# Mass Transfer II

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## Lecture No. # 14

In today’s lecture, we continue our discussion on vapor liquid equilibrium. If you recall we talked about degree of freedom, if you have binary component and then if you fixed pressure and temperature then the mole fraction of two components in liquid and vapor phase will be fixed, so we apply this rule degree of freedom f equal to c minus p plus 2, which means if T and pressure are known mole fraction of A and B in V and l two phases will be fixed. Of course, we can applied Raoult's Law and equate with the total pressure or the partial pressure to calculate x and y. In today’s lecture, we do this, we prepare T x y diagram, if you recall in absorption also we started with the thermodynamics. First thing is that we must establish the equilibrium conditions between the two phases so in other words given mole fractions of y given mole fractions of A in vapor phase what is the mole fraction in the liquid phase for one component or for both the components.

The first thing we have to do in this distillation the second unit operation is to establish this T x y diagram. For this one has to do the experiment so in batch experiment you start with the system of liquid A plus B heat the liquid and monitor it composition and monitor the amounts of liquid and vapor formed in that closed system and then plot this T x y diagram. We one has to do this experiment and one has to; one can also apply this Raoult’s Law to corroborate is in a finding or observation, so we will do this exercise here in plotting this T x y diagram, which is the first thing one has to do before we get into this distillation column.

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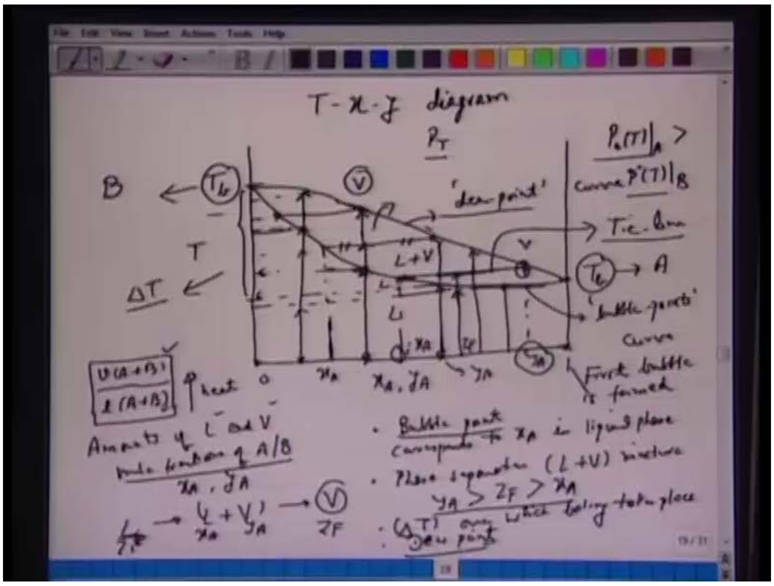

Let us start with this T x y diagram, which will look like this, so essentially this is what we want to plot here or we want to establish here, we have temperature here, and we have mole fraction of A in liquid and vapor. What we are looking here at a batch system, suppose we take a batch system here of liquid say l A plus B, there be some amount of vapor in contact with liquid here also containing A plus B. And if we heat this liquid slowly, if you have say pure component of you know A or B it says zero here, and if it is one at this end, so if you take pure component of B and heated you will expect that at boiling temperature T b corresponding to the total pressure P t, the system will boil or this component B will boil.

Similarly, if we have A if your component A mole fraction one, and heat this liquid then at a certain temperature corresponding to the boiling temperature of A write the component A will boil here, and will be vaporize and entire liquid will converted into vapor. When we have component - the binary component of A plus B then start with certain mole fractions and heat this system here, one can do this experiment, one can monitor the amount amounts of l and vapor, and mole fractions and or compositions mole fractions of A or B in two phases. Essentially, we one can monitor x A and y A, so 1 minus x A will be the mole fraction of B and one  minus y A will be mole fraction of B in vapor and the liquid phase.

If you do this experiment, what we observed here that as we increase the temperature. A certain temperature is reached, at which the first bubble is found. This is very important that we understand the difference between the boiling of a binary components, and boiling of a pure components A and B here. When we take this cold fluid liquid and we increase a temperature, a temperature is reached here at which the first bubble is formed.

If you chose another mole fraction here, let us say some mole fraction is smaller than this and heat this liquid, we will get another boiling temperature here, at which the first bubble will be found. Essentially, we will have a locus of all boiling temperature like this; if you take the mole fraction here and heat it we have another boiling temperature. Essentially, we have a locus of bubble points curve, so we call it bubble points curve. What are the bubble points curves. It is a locus of the temperature depending upon the mole fractions of A in the liquid phase, at which the first bubble is formed. This is the temperature, at which the boiling just starts taking place.

If further heated, then we will see this where significant amount of vapor is formed, in other words now we will have two phases one vapor containing A plus B and another phase we have the liquid containing A plus B also, in this case the amount of liquid and vapor will be different one can measure this amount of liquid and vapor one can also measure the composition of A in vapor phase and the liquid phase. We have now two phases here, so this is the liquid, now we have l plus P a liquid phase and the vapor phase, if we take another mixture here let us say we have heated here reach this bubble point if further heat then again there is a separations observe, we have some amount of liquid form, some amount of vapor form.

We will talk about this later what is the total amount. Essentially, we have now another locus curve like this, in which for different compositions there will be a separation of two phases in vapor phase and the liquid phase, in which the amount of liquid and vapor is different and amount of vapor compositions and amount of liquid compositions are different. Now, you further heated continue with this heating then temperature is reached, at which the entire liquid is now converted into vapor. So, similar to all this bubble point curves we have a locus of what we call dew points curve. This is dew points curve.

Now, what we have here is the when we reach this temperature for this binary components of A plus B depending upon what mole fraction, we has starting here is a temperature at which the entire liquid is now converted into vapor phase. Essentially for this binary phase, there is a temperature range right one is T B for a pure component B and we have this boiling temperature for a pure component A and if you choose any binary components of A plus B, a mixture of A plus B, then there is a temperature range between here and here.

There is a temperature range, at which the boiling takes place. First boiling or first bubble is observed at certain temperature you call it bubble point. If further heated there is separations liquid plus vapor the vapor phase contain so much mole fraction of y A given by this curve here and the liquid phase will contains so much mole fraction of x A given by this curve. If you further heated boiling continues till we reach this point and entire liquid is now converted into vapor phase, this temperature we call it dew point curve. So, we make three very important points here, one there is a bubble point this corresponds to x A in liquid phase.

This is the temperature, at which the first bubble is formed or the liquid just starts boiling, after that there is a phase separation. There is a phase separation or we have liquid plus vapor mixture, in which you can see the vapor phase composition is greater than feed compositions, if you call it Z f, which is in turn is greater than x A. Let us see what we trying to say here, suppose we start with certain mole fraction here, this is you call it Z f. We start with a composition of feed with Z f mole fractions say sixty percent of A and we start heating it, first we will reach a bubble point, so this is the temperature at which the first bubble will be formed if further heated, now there is a separation l plus B you call this as a tie line.

Now, there is liquid and vapor form vapor phase composition is given by this y A and the liquid phase composition will be given by x A, you can see y A is greater than Z f and Z f is greater than x A, which means there is a enrichment, we starting with sixty percent mole fraction of A now, we have been able to achieve eighty percent of A in the vapor phase and forty percent for example, lesser than the feed composition in this liquid phase. This is essentially we have y A greater than Z f greater than x A and here also once should note that with the boiling temperature of B is higher than the boiling temperature of a because vapor pressure of A is greater than the vapor pressure of B at any temperature.

We have the boiling temperature A smaller than the boiling temperature at means there is a temperature range, there is a del T, which is in between the boiling temperature of a pure component B and the boiling temperature of A over which the boiling takes place and as a consequence similar to this bubble point there is a dew point, so dew point is a temperature or is a locus of a different temperatures, at which entire liquid is now converted into vapor pressure, so starting with liquid you have now liquid plus vapor and then we have this vapor phase.

We start with a certain compositions Z f at any instance liquid has x A vapor has y mole fractions and now entire liquid has been converted into vapor, which means the final composition will be same as the starting composition, which we have Z F. The same experiment one can also do starting with a vapor, which means here we start with a liquid in an close container fix the pressure, composition is 40 percent A, 60 percent B heated with the temperature is raise from room temperature for example, 30 degree centigrade to 80 degree centigrade, when the temperature reaches 80 degree centigrade one can physically observe that there is now the liquid has started boiling or just above to boil that point is your dew point.

And this dew point will depend up on what is your mixture composition, if you start with some other composition higher compositions then if you increase the temperature now the dew point will be form or dew will be form at a temperature lower than the previous temperature so just follow this curve qualitatively to understand this physical meaning of this. Now, we have in the in case of binary mixtures, there is a temperature range, at which over which the liquid boils before it converted into vapor phase.

We start with A plus B pure liquid first bubble point further heated now there is a vapor phase and the liquid phase one can calculate the amount one can also measure the amount to make a to ensure that it is a consistent with our material balance, so we have certain amount of vapor form certain amount of liquid form vapor is now enriched in A that means the vapor composition an given by y A is not greater than the Z F initial mixture concentrations, which in turn as greater than your mole fraction, you further heat it liquid is still the mixture is still boiling more amount of vapor is formed less amount of liquid is now left in the container till you reach a temperature, which you call it dew point at which the entire liquid is now converted into vapor phase.

Now, the vapor phase composition will be is natural that will be same as what we have studied you just follow this vertical line here and every point in between del T dew point and the bubble point there is a tie line, the tie line decides how much is your mole fractions of a in the vapor phase ? How much the mole fraction of a in the liquid phase? And also decides how much is the amount of liquid and vapor formed? We will talk about this later. Why it is called dew point because I was talking about this earlier that the state of doing this experiment from liquid to vapor one can start with the vapor phase so super heated vapor. A vapor temperature is greater than the boiling temperature of less boiling less volatile component, which is B here that is why it is as higher temperature.

We have T b and we T a here and you take a temperature higher than this T B and start now cooling it, just do it reversible, if you cool it then you reach a temperature, which we call it dew point curve, at which the first dew is formed, that means the first drop of the liquid is formed. Further cool it there is separation vapor liquid it follow the same exactly for and till you reach a further cool it, till you reach a bubble point curve at which the entire now this liquid and entire vapor has been converted into liquid.

Now, I start with the vapor l plus V and you have l e to this what we have this T x y diagram one can observe experimentally, if we can measure the amount of liquid vapor form we can do some chemical analysis to find the composition of vapor and liquid to obtain, but you must not forget that this curve can also be obtain analytically by applying this Raoult’s law. Let us redraw this curve and make you know similar observations what we had in case of heating the vapor, so heating the liquid now let us start with the vapor and let us follow the locus of this line.

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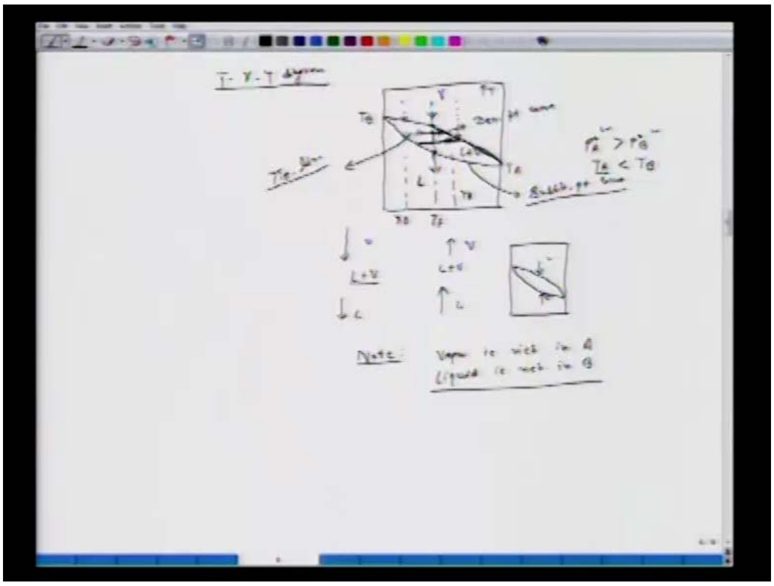

Note: Vapor is rich in A
Liquid is rich in B

Now, we have T x y diagram. So, here are we trying to understand the change in the compositions, if we have condenses in other words we are starting with the pure vapor, so let us say we have this general T x y diagram like this we have fixed total pressure, if you write T B and T A like this that means we are saying that vapor pressure of a is greater than vapor pressure of B it is more volatile compounds and as you consequence boiling temperature of a is smaller than the boiling temperature of B here. Now, let us see if you start with a pure vapor say the compositions of this pure vapor is Z f and start cooling it. When you start cooling it what will happened the first bubble; first dew will occur right here and if so we call it dew point curve, which is nothing but the locus of all such dews here.

If you start with different compositions the first you will appear if you start with different compositions that first you will appear right here, so we have this locus which we call it dew point curve. Now, if you further cool from here then we will get a liquid and vapor mixtures here, so we can call this as x A, we can denote this as y A the idea here is that the amount of the liquid form will be in the ratios of this by this. It is all tie line and we can apply the lever rule, which we discuss in the previous slide here if further cool it cool it the amount of liquid will be more and all the time the amount ratios of the liquid amount and this vapor amount will be given by this ratio by this ratio, if you keep on further cooling it till we heat this point we can say that we have heat what do we call bubble point curve and we further cool it we have now this pure liquid so starting with pure vapor we have l plus V then we have this liquid, the idea is that either we start from the pure vapor to reach there is own up your liquid through this l plus V by condensations or we start like in the previous class with the pure liquid and heat it till we reach l plus V and then we have this pure vapor, both of them will trace the same T x y diagram in a general curve like this, so either you go from here or you starts from here it will give the same results. We can make a note that all the time vapor is rich in A, it is a more volatile compound we said the vapor pressure of A is more greater than vapor pressure of the B or the boiling temperature of A is a smaller than boiling temperature of B or and all the time liquid fraction is rich in B.

We have this T x y diagram either way you starting from the pure vapor or heating of this pure liquid.

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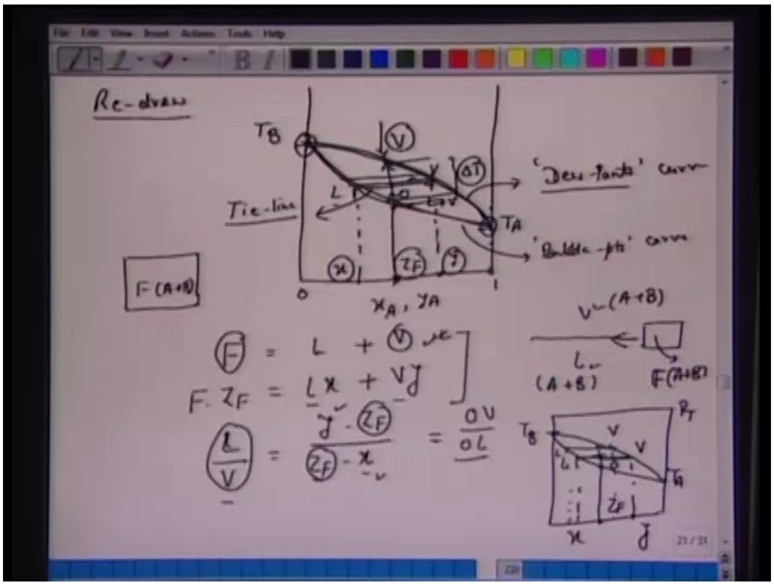

We will like to redraw this again, so let us redraw this T x y diagram. We are plotting x A and y A 0 to 1 we have T b we have T a, this is a bubble point curve and this is dew point curve. If you take any compositions of Z f and we reach this zone of liquid plus vapor we have compositions given by this bubble points curve given as x and we have this composition y given by dew points curve.

This is you calling it is tie line, because we are going to apply what do we call tie rule and of course, we know that if further heated then we will reach this dew point curve then the entire vapor liquid will be converted into this vapor phase. There is a boiling temperature range for binary compound. For a pure component entire liquid gets converted into vapor at one temperature for pure a entire liquid gets converted into vapor at one temperature above A for binary mixture there is a temperature range between T b and T a, at which the entire liquid boils. This composition for Z f is composition can say that this is del T range of temperature at which the boiling takes place. First boiling starts from here and ends here. Similarly, if we condense first condensation takes place this temperature then entire vapor is converted into liquid at this temperature. This is a temperature range for these binary component mixtures.

If you are doing this batch experiments and start with some feed of A plus B at any time we can write that f equals l plus V, at any instance between here and here feed is now converted or feed has two components, so initially we have hundred moles now we are saying that spot of this hundred moles is as the liquid phase and part of this as the vapor phase and part of this as a liquid phase so we can make a material balance to say that f equal to l plus V.

We are looking at starting with now we have vapor phase and we have liquid phase is started with a pure say one liquid phase F which is consisted of A plus B and we have heated it to bring it two phases l and V, each l each phase A l and vapor will contain A plus B. Now, we are made this, we have written this total material balance, you can now make the balance for A alone. If you have f and starting composition was Z F so f dot Z F, this would be the moles in this moles of a in this feeds and now this is distributed in liquid and vapor.

This is y this is x this is z, now you should be able to understand the meaning of this tie line and this horizontal tie line, which we have drawn here was point this Z F anywhere in between, this gives you Y 1 X 1, Y 2 X 2, Y 3 X 3 over this temperature, so essentially this A is distributed now between the liquid phase and the vapor phase with these two equations one can write l over V as y minus Z F over Z F minus x. If we chose say this o in between and we call this as v vapor which is a point, which is a coordinate on this dew points and we call this for corresponding to this o or v if a l on this bubble points nothing but y minus Z F is nothing but O V and Z F minus l is nothing but O L.

This what we have so we have this T x y diagram at a given pressure we have fix the pressure we have this T x y diagram T b, T a and let us do this calculation for Z F, so this mixture had brought to this temperature, now we have o this point here, this is v, this is l, this is y, this is x, so y minus Z F, y minus Z F is nothing , but O V and Z F minus x is nothing but O L, so l by v amount of liquid form reduces of amount of liquid form to that of vapor is given by this time line O V by O L this what it says.

If we know the compositions y and x the vapor phase, we know the feed composition Z F and Z F one can obtain the ratios of l and v form since we know the amount of f one can calculate out of 100 moles may be 40 moles are liquid 60 moles are vapor depending upon what temperature the feed mixtures and follow this locus the way it moves, we further heated now we are here Z F is fixed, but now, we have v reach be here and reach l here now look at his ratios now, o has reached here now we have new y, y minus Z F and we have new x, Z F minus x, so every time the amount of liquid and vapor the change as between as you increase the temperature between the first bubble point and the dew point and how does the liquid of vapor amount change ? This quite expected that in the beginning you have pure liquid l is almost equal to f when the temperature reaches bubble points and just you further heat more amount of vapor is formed so the tie lines can be we can look at this l by v right ? Now you have the small segments becoming a larger here.

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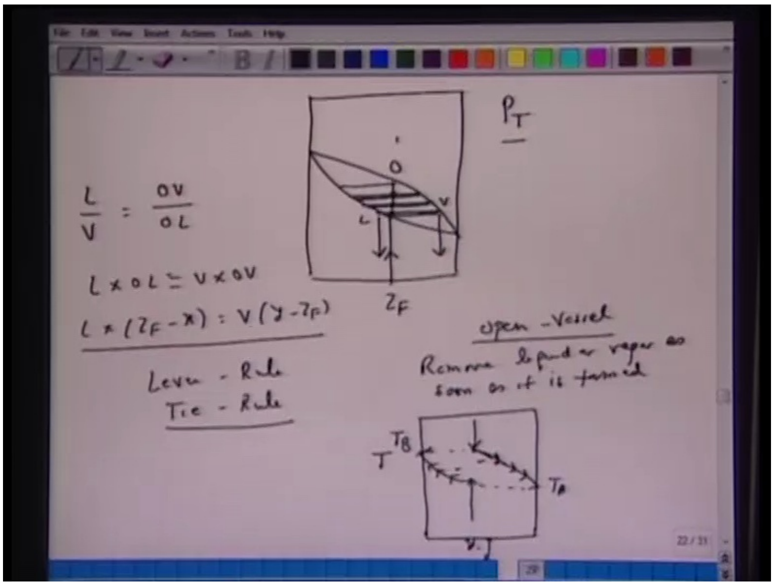

$$\frac{L}{V} = \frac{OV}{OL}$$

$$L \times OL \simeq V \times OV$$

$$L \times (Z_F - x) = V(y - Z_F)$$

Lever - Rule

Tie - Rule

open - Vessel

Remove liquid or vapor as soon as it is formed

We will one can let us redraw this and follow how does the segments of tie lines in the change? So you have tie line here suppose you are starting with this Z F you have just very small amount very small increment the temperature now we have this so this is a tie line Z F is fixed here this v this is one further increase, now we have another v another one further increase now we have this, so follow the segments. This segment, this segment, this segment it decreases this segment, this segment, this segment increases, so this what we wrote here l by v equals O V over O L or we can write l into O L equals v into O V or l into Z F minus x equals v into y minus Z F so what we have here l this is l and this is v l into this so we are applying essentially a lever rule or this also known as tie rule.

The amount of liquid and vapor form it varies along this, initially we have very small amount of vapor form then the vapor amount increases till it reaches here and everything is now the vapor, so starting with pure liquid we have reach now the vapor the amount will be just inverse of the segment, l by v is now O V if this all this locus is of course, Z F is o then l by v is O V over O L, so you should monitor this one can do this experiment, one can also apply this material balance and you know to determine how much is the amount of liquid? And how much amount of vapor is form? What is the mole fraction of x? And what is the mole fraction of y? You should also note that this is consistent with our you know we talked about this degree of freedom.

If fix the pressure say one atmosphere and any temperature between the boiling temperature of A and the boiling temperature of B, we assume that A is more volatile than B that means the vapor pressure of A is larger than B and the boiling temperature of A will be smaller than B. If you chose any temperature in between right for a given pressure then y and x is fixed given by the tile and once y and x are fixed we know the initial amount of mixture the compositions or amounts of liquid and vapor there also fixed this all consistent with your degree of freedom fix P and t, x and y are fixed degree of freedom is two here.

The idea of this small exercise is to generate this T x y diagrams they we want to distill acetone from methanol water from benzoic acid acetic acid from formic acid so they are two binary component one can create this T x y diagram by batch experiments. If you know some chemical analytical tools to measure the composition of vapor and liquid for example, gas chromatography, liquid chromatography one can also find the amount of liquid and vapor one can generate this T x y, , but T x y diagram can also be generate by Raoult’s Law, which we will do in a minute. This is also very important to note that instead of this batch experiment, which we are doing in a close system suppose you do this experiment in open vessel that means as soon as you start with a liquid.

And you heat it once the vapor is formed you remove the vapor again heat it again you remove the vapor or alternatively you start with the vapor phase of A plus B and load the temperature till it reaches this dew point that time as soon as the liquid amount is formed you remove it essentially one can do this experiment in open vessel if you do this experiment in open vessel what T x y will obtain that is very interesting and you should must understand that this is consistent with your experiment.

If we do this experiment in open vessel where you remove liquid or vapor as soon as it is formed so if you do this it is not difficult to understand that now we have this T x y diagram if you start with the vapor suppose it condenses here that is your first dew point and remove the liquid, now further cool it, now you have the locus, which will go like this, because you are removing the liquid as soon as this form so there is no liquid here of course, there is phase separation there will be vapor and the liquid like in the previous case, but you are just moving all the dew similarly, if you start with the vapor with a liquid phase a same compositions and as soon as the vapor is formed you remove it you will reach follow this path like this, which is same as T B and same as T A.

This is very similar to what we have to the previous case except you are removing the liquid form or the vapor form here as soon as you know you reach dew point of the bubble point curves, Now what will do next is we will show that this T x y diagram one can also calculate from or obtain from Raoult’s Law.

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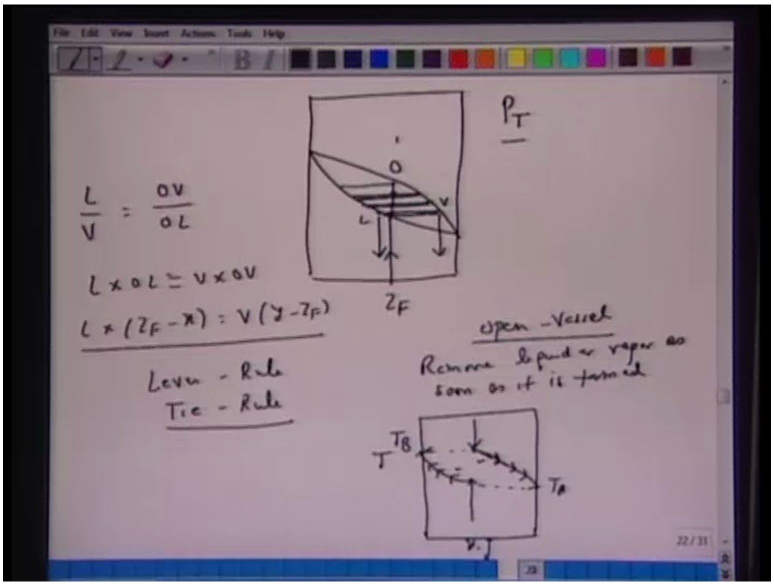

$$\frac{L}{V} = \frac{OV}{OL}$$

$$L \times OL \simeq V \times OV$$

$$L \times (z_F - x) = V(y - z_F)$$

Lever - Rule
Tie - Rule

Open - Vessel
Remove liquid or vapor as soon as it is formed

So experimental observation is one thing for most of the binary components you know you look at the Perris hand book or you look at the Treybals or McCabe Smith they have given this T x y diagram. If you have new systems A plus B new type of liquid mixture of course, one has to do this experiment, otherwise one has to rely on this vapor pressure curve and to an equation which you must have to done in thermodynamics to calculate this vapor pressure at a given temperature, but it still one can calculate the T x y diagram by calculation so let us see how we can do it.

These are the governing equations we are fixing temperature that means we are fixing vapor pressure and of A vapor pressure of B, so for example, we have this Antoine’s equation or you have some hand out tables to calculate or estimate the vapor pressure of A and B, so total pressure is P t is fixed that means the partial pressure of P t will equal to partial pressure of A and partial pressure of B. What is the partial pressure of A? The Raoult’s Law now assuming ideal gas law, ideal systems you have x A, P a 0 T and similarly for P v we can write x B as vapor into vapor pressure of T so we are assuming the ideal component, they behave as a ideal solutions and x A, P a 0 T is a partial pressure it can also be equated as y A into , so essentially partial pressure in the liquid phase we have equated with the partial pressure in the vapor pressure this will also equal to y B into P.

So, P is fixed and P t is fixed to and what are the unknowns here, unknowns are x A and y A because x B is nothing but one minus x A and y B is nothing but one minus y A, so we have two equations so these are the two equations we have and we have two unknowns to solve for x A and y A, one can solve for x A and y A for different temperature to obtain this T x y diagram. Essentially, we have this T x y diagram generated for a binary component of A and B at a given pressure P t, at chose P is one atmosphere, two atmospheres and chose a temperature I have y and x given from two point in the bubble. This small x exercise, we have done small calculation; we have done to calculate x and y for a given pressure and temperature of course, we need to know the vapor pressure of A and B given by some correlations or Antoine's equation so out are from some hand out.

Now, in principle it is also possible that we plot P x y in other words. We say that temperature is fixed and if you vary pressure there also we have a same degree of freedom two, if you apply you know the rule of degree of freedom f P equal to c minus P plus two. So, if you fix temperature and vary p one can also obtain P x y and generally P x y is not very popular or not very convenient to calculate the calculus in distillation one extensively relays on p a and x y, but theoretically one can also P x y and if you plot P x y you will get this equilibrium curve P x y like this.

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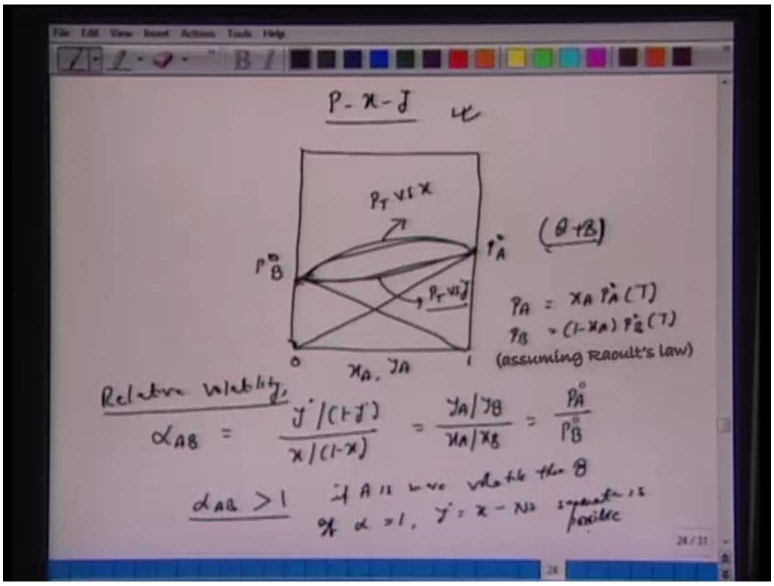

$p_A = x_A P_A^o(T)$

$p_B = (1 - x_A) P_B^o(T)$

(assuming Raoult's law)

Relative volatility,

$\alpha_{AB} = \frac{y^*/(1-y^*)}{x/(1-x)} = \frac{y_A/y_B}{x_A/x_B} = \frac{P_A^o}{P_B^o}$

$\alpha_{AB} > 1$ if A is more volatile than B

If $\alpha = 1$, $y^* = x$ – No separation is possible

Now, we have same x A y A 0 1 now if we vary the mole fraction of x A then it is not difficult to so that partial pressure of A will vary like this and the partial pressure of B will vary like this, so what we have plotted here is partial pressure of A so P a one can write as x A vapor pressure of a at any temperature, so it is linear similarly, 0 x 0 that means of vapor pressure of pure component B, which would be A B would be one minus x A into vapor pressure of B. With this one can then plot P t versus x and P t versus y and leave as an exercise to plot this, we have this P t versus x and we a have P t versus y. This is also equilibrium curve for the binary mixture of A and B, P x y instead of P x y, but generally as I said earlier that P x y is more convenient to use and widely used is most popular.

In distillation, there is one more variable called relative volatility, which is widely used in several calculations if you recall we said that if you have a binary components of A and B and we plot T x y diagram, A is more volatile it has a larger vapor pressure than B so it has a smaller boiling point than A than B. Larger the volatility you will see that larger the separations, so we like to plot this T x y diagram for different volatility as per. Let us define this relative volatility, which is use nomenclatures use alpha A B, so relative volatility of a with respect to B is defined as Y star over one minus Y star, so star means it is an equilibrium with x and one minus in other words for a and b this would be y A over y B over x A over x B or which would be same as P a over P b.

Volatility must be larger than one in fact much larger than one, one much larger than one, if A is more volatile than B and 1 can also that if alpha equal to 1 that means Y star equal to x and there is no separation is possible. This alpha relative volatility signifies what extent A is more volatile than B or from the practical point of view to what extent separation is possible right. This T x y diagram, which we have plotted for temperature n x and y can also be plotted as y versus x and we will do this by taking the projections of x and y for T x y plot.

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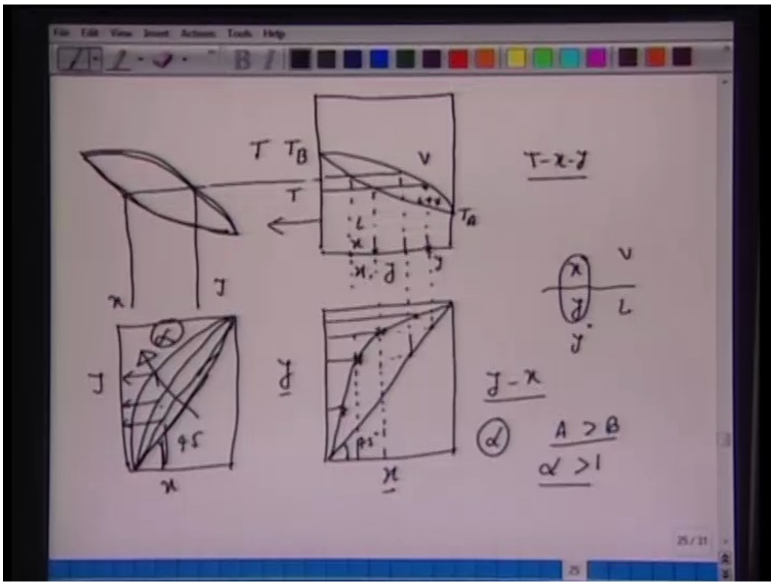

Let us again redraw this T x y diagram, so we have T x y diagram like this, which is T b here and we have t a, now just underneath this. Let us plot y versus x right where y and x they are in equilibrium phase, so we are talking of vapor phase l phase liquid y and x in equilibrium, so liquid and vapor they are in equilibrium phase so very often we use y or y star here, now in T x y diagram as you said earlier if you chose any temperature between T a and T b at this temperature here, then we have vapor phase this is v, this is l we have l plus v, now all it means that they will be two phases vapor in the liquid and the vapor will have this mole fraction and this liquid will have mole fraction of A and the liquid phase and here we have this y and this x and if you want to plot y versus x the best would be first to draw this 45 degree line here.

This is the 45 degree line and we take this projection here x and corresponding to this x this liquid phase vapor is in equilibrium, this y we can extend here to 45 degree line and move in this directions to obtain this coordinate, suppose I chose this temperature and this tie line we have x mole fraction of A in the liquid phase mole fraction of A in the vapor phase, I extend this, so this is x here corresponding to this x now i have this y here, which as take to the 45 degree line I come to this direction I have another coordinates.

Similarly, we can plot different x and y to obtain this what do we call x y diagram, so this is also an equilibrium curve y versus x, the more important here to notice that at every coordinate y and x the temperature is different. It is very important that you understand this all the we do not specified temperature here and temperature is different for every y and x, so T x y diagram is one type of equilibrium curve and more simplified version if you call it is y versus x, which is also very more widely used here.

We were talking about the relative volatility, A is more volatile than B, you will expect that alpha will be greater than 1 and larger is volatile than B alpha will be larger than 1 from here we can show that or one can see that, now if you want to plot this liquid vapor equilibrium curve for a larger volatility and there will be a separations more separations, in other words if you plot it here this will be now wider liquid and vapor curve oval point curve and the dew point curves will be wider here that means for the same temperature you go this way now you look at the this difference between y and x will be larger, so that means it is more separation here. This phase is much richer in A and here.

And similarly, for this if you want to plot y or x versus diagram by the same technique while taking the projection here one can show that this 45 degree line now y versus x curve will also be y versus x curve be x curve will also be away from this forty five degree line. For the same curve same plot if you want to plot for different relative volatility it is easy to show that there what we have done is increasing relative volatility, it is 45 degree line and away you are from 45 degree lines you have y much larger than y one greater than y two greater than y three for the same x, so we have plotted y x diagram for different relative volatility.

These are the things, which we have to understand from both physically and also from mathematically. We can write down all these Raoult’s Law equations, we can also write down this relative volatile expressions alpha to convince our self the shape of T x y diagram wider it is that means more separations y is much larger than Z f, Z f is much larger than x and we have very small relative volatility this curves take one side or they come closer we have very separations you can do these equations for Raoult’s Law and one can do this kind of exercise as I leave this an exercise you must try to convince yourself.

Similarly, if you plot y versus x diagram and draw this forty five degree line if you are very small relative volatility this curve will be very close to this y this forty five degree line and your larger relative volatility that means A is more volatility than B it has more vapor pressure than B then the curve will be away from this x y diagram this what we have done here. Now, these are all for ideal system and we said that we are fixing the pressure here now if you change the pressure T x y diagram will also change. Now we are saying that T x y diagram we want to plot for different pressures P 1, P 2, P 3 etcetera.

There also qualitatively you will an you should try to understand that increase the pressure then there is a possibility of that means we are trying to approach critical pressure of A or B since A is more volatile than B then at the certain pressure there is risk of pressure reaching the critical pressure of A, in that case there is no phase separations right if you recall from thermodynamics one is you reach a critical pressure, then you essentially you have reach a stage where there is no l and v separations so if you want to plot T x y diagram for different pressure one can plot qualitatively like this.

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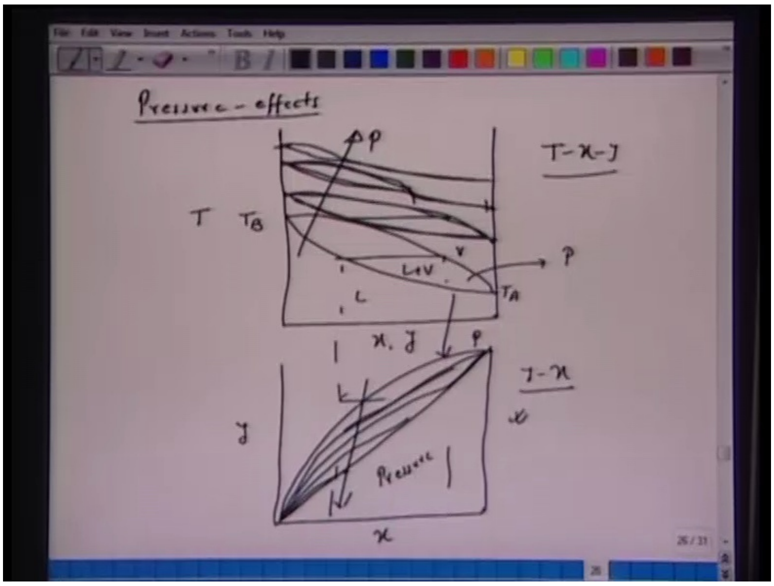

Let us plot this pressure effects so we have T x y diagram what we did earlier x y we have T x y, so let us say that we have plotted this, T x y for certain pressure, we have T b T a and this at corresponding to some pressures P, now if increase the pressure then you will expect that this now we have the new T x y diagram, which will be slightly more compact, in other words now the separation between two phases as gone the smaller, if further increase the pressure there is a possibility that we will might reach the critical pressure of A in that case this curve will shrink it will come like this, so that means now there is no separation corresponding to this zone here. We have liquid plus vapor, we have vapor again for the system only this region where we have liquid and vapor if you further increase this curve will further become narrower till we reach a pressure where we have exceeded the critical pressure of B components.

This is like increasing pressure we have plotted T x y diagram, corresponding to this T x y diagram if you just underneath this, if you plot y versus x again qualitatively you should be able to just that if this is the curve for the lower part right for A pressure and then if increase a pressure then this will become flatter and flatter, it will approach y this forty five degree lines till you will have situations like this where there is no liquid and vapor separations, it has heat the forty five degrees like this and like this, so this is now increasing pressure. Again T x y diagram, which we have plotted from this y x diagram, which we have plotted from here one can take the projections of y and x take x here take y here go to the forty five degree line connect with this etcetera, so one can do this.

The idea is that here we have plotted this T x y diagram or x y diagram or y x diagram for change of the pressure at higher pressures in general most of the ideal solutions they behave like this the separation is less the curve becomes narrower and narrower. Now, these are all for your ideal solutions. Right now, there are some non-ideal solutions, where we have very typical you know things what do you call as azeotropic mixtures, in which case the total pressure is actually more than what we predicted by the Raoult's Law, so we call it positive deviations from ideality. Similarly, you can have different types of A plus B binary components whether deviation is negative that means the pressure total pressure is exerted is smaller than theoretical calculation.

Now, when we have this type of situation as azeotropic compositions, a very peculiar thing happens that at certain temperature in between the boiling temperature of pure component B and A there is a azeotropic compositions, at which entire liquid will be converted vapor pressure without any phase separations. Now, if that happens you can imagine that in distillation column at that trey wherever it happens the distillation will stop there is no enrichment, remember if you started with A plus B for a liquid phase you had Z f we heated we reach a bubble points we further heat it the liquid mixture is now boiling we have vapor phase composition y which is greater than Z F and Z F is greater than x.

So, there is a separation here we are reaching we are doing enrichment, we are purifying it we have vapor, which is richer in A and liquid which is richer in B, so this is the way we have achieved this separations or if you have this azeotropic mixture or what do we call constant boiling mixture then at that compositions you will see that entire liquid is converted into vapor phase, that means there is no separation there and one has to avoid this azeotropic boiling mixture. For this course, most of the discussion will be confined to this ideal system, , but now we should must make a note of this non-ideal mixture. So today's lecture, we complete with this qualitative description or this non-ideality in binary component mixtures.

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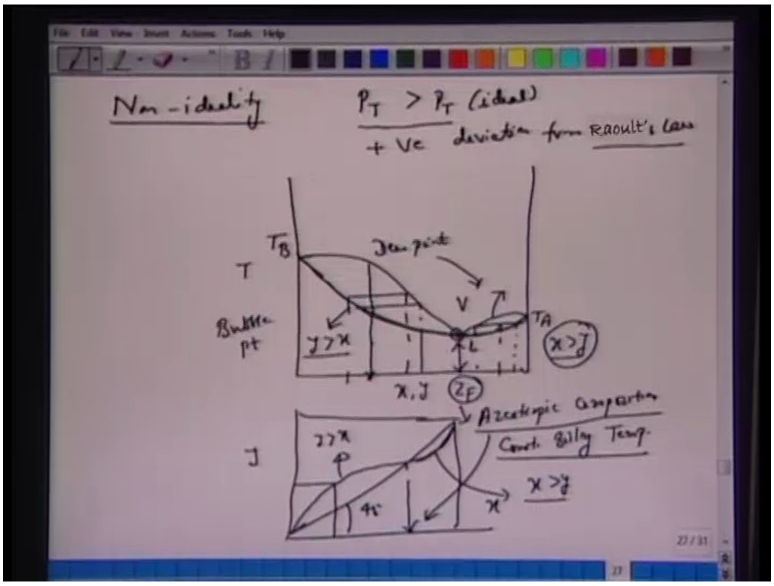

Non-ideality

$P_T > P_T$ (ideal)

+ Ve deviation from Raoult's Law

We have non-ideality gave say let us take P t is greater than P t ideal so what we call is positive deviation from Raoult's Law. What Raoult's Law predicts? Now, we have pressure greater than this, for that such type of system as we said earlier that if we plot T x y diagram then what we obtain is something like this qualitatively. Now, we have T b and we have T a and the bubble point curve reaches the minimum and before it increases to this T a and we plot the dew point then we have curve like this.

Notice here, if we have this composition mixture of Z F as a feed and if heat it then entire liquid will be converted into vapor without any separations. There will be a separations, if we take a mixture smaller than Z F, if increase it we have the bubble point curve here bubble point, first bubble is form, liquid is starts boiling, there is a separation here, this y is greater than Z F further heated y is greater than Z F till we reached this dew point.

So any region any composition smaller than this Z F or we call it isotropic composition, we should notice that y is greater than x alright and if you are here and draw a tie line is not difficult to show that now we have a just reverse situations this is also dew point curve and this is also a bubble point curve here. Now, we have x greater than y and if you have a mixture here that means there is no separation at all, entire liquid is converted into this azeotropic composition that was it also known as constant boiling temperature.

So only in this reason as long as feed composition is smaller than Z F we have vapor in rich and richer than your feed composition and the liquid is linear in A and richer in B, on the other hand if the feed composition is greater than isotropic composition and we just have a reverse conditions x is greater than y, A is richer in the liquid phase rather than in this vapor phase except non-ideality situations it raises because total pressure exhausted by such component is greater than you know what is predict by the Raoult's Law. Corresponding to this T x y diagram, if it plot y x diagram and if we have this 45 degree line here when you take the projections from the top to the bottom you should be able to convince yourself that you will get a curve like this here, now this is the isotropic composition and notice here y is greater than x it is above 45 degree line.

This range y is greater than x and this range here is curve is below this forty five degree line x is greater than y, so this is a non-ideality situation, non-ideal components, which view main counter depending upon type of binary components we have, for example, water with most of the alcohols right it is a kind of immiscible fluids and there is certain isotropic compositions at a given pressure at which if you have that compositions then entire liquid will converted into vapor and they will not be in a separation. If you want to separate this type of mixture one of course, the feed composition should be smaller than this isotropic composition or if you increase the pressure there is a possibility of removing this isotropic composition, just now in the case of ideal mixtures we plotted the effect of pressure and the curve of T x y diagram changes.

Similarly, one can show that we take a increase the pressure they will be locus of isotropic mixture and this point will move away to you know one or pure component of A in which case is a possible to increase our feed compositions at which the distillation or the separation is possible. As, we said earlier that for this course distillations we confine our discussion, calculations, or the design of a distillation column for an ideal binary component system. We can apply Raoult’s Law without bring in this activity coefficient etcetera, which accounts for non-ideality.