

Thermodynamics of Fluid Phase Equilibria
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Lecture - 31
Algorithms for Vapour-Liquid Equilibria

Welcome back, in this lecture we will be continuing the thermodynamic property evaluation from volumetric data. In particular, we will be looking at the algorithms for a vapour liquid equilibrium using phi gamma approach ok.

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Thermodynamic Properties from Volumetric Data

- **Algorithms for Vapor-Liquid Equilibrium Using the Phi-Gamma Approach**
 - First, here are some important equations:

$$y_i \phi_i(T, P, \mathbf{y}) P = x_i \gamma_i(T, P, \mathbf{x}) P_i^{sat}(T) \phi_i^{sat}(T) \exp \left[\int_{P_i^{sat}}^P \frac{v_i^L}{RT} dP \right] \quad (1)$$

$$y_i = \frac{x_i \gamma_i P_i^{sat} \phi_i^{sat} \exp \left[\frac{(P - P_i^{sat}) v_i^L}{RT} \right]}{\phi_i P} \quad (2)$$

$\sum y_i = 1$

$$x_i = \frac{y_i \phi_i P}{\gamma_i P_i^{sat} \phi_i^{sat} \exp \left[\frac{(P - P_i^{sat}) v_i^L}{RT} \right]} \quad (3)$$

$\sum x_i = 1$

So, we will start with the basic phi gamma approach equation, which is this ok. And now what we are going to do is, we are going to rearrange it is expression in different forms, and that would be useful depending on what particular data are available. So, you can write y i mole fraction in the vapor phase or gas phase as this. Or x i in this form ok. So, if you take consider y here, you take this in a denominator, you get phi ip. So, this is the expression ok, or if you are interested to evaluate x i ok, you divide this term in the denominator, which is this ok.

So, these 2 terms can be evaluated we can get it from the general expression which we have ok. Now since we know that summation y i is one our summation x i is equal to 1. So, we can also use these expressions in order to come up with the falling one. So, for this one is the case, when we try to use equation 2, and this expression.

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Thermodynamic Properties from Volumetric Data

$$\sum y_i = 1 \Rightarrow 1 = \sum_{i=1}^m \left\{ \frac{x_i \gamma_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp\left[\frac{(P - P_i^{\text{sat}})v_i^L}{RT}\right]}{\phi_i P} \right\} \quad (4)$$

$4 \times P$

\Rightarrow

$$P = \sum_{i=1}^m \left\{ \frac{x_i \gamma_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp\left[\frac{(P - P_i^{\text{sat}})v_i^L}{RT}\right]}{\phi_i} \right\} \quad (5)$$

$\sum x_i = 1 \Rightarrow$

$$1 = \sum_{i=1}^m \left\{ \frac{y_i \phi_i P}{\gamma_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp\left[\frac{(P - P_i^{\text{sat}})v_i^L}{RT}\right]} \right\} \quad (6)$$

So, if you do that so, this is due to y_i equal to 1, which will give us this, and if we multiply P both side, we are going to get this expression. So, if this 4 if you multiply P then this will give us this expression. Similarly, we know that this expression if we can use this and plug x_i from here we get this expression ok. So, this is so, these are the 4 6 equations which are going to be extremely useful for us in the later part when we are going to discuss the algorithms, depending on where there is a bubble point calculation or d point calculation. For when we consider summation y equal to 1, we got P in this expression.

Similarly, here what we can do is we can also evaluate p , we can take out P here and P is equal to 1 divided by this expression or in other word, it will be simply the inverse of this ok.

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Thermodynamic Properties from Volumetric Data

$$P = \left(\sum_{i=1}^m \left[\frac{y_i \phi_i}{\gamma_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp \left[\frac{(P - P_i^{\text{sat}}) v_i^{\text{L}}}{RT} \right]} \right] \right)^{-1} \quad (7)$$

- Initial guess for T in BUBBLE T: *x_i are given*

$$T = \sum_{i=1}^m x_i T_i^{\text{sat}} \quad (8)$$

$$T_i^{\text{sat}} = \frac{B_i}{A_i - \ln P} - C_i \quad (9)$$

$$P_1^{\text{sat}} = \sum_{i=1}^m \left[\frac{x_i \gamma_i \left(\frac{P_i^{\text{sat}}}{P_1^{\text{sat}}} \right) \phi_i^{\text{sat}} \exp \left[\frac{(P - P_i^{\text{sat}}) v_i^{\text{L}}}{RT} \right]}{\phi_i P} \right]^{-1} \quad (10)$$

$s \rightarrow$

Now this 7 equations, we are going to try to use it depending on what kind of calculation we are talking about. Now let us also consider cases, where we have to come up with the initial cases. So, for example, for the case of bubble point where T, where the temperature has to be estimated or initial guess has to be given. Then we will be considering so, considering this a bubble point, which essentially means that information of x is are given right. So, the bubble of vapor we have to evaluate at which conditions the bubble is formed.

So, if x is are given then we can consider in a showcase of the temperature at which this is happening or at which this equilibrium exists, by taking the mean value or weighted value of this T_i sat; where T_i sat is for the saturation temperature for individual pure components. Where T_i can be also related to the pressure of this you know a system whereby his entire equation ok. In addition, we can also consider where P 1 sat, you know, if you are just looking at one of the equation, then we can look at here.

Since x is are given; that means, we do not know the y I so, we consider this equation first. And here what we can do is we can take out a one we can divide this by P 1 sat multiplied by P 1 sat ok, take out P 1 sat outside right, and this rest of the things will go to the denominator part. And this can be written in this form. So, P 1 sat is x 1 as summation of x i gamma i this term, and multiply with the rest of the term, and this is inverse of that. Now this is useful because you can just focus on one of the pressure

component of one of the saturation pressure of a component let us say one. And we use this information to solve problems ok.

Again, you can connect this thing by the temperature by the central equation relations.

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Thermodynamic Properties from Volumetric Data

$$T = \frac{B_1}{A_1 - \ln P_1^{sat}} - C_1 \quad (11)$$

Initial guess for T in DEW_T:

$$T = \sum_{i=1}^m y_i T_i^{sat} \quad (12)$$

$$P_1^{sat} = \sum_{i=1}^m \left\{ \frac{y_i \phi_i P_i^{sat}}{\gamma_i \phi_i^{sat} \exp\left[\frac{(P - P_i^{sat}) v_i^L}{RT}\right]} \right\} \quad (13)$$

Eq. 7

$\{x_i\}$
 $\{y_i\}$ are given

Of course, be a cs are the constants for a given component. Similarly, for d point particular temperature calculation you have to guess temperature. So, we are talking about dew point which essentially means, the composition of the x are unknown, but ys are given. So, again you start with a narrated value of temperatures of the individual component saturation temperature with respect to the composition in the vapor phase. And here this since summation x our x are known.

So, you are going to make use of equations where y is available. So, here what we have done is we have taken the ps, here if you realize this expression and take out the P 1 multiplied by the same P 1 here. Then you should be able to show that the same expression here equation 7 can be written in this form particularly relating P 1 to this ratios or the P 1 and P i ok.

So, this is also useful to make use of it. So, remember that equation 7 rearranging would lead to 13 ok. And for the case of the bubble point it is equation 5; which allows you to get equation 10 ok. So now, these are the set of equations which are available for us, and now we should be able to come up with an algorithms depending on what kind of data is

which we are given. So, instead of going into details I will just discuss the procedural aspect of it in order to understand how to solve the problem for given set of data.

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Thermodynamic Properties from Volumetric Data

- **BUBBLE_P:** Given $T, \{x\}$ calculate $P, \{y\}$
 1. Read in $T, \{x\}$, all constants (Antoine constants, pure liquid molar volumes, etc). Set all $\phi_i = 1$ and Poynting corrections to 1.
 2. Evaluate $P_i^{sat} \Rightarrow \phi_i^{sat}$ and v_i^L (since they only depend on temperature)
 3. Evaluate P from,

$$P = \sum_{i=1}^n \frac{x_i y_i P_i^{sat} \phi_i^{sat} \exp\left(\frac{(P - P_i^{sat}) v_i^L}{RT}\right)}{\phi_i}$$

y_i from

$$y_i = \frac{x_i y_i P_i^{sat} \phi_i^{sat} \exp\left(\frac{(P - P_i^{sat}) v_i^L}{RT}\right)}{\phi_i P}$$

1. Evaluate ϕ_i and Poynting corrections
2. Is this the first iteration? If yes, go to step 3.
3. Is δP , the change in P between the last and present iteration, less than ε (a convergence criterion)? If not, go to 3.
4. Print $P, \{y\}$.

So, we will consider now for the bubble point. So, bubble point essentially means, the information of the liquid are given, now it depends by the temperature is given or pressure is given. So, in this case bubble point P means, that we have to calculate the pressure for a given temperature and composition ok. Bubble point T would mean that we have to calculate temperature for a given pressure and composition. So, let us look at this case which is both point P ok.

So, you read the information of temperature, and all composition for all constant now this constants would be entering constants for pure liquid molar volume etc ok because now you have n number of components. So, you have to get the information of n to n constants which would relate the saturation temperature and pressure. And that is important force in the set of equations which we are going to consider. Now remember that since initially we do not have any information.

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Thermodynamic Properties from Volumetric Data

- Algorithms for Vapor-Liquid Equilibrium Using the Phi-Gamma Approach
 - First, here are some important equations:

$$y_i \phi_i(T, P, \mathbf{y}) P = x_i \gamma_i(T, P, \mathbf{x}) P_i^{\text{sat}}(T) \phi_i^{\text{sat}}(T) \exp \left[\int_{P_i^{\text{sat}}}^P \frac{v_i^L}{RT} dP \right] \quad (1)$$

$$y_i = \frac{x_i \gamma_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp \left[\frac{(P - P_i^{\text{sat}}) v_i^L}{RT} \right]}{\phi_i P} \quad (2)$$

$$x_i = \frac{y_i \phi_i P}{\gamma_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp \left[\frac{(P - P_i^{\text{sat}}) v_i^L}{RT} \right]} \quad (3)$$

$\sum y_i = 1$
 $\sum x_i = 1$

And at the end we are trying to solve you know this is the relation of the equilibrium. So, in this case what we are going to do is we are going to start with an approximation. So, we always start with an approximation considering the ideality of the saturation fugacity of component i that will be one; that means, we can see consider to be like an ideal gas as far as the situation is concerned and then as well as the, we considering the pointing correction to be one.

So, this is what we always start with that set phi i equal to 1, and pointing correction to one ok. And then you will try to get the more realistic value by using iterations. Now given this information, and as well as your given T, for a given T and n to n constant you can find out for all the component P i set all is all right. So, you can also find out phi i sat also and gamma i ok. Now phi i sat you can try you can find out by using the volumetric information.

This is for the pure system remember that. So, we should be able to directly use the molar volume properties given here for pure liquid volume. And with their integrated with respect to the pressure from 0 to P sat, given that you have calculated P i said you should be able to get phi i sat. And as well as gamma i, now gamma i is depends only on the temperature, and this is something which we have not given information as far as the models are concerned. So, the activity models we are going to consider later part of it. As of now we are just telling you know emphasizing that we have to also calculate the

gamma is given that information is available. So, without going to details of the models, we are just stating that gamma i we can calculate now.

Now, you have the information of phi you have the information of P_i and ϕ_i and gamma i, you can evaluate now the pressure from which equation. So, if you look at it this is the equation 5 x is are given gamma i ϕ_i sat you have calculated ϕ_i you calculated molar volume informations are available. V_i sat is informations available and of course, the initial value we have considered ϕ_i to be 1, ok. So, hey this is what we have got back here. So, we can evaluate here now initially we have said this to be 1 and this to be 1. So, we get an estimate of pressure from here. Once we have got an estimation of the pressure, we can use y_i from here ok. So, remember in the first iteration, we have got ϕ_i to be one, and pointing corrections to be one ok.

Now, after evaluating y_i you have new information, now you can calculate ϕ_i also. Because ϕ_i depends on the partial molar volume in properties. And now using the expression which we have derived earlier, we can get ϕ_i . Also, and of course, you can also get pointing correction, because you know the P_i said P and other information.

Now since if it is the first iteration, then you go back to this 3 ok, and collect this information p. So, you keep doing that until your ΔP the changes in the pressure value, and the current iteration in the present iteration is much less than some value epsilon which should be very small which would be a convergence criteria ok. If not, you keep doing this exercise that is how we obtain this pressurizer, and as well as the composition. So, this is what we call it bubble point pressure ok. Now these type over here so, this should have been actually 3, 4, 5, 6 and so forth, but I hope that you understand the meaning of this going back and iterating here.

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Thermodynamic Properties from Volumetric Data

- **DEW_P:** Given $T, \{y\}$ calculate $P, \{x\}$
 1. Read in $T, \{y\}$, all constants. Set all ϕ_i, γ_i and Poynting corrections to 1.
 2. Evaluate P_i^{sat}, ϕ_i^{sat}
 3. Evaluate P from Eq. ,

$$P = \left[\sum_{i=1}^n \frac{y_i \phi_i}{\gamma_i P_i^{sat} \phi_i^{sat} \exp\left[\frac{(P - P_i^{sat})v_i^L}{RT}\right]} \right]^{-1}$$
 4. x_i from Eq. $x_i = \frac{y_i \phi_i P}{\gamma_i P_i^{sat} \phi_i^{sat} \exp\left[\frac{(P - P_i^{sat})v_i^L}{RT}\right]}$
 1. Evaluate ϕ_i, γ_i and Poynting corrections
 2. Is this the first iteration? If yes, go to step 3.
 3. Is $\delta P_i < \epsilon$? If not, go to 3.
 4. Print $P, \{y\}$

So, let us also look at this temperature there is another case which is basically the dew point calculations; where the composition in the vapor phase is given, and here the pressure has to be evaluated, that is why it is called dew point pressure calculations or dew P which we are written in the short form. So, here again the temperature is given composition of the vapor vapour phase is given and we have 2 valid pressure n x here.

So, what we are going to do is we are going to read this value all the constants and the molar informations, set this informations to one, initially evaluate again the same way as we have done for the P i sat and as well as the fugacity coefficient of the saturation system. Now since it is ys are given you have to come up with a different equation, this equation would be this one, with y is a given. So, initially gamma is we are going to take in one P i sat we know y i sat we know, this is one. So, we got an information of P from here ok.

So, this is what we got. We got the information of P here. Now xiv calculate going back to the original phi gamma expression xi, we calculate from here ok, now again we are keeping the same like we are keeping gamma is to be one in this case and the important correction to be one phi to be one. Now we can evaluate phi i and gamma in point correction considering that we have this information available. We weathered the phi again if this is the first then the first iteration then we will go back to this thing.

So, we can keep doing this exercise until delta P is less than eq, less than some epsilon which is basically the convergence criteria. And then we finally, print out the pressure ok. Now the previous exercise was all bubble point calculation dew point calculation, this is going to be bubble temperature and dew temperature.

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Thermodynamic Properties from Volumetric Data

- **BUBBLE_T:** Given $P, \{x\}$, calculate $T, \{y\}$
 1. Read in $P, \{x\}$, all constants. Set all $\phi_i = 1$ and Poynting corrections to 1.
 2. Calculate initial guess for T from Eq. $T = \sum x_i T_i^* \phi_i^{sat}$. Evaluate P_i^{sat} / P^{sat} , ϕ_i^{sat} and y_i (since they only depend on temperature).
 3. Evaluate P_i^{sat} from Eq. 10, T from Eq. 11.

$$P_i^{sat} = \left(\frac{x_i \left(\frac{P_i^{sat}}{P_i^*} \right)^{\phi_i^{sat}} \exp \left[\frac{(P - P_i^{sat}) V_i^L}{RT} \right]}{\phi_i^P} \right)^{1/y_i}$$
 4. Using the new value of T , evaluate P_i^{sat} , ϕ_i^{sat} and y_i from Eq. (2)

$$y_i = \frac{x_i \gamma_i P_i^{sat} \phi_i^{sat} \exp \left[\frac{(P - P_i^{sat}) V_i^L}{RT} \right]}{P}$$
 5. Evaluate ϕ_i , γ_i (since they may be temperature dependent) and Poynting corrections and P_i^{sat} / P^{sat} .
 6. Is this the first iteration? If yes, go to step 3.
 7. Is δT , the change in T between the last and present iteration, less than ϵ (a convergence criterion)? If not, go to 3.
 8. Print $T, \{y\}$

So, in this case for the case of bubble temperature you have the pressure information available, and then you have to calculate temperature ok. So, bubble again means the composition of the liquid phase is available. So, that the pressure is given that is why it is (Refer Time: 14:21) because T we have to evaluate. Now again read this information all constant set this information to 1. So now, the remember that you may ask this question that in this case why we had to keep gamma i equal to 1 ok. Now you actually could have simply calculate gamma also as well because gamma depends on the temperature, but this is one of the simplest way to do that here also we have kept. So, gamma to be 1, but you can evaluate gamma also directly if the models available ok.

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Thermodynamic Properties from Volumetric Data

- **DEW (T)** Given $P, \{y\}$ calculate $T, \{x\}$
 1. Read in $P, \{y\}$, all constants. Set all ϕ, γ , and Poynting corrections equal to 1. Σ y_i T_i^{sat}
 2. Calculate initial guess for T from Eq. (12). Evaluate P_1^{sat} / P_1^{sat} and ϕ_1^{sat}
 3. Evaluate P_1^{sat} from Eq. (13), T from Eq. (12). Using the new value of T , evaluate P_1^{sat} , ϕ_1^{sat} and x_1 from Eq. (2). φ-y emp
 4. Evaluate ϕ, γ (since they may be temperature dependent) and Poynting corrections and P_1^{sat} / P_1^{sat}
 5. Is this the first iteration? If yes, go to step 3.
 6. Is δT less than ϵ ? If not, go to 3.
 7. Print $T, \{x\}$

Here again we are doing the same exercise, that for bubble T when the composition of the liquid phase is available. We read this information set all the files to be one pointing correction to be 1, calculate initial temperature because temperature is in it by simply there taking the weighted value of the T sat. Evaluate this information which is now P i sat divided by P 1 sat and phi i sat and gamma i ok.

So, you evaluate because now you have the temperature information you value it. So, P i sat for all the saturation pressure components is based on the of course, the n to an equation and the temperature is given here now is estimated or initial guess is this. So, once you have done that we can evaluate P 1 sat from here, the new P 1 sat based on this expression, which is nothing but equation 11 if you recall this was what was the initial guess for temperature, for in the bubble temperature curve portion. So, we are valuate from this and now using the new T value of T and P i sat phi i sat, we evaluate for y one from the basic phi gamma expression.

Using this information, we can evaluate phi i gamma i ok, and pointing correction and as well as new value of this. Now if this is the first iteration we go back ok, and do this. So, this is how we can work on it ok. Now similarly for the dew temperature calculation, again, let me just go quickly here. Here in this case the is the temperature we have to evaluate; that means, pressure and the composition of the vapor phase is given you read all the information. Set initially the phi i gamma is in pointing to one initial temperature

is from the weighted value of d_i^{sat} ok. The same way as we have done this one ok, evaluate the ratios of the P_1^{sat} and P_i^{sat} and ϕ_i^{sat} .

Now P_1^{sat} from equation 13 we are going to use which was this ok. This is again the estimate the P_1^{sat} because this is estimated. And these are the constant this is one we have considered this is one way of considered and we have evaluated. This this is one we have considered ok.

You estimated P_1^{sat} from equation 13 ok. Temperature from again equation 2 which is a weighted value of T_1^{sat} with respect to the composition. Using the new value of T , we evaluate P_y^{sat} ϕ_i^{sat} and x_i from equation 2 ok. This is again from the basic ϕ_i^{sat} γ_i expression. Evaluate ϕ_i^{sat} γ_i ok, n pointing correction as well as ratio and if this is the first iteration you go back and do that ok. So, this is typical so, the major important aspect of this kind of algorithm is that you are basically relying on the ϕ_i^{sat} γ_i expression.

Now irrespective of whether is a dew point temperature or bubble point temperature, what you are going to do is basically you are going to manipulate this expression, and make some certain assumption. So, the initial guess becomes an important. For temperature it becomes straightforward you take a mean value of that. You make us make a use of the antoine equation to connect to the pressure and temperature which is quite valid, because of the usually the logarithmic relation between the saturation pressure and temperature. And then you make use of the ϕ_i^{sat} information which you connect to the volumetric data, and the γ_i information which is activity using a certain model; which we have not disclosed at this point, but this is the usual algorithm.

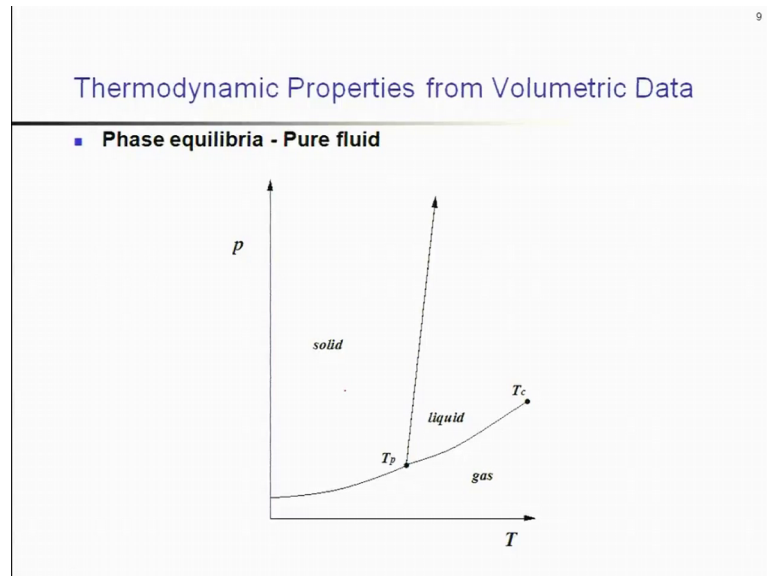
Now, we are not showing any detailed exercise, because this kind of algorithms are used to solve some more complicated which usually is not easy to depict using this simple hand, you know, pen and paper you may have to employ excel sheet, or some MATLAB code in order to solve this much much easily, excel sheet has a goal seek pro approach you can use the function goal seek to solve iteratively certain solution based on this algorithm which we have shown ok.

So, I hope that this gives an idea how to solve problems related to phase equilibria using ϕ_i^{sat} γ_i approach, and using the set of equations which we have written based on the

phi gamma expression. Now in the last few minutes of this lecture, I will just describe a bit on the types of the phase equilibria are which we see in the mixtures ok.

You are well aware of at least this phase diagram or P T diagram for pure fluid ok.

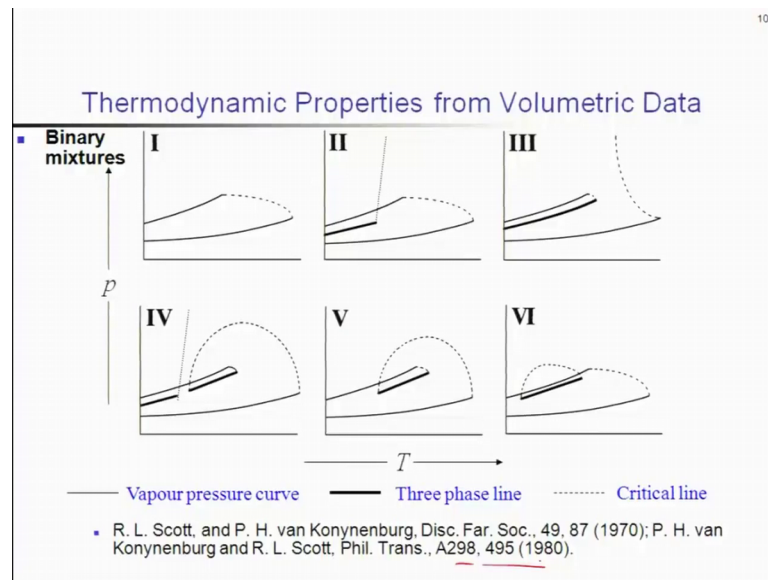
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Where you have this saturation vapour line here ok, which range starts from T P ends at T C, T C is a critical point. And this is the maximum temperature at which the vapor gas can coexist. So, solid liquid line is here and this is the gas liquid and solid phases stable phases. Now it appears to be simple as far as a few pure fluid is concerned, but as we add components, as we introduce mixtures, we have in addition to pressure and temperature.

And volume we have an additional variable called composition ok. And thus, we cannot easily draw typical phase diagram of a binary mixture for example, ok. But fortunately, the binary phase diagram has been classified by Scott and van in 70's and I am going to describe the types of different binary phase diagram which we see in in experiments ok.

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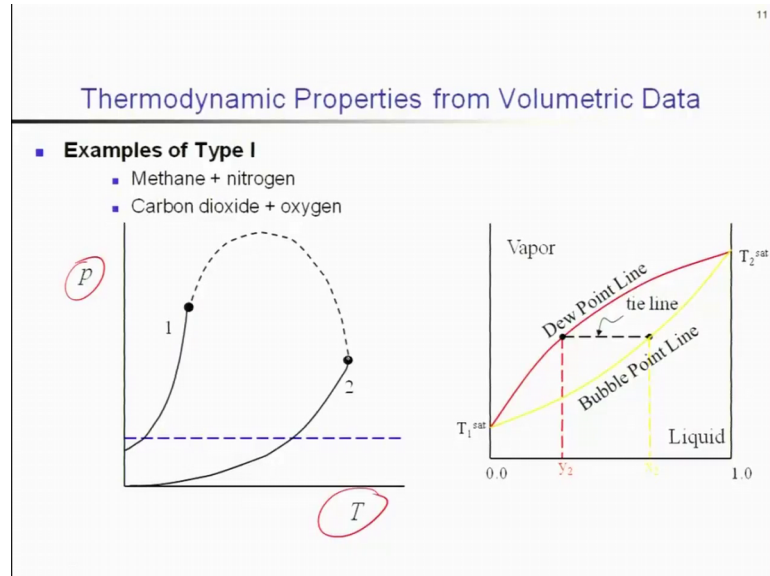
So, this is a typical binary mixture phase diagrams. And there are different types which have been which has been considered or categorized by Scott and van, using some classification scheme ok. So, this is type one so, this line basically is a vapor pressure curve and this is a pressure against temperature. Just like what you have seen here ok, this was nothing but the line saturation line. So, this is the same as this, but here these are 4 different components ok. And the dotted line here is basically critical line.

So, in this case for the pure system you have just one point, but for the binary mixture there is in there is a line of critical point. So, that each point this is the maximum temperature at which the phase equilibria can coexist for a given composition ok. So, that becomes one point. And so, for the u value the composition you would have a different critical point, and when you connect them you be get a critical line, alright. Which range from the end point of the vapor pressure for the pure system to another one ok.

So, this is the way it has been drawn. Now in addition to vapor pressure line critical line, you have 3 phase line where the 3-phase coexistence again remember here this is one only one point, as far as 3 phases are concerned on a P T diagram ok, but here there will be line of such points ok, which is called 3 phase line ok. And that again depends on the composition right. So, this is what we are drawing here. And now different types here

would lead to different types of binary emissions ok, and this is well described in this paper ok. So, I would not go through the details because it is a bit messy here.

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But to just to illustrate at least to give a idea what I am going to do is I am going to spend some time on this example of type one which is a commonly seen binary mixtures phase diagram, and examples of the methane and nitrogen or carbon dioxide and oxygen.

So, type one basically is a simplest class of phase diagram of phase behavior usually seen for mixtures of nonpolar substances of a similar chemical type such as mixture of homologous series such as alkanes ok. So, here what we have is a P T projection of type one phase diagram, pressure on on y axis ok. And temperature on the x axis so, here the vapor pressure curve of component 1 and 2 are ending in a gas liquid critical point.

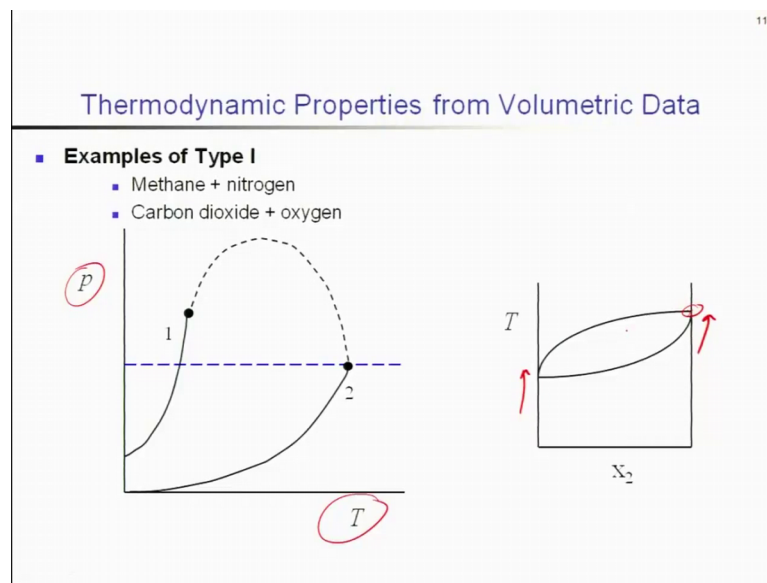
And having a continuous a gas liquid critical line connecting the critical points of the 2 pure components, and this type of the phase diagram, you must have seen in some earlier thermodynamics courses ok. Now if we take a slice of the pressure constant pressure line, we have a familiar Tx diagram, which is this this is temperature, this is x. Now here what we have is basically vapor up here, and the low temperature liquids are there. So, there is a dew point line and the bubble point line ok.

And here at this point if you draw a straight line that becomes this 2 point represent the phases which are at equilibrium having a composition y and this is composition x ok. So,

at low pressure below the critical point either pure component or the pretty critical point, the gas liquid coexistence envelope spans the full composition range. So, this is a full composition range ok. From the vapor pressure point 1, component to the vapor pressure of component 2, that is what we are talking from this point to this point ok.

So, now if we take consider different lines here such that the pressure line now connects to the critical point of phase 2.

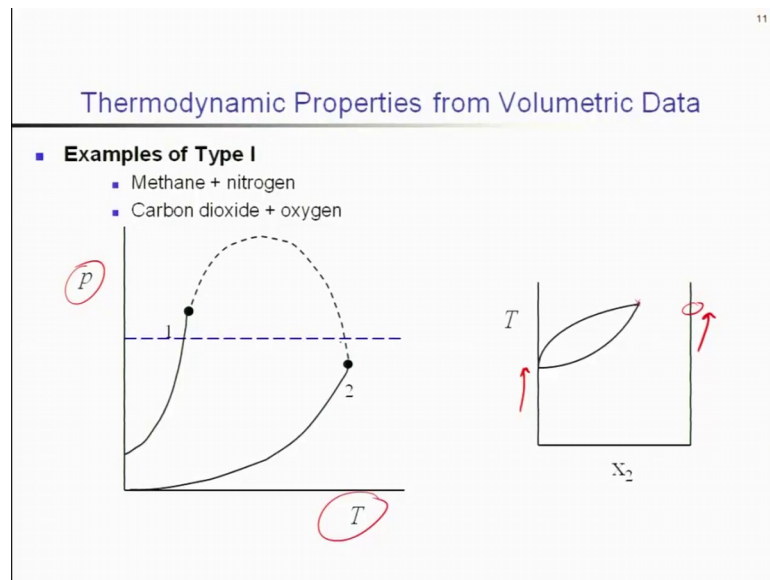
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Remember, this one is more volatile, but at low temperature you see the critical point. So, at low pressure of course, you get the complete one. Now if you increase the pressure here, such that it is increased to the critical pressure of the component 2. The gas liquid critical point of pure component appears at the axis here ok. So, this is shifted up here remember this let me just show this.

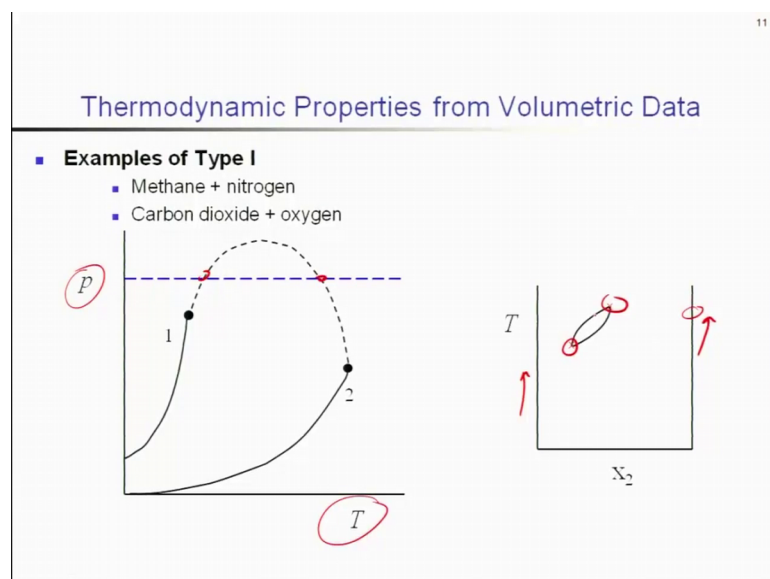
So, this is as we increase the temperature you see this is shifted up here. So, this goes up in the direction ok. And when this line the constant pressure line is here, then basically this point is represented by this cross; which means this is the gas liquid critical point of the pure component appears on the axis, and this becomes the the region which which is a critical; that means, the 2-phase region is now constrained it from here to here here.

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Now, if you go a little bit up also in the pressure what do you see? This always from gets away from this axis, and this is bound by this particular critical point which is here a critical line represented here ok. So, that means, at higher pressure, now wave P C of component 2 the region of gas liquid coefficient retreats from the axis giving a gas liquid critical point for the binary mixture; which is a point on the gas liquid critical line here in the P T projection; if you look at higher pressure still, yes.

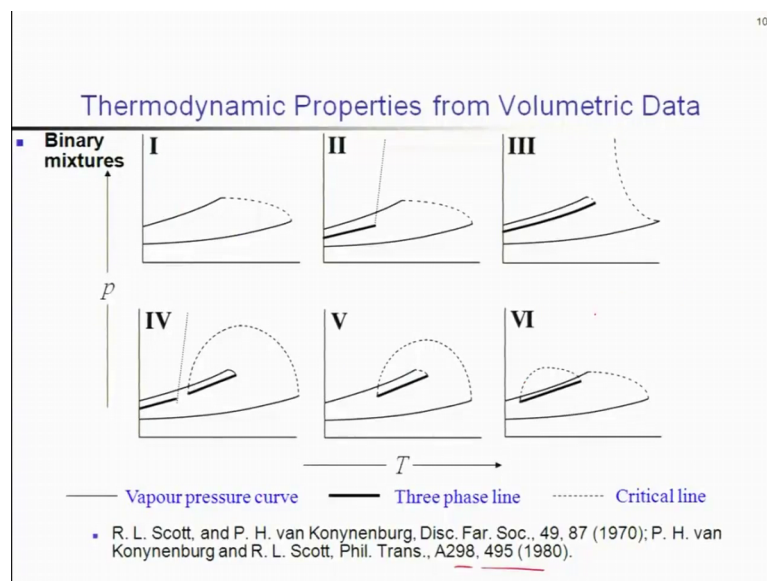
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So, this is the high pressure, where we are now you have the critical point of both the pure component the gas liquid coexistence envelope is now bound by 2 gas liquid critical point ok, which corresponds to this point. So, this regions are shrunk, and does it can it does not span the whole composition range.

So, you can clearly see that this phase diagram in binary mixtures a simple addition of one component creates a lot of different variety of phase diagrams. And hence it requires more in depth understanding of the variations in different components in order to appreciate the phase diagram. So, particularly what you saw just now by changing the variations in the pressure, and how that affects the 2 phase regions you know Tx diagram. And this was only type one type 2 type 5 and all this have more complicated behavior. And I just wanted to illustrate this without going through details and the more details of course, you can see in the paper which we mentioned here ok.

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But I will stop here, and this would be the end of the exercise on the thermodynamic property from volumetric data. There will be examples or assignments which will help you to work on these concepts. And the next lecture we will start a new topic based on statistical mechanics. So, a bit to give you an idea about relations of thermodynamic property to the microscopic informations, and as well as will be also looking at the different types of the intermolecular forces experienced by molecules in systems ok.

So, I will see you in the next lecture.