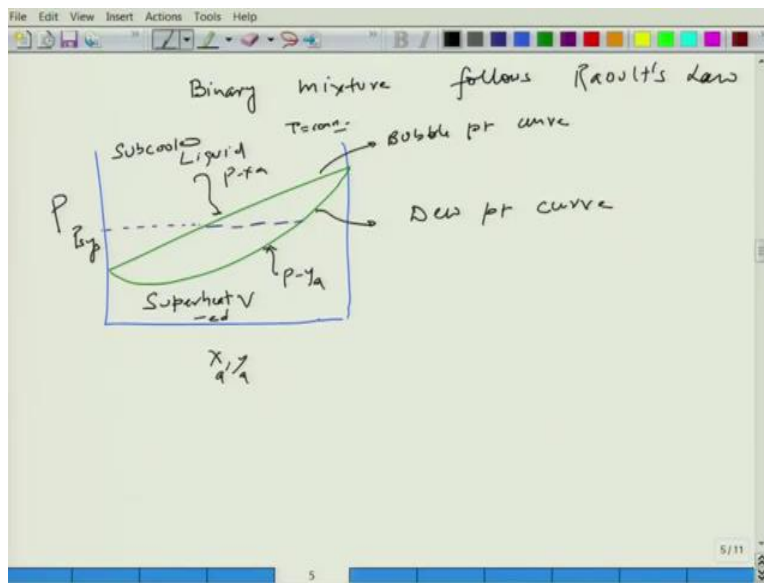


**Chemical Engineering Thermodynamics**  
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**Lecture 50**  
**Vapor Liquid Equilibrium (non-ideal mixtures)**

Welcome back, we have been talking about vapor liquid equilibrium phase diagram calculation and particularly we have focused on the binary mixtures. So, today I will start and again with basic construct of the phase diagram of the binary mixtures and we will discuss about something called lever rule which many of you must be aware of it but for the sake of completion I will do that and subsequently we will talk about non-ideal mixtures and how do we generate the phase diagram for that.

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So, as you already know that if it is as binary mixtures which follows let us say Raoult's law. In such case we can clearly draw pxy diagram, where the liquid line which we call as, this is p and this is xy. So, this would be a straight line ok, this is pxya let us say a px a particularly x and y we are referring to a which is let us say the one which could be above volatile.

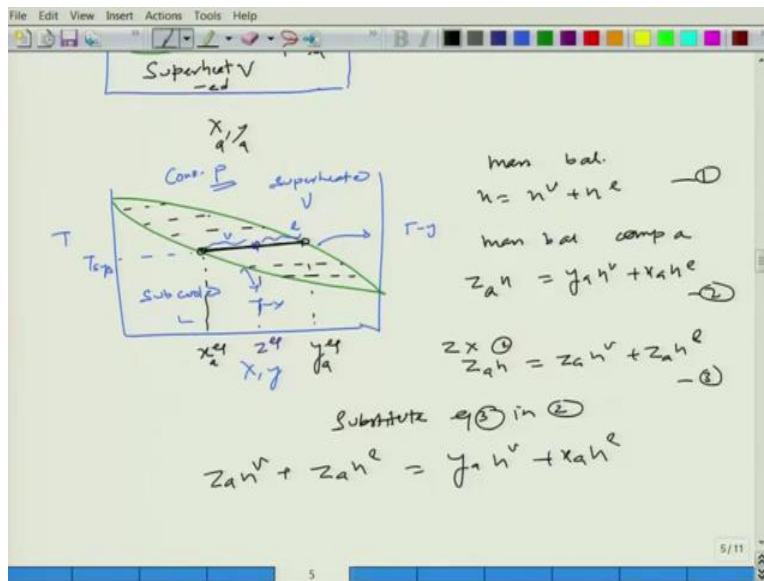
So, this is the something which we have looked at earlier and this sometime this line which is a liquid line also called bubble point curve. Then you have this other line which is a curve which is for the gas phase this is the saturation kind of vapor line and this is pya line, you can clearly see

that this is a bubble point curve that is the first bubble of vapor one can obtain from here for given pressure right.

So if the pressure is fixed  $p$  system is let say fixed then we can have an equilibrium between the liquid phase here and a vapor phase here and this would be called dew point curve, this is your  $p$  system. Now I mention about this is liquid but this is a liquid and this a vapor but, so this is a saturation liquid line, this is a saturation vapor line but this will be also one can say a sub cooled liquid and the similar line which we have done in engineering thermodynamics this would be your super-heated vapor.

So, this was the  $p$ - $x$  curve we can do the similar analysis for  $t$ - $x$  but note that we have clearly considered one of the components because the thing is here the pure  $a$ , the  $p$  sat for pure  $a$  is more than that of pure  $b$  that something for given temperature. So this is when it is  $p$ - $x$  means that  $t$  is constant right. So, that is important that we have just considered that  $x_p$  of pure  $a$ , saturation point of  $p$  saturation vapor for  $p$  is more than that of  $p_b$ .

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Substitute eq (1) in (2)

$$z_a n^v + z_a n^l = y_a n^v + x_a n^l$$

$$(z_a - x_a) n^l = (y_a - z_a) n^v$$

$$\therefore \frac{n_v}{n_l} = \frac{z_a - x_a}{y_a - z_a} = \frac{\text{line seg } v}{\text{line seg } l}$$

Lever Rule

Now we can extend this thing for liquid T xy in this case we will be having this kind of curve and the tie line this is also called tie line. We will be somewhere like this so let us consider that for given system. We have something like  $T_{sys}$  for the particular case here. So, now if you look at it here this is x and y and the composition of y has to be more if it a volatile so that way this would be your Ty curve, this would be your Tx curve and this will be liquid and this will be vapor again the liquid will be sub-cooled liquid.

And this will be your super-heated vapor, and this is at constant pressure p now make a note of this fact that for given  $T_{sys}$  you have your x equilibrium, y composition for considering a tie line. So, this is the points which represent the phases at equilibrium with this composition. Is a vapor phase, is a liquid phase and the components let us say a will be like this.

$$\text{Mass balance: } n = n^v + n^l$$

$$\text{Mass balance of component a: } z_a n = y_a n^v + x_a n^l$$

$$z_a n = z_a n^v + z_a n^l$$

$$z_a n^v + z_a n^l = y_a n^v + x_a n^l$$

$$(z_a - x_a) n^l = (y_a - z_a) n^v$$

$$\frac{n_v}{n_l} = (z_a - x_a)/(y_a - z_a) = \text{line seg } v/\text{line seg } l$$

Now, if it is a mixture of both somewhere let us say here then it is going to be a  $z$  equilibrium but of course this will have, this is like an effective composition but this is something which is combined in the vapor and liquid together but there is the phase separation indeed right.

So, how do you find an equilibrium or in general if you have this how do you connect this thing to diagrammatically, if you have been asked that composition of  $z$ ,  $z$  equilibrium is given to you and it phase separates and the diagrams are given to you then how do you use this diagram to obtain the information such as  $z_a$  or  $y_a$ .

So, one uses the lever rule, lever rule essentially kind of uses these diagrams and let us say if this is  $z$  equilibrium and if I am going to say that this is length  $l$  and this is length let us say  $v$ , this a branch or segment  $v$  and this is the segment  $l$ . then I can use this information to obtain the information of the compositions.

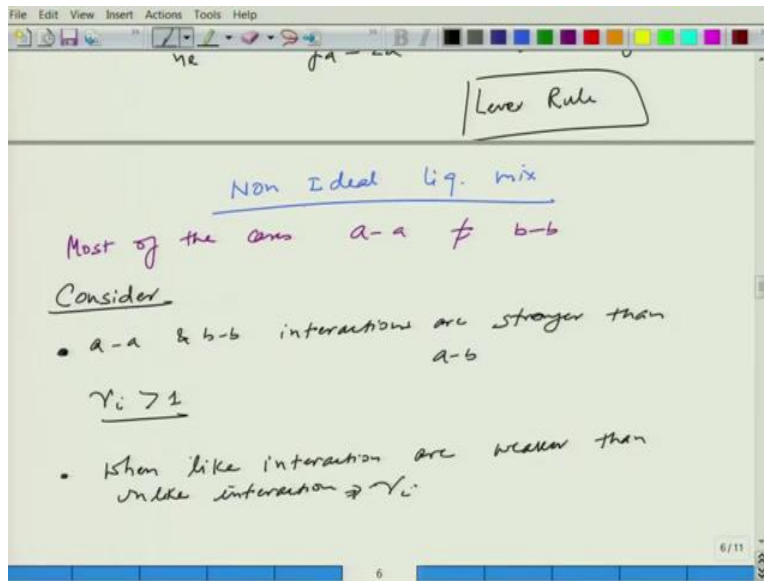
So, how do I do that let me start with this simple material balance. So if you are considering the mass parents here, the total mass would be something like mass in the vapor phase plus mass on the liquid phase and then if you looking at the mass balance for component  $a$  so it would be something like  $z$  which is total composition multiplied by mass is equal to  $y_a$  and  $v$  plus  $x_a$  and  $l$ .

So, this is let us say equation 1 and then equation 2 so if you multiply  $z$  here in the first one then I am going to get  $z$  multiplied by equation 1,  $z_n$  is equal to  $z_a n_v$  plus  $z_a n_l$ . So, I can now subtract these 2 equations so in other words I can substitute equation 3 in 2. And I can get  $z_a n_v$  plus  $z_a n_l$  this is  $y_a n_v$  plus  $x_a n_l$ . So this is now the expression I have, I get  $z_a$  minus  $x_a$ , I am now subtracting this with the common terms here so  $n_l$  is common here  $n_v$  is common, this is going to be  $y_a$  minus  $z_a n_v$ . Therefore,  $n_v$  minus  $n_l$  can be written as  $z_a$  minus  $x_a$  divided by  $y_a$  minus  $z_a$ .

Now if you look at it this is the mass information if it is available to you in the vapor phase or liquid phase and if you are aware if that is  $a$  or one of these two compositions then you can use this equation to find out. So, this nothing but the segment if you look at this, this is nothing but the segment, line segment  $v$ , so this is nothing but this right. Because this is  $z_a$  and this is your  $x_a$ , so this  $z_a$  minus  $x_a$  is the segment and  $y_a$  minus  $z_a$  is this segment so this is line segment  $v$  divided by line segment  $l$ .

So, that is how we can use this approach to find out some of the unknown, so you can use graphs also if it available to you. So this is our famous lever rule, so now I can extend this understanding and we been just talking about only their more or less ideal case. Now let me just consider the case where gamma is not equal to 1 that means activity coefficient is not equal to 1 and that will be the case of non-ideal liquids.

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So, this is not very unusual because real system hardly follows Raoult's law since most of the cases you will find aa not equal to bb. So, aa is hardly unlikely related to or identical to bb and that means that there is non-ideality is usually common in the real system. So, we will be considering a couple of cases to understand it. So, let us consider aa and bb interactions are stronger than ab, so ab interaction is a unlike interaction. aa and bb are like like interactions.

Now if you something like this, your gamma of i should be greater than 1, that is something which suggest that these interactions are stronger hence gamma is equal to 1. We will talk about it this expect of that, but usually or rather for such cases your gamma will deviate from 1, that is true but gamma will be more than 1. When like interactions are weaker that means aa and bb are weaker than unlike in such case gamma is less than 1.

So, these are the two important cases, the first one we often say is a positive deviation from ideality, the second one we often say is the negative deviation from ideality. We will talk about this more

once we understand its molecular nature. So let us consider the case of a binary mixture, so we will consider binary mixture to illustrate this understanding. Consider a low pressure which essentially means so I can consider vapor phase as ideal.

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Binary mix

- low  $P \Rightarrow$  vap phase as ideal
- Lewis/Randall ref
- chemically dissimilar species

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

$\gamma_a x_a P_a^S = y_a P$   
 $\gamma_b x_b P_b^S = y_b P$

Adding  $\Rightarrow$

$$\gamma_a x_a P_a^S + \gamma_b (1-x_a) P_b^S = P$$

$\gamma_a x_a P_a^S = y_a P$   
 $\gamma_b x_b P_b^S = y_b P$

Adding  $\Rightarrow$

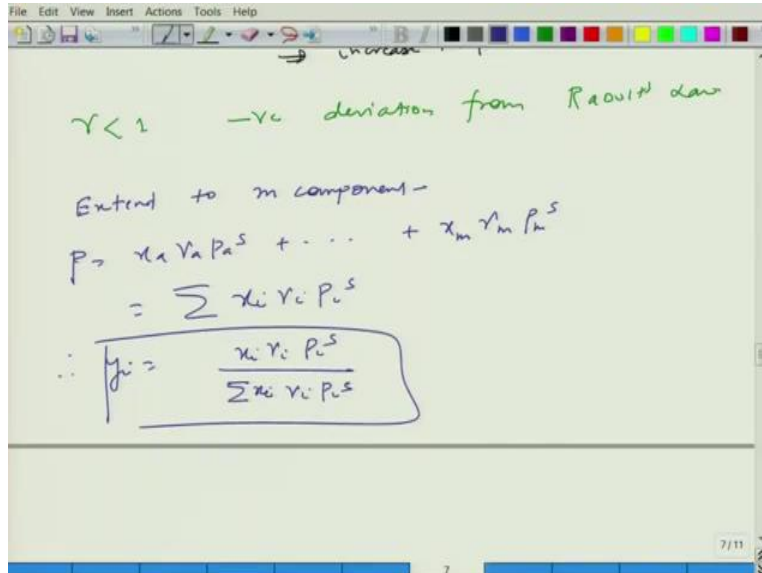
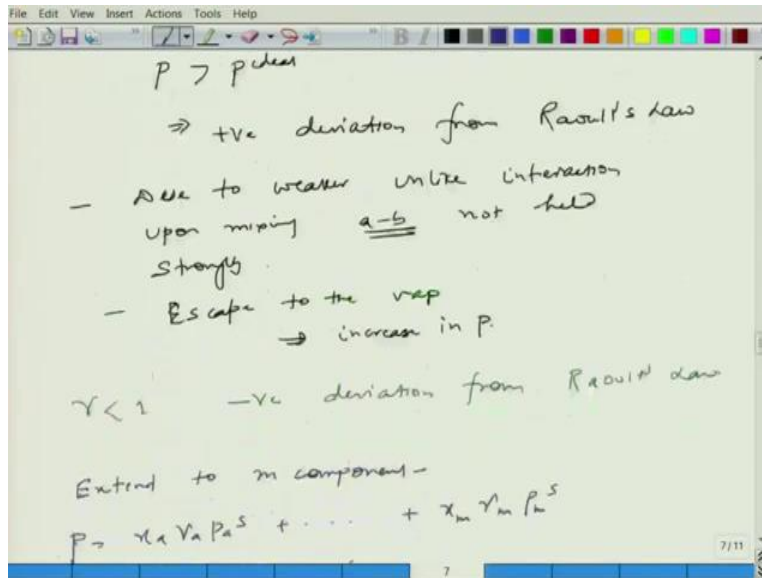
$$\gamma_a x_a P_a^S + \gamma_b (1-x_a) P_b^S = P$$


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$$y_a = \frac{\gamma_a x_a P_a^S}{P} = \frac{\gamma_a x_a P_a^S}{\gamma_a x_a P_a^S + \gamma_b (1-x_a) P_b^S}$$

Consider the case  $\gamma_a > 1$   
 $\Rightarrow \gamma_b > 1$

$P > P^{ideal}$



The second thing which we can consider is that now we will be using the reference of Louis Randall and we will be considering the chemically dissimilar species, so they are not similar species it is a dissimilar species. So, now given this that your you have a Louis Randall reference, what we can consider now is the ideal gas mixture that is the right hand side, what about the liquid, it is a  $\gamma_i x_i p_i^s$ , since it is low pressure we are going to consider  $\phi_i$  sat 1 and the pointing correction to be 1.

So, you have this now relation which we are going to use for such a case. Now if it a binary mixture it means you have  $\gamma_a x_a p_a^s$  is equal to  $y_a p$ ,  $\gamma_b x_b p_b^s$  is equal to  $y_b p$  and  $p$  so these are the 2 equations. You can add this up so adding would mean that you get the following

$\gamma_a x_a P_a^S$  plus  $\gamma_b (1 - x_a) P_b^S$  and this is going to be  $P$ . So, this is the relation we have got.

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

$$\gamma_a x_a P_a^S = y_a P$$

$$\gamma_b x_b P_b^S = y_b P$$

$$\gamma_a x_a P_a^S + \gamma_b (1 - x_a) P_b^S = P$$

$$y_a = \frac{\gamma_a x_a P_a^S}{P} = \frac{\gamma_a x_a P_a^S}{\gamma_a x_a P_a^S + \gamma_b (1 - x_a) P_b^S}$$

Now this is rather interesting because in our ideal case scenario when we had Raoult's law completely the same equation was used but with a gamma equal to 1 right, but here and of course you could see that in such for a case you had a linear relation of  $x$  with pressure but now with this the linear relation is not anymore true. Now how do you find  $y_a$  if you have this relation so  $y_a$  is going to be from here is going to be  $\gamma_a x_a P_a^S$  divided by  $P$ , and this  $P$  now is something which we can use this expression so you have  $\gamma_a x_a P_a^S$  divided by  $\gamma_a x_a P_a^S$  plus  $\gamma_b (1 - x_a) P_b^S$  all right, so this is the expression we have now.

*Extending to m components*

$$P = x_a \gamma_a P_a^S + \dots + x_m \gamma_m P_m^S = \sum x_i \gamma_i P_i^S$$

$$y_i = \frac{x_i \gamma_i P_i^S}{\sum x_i \gamma_i P_i^S}$$

So, we can take couple of cases and solve such cases where if we can use gamma relation with a composition, so there we can use some other models such are your 2 suffix models can be used, or 3 suffix models can be used and we can solve this problem. So, we will do that one of the cases in the later part of this particular topic. So now we have 2 specific cases one is the gamma is less than 1, and the other one is gamma is greater than 1.

So, let us consider the case gamma 1 is greater than 1 right, now this essentially means that like like interactions are stronger than unlike interactions, now one can show that if gamma a is equal to greater than 1 then this also implies through the equation gamma b should also be greater than 1. Now if that is the case that means if gamma 1 is greater than 1, this is also greater than 1. That



means the pressure here would be more than the pressure ideal that essentially mean that a pressure in the vapor phase of course is going to be more than the ideal.

And this is why we call it as a positive deviation from Raoult's law, now what is the molecular description or understanding of this, why does it happen if it is a pressure more. Now, the pressure is more that means the more particles have gone up in the air or rather vaporized, it prefers the vapor phase and hence the this enhance the pressure or it increases the pressure. Now which essentially means if the particles are going up that means their interaction there in the liquid phase have kind of less compared to the case pure phase, compared to the case of ideal phase.

So, this happens because of the fact that due to the weaker unlike interaction upon mixing ab is not held strongly, so your mixing it a and a of course it is stronger and b and b is stronger but when you mix you have lot of coordination number between a and b and that means there is a lot of particle between a around b or b around a. However, because of the weaker in unlike interaction it is not held and thus there is a preference to go in the vapor phase.

So, it means that thus the particles or molecules escape to the vapor phase which essentially means that increase in pressure. Now similar to the understanding of what we did for gamma greater than 1, 1 can also extend this understanding for gamma less than 1, where we call it this as negative deviation from Raoult's Law. Now we have done this exercise for binary mixtures we can also try to extend this exercise for many components, so is need not be just one because for each of them you will have this equality for the case of a Louis Randall for the case of the vapor phase so this expression will be extended for all different components and then you can submit of all different components.

So, that means you can have pressure and this term here so there are 2 terms, this term with the increase if increase the number of components. So, if we extend to m component we are going to get the following, so this means simply summation  $\sum x_i \gamma_i$  therefore what is y. y is the same, if you look at it y, y is always this term divided by total pressure so for y let us say i is going to be  $x_i \gamma_i$  and summation  $\sum x_i \gamma_i$ .

So, this is something which clearly make use of the assumptions and is a straight forward exercise for the case of the binary mixtures. Let us try to do a little bit of example which will be still simpler

and then we will try to do more complicated where the iterative and other aspects of the numerical analysis will come into the picture.

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### Dew-Point Calculation of a Nonideal Liquid with $T$ Known

A binary vapor mixture contains 48% ethanol (1) in water (2) at 70°C. Determine the pressure at which this vapor develops the first drop of liquid. What is the liquid composition? The excess Gibbs energy can be described by the three-suffix Margules equation with parameters:

$A = 3590 \text{ J/mol}$  and  $B = -1180 \text{ J/mol}$

Assume ideal vapor phase

$P = x_1 \gamma_1 P_1^{sat} + (1 - x_1) \gamma_2 P_2^{sat}$

Three-suffix Margules equation

$\ln \gamma_1 = \frac{(A + 3B)}{RT} x_2^2 - \frac{4B}{RT} x_2^3$

$\ln \gamma_2 = \frac{(A - 3B)}{RT} x_1^2 + \frac{4B}{RT} x_1^3$

*Handwritten notes:*  $\gamma_1 = \text{Exp}(\dots)$ ,  $\gamma_2 = \text{Exp}(\dots)$ ,  $x_1 \gamma_1 P_1^{sat} = \gamma_1 P_1^i$ ,  $x_2 \gamma_2 P_2^{sat} = \gamma_2 P_2^i$

$$P = x_1 \gamma_1 P_1^{sat} + (1 - x_1) \gamma_2 P_2^{sat}$$

$$\ln \gamma_1 = \frac{A + 3B}{R} x_2^2 - \frac{4B}{RT} x_2^3$$

$$\ln \gamma_2 = \frac{A - 3B}{RT} x_1^2 + \frac{4B}{RT} x_1^3$$

$\gamma_1$

$$P = x_1 \exp \left[ \frac{(A + 3B)}{RT} x_2^2 - \frac{4B}{RT} x_2^3 \right] P_1^{sat} + x_2 \exp \left[ \frac{(A - 3B)}{RT} x_1^2 + \frac{4B}{RT} x_1^3 \right] P_2^{sat}$$

$\gamma_2$

$$y_1 = \frac{x_1 \exp \left[ \frac{(A + 3B)}{RT} x_2^2 - \frac{4B}{RT} x_2^3 \right] P_1^{sat}}{x_1 \exp \left[ \frac{(A + 3B)}{RT} x_2^2 - \frac{4B}{RT} x_2^3 \right] P_1^{sat} + x_2 \exp \left[ \frac{(A - 3B)}{RT} x_1^2 + \frac{4B}{RT} x_1^3 \right] P_2^{sat}}$$

*Handwritten notes:*  $y_1 = \frac{x_1 \gamma_1 P_1^{sat}}{P}$ ,  $y_2 = \frac{x_2 \gamma_2 P_2^{sat}}{P}$

$$P = x_1 \exp \left[ \frac{A + 3B}{RT} x_2^2 - \frac{4B}{RT} x_2^3 \right] P_1^{sat} + x_2 \exp \left[ \frac{A - 3B}{RT} x_1^2 + \frac{4B}{RT} x_1^3 \right] P_2^{sat}$$

$$y_1 = \frac{x_1 \exp \left[ \frac{A + 3B}{RT} x_2^2 - \frac{4B}{RT} x_2^3 \right] P_1^{sat}}{x_1 \exp \left[ \frac{A + 3B}{RT} x_2^2 - \frac{4B}{RT} x_2^3 \right] P_1^{sat} + x_2 \exp \left[ \frac{A - 3B}{RT} x_1^2 + \frac{4B}{RT} x_1^3 \right] P_2^{sat}}$$

- Calculate the saturation pressure from Antoine equation for ethanol ✓
- Obtain the saturation pressure from Steam table ✓

Since sum of y would be 1  
Thus, equation in one variable.

$x_1 = 0.12$  Exact ✓  
Solve ✓

Plug in the P equation ✓

Compare with experiments ✓

$x_1 = 0.13$  and  $P = 0.57$  [bar]

So, this is the first question, so again we are talking about non ideal vapor liquid equilibrium and the first question is on the Dew point calculation of a non-ideal liquid with T known. So here essentially what we need to find out is dew point that means dew point calculation of a non-ideal liquid with T known.

So, if you look at the question you have a binary vapor mixture which contains 48 percent ethanol in water and the temperature is given determine the pressure at which the vapor develops the first drop of the liquid, that is why it is a dew point calculation and what is the liquid composition.

So, y are given to you, we do not know x here, and what is been asked us to do is to use the 3 suffix Margules equation for the excess Gibbs energy that means essentially we just have to use it, otherwise you can solve the problem for different models also and the parameter for 3 suffix model is given here first.

So, we will start again with the fact that since it is a ideal vapor phase essentially, so you have  $\gamma_i p_i = y_i p$ . So we are assuming to be a low pressure that is why we ignored the fugacity, fugacity of i at saturation and then at the pointing correction. So, now for the case of binary you

will add it up, this right-hand side become total pressure and the left hand side is basically is given here.

So, this is the first term, this is the second term and this is the total pressure so this comes from the first equation, you can also add here and it will be  $x_2 \gamma_2 p_{2s}$  is equal to  $y_2 p$ . Now here the gamma information is given in the form of Margules equation, the textbook clearly has its expression so the LN gamma expression based on the 3 suffix Margules equation as this and similarly LN gamma 2 is given to you like this.

So, this you can derive it or you can take it from the textbook, so this is widely available. The excess Gibbs energy modal is also known is also summarized or stabilized in the textbook. So I have just directly taken it from there. So, this is the expression here, I know a and b so essentially what I can do is, I can plug in this expression here, however these are depends on  $x_2$  and  $x_1$ . So that is what I did, I represent gamma in terms of exponential term here and similarly here also exponential and then I plug in in this expression.

So, this is how it looks like exponential this multiplied by  $p_{1sat}$ , so this is nothing but gamma 1 and this is nothing but gamma 2. Now as we have done for y, y is again can be written as  $x_1 \gamma_1 p_{1sat}$  divided by total pressure. Now total pressure is this, so this is where it comes here and gamma 1 is basically the exponential term. So, this now the expression we have so what we need to find out is clearly the first thing is that we have to determine the pressure to which this vapor develops the first drop at that particular temperature and the liquid composition.

So, now what is remaining to be solved is the  $p_{1sat}$  and the  $p_{2sat}$ , so here the easiest way to do that is take the help of Antoine equation, so one of them is the ethanol so for that the Antoine equation is clearly available in the nist way of data or of course you can also look as the appendices of the textbook which we are following. The other thing which one can do is particularly for water one can take the  $p_{1sat}$  from the steam table.

So, calculate the saturation pressure from Antoine equation for ethanol, obtain the saturation pressure from steam table for water. Since the sum of y would be 1 that means you can clearly take this as well as you can also write  $y_2$ , and then you can submit up. Then you have this 1 is equal to the first term which is this plus the second term and since  $x_1$  can written terms of  $x_2$ ,  $x_2$  can be written in terms of  $x_1$ . So, you will have this right-hand side only in one particular variable

considering that you have calculated  $p_{1sat}$  from the Antoine equation or obtained that from the steam table for the case of water.

So, you have a simple equation here which is dependent on one variable which you can plug in, or you can plug in those equations in excel sheet and you can use the solver to obtain  $x_1$ . So once you obtain  $x_1$  you can plug back this expression to the same expression here pressure. Now  $x_1$  is available that means  $x_2$  is also available,  $a$  and  $b$  we know  $t$  we know,  $p_{1sat}$  and  $p_{2sat}$  we know. So, that from there you can obtain the pressure, so this is a simple from the mathematical part of way is very simple. This part of this analysis is bit numerical and that is why you have to use sometime kind of tools, such as excel tool and that is very handy for that.

Now, if you look at the data which we obtained using the 3 suffix Margules equation and compare that with the experiment it is very close by, that tells you how well this analysis can be done using simple approximation which we have made and that is the one where we consider this low pressure, we consider the vapor phase to be ideal gas.

So, I hope you have got this understanding a bit, this is the first set of examples which we solved we will be using another one where you need to use iterative ways to obtain the answers. So we will continue this exercise and I will stop here, and we will see you next time with a more complicated and interesting problems at hand. So see you soon.