

**Chemical Engineering Thermodynamics**  
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**Lecture-51**

**Vapor Liquid Equilibria (non-ideal mixture-ii)**

Welcome back in the last few classes what we have learned is basically the phase equilibria calculation where phi gamma approach was introduced basically the fugacity equality and the vapor phase was related to the fugacity coefficient and the liquid phase fugacity was related to the activity coefficients. Some example we have conducted where we have considered non ideal liquid and ideal gas, in today's class we will start with an example where we will be considering both the phases non ideal and then we will realize the complexity of the systems, simple binary mixture for example.

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**Dew-Point Calculation of a Nonideal Liquid and Nonideal Gas with  $T$  Known**  $y_a, y_b$

At high pressures, both the vapor and liquid phases may be nonideal. Consider a binary mixture of a and b with vapor-phase mole fraction and  $T$  known. Develop a set of equations and a solution algorithm to determine the composition in the liquid phase and the system pressure. Use the van der Waals equation to quantify deviations from ideality in the vapor and the three- suffix Margules equation to model the nonideal liquid. Assume that critical properties, liquid volumes, and Antoine coefficients for each species are readily available and that the three- suffix Margules parameters have been determined.

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

$$x_i = \frac{y_i \phi_i P}{\gamma_i f_{i,pure}} = \frac{y_i \phi_i P}{\gamma_i \phi_i^s p_i^s \exp\left[\frac{v_i^L (P - p_i^s)}{RT}\right]}$$

$$x_a + x_b = 1 = \frac{y_a \phi_a P}{\gamma_a \phi_a^s p_a^s \exp\left[\frac{v_a^L (P - p_a^s)}{RT}\right]} + \frac{y_b \phi_b P}{\gamma_b \phi_b^s p_b^s \exp\left[\frac{v_b^L (P - p_b^s)}{RT}\right]}$$

And this can be extended to multiple mixtures as well, so let me describe the problem here, so this dew point calculation of a non-ideal liquid and non-ideal gas with temperature known. So, at high pressure both the vapor liquid phases maybe non-ideal. So, consider a binary mixture of a and b with vapor phase mole fraction and  $T$  known, that means we know  $y_a$  and  $y_b$ . Develop a set of equation and a solution algorithm to determine the composition in the liquid phase and the system pressure.

So we need to find out how to solve this that means we can have to we have to design an algorithm to solve the constraints and find a solution of the equations and solution of  $b$  basically the composition in the liquid phase and the system pressure, so since we are saying that a non-ideal gas is there, so we have to also come up with a expression for equational state to get a fugacity coefficient so for that the van der waals equational state can be used to quantify the deviation from the ideality and three suffix margules equation can be used to expresses non ideality in the liquid phase.

Assume that the critical properties, liquid volumes and Antoine coefficient of each species are readily available and the three suffix margules parameters have been determined. So these are the things which are given to us in some form whether it is a table for example. Though the solution which whatever we are going to do is use van der waals equation but of course you can use many other equation like such as pang robinson and you know van law for example and similarly for the liquid phase non ideality we can use other models also but the systematic approach which we are going to work on should be extensible to different model as well.

So let us start with a basic equation, equation is of course the fugacity of component  $I$  in vapor phase should be same as that of a component  $I$  in the liquid phase and this we can write in terms of  $\phi$   $\gamma$  representation where we write  $x_i \gamma_i f_i^{pure}$  where we assuming this Randall scale which basically is valid for zero to one and this must be equal to  $y_i \phi_i P$ . So this is basic constraint at the phase equilibria where  $I$  in this case could be  $B$ . I can rewrite these things in terms of something like this and they have  $\gamma_i$  and  $f_i^{pure}$  now I can write this as  $y_i \phi_i P$  by  $\gamma_i$  and this can be written as  $\phi_i^{sat}$  and  $P_i^{sat}$  and then pointing correction. This would be your  $P$  minus  $P_i^{sat}$ , so this is a molar volume of the liquid phase.

So this is we know that from our earlier analysis, now this is for  $x_1$  or  $x_i$  for the case of the binary mixture you will have two of them for  $a$  and  $B$ , so if you add it up you will have  $x_a$  plus  $x_b$  and that must be equal to 1, so you will have two terms  $y_a \phi_a P$  divided by  $\gamma_a \phi_a^{AS}$ ,  $P_a^S$  exponential this part plus  $y_b \phi_b P$   $\gamma_b \phi_b^{BS}$   $P_b^S$  exponential this part.

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

$$x_i = \frac{y_i \phi_i P}{\gamma_i f_{i,pure}} = \frac{y_i \phi_i P}{\gamma_i \phi_i^s P_i^s \exp\left[\frac{v_i^l}{RT}(P - P_i^s)\right]}$$

$$x_a + x_b = 1 = \frac{y_a \phi_a P}{\gamma_a \phi_a^s P_a^s \exp\left[\frac{v_a^l}{RT}(P - P_a^s)\right]} + \frac{y_b \phi_b P}{\gamma_b \phi_b^s P_b^s \exp\left[\frac{v_b^l}{RT}(P - P_b^s)\right]}$$

So these are the two parts, two terms which you should yield one. Now you can solve this thing in order to obtain let us say pressure but then you have to worry about fugacity coefficients for a and B. Now for the case of the Pa sat off course which comes here Pa sat is there this we can use Antoine equation.

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$\ln P^s = A - \frac{B}{T+C} \Rightarrow P_a^s, P_b^s \text{ anti } T$   
 $-\phi_a, \phi_b^s$   
 $- P = \frac{RT}{v-b} - \frac{a}{v^2} \Rightarrow v_a^s, v_b^s$

## Dew-Point Calculation of a Nonideal Liquid and Nonideal Gas with $T$ Known $y_i, y_b$

At high pressures, both the vapor and liquid phases may be nonideal. Consider a binary mixture of a and b with vapor-phase mole fraction and  $T$  known. Develop a set of equations and a solution algorithm to determine the composition in the liquid phase and the system pressure. Use the van der Waals equation to quantify deviations from ideality in the vapor and the three-suffix Margules equation to model the nonideal liquid. Assume that critical properties, liquid volumes, and Antoine coefficients for each species are readily available and that the three-suffix Margules parameters have been determined.

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$$x_i = \frac{y_i \phi_i P}{\gamma_i f_{i, pure}} = \frac{y_i \phi_i P}{\gamma_i \phi_i^s p_i^s \exp\left[\frac{v_i^L (p - p_i^s)}{RT}\right]}$$

$$x_a + x_b = 1 = \frac{y_a \phi_a P}{\gamma_a \phi_a^s p_a^s \exp[\dots]} + \frac{y_b \phi_b P}{\gamma_b \phi_b^s p_b^s \exp[\dots]}$$

So for the case of  $P_{a, sat}$  we can use LNP sat is a minus B, T plus C so since first a b C's are given to us so we can obtain certainly  $P_{a, S}$  and  $P_{b, S}$  as a function of T that is something which you can evaluate. Now one of the thing which we have to worry about now is the question is how do you get phi a of phi a sat and the other thing is that if you want to make use of the expression of the Vander waal then we have to also obtain one of the important thing is we have to also obtain this molar volume, so that means that you should be able to use this Vander waal equation of state for the case a and b for the pure case, so from here we can get  $V_A, sat$   $V_B, sat$  that we can approximate that to the liquid phase, so from here we can obtain it.

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Van der Waals Equation of State	
Pure species $i$	$\ln \phi_i = \frac{b_i}{v_i - b_i} - \ln\left(\frac{(v_i - b_i)P}{RT}\right) - \frac{2a_i}{RTv_i}$
Species 1 in a binary mixture	$\ln \phi_1 = \frac{b_1}{v - b} - \ln\left(\frac{(v - b)P}{RT}\right) - \frac{2(y_1a_1 + y_2a_{12})}{RTv}$
Species $i$ in a mixture	$\ln \phi_i = \frac{b_i}{v - b} - \ln\left(\frac{(v - b)P}{RT}\right) - \frac{2\sum_{k=1}^m y_k a_{ik}}{RTv}$

Solve pure  $v$  using vDW EOS

$$a_{mix} = y_a^2 a_a + 2y_a y_b \sqrt{a_a a_b} + y_b^2 a_b$$

$$b_{mix} = y_a b_a + y_b b_b$$

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$a = \frac{27}{64} \frac{(RT_c)^2}{P_c} \left[ \frac{\text{m}^3}{\text{mol}^2} \right]$$

$$b = \frac{(RT_c)}{8P_c} \left[ \frac{\text{m}^3}{\text{mol}} \right]$$

(T<sub>c</sub>, P<sub>c</sub>)

Using the three-suffix Margules equation for activity coefficients gives:

$$\gamma_a = \exp\left[\frac{(A + 3B)}{RT} v_1^2 - \frac{4B}{RT} v_1 v_2\right]$$

$$\gamma_b = \exp\left[\frac{(A - 3B)}{RT} v_2^2 + \frac{4B}{RT} v_1 v_2\right]$$

$$\text{Pure species } i: \ln \phi_i = \frac{b_i}{v_i - b_i} - \ln\left(\frac{(v_i - b_i)P}{RT}\right) - \frac{2a_i}{RTc_i}$$

$$\text{Species 1 in binary mixture } \ln \phi_1 = \frac{b_1}{v - b} - \ln\left(\frac{(v - b)P}{RT}\right) - \frac{2(y_1 a_1 + y_2 a_{12})}{RTc}$$

$$\text{Species } i \text{ in a mixture } \ln \phi_i = \frac{b_i}{v - b} - \ln\left(\frac{(v - b)P}{RT}\right) - \frac{2\sum_{k=1}^m y_k a_{ik}}{RTc}$$

Solve pure  $v$  using vdw EOS

$$a_{mix} = y_a^2 a_a + 2y_a y_b \sqrt{a_a a_b} + y_b^2 a_b$$

$$b_{mix} = y_a b_a + y_b b_b$$

So essentially we need to obtain use this which relate pressure, volume and T B's we can obtain from the parameters of the a and b because it is written that TC and PC is given to you which means basically for both the species you should be able to obtain a and b that is possible for you that means you can relate you can have the handle to the equational state for both the species. Now in addition to that if you have it you can also use this expression of a fugacity coefficient for using the van der waal equation state, so without deriving it I am using the expression which is already

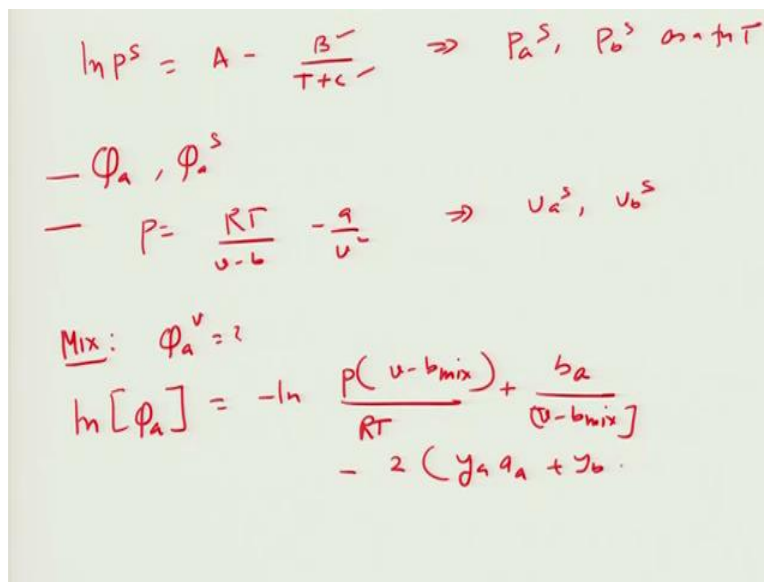
derived or you can do the same thing using the expression of LN phi with Z the compressibility factor integral of that for zero to V.

So, something which you can easily derive it, so were not putting it here. Now this gives you a relation of fugacity with the other terms, so from here we can obtain certainly we can obtain phi of sat and as well as phi so we can obtain phi's a and b and as well as phi a and phi sat for the case of phi sat you have to use the T sat and the corresponding the V sat here.

So essentially you have the complete understanding of the pure spaces and for the case of something which is phi which is written here.

This one is for the pure this one is off course for the mixture, so for mixtures you have to use the other expression which comes here, so this is the fugacity coefficient in the mixture in some textbook they use this in order to describe that this is for the mixture but if you look at it here for the binary mixture you have LN phi here LN phi a a so let me just try to use the other space available.

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$$\ln p^s = A - \frac{B}{T+c} \Rightarrow P_a^s, P_b^s \text{ as a function of } T$$

$$- \phi_a, \phi_a^s$$

$$- P = \frac{RT}{v-b} - \frac{a}{v^2} \Rightarrow u_a^s, u_b^s$$

Mix:  $\phi_a^v = ?$

$$\ln[\phi_a] = -\ln \left[ \frac{P(v-b_{mix})}{RT} + \frac{b_a}{(v-b_{mix})} \right] - 2(y_a a_a + y_b a_b)$$

So for the case of the mixture the fugacity coefficient would be something like this, this is LN phi a in the mixture would be minus LN P V minus b mix, so instead of B, so we was just writing out b mix and this we are talking about let us say certain phase here plus b of component a because this is a and then you have this V minus b mix. Then the last term is 2 y<sub>a</sub> a<sub>a</sub> of a plus y<sub>b</sub>.

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Van der Waals Equation of State	
Pure species $i$	$\ln \phi_i = \frac{b_i}{v_i - b_i} - \ln\left(\frac{(v_i - b_i)P}{RT}\right) - \frac{2a_i}{RTv_i}$
Species 1 in a binary mixture	$\ln \phi_1 = \frac{b_1}{v - b} - \ln\left(\frac{(v - b)P}{RT}\right) - \frac{2(y_1 a_1 + y_2 a_{12})}{RTv}$
Species $i$ in a mixture	$\ln \phi_i = \frac{b_i}{v - b} - \ln\left(\frac{(v - b)P}{RT}\right) - \frac{2\sum_{j=1}^n y_j a_{ij}}{RTv}$

Solve pure  $v$  using vDW EOS

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$a_{\text{mix}} = y_a^2 a_a + 2y_a y_b \sqrt{a_a a_b} + y_b^2 a_b$$

$$b_{\text{mix}} = y_a b_a + y_b b_b$$

Using the three-suffix Margules equation for activity coefficients gives:

$$\gamma_a = \exp\left[\frac{(A + 3B)}{RT}x_a^2 - \frac{4B}{RT}x_a\right]$$

$$\gamma_b = \exp\left[\frac{(A - 3B)}{RT}x_b^2 + \frac{4B}{RT}x_b\right]$$

Now here if you look at it here this is minus 2  $y_a a_{12}$  where this  $a_{12}$  is like you know  $\sqrt{a_1 a_2}$  for the case of two component mixture, so this could be your  $a$  so that is make a little difficult because you are using the same sign, so we can write a here and essentially this for the sake of clarity I will simply say  $a_{12}$  this could be your simply  $J$ . so now this  $a_{12}$  is a mixed term is a cross term this we can use the approximation of under root because this is energy parameter.

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$$\ln p^S = A - \frac{B}{T+C} \Rightarrow p_a^S, p_b^S \text{ as a f of } T$$

$$-\phi_a, \phi_a^S$$

$$- P = \frac{RT}{v-b} - \frac{a}{v^2} \Rightarrow v_a^S, v_b^S$$

Mix:  $\phi_a^V = ?$

$$\ln[\phi_a] = -\ln \frac{P(v - b_{\text{mix}})}{RT} + \frac{b_a}{(v - b_{\text{mix}})} - \frac{2(y_a a_a + y_b \sqrt{a_a a_b})}{RTv}$$

So, we can use expression of this that this could be a simple geometric mean of  $a$  of A,  $a$  of b and divided  $RTV$ .

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Species $i$ in a binary mixture	$\ln \hat{\phi}_i = \frac{b_i}{v - b} - \ln\left(\frac{(v - b)P}{RT}\right) - \frac{2(y_i a_i + y_j a_j)}{RTv}$
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$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$a_{\max} = y_a^2 a_a + 2y_a y_b \sqrt{a_a a_b} + y_b^2 a_b$$

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$\ln p^S = A - \frac{B}{T+C} \Rightarrow P_a^S, P_b^S \text{ on } T$   
 $-\phi_a, \phi_b^S$   
 $P = \frac{RT}{v-b} - \frac{a}{v^2} \Rightarrow v_a^S, v_b^S$   
 Mix:  $\phi_a^v = ?$   
 $\ln[\phi_a] = -\ln \frac{P(v-b_{\text{mix}})}{RT} + \frac{b_a}{(v-b_{\text{mix}})} - \frac{2(y_a a_a + y_b \sqrt{a_a a_b})}{RTv}$

So this is nothing but the same expression as this but making sure that here this is your  $b_{\text{mix}}$  this is pure component one this is again  $b_{\text{mix}}$ , so the way I have written is I have written the first part this part and then this is the second term, so this is I have written here so now you have you know how to use this expression which is given to you otherwise you can derive it also but this is simple extension of this part were basically we have used the term volume here subtracted by the, the effective  $b$  of the mixture and same with that one, but the rest of the term we use a typical  $V$  mixture part.



So now the point is that you know you have handle to phi also, similarly you can do that for the other term that is phi a and phi B. Now the question is how do you find a mix because you have to use a mix and b mix that you can do that from here, so a mix and b mix can be done like this and the other question is that now given that this is phi information is available now with all this variables given to you so you have the complete expression of this.

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**Dew-Point Calculation of a Nonideal Liquid and Nonideal Gas with  $T$  Known**

At high pressures, both the vapor and liquid phases may be nonideal. Consider a binary mixture of a and b with vapor-phase mole fraction and  $T$  known. Develop a set of equations and a solution algorithm to determine the composition in the liquid phase and the system pressure. Use the van der Waals equation to quantify deviations from ideality in the vapor and the three-suffix Margules equation to model the nonideal liquid. Assume that critical properties, liquid volumes, and Antoine coefficients for each species are readily available and that the three-suffix Margules parameters have been determined.

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

$$x_i = \frac{y_i \phi_i P}{\gamma_i f_{i, pure}} = \frac{y_i \phi_i P}{\gamma_i \phi_i^s P^s \exp\left[\frac{v_i^L (P - P^s)}{RT}\right]}$$

$$x_a + x_b = 1 = \frac{y_a \phi_a P}{\gamma_a \phi_a^s P^s \exp\left[\frac{v_a^L (P - P^s)}{RT}\right]} + \frac{y_b \phi_b P}{\gamma_b \phi_b^s P^s \exp\left[\frac{v_b^L (P - P^s)}{RT}\right]}$$

And now the second question is that if you want to find out gamma then you have to worry about the equation of excess gibbs free energy and so we are using this here AB, so I am directly using the expression of gamma a and gamma b were it is related AB and the composition. Now once you plug in this expression with LN phi and this expression, you have a very complicated set of equation were this is depends on very parameters and this also depends on parameters, so that means phi and gamma both depends on parameters some are unknown and now you have to solve this equation for there will be two equation such for xa and xb and that is what we can come up with this constraints, so we have to plug in this expression were the left hand side is one and the right hand side you plug in phi P phi a phi b and similarly for saturation and this one is we know because this is Antoine equation based and then you have pointing expression and gamma we will be using the three suffix Margule's equation.

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- Three unknown to solve
  - $P, x_a, x_b$
  - Fugacity depends on P also
  - Activity depends on x
  - Therefore, iterative scheme is needed

Set  $\phi_a, \phi_b, \gamma_a, \gamma_b = 1$

↓

calculates P

So you have some set of equation now the thing is there constraints, so what we know, we know only the temperature and  $y_a$ 's and the things which you do not know is pressure, composition and the liquid phase. Now we also know now that fugacity depends on the pressure because pressure unknown but fugacity depends on the pressure, fugacity coefficient will be depending on the pressure and similarly activity depends on composition of the liquid phase, so which we need to find it out.

So essentially we have a very complicated structure so let us think about a solution and this solution is something which is just for the sake of illustration they could be better algorithm to solve this, so can start from very simple thing for example you can start assuming that your  $\phi$  is initially and  $\gamma$ 's are all 1 which means you start with a assumption that this is let us take this case of a ideal gas mixture in solution. Now you solve for P so that means you calculate P.

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**Van der Waals Equation of State**

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Solve pure  $v$  using vdW EOS

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$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$a = \frac{27}{64} \frac{(RT_c)^2}{P_c} \left[ \frac{\text{m}^3}{\text{mol}^2} \right]$$

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Using the three-suffix Margules equation for activity coefficients gives:

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$$\gamma_b = \exp\left[\frac{(A-3B)}{RT}x_a^2 + \frac{4B}{RT}x_a\right]$$

$$P = \left[ \frac{y_a \phi_a}{\gamma_a \phi_a^s P_a^s \text{exp}[...]} + \frac{y_b \phi_b}{\gamma_b \phi_b^s P_b^s \text{exp}[...]} \right]$$

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Assume that critical properties, liquid volumes, and Antoine coefficients for each species are readily available and that the three-suffix Margules parameters have been determined.

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

$$x_i = \frac{y_i \phi_i P}{\gamma_i f_{i, \text{pure}}} = \frac{y_i \phi_i P}{\gamma_i \phi_i^s P_i^s \text{exp}\left[\frac{v_i^L}{RT}(P - P_i^s)\right]}$$

$$x_a + x_b = 1 = \frac{y_a \phi_a P}{\gamma_a \phi_a^s P_a^s \text{exp}[...]} + \frac{y_b \phi_b P}{\gamma_b \phi_b^s P_b^s \text{exp}[...]}$$

So to calculate  $P$  you have to use the following, so from here how do I get my pressure, so we need to calculate  $P$  so  $P$  can be written as the following  $P$  would be I am rewriting that expression which will be  $y_a \phi_a$  divided by  $\gamma_a \phi_a^s P_a^s$  and let us say this pointing expression is 1 plus  $y_b \phi_b$  by  $\gamma_b \phi_b^s P_b^s$  pointing expression 2, so this was inverse of this so this is something which comes from this expression, so I am using this and taken common and rest come to the denominator and that is what you see here.

So if you fixing  $\phi_a$   $\gamma_a$  to be 1  $\phi_b$  and  $\gamma_b$  to be 1 you can use this equation to calculate the pressure and that is what the pressure is.

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- Three unknown to solve
  - $P, x_a, x_b$
  - Fugacity depends on P also
  - Activity depends on x
  - Therefore, iterative scheme is needed

Set  $\phi_a, \phi_b, \gamma_a, \gamma_b = 1$

calculates P

Solve v using vdw

$\phi_a, \phi_b^{ca}$

So, once we calculate the pressure we have to solve for volume using van der waal. Because now you have the pressure, so van der waal equational state can be used so you know the pressure, you know the temperature and the B's of the pure are available A's are also available and in general you can now calculate the volume, so you can get the volume of the mixture also from here, so that we know from here we can get the volume then the next important thing is we need to calculate the fugacity coefficients.

So now next is that we calculate the fugacity  $\phi_a$  for the mixture and  $\phi_b$  for the mixture, so you calculate that and how do you do that will use this expression.

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**Van der Waals Equation of State**

Pure species $i$	$\ln \phi_i = \frac{b_i}{v_i - b_i} - \ln \left( \frac{(v_i - b_i)P}{RT} \right) - \frac{2a_i}{RTv_i}$
Species 1 in a binary mixture	$\ln \phi_1 = \frac{b_1}{v - b} - \ln \left( \frac{(v - b)P}{RT} \right) - \frac{2(y_1 a_1 + y_2 a_{12})}{RTv}$
Species $i$ in a mixture	$\ln \phi_i = \frac{b_i}{v - b} - \ln \left( \frac{(v - b)P}{RT} \right) - \frac{2 \sum_{j=1}^n y_j a_{ij}}{RTv}$

Solve pure  $v$  using vdW EOS

$$F = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$a_{\text{mix}} = y_a^2 a_a + 2y_a y_b \sqrt{a_a a_b} + y_b^2 a_b$$

$$b_{\text{mix}} = y_a b_a + y_b b_b$$

Using the three-suffix Margules equation for activity coefficients gives:

$$\gamma_a = \exp \left[ \frac{(A + 3B)}{RT} x_b^2 - \frac{4B}{RT} x_b^3 \right]$$

$$\gamma_b = \exp \left[ \frac{(A - 3B)}{RT} x_a^2 + \frac{4B}{RT} x_a^3 \right]$$

$$P = \left[ \frac{y_a \phi_a}{\gamma \phi_a^s P_a^s P \Delta y_1} + \frac{y_b \phi_b}{\gamma \phi_b^s P_b^s P \Delta y_2} \right]$$

$$P = \left[ \frac{y_a \phi_a}{\gamma \phi_a^s P_a^s P \Delta y_1} + \frac{y_b \phi_b}{\gamma \phi_b^s P_b^s P \Delta y_2} \right]$$

So, because the pressure is known the volume is known now because you just calculated, so you can calculate the fugacity. Now there are two ways to do that once you calculate the fugacity you can also use the expression here because now you have calculated the fugacity from here for example here you can get this composition X here.

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- Three unknown to solve
  - $P, x_a, x_b$
  - Fugacity depends on P also
  - Activity depends on x
  - Therefore, iterative scheme is needed

Set  $\phi_a, \phi_b, \gamma_a, \gamma_b = 1$

```

    graph TD
      A[Set φa, φb, γa, γb = 1] --> B[calculate P]
      B --> C[Solve v using vdW]
      C --> D[calculate φa, φb]
      D --> E[xa, xb]
      E --> F[γa, γb]
      F --> G[P]
      G --> H(( ))
      H --> B
      H --> I[|ΔP/P| < ε]
      I --> G
    
```

So, I can do that, I can simply say as well after this I can calculate the composition X here  $x_b$  if I get  $x_b$ ,  $x_a$  and  $x_b$  then I have to handle to obtain this so I can get my gammas,  $\gamma_a$  and  $\gamma_b$ . Now once I get  $\gamma_a$  and  $\gamma_b$  then I go back to this and calculate the pressure again and then you check off course that if the new pressure if  $\Delta P$  the old pressure and new pressure if you subtracted divided by earlier the change in the pressure is less than some kind of criteria and if it is less than that of course you can stop if it is not then you go back and try to solve  $V$  again.

Now this is a typical algorithm now I did not put it in a way which clearly explain how to solve complicated system in fact there could be many variants. Why there could be many variant because for example in this here when you calculate this  $\phi$  at this point you can actually check the pressure again, so you can also have a interior loop and keep getting the correct pressure for this assumption and then you move to the next part, so can have one of the test here again.

So this clearly tells you that iterative process is a bit more complicated and there is proper skill which is necessary. Now it turns out that many software does exist which helps you out to solve this problem but if you have to develop something on your own then it may take some little more time to do that and that depends on what kind of system you are working on, so if it is for example highly non ideal you may have some difficulty, you may face some difficulty in converging the data's that means for all this  $\phi$  getting the correct  $\phi$  and correct  $\gamma$  and then effectively the correct pressure.

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### Dew-Point Calculation of a Nonideal Liquid and Nonideal Gas with $T$ Known $\gamma_i, \gamma_i^L$

At high pressures, both the vapor and liquid phases may be nonideal. Consider a binary mixture of a and b with vapor-phase mole fraction and  $T$  known. Develop a set of equations and a solution algorithm to determine the composition in the liquid phase and the system pressure. Use the van der Waals equation to quantify deviations from ideality in the vapor and the three-suffix Margules equation to model the nonideal liquid. Assume that critical properties, liquid volumes, and Antoine coefficients for each species are readily available and that the three-suffix Margules parameters have been determined.

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

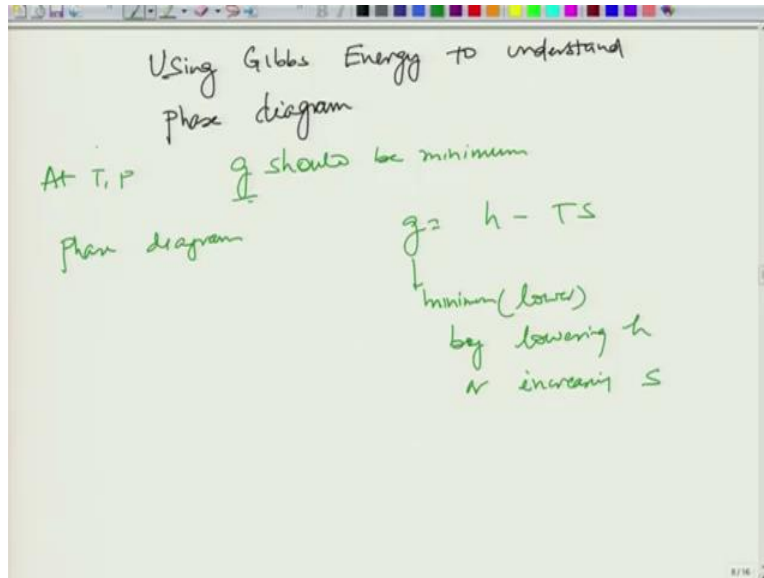
$$x_i = \frac{y_i \phi_i P}{\gamma_i f_{i, pure}} = \frac{y_i \phi_i P}{\gamma_i \phi_i^s P^s \exp\left[\frac{v_i^L (P - P^s)}{RT}\right]}$$

$$x_a + x_b = 1 = \frac{\gamma_a \phi_a P}{\gamma_a \phi_a^s P^s \exp[\dots]} + \frac{\gamma_b \phi_b P}{\gamma_b \phi_b^s P^s \exp[\dots]}$$

So I just wanted to describe the typical issues in this kind of equilibria when you have non ideality in the liquid and the gas phase were you have to worry you have to calculate the make use of the fugacity coefficient and as well as the activity coefficient and then you have to use iterative process to solve certain problem as we have tried to do this today. So we have only few things you know we have not looked into many complicated systems for simply for the lack of time in this course, so I will not be dwelling more into solving complicated system or showing you how to do that in excel sheets or using software, so it is more about explaining the fundamental aspect of the usual kind of problems which face and how do we proceed with those solutions step by step.

So let us little bit try to understand this phase equilibria from a free energy point of view, so we know that when a given a temperature and a pressure the system is at equilibrium when the Gibbs free energy is minimum. Now if there is a phase equilibria or when you change the composition you may see a change in the phases from the vapor, liquid and so forth it also indicates that the Gibbs free energy curve or the plot is also going to change that means there would be a change in the curvature for example or minima would shift from the vapor phase to the liquid phase.

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*At T, P  $g$  should be minimum*

*Phase diagram:  $g$  (minimum by lowering  $h$  or increasing  $S$ ) =  $h - TS$*

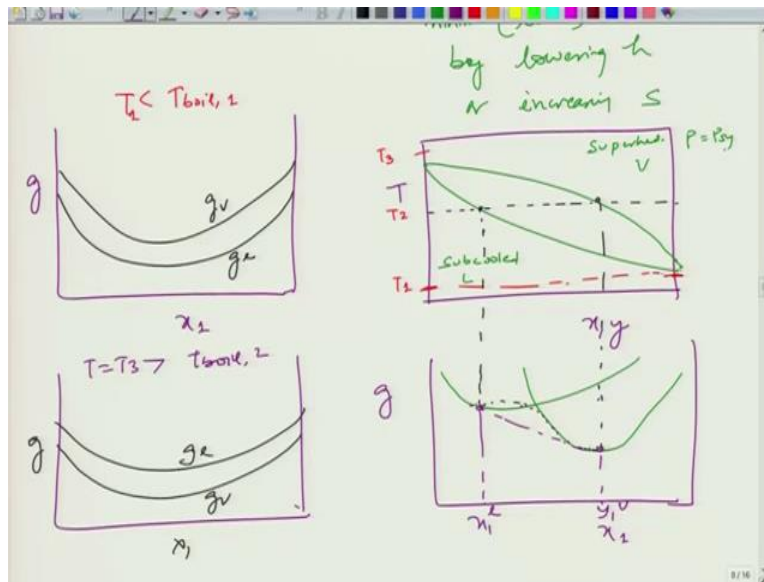
So how do you explain those from graphically, so let me try to do that in a quick kind of introduction of this understanding phase diagram using Gibbs free energy. So as I said at a given T and P, G should be minimum, so essentially the phase diagram what we obtain is basically because our G shift with the changes in the temperature, pressure and so forth and thus you keep saying different kind of phases because Gibbs free energy is function of temperature, pressure and of course in this composition.

So but if we look at G, G can written as also in a molar form H minus TS, so if the G to be minimum or you can lower the G by lowering H or by increasing entropy. Now think from molecular picture if you want to lower enthalpy it is indicative that liquid phase is more preferred for doing that and increasing entropy means that in a vapor phase will be more preferred, so that is there is some kind of competition between this enthalpic and entropic behavior of the system, so there is a trade off in order to obtain a phase there will always be a competition between this two different element.

One would like to condense other would like to expand in order to increases the entropy.



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So let us little bit try to look at from the phase diagram point of view, so I am going to draw a Txy plot, so this is a typical Txy plot for binary mixture. Now here P is P system, so this is your vapor phase which could be your which we can say super-heated. This is your liquid phase sub cooled. Now I am going to consider three temperatures one in the super-heated vapor phase the other one is in the two phase and third is in a sub cooled liquid phase. So let us consider three of them, so first is let us look at sub cooled liquid and as the question that what would be the behavior of molar fuel energy  $G$  as a function of  $x_1$  and here if we look at the  $T$ , so the important thing is that this  $T$  here is less than the boiling point of 1.

So that is something which is there because lower this  $T$  here is here. Now if that is the case you can clearly say that well it is sub cooled liquid and only one phase exist in this and hence, the for any given point which we are looking at let us  $x_1$  you would see that the liquid Gibbs free energy would be lower than that of the vapor phase. Now similarly you can consider  $T_3$ , so  $T_3$  would be something like this where  $T$  is equal to  $T_3$  greater than  $T$  bond of 1 and in this case in fact 2 also because more than here also, now in this case off course I can consider looking at it here this is only one phase and hence it is clear that the vapor phase is going to be stable and we may have something like this were this is your  $G_v$  and this is your  $G_l$  and this is  $G$  as a function of  $x_1$ .

Now what about  $T_2$ , so  $T_2$  is something like this, so here at a certain intermediate composition you see this two phase region and this is a indicative of that there would be some competition

around which would like to phase aggregate and if this you can see I can draw it that at a given temperature, these are the two points which indicates a coexistence composition which means essentially at this point one minima I should see here and this is another point where I should another see minima in the Gibbs free energy plot, because this has two stable phases, so any composition here will face segregate leading to two stable phases.

So let me draw  $G$  verses  $X$  of 1, so I expect that at this point there will be minima and decays that and since, this is something this is vapor phase, so I think that we are going to get something like this, so this is one of those point and the other point is something like this, so this is indicative that around this point of course this also means that you know eventually this was something going like this and that is why it is change in the curvature of the effective  $G$  mix and thus point the here which we can draw a tangent indicates this two point to be the stable ones which are the composition of this two that is  $x_1$  liquid and here  $Y_1$  vapor, so this is how it appears that at intermediate composition if you take any of this intermediate composition this  $G$  mix would not be favorable because of the nature of the curve here it will try to split and leading to this two points as a phase separated stable phases.

So this how we may use to understand the phase aggregation in respect to the Gibbs free energy so I will stop here and in the next class I am going to start about I will discuss about azeotrope and some of the problem related to azeotrope, so hope to see you in the next lecture.