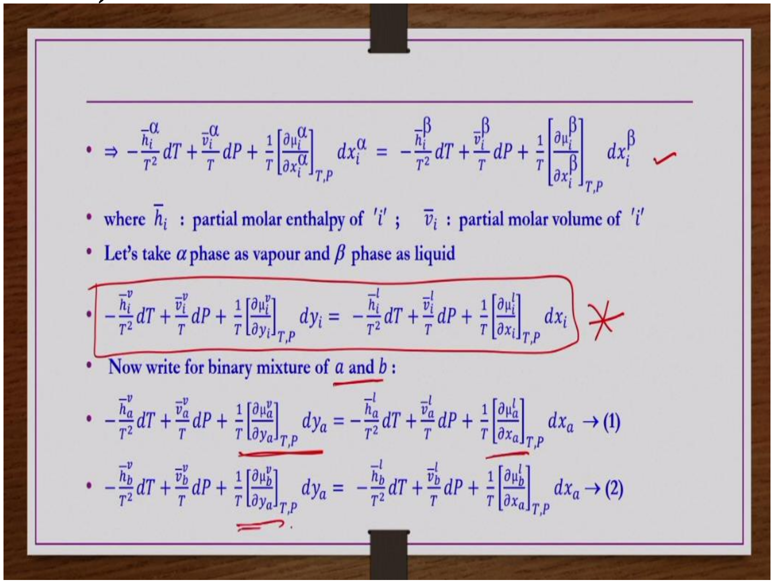

- $\Rightarrow -\frac{\bar{h}_i^\alpha}{T^2}dT + \frac{\bar{v}_i^\alpha}{T}dP + \frac{1}{T}\left[\frac{\partial\mu_i^\alpha}{\partial x_i^\alpha}\right]_{T,P} dx_i^\alpha = -\frac{\bar{h}_i^\beta}{T^2}dT + \frac{\bar{v}_i^\beta}{T}dP + \frac{1}{T}\left[\frac{\partial\mu_i^\beta}{\partial x_i^\beta}\right]_{T,P} dx_i^\beta$ ✓
- where $\bar{h}_i$: partial molar enthalpy of $'i'$; $\bar{v}_i$: partial molar volume of $'i'$
- Let's take α phase as vapour and β phase as liquid
- $\boxed{-\frac{\bar{h}_i^v}{T^2}dT + \frac{\bar{v}_i^v}{T}dP + \frac{1}{T}\left[\frac{\partial\mu_i^v}{\partial y_i}\right]_{T,P} dy_i = -\frac{\bar{h}_i^l}{T^2}dT + \frac{\bar{v}_i^l}{T}dP + \frac{1}{T}\left[\frac{\partial\mu_i^l}{\partial x_i}\right]_{T,P} dx_i}$ ✱
- Now write for binary mixture of $\underline{a \text{ and } b}$:
- $-\frac{\bar{h}_a^v}{T^2}dT + \frac{\bar{v}_a^v}{T}dP + \underline{\frac{1}{T}\left[\frac{\partial\mu_a^v}{\partial y_a}\right]_{T,P}} dy_a = -\frac{\bar{h}_a^l}{T^2}dT + \frac{\bar{v}_a^l}{T}dP + \frac{1}{T}\underline{\left[\frac{\partial\mu_a^l}{\partial x_a}\right]_{T,P}} dx_a \rightarrow (1)$
- $-\frac{\bar{h}_b^v}{T^2}dT + \frac{\bar{v}_b^v}{T}dP + \frac{1}{T}\underline{\left[\frac{\partial\mu_b^v}{\partial y_a}\right]_{T,P}} dy_a = -\frac{\bar{h}_b^l}{T^2}dT + \frac{\bar{v}_b^l}{T}dP + \frac{1}{T}\left[\frac{\partial\mu_b^l}{\partial x_a}\right]_{T,P} dx_a \rightarrow (2)$

That if you do you will get this equation $-\frac{\bar{h}_i^\alpha}{T^2}$dT + $\frac{\bar{v}_i^\alpha}{T}$dP + $\frac{1}{T}\left[\frac{\partial\mu_i^\alpha}{\partial x_i^\alpha}\right]$ dx_i^α and then same is true for the β phase in the right hand side. Then, here in this equation what we have this $\bar{h}_i$ is nothing but partial molar enthalpy of component i and then $\bar{v}_i$ is nothing but partial molar volume of i. Now, let us write this equation by taking α phase as vapour phase and β phase as liquid phase because this is we are trying this in mathematical thermodynamic simplification.

We are trying to find out thermodynamically can we prove that $x_i = y_i$ or not that is vapour and liquid phases are there. So, then α phase we are taking as vapour phase and β phase we are taking as the liquid phase then same equation exactly the same thing that α is replaced by v and then β is replaced by l indicating vapour and liquid phases respectively. Now, this equation we write for binary mixture simplicity, just for simplicity we write it for a binary mixture.

So, this is a generalized equation for any component i in the mixture, if there are m number of components, there are m number of such relations would be there. So, now, for simplicity we take binary mixture a b. So, 2 relations would be there. So, for component a this relation for component b, we have this relation. Now, what we do whatever the $\frac{\partial\mu_i}{\partial y_i}\frac{\partial\mu_i}{\partial x_i}$terms are there, they those terms will be keeping one side and then remaining terms will be taking to the other side for both of these equations.

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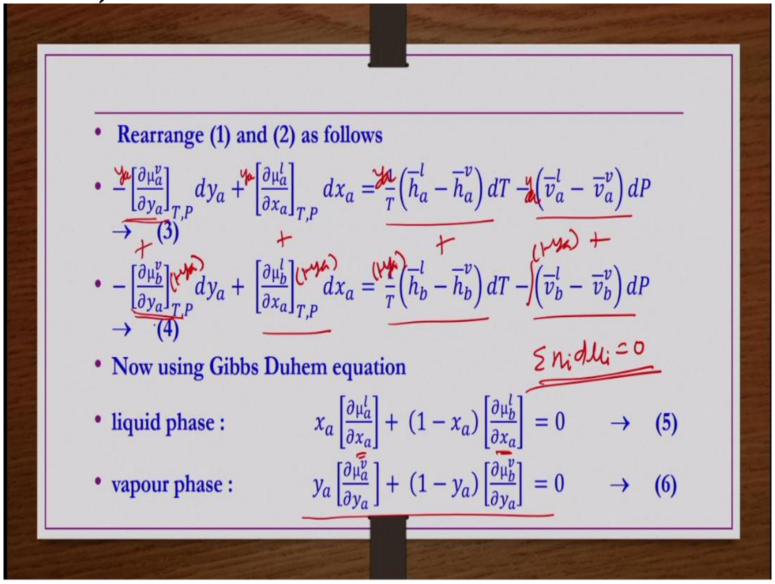

- Rearrange (1) and (2) as follows
- $-\left[\frac{\partial \mu_a^v}{\partial y_a}\right]_{T,P} dy_a + \left[\frac{\partial \mu_a^l}{\partial x_a}\right]_{T,P} dx_a = -\frac{1}{T}\left(\bar{h}_a^l - \bar{h}_a^v\right) dT - \left(\bar{v}_a^l - \bar{v}_a^v\right) dP \rightarrow (3)$
- $-\left[\frac{\partial \mu_b^v}{\partial y_a}\right]_{T,P} dy_a + \left[\frac{\partial \mu_b^l}{\partial x_a}\right]_{T,P} dx_a = -\frac{1}{T}\left(\bar{h}_b^l - \bar{h}_b^v\right) dT - \left(\bar{v}_b^l - \bar{v}_b^v\right) dP \rightarrow (4)$
- Now using Gibbs Duhem equation $\quad \Sigma n_i d\mu_i = 0$
- liquid phase : $\quad x_a \left[\frac{\partial \mu_a^l}{\partial x_a}\right] + (1 - x_a)\left[\frac{\partial \mu_b^l}{\partial x_a}\right] = 0 \rightarrow (5)$
- vapour phase : $\quad y_a \left[\frac{\partial \mu_a^v}{\partial y_a}\right] + (1 - y_a)\left[\frac{\partial \mu_b^v}{\partial y_a}\right] = 0 \rightarrow (6)$

When we do then we get this equation number 3 and then equation number 4 like this. But we have Gibbs Duhem equation for liquid phase if you write this is what you can have $x_a\, d\mu_a^l + x_b\, d\mu_b^l = 0$ that I have written with respect to partial differentiation x_a here for simplicity. Same is true for the vapour phase also if you write Gibbs Duhem equation then you have this equation that is simply $\sum n_i d\mu_i = 0$ or $\sum x_i d\mu_i = 0$ either why we could write this we are writing for both vapour and liquid phase.

So, then we have this equation. Now what I do this equation number 3. I will multiply by y_a both sides and then equation number 4 what I do I will multiply both sides by $1 - y_a$ like this and then add them together and then if you add them together, so what you have here $y_a \frac{\partial \mu_a^v}{\partial y_a}$ you are having 1 term, and then another term you will be having $(1 - y_a) \frac{\partial \mu_b^v}{\partial y_a}$ this term you are having.

So, if you take the $-$ common so then some this term, + this term, when you do what will happen that is nothing but, 0 according to equation number 6. And then remaining terms would be there so these 2 terms y_a multiplied by this term + $1 - y_a$ multiplied by this term = y_a multiplied by this term, + $1 - y_a$ multiplied by this term, then + y_a multiplied by this term + $1 - y_a$ multiplied by this term that is what you have.

So, then finally, when you strike out these 2 terms using equation number 6, this first terms would be 0 and then remaining 6 terms if you re write after making use of this expression also and then doing some kind of algebraic simplifications, then you will have this term.

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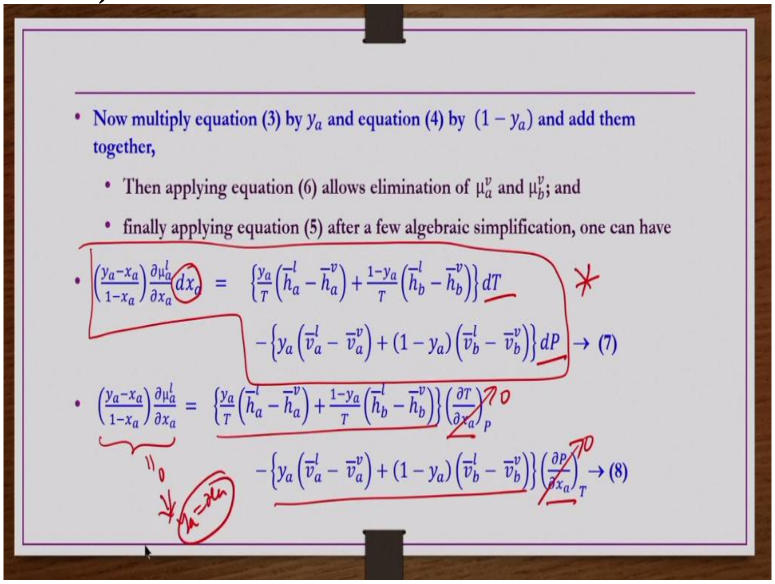

- Now multiply equation (3) by y_a and equation (4) by $(1-y_a)$ and add them together,
  - Then applying equation (6) allows elimination of μ_a^v and μ_b^v; and
  - finally applying equation (5) after a few algebraic simplification, one can have
- $$\boxed{\left(\frac{y_a-x_a}{1-x_a}\right)\frac{\partial\mu_a^l}{\partial x_a}dx_a} = \left\{\frac{y_a}{T}\left(\bar{h}_a^l-\bar{h}_a^v\right)+\frac{1-y_a}{T}\left(\bar{h}_b^l-\bar{h}_b^v\right)\right\}dT \quad *$$
  $$-\left\{y_a\left(\bar{v}_a^l-\bar{v}_a^v\right)+(1-y_a)\left(\bar{v}_b^l-\bar{v}_b^v\right)\right\}dP \rightarrow (7)$$
- $$\underbrace{\left(\frac{y_a-x_a}{1-x_a}\right)\frac{\partial\mu_a^l}{\partial x_a}}_{=0 \Rightarrow y_a=x_a} = \left\{\frac{y_a}{T}\left(\bar{h}_a^l-\bar{h}_a^v\right)+\frac{1-y_a}{T}\left(\bar{h}_b^l-\bar{h}_b^v\right)\right\}\cancel{\left(\frac{\partial T}{\partial x_a}\right)_P}^{\,0}$$
  $$-\left\{y_a\left(\bar{v}_a^l-\bar{v}_a^v\right)+(1-y_a)\left(\bar{v}_b^l-\bar{v}_b^v\right)\right\}\cancel{\left(\frac{\partial P}{\partial x_a}\right)_T}^{\,0} \rightarrow (8)$$

Final equation you will get this one + this term is also be there. So, that is by multiplying this equation number (3) by y_a and then multiplying equation number (4) by $1 - y_a$ this side and then adding them together what we can understand we will be having a term $y_a \frac{\partial\mu_a^v}{\partial y_a} + (1 - y_a)\frac{\partial\mu_b^v}{\partial y_a}$ will be having that is nothing but 0, according to Gibbs Duhem equation for the vapour phase.

And then similarly, remaining terms also if you apply the Gibbs Duhem equation terms for the liquid phase and then simplify then if you do some kind of algebraic simplification then you get this equation. So, now this dx_a if I take to the right hand side, then what we will have I will be having $\left(\frac{y_a-x_a}{1-x_a}\right)\frac{\partial\mu_a^l}{\partial x_a}$ = this entire term multiplied by $\frac{\partial T}{\partial x_a}$at constant P minus this entire term multiplied by $\frac{\partial P}{\partial x_a}$ constant T.

Now, from the azeotropic discussions that what we understand there is a kind of maxima in T-x_a curve and then P-x_a curve also. So, that means if the maxima is occurring at certain composition, then at that composition $\frac{\partial T}{\partial x}$ is 0 $\frac{\partial T}{\partial y}$is 0 if it is you know T-x-y curve and then similarly in the case of a P-x-y curve also there is a maxima then at that maxima composition at that particular composition where the maxima is occurring for P-x and P-y curve then at that point we can write $\frac{\partial P}{\partial x_a}$= 0 as well as $\frac{\partial P}{\partial y_a}$= 0.

That means, at the azeotrope $\frac{\partial T}{\partial x_a}$is 0 $\frac{\partial P}{\partial x_a}$ is also 0. That means, altogether right hand side both the terms are 0. So, that means left hand side is equal to 0 then, what we can understand if this left hand side = 0. From here what we can understand we can understand y_a = x_a. So, even thermodynamically it is proved that azeotrope is possible. That is what it means by.

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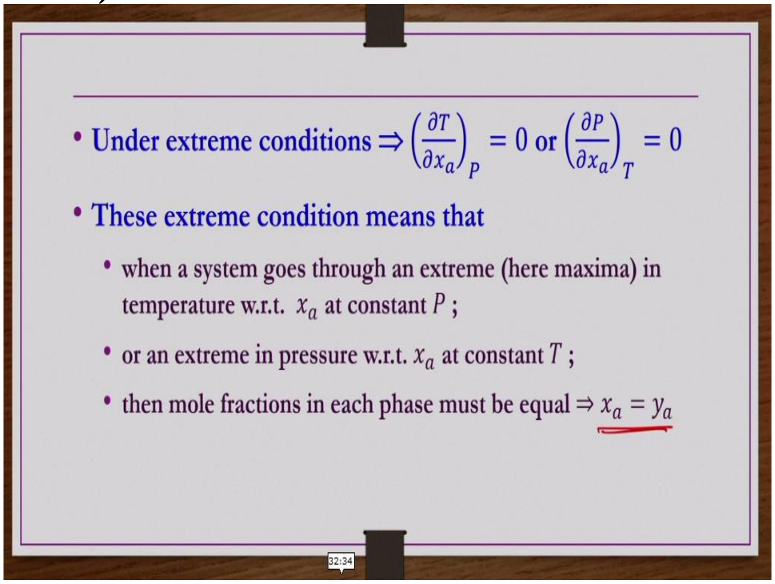

- Under extreme conditions ⇒ $\left(\frac{\partial T}{\partial x_a}\right)_P = 0$ or $\left(\frac{\partial P}{\partial x_a}\right)_T = 0$
- These extreme condition means that
  - when a system goes through an extreme (here maxima) in temperature w.r.t. x_a at constant P ;
  - or an extreme in pressure w.r.t. x_a at constant T ;
  - then mole fractions in each phase must be equal ⇒ $x_a = y_a$

So, under extreme conditions $\frac{\partial T}{\partial x_a}$= 0 or $\frac{\partial P}{\partial x_a}$= 0 these extreme conditions means that when system goes through an extreme here maxima in temperature with respect to x_a at constant P or an extreme in pressure with respect to x_a at constant T, then mole fractions in each phase must be equal, that is x_a = x_a as we have seen proved in the previous slide.

So, that is about the thermodynamic proof of existence of an azeotropic or at azeotropic point the composition of a component in either of the phase is equal if at all there is as azeotrope is forming or at an azeotropic point, the combination of component i in the vapour phase = the combination of component i in the liquid phase that is what we have already proved. Now, having seen the same characteristics of this azeotropic behavior and then having seen the proof thermodynamic proof of this equal composition at azeotropic point. Now, what we do we go to a few example problem to make sure how we can use this azeotropic conditions?

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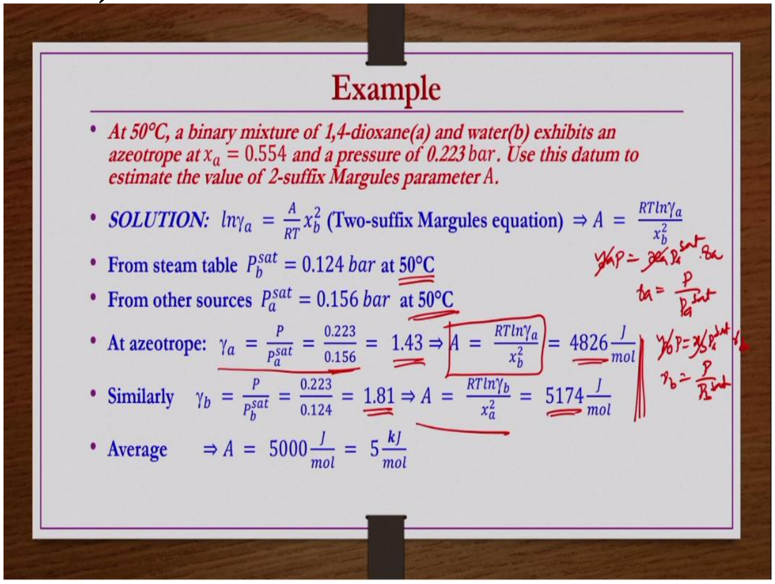

Example

- At 50°C, a binary mixture of 1,4-dioxane(a) and water(b) exhibits an azeotrope at $x_a = 0.554$ and a pressure of 0.223 bar. Use this datum to estimate the value of 2-suffix Margules parameter A.
- SOLUTION: $ln\gamma_a = \frac{A}{RT}x_b^2$ (Two-suffix Margules equation) $\Rightarrow A = \frac{RTln\gamma_a}{x_b^2}$
- From steam table $P_b^{sat} = 0.124\ bar$ at 50°C
- From other sources $P_a^{sat} = 0.156\ bar$ at 50°C
- At azeotrope: $\gamma_a = \frac{P}{P_a^{sat}} = \frac{0.223}{0.156} = 1.43 \Rightarrow \boxed{A = \frac{RTln\gamma_a}{x_b^2}} = 4826\frac{J}{mol}$
- Similarly $\gamma_b = \frac{P}{P_b^{sat}} = \frac{0.223}{0.124} = 1.81 \Rightarrow A = \frac{RTln\gamma_b}{x_a^2} = 5174\frac{J}{mol}$
- Average $\Rightarrow A = 5000\frac{J}{mol} = 5\frac{kJ}{mol}$

$\cancel{y_a}P = \cancel{x_a}P_a^{sat}\gamma_a$

$\gamma_a = \frac{P}{P_a^{sat}}$

$\cancel{y_b}P = \cancel{x_b}P_b^{sat}\gamma_b$

$\gamma_b = \frac{P}{P_b^{sat}}$

So, here at 50 degrees centigrade a binary mixture of 1, 4-dioxane and water exhibits an azeotrope at $x_a = 0.554$ and a pressure of 0.223 bar and then use this datum to estimate the value of two suffix margules parameter A. So, to suffix Margules equation we know $\ln \gamma_a = \frac{A}{RT} x_b^2$ that means $A=\frac{RT\ln\gamma_a}{x_b^2}$. Now from steam table said 50 degrees integrate we know for water the saturation pressure is $P_b^{sat} = 0.124$ bar.

And then similarly, if you obtain the unknown constant for this 1, 4-dioxane and then apply the Antoine equation to find out the saturation pressure of this component A then you can find out this P_a^{sat} as 0.156 bar at 50 degrees centigrade this I am not doing just take it because such kind of things we have already done several problems, how to find out the saturation pressures. And then at azeotrope what we know that γ_a is nothing but $\frac{P}{P_a^{sat}}$ isn't it?

Because we have this $y_a P = x_a P_a^{sat}$ and then there is γ_a, if it is a non idealities there in the liquid phase only, then it azeotrope this x_a y_a equal that means $\gamma_a = \frac{P}{P_a^{sat}}$. So, that we have seen, so, that we apply then you get $\gamma_a = 1.43$ once γ_a is known, so, this $A = \frac{RT\ln\gamma_a}{x_b^2}$ you can use to find out A value that x_a given as 0.554. So, x_b is nothing but, 0.446. So, that you can substitute so, here and then γ_a you find just now as 1.43 then you get A = 4826 joule per mole, then you get A = 4826 joule per mole.

Then similarly for the component b also y_b P = x_b $P_b^{sat}\gamma_b$ x_b y_b is equal to each other at azeotropic point. So, γ_b is nothing but $\frac{P}{P_a^{sat}}$. And then when you apply this 1, you get γ_b = 1.81. And then from this γ_b information ln γ_b is nothing but $\frac{A}{RT}$ x_a^2. That means A = $\frac{RT\ln\gamma_b}{x_a^2}$ for two suffix Margules equation ln γ_b you substitute whatever 1.81 and x_a is nothing but 0.554 when you do it, you get 5174 joule per mole as this parameter a.

Now you can see by either of these 2 approaches we are getting different values of A, 1 is 4826 another 1 is 5174. Though the difference is not much. So, that can be avoided any of this value can be taken are better you take the average value, average value comes out to be 5000 joule per mole or 5 kilo joules per mole is the value of this two suffix parameter or two suffix Margules parameter A.

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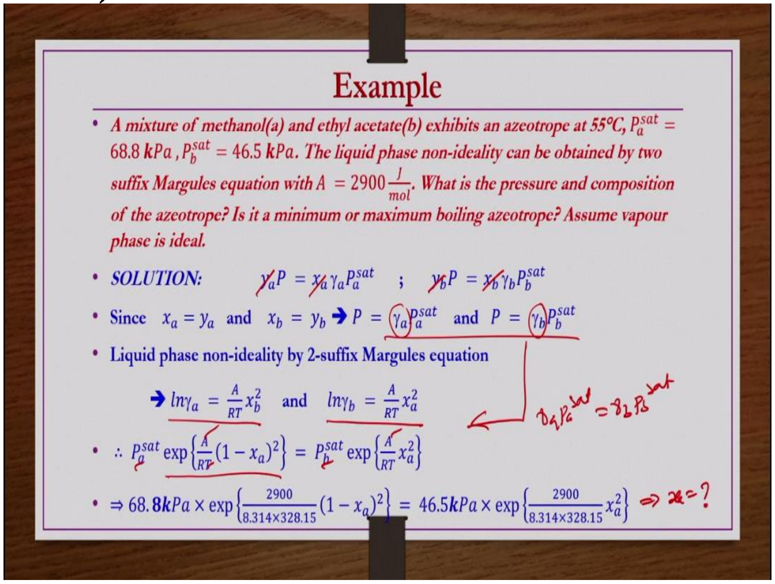

Example

- *A mixture of methanol(a) and ethyl acetate(b) exhibits an azeotrope at 55°C, P_a^{sat} = 68.8 kPa , P_b^{sat} = 46.5 kPa. The liquid phase non-ideality can be obtained by two suffix Margules equation with A = 2900 $\frac{J}{mol}$. What is the pressure and composition of the azeotrope? Is it a minimum or maximum boiling azeotrope? Assume vapour phase is ideal.*
- *SOLUTION:* $\cancel{y_a}P = \cancel{x_a}\gamma_a P_a^{sat}$; $\cancel{y_b}P = \cancel{x_b}\gamma_b P_b^{sat}$
- Since $x_a = y_a$ and $x_b = y_b$ ➔ $P = \gamma_a P_a^{sat}$ and $P = \gamma_b P_b^{sat}$
- Liquid phase non-ideality by 2-suffix Margules equation

  ➔ $ln\gamma_a = \frac{A}{RT}x_b^2$ and $ln\gamma_b = \frac{A}{RT}x_a^2$

  $\gamma_a P_a^{sat} = \gamma_b P_b^{sat}$
- $\therefore P_a^{sat} \exp\left\{\frac{A}{RT}(1-x_a)^2\right\} = P_b^{sat} \exp\left\{\frac{A}{RT}x_a^2\right\}$
- $\Rightarrow 68.8kPa \times \exp\left\{\frac{2900}{8.314\times328.15}(1-x_a)^2\right\} = 46.5kPa \times \exp\left\{\frac{2900}{8.314\times328.15}x_a^2\right\}$ $\Rightarrow x_a = ?$

Now we take another example, a mixture of methanol and ethyl acetate exhibits an azeotrope at 55 degrees centigrade $P_a^{sat}$is given as 68.8 kilo Pascal P_b^{sat}that is given us 46.5 kilo Pascal's the liquid phase non ideality can be obtained by two suffix margules equation with parameter A = 2,900 joule per mole. What is the pressure and composition of the azeotrope? Now, the question is the other way, in previous problem is that azeotropic composition and then pressure is given.

So we were to find out the parameter A now the parameter A and then saturation pressures are given temperature is given. So, we have to find out the pressure and then azeotropic composition. Azeotropic composition and then corresponding pressure we have to find out and then we have to check whether is it a minimum or maximum boiling azeotrope assume vapour phase is ideal. So, non ideality is there only in the liquid phase if you wanted to know whether it is a minimum boiling azeotrope or maximum boiling azeotrope.

You have to find out the pressure at the azeotropic competition. If that pressure is higher than the saturation pressure of both the components, then we can say it is a minimum boiling azeotrope. Otherwise it is maximum boiling azeotrope. So, first we have to find out pressure. So, for component a and b if you write equilibrium relation then y_a P = x_a γ_a $P_a^{sat}$and then y_b P = x_b γ_b P_b^{sat}if you apply this azeotrope that is $y_a = x_a$ and then $y_b = x_b$ at azeotrope then we have P = γ_a $P_a^{sat}$and then P = γ_b P_b^{sat}.

And then two suffix Margules equation we know that ln γ_a = $\frac{A}{RT}\, x_b^2$ and then ln γ_b = $\frac{A}{RT}\, x_a^2$ this we have already derived then. This γ_a in place of γ_a and then in place of γ_b, we can have this information whatever exponential of $\frac{A}{RT}(1 - x_b)^2$ and then exponential of $\frac{A}{RT}\, x_a^2$ respectively. For γ_a and γ_b because from this relation what we are having we are having γ_a P_a^{sat}= γ_b P_b^{sat}.

Now, $P_a^{sat} P_b^{sat}$are given a is also given only thing unknown is x_a here, temperature is also given 55 degrees centigrade. So, you substitute all of them here and then solve this equation for x_a.

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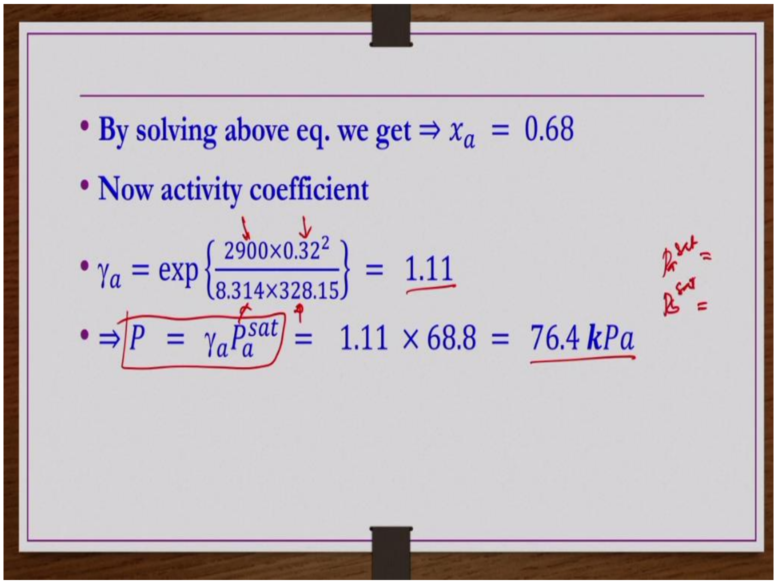

- By solving above eq. we get ⇒ $x_a = 0.68$
- Now activity coefficient
- $\gamma_a = \exp\left\{\frac{2900\times0.32^2}{8.314\times328.15}\right\} = \underline{1.11}$
- $\Rightarrow \boxed{P = \gamma_a P_a^{sat}} = 1.11 \times 68.8 = \underline{76.4\ kPa}$

$P_a^{sat} =$
$P_b^{sat} =$

Then you will find it out as 0.68. So, azeotropic composition is nothing but $x_a = 0.68$ and then $y_a = 0.68$ but we have to find out the pressure also P is nothing but $\gamma_a P_a^{sat}$ or $\gamma_b P_b^{sat}$. So, you have to find out what is γ_a γ_b, if you wanted to find out the pressure since x_a x_b are already known, already calculated. So, γ_b can be or γ_a can be calculated easily, γ_a = exponential of $\frac{A}{RT} x_b^2$.

So, this is a given x_b we found it as 0.32, this is R, this is T. So, γ_a you will get 1.11 then P is nothing but $\gamma_a P_a^{sat}$ as azeotropic composition at azeotropic composition P is nothing but $\gamma_a P_a^{sat}$ when you do it you will find it out as 76.4 kilo Pascal's. Now, what is P_a^{sat}? What is P_b^{sat} you have to compare this P with these 2 values then only you can serve whether it is maximum boiling or minimum boiling mixture.

So, P_a^{sat} is 68.8 P_b^{sat} is 46.5 so the system pressure at the azeotropic composition is higher than the either of saturation pressure values for component a and b respectively. So that means it is a minimum boiling azeotrope. Now, we see a few details about solubility of gases and liquids using these same principles of vapour liquid equilibrium that is fugacity of component i in gases phase = fugacity of component i in the liquid phase that principle we use and then we try to establish some relationship.

But before going into details, what we should understand whatever the analysis that we have done vapour liquid equilibrium analysis fully ideal for ideal non ideal system as well even for the azeotropic calculations also, the reference state mostly we have taken either Lewis Randall reference state Raoult's law and kind of thing those things only we have taken. But we already know that Henry's law is also a kind of reference state further defining in a non ideality or ideality of a liquid phase.

When we take Henry's law as a kind of reference state, if T unlike interactions are dominating and they are different from the like interactions, then we should have a kind of information about Henry's law constant under such conditions we can use this Henry's law as a kind of a reference state or when $x_i \to 0$ then that means, we can say the component i is very sparingly soluble in the solvent.

So, under such conditions also we can use this Henry's law as a kind of referenced it and then solubility of gases in liquid is in general falls on in that category only these gases soluble in the liquid but they are soluble in very small amount. So, under such conditions, we can use the same vapour liquid equilibrium principles that if $f_i^v = f_i^l$, but you know here the reference state has to be Henry's law reference state, because this gasses components are very sparingly soluble in the liquids in general.

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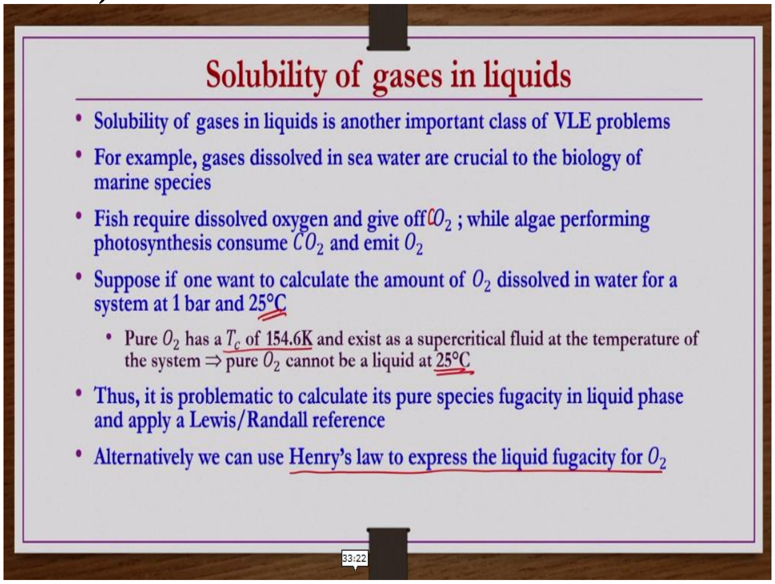

Solubility of gases in liquids

- Solubility of gases in liquids is another important class of VLE problems
- For example, gases dissolved in sea water are crucial to the biology of marine species
- Fish require dissolved oxygen and give off CO_2 ; while algae performing photosynthesis consume CO_2 and emit O_2
- Suppose if one want to calculate the amount of O_2 dissolved in water for a system at 1 bar and 25°C
  - Pure O_2 has a T_c of 154.6K and exist as a supercritical fluid at the temperature of the system ⇒ pure O_2 cannot be a liquid at 25°C
- Thus, it is problematic to calculate its pure species fugacity in liquid phase and apply a Lewis/Randall reference
- Alternatively we can use Henry's law to express the liquid fugacity for O_2

For those cases we are going to see now here solubility of gases in liquids is another important class of VLE problem for examples gases dissolved in seawater are crucial to the biology of marine species. Also, fish require dissolved oxygen and give off CO_2 well, algae perform photosynthesis, consume CO_2 and then emit oxygen? Suppose if one want to calculate the amount of oxygen dissolved in water for a system at 1 bar and 25 degrees centigrade.

Then how should it be done? Is it possible or not? But pure O_2 has a critical temperature of 150 4.6 Kelvin so obviously, at 25 degrees centigrade we wrote O_2 cannot be liquid, because for pure O_2 C are critical temperature is nothing but 154.6 Kelvin. So, obviously it will exist as a supercritical fluid a temperature of the system that is whatever 25 degrees centigrade. So, does it is problematic to calculate its pure species fugacity in liquid phase and apply Lewis Randall reference state. So, that is not possible. So, alternatively what we can use, we can use Henry's law to express the liquid fugacity for oxygen O_2.

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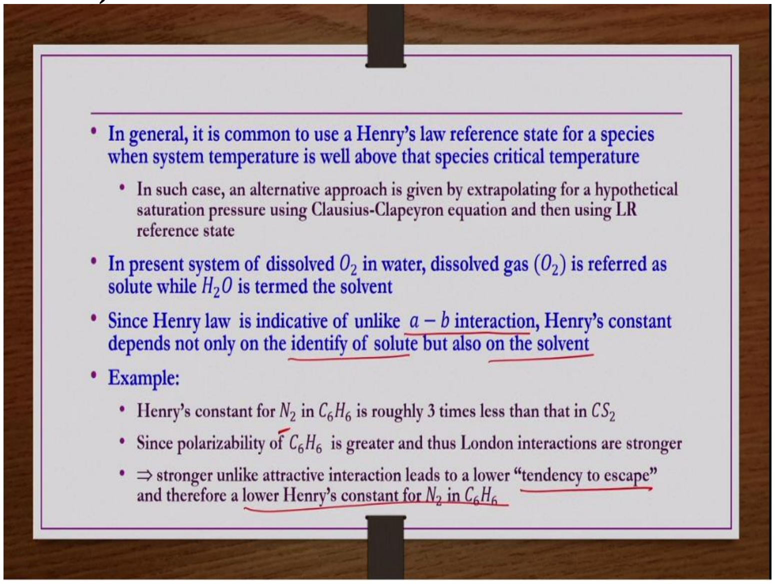

- In general, it is common to use a Henry's law reference state for a species when system temperature is well above that species critical temperature
  - In such case, an alternative approach is given by extrapolating for a hypothetical saturation pressure using Clausius-Clapeyron equation and then using LR reference state
- In present system of dissolved O_2 in water, dissolved gas (O_2) is referred as solute while H_2O is termed the solvent
- Since Henry law is indicative of unlike $a-b$ interaction, Henry's constant depends not only on the identify of solute but also on the solvent
- Example:
  - Henry's constant for N_2 in C_6H_6 is roughly 3 times less than that in CS_2
  - Since polarizability of C_6H_6 is greater and thus London interactions are stronger
  - $\Rightarrow$ stronger unlike attractive interaction leads to a lower "tendency to escape" and therefore a lower Henry's constant for N_2 in C_6H_6

In general it is common to use a Henry's law reference sate for a species when system temperature is well above that species critical temperature as we have seen the example of oxygen. In such case, an alternative approach is given by extrapolating for the hypothetical saturation pressure using Clausius Clapeyron equation, and then using LR reference state that is also possible, but in present system of dissolved oxygen in water, dissolved gas is referred as a solute while H_2O is termed as the solvent.

Since Henry's law is indicative of unlike interactions, a-b interactions and these constants depends not only on the identity of solute, but also on the identity of the solvent because solute you know the same solute if you dissolve in different solvent the solubility is going to be different. So, basically this law constant is going to be different for the same solute in different solvent. For example, if you take Henry's constant for N_2 in $C_6 H_6$ is roughly 3 times less than that in CS_2. Solute is same, but solvent is different in 2 cases.

That is because why it happens polarizability of $C_6 H_6$ is greater than that of CS_2 and thus London attractions or London interactions are stronger in the case of $C_6 H_6$. So, since the stronger unlike attractive interaction leads to lower the tendency to escape and therefore, a lower Henry's constant for N_2 in $C_6 H_6$. One can find the discretion. So, this is one of the examples and then other examples may also be there and then similar analysis one can find out why solubility of one particular solute in different solvents are going to be different.

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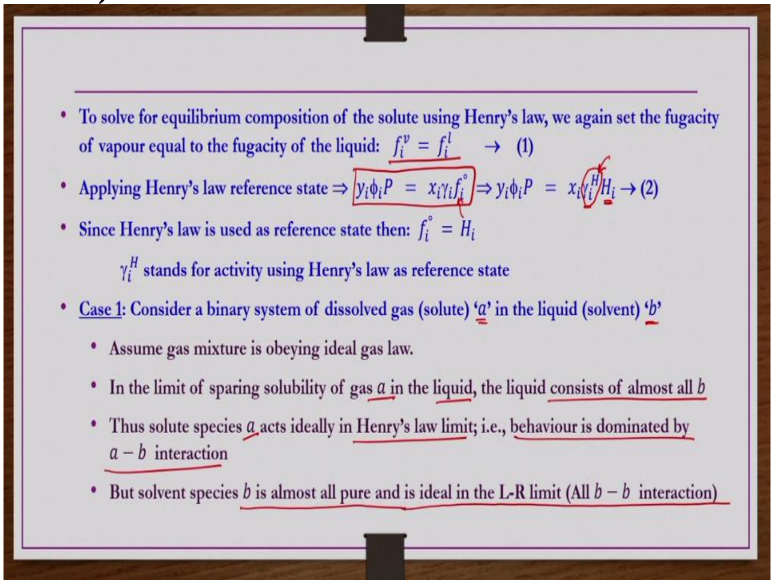

- To solve for equilibrium composition of the solute using Henry's law, we again set the fugacity of vapour equal to the fugacity of the liquid: $\underline{f_i^v = f_i^l} \rightarrow (1)$
- Applying Henry's law reference state $\Rightarrow \boxed{y_i\phi_i P = x_i\gamma_i f_i^\circ} \Rightarrow y_i\phi_i P = x_i\gamma_i^H H_i \rightarrow (2)$
- Since Henry's law is used as reference state then: $f_i^\circ = H_i$

  γ_i^H stands for activity using Henry's law as reference state
- Case 1: Consider a binary system of dissolved gas (solute) 'a' in the liquid (solvent) 'b'
  - Assume gas mixture is obeying ideal gas law.
  - In the limit of sparing solubility of gas a in the liquid, the liquid consists of almost all b
  - Thus solute species a acts ideally in Henry's law limit; i.e., behaviour is dominated by $a - b$ interaction
  - But solvent species b is almost all pure and is ideal in the L-R limit (All $b - b$ interaction)

So, now in order to solve equilibrium composition of the solute using Henry's law we can apply this principle $f_i^v = f_i^l$ and then applying Henry's law constant when we have both phases non ideality generalized one we are writing. So, then for the vapour phase or the gasses phase $y_i \phi_i P$ = for the liquid phase whatever the $x_a \gamma_i f_i^0$. Till now what we have taken f_i^0 with reference to by Lewis Randall rule f_i^0 we have taken as $f_{\text{pure i}}$ and then for pure component $f_{\text{pure i}}$ is nothing but P_a^{sat}.

Saturation pressure of that component i the pressure is low to moderate that is what we have taken. But now, we are taking Henry's law as a kind of reference here. So, f_i^0 has to be H_i that is the solubility of component i in the solvent and then whatever the activity coefficient is there that γ_i we are representing $\gamma_i H_i$ because whatever the activity coefficients those we have derived there also we have taken either the Lewis Randall reference rule or the Raoult's law slide as you can of reference and then we got this activity coefficient etc.

Indirectly whatever that g expression $g^E \rightarrow 0$ when $x_1 \rightarrow 0$ or $x_2 \rightarrow 0$ that is what we have taken that is nothing but with reference to the Raoult's law. So, but here we are taking this activity coefficient translate one has to calculate by taking that you know $x_i \rightarrow 0$ then $f_i^0 = H_i$ that we are taking. So, the active corresponding activity coefficient whatever is there that is we are representing as γ_i^H, how to calculate γ_i^H that is what we are going to see anyway.

So, case one first case we take dissolved gas solute a in the liquid solvent b and then when both the phases are obeying ideal behavior and then that is assume gas mixture is obeying ideal gas law and in the limit of sparing solubility of gas a in the liquid, the liquid consists of almost all b the solute species a has ideally in Raoult's law limit that is behavior is dominated by the a b interactions.

Whereas, the for b it is same by Lewis Randall difference law is applicable, but the solvent species b is almost all pure b and is ideal in the LR limit that is all b interactions are there for species b. So, with respect to component a which is sparingly soluble in the solvent, $x_i \rightarrow 0$ or very small. So, for that component whatever f_i^0 is there that can be taken as H_i whereas, with respect to b, b is almost pure. So, then for this case f_i^0 should be taken as $f_{\text{pure } i}$. So, that is nothing but P_a^{sat} we can take so, that is to differentiate compared to the previous 1.

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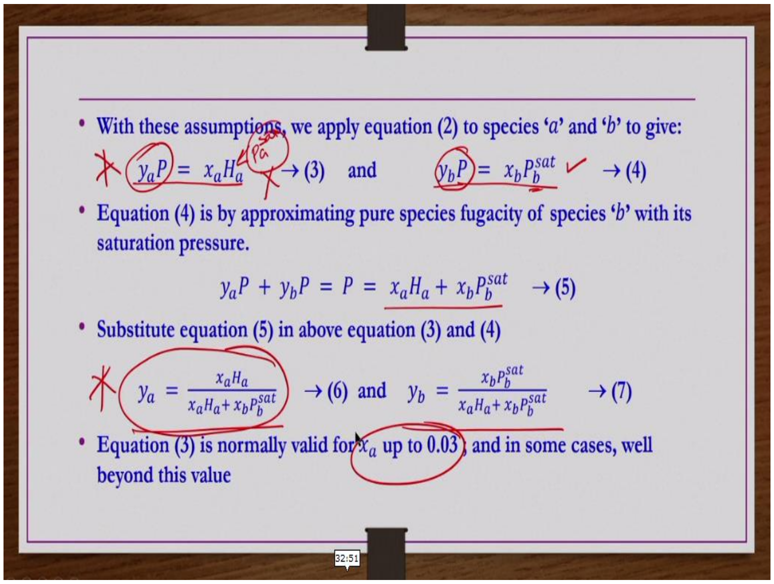

- With these assumptions, we apply equation (2) to species '*a*' and '*b*' to give:

$$y_aP = x_aH_a \rightarrow (3) \quad \text{and} \quad y_bP = x_bP_b^{sat} \rightarrow (4)$$

- Equation (4) is by approximating pure species fugacity of species '*b*' with its saturation pressure.

$$y_aP + y_bP = P = x_aH_a + x_bP_b^{sat} \rightarrow (5)$$

- Substitute equation (5) in above equation (3) and (4)

$$y_a = \frac{x_aH_a}{x_aH_a + x_bP_b^{sat}} \rightarrow (6) \quad \text{and} \quad y_b = \frac{x_bP_b^{sat}}{x_aH_a + x_bP_b^{sat}} \rightarrow (7)$$

- Equation (3) is normally valid for x_a up to 0.03; and in some cases, well beyond this value

So, then what we have for component a y_a P = x_a γ_a and then f_i^0 is H_a here and then γ_a we are taking liquid phase is ideal. So, γ_a^H will also be 1 and then for component b here y_b P for the vapour phase is but for the liquid phase x_b γ_b and then $f_i^0 \gamma_b$ is also 1 because we are taking ideal liquid phase and then f_i^0 with respect to b what we are seeing almost pure b is there so, f_i^0 should be $f_{pure\ i}$ so, that is $f_{pure\ b}$ and then that is nothing but P_b^{sat}.

And that is nothing but P_b^{sat} at low to moderate pressures when it is low to moderate pressures then only you can say it shows ideal behavior for the vapour phase or gas phase. So, this is the difference now, here in the previous case, when we take you know for both the components if you take the Lewis Randall rule as a reference state then here we previously we got P_a^{sat}, but now, it is not true here in this case, here in this case of sparingly soluble a it is not true.

Whereas, for the component b, it is same as in the previous case of vapour liquid equilibrium whatever we have done so, now, if you add them together y_a P + y_b P is nothing but P that is nothing but x_a H_a + $x_bP_b^{sat}$. So, now this if you substitute in equation 3 and 4 then you can find it out $y_a = \frac{x_aH_a}{x_aH_a+x_bP_b^{sat}}$ and then $y_b = \frac{x_bP_b^{sat}}{x_aH_a+x_bP_b^{sat}}$. So, in general this whatever this equation number 6 is there are this equation number 3.

Whatever these 2 are there they are valid only when x$_a$ is up to 0.03 only. Sometimes it is well beyond this limit also if it is more than 0.05 in general you cannot take as a kind of Henry's law as a reference it is true only when x$_a$ → 0, very small.

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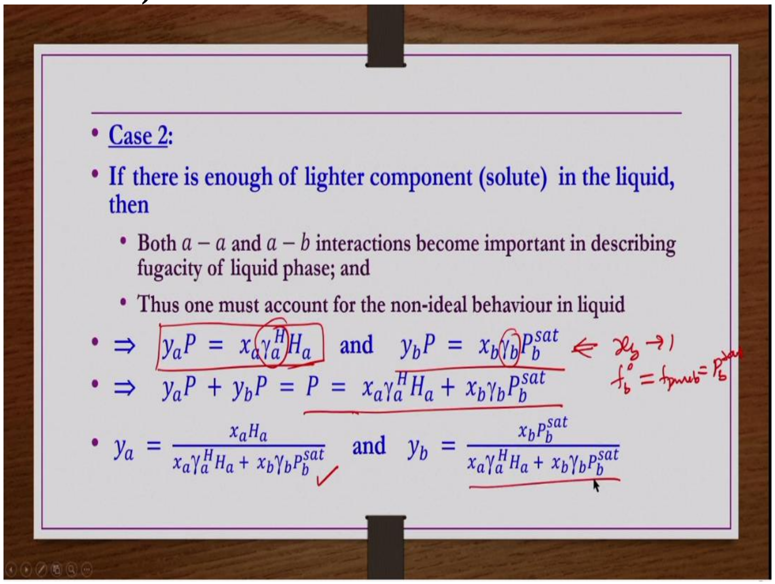

- Case 2:
- If there is enough of lighter component (solute) in the liquid, then
  - Both $a - a$ and $a - b$ interactions become important in describing fugacity of liquid phase; and
  - Thus one must account for the non-ideal behaviour in liquid
- $\Rightarrow \boxed{y_a P = x_a \gamma_a^H H_a}$ and $y_b P = x_b \gamma_b P_b^{sat}$ $\Leftarrow x_b \to 1$
- $\Rightarrow y_a P + y_b P = P = x_a \gamma_a^H H_a + x_b \gamma_b P_b^{sat}$

$f_b^0 = f_{pure\,b} = P_b^{sat}$

- $y_a = \dfrac{x_a H_a}{x_a \gamma_a^H H_a + x_b \gamma_b P_b^{sat}}$ ✓ and $y_b = \dfrac{x_b P_b^{sat}}{x_a \gamma_a^H H_a + x_b \gamma_b P_b^{sat}}$

So, now, we take the case 2 if there is enough of a lighter component in the liquid solute there is a non ideality in the liquid phase but the vapour phase is still ideal, then, both a-a and a-b interactions become important in describing fugacity of liquid phase and thus one must account for non ideal behavior in the liquid phase then we have for component a y$_a$ P vapor phase is still ideal and then liquid phase x$_a$ γ_a^HH$_a$ we have and then this component b y$_b$ P and then x$_b$ this γ$_b$ and then P_b^{sat} because x$_b$ → 1.

So, then f_b^0 is nothing but f$_{\text{pure b}}$ is nothing but P_b^{sat} whereas, such one such reference state we cannot use because here in the case of x$_a$ → 0. So, then f_a^0 is nothing but H$_a$ and then corresponding activity coefficient is nothing but γ_a^H. This is the difference whatever the difference compare to the previous 2 lectures that equation that we have used that is coming in this component a because component a is only sparingly soluble in component b.

So, when you add them together what we have y$_a$ P + y$_b$ P = P = x$_a$ γ_a^H H$_a$ + x$_b$ γ$_b$ P_b^{sat}then y$_a$ you will get x$_a$ H$_a$ by this 1 and then y$_b$ is nothing but x$_b$ $P_b^{sat}$by this 1, P whatever the total P.

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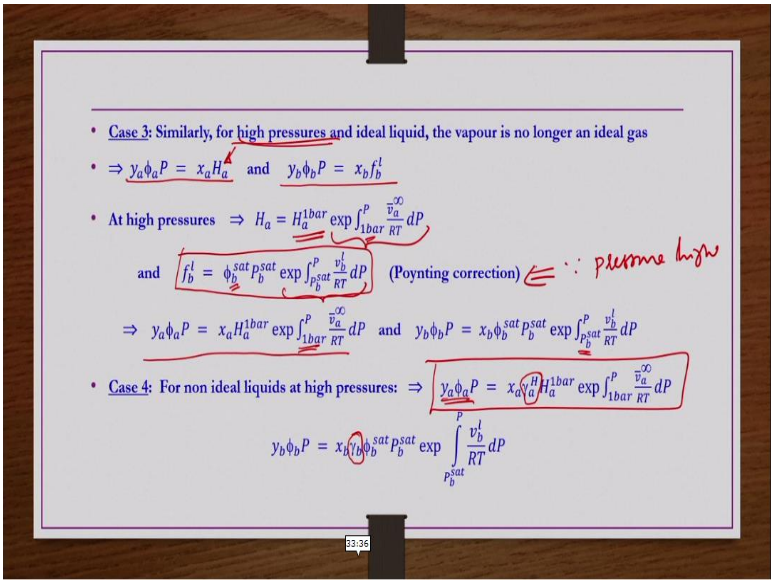

- **Case 3**: Similarly, for high pressures and ideal liquid, the vapour is no longer an ideal gas
- $\Rightarrow \underline{y_a \phi_a P = x_a H_a}$ and $\underline{y_b \phi_b P = x_b f_b^l}$
- At high pressures $\Rightarrow H_a = H_a^{1bar} \exp \int_{1bar}^{P} \frac{\bar{v}_a^{\infty}}{RT} dP$

  and $\boxed{f_b^l = \phi_b^{sat} P_b^{sat} \exp \int_{P_b^{sat}}^{P} \frac{v_b^l}{RT} dP}$ (Poynting correction) $\Leftarrow$ ∵ pressure high

  $\Rightarrow \underline{y_a \phi_a P = x_a H_a^{1bar} \exp \int_{1bar}^{P} \frac{\bar{v}_a^{\infty}}{RT} dP}$ and $y_b \phi_b P = x_b \phi_b^{sat} P_b^{sat} \exp \int_{P_b^{sat}}^{P} \frac{v_b^l}{RT} dP$
- **Case 4**: For non ideal liquids at high pressures: $\Rightarrow \boxed{y_a \phi_a P = x_a \gamma_a^H H_a^{1bar} \exp \int_{1bar}^{P} \frac{\bar{v}_a^{\infty}}{RT} dP}$

$$y_b \phi_b P = x_b \gamma_b \phi_b^{sat} P_b^{sat} \exp \int_{P_b^{sat}}^{P} \frac{v_b^l}{RT} dP$$

33:36

Now, similarly, if you take high pressures but liquid is ideal high pressure that means vapour is non ideal but liquid we are taking as a kind of ideal behavior then for component by y_a ϕ_a P = x_a H_a and then component b y_b ϕ_b P = x_b f_b^l. Now, here what happens at high pressures this whatever the H_a you know in general available at 1 bar pressure but the pressure is higher one then we have to make a kind of correction to this Henry's constant that correction is nothing but exp $\int_1^P \frac{\bar{v}_a^\infty}{RT}$ dP.

Now here i is nothing but pure and then integration from 1 bar to the pressure at which you want it to update this and Henry's constant are correct this Henry's law constant. So, that is what you should have and then f_b^l is nothing but ϕ_b^{sat} P_b^{sat}exp$\int_{P_b^{sat}}^{P} \frac{v_b^l}{RT}$. This is also we have seen for pure component because b component is almost pure competent now here, and then pressure is high. So, here if the pressure is high. That is the reason we are writing this 1.

Pressure is high, that is the reason we have to write this one. If the pressure is low to moderate, then we can write this f_b^l or simply nothing but P_b^{sat} we can write, if the pressure is low to moderate, but the pressure is not low to moderate, because when the pressure is low to moderate, then what happens is $P_b^{sat}$is close to one. And then this exponential term pointing direction, what we have seen it is close to 1, if the pressure or delta P is less than 10 bar that is what we have seen for typical cases.

There under such conditions $f_b^l$is obviously, becomes P_b^{sat}, but in this case the pressure is high. So, we cannot say this exponential term pointing correction is close to one it is having certain value and then we cannot say that P_b^{sat} = 1, it will also have some kind of value. So, that is the reason this is what we are having. So, that means y_a ϕ_a P = x_a H_a at 1 bar exponential of $\bar{v}_a^{\infty}$ by RT dP integration from 1 bar to P and then y_b phi_b P = x_b $phi_b^{sat} P_b^{sat}$ exp $\int_1^P \frac{\bar{v}_a^{\infty}}{RT}$ dP.

So, these are the equations. Now, in the last case, non ideal liquid and then pressure is also very high. Then both phases liquid is not even ideal we are saying if the pressure is also very high then vapor is also non ideal, then under such conditions, we have the same expression whatever we are having you know, this one that will be in the right hand side multiplied with this activity coefficient, only difference from case 4 to case 3 is the non-ideality.

In the liquid phase also that non ideality in the liquid phase 4 component a is brought through the γ_a^H. So, that is added here and then for component b non ideality is added through this γ_b here that is it. These are the corresponding equations, if you wanted to find out solubility of gases and liquids, and then depending on the pressure, low pressure, high pressure or the ideal vapour or ideal liquid or 1 of them is ideal.

Another one is non ideal or both of them are non ideal then accordingly out of these 4 cases which case is matching when asked to find out and then apply to find out the problems or to solve the problems associated with the solubility of gases and liquids. So, with this we completed almost all required information about a vapour liquid equilibrium.

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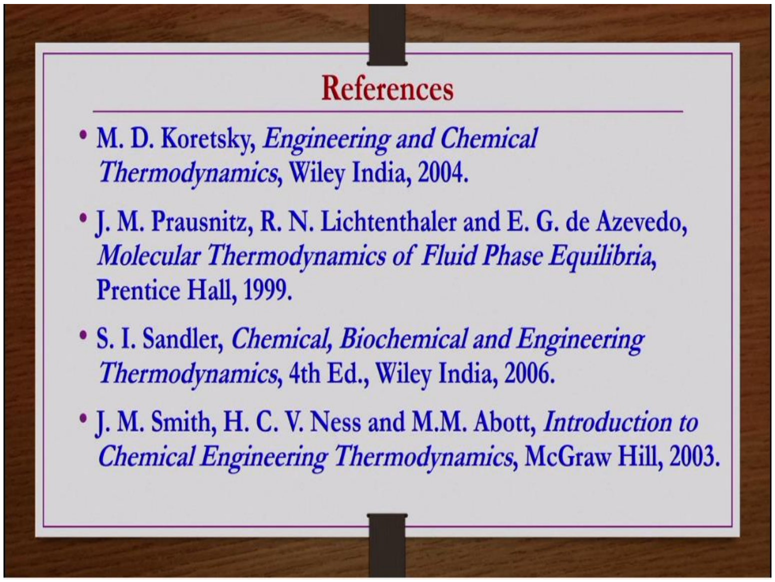

References

- M. D. Koretsky, *Engineering and Chemical Thermodynamics*, Wiley India, 2004.
- J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice Hall, 1999.
- S. I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, 4th Ed., Wiley India, 2006.
- J. M. Smith, H. C. V. Ness and M.M. Abott, *Introduction to Chemical Engineering Thermodynamics*, McGraw Hill, 2003.

The references for this lecture are provided here, but the entire lecture is prepared from this reference book by Koretsky. Thank you.