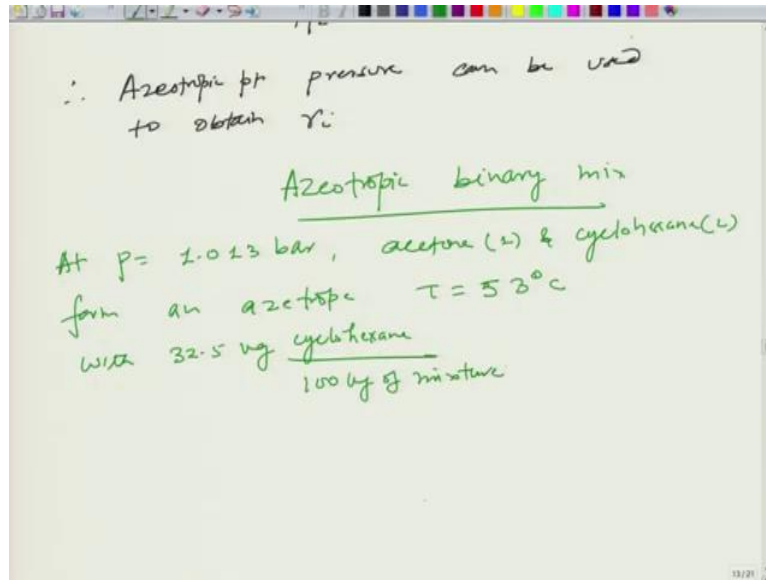


Chemical Engineering Thermodynamics
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Lecture 53

Azeotrope (binary mixture)

Welcome back. So, I was discussing about Azeotrope and Azeotropic mixtures where we talked about the minimum and maximum boiling point scenario particularly for the cases where you have azeotrope that means a significant deviation from Raoult's law.

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So, I will start with an example now to list some of the things which often is relevant for the azeotropic mixture. We will consider the binary mixture. So, so let us consider that you have a case where the pressure is given to you. And this is the case where you have acetone let us say this is 1 and cyclohexane which we represent as 2. It forms an azeotrope at a specific temperature. Which is 53 degrees Celsius with a certain concentration that means you have 32, let us say this the information given to us where 32.5 kilo kg of cyclohexane per 100 kg of mixtures.

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form an azeotrope $T = 53^\circ\text{C}$
with $32.5 \text{ kg cyclohexane}$
 $100 \text{ kg of mixture}$

Obtain Txy diagram
Van Laar activity model with T, C_1, C_2

$$\ln \gamma_1 = \frac{C_1}{RT} \left(1 + \frac{C_1 x_1}{C_2 x_2} \right)^{-2}$$
$$\ln \gamma_2 = \frac{C_2}{RT} \left(1 + \frac{C_2 x_2}{C_1 x_1} \right)^{-2}$$

Azeotropic binary mix

At $p = 1.013 \text{ bar}$, acetone (1) & cyclohexane (2)
form an azeotrope $T = 53^\circ\text{C}$
with $32.5 \text{ kg cyclohexane}$
 $100 \text{ kg of mixture}$

Obtain Txy diagram
Van Laar activity model with T, C_1, C_2

$$\ln \gamma_1 = \frac{C_1}{RT} \left(1 + \frac{C_1 x_1}{C_2 x_2} \right)^{-2}$$
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$$\ln \gamma_2 = \frac{C_2}{RT} \left(1 + \frac{C_2 x_2}{C_1 x_1} \right)^{-2}$$

So, this is the primary the question, primary information the question is that we need to obtain Txy diagram for the system. So, we assume that Van Laar activity model. With t independent. Okay, with independent t and basically the constant let us say at C_1 and C_2 . So, we know the Van laar activity equation is given as if you look at the textbook or earlier developed relations it is given the relation between activity is given in this form. So, you have relations between the gammas and basically with the composition.

So essentially, we need to find out C_1 for sure and C_2 . So, the constant need to be evaluated. So, once we have that of course we can make use of typical process for VLE. So, let us first look at the composition because what we are given is this 32.5 kilo joules sorry kg of cyclohexane per 1000 kg of mixture, so we can obtain the composition at which the azeotrope is same.

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$$\ln y_2 = \frac{c_2}{RT} \left(1 + \frac{c_2 x_2}{c_1 x_1} \right)$$

$$MW_2 = 58.0791 \text{ g/mol}$$

$$MW_1 = 84.1595 \text{ g/mol}$$

$$x_2 = \frac{32.5 / MW_2}{\frac{32.5}{MW_2} + \frac{(100 - 32.5)}{MW_1}} = 0.249$$

$$x_1 = 1 - x_2 = 0.751$$

\therefore Azeotropic pt pressure can be used to obtain γ_i

Azeotropic binary mix

At $p = 1.013 \text{ bar}$, acetone (1) & cyclohexane (2)
form an azeotrope $T = 53^\circ \text{C}$
with $\frac{32.5 \text{ kg cyclohexane}}{100 \text{ kg of mixture}}$

Obtain Txy diagram
van Laar activity model with T, c_1, c_2

$$\ln \gamma_1 = \frac{c_1}{RT} \left(1 + \frac{c_1 x_1}{c_2 x_2} \right)^{-2}$$

So, let us look at it, so the molecular weight of component 1 is 58.071 gram per mole. Molecular weight of component 2 is 84.1595 gram per mole. So, these are the 2 molecular weights which we know for the case of acetone is 1, this is the 1 and for cyclohexane that is the molecular weight. Now given this we can find X_2 that is the composition in the liquid phase of for cyclohexane for which we obtain the azeotrope at t is equal to 53 degree Celsius and the pressure of 1.013 bar that is the atmosphere. So this is going to be 32.5 molecular weight of 2 divided by 32.5 by MW_2 and we can take because 100 kg is the mixture so the remaining amount would be of acetone.

Now, if you plug-in this information of molecular weights, we obtain 0.249 that is the composition of cyclohexane in the mixture, where the azeotrope occurs. Similarly, from here since X_2 is this, X_1 is 1 minus X_2 that is 0.751. Ok, so now you have the composition that is fantastic, but we also need to find out the pressures particularly the saturation pressures of this component because that will be needed for us to obtain the finally the phase diagram.

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$$x_1 = 1 - x_2 = 0.751$$

Antoine ϵ_1 $\log_{10} P_i^S$

$$T = 53^\circ\text{C} = 326.15\text{K} \Rightarrow P_1^S = 0.905 \text{ bar}$$

$$P_2^S = 0.406 \text{ bar}$$

At azeotropic point-

$$\left. \begin{aligned} x_1 &= y_1 \\ x_2 &= y_2 \end{aligned} \right\} \text{A system for which no change is possible by boiling}$$

VLE

$$\begin{aligned} \gamma_1 x_1 P_1^S &= y_1 P \\ \gamma_2 x_2 P_2^S &= y_2 P \end{aligned}$$

$$\Rightarrow \gamma_1 = P/P_1^S \quad \text{or} \quad \left| \frac{\gamma_1}{\gamma_2} = \frac{P_2^S}{P_1^S} \right|$$

\therefore Azeotropic pt pressure can be used to obtain γ_i

$x_2 = y_2$ } change is possible by boiling

VLE

$$\begin{aligned} \gamma_1 x_1 P_1^S &= y_1 P \\ \gamma_2 x_2 P_2^S &= y_2 P \end{aligned}$$

$$\Rightarrow \left| \begin{aligned} \gamma_1 &= P/P_1^S \\ \gamma_2 &= P/P_2^S \end{aligned} \right| \quad \text{or} \quad \left| \frac{\gamma_1}{\gamma_2} = \frac{P_2^S}{P_1^S} \right|$$

\therefore Azeotropic pt pressure can be used to obtain γ_i

Azeotropic binary mix

At $P = 1.013 \text{ bar}$, acetone (1) & cyclohexane (2)
 $T = 53^\circ\text{C}$

$$\text{VLE: } \gamma_1 x_1 P_1^S = y_1 P$$

$$\gamma_2 x_2 P_2^S = y_2 P$$

$$\gamma_1 = \frac{P}{P_1^S} \quad \gamma_2 = \frac{P}{P_2^S} \quad \text{or,} \quad \frac{\gamma_1}{\gamma_2} = \frac{P_2^S}{P_1^S}$$

So, we can make use of Antoine equation to get $\log_{10} P_i^s$. Okay, so for the case of because the temperature is known so which is 326.15 K so using Antoine equation, I can get P_1^s which turns out to be 0.905 bar and P_2^s turns out to be 0.406 bar. Okay, so now we have this information that P is, now, if you go back to the what we wanted you know one which derives in the last (term) lecture.

So, you remember that we looked into the, we calculated the saturation pressure, but the saturation pressures of these components are related to the activities coefficients of component in particularly in azeotropic condition. So, in azeotropic state the ratio of the gammas are related to the ratio of the saturation pressures of the pure component or inverse of that. But you can also obtain the, this activity coefficient by just dividing the pressure, system pressure by the same saturation pressures of the same component.

So, essentially, we know the P system, so with this information is good enough for us in order to find out the γ_1 . So, we know P , we know P_1^s and similarly we know P_2^s , so we can obtain γ_1 and γ_2 and that is what we are going to do because we have evaluated P_1^s and P_2^s .

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$x_2 = 1 - x_1 = 0.751$
 Antoine $\log_{10} P_i^S$
 $T = 53^\circ\text{C} = 326.15\text{K} \Rightarrow P_1^S = 0.905 \text{ bar}$
 $P_2^S = 0.406 \text{ bar}$
 for azeotropic condition
 $\gamma_1 = P/P_1^S = 1.013$
 $\gamma_2 = P/P_2^S = 1.013$

Therefore for or rather for the azeotropic condition. Okay, we are saying that gamma 1 is nothing but P by P1s that is going to be 1.013 divided by, okay so with this you can plug in this information here. Similarly, gamma 2 is P by P2s that is going to be 1.013 and again this information can be plugged here. So, with this we have handled our information of gammas.

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with 32.5 wt% cyclohexane in 100 kg of mixture
 Obtain T_{xy} diagram with Van Laar activity model with T, c_1, c_2
 $\ln \gamma_1 = \frac{c_1}{RT} \left(1 + \frac{c_1 x_1}{c_2 x_2} \right)^{-2} \quad \text{--- (1)}$
 $\ln \gamma_2 = \frac{c_2}{RT} \left(1 + \frac{c_2 x_2}{c_1 x_1} \right)^{-2} \quad \text{--- (2)}$
 $MW_{c_1} = 50.0791 \text{ g/mol}$

Now this gamma is given here, so these are two equations. Now you have one equation where the right-hand side is you know, sorry left inside you are aware of it, as well as another equation you know this this expression is equal to the log of gamma 2 which you now know. So, you have two equations, you have the compositions X2. So, with these two equations. 1 and 2 you can solve two variables which is C1 and C2 ok.

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Solve ① & ② $\Rightarrow C_1$ & C_2

$\gamma = f(T, x)$

VLE $\gamma_i x_i f_{i,pure} = \phi_i y_i P$

$\therefore \gamma_i x_i P_i^s = y_i P$

$\gamma_2 x_2 P_2^s = y_2 P$

$\Rightarrow \begin{cases} \gamma_1 = P/P_1^s \\ \gamma_2 = P/P_2^s \end{cases}$ or $\begin{cases} \frac{\gamma_1}{\gamma_2} = \frac{P_2^s}{P_1^s} \end{cases}$

\therefore Azeotropic pt pressure can be used to obtain γ_i

Azeotropic binary mix

At $P = 2.013$ bar, acetone (L) & cyclohexane (L) form an azeotrope $T = 53^\circ\text{C}$ with 32.5 wt% cyclohexane in 100 kg of mixture

$$\gamma = f(T, x)$$

$$\text{VLE: } \gamma_i x_i f_{i,pure} = \phi_i y_i P$$

$$\gamma_i x_i P_i^s = y_i P$$

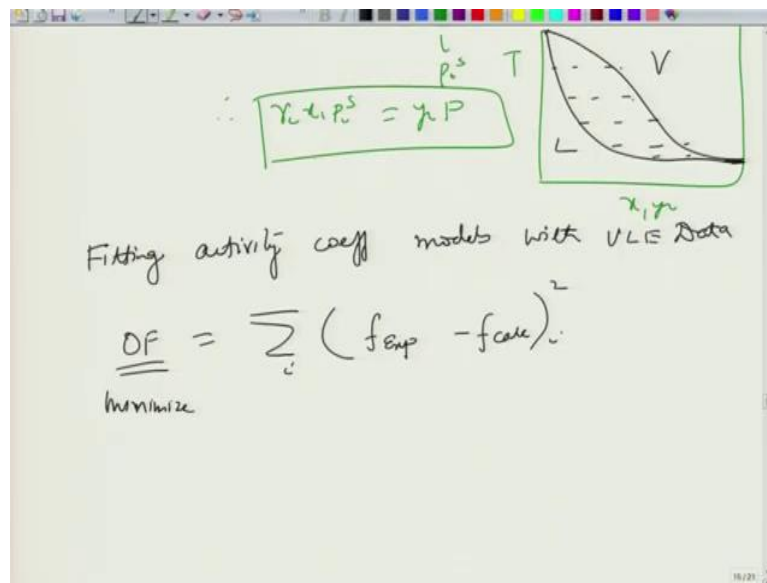
So, solve 1 and 2. Because now you have two equations. Solve equations 1 and 2 and you will get C_1 and C_2 . So, you will obtain C_1 and C_2 . I am not going to write down the numbers here, but once you know now C_1 and C_2 that that means you are completely you have now the information of gamma as a function of only its temperature and the composition so that is good enough for us and thus we can now make use of the VLE equations which we try to solve usually that is going to be $x_1 \gamma_1 f_{i,pure} = \phi_i y_i P$ so we can consider this to be 1, we can consider this to be simply P_i^s , so we have now $\gamma_i x_i P_i^s = y_i P$ and this you can now try to solve it for the two binary conditions which are considered.

So, if you do that, we get this expression or rather we will get this phase diagram where you have something like this, this is volume, this is vapour and this is your liquid. So, that is a way to solve a problem related to Azeotropic mixture of course there could be certain variant in the

problem, but essentially the emphasis of this particular case was to make use of the expression we have used, or we have developed here. Alright. This was the point we used here in this particular case.

Now in general you may not get a very specific case such as this azeotropic conditions may get some kind of experimental data and there we can also use those experimental data to fit the variables and so let me just try to summarise, a typical way of fitting the model data to the experimental value. So, you can come up with objective functions such that certain functions, certain objective functions basically match with that of the experiment that means the difference of that turns out to be almost negligible.

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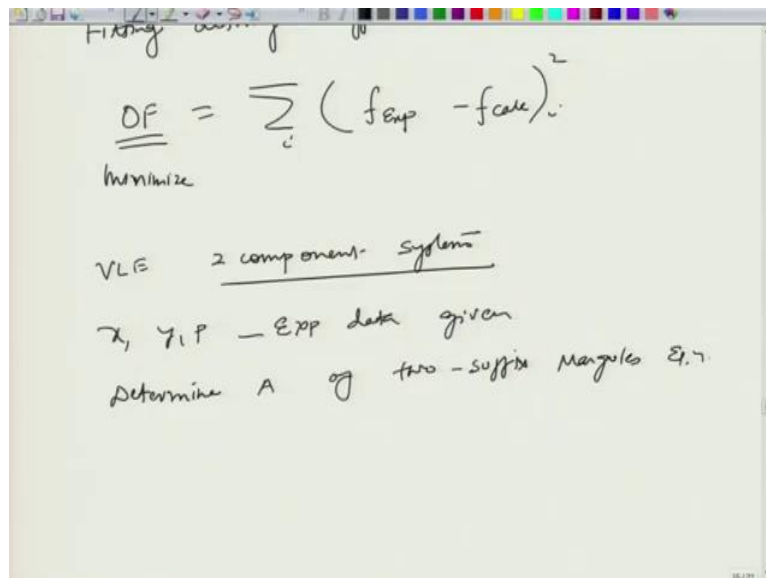


Fitting activity coefficient models using VLE data:

$$OF = \sum_i (f_{ex} - f_{calc})_i^2$$

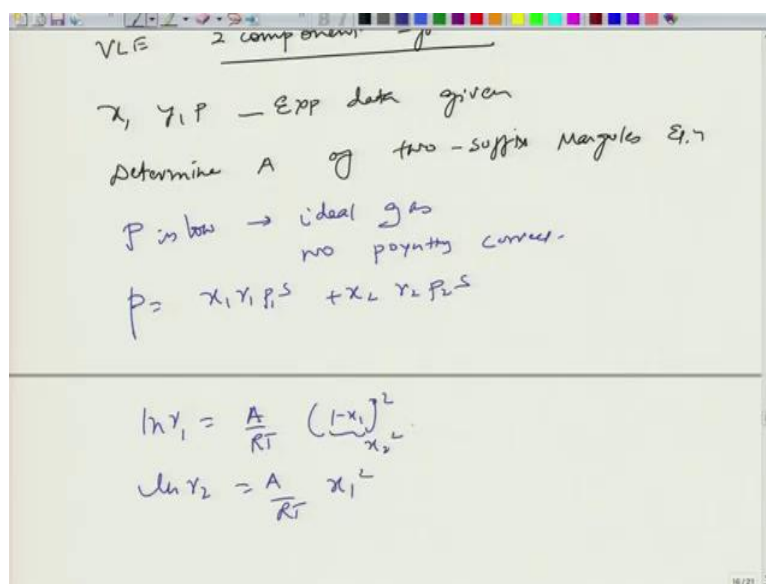
So how do we do that? So, that is the normal numerical method, but we apply for the case of activity coefficients. So we define the function usually let us say its objective function and we say well for because there could be many data point, could be a function of X, could be a function of t, so usually we say well this is f of experiment minus f of calculated and this is over all the points which we are interested and sum of that. So, that is the, that is the objective function we would like to minimise. Right?

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So, we can consider the simple example. So for example, the VLE information is given for 2 component system. Okay, where X, Y, P is given, experimental data is given. Ok, so if we have a 2-component system that is binary system where X, Y and P experimental data is given and the question may be like let us say determines A of the two-suffix Margules Equation.

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So, one approach is the way I am going to show here could be return here. So, if you are considering let us say pressure is low. We are considering ideal gas-phase. Ok, no pointing correction. Which means I can write pressure as simply $x_1 \gamma_1 P_1^s$ plus $x_2 \gamma_2 P_2^s$. And we know this two-suffix Margules Equation which is written as $\ln \gamma_1 = \frac{A}{RT} (1 - x_1)^2$ and $\ln \gamma_2 = \frac{A}{RT} x_1^2$ so this nothing but saying is x_2 square, right?

$$p = x_1 \gamma_1 P_1^s + x_2 \gamma_2 P_2^s$$

$$\ln \gamma_1 = \frac{A}{RT} (1 - x_1)^2$$

$$\ln \gamma_2 = \frac{A}{RT} x_1^2$$

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$$p = x_1 \gamma_1 P_1^s + x_2 \gamma_2 P_2^s$$

$$\ln \gamma_1 = \frac{A}{RT} \frac{(1-x_1)^2}{x_2}$$

$$\ln \gamma_2 = \frac{A}{RT} x_1^2$$

$$p_{calc} = x_1 \exp \left[\frac{A}{RT} (1-x_1)^2 \right] P_1^s + (1-x_1) \exp \left[\frac{A}{RT} x_2^2 \right] P_2^s$$

$$p_{calc} = x_1 \exp \left[\frac{A}{RT} (1 - x_1^2) \right] P_1^s + (1 - x_1) \exp \left[\frac{A}{RT} x_2^2 \right] P_2^s$$

Ok, so given this you can plug in here, right? So, now I have an expression of pressure this is a calculator that means you are trying to calculate it is nothing but x_1 and γ_1 can be written as exponential $\frac{A}{RT} (1 - x_1^2) P_1^s$ plus $(1 - x_1) \exp \left[\frac{A}{RT} x_2^2 \right] P_2^s$. Okay? So, this would be the one which calculates.

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$$\ln \gamma_1 = \frac{A}{RT} (1-x_1)^2$$


$$\ln \gamma_2 = \frac{A}{RT} x_1^2$$

$$P = x_1 \exp \left[\frac{A}{RT} (1-x_1)^2 \right] P_i^s \quad P-x$$

$$+ (1-x_1) \exp \left[\frac{A}{RT} x_1^2 \right] P_2^s$$

$$OF = \sum (P_{exp} - P_{calc})^2$$

Minimize by A

$$\gamma_2 x_2 P_i^s = \gamma_2 P$$


Fitting activity coeff models with VLE Data

$$OF = \sum (f_{exp} - f_{calc})^2$$

Minimize

VLE 2 component systems

$x_1, \gamma_1 P$ - EXP data given

So essentially now the question is, if you have the data given to you already which is as I said earlier is my P-x let us say is information is given to you and A here is basically is unknown, so A we have to determine. So, essentially you can vary A such that your P calculations are same as that of the experiment for given X, but there are many data points, right?

So, essentially you can come up with an objective function which is nothing but for the pressure and we are saying that well the summation for each particular point, the experimental data point should be same as or should be close enough to the calculated data point for each point and thus we take the square and we try to minimise this. That means this root-mean-square or rather this sum of the squares of this difference should be minimum.

Okay, so if you minimise this. This by varying A. Okay, you would get a appropriate A which would fit all the data very close to the experimental one and would be suitable for this thing. So, usually this kind of exercise is done in order to find the variables if you have usually, if you have all the data points. Because A can be a little bit variable at each point not usually you know because A is just effective parameter and sometimes you have to use all the data points

if it is available to obtain it. But this is the good way of approaching you know to find out the informations from the experimental data.

Ok, so there is one thing which is still left in our discussion as far as the Azeotropic mixtures are concerned that how do you check or how do you verify that the compositions are same. That means X is equal to Y for the azeotropic mixture so, how do you verify that?

So, let us try to do this. So, one the important thing for the azeotropic mixture is that it undergoes the maxima or minima depending on whether it is unlike interactions are very large compared to the like or otherwise you know on the contrary if unlike interactions are weaker. So, how do you now check? So, now these both the conditions of minimum and maximum as far as this deviation from the ideal gas is concerned would lead to the first derivative of the pressure to be 0 or similarly vice versa you can do the same thing for temperature.

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Q. Show that VLE, $x_a = y_a$ hold for azeotrope

$$\frac{\mu_i^\alpha}{T} = \frac{\mu_i^\beta}{T}$$

$$\frac{\partial(\mu_i^\alpha/T)}{\partial T} dT + \frac{\partial(\mu_i^\alpha/T)}{\partial P} dP + \frac{\partial(\mu_i^\alpha/T)}{\partial x_i^\alpha} dx_i^\alpha$$

$$= \frac{\partial(\mu_i^\beta/T)}{\partial T} dT + \frac{\partial(\mu_i^\beta/T)}{\partial P} dP + \frac{\partial(\mu_i^\beta/T)}{\partial x_i^\beta} dx_i^\beta$$

So, can we use this observation to in the experiment to find out whether the X is equal to Y.? So that is the question which would I would like to pose that show that for VLE, show that for VLE, XA is equal to YA this must be that means XA is equal to YA is the condition or composition of component A in X is equal to composition of all fraction in the vapour phase so this is. This must hold for azeotrope. So, if you want to prove this, how to go about it, let us try to quickly work on it.

Ok, so let us look at let us say mu i particularly we can take it here just a generic i. So, it could be Xi and Yi. So, mu i should be same if it is the 2 phases at equilibrium, so we can divide by temperature also. And then we can look at the differential part of this. So, if you would look at this in the differential form, then I can write this thing because mu is a function of temperature, pressure and the composition.

Considering mu is a function of temperature, pressure and the composition. I can differentiate this thing in this way that I can write this mu i by T and let us say putting alpha here. So, which also means mu by T is also function of this. So, I am looking at this together. And taking

differential form and then equating to the right-hand side, so let me just write it down first on the left-hand side.

So, this is going to be μ_i^α by $T P$ at constant T and this is going to be constant P and X here and this is going to be constant T plus μ_i^α by T by DX_i and this is DX_i^α . So, this is the left-hand side, the other side is the right-hand side. So, this is going to be similar way, μ_i^β by T divided by dT plus so this, when I say X here this is like you know considering only binary, but otherwise you have to consider all of the X here. And then you have $D\mu_i^\beta$ by T by DP by T dT plus with that of the composition. So, this is DX_i^β and DX_i^β . So similarly, this would be alpha here.

$$\frac{\mu_i^\alpha}{T} = \frac{\mu_i^\beta}{T} \quad \frac{\mu(T, P, x)}{T}$$

$$\frac{\partial \left(\frac{\mu_i^\alpha}{T} \right)}{\partial T} \Big|_{P,x} dT + \frac{\partial \left(\frac{\mu_i^\alpha}{T} \right)}{\partial P} \Big|_{T,x} dP + \frac{\partial \left(\frac{\mu_i^\alpha}{T} \right)}{\partial x_i^\alpha} dx_i^\alpha$$

$$= \frac{\partial \left(\frac{\mu_i^\beta}{T} \right)}{\partial T} \Big|_{P,x} dT + \frac{\partial \left(\frac{\mu_i^\beta}{T} \right)}{\partial P} \Big|_{T,x} dP + \frac{\partial \left(\frac{\mu_i^\beta}{T} \right)}{\partial x_i^\beta} dx_i^\beta$$

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The image shows a handwritten derivation on a whiteboard. At the top, it shows the partial derivative of $\frac{\mu_i^\alpha}{T}$ with respect to T , P , and x_i^α . A red circle highlights the $\frac{\partial \left(\frac{\mu_i^\alpha}{T} \right)}{\partial T} \Big|_{P,x}$ term, with an arrow pointing to a green circle containing $\frac{1}{T} \left(\frac{\partial \mu_i^\alpha}{\partial T} \right)_{P,x}$. Below this, the same derivative is written for μ_i^β . At the bottom, the derivation connects these terms to partial molar enthalpy and volume:

$$\frac{-H_i^\alpha}{T^2} = \frac{-H_i^\beta}{T^2} = \frac{-V_i^\alpha}{T} \frac{dp}{T} + \frac{1}{T} \left[\frac{\partial \mu_i^\alpha}{\partial x_i^\alpha} \right] dx_i^\alpha$$

Now, if we look at this derivative, derivative of the mu by T, this one, okay? This is related to minus H_i partial molar enthalpy by T square and this the second one is related to 1 by T del μ_i^α by P . Right? DP this is here should be this should be dP . Ok, we have this whole thing is basically is minus V_i^α . Right? Partial molar volume for this case.

So, if I use this derivative information which one can find it out from the in general this partial derivatives which we have done it earlier, now I am going to make use of that and connect this partial derivatives of the chemical potential with respect to the temperature and pressure to the enthalpy, partial molar enthalpy and the volume.

So, if I do that, I have an equation on the left-hand side like, therefore \bar{H}_i^α by T^2 that is this part minus \bar{V}_i^α by T dP this is this plus 1 by T again because T is independent to X here so it can be taken out and this is $d\mu_i^\alpha$ by dx_i^α putting here α here. Similarly, this would be for minus \bar{X}_i^β by T^2 minus \bar{V}_i^β here plus 1 by T . Okay? Alright.

$$-\frac{\bar{H}_i^\alpha}{T^2} - \frac{\bar{V}_i^\alpha}{T} dP + \frac{1}{T} \left[\frac{\partial \mu_i^\alpha}{\partial x_i^\alpha} \right] dx_i^\alpha = -\frac{\bar{H}_i^\beta}{T^2} - \frac{\bar{V}_i^\beta}{T} dP + \frac{1}{T} \left[\frac{\partial \mu_i^\beta}{\partial x_i^\beta} \right] dx_i^\beta$$

Apply for a & b and VLE

$$\left(\frac{\partial \mu_a^l}{\partial x_a} \right)_{T,P} dx_a - \left(\frac{\partial \mu_a^v}{\partial y_a} \right)_{T,P} dy_a = \frac{1}{T} (\bar{H}_a^l - \bar{H}_a^v) dT - (\bar{v}_a^l - \bar{v}_a^v) dP$$

$$\left(\frac{\partial \mu_b^l}{\partial x_b} \right)_{T,P} dx_b - \left(\frac{\partial \mu_b^v}{\partial y_b} \right)_{T,P} dy_b = \frac{1}{T} (\bar{H}_b^l - \bar{H}_b^v) dT - (\bar{v}_b^l - \bar{v}_b^v) dP$$

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dT P, X

$$\frac{-H_i^L}{T^2} = -\frac{H_i^L}{T^2} - \frac{V_i^L}{T} dp + \frac{1}{T} \left[\frac{\partial \mu_i^L}{\partial x_i^L} \right]_{T,P} dx_i^L$$

$$= -\frac{H_i^V}{T^2} - \frac{V_i^V}{T} dp + \frac{1}{T} \left[\frac{\partial \mu_i^V}{\partial x_i^V} \right]_{T,P} dx_i^V$$

Apply for a & b (VLE)

$$\left(\frac{\partial \mu_a^L}{\partial x_a} \right)_{T,P} dx_a - \left(\frac{\partial \mu_a^V}{\partial x_a} \right)_{T,P} dx_a$$

$$= \frac{1}{T} \left(-L_{H_a} - H_a^V \right) dT - \left(V_a^L - V_a^V \right) dP$$

So, if you apply. So, now the thing is this is a general equation ok now since we are talking about VLE. So, if we apply for component a and b and for vapour liquid equilibria. I can write this expression now in terms of the following. And let me do here you know rewrite this part so a kind of little bit distribute this so I can bring this together and I can take this thing to the right-hand side.

If I do that, I can get the following expression. $\Delta \mu_{\text{liquid a}} / \Delta x_a$ at T, P minus $\Delta \mu_{\text{vapor a}} / \Delta x_a$ at T, P dx_a . So, this apparently would be at a constant T and P here is T, P minus $\Delta \mu_{\text{a V}} / \Delta x_a$ at T, P dx_a . So instead of saying x_i^L since we are talking about only liquid and vapour which means we are talking about X and Y . Okay?

Because usually we use X in a liquid phase. So here, I am just replacing this Y to, replacing this X to Y particularly considering this to be vapour phase. So, these are the two component, two terms which comes directly from here, these two terms I am going to take it to the right-hand side and now I will take the T common, okay?

And one of the thing I can do is I can get rid of this T , so if I can get rid of this T here considering this case so the only thing remains is 1 of the T here, that means I have this 1 by T $H_a^{\text{liquid}} - H_a^{\text{vapor}}$ dT minus of $V_a^{\text{liquid}} - V_a^{\text{vapor}}$ dP . So, this is the final expression I have got from this simple exercise. And the use of this, so this was only for component A. I can extend this thing to component B be also.

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Apply for a & b & (V, L)

$$\left(\frac{\partial \mu_a^l}{\partial x_a}\right)_{T,P} dx_a - \left(\frac{\partial \mu_a^v}{\partial x_a}\right)_{T,P} dy_a$$

$$= \frac{1}{T} \left(\bar{H}_a^l - \bar{H}_a^v \right) dT - \left(\bar{V}_a^l - \bar{V}_a^v \right) dp$$

$$\left(\frac{\partial \mu_b^l}{\partial x_a}\right)_{T,P} dx_a - \left(\frac{\partial \mu_b^v}{\partial y_a}\right)_{T,P} dy_a = \frac{1}{T} \left(\bar{H}_b^l - \bar{H}_b^v \right) dT - \left(\bar{V}_b^l - \bar{V}_b^v \right) dp$$

So, I can do the same exercise just for component b that means μ_b . But I am keeping the same composition because these are related x_a and b . Ok, so you have now two equations. Now, how do you get rid of these terms now if you think about when you look at this kind of conditions you always make sure that you make use Gibbs–Duhem relation and that is something which now we are going to make resort to in order to simplify this.

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$$\left(\frac{\partial \mu_a^l}{\partial x_a}\right)_{T,P} dx_a - \left(\frac{\partial \mu_a^v}{\partial x_a}\right)_{T,P} dy_a = \frac{1}{T} \left(\bar{H}_a^l - \bar{H}_a^v \right) dT - \left(\bar{V}_a^l - \bar{V}_a^v \right) dp \quad \text{--- (3)}$$

$$\left(\frac{\partial \mu_b^l}{\partial x_a}\right)_{T,P} dx_a - \left(\frac{\partial \mu_b^v}{\partial y_a}\right)_{T,P} dy_a = \frac{1}{T} \left(\bar{H}_b^l - \bar{H}_b^v \right) dT - \left(\bar{V}_b^l - \bar{V}_b^v \right) dp \quad \text{--- (4)}$$

G-D rel.

$$x_a \frac{\partial \mu_a^l}{\partial x_a} + (1-x_a) \frac{\partial \mu_b^l}{\partial x_a} = 0$$

$$y_a \frac{\partial \mu_a^v}{\partial y_a} + (1-y_a) \frac{\partial \mu_b^v}{\partial y_a} = 0$$

Multiply (3) by y_a & (4) by $(1-x_a)$
& add them & use G-D rel.

$$G - D \text{ relation: } \frac{x_a \partial \mu_a^l}{\partial x_a} + \frac{(1-x_a) \partial \mu_b^l}{\partial x_a} = 0$$

$$\frac{y_a \partial \mu_a^v}{\partial y_a} + \frac{(1-y_a) \partial \mu_b^v}{\partial y_a} = 0$$

Multiply (3) by y_a & (4) by $(1-y_a)$
& add them & use G-D rel.

$$\frac{(y_a - x_a)}{(1-x_a)} \frac{\partial \mu_a^l}{\partial x_a} dx_a = \left[\frac{y_a}{T} (\bar{H}_a^l - \bar{H}_a^v) + \frac{(1-y_a)}{T} (\bar{H}_b^l - \bar{H}_b^v) \right] dT - \left[y_a (\bar{v}_a^l - \bar{v}_a^v) + (1-y_a) (\bar{v}_b^l - \bar{v}_b^v) \right] dP$$

Azeotropic
 $\left. \frac{\partial T}{\partial x_a} \Big|_P = 0 \text{ or } \frac{\partial P}{\partial x_a} \Big|_T = 0 \right] \rightarrow \text{R.H.S.} = 0$

$$\frac{y_a - x_a}{1 - x_a} \left(\frac{\partial \mu_a^l}{\partial x_a} \right) dx_a = \left[\frac{y_a}{T} (\bar{H}_a^l - \bar{H}_a^v) + \frac{1 - y_a}{T} (\bar{H}_b^l - \bar{H}_b^v) \right] dT - \left[y_a (\bar{v}_a^l - \bar{v}_a^v) + (1 - y_a) (\bar{v}_b^l - \bar{v}_b^v) \right] dP$$

Azeotropic: $\frac{\partial T}{\partial x_a} \Big|_P = 0$ or, $\frac{\partial P}{\partial x_a} \Big|_T = 0$ or, $\text{RHS} = 0$

Apply for a & b & (v & l)

$$\left(\frac{\partial \mu_a^l}{\partial x_a} \right)_{T,P} dx_a - \left(\frac{\partial \mu_a^v}{\partial x_a} \right)_{T,P} dy_a = \frac{1}{T} (\bar{H}_a^l - \bar{H}_a^v) dT - (\bar{v}_a^l - \bar{v}_a^v) dP \quad \text{--- (3)}$$

$$\left(\frac{\partial \mu_b^l}{\partial x_a} \right)_{T,P} dx_a - \left(\frac{\partial \mu_b^v}{\partial y_a} \right)_{T,P} dy_a = \frac{1}{T} (\bar{H}_b^l - \bar{H}_b^v) dT - (\bar{v}_b^l - \bar{v}_b^v) dP \quad \text{--- (4)}$$

G-D rel:

$$x_a \frac{\partial \mu_a^l}{\partial x_a} + (1-x_a) \frac{\partial \mu_b^l}{\partial x_a} = 0$$

$$y_a \frac{\partial \mu_a^v}{\partial y_a} + (1-y_a) \frac{\partial \mu_b^v}{\partial y_a} = 0$$

So, if you look at the Gibbs–Duhem relation because this will put a constraint on this chemical potential. So, we will have $x_a \text{ del } \mu_a^l \text{ del } x_a + (1 - x_a) \text{ del } \mu_b^l \text{ del } x_a = 0$. Similarly, I can do that for Y. So now this, this is something which is good because we have now this relation the Gibbs–Duhem relation. So, if we multiply, so, let us say if you have this is a relation this is an equation let us say 3 and this is your 4. Ok, so if you multiply 3 by y_a and 4 by $(1 - y_a)$. And add them and use this Gibbs–Duhem relation.

So, this is something which you have to do. You know this is more numerical aspect. So, the idea is that, now you have to these relations which you have written. 3 and 4 and then you have

to make use of Gibbs–Duhem relation, so you have to play with little bit of this arithmetic's here to simplify this expression.

So, when you do this. When you multiply 3 by Y_A and 4 by $1 - Y_A$ and add them and use Gibbs–Duhem relation the following you get. So, I am trying to just simplify the expression without going into details how I did that. So I am going to just write down the final expression.

So, this is for this is combined with this term T and now for the case of the terms related to P . So, right. So, this is the final expression which comes with this exercise. Now the thing is what we know from this, I mean we cannot calculate it but the only thing which we know about as far as the azeotropic conditions are concerned that you have this maxima in your P vs X or minima in your T vs Y or in general you have this extremum in those condition and hence for azeotrope we have this $\frac{\partial T}{\partial X_A}$ at constant pressure is equal to 0. Or $\frac{\partial P}{\partial X_A}$ at constant T is equal to 0. That means this is at maximum or minimum.

So, when you consider the pressure is constant so essentially you have both the conditions, that means you basically this means that the right-hand side has to be 0, this whole part, this has to be 0 because of the conditions of the azeotropic which will give us a strict condition that this implies.

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$$\frac{\partial G}{\partial x_a} = (-x_a) \frac{\partial \mu_a}{\partial x_a} + \frac{(1-y_a)(\bar{H}_b - \bar{H}_a)}{T} - \left[y_a (\bar{v}_a^L - \bar{v}_a^V) + (1-y_a)(\bar{v}_b^L - \bar{v}_b^V) \right] \frac{\partial P}{\partial x_a}$$

Azeotropic
 $\left. \frac{\partial G}{\partial x_a} \Big|_P = 0 \text{ or } \frac{\partial P}{\partial x_a} \Big|_T = 0 \right\} \Rightarrow \text{R.H.S} = 0$

This implies $(y_a - x_a) = 0$
 $\Rightarrow y_a = x_a$
 System goes through extremum in T vs P vs X
 \Rightarrow azeotrope

This implies, $(y_a - x_a) = 0$ or, $y_a = x_a$

This implies that your Y_A minus X_A is equal to 0 or Y_A is equal to X_A . So, this tells you that if the system goes through extreme in extremum in T or P versus X this will be the case of azeotrope that means your Y_A will be equal to X_A . Okay, so I thought this would give us a clear idea how we can also thermodynamically prove that and gives you the glimpse of the mathematical expression which one must use in order to solve such a problem. So that will be the end of Azeotrope. We will, we will take up, we have just finished the VLE part, now we will take up the liquid-liquid equilibria and that will be done in the next class. So, I will see you in next class.

