Advanced Thermodynamics
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Lecture-23
Vapour - Liquid Equilibrium

Welcome to the MOOCs course advanced thermodynamics, the title of this lecture is vapour liquid equilibrium. Now, having seen almost all details of non-ideality of vapour as well as the liquid phase now, we have come to a stage where we can apply those fundamental basic principles to realistic problems. So, now that is what we are going to start with today's lecture and then coming few lectures. So, today we start with the vapour liquid equilibrium problems.

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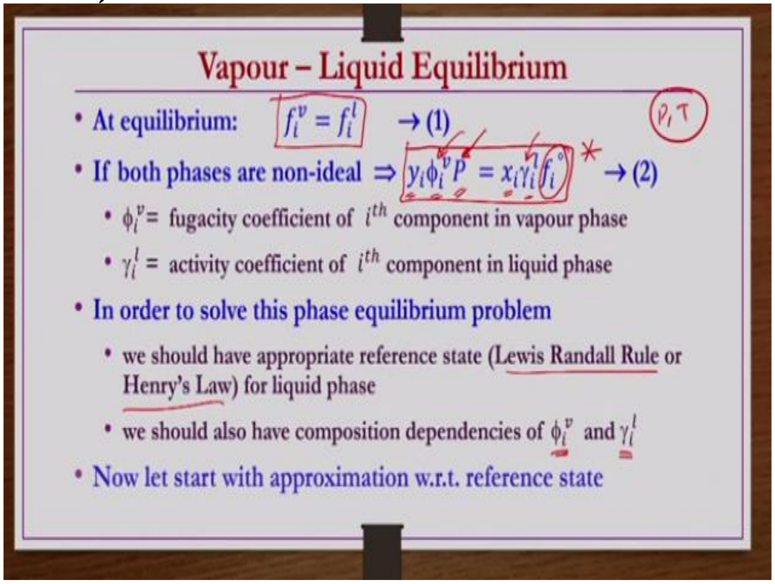

Vapour – Liquid Equilibrium

P, T

- At equilibrium: $\boxed{f_i^v = f_i^l}$ → (1)
- If both phases are non-ideal ⇒ $\boxed{y_i\phi_i^v P = x_i\gamma_i^l f_i^\circ}$ * → (2)
  - ϕ_i^v = fugacity coefficient of i^{th} component in vapour phase
  - γ_i^l = activity coefficient of i^{th} component in liquid phase
- In order to solve this phase equilibrium problem
  - we should have appropriate reference state (Lewis Randall Rule or Henry's Law) for liquid phase
  - we should also have composition dependencies of ϕ_i^v and γ_i^l
- Now let start with approximation w.r.t. reference state

At equilibrium what we know they fundamentally very first week we realized that the chemical potential of each component in all coexisting phases which are at equilibrium are same. So, that is what our chemical potential of any component is same in all the phases that are coexisting and which are at equilibrium that is what we have seen. So, from there what we realized? We realized that not only chemical potential fugacity of that particular component is also same in all the phases which are coexisting and equilibrium that is what we have seen.

And then we have this $f_i^v = f_i^l$ for vapour and liquid equilibrium because now we have started discussing the vapour liquid equilibrium problems and then for the vapour phase if it is having non-ideality fugacity we can obtain by y_i ϕ_i^v P = and then if it is liquid phase non ideality can be brought into the picture by x_i γ_i^l f_i^0that is what we have already seen.

So, that is both vapour and liquid phases are having non ideality. So, then this equation we will be having. So, now, if you wanted to know equilibrium composition let us say y_i x_i you wanted to know y_i x_i are nothing but the mole fraction of component i in the vapour phase which is in equilibrium with the liquid phase composition. So, the vapour phase composition is nothing but y_i. And then liquid phase composition is nothing but x_i these 2 are in equilibrium with each other.

So, if you wanted to find out this is y_i and x_i you should know what is ϕ_i^v that we have already seen how to obtain it for several cases and then you should also know for the liquid phase what is γ_i^l, this also we know depending on the information about the excess molar Gibbs energy if you have that information then activity coefficient of component A. You can find it out and then pressures usually given are available.

And that depends on the degrees of freedom if it is a 2 component binary mixture 2 faced binary mixture then degrees of freedom are 2. So, if you know any 2 independent variables the rest all other you can calculate without any difficulty that is what says the Gibbs phase rule. So, let us say P and T are known. So, P is also known x_i, y_i you have to calculate so now; if you wanted to solve this equation not only about information ϕ_i^v.

And then γ_i^l, you also need to know information about this f_i^0 because in the vapour phase or the gaseous phase reference state are general fixed in terms of ideal gas behavior or with reference to the ideal gas behavior we define this fugacity of non-ideal vapour phase or gas phase. So, there we have directly pressure. But in the case of liquids, the reference states are you know not one single reference states so different reference states are possible.

So, $f_i^0$is nothing but the fugacity of component i in the liquid phase so f_i^0, what it is if you know this one also then we can solve this problem without any difficulty. So, ϕ_i^v is fugacity coefficient of ith component in the vapour phase γ_i^l is nothing but activity coefficient of ith component in the liquid phase. Now, in order to solve this problem you need to know reference state for f_i^0 and then you should also know composition dependent ϕ_i^v and γ_i^l reference state for f_i^0.

It can be Lewis Randall Rule it can be Henry's law as well as we have seen. So, now, what we do for simplicity we take the case of ideal mixture that is both the liquid and vapour phases are obeying ideal behavior and then start doing the problems because from there it will be easy to develop and bring into non-ideality of the liquid phase and the non-ideality of the vapour phase simultaneously as a kind of gradual incremental order.

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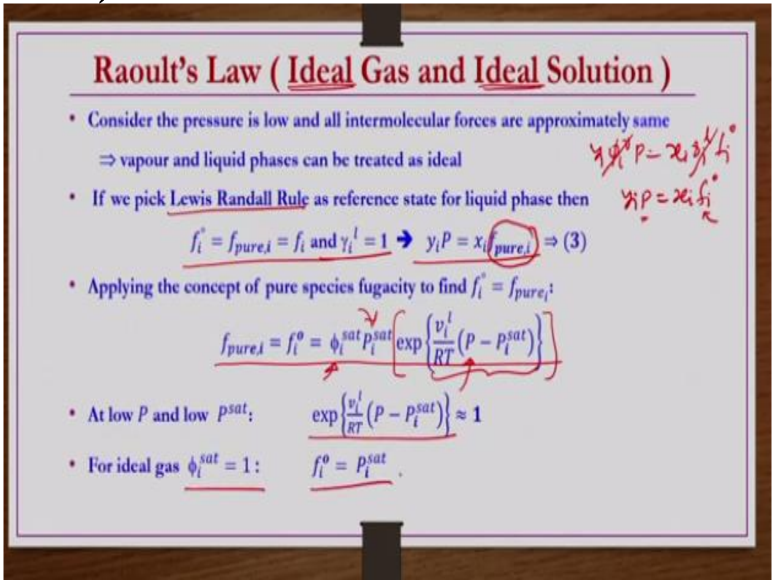

Raoult's Law (Ideal Gas and Ideal Solution)

- Consider the pressure is low and all intermolecular forces are approximately same
  $\Rightarrow$ vapour and liquid phases can be treated as ideal
- If we pick Lewis Randall Rule as reference state for liquid phase then

$$f_i^\circ = f_{pure,i} = f_i \text{ and } \gamma_i^l = 1 \rightarrow y_i P = x_i \boxed{f_{pure,i}} \Rightarrow (3)$$

- Applying the concept of pure species fugacity to find $f_i^\circ = f_{pure_i}$:

$$f_{pure,i} = f_i^o = \phi_i^{sat} P_i^{sat} \left[\exp\left\{ \frac{v_i^l}{RT}(P - P_i^{sat}) \right\} \right]$$

- At low P and low P^{sat}: $\exp\left\{ \frac{v_i^l}{RT}(P - P_i^{sat}) \right\} \approx 1$
- For ideal gas $\phi_i^{sat} = 1$: $f_i^o = P_i^{sat}$.

$y_i \cancel{\phi_i^v} P = x_i \cancel{\gamma_i^l} f_i^\circ$

$y_i P = x_i f_i^\circ$

So, now, we take a case where the vapour phase is also ideal and then liquid phase is also ideal then under such conditions we can say whatever the principle that we are going to develop that is known as the Raoult's law that is what we are going to see. Now, consider the pressure as low, if the pressure is low then only you can say that the vapour phase is ideal and in addition to the low pressure also assume.

That the intermolecular interactions are like interactions unlike interactions whatever the interaction that we have seen, all the interactions are same in the given liquid phase so, that the liquid phase is also always a kind of ideal behavior. So, when you have the pressure is low and in all intermolecular forces are approximately same then we can say vapour and liquid faces both can be treated as ideal.

Now, if we take Lewis Randall Rule as reference state for liquid phase because whatever this y_i ϕ_i^v P = x_i γ_i^l f_i^0. So, now here ideal phases we have taken, so, fugacity coefficient and activity coefficients are equals to one for both of them then we get this equation as y_i P = x_i f_i^0 still though the pressure is known you how to find out x_i and y_i. So, but still you do not know f_i^0 so, for f_i^0 we have to make a kind of a reference state we have to consider a reference state.

So, let us say if you take the Lewis Randall Rule as a kind of reference state in order to define the fugacity of liquid phase it reference temperature pressure so, if you take Lewis Randall reference state then f_i^0 is nothing but $f_{\text{pure } i}$ that is what we have already seen. So, that means, f_i^0 equals to $f_{\text{pure } i}$ and then γ_i^l = 1. So, that we have this y_i P = x_i $f_{\text{pure } i}$. Now, still you need to have some information about $f_{\text{pure } i}$ then only you can further solve this problem easily.

Otherwise, because fugacity are of kind of much more related to the measurable temperature pressure and then composition of the system. But still though it is better than the chemical potential, but still we need to have a kind of final form of this $f_{\text{pure } i}$ then only we can solve this equation. So, now, getting back to, you know fugacity calculation for a pure condensed phase now, $f_{\text{pure } i}$ is nothing but is a pure component. This is the reference state $f_{\text{pure } i}$ is pure and then it is the liquid phase.

So, it is the condense phase for the pure condensed phase, we have already seen this $f_{\text{pure } i} = \phi_i^{sat}\ P_i^{sat}\ \exp\left\{\frac{v_i^l}{RT}(P - P_i^{sat})\right\}$. So, now, here we have taken the pressure total pressure as a very small low pressure kind of thing we have taken in order to have a kind of ideal vapour phase. So, if the pressure is low, then obviously, P_i^{sat} is going to be much lower.

Than that because, you know below P_i^{sat} we have the vapour phase and then above P_i^{sat} we can have a kind of condensed phase etc. So, that is what the you know saturation equilibrium pressure means way so, that means if you have, you know, on both low P and then low P_i^{sat}this exponential for this term is going to be whatever in the parenthesis this entire time is going to be very small.

So, exponential of a very small quantity close to 0 is nothing but close to 1. So, that whatever the exponential of this entire time is nothing but it is very close to 1 that is also we have seen in one of the previous lectures and then for ideal phases this ϕ_i^{sat} = 1, So, then what we get $f_{pure\ i}$ is nothing but what is remaining in this term P_i^{sat}. So, at low P and low P_i^{sat} what we have we can expect this exponential term close to 1 or very close to 1 and then for ideal gas ϕ_i^{sat}= 1 so, then we have f_i^0= P_i^{sat}.

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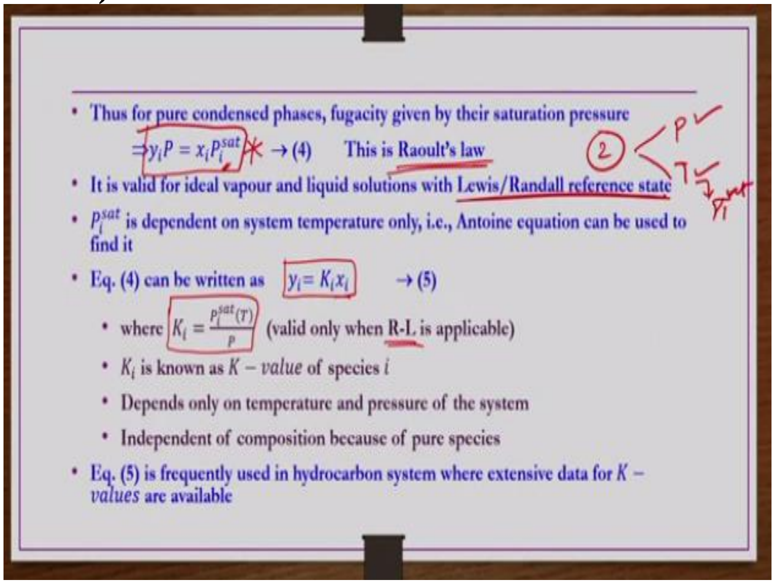

- Thus for pure condensed phases, fugacity given by their saturation pressure

  $\Rightarrow \boxed{y_iP = x_iP_i^{sat}}$ * → (4)   This is Raoult's law

- It is valid for ideal vapour and liquid solutions with Lewis/Randall reference state
- P_i^{sat} is dependent on system temperature only, i.e., Antoine equation can be used to find it
- Eq. (4) can be written as $\boxed{y_i = K_ix_i}$ → (5)
  - where $\boxed{K_i = \frac{P_i^{sat}(T)}{P}}$ (valid only when R-L is applicable)
  - K_i is known as $K - value$ of species i
  - Depends only on temperature and pressure of the system
  - Independent of composition because of pure species
- Eq. (5) is frequently used in hydrocarbon system where extensive data for $K - values$ are available

② P ✓ T ✓ → P_i^{sat}

So, that means, this equation thus for pure condensed phase fugacity to given by their saturation pressure. So, this equation whatever we have y_i P = x_i f_i^0that we can write as y_i P = x_i P_i^{sat}we are taking binary mixture and then 2 phases are there vapour and liquid. So, then degrees of freedom are nothing but 2. So, then if you fix the pressure and then temperature you can find out this x_i y_i easily.

That is what we are going to see because P is given then if T is given then you can know P_i^{sat} through the Antoine equations, because those Antonie constants almost known for all components. So, if you know those Antonie constant for a given component at a given temperature, you can find out the saturation pressure of for that particular component. So, that means, if the temperature is known $P_i^{sat}$is also known indirectly.

So, now, if you have a binary mixture a and b So, then 2 equations you will be having for a component for b component, so, 2 equations 2 unknowns would be there. So, those things you can comfortably calculate. And then, under these conditions where this vapour and liquid phase both faces are ideal then we came to final equation of this form y_i P = x_i P_i^{sat}that is, this is known as the Raoult's law.

It is valid for ideal vapour and like liquid solutions with Lewis Randall reference state with Lewis Randall reference state. Remember, if you take for liquid phase of Henry's law as a kind of reference state then f_i^0will become H_i^0 or H_i whatever the Henry's law constant state for that particular component that is the solubility of that particular component that one will be coming as a kind of additional term in the right hand side not additional term that is what we will be having a f_i^0= H_i.

So, when you say Raoult's law it is with reference to Lewis Randall reference state it is not with respect to the Henry's law reference state. So, as mentioned $P_i^{sat}$is dependent on the system temperature only that is Antonie equation can be used to find it out without any difficulty. So, equation 4 what we can write for ideal liquid phase and an ideal vapour phase we can write y_i = some constant K_i x_i and then $K_i = \frac{P_i^{sat}}{P}$.

And then $P_i^{sat}$is nothing but it is a function of temperature. So, that means, whatever this K_i that we are having it is independent of the composition. If the both vapour and liquid phases are ideal, then this K_i is independent of composition and that is what we can say and then this is valid only when RL is applicable. So, this K_i is known as the K value of species i it depends only on temperature and pressure of the system. It is independent of composition because of pure species that we are taking. So, this equation 5 is frequently used in hydrocarbon system, where extensive data for K values are available.

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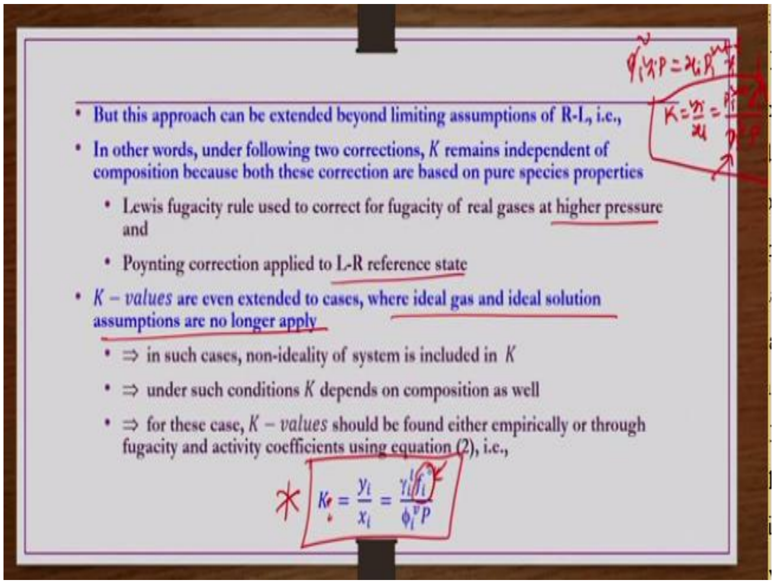

$\tilde{\phi}_i y_i P = x_i P_i^{sat}$

$K = \frac{y_i}{x_i} =$

- But this approach can be extended beyond limiting assumptions of R-L, i.e.,
- In other words, under following two corrections, K remains independent of composition because both these correction are based on pure species properties
  - Lewis fugacity rule used to correct for fugacity of real gases at higher pressure and
  - Poynting correction applied to L-R reference state
- $K - values$ are even extended to cases, where ideal gas and ideal solution assumptions are no longer apply
  - ⇒ in such cases, non-ideality of system is included in K
  - ⇒ under such conditions K depends on composition as well
  - ⇒ for these case, $K - values$ should be found either empirically or through fugacity and activity coefficients using equation (2), i.e.,

$$* \boxed{K_i = \frac{y_i}{x_i} = \frac{\gamma_i^l f_i^l}{\phi_i^v P}}$$

So, but this approach can be extended beyond limiting assumptions of RL also that obviously you are writing this y_i P = x_i P_i^{sat}, if you have this, you know, non-idealities also coming into the picture then K = $\frac{y_i}{x_i} = \frac{P_i^{sat}\gamma_i^l}{\phi_i^v \text{P}}$ this is what you have. So, now here $\phi_i^l$and ϕ_i^v and then γ_i^l are again composition dependent. That is the only difference.

If you apply this K value principle for the things beyond the assumption of Raoult's law that is beyond the cases of ideal vapour and an ideal liquid phase, then obviously this ϕ_i^l, then obviously this ϕ_i^v γ_i^l would be coming into the picture. So, then obviously, they will be composition dependent that is the only additional thing that is in other words for non-ideal systems non-ideal vapour and non ideal liquid phase.

If you wanted to find out these K_i values, this is going to be dependent on the composition also in addition to temperature and pressure. For the case of ideal behavior, it is this K_i value is going to be dependent only on pressure in temperature for non-ideal system it is also going to depend on the composition of the system. So, in other words under the following 2 correction K remains independent of composition because both these corrections are based on pure species of properties, that is Lewis fugacity rule use to correct for fugacity of real gases at high pressure.

And then poynting correction applied to LR reference states. K values are even extended to cases where ideal gas and ideal assumptions are no longer apply. But in such cases non-ideality of the system is included in K under such conditions K depends on competition as well as I mentioned here for these cases, K values should be found either empirically or through fugacity and activity coefficient using the equation to that is K = $\frac{y_i}{x_i} = \frac{f_i^0 \gamma_i^l}{\phi_i^v \text{P}}$ so, here since we are saying for non-ideal system.

So, f_i^0 that you have to take as per different state if you take a Lewi's Randall reference state in this f_i^0 is going to be P_i^{sat} if you take the hand this law as a kind of reference state this f_i^0 is going to be H_i and this constant or the solubility of that component i that is it that is the only difference. But beyond the limiting assumptions of RL also it can be applicable under 2 conditions are because under such conditions.

Lewis fugacity rule use to correct fugacity of real gases at high at very higher pressures and the poynting correction apply to LR reference state. So, under these 2 conditions also this K remains to be independent of composition but if you how extended to the cases where ideal gas and an ideal solution is no longer applying. So, then you have this K_i defined by this one where this K_i is dependent in composition as well in addition to the pressure and temperature.

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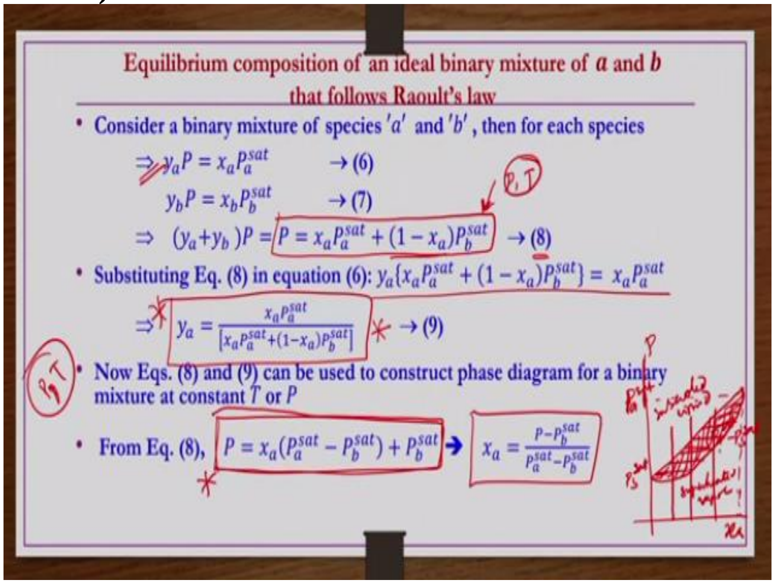

Equilibrium composition of an ideal binary mixture of *a* and *b* that follows Raoult's law

- Consider a binary mixture of species '*a*' and '*b*', then for each species

$$\Rightarrow y_a P = x_a P_a^{sat} \quad \rightarrow (6)$$

$$y_b P = x_b P_b^{sat} \quad \rightarrow (7)$$

$$\Rightarrow (y_a + y_b) P = \boxed{P = x_a P_a^{sat} + (1 - x_a) P_b^{sat}} \quad \rightarrow (8)$$

- Substituting Eq. (8) in equation (6): $y_a\{x_a P_a^{sat} + (1 - x_a) P_b^{sat}\} = x_a P_a^{sat}$

$$\Rightarrow \boxed{y_a = \frac{x_a P_a^{sat}}{[x_a P_a^{sat} + (1 - x_a) P_b^{sat}]}} \quad \rightarrow (9)$$

- Now Eqs. (8) and (9) can be used to construct phase diagram for a binary mixture at constant *T* or *P*
- From Eq. (8), $\boxed{P = x_a(P_a^{sat} - P_b^{sat}) + P_b^{sat}} \rightarrow \boxed{x_a = \frac{P - P_b^{sat}}{P_a^{sat} - P_b^{sat}}}$

Now, what we do we calculate we make equilibrium composition of an ideal binary mixture of a and b that follow Raoult's law. So, whatever y_a P = x_a P_a^{sat} that the equation we have taken so that we are going to find out what is y_a what is x_a how to find out this y_a x_a or both at a given temperature and pressure that is what we are going to see now. So, we start with a binary system.

So that it can be easy to develop on this ideal behavior and then bring it in non-ideality in the later cases. Consider a binary mixture of our species a and b then for 2 components this $y_a P = x_a P_a^{sat}$ we can write it as $y_a P = x_a P_a^{sat}$, $y_b P = x_b P_b^{sat}$. Now, if you add them together $(y_a + y_b) P = P$ because $y_a + y_b = 1$ for a binary mixture.

So, left hand side is P and then right hand side $x_a P_a^{sat} + x_b P_b^{sat}$. So, now here what we understand from this equation number 8 if the pressure and temperature are known you can find out x_a without any difficulty because at a given temperature P_a^{sat} P_b^{sat} can be known and then P is given. So, x_a you can find it out. Now, if you substitute this particular P in equation number 6 then you have this $y_a \{x_a P_a^{sat} + (1 - x_a) P_b^{sat}\} = x_a P_a^{sat}$.

So, that means, $y_a = \frac{x_a P_a^{sat}}{[x_a P_a^{sat} + (1 - x_a) P_b^{sat}]}$ that is what you can have now here. At a given pressure and temperature, you know, this x_a you have already found out from this equation number 8, and then the x_a is already known. So, then you using the equation number 9 you can find out y_a. So, for simply given pressure and temperature, you are comfortably able to calculate equilibrium composition of this vapour liquid system forever vapour liquid binary system because degrees of freedom is 2 for this binary system having 2 phases. So, the degrees of freedom is 2 that means 2 independent variables we are fixing we can fix. So, let us say if I fixed pressure and temperature, then remaining 2 independent variables that is y_a you can find out and then x_a also you can find out.

So, that is what we can do from this equation number 8 and 9 not only the pressure and temperature you can fix anything let us say P and y_a you fix then T and x_a you can find out or P and x_a you fix then T and y_a you can find out without any difficulty, we are going to solve a few problems as well on this. So, this equation 8 and 9 would be help us in constructing the phase diagram, phase diagram in the sense at a given temperature and pressure.

If you have this binary system, and then there is a kind of vapour liquid equilibrium is existing. So, what kind of phases are existing at given temperature, pressure and then under what composition kind of phase pure phase; a pure vapour phase, pure liquid phase or binary phases existing all those kinds of things we can construct from these equations, these 2 equations, that is what we are going to do for the ideal liquid and ideal vapour phase today.

And then later on we take the non-ideal liquid phases also coming into the picture. So, now the from equation 8 what we understand, so, we have this rearrangement of the same equation number 8, P = x_a $(P_a^{sat} - P_b^{sat}) + P_b^{sat}$that means $x_a = \frac{P-P_b^{sat}}{P_a^{sat}-P_b^{sat}}$ that is a straight forward but what is the important thing to see this P versus x_a is a linear relation from this equation number 6 is not it?

It is a linear relation and then it is having a slope of nothing but $P_a^{sat} - P_b^{sat}$. And then when x_a =1 whatever the P is there that is nothing but $P_a^{sat}$and then when x_a = 0 whatever the P is nothing but that is P_b^{sat}. So, this P versus x_a curve for ideal liquid phase, it is going to be linear straight line like this. So, that is what we have to understand from here, because now let us if when you are constructing phase diagram.

So, P x_a information or the curve already drawn it. So, now, we understand at higher pressures liquid phases would be there liquid or condensed phase is going to exist. So, above whatever the composition you take this co point, any point if you take this composition. So, if the composition and the pressure for a given composition of x_a the pressure is going beyond the straight line.

So, then what we can have a kind of sub cooled liquid only liquid phase is existing. So, that is what we can say and then vapour phase is going to be there below on this line, but not entire amount, but there may be a kind of region of where both vapour and liquid phases may be coexisting that information, we can understand if you plot this P versus y_a, P versus y_a if you plot it is not going to be linear like this.

Now equation 8, if you rewrite like this, you can clearly understand this y = mx + c form. It is a linear equation, but equation number 9 P versus y_a it is not linear, it is not linear. So, that is the important difference one has to realize here though, vapour phase is also ideal, but, P versus composition P versus y_a curve is not linear here. Whereas liquid phase is ideal, but P versus x is a linear curve so, let us say P versus y_a curve it is having some form like this.

So, now this is $y_a = 1$. So, now, here in this region whatever this between the 2 end close region whatever is there in these 2 reasons we are going to have a kind of binary image that is both vapour and liquid are coexisting below this P y_a curve. So, because this is P y_a curve, so, below this one we will be having superheated vapour only the vapour phase we are going to have and then above this P x_a curve we are going to have only sub cooled liquid in between we are going to have both a vapour and liquid but they are at equilibrium so this exactly the same thing from this information of equation 8 and 9.

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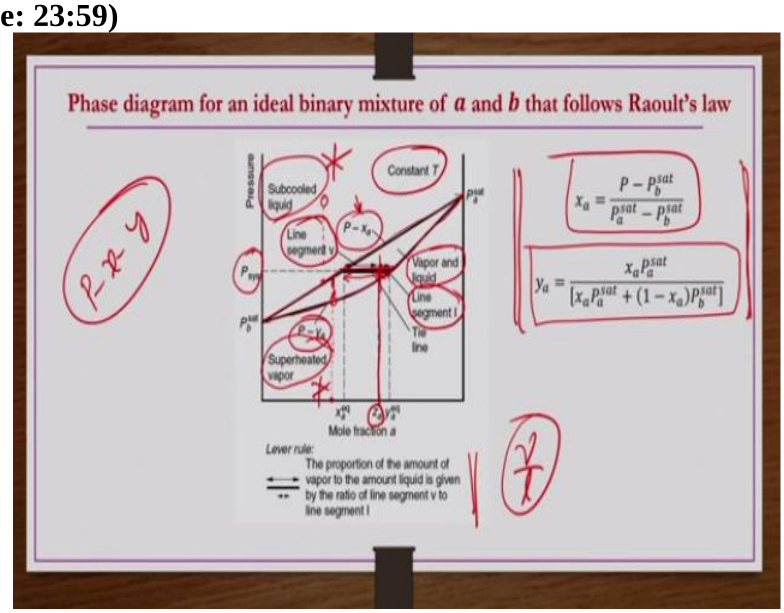

Phase diagram for an ideal binary mixture of *a* and *b* that follows Raoult's law

$$x_a = \frac{P - P_b^{sat}}{P_a^{sat} - P_b^{sat}}$$

$$y_a = \frac{x_a P_a^{sat}}{[x_a P_a^{sat} + (1 - x_a) P_b^{sat}]}$$

Lever rule:

The proportion of the amount of vapor to the amount liquid is given by the ratio of line segment v to line segment l

I have redrawn here. So, this is what we had. So, at constant temperature, I am trying to draw P-x-y diagram. So, at system pressure this is what we are having. So, pressure we are changing pressure and in composition we are changing and then trying to find out at constant temperature how this curve look like. So, this P versus x_a is a straight line that we already mentioned. So this is what one, this is the one with a slope we are having $P_b^{sat} - P_a^{sat}$.

So, this P x_a curve we know that it is a linear and then we know the slope of this curve is nothing but P_a^{sat} minus P_b^{sat} that is what we understand. And then P y_a curve is not a linear one it is a nonlinear one and then that is having shaped like this, that equation number 9, whatever this equation. So, then this is what we are having this is known as a P y_a curve and this is P x_a curve.

So, any combination of this composition x_a y_a, if the pressure is above this pressure is falling above this P x_a line, so, then we can have the system you know only sub cooled liquid. Or if the pressure and then composition combination in such a way that the data point is falling above this P x_a curve then we can say that only sub cooled liquid single phase is existing. For the combination of pressure and then composition any combination of pressure and composition if the data point is following, below this P y_a curve that means we are having only super-heated vapour phase.

And then let us say if you have a combination of pressure and composition such a way that the data point is falling in this encapsulation between these 2 curves. That is P x_a and P y_a curve then we can say both vapour and liquid phases are coexisting and they are at equilibrium that is what we can see. So, now, this P x_a curve is also known as a kind of bubble point curve, because let us say, at certain composition x_a the pressure if you gradually decrease the pressure that is initially the composition is having some value here.

And then pressure you are gradually decreasing. So, when the pressure comes out to this point where it touches the P x_a curve that is the point where the first bubble has formed. Above it only liquid is there and then the pressure comes to the point where it touches this P x_a line that is the point where the first bubble forms with certain y_a value otherwise initially it was only x_a value it having. So, that is the point you know first bubble forms.

And then as you that is that is the reason this P x_a occur is also known as the bubble point curve. And then whatever the P y_a is there it is also known as the dew point curve**.** Because let us say, any composition y_a you are having here and then gradually isothermally at constant temperature you are increasing the pressure. So, initially it was superheated vapour and then as in gradually increasing the pressure, so, condensed phase will start forming at certain point.

So, the pressure when it touches this P y_a curve so, that is the point where the first dew is forming from this vapour phase. So, liquid started forming and then further increase. So, then there will be a kind of condition where both vapour and liquid would be there and then after crossing this P x_a curve again only liquid form liquid phase of pure liquid phase is going to be. So, that is the reason P y_a curve is also known as the dew point curve because on this point, the first point where the first dew is forming.

So that is the reason dew point curve it is also known as dew point curve. So now it certain system pressure P system let us say if you have a kind of a draw a horizontal line so, that is known as the tie line. Tie line in the sense it ties the composition of a vapour phase and liquid phase which are at equilibrium. So that is the reason they are known as to tie line. So, and then if z_a is a kind of a feed composition, the point with joins this feed system in z_a. So, now here you can have a kind of 2 segmenting this line in 2 parts.

Whatever this tie line is there for this combination of P system and z_a this tie line is segmented in 2 parts. So, one is this part, which is known as line segment v. And then this is the other part which is known as the line segment l. Line segment v here and the left hand side line segment l and the right hand side. So, this will also give you the ratio if you take the proportion of the amount of vapour to the amount of liquid is given by the ratio between this line segments $\frac{v}{l}$.

So, now this phase diagram not only from this from this phase diagram picture. It is not only that we get the what kind of phase is existing with our sub cooled liquid or superheated vapour or both phases are existing not only that information we can also find out the composition at a given temperature and pressure not only that composition equilibrium composition but also we know what is the ratio between the amount of vapour form to the amount of liquid that this formed at given system pressure.

And then composition that is also we can find out. So, this is what about the phase diagram. So, this is known as a kind of phase diagram because now it says, you know, which phase is existing at what composition it is existing and what is the corresponding pressure and all that information we know it is we are doing T constant isothermal system, but by changing the pressure you can also have the T-x-y curves also it is possible.

So, now if you have a T-x-y curves so then what happens the liquid phase would be at the bottom because at the lower temperature liquid phase would be there and then at the higher temperature larger temperature beyond that T y_a curve you will be having in a vapour phase superheated vapour phase would be they would be having. So, those kinds of things you might already being knowing through your undergraduate courses are even construct T x_a diagrams also simultaneously using the same equations are written those 2 equations yes, that I leave it to you to do yourself as a kind of a self-exercise problem.

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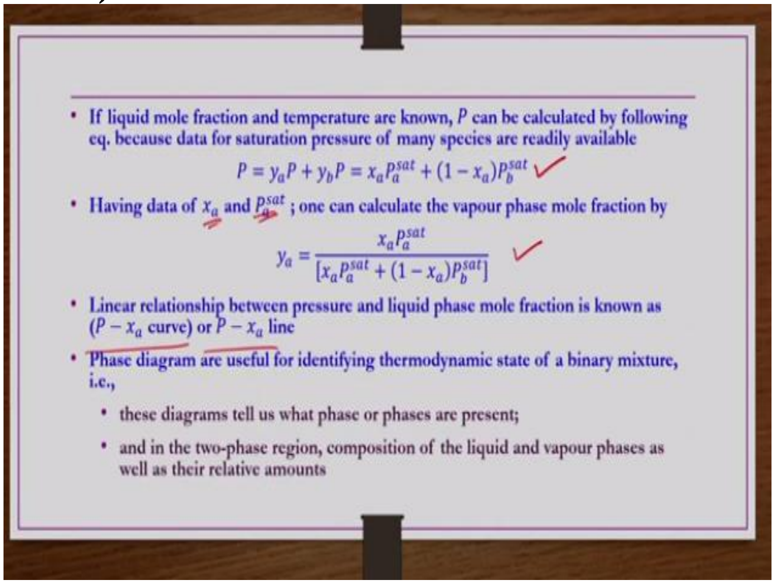

- If liquid mole fraction and temperature are known, P can be calculated by following eq. because data for saturation pressure of many species are readily available

$$P = y_aP + y_bP = x_aP_a^{sat} + (1 - x_a)P_b^{sat} ✓$$

- Having data of x_a and P_a^{sat} ; one can calculate the vapour phase mole fraction by

$$y_a = \frac{x_aP_a^{sat}}{[x_aP_a^{sat} + (1 - x_a)P_b^{sat}]} ✓$$

- Linear relationship between pressure and liquid phase mole fraction is known as ($P - x_a$ curve) or $P - x_a$ line
- Phase diagram are useful for identifying thermodynamic state of a binary mixture, i.e.,
  - these diagrams tell us what phase or phases are present;
  - and in the two-phase region, composition of the liquid and vapour phases as well as their relative amounts

So, all this is provided as a kind of notes here. So, if you know the liquid mole fraction and temperature then P can be calculated by this equation once P is known, so, at given temperature P_a^{sat} can also be known and then x_a is known for this case let us say then you can find out y_a using this expression that is what we are doing. Now, linear relationship between pressure and liquid phase we have seen that is known as P x_a curve or P x_a line.

If it is linear then we call P x_a line for ideal liquid system, let us say if you have a kind of non-ideal liquid system then whatever the P x_a line is that is not going to be linear as we are going to see later course, phase diagram useful for identifying thermodynamic state of a binary mixture, that is these diagrams tell us what phase or phases are present. And in the 2 phase region combination of the liquid and vapour phases as well they are related amongst that is x_i y_i, not only x_i y_i. Also $\frac{v}{l}$ information we get.

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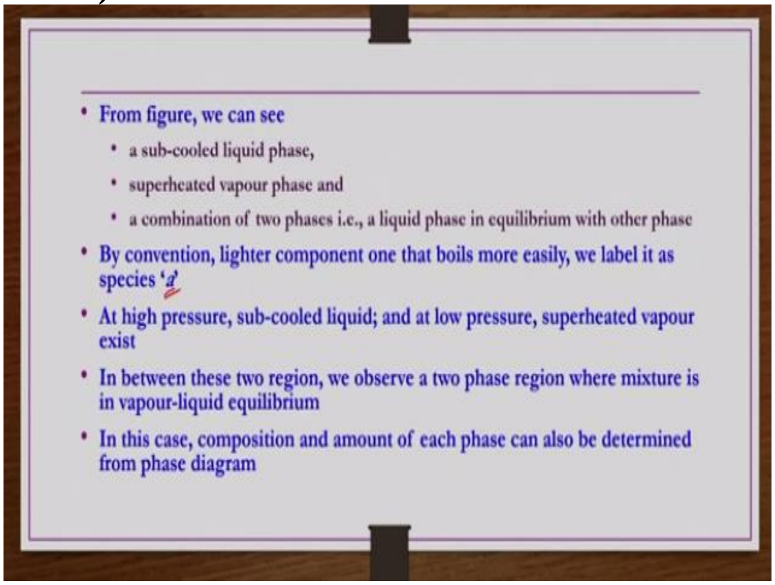

- From figure, we can see
  - a sub-cooled liquid phase,
  - superheated vapour phase and
  - a combination of two phases i.e., a liquid phase in equilibrium with other phase
- By convention, lighter component one that boils more easily, we label it as species '*a*'
- At high pressure, sub-cooled liquid; and at low pressure, superheated vapour exist
- In between these two region, we observe a two phase region where mixture is in vapour-liquid equilibrium
- In this case, composition and amount of each phase can also be determined from phase diagram

How much I want related vapour is present related to the liquid amount all those things also we can find out from this diagram. So, from this phase diagram we understand there is a sub cooled liquid phase, there is a superheated vapour phase and there is a combination of 2 phases that is the liquid phase in equilibrium with the vapour phase that is the area constraint between P x_a and P y_a curves.

So, by convention, obviously, you know lighter component or that one boils more easily is labeled as a kind of more volatile component and then more volatile components are given convention a x_a, if you have a binary mixture of a and b. So, a is more relative to the b. So, whatever this curve if you have written drawn with respect to mole fraction of a that means, in the mixture a is more volatile than the b that is what it means, it high pressure sub cooled liquid.

And at low pressure superheated vapour to exist in this P-x-y diagrams in between these 2 reasons we observe a 2 phase region where mixture is in vapour liquid equilibrium in this case composition and an amount of each phase can also be determined from the phase diagram as I already explained.

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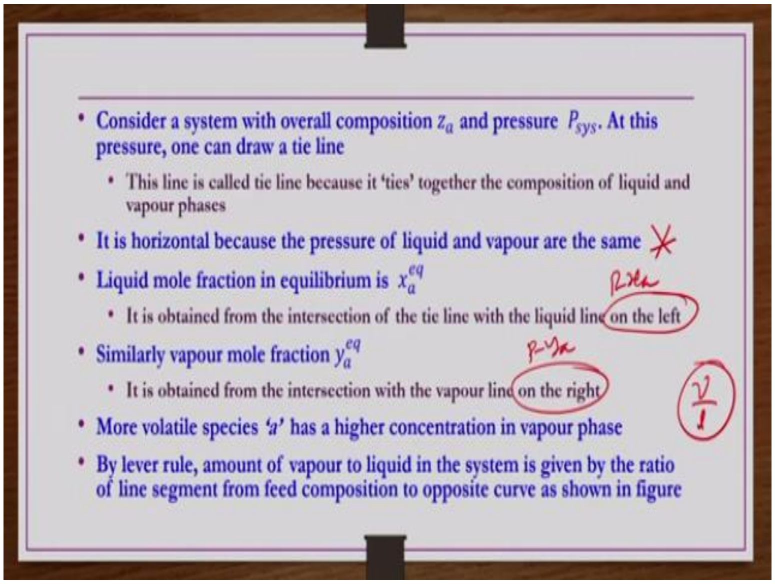

- Consider a system with overall composition z_a and pressure P_{sys}. At this pressure, one can draw a tie line
  - This line is called tie line because it 'ties' together the composition of liquid and vapour phases
- It is horizontal because the pressure of liquid and vapour are the same *
- Liquid mole fraction in equilibrium is x_a^{eq} $P\text{-}x_a$
  - It is obtained from the intersection of the tie line with the liquid line on the left
- Similarly vapour mole fraction y_a^{eq} $P\text{-}y_a$
  - It is obtained from the intersection with the vapour line on the right $\frac{V}{L}$
- More volatile species *'a'* has a higher concentration in vapour phase
- By lever rule, amount of vapour to liquid in the system is given by the ratio of line segment from feed composition to opposite curve as shown in figure

Now, consider the system with overall combinations z_a and pressure P system at this pressure, one can draw a tie line at the P system if you draw a horizontal line. So that line that intersects both P x_a curve and then P y_a curve is known as the tie line because it ties the composition at that system pressure species. So, this line is called the tie line because it ties together the composition of liquid and vapour phases which are coexisting and which are at equilibrium.

It is horizontal because the pressure of the liquid and vapour are the same. This is what we have seen. And at the beginning, when we are discussing the defining the equilibrium of a system with respect to 3 processes, mechanical equilibrium, thermal equilibrium and chemical equilibrium. If the system to be said as a kind of equilibrium, the system has to be in equilibrium with respect to all internal 3 equilibrium processes internally equilibrium.

With respect to pressure, with respect to the temperature, and with respect to the chemical potential so, we know that they know for a system to be mechanical equilibrium at mechanical equilibrium pressure has to be same. So, that is the region this horizontal line tie line whatever is there it is horizontal liquid mole fraction is x_a equilibrium which is obtained from the intersection of the tie line.

With the liquid line on the left this on the left is a kind of relative kind of thing if you write T-x-y then it is going to be other side. So, that is simply in the intersection of the tie line with P x_a curve and then similarly vapour mole fraction is y_a equilibrium it is obtain from the intersection with a vapour line that is on the P y_a curve here in the case it is the dew point curve. It is also known as dew point curve.

And then more volatile phases “a” has a higher concentration in the vapour phase obviously, because it is more volatile. So, it can easily boil and it can easily vaporize and go into the vapour phase. And then by lever a rule amount of vapour to liquid in the system is given by the ratio of line segment from feed composition to opposite curve are shown in the figure that $\frac{v}{l}$ line segment v and then line segment l if you take these ratios that you will get relative amount of vapour to liquid in the system at that system pressure.

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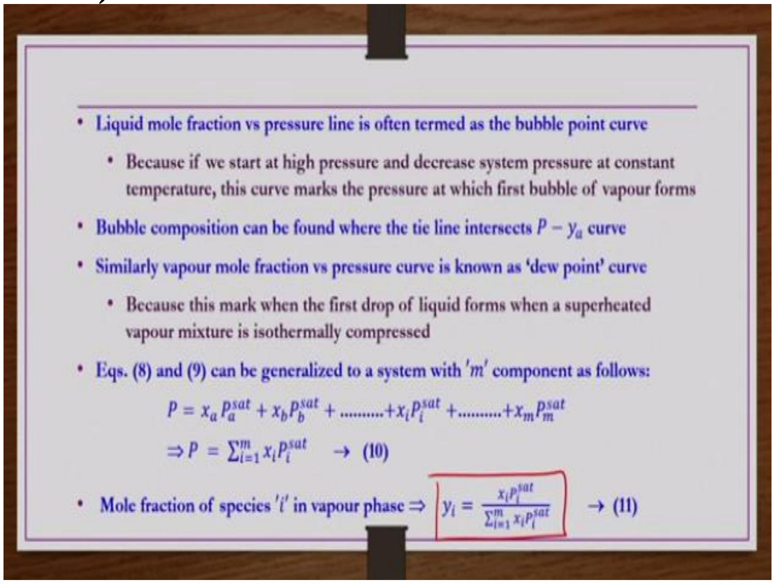

- Liquid mole fraction vs pressure line is often termed as the bubble point curve
  - Because if we start at high pressure and decrease system pressure at constant temperature, this curve marks the pressure at which first bubble of vapour forms
- Bubble composition can be found where the tie line intersects $P - y_a$ curve
- Similarly vapour mole fraction vs pressure curve is known as ‘dew point’ curve
  - Because this mark when the first drop of liquid forms when a superheated vapour mixture is isothermally compressed
- Eqs. (8) and (9) can be generalized to a system with $'m'$ component as follows:

$$P = x_a P_a^{sat} + x_b P_b^{sat} + \text{.........} + x_i P_i^{sat} + \text{.........} + x_m P_m^{sat}$$

$$\Rightarrow P = \sum_{i=1}^{m} x_i P_i^{sat} \rightarrow (10)$$

- Mole fraction of species $'i'$ in vapour phase $\Rightarrow \boxed{y_i = \frac{x_i P_i^{sat}}{\sum_{i=1}^{m} x_i P_i^{sat}}} \rightarrow (11)$

Liquid mole fraction versus pressure line is often termed as bubble point curve. Because if we start at high pressure and decrease the system pressure at constant temperature this curve marks the pressure at which the first bubble of vapour performs. Bubble composition can be found where the tie line intersects P y_a curve. And then similarly, the vapour mole fraction was this pressure curve is known as the dew point curve because this mark when the first drop of liquid forms.

When a superheated vapour mixture is isothermally compressed by increasing the pressure and an equation 8 and 9 can be generalized to a system with m component as follows that is P = $\sum x_i P_i^{sat}$ i = 1 to n. So, this is given as a note as I already explained all these points in, you know P-x-y curve diagram itself. So, If you know the relation between x_a and P for m number of components, so, then you can also find out y a for those m number of components by using $y_i = \frac{x_i P_i^{sat}}{\sum_{i=1}^{m} x_i P_i^{sat}}$.

Now, quickly what we do we take a few simple problems to understand these things, then we go into non-ideal behavior of vapour liquid system. So, before going to the problems what we do we see a few common types of VLE calculations. So, VLE calculations are 4 types.

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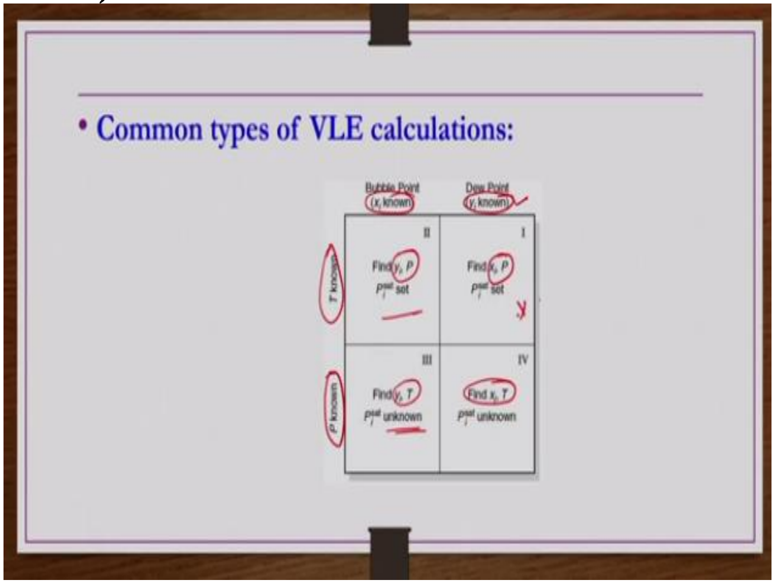

- Common types of VLE calculations:

	Bubble Point (x_i known)	Dew Point (y_i known)
T known	II Find y_i, P P_i^{sat} set	I Find x_i, P P_i^{sat} set y
P known	III Find y_i, T P_i^{sat} unknown	IV Find x_i, T P_i^{sat} unknown

You can have a kind of this T known and then P known kind of system. If T known and then x_i is also known. Then those things are known as the bubble point calculations where you can find out y_i and then P. $P_i^{sat}$is said because T is known then if P known and then x_i known then also it is known as the bubble point calculation where you can find out y_i T P_i^{sat}unknown. So, by trial and error you can find out these things temperature.

And then P_i^{sat}that is what we are going to do anyway then if T known and then y_i known it is known as the dew point calculations where you will be finding x_i and P. If P_i is known and then y_i is known as a kind of dew point calculation where you will be finding x_i and T. If you are finding simply to memorize or simply to have a kind of you know as a kind of simple principles to realize which whether it is the dew point calculation or a bubble point calculation. If you are finding x_i values it is a dew point calculations. If you are finding y_i values it is a bubble point calculation Fine.

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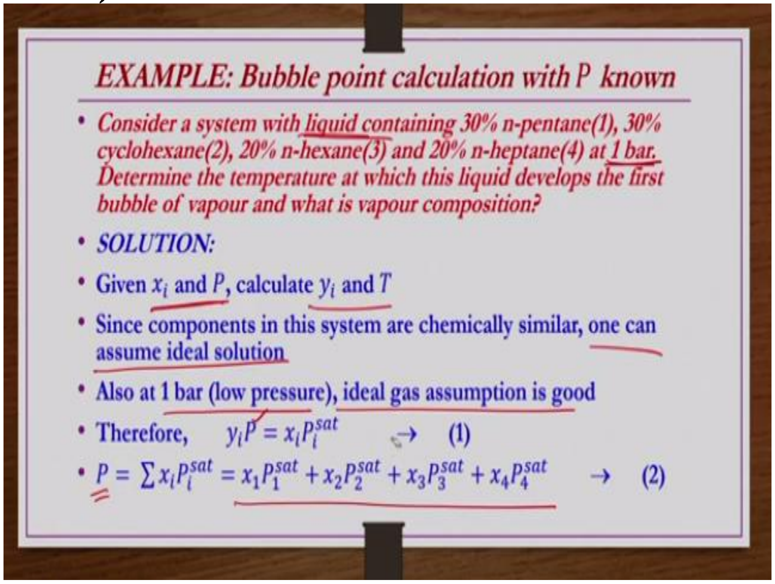

EXAMPLE: Bubble point calculation with P known

- *Consider a system with liquid containing 30% n-pentane(1), 30% cyclohexane(2), 20% n-hexane(3) and 20% n-heptane(4) at 1 bar. Determine the temperature at which this liquid develops the first bubble of vapour and what is vapour composition?*
- *SOLUTION:*
- Given x_i and P, calculate y_i and T
- Since components in this system are chemically similar, one can assume ideal solution
- Also at 1 bar (low pressure), ideal gas assumption is good
- Therefore, $y_i P = x_i P_i^{sat}$ → (1)
- $P = \sum x_i P_i^{sat} = x_1 P_1^{sat} + x_2 P_2^{sat} + x_3 P_3^{sat} + x_4 P_4^{sat}$ → (2)

So, example one bubble point calculation with P known. So, y_i T we are going to find out. Consider a system with liquid containing 30% n-pentane 30% cyclohexane 20%, n-hexane 20% and heptane at 1 bar pressure is given 1 bar. It is low pressure, so, we can say that the vapour phases ideal phases though it is not given determine the temperature at which this liquid develops the first bubble or vapour and what is vapour compression.

So, x_i and P are given liquid mole fractions are given 4 components, multi component system we are doing 4 components, but it is a 2 phase system but multi component and then ideal phases. So calculate y_i and T, here. Since components in the system are chemical is similar, one can assume ideal solution and then since pressure is low one can also assume ideal gas assumption for the vapour phase.

Then we have y_i P = x_i P_i^{sat} that you need to find out y_i. P is given x_i is given. So, y_i you can find out only if you know P_i^{sat} and then P_i^{sat} you can only win if you know the temperature which is not given. So, what we do we write this equation for 4 components like this and then add them together when you add them together sigma y_i P is nothing but P and then $\sum x_i P_i^{sat}$ is nothing but $x_1 P_1^{sat} + x_2 P_2^{sat} + x_3 P_3^{sat} + x_4 P_4^{sat}$ this is what we have.

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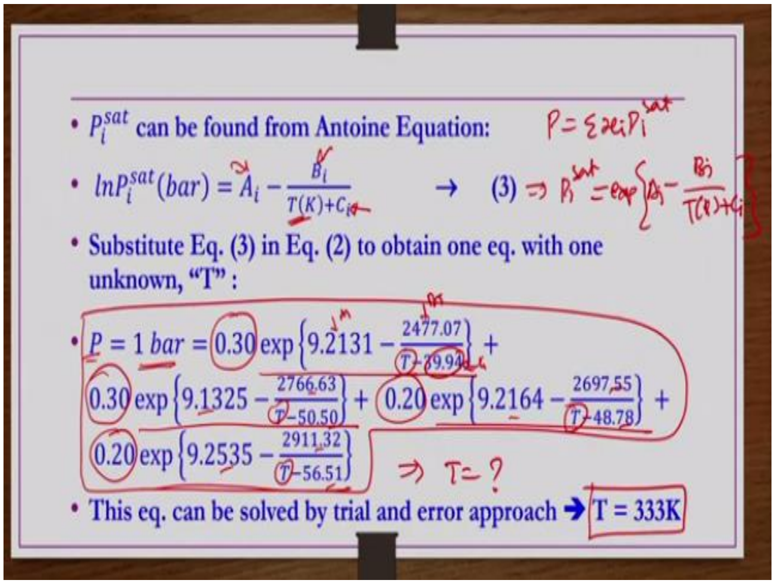

- P_i^{sat} can be found from Antoine Equation: $P = \Sigma x_i P_i^{sat}$
- $\ln P_i^{sat}(bar) = A_i - \frac{B_i}{T(K)+C_i}$ → (3) $\Rightarrow P_i^{sat} = \exp\left\{A_i - \frac{B_i}{T(K)+C_i}\right\}$
- Substitute Eq. (3) in Eq. (2) to obtain one eq. with one unknown, "T" :
- $P = 1\ bar = 0.30 \exp\left\{9.2131 - \frac{2477.07}{T-39.94}\right\} + 0.30 \exp\left\{9.1325 - \frac{2766.63}{T-50.50}\right\} + 0.20 \exp\left\{9.2164 - \frac{2697.55}{T-48.78}\right\} + 0.20 \exp\left\{9.2535 - \frac{2911.32}{T-56.51}\right\}$ $\Rightarrow T = ?$
- This eq. can be solved by trial and error approach ➔ $\boxed{T = 333K}$

So, now P_i^{sat} can be found from Antoine equation. So, ln P_i^{sat} in bars = $A_i - \frac{B_i}{T(K)+C_i}$. T is in Kelvin his A$_i$ B$_i$ and then C$_i$ are nothing but unknown constants, they are available for almost all components in standard chemical engineering thermodynamics books. So, now, this equation if you substitute in our previous equation P = $\sum x_i\, P_i^{sat}$ for each component then expand.

So, you have this equation in place of P_i^{sat} what we are writing P_i^{sat} = exp $\left\{A_i - \frac{B_i}{T(K)+C_i}\right\}$, this is what we are writing. This is what the component 1 this is for the component 2, this is for the component 3 and this is for the component 4 and these are nothing but x_1 x_2 x_3 x_4 and then P is nothing but 1 bar it is given. So, now in this equation except this temperature everything is known these are nothing.

But A$_i$ B$_i$ and then this C$_i$ for component 1, similarly for component 2 also these are available I have tabulated in this next slide. So, this equation you can solve you can find out T that is the only unknown. So, by trial and error you can solve this equation and then you will find it out as 333 Kelvin. So, now the temperature is known out of y_i and T, T is not only y_i is remaining.

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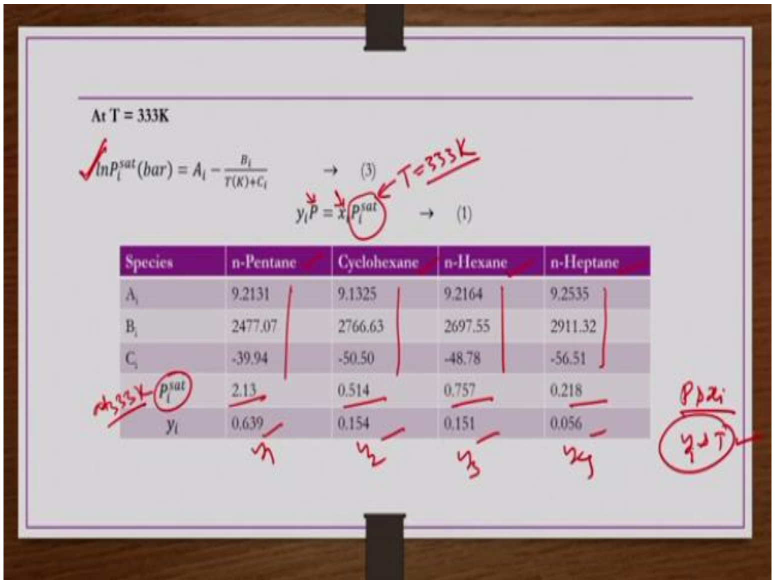

At T = 333K

$\ln P_i^{sat}(bar) = A_i - \frac{B_i}{T(K)+C_i}$ → (3)

$y_i P = x_i P_i^{sat}$ → (1)

Species	n-Pentane	Cyclohexane	n-Hexane	n-Heptane
A_i	9.2131	9.1325	9.2164	9.2535
B_i	2477.07	2766.63	2697.55	2911.32
C_i	-39.94	-50.50	-48.78	-56.51
P_i^{sat}	2.13	0.514	0.757	0.218
y_i	0.639	0.154	0.151	0.056

So, y_i you can find it out using $y_i P = x_i P_i^{sat}$, x_i is given x_i is given P_i is also given. Now, temperature we already find it out as it if we found as 333 Kelvin. At 333 Kelvin you can find out P_i^{sat} for each component using this Antoine equation calculating back. So, for this n-Pentane, cyclohexane, n-Hexane, n-Heptane this ABC or A_i B_i C_i values are given at 333 Kelvin if you find it out P_i^{sat} for each of these component you get these values in bar.

So, if you substitute this P_i^{sat} in this equation 1 then $y_i = \frac{x_i P_i^{sat}}{P}$. So, then you get this y_1 y_2 y_3 y_4 values like this. So, simply P_i and x_i is given. So, y_i and T you able to calculate without any difficulty here. Now, we take the similar problem.

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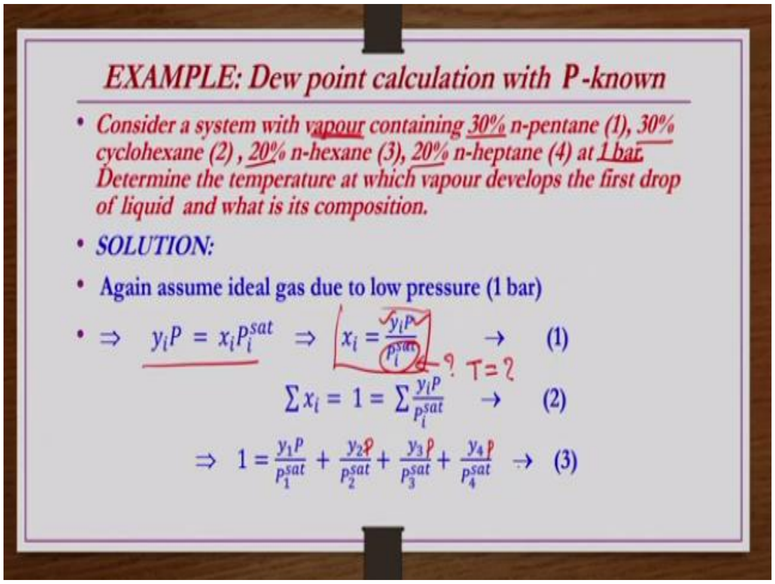

EXAMPLE: Dew point calculation with P-known

- *Consider a system with vapour containing 30% n-pentane (1), 30% cyclohexane (2), 20% n-hexane (3), 20% n-heptane (4) at 1 bar. Determine the temperature at which vapour develops the first drop of liquid and what is its composition.*
- ***SOLUTION:***
- Again assume ideal gas due to low pressure (1 bar)
- $\Rightarrow \quad y_iP = x_iP_i^{sat} \quad \Rightarrow \quad \boxed{x_i = \frac{y_iP}{P_i^{sat}}} \quad \rightarrow \quad (1)$

? T=?

$$\sum x_i = 1 = \sum \frac{y_iP}{P_i^{sat}} \quad \rightarrow \quad (2)$$

$$\Rightarrow \quad 1 = \frac{y_1P}{P_1^{sat}} + \frac{y_2P}{P_2^{sat}} + \frac{y_3P}{P_3^{sat}} + \frac{y_4P}{P_4^{sat}} \quad \rightarrow \quad (3)$$

So, here dew point calculation with P known, so, that is P and that is you have to find out the x_i and T, you have to find out P and y_i are given. So, now, consider the system with vapour containing this is vapour mixture. So, y_1 is 0.3 y_2 is 0.3 y_3 is 0.2 and y_4 is 0.4. 4 components P is 1 bar P and y_i are given x and T you have to find out in the previous problem P and x_i were given T and y, you have to find out.

So, now here P and y_i are given T and x_i you are finding out the difference same equations and then assume ideal gas because the pressure is low and then these components are chemical similar So, then you can assume the liquid phase is also ideal if the chemicals are similar in nature so then their interactions going to be similar if the interactions are similar, so, then we can say that ideal liquid solution. So, the same equation we have to use y_i P = x_i P_i^{sat}.

So, now x_i you have to find out. So, $x_i = \frac{y_iP}{P_i^{sat}}$. P is given y_i is given, but P_i^{sat} is not given. So, if you know the temperature, then you can know P_i^{sat} but the temperature also not given. So, temperature you have to find out then only you can find out x_i. So, temperature how you can find out, this equation you can write $\sum x_i = \sum \frac{y_iP}{P_i^{sat}}$ this is what we can write sigma x_i = 1. So, that mean if you extend one = $y_1 \frac{P}{P_1^{sat}}$ + $y_2 \frac{P}{P_2^{sat}}$+ $y_3 \frac{P}{P_3^{sat}}$ and then + $y_4 \frac{P}{P_4^{sat}}$. So, P is common that you can take it as a common.

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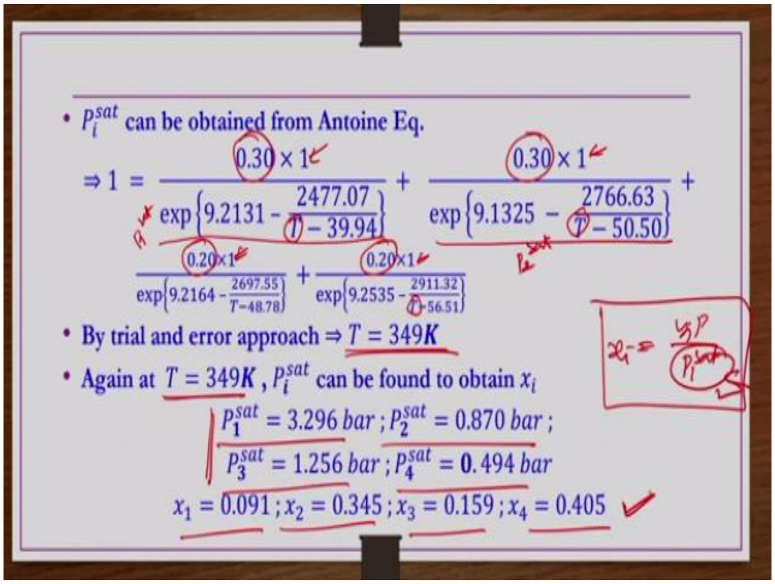

- P_i^{sat} can be obtained from Antoine Eq.

$$\Rightarrow 1 = \frac{0.30 \times 1}{\exp\left\{9.2131 - \frac{2477.07}{T - 39.94}\right\}} + \frac{0.30 \times 1}{\exp\left\{9.1325 - \frac{2766.63}{T - 50.50}\right\}} + \frac{0.20 \times 1}{\exp\left\{9.2164 - \frac{2697.55}{T - 48.78}\right\}} + \frac{0.20 \times 1}{\exp\left\{9.2535 - \frac{2911.32}{T - 56.51}\right\}}$$

- By trial and error approach $\Rightarrow T = 349K$
- Again at $T = 349K$, P_i^{sat} can be found to obtain x_i

$P_1^{sat} = 3.296\ bar$; $P_2^{sat} = 0.870\ bar$;

$P_3^{sat} = 1.256\ bar$; $P_4^{sat} = 0.494\ bar$

$x_1 = 0.091$; $x_2 = 0.345$; $x_3 = 0.159$; $x_4 = 0.405$ ✓

$x_i = \frac{y_i P}{P_i^{sat}}$

So, now P_i^{sat} that you can find out from the Antoine equation like this. So, this is the nothing but P_i^{sat} using the Antoine equations, this is P_1^{sat}, this is P_2^{sat} and this is P_3^{sat} and this is P_4^{sat}. This is y_1, this is y_2, this is y_3 this is y_4 and this is pressure is 1 bar. So, in this equation also except the temperature everything is known. So, here also what you can do you can do the trial and error approach and then find out this temperature as 349 Kelvin.

So, now the temperature is no out of T and x_i calculations T already you got so x_i is very straightforward, because x_i is nothing but $\frac{y_iP}{P_i^{sat}}$. So, now if T is known, so, then this P_i^{sat} is known through the Antoine equation. So, P_1^{sat} you can find it out P_2^{sat}, P_3^{sat} and then P_4^{sat} you can find it out. This Antoine constants etc. same like in a previous problem, because same components are this or have not written them back. So, once you find out this P_i^{sat}, for 4 components at 349 Kelvin, then x_i you can find it out using this equation $x_i = \frac{y_iP}{P_i^{sat}}$ as x_1 x_2 x_3 x_4 as these values straightforward and simple.

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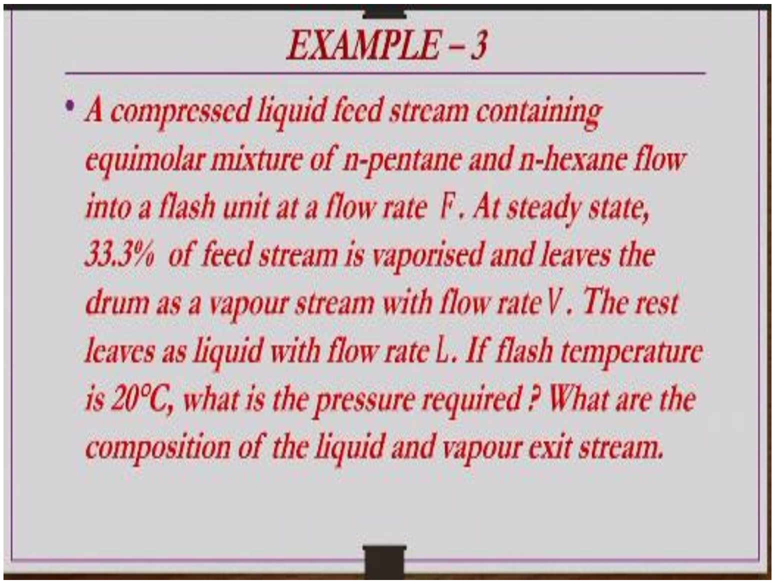

EXAMPLE – 3

- A compressed liquid feed stream containing equimolar mixture of n-pentane and n-hexane flow into a flash unit at a flow rate F. At steady state, 33.3% of feed stream is vaporised and leaves the drum as a vapour stream with flow rate V. The rest leaves as liquid with flow rate L. If flash temperature is 20°C, what is the pressure required ? What are the composition of the liquid and vapour exit stream.

So quickly look at one last problem for the day. A compressed liquid feed stream containing a equimolar mixture of n-pentane and n-hexane flow into your flash unit at a flow rate F at steady state 33.3% of feed stream is vaporized and leaves the drum as a vapour stream with flow rate V the rest leaves as a liquid with flow rate L. If flash temperature is 20 degrees centigrade, what is the pressure required? What are the composition of the liquid and vapour exit stream.

So, previous 2 examples were finding the equilibrium composition and temperature those things we have seen now, here we are going to do find out in addition to this composition we are going to find out the relative amounts of this v_2^l that is also we are going to find out here.

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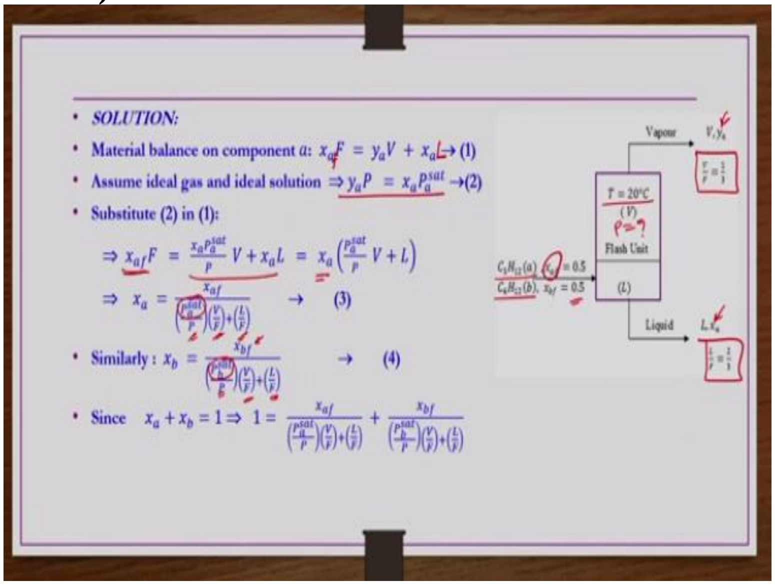

- SOLUTION:
- Material balance on component a: $x_{af}F = y_aV + x_aL \rightarrow (1)$
- Assume ideal gas and ideal solution $\Rightarrow y_aP = x_aP_a^{sat} \rightarrow (2)$
- Substitute (2) in (1):

$$\Rightarrow x_{af}F = \frac{x_aP_a^{sat}}{P}V + x_aL = x_a\left(\frac{P_a^{sat}}{P}V + L\right)$$

$$\Rightarrow x_a = \frac{x_{af}}{\left(\frac{P_a^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)} \rightarrow (3)$$

- Similarly : $x_b = \frac{x_{bf}}{\left(\frac{P_b^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)} \rightarrow (4)$
- Since $x_a + x_b = 1 \Rightarrow 1 = \frac{x_{af}}{\left(\frac{P_a^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)} + \frac{x_{bf}}{\left(\frac{P_b^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)}$

So, pictorially we have a flash unit, you know, in which we are sending these 2 components, having equal molar compression in the unit temperature is maintained 20 degrees centigrade. So, then a flash has to be carried out. So then, certain pressure has to be given at this temperature. So, that the separation of vapour liquid takes place. So, how much the pressure is required that is what we have to calculate.

So, when the vapour is going out, so, what is this y a after the flash, the vapour composition is how much and then what is the liquid this x_a composition that liquid composition is how much that we have to find out this amount wise $\frac{V}{F}$is given and then $\frac{L}{F}$ is also given. $\frac{1}{3}$ of feed is going into the vapour phase. And then $\frac{2}{3}$ of the feed is going into the liquid phase after this and the flash operation taking place in the splash chute.

So, y_a and x_a and then v and also we have to find out so, material balance for component if you do x_{af} F = y_a V + x_a L. Then assume ideal gas, so then y_a P = x_a P_a^{sat}then substitute this equation number 2 in equation number 1. So, then x_{af} F = y_a V, y_a =$\frac{x_a P_a^{sat}}{P} V$ + x_a L. So, this feed composition whatever is said that we are indicating x_{af}. So, that is the reason x_{af} we are writing here. In the right hand side what you can do you can take x_a common which is there in both of the components both of the terms in the right hand side.

So, $\frac{x_a P_a^{sat}}{P} V$ + L this is what we have, that means x_a = $\frac{x_{af}}{\left(\frac{P_a^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)}$, this is what we have. So, here now, x_{af} is giving as 0.5 equimolar feed composition and then $\frac{V}{F}$is given as $\frac{1}{3}$, $\frac{L}{F}$is given as $\frac{2}{3}$. Now, only thing you know, if you know $P_a^{sat}$and then P then you can find out x_a P_a^{sat}you can find out because temperature is given 20 degrees centigrade, but P is not given. So, you cannot solve this equation directly. So, what we do? Similarly we read for the second component.

Second component x_b similarly you get x_b = $\frac{x_{bf}}{\left(\frac{P_b^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)}$ this $\frac{L}{F}$ is given, $\frac{V}{F}$is given, x_b F is given P_b^{sat}you can find out because T is given. So, P is not known here also you can then you cannot find out x_a directly. So, but what you do you have 2 equations only one unknown if you add them together you can find out easily. So, when you add them together $x_a + x_b$ in the left hand side that is nothing but one so, one = additional this right hand side terms.

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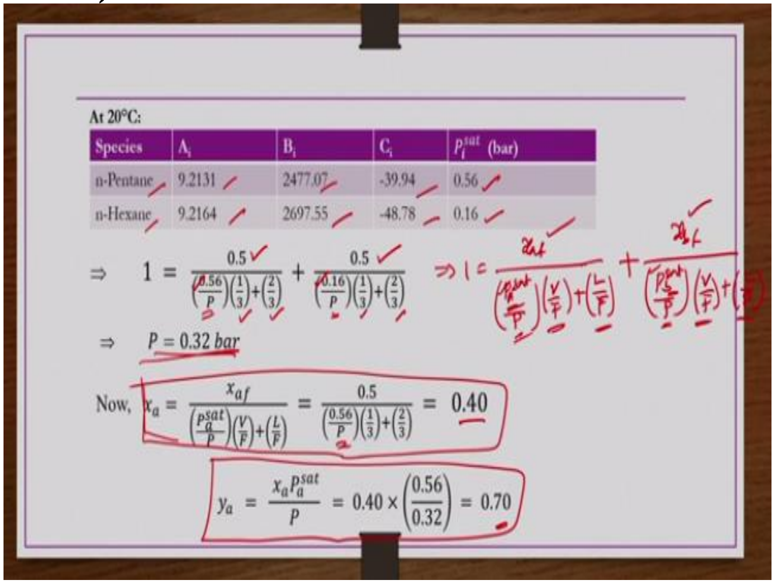

At 20°C:

Species	A_i	B_i	C_i	P_i^{sat} (bar)
n-Pentane	9.2131	2477.07	-39.94	0.56
n-Hexane	9.2164	2697.55	-48.78	0.16

$$\Rightarrow \quad 1 = \frac{0.5}{\left(\frac{0.56}{P}\right)\left(\frac{1}{3}\right)+\left(\frac{2}{3}\right)} + \frac{0.5}{\left(\frac{0.16}{P}\right)\left(\frac{1}{3}\right)+\left(\frac{2}{3}\right)} \quad \Rightarrow 1 = \frac{x_{af}}{\left(\frac{P_a^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)} + \frac{x_{bf}}{\left(\frac{P_b^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)}$$

$$\Rightarrow \quad P = 0.32\ bar$$

$$\text{Now, } x_a = \frac{x_{af}}{\left(\frac{P_a^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)} = \frac{0.5}{\left(\frac{0.56}{P}\right)\left(\frac{1}{3}\right)+\left(\frac{2}{3}\right)} = 0.40$$

$$y_a = \frac{x_a P_a^{sat}}{P} = 0.40 \times \left(\frac{0.56}{0.32}\right) = 0.70$$

So, at 20 degrees centigrade for this n-pentane and n-hexane system A_i B_i C_i values are given Antoine constants are given or we can find out from the chemical engineering thermodynamics books. Then corresponding P_i^{sat} you can find it all you can find them as 0.56 and 0.16 bar respectively. So, P_i^{sat} is also known. So, simply in this equation, whatever $1 = \frac{x_{af}}{\left(\frac{P_a^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)} + \frac{x_{bf}}{\left(\frac{P_b^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)}$.

In this equation, now, $P_a^{sat} P_b^{sat}$ are also known, in addition to the rest everything that is $\left(\frac{V}{F}\right) + \left(\frac{L}{F}\right)$ are known, x_{af} x_{bf} are also known $P_a^{sat} P_b^{sat}$ you just calculate it is only unknown is P. So, that if you substitute here x_{af} x_{bf} are 0.5 $\frac{V}{F}$ are $\frac{1}{3}$ and $\frac{L}{F}$ are $\frac{2}{3}$. So, they are given P_a^{sat} is 0.56 P_b^{sat} is 0.16. So, this equation except P everything is known, so, P you can find it out it comes out to be as 0.32 bar.

So, that means when this equal molar make sure you take in a flash unit at 20 degrees centigrade in order to have one third of these feed into the vapour phase and 2 thirds of the feed into the liquid phase as a kind of separate 2 separate phases, then you have to apply a pressure of 0.32 bar pressure you have to apply. So, then once P is known, so, x_{af} you can easily find out from this equation that is x_a = x$\frac{x_{af}}{\left(\frac{P_a^{sat}}{P}\right)\left(\frac{V}{F}\right)+\left(\frac{L}{F}\right)}$.

Because these things are given P you just found it as a 0.32 bar, so, it comes out to be 0.4 and then y_a comes out to be 0.7. Similarly, because if once x_a is known then y_a nothing but once x_a $\frac{P_a^{sat}}{P}$ for that comes out to be 0.7. This is how we can apply these principles to solve any vapour liquid problems. Today we have taken only the cases where both phases are ideal phases.

In the next lecture we will be taking the cases where start with a case where the liquid phase having non ideality, positive deviation from ideality negative deviation from the ideality those things we incorporate in liquid phase then again for those cases we are going to draw the phase diagram and then we are going to solve a few problems in the next lecture.

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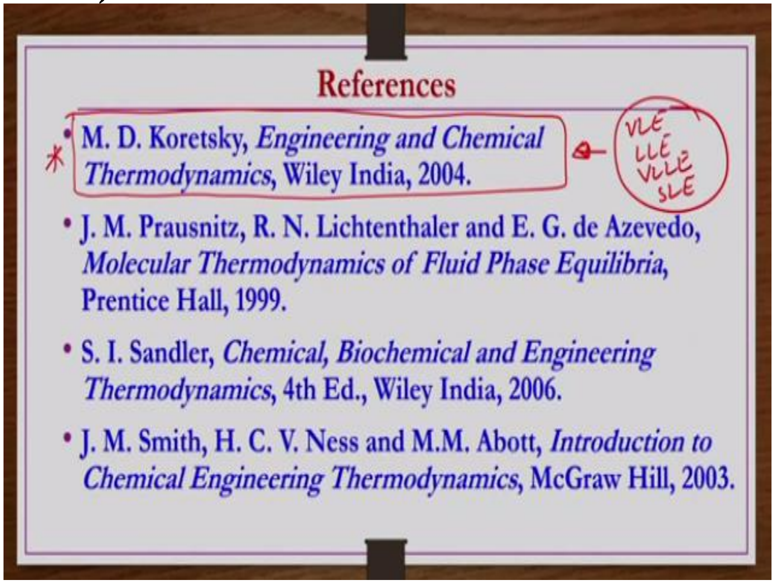

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VLE
LLE
VLLE
SLE

References for this lecture are given here, but henceforth, the entire course all notes would be prepared from this reference book that is for this VLE, LLE and VLLE, SLE cases the entire notes is going to be prepared from this lecture notes that is engineering and chemical thermodynamics by Koretsky. Though there are many other books available which can serve as a kind of better reference. Thank you.