Chemical Engineering Thermodynamics
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Lecture: 48 Vapor-Liquid Equilibria

Welcome back in last couple of weeks what we have done is we have looked into the models related for the vapor phase where basically the deviation from the ideality was you know described in the form of fugacity, ok and rather fugacity coefficient. Similarly, in the liquid phase, we have used the activity coefficient to describe that and we have looked into the different possible models which could represent you know the behavior of excess Gibbs free energy, molar Gibbs free energy.

So essentially what you have now is, you have now tools to represent vapor phase using equation of state from there calculating the fugacity coefficients right and now you also have tools to represent or evaluate the liquid phase. Here you have now activity models. So, using this understanding we can now apply this understanding to the vapor-liquid equilibria which is the major focus of the rest of the lectures in this course.

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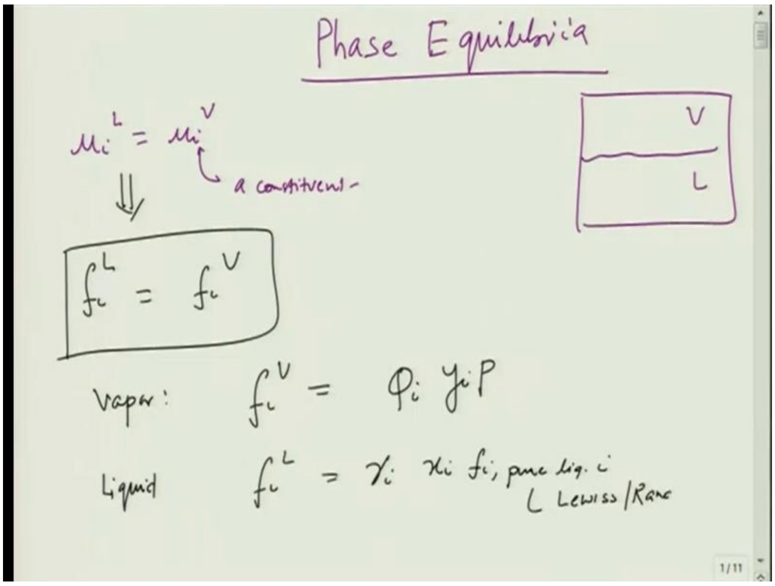

Phase Equilibria

$\mu_i^L = \mu_i^V$ ← a constituent

$\Downarrow$

$$\boxed{f_i^L = f_i^V}$$

Vapor: $f_i^V = \varphi_i y_i P$

Liquid $f_i^L = \gamma_i x_i f_{i,\text{pure liq. } i}$ ← Lewiss/Rand

So, essentially when we talk about the vapor phase equilibria or phase equilibria, you are talking about equilibria between two phases. We are going to consider vapor and liquid ok as our case and later once we understand we can take it to more complicated systems. So we have vapor and liquid alright. Now, this vapor and liquid phases may have many constituents and if they are at equilibrium then essentially the chemical potential in this phase vapor should be same as in this phase liquid right.

So, in that case, I can write this like Mu i let us say in liquid phase should be same as Mu i in the vapor phase where i is nothing but a constituent of the phase. Now based on the definition of the chemical fugacity we can clearly show that this implies if you consider the same difference state then essentially fl should be equal to fiV. So, the fugacity of the component i in the liquid phase should be same as in the vapor phase, alright. Now here comes the understanding of the last few lectures where one can relate these fugacities to the relevant diameters in the gas phase and the liquid phase.

For the liquid phase, we prefer to use the activity that is what we said that. For the gas phase, we prefer to use fugacity or fugacity coefficient in this case. So, let me write down particularly for vapor now. So for the case of vapor the fugacity of the component i can be written as the fugacity coefficient multiplied by the partial pressure or yi times P here ok, so this is the definition of the fugacity right where basically this Phi i is nothing but the fugacity coefficient for the ideal case Phi i is going to be 1 which essentially means that fugacity is nothing but the partial pressure that in the case of ideal gas mixtures.

Now for the case of a liquid ok we can use the definition of activity coefficient which suggests that fil is nothing but your Gamma i that is a deviation from ideality and ideal part is fi, so xi times fi of the pure liquid i ok. So, this will be the case essentially when you use pure liquid as a reference ok. This part is ideal part here then you are saying that we are considering Lewis Randall reference where essentially their composition is range from 0 to 1.

$$\mu_i^L = \mu_i^V$$

$$f_i^L = f_i^V$$

$$Vapor\!: \; f_i^V = \phi_i y_i P$$

$$Liquid\!: f_i^L = \gamma_i x_i f_{i,pure} \rightarrow Lewis\ Randall\ Rule$$

$$Vapor\ Liquid\ Equilibrium\!: \; \gamma_i x_i f_{i,pure} = \phi y_i P$$

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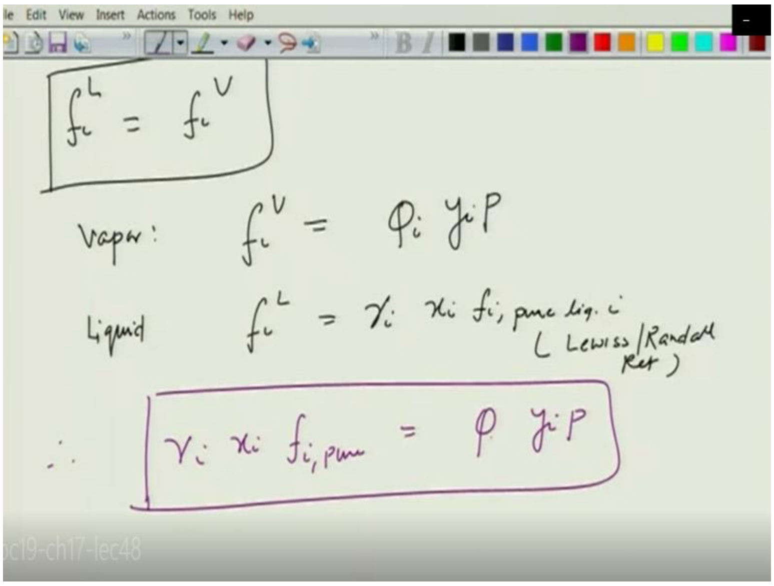

$$\boxed{f_i^L = f_i^V}$$

Vapor: $f_i^V = \phi_i y_i P$

Liquid $f_i^L = \gamma_i x_i f_{i,\text{pure liq. } i}$ (Lewiss/Randall Ref)

$$\therefore \boxed{\gamma_i x_i f_{i,\text{pure}} = \phi y_i P}$$

Ok, so given this now we plug in this equality conditions of the fugacity of the component i. So now we have a generic equilibrium equality or equilibrium conditions in terms of fugacity and activity. So, this is i, pure i, we will simply say pure we will drop the liquid part because this will indicate actually it is liquid phase and this is Phi i yi P. So, you have now a generic expression, ok. Ok so at this point we do not have any approximation other than the fact that this single condition which we have considered and that is the Lewis Randall reference.

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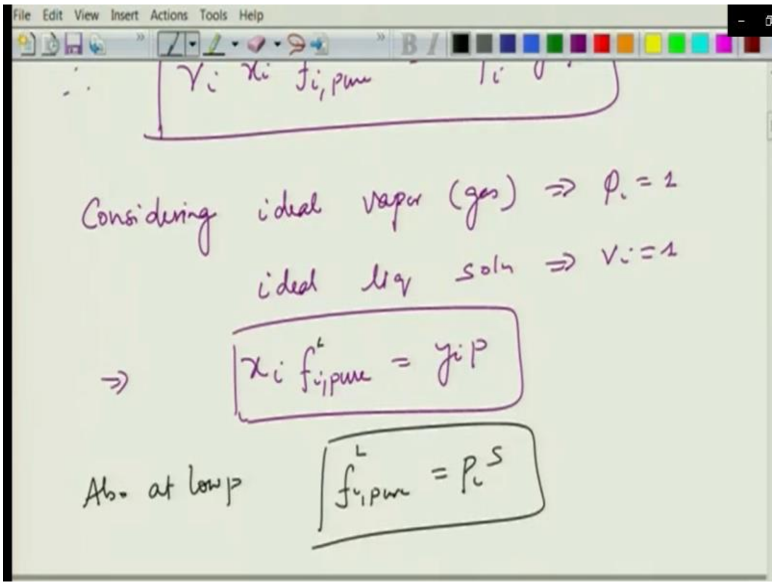

$\therefore \gamma_i x_i f_{i,\text{pure}}$

Considering ideal vapor (gas) $\Rightarrow \phi_i = 1$

ideal liq soln $\Rightarrow \gamma_i = 1$

$$\Rightarrow \boxed{x_i f_{i,\text{pure}}^L = y_i P}$$

Ab. at low p $\boxed{f_{i,\text{pure}}^L = P_i^S}$

Ok, so now from here we can bring some kind of approximation ok we can consider either phase we can consider vapor to be ideal gas mixtures and if that is the case that means your Phi i can be considered to be 1 ok gas phase that means phi i is equal to 1. The other thing which we can do is we can also consider the liquid phase to be an ideal mixture and which means that the Gamma the activity coefficient should be 1.

So, if we consider again that ideal liquid solution this means your Gamma i is equal to 1. For such a case, you have, this means you have this relation now xi fi pure is equal to yi P, right. Now what we can do is that we have done this exercise earlier. We have shown this clearly that for the case of a low-pressure fi pure ok liquid and of course this is a liquid is nothing but Pi sat, ok. At a low pressure, you can ignore the pointing connection and the fugacity of the component i at a given temperature can be simply you know simply can be replaced by the saturation pressure of that particular component i of that temperature, ok.

$$Considering\ ideal\ vapor\ (gas){:}\ \ \phi_i = 1$$

$$Considering\ ideal\ liquid\ soln.{:}\ \ v_i = 1$$

$$or, \qquad x_i f_{i,pure}^{L} = y_i P$$

$$Also, at\ low\ pressure, \qquad f_{i,pure}^{L} = P_i^{S}$$

$$x_i P_i^{S} = y_i P \quad Raoult's\ Law$$

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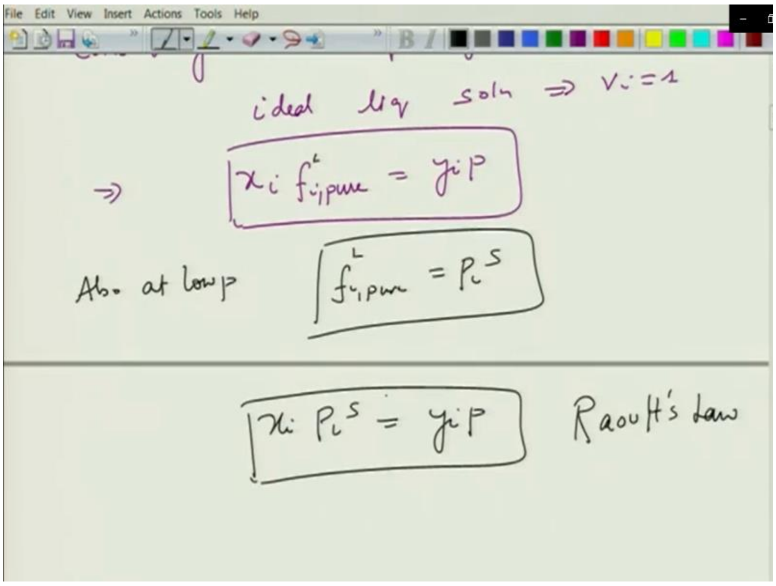

ideal liq soln $\Rightarrow$ $\nu_i = 1$

$\Rightarrow$ $\boxed{x_i f_{i,pure}^{L} = y_i P}$

Also at low p $\boxed{f_{i,pure}^{L} = P_i^{S}}$

$\boxed{x_i P_i^{S} = y_i P}$ Raoult's law

So this is something which will give us a very interesting expression which we now write as xi Pi sat ok and is equal to yi P and this famous relation is called Raoult’s Law, ok. So this is a very well-known expression which relates basically the partial pressure to the saturation pressure in a composition in the liquid phase. Now, we can solve phase equilibrium problem.

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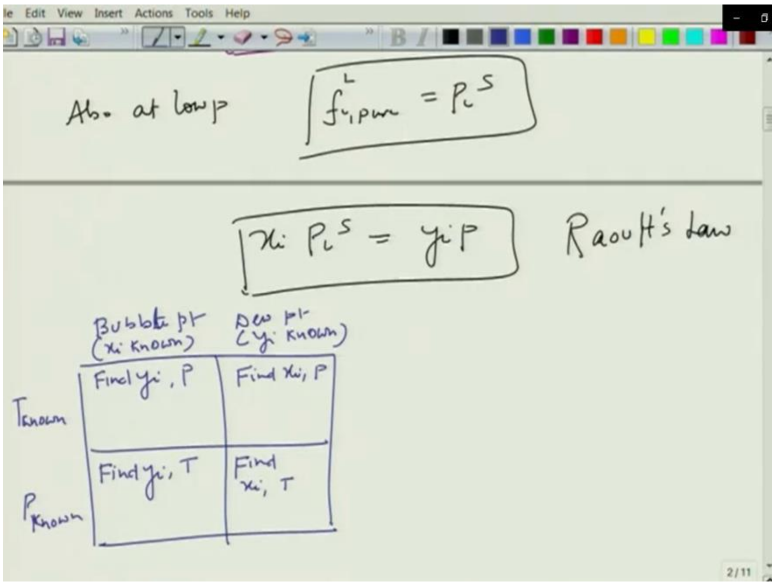

Abs. at low p $\boxed{f^L_{i,pure} = P_i^S}$

$\boxed{x_i P_i^S = y_i P}$ Raoult's Law

	Bubble pt (xi known)	Dew pt (yi known)
T known	Find yi, P	Find xi, P
P known	Find yi, T	Find xi, T

There could be many possibilities so many times the pressure may be given and the compositions are not known and so similarly the temperature is given and one of the phase compositions should be given and the rest you have to find.

So we can actually divide the possible combination into four quadrant. This could be something like this, ok so, here we can say that this is T is known, pressure is known, so in this row the temperature is known ok and then we may have to find yi that is the composition in the vapor phase and the total pressure ok and here it could be find xi and the total pressure here since the temperature is unknown you have to find let us say yi and T and here is going to be find xi and T. So if you look at it here, here what we are looking at is find the composition in the vapor phase for the given temperature or pressure.

So when you have to find this composition essentially in the vapor phase we say those say those, this conditions as bubble point calculations because what you are looking at is is basically the first bubble coming from the liquid phase essentially the composition of that.

So this should be a bubble point calculation where essentially x is known ok. Ok and this should be your dew point calculation because what you are looking at is a calculating the y, sorry calculating the x essentially that means composition of the liquid phase the first drop of the liquid and for that, you need to have the yi is known, ok. So this is a typical four-quadrant so if your x is known then you are looking only at y that means basically bubble point calculation, if y is known you are looking at x but then it depends on whether T is known or P is known ok.

So what we can do is, we can try to solve a simple problem to understand how such a problem in general vapor phase equilibria calculations are done.

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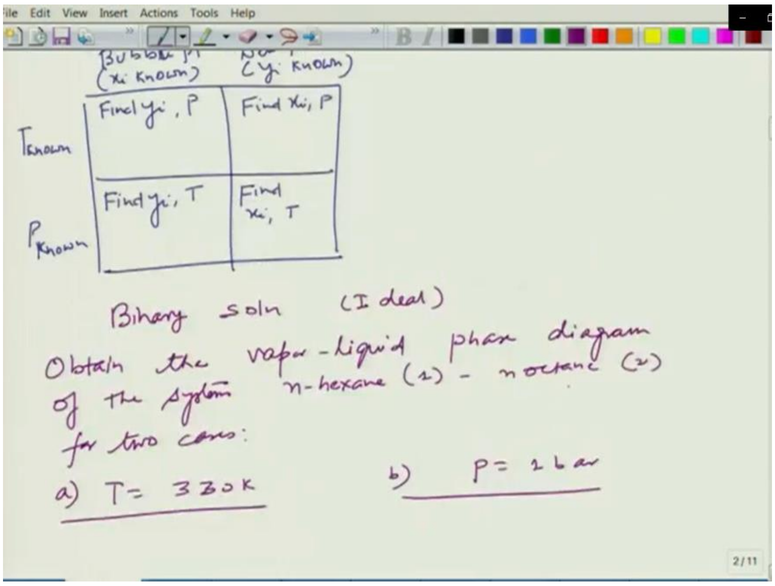

	Bubble Pt (x_i known)	(y_i known)
T_{known}	Find y_i, P	Find x_i, P
P_{known}	Find y_i, T	Find x_i, T

Binary soln (Ideal)

Obtain the vapor-liquid phase diagram of the system n-hexane (1) - n octane (2)

for two cases:

a) T = 330 K

b) P = 1 bar

For that, we can consider of course the ideal solution to start with. So let us say it is a binary solution and we have ideal ok considering it is a liquid phase is ideal and gas phase is ideal and the question is to is basically to obtain the phase equilibria or phase diagram of the system n-hexane 1 and n-octane 2 for two cases, ok.

So it could be something like this where you are saying that you know temperature is constant and so T is fixed here 330 Kelvin or it could be the constant pressure where basically the pressure is fixed and is P is equal to 1 bar. So this is a constant, this is also a constant. So these are two cases where temperature is fixed and the other case the pressure is fixed, ok and it is a binary mixture so obtain the vapor-liquid phase diagram of the system n-hexane and n-octane for two cases.

Now, if you look at this again this expression you one of the thing which you have to calculate is this saturation pressure, right which depends on the temperature and so for that what we are going to do is we are going to use Antoine equation which is basically dependent on three parameters and in most of the cases for simple fluid this information is given to us in the form of table, ok.

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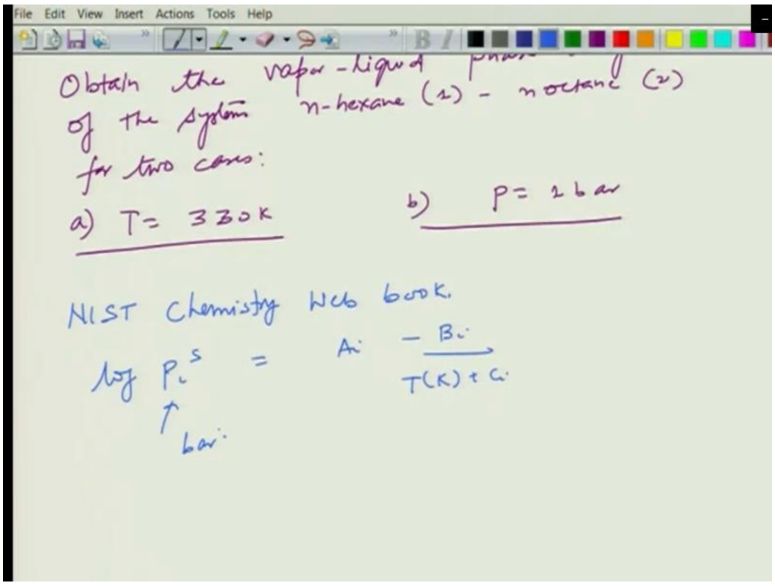

Obtain the vapor-liquid pha

of the system n-hexane (1) - n octane (2)

for two cases:

a) T = 330K

b) P = 1 bar

NIST Chemistry Web book.

$\log P_i^s = A_i - \frac{B_i}{T(K) + C_i}$

$\uparrow$ bar.

$$NIST\ Chemistry\ web\ book$$

$$\log P_i^s = A_i - \frac{B_i}{T(K) + C_i} \quad Antoine\ Eqn.$$

So one can use the textbook with the table behind the textbook or we can try to find out use this information or obtain this information from NIST Chemistry web book ok, where essentially you have to use this minus Bi T temperature plus Ci, ok and usually, this is in bar, ok. Alright so let us assume that you have handle to this information that means you know A and B and C for these two components which is hectane and octane then essentially you have an expression of Pi as a function of T and for the case of the first essentially you have you do know the Pi sat for hexane and octane for part A, ok.

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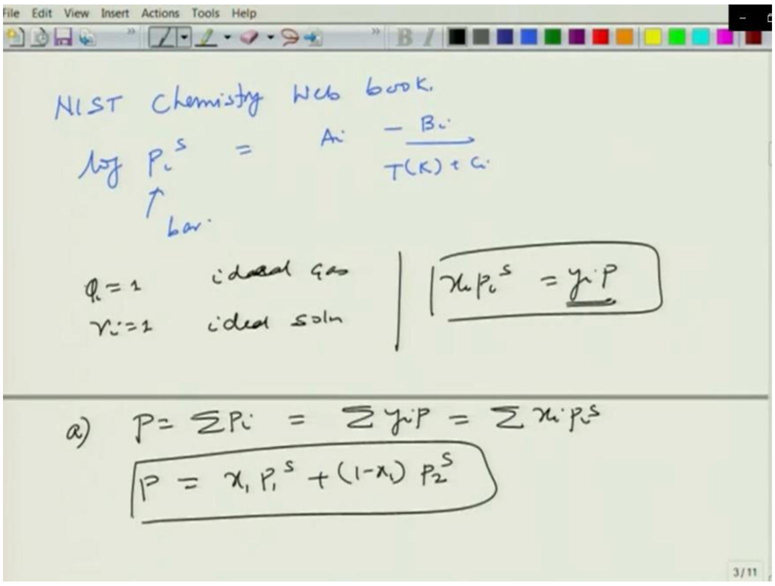

NIST Chemistry Web book.

$\log P_i^S = A_i - \frac{B_i}{T(K) + C_i}$

$\uparrow$ bar.

$\phi_i = 1$ ideal gas

$\gamma_i = 1$ ideal soln

$\boxed{x_i P_i^S = \underline{y_i P}}$

a) $P = \sum P_i = \sum y_i P = \sum x_i P_i^S$

$\boxed{P = x_1 P_1^S + (1 - x_1) P_2^S}$

$$a) \quad P = \sum P_i = \sum y_i P = \sum x_i P_i^S$$

$$P = x_1 P_1^S + (1 - x_1) P_2^S$$

So considering liquid ideal solution and ideal gas mixture which means that Phi i is equal to 1 and Gamma i is equal to 1 for ideal solution, ok, it is an ideal case ideal gas, ok, so I can use xi Pi sat, xi Pi sat is equal to yiP, ok alright, so now the question is that how do you solve this thing because in the first case the temperature, so that means that the total pressure is not known right so essentially what we can do is we can see this expression and write it for both the component and let us see what we can do about it.

So this would be a typical solution for such a case where basically pressure is some of the partial pressures, ok, so and this can be written as summation yi P and this can be written as because yi P is nothing but xi Pi sat right this for the binary case. I can write this as Pi sat plus 1 minus x1 P2 sat right.

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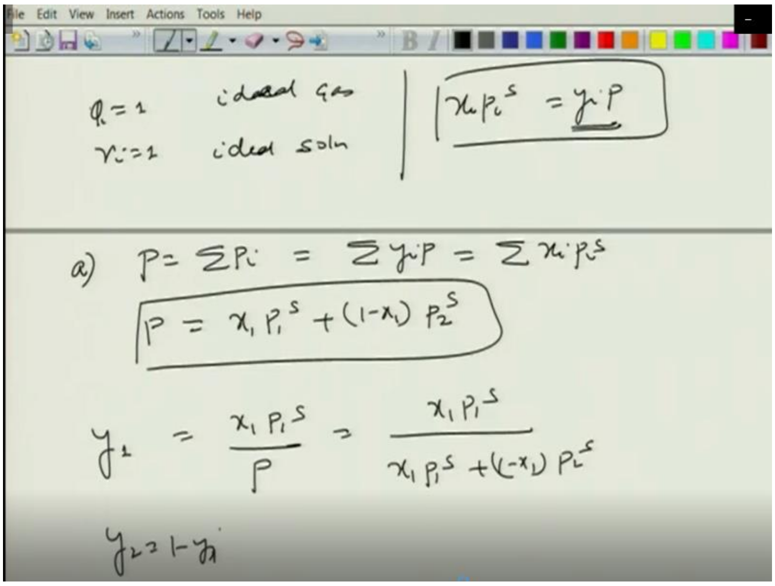

$\phi_i = 1$ ideal gas

$\gamma_i = 1$ ideal soln

$$\boxed{x_i P_i^s = \underline{y_i P}}$$

a) $P = \sum P_i = \sum y_i P = \sum x_i P_i^s$

$$\boxed{P = x_1 P_1^s + (1-x_1) P_2^s}$$

$$y_1 = \frac{x_1 P_1^S}{P} = \frac{x_1 P_1^S}{x_1 P_1^S + (1-x_1) P_2^S}$$

$y_2 = 1 - y_1$

So I have an expression here ok which tells you that if I plot P as a function of x1 is going to be a straight line right. So this is something which clearly tells me that. Now the other part is to find out the relation of the pressure with respect to y. So let us again look at this part here this is can be written as for example y1 can be written as y1 is equal to x1 p1 S by P right and I can now write P as this so this is going to be x1 P1 S plus one minus x1 P2S and this is x1 P1 S, right, so given x ok I can find out the P right and then I can also find out the y from this relation right. So and y2 is, of course, one minus y1 ok.

$$y_1 = \frac{x_1 P_1^S}{P} = \frac{x_1 P_1^S}{x_1 P_1^S + (1 - x_1) P_2^S} \; ; \quad y_2 = 1 - y_1$$

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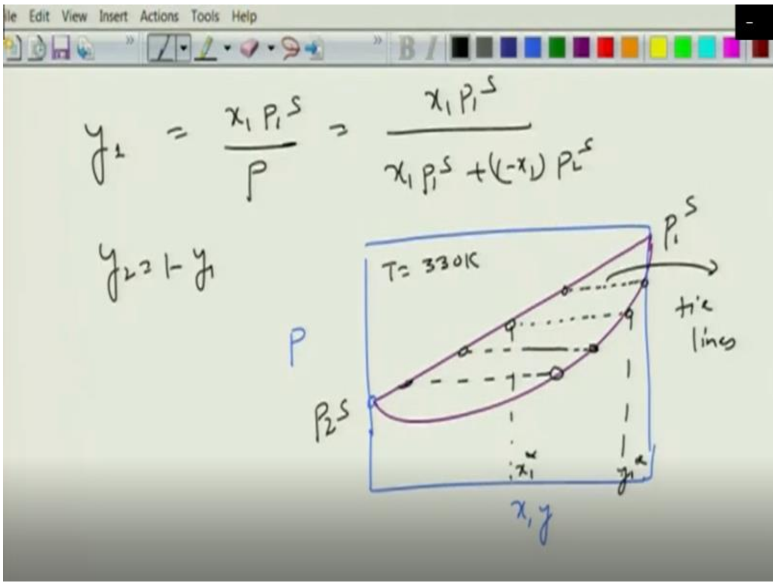

$$y_1 = \frac{x_1 P_1^s}{P} = \frac{x_1 P_1^s}{x_1 P_1^s + (1-x_1) P_2^s}$$

$$y_2 = 1 - y_1$$

So let me just draw the kind of expression or a kind of a diagram we obtain for such a case. So I will be considering P versus ok P versus x comma y ok because we will be taking x1 and y1 so in that case when this y1 is 0 essentially you have all component 2, in that case, the difference here is P2s, ok and this relation tells you that if we plot P as a function of x1 is going to be something like straight line right in that case this is P1s right so this is basically the liquid saturation line and this is liquid side and if you plot this ok for given ys one can come with an expression or rather I can get something like this where I have equality between two phases in the form of this, it tells you that, this tells you that this two points that phases which are at a equilibrium with the corresponding is this x1 Alpha and this is y1 Alpha correct, ok. Similarly, you can have other tie lines. So these are called tie lines ok which is to connect these two phases which are at equilibrium and the composition you can get it if you take the projections vertically to the to the x-axis ok.

Now, this was first case where essentially you had temperature known ok. So, this is T say let us say 330. So let us assume that we have done the calculations and you have access to P1s with this information you have the value P1s and P2s and then you can obtain this straight line for the liquid phase and this is the vapor phase.

Now for the second case, which is the case where only the pressure is known. This is to obtain vapor liquid phase equilibria at constant pressure of 1 bar ok. So if you put it at a second case ok.

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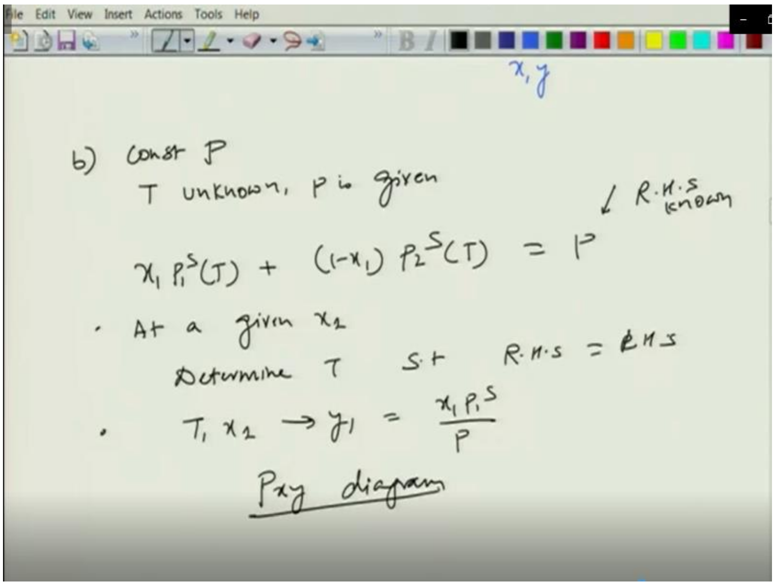


x, y

b) const P

T unknown, P is given ↙ R.H.S known

$x_1 P_1^S(T) + (1-x_1) P_2^S(T) = P$

- At a given x_1

  Determine T s.t R.H.S = L.H.S

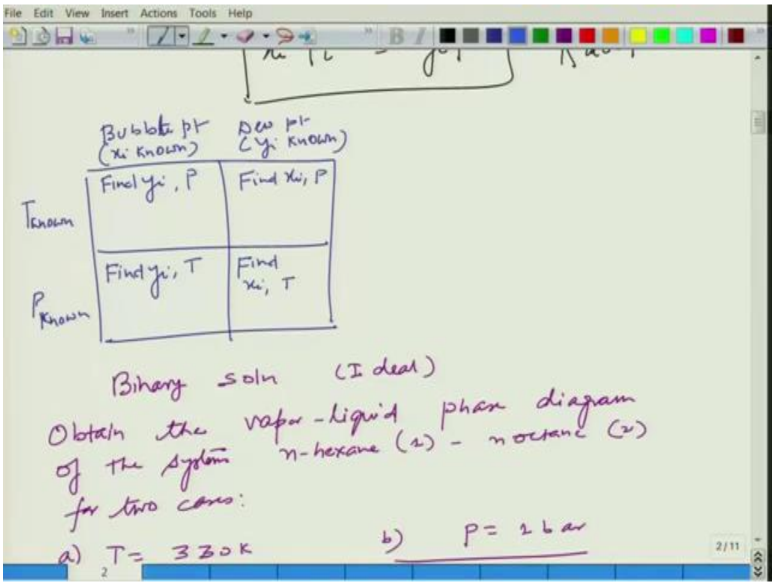
- $T, x_1 \to y_1 = \frac{x_1 P_1^S}{P}$

Pxy diagram

$$b)\ const\ P\quad T\ unknown, P\ is\ given$$

$$x_1 P_1^S(T) + (1 - x_1) P_2^S(T) = P$$

$$T_1 x_1 \to y_1 = \frac{x_1 P_1^S}{P}$$



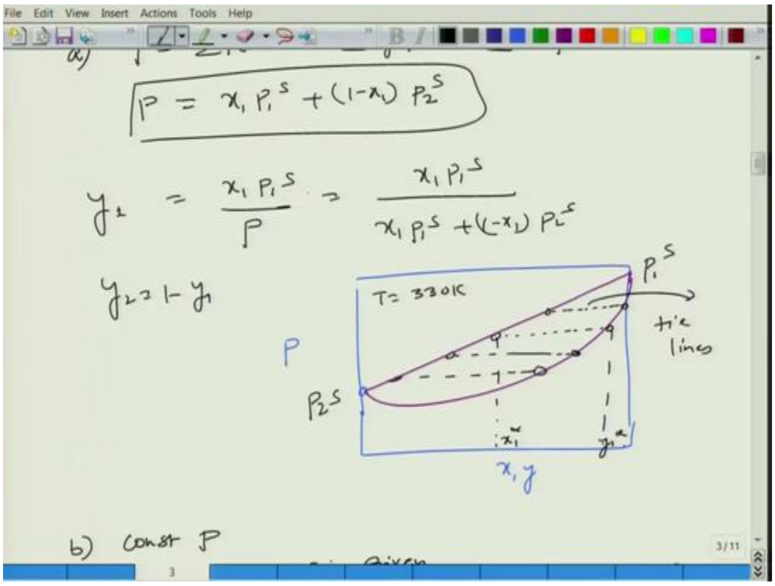
	Bubble pt (x_i known)	Dew pt (y_i known)
T known	Find y_i, P	Find x_i, P
P known	Find y_i, T	Find x_i, T

Binary soln (Ideal)

Obtain the vapor-liquid phase diagram of the system n-hexane (1) - n-octane (2) for two cases:

a) T = 330 K

b) P = 1 bar



$$\boxed{P = x_1 P_1^S + (1-x_1) P_2^S}$$

$$y_1 = \frac{x_1 P_1^S}{P} = \frac{x_1 P_1^S}{x_1 P_1^S + (1-x_1) P_2^S}$$

$$y_2 = 1 - y_1$$

b) Const P

So second is a constant pressure and here your T is basically unknown and of course P is given. So we look at again at the same expression, which we have written earlier, ok, this one right, look at again this one and so this is the pressure is of course known. So x1 P1 S plus 1 minus x1 P2S, this is P and this P2S is now a function of T because T we do not know so T is something which we have to find it out.

So if you are looking at this the right-hand side is known ok so how do we solve this, how do we obtain phase equilibria for such a condition, now this condition which falls in which quadrant your T is unknown ok and your is a binary mixture right ok so we do not know the composition here, so P is known, so we need to find in this way.

So at this point it is like generating there complete phase diagram here but it will be in this row as far as this diagram is concerned ok. So let us think about the algorithm. So you have right-hand side which is known. We know the expression of P2 and PS, P1 because this comes from the Antoine relation and A, B, C are known. Only the temperature is something which is unknown. So what we can do is at a given we can vary the x. So for given x1 we just have to find the temperature which satisfies this relation or constraint.

So at a given x1 determine T such that right-hand side is equal to left-hand side ok. Now this can be used or this can be evaluated using many different tools so you can actually plug in and we can put this thing as a constraint in excel sheet using a goal seek a function you can obtain the solution for this equation ok, and it will return temperature T and you can now iterate this you can have it from x close to 0 to 1 and you can have this complete you know the liquid saturation line for the case of this which is this.

Now once you know this x ok, then essentially you have temperature and then you have x1 right then from here you can easily calculate y1 ok for given x and pressure is already known right P1 Sat is known because temperature is calculated. So essentially you can use this expression to calculate the right. So you can calculate the y1 and thus if you do iteratively you do have means now to obtain P versus x and P versus y. Sometimes we say Pxy diagram ok. So you can calculate through this exercise.

So let me also draw for the case of this particular mixture. How does this diagram look like? So in this case actually this is the. So this is the Pxy diagram right because the Pressure is variable and x y you wanted to find here. This will be since pressure is fixed this should be, this should be Txy diagram ok. So how does the Txy diagram look like for this particular case?

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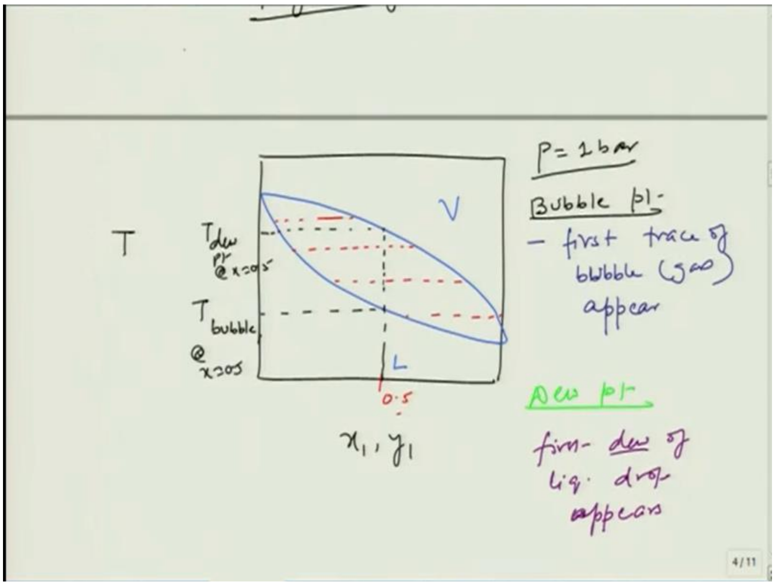

So here the pressure is 1 bar ok, this is your temperature and this is your x1, y1 ok, ok so this how it is, it will be something like this ok where v is here l is here ok and what you are looking for is this tie lines are going to be like this ok. Now the question is for given let us say 0.5 binary mixture, equal mixture, what would be the bubble point for such a case? Ok, if it is a mixture is like you know equally equal molar mixture so for such a case, you can think about it in this way that you are taking a let us say a vertical line and the cross-section with the liquid phase will give you a certain temperature ok at which the first, first bubble of vapor is seen and similarly this would be the temperature where the first drop of liquid is seen.

So this means that for a pressure 1 bar for equimolar mixture, this will be your bubble point temperature at x is equal to 0.5 and this will be your dew point temperature at x is equal to 0.5

ok, and you can do that for other cases also, alright. So essentially this is something which is often used that when I have to calculate bubble point temperature or bubble point pressure and so forth so one need to understand this phase diagram very well in order to get appropriate temperature in this case for example.

So bubble point again is the first trace of bubble which is gas which appears right ok so in this case here is a liquid is a vapor so this is the so here this is the one which is going towards this ok so that means there is a transition from this point to this point along the way. So this is here the first bubble would be appearing and that is why this is the reason that we call this as a temperature ok at this particular composition.

Similarly, you can have this dew point ok where the first dew of liquid ok dew stands for liquid, or trace of (bubble) trace of liquid drop which appears or appears ok. So, first dew of liquid drop appears, right. So that will be your dew point which is here, ok. Ok, I think this is something which I wanted to cover to give a first-hand introduction to the phase equilibria ok where what we did is, we consider the generic expression of equality of the fugacity. Express the fugacity in terms of fugacity coefficient and then we consider a simple example where we consider that the phases are ideal ok and then the proximation leads to the Raoult's Law and for the case of binary mixtures we obtained Txy and Pxy for simple case to illustrate how this phase diagrams are generated.

I would be taking this exercise further and providing more insight to other cases in the next few lectures so today that is the end. So, I will see you next time.