Mass Transfer Operations - I
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Lecture - 26
Distillation

Welcome to the next module that is module 5 on Mass Transfer Operation. In this module, we will discuss Distillation. Before going to the first lecture on distillation, let us have small recap on our previous lecture.

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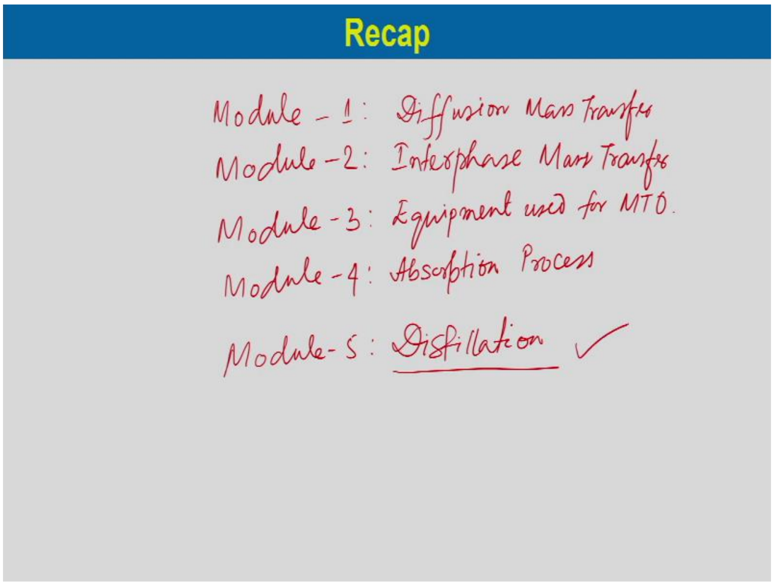

Recap

Module - 1: Diffusion Mass Transfer
Module - 2: Interphase Mass Transfer
Module - 3: Equipment used for MTO.
Module - 4: Absorption Process
Module - 5: Distillation ✓

In module 1 we have considered Diffusion Mass Transfer, in module 2 we have considered Interface Mass Transfer and in module 3 we have considered the different equipments used for the Mass Transfer Operation and module 4 we have considered the Absorption Process and we have looked into different aspects of Mass Transfer Operation and this is the final module we will consider Distillation Operation.

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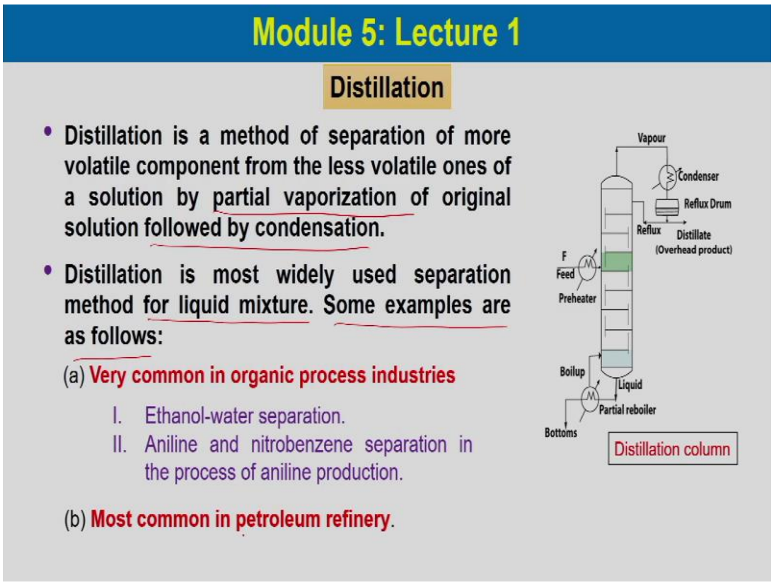

Module 5: Lecture 1

Distillation

- Distillation is a method of separation of more volatile component from the less volatile ones of a solution by partial vaporization of original solution followed by condensation.
- Distillation is most widely used separation method for liquid mixture. Some examples are as follows:

(a) Very common in organic process industries

I. Ethanol-water separation.
II. Aniline and nitrobenzene separation in the process of aniline production.

(b) Most common in petroleum refinery.

So, this we will cover now. So, in our first lecture we will consider Introduction to the Distillation Operation. Distillation is a method of separation of more volatile component from the less volatile ones of a solution by partial vaporization of the original solution followed by condensation. So, in this case unlike in absorption where we add a solvent the third component to separate a gaseous mixture, but in this case we have a liquid mixture that is partially vaporized and then, the solution generates the vapor of the more volatile components and then by condensation it separates the mixture of components. That is why in case of distillation, we do not use any third components. So, we take the mixture and then, we separate them by based on its boiling point.

So, this is typical distillation column we have discussed already. So, distillation is most widely used separation method for liquid mixture. So, this is very widely used and some of the examples as you know one is very common in organic process industries like if we consider ethanol water separation where we use distillation. Another one is aniline and nitrobenzene separation in the process of aniline production; for producing aniline, we have byproduct of nitrobenzene and that has to be separated and that is done by distillation. And most common in the industry as you can see in different industries most common particularly in petroleum refinery. So, refinery has plenty of application of the distillation operations and you could see a huge plant for most of the refineries on distillation

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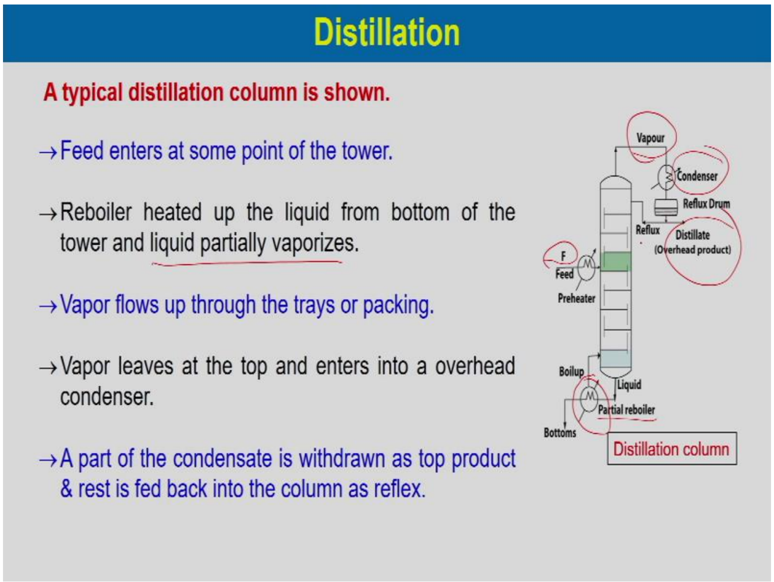

Distillation

A typical distillation column is shown.

→Feed enters at some point of the tower.

→Reboiler heated up the liquid from bottom of the tower and liquid partially vaporizes.

→Vapor flows up through the trays or packing.

→Vapor leaves at the top and enters into a overhead condenser.

→A part of the condensate is withdrawn as top product & rest is fed back into the column as reflex.

So, a typical distillation column is shown over here as we said and we will just tell you how is the operation of the distillation happened in a distillation column. This is typical tray column which we have shown over here. So, in the tray column it may be packed towers, but in case of tray towers as shown over here feed enters at some point of the tower. You can see over here the feed is entered at some point of the column and then, reboiler heated up the liquid from the bottom of the tower and liquid is partially vaporized.

So, we have a reboiler here which is shown over here is a partial reboiler and which boils up the liquid and then, boils up return back to the column and the less volatile components they comes out as a bottom. So, reboiler heated up the liquid from the bottom of the tower and liquid is partially vaporized, that is why it is partial reboiler over here it is used, it is not completely vaporized. So, vapor flows up through the trays or packing; if it is packed towers, it flows through the packing and if it is tray, it flows from tray to tray.

So, vapor flows up and the vapor leaves at the top and enters into a overhead condenser. So, you can see vapor is leaving at the top of the tower and at the top of the tower you have a condenser. So, through the overhead it goes to the condenser. So, once it enters into the condenser, a part of the condensate is withdrawn; that is as a top product and rest is fed back into the column as reflux. So, some part of the condensate which is returned back to the column and some part is taken out as a top product and raised is feedback to the column as reflux.

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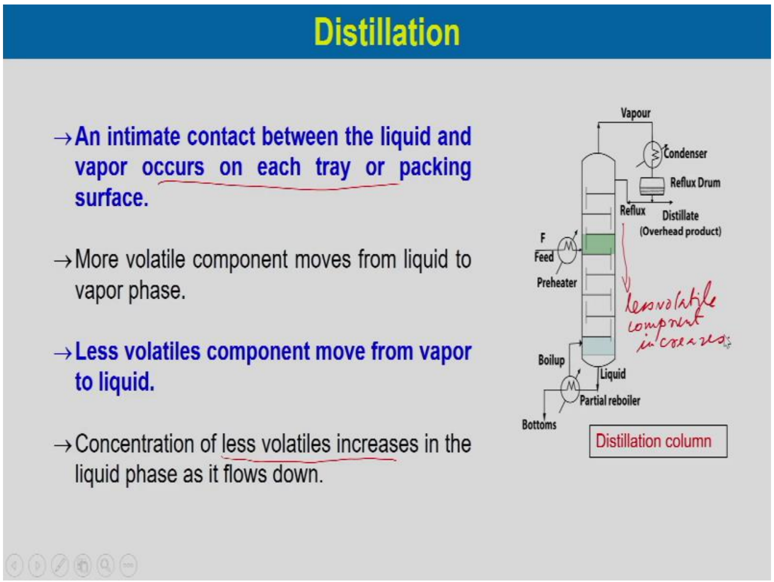

Distillation

- →**An intimate contact between the liquid and vapor occurs on each tray or packing surface.**
- →More volatile component moves from liquid to vapor phase.
- →**Less volatiles component move from vapor to liquid.**
- →Concentration of less volatiles increases in the liquid phase as it flows down.

Distillation column

Now, what happens during this flows of gas and liquid from top to bottom as the reflux liquid as well as the feed flows down and intimate contact between the liquid and the vapor occurs on each tray or packing surface. More volatile components moves from liquid to the vapor phase. So, throughout the column the more volatile components will move from the liquid phase to the vapor phase and the less volatile component from the vapor phase to the liquid phase. So, mass transfer happens both from the liquid to the vapor and vapor to the liquid. Concentration of the less volatile increases in the liquid phases as it flows down; so, less volatile components will increase in the liquid flows down from top, the less volatile component will enrich in the liquid phase.

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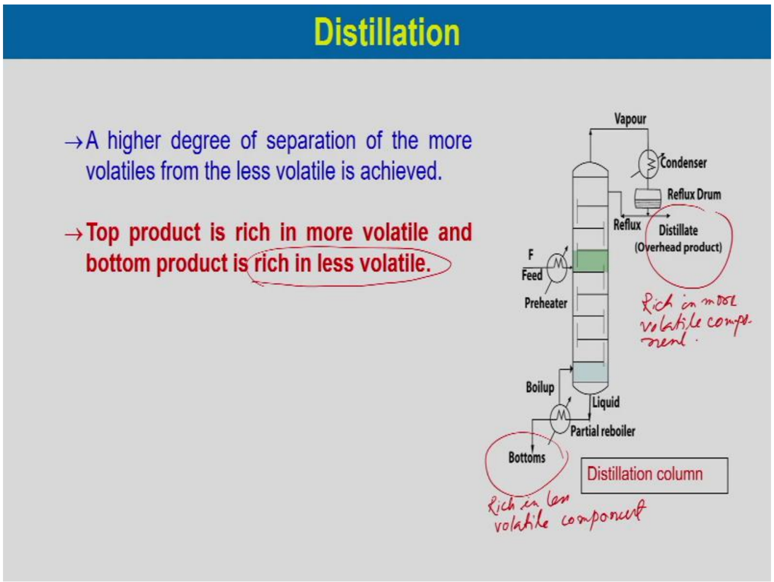

Distillation

→A higher degree of separation of the more volatiles from the less volatile is achieved.

→Top product is rich in more volatile and bottom product is rich in less volatile.

And the vapors which goes up it will increase the more volatile component. So, a higher degree of separation of the more volatile from the less volatile is achieved in this way. So, top product what we will get over here in the distillate is a more volatile component and the bottom product will be rich in less volatile component.

So, this is and this will be rich in. So, the top product distillate will be rich in more volatile component and the bottom product will be rich in less volatile component.

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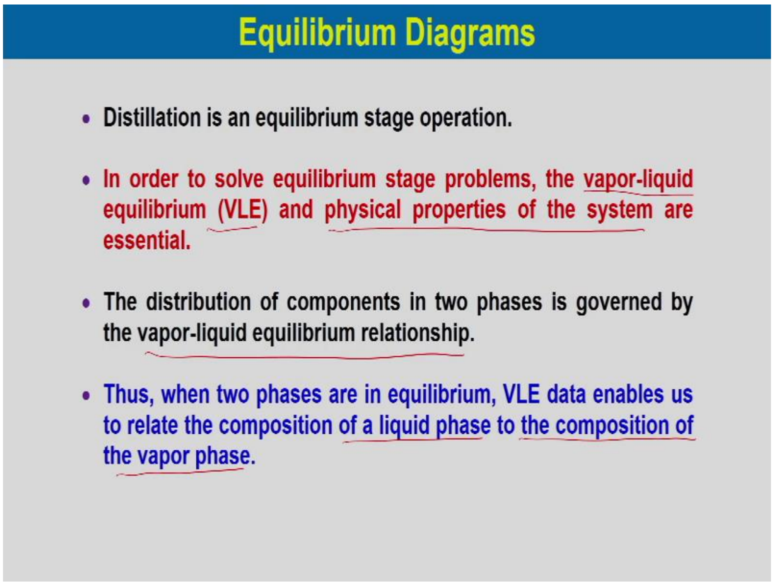

Equilibrium Diagrams

- Distillation is an equilibrium stage operation.
- In order to solve equilibrium stage problems, the vapor-liquid equilibrium (VLE) and physical properties of the system are essential.
- The distribution of components in two phases is governed by the vapor-liquid equilibrium relationship.
- Thus, when two phases are in equilibrium, VLE data enables us to relate the composition of a liquid phase to the composition of the vapor phase.

Now, distillation is an equilibrium stage operation. So, as you can see if there is an intimate contact between the gas and liquid and each tray and we consider it is it reaches the equilibrium between the liquid and vapor. So, distillation is considered is an equilibrium stage operation. So, in order to solve the equilibrium stage problems, the vapor liquid equilibrium and physical properties of the systems are essential.

So, one is the vapor liquid equilibrium data VLE data and the physical properties of the system. These two things are required to solve the equilibrium stage problem. The distribution of the component in two phases is governed by the vapor-liquid equilibrium relationship and thus, when two phases are in equilibrium vapor liquid equilibrium data enables us to relate the composition of a liquid phase to that of the composition of the vapor phase. So, two phases if we have a relation between the vapor phase and liquid phase and there is equilibrium, then we can obtain the liquid phase composition to that of the composition in the vapor phase.

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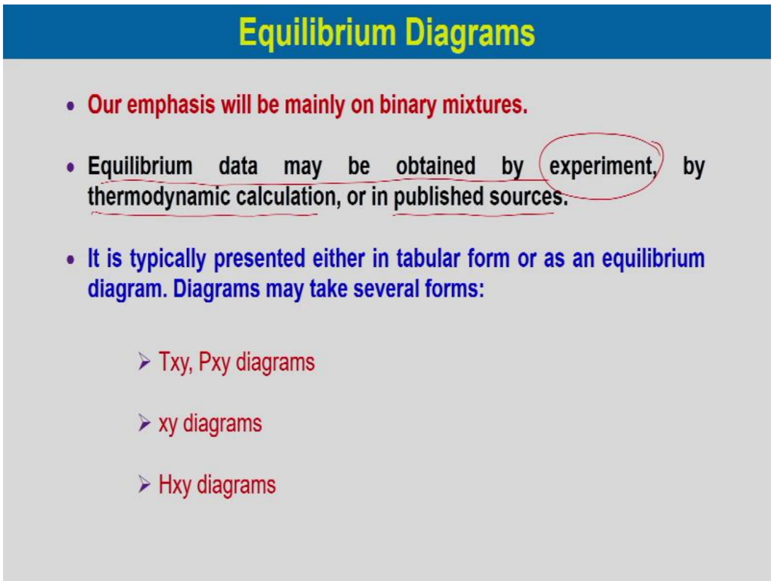

Equilibrium Diagrams

- Our emphasis will be mainly on binary mixtures.
- Equilibrium data may be obtained by experiment, by thermodynamic calculation, or in published sources.
- It is typically presented either in tabular form or as an equilibrium diagram. Diagrams may take several forms:
    - ➢ Txy, Pxy diagrams
    - ➢ xy diagrams
    - ➢ Hxy diagrams

So, our emphasis will be mainly on binary mixture over here. So, equilibrium data may be obtained by experiments or by thermodynamics calculation or in published sources. So, equilibrium data has to be obtained either we can get from the experimental measurements or it may be some thermodynamics calculations or it will have some published sources. Now, it is typically presented either in tabular form or as an equilibrium diagram. So, equilibrium diagram may take several forms, these are Txy

Temperature and Pressure Mole Fraction diagram or Mole Fractions diagram xy diagram or Hxy diagram that is Enthalpy Mole Fraction diagram. So, we will discuss each of them systematically to understand how we can obtain the equilibrium data and how we can solve the stage problem when there is an equilibrium operation.

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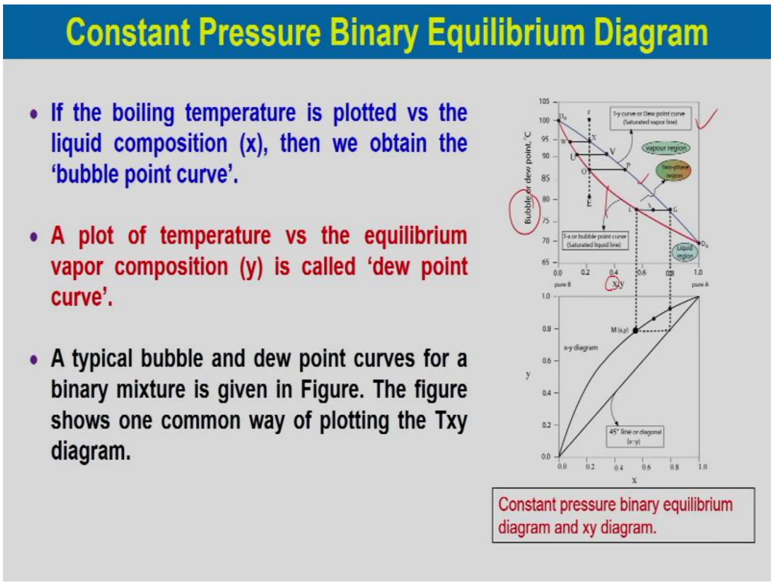

Constant Pressure Binary Equilibrium Diagram

- If the boiling temperature is plotted vs the liquid composition (x), then we obtain the 'bubble point curve'.
- A plot of temperature vs the equilibrium vapor composition (y) is called 'dew point curve'.
- A typical bubble and dew point curves for a binary mixture is given in Figure. The figure shows one common way of plotting the Txy diagram.

Constant pressure binary equilibrium diagram and xy diagram.

So, first we will consider constant pressure binary equilibrium diagram. So, if the boiling point temperature is plotted versus the liquid composition x, then we obtained the bubble point curve. So, in the top figure over here you can see, if we plot x versus bubble point, so then we can obtain the bubble point curve. So, this is Tx the bottom curve red line over here, this one is the Tx or bubble point curve or saturated liquid line.

Now, a plot of temperature and the equilibrium vapor composition that is y is called the dew point curve. In the upper figure you can see, blue line over here which is Ty curve or the dew point curve or saturated vapor line so, which is shown over here. So, the y axis we have a bubble point or dew point and then the x axis you have mole fractions x or y. A typical bubble and dew point curve for a binary mixture is given in this figure. The figure shows one common way of plotting the Txy diagram. So, this is called the Txy diagram.

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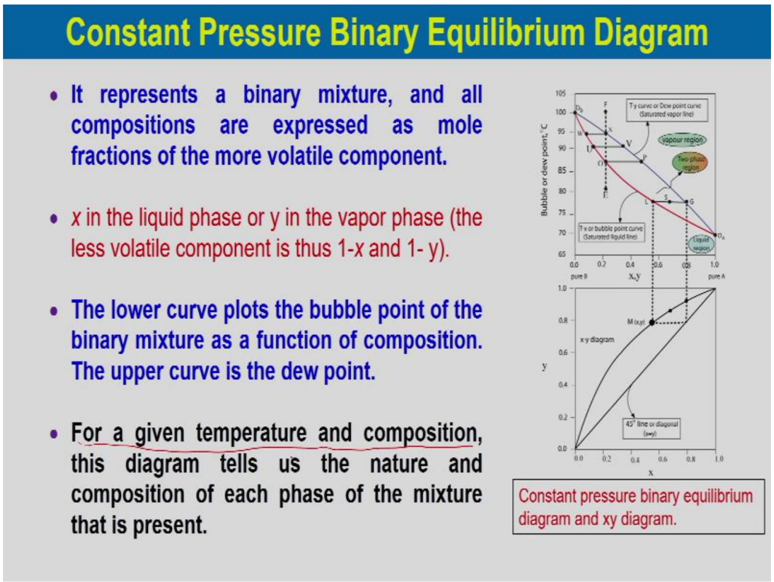

Constant Pressure Binary Equilibrium Diagram

- It represents a binary mixture, and all compositions are expressed as mole fractions of the more volatile component.
- *x* in the liquid phase or y in the vapor phase (the less volatile component is thus 1-*x* and 1- y).
- The lower curve plots the bubble point of the binary mixture as a function of composition. The upper curve is the dew point.
- For a given temperature and composition, this diagram tells us the nature and composition of each phase of the mixture that is present.

Constant pressure binary equilibrium diagram and xy diagram.

It represents a binary mixture and all composition are expressed as mole fractions of the more volatile component. So, these mole fractions x and y it represents the mole fraction of the more volatile component, not the less volatile component. So, all the compositions are expressed over here in mole fraction unit. So, x is the liquid phase and y in the vapor phase. If we know x and y, we can also calculate the composition of the less volatile one by subtracting from 1. So, 1 minus x would be the less volatile in the liquid phase and 1 minus y would be the more volatile in the vapor phase. The lower curve plots the bubble point of the binary mixture as a function of composition. The upper curve is the dew point curve. So, upper curve is the dew point and lower curve is the bubble point curve.

So, for a given temperature and composition, this diagram what does it tell us the nature and the composition of each phase of the mixture that is present when the temperature and composition is given. From this diagram we can tell the nature and the composition of each phase of the mixture that is present. So, we can tell about the nature as well as the composition.

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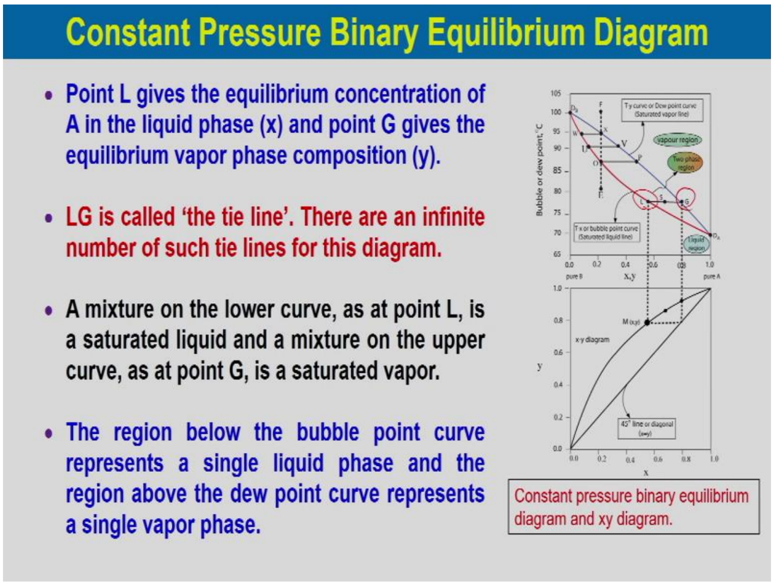

Constant Pressure Binary Equilibrium Diagram

- Point L gives the equilibrium concentration of A in the liquid phase (x) and point G gives the equilibrium vapor phase composition (y).
- LG is called 'the tie line'. There are an infinite number of such tie lines for this diagram.
- A mixture on the lower curve, as at point L, is a saturated liquid and a mixture on the upper curve, as at point G, is a saturated vapor.
- The region below the bubble point curve represents a single liquid phase and the region above the dew point curve represents a single vapor phase.

Constant pressure binary equilibrium diagram and xy diagram.

Point L gives the equilibrium concentration of A over here you can see at any point at L gives the equilibrium concentration of A in the liquid phase x and point G gives the equilibrium vapor composition y. If we just join these two points L and G is called the tie line. We can draw infinite number of such tie lines for this diagram; Txy diagram. A mixture on the lower curve at point L, at this one is a saturated liquid and a mixture on the upper curve that is at point G is saturated vapor.

Now, what about the region in between these two points L and G region which is below L and what is the region which is above G? So, the region below the bubble point curve, so that is red line below that represents a single liquid phase and the region above the dew point curve represent a single vapor phase. So, the region over here this region is basically the liquid region and this region is basically the vapor region.

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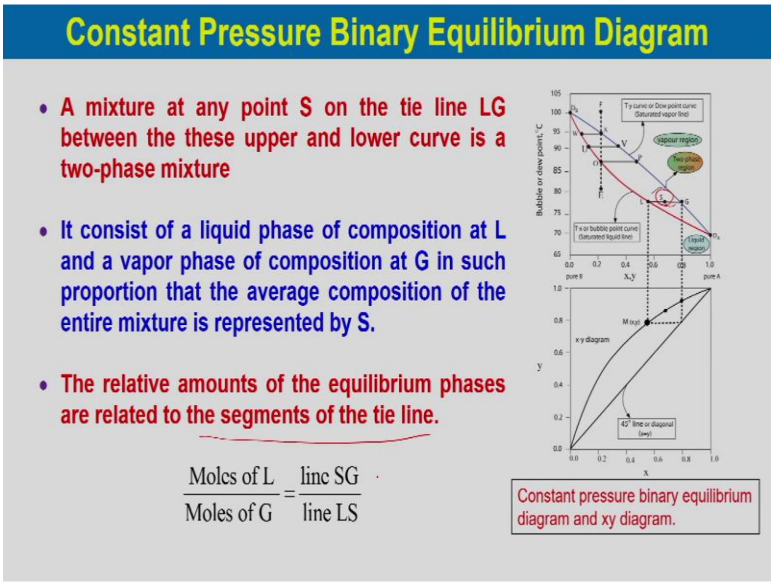

Constant Pressure Binary Equilibrium Diagram

- A mixture at any point S on the tie line LG between the these upper and lower curve is a two-phase mixture
- It consist of a liquid phase of composition at L and a vapor phase of composition at G in such proportion that the average composition of the entire mixture is represented by S.
- The relative amounts of the equilibrium phases are related to the segments of the tie line.

$$\frac{\text{Moles of L}}{\text{Moles of G}} = \frac{\text{line SG}}{\text{line LS}}$$

Constant pressure binary equilibrium diagram and xy diagram.

Now, a mixture at any point S on the tie line; so, at any point if you considered over here say S on the tie line LG between this upper and lower curve is a two phase mixture. So, any point between L and G so, inside this envelope is a two phase mixture it is a vapor and liquid mixture. It consist of a liquid phase of composition at L and a vapor phase of composition at G, in such proportion that the average composition of entire mixture is represented by S. The relative amount we can obtain for this equilibrium phases and that can be related with the segment of the tie lines. The segment of the tie lines is basically LS and GS. So, that is the segment of the tie line. So, the relative composition moles of L divided by moles of G, liquid and gas would be equal to line SG divided by line LS, SG divided by line LS.

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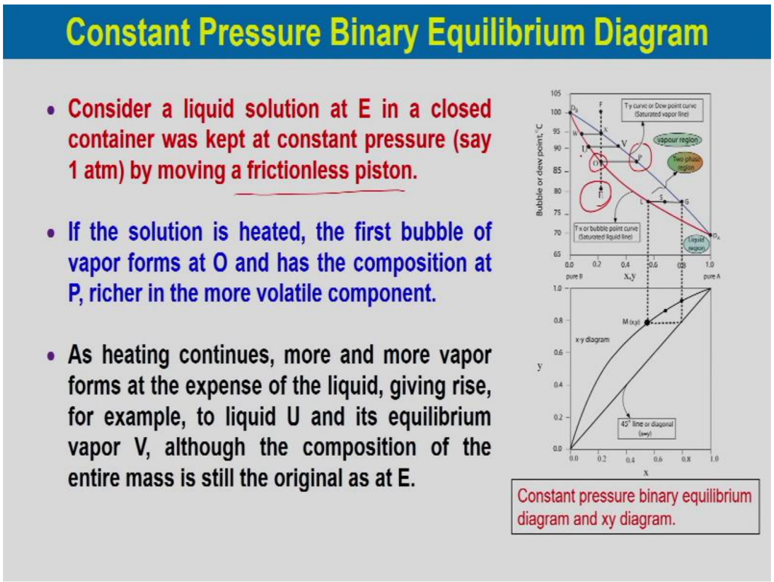

Constant Pressure Binary Equilibrium Diagram

- Consider a liquid solution at E in a closed container was kept at constant pressure (say 1 atm) by moving a frictionless piston.
- If the solution is heated, the first bubble of vapor forms at O and has the composition at P, richer in the more volatile component.
- As heating continues, more and more vapor forms at the expense of the liquid, giving rise, for example, to liquid U and its equilibrium vapor V, although the composition of the entire mass is still the original as at E.

Constant pressure binary equilibrium diagram and xy diagram.

Now, consider a liquid solution at any point E in a closed container kept at constant pressure say at one atmosphere and by moving a frictionless piston. So, it is kept at one atmosphere in a closed container. Now if the solution is heated the first bubble of the vapor forms at O. So, as it will be heated this liquid its temperature no at a constant pressure, a temperature will gradually increase through this line vertically and the first drop of bubble will form at point O, when it meets the bubble point curve and has the composition of P which is over here the vapor composition will be a P richer in more volatile component.

So, as heating continues, more and more vapor forms at the expense of the liquid giving rise for example to liquid U so, over here and its equilibrium vapor V, although the composition of the entire mass is still the original as at E. So, its composition so once it reaches the first drop of bubble which will vaporize and then its composition will be at its original composition at E and it will continue to follow this line and having the equilibrium composition changed from P to V.

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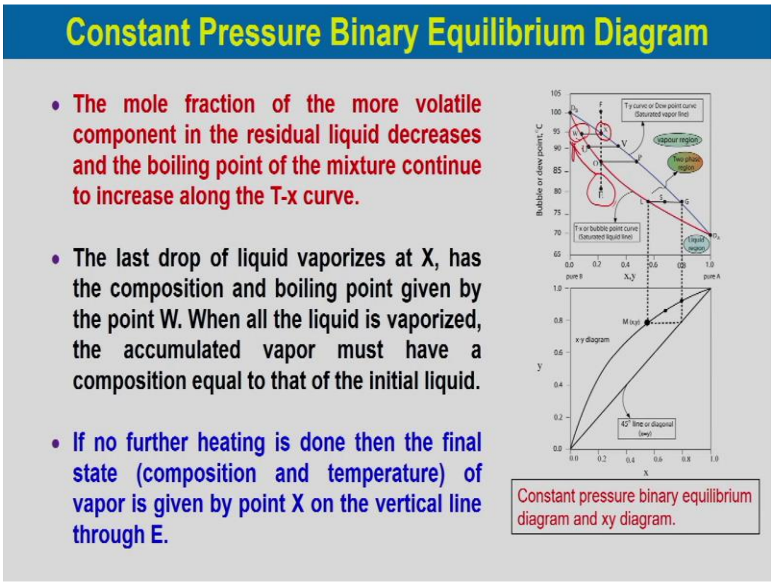

Constant Pressure Binary Equilibrium Diagram

- The mole fraction of the more volatile component in the residual liquid decreases and the boiling point of the mixture continue to increase along the T-x curve.
- The last drop of liquid vaporizes at X, has the composition and boiling point given by the point W. When all the liquid is vaporized, the accumulated vapor must have a composition equal to that of the initial liquid.
- If no further heating is done then the final state (composition and temperature) of vapor is given by point X on the vertical line through E.

Constant pressure binary equilibrium diagram and xy diagram.

So, now the mole fraction of the more volatile component in the residual liquid decreases and the boiling point of the mixture continuous to increase along the line. So, along this line Tx curve, so it’s boiling point gradually increases along this line. The last drop of liquid vaporizes at X over here has the composition and boiling point given by the point W. So, it will be here its composition and when all the liquid is vaporized, the accumulated vapor must have the composition which to that of the initial liquid because after this point all the liquid vaporized.

So, the composition which was in the liquid phase would, should be the same which is now in the vapor phase that is the initial liquid composition. So, if no further heating is done, then the final state composition temperature of the vapor is given by point X on the vertical line and through E. So, from here we will go through the upper curve which is the dew point curve. No further heating is done, then there the state, final state which will attend will have the composition and temperature corresponding to X.

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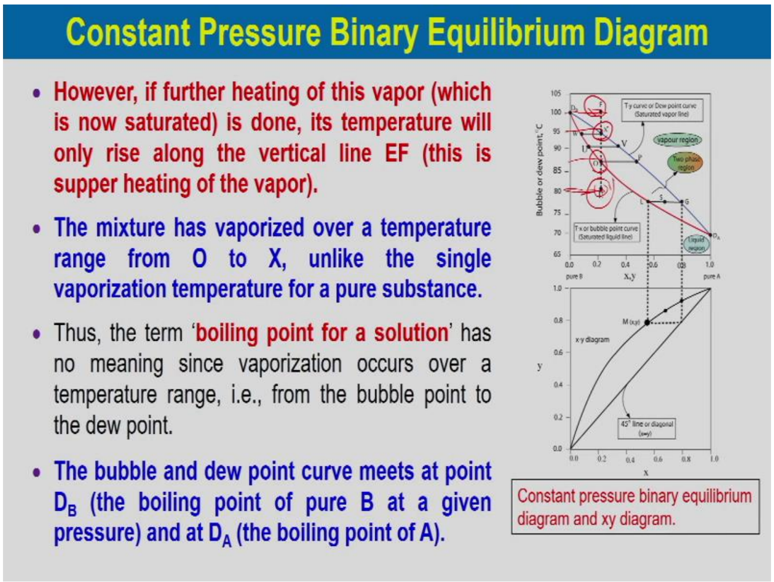

Constant Pressure Binary Equilibrium Diagram

- However, if further heating of this vapor (which is now saturated) is done, its temperature will only rise along the vertical line EF (this is supper heating of the vapor).
- The mixture has vaporized over a temperature range from O to X, unlike the single vaporization temperature for a pure substance.
- Thus, the term '**boiling point for a solution**' has no meaning since vaporization occurs over a temperature range, i.e., from the bubble point to the dew point.
- The bubble and dew point curve meets at point D_B (the boiling point of pure B at a given pressure) and at D_A (the boiling point of A).

Constant pressure binary equilibrium diagram and xy diagram.

If we further heat, this vapor which is now saturated vapor at this location, if we further heat its temperature will only rise along the vertical line EF. So, from these E, it will vertically go to F.

So, its temperature will increase along the vertical line and this is called the superheated vapor. The mixture has vaporized as you can see over the temperature range. So, starting from this no temperature over here at say, close to 80 degree and it vaporize no up to this location and then heated up and it goes to say 100 degree centigrade. So, the liquid mixture which is vaporized over a temperature range from is basically from the liquid to the vapor is from O to X. So, this is the temperature range where it is vaporized and this is the final temperature change if we take a liquid at this temperature at 80 degree to heated up to 100 degree centigrade temperature.

So, this is the overall temperature change, but from liquid to vapor formation the change of temperature will vary between O to X. So, for a single liquid there is a single temperature for the vaporization, but in this case you can see the range of temperature. Thus, the term boiling point for a solution has no meaning since vaporization occur over a temperature range that is from the bubble point to the dew point. So, for a mixture its vaporization which happens from the liquid phase to the vapor phase, it occurs over a range of temperature. So, for this no liquid mixture or for this solutions, we do not have any meaning to call boiling point for a solution or for a mixture the bubble and dew point curves meet at a point D B. So, you can see over here D B at this point where the both bubble point curves the bottom rate line curve and the blue line curve meets at this point D B.

So, the boiling point of pure component B at a given pressure and at D A the boiling point of A so, over here. So, both the curves meet at this location.

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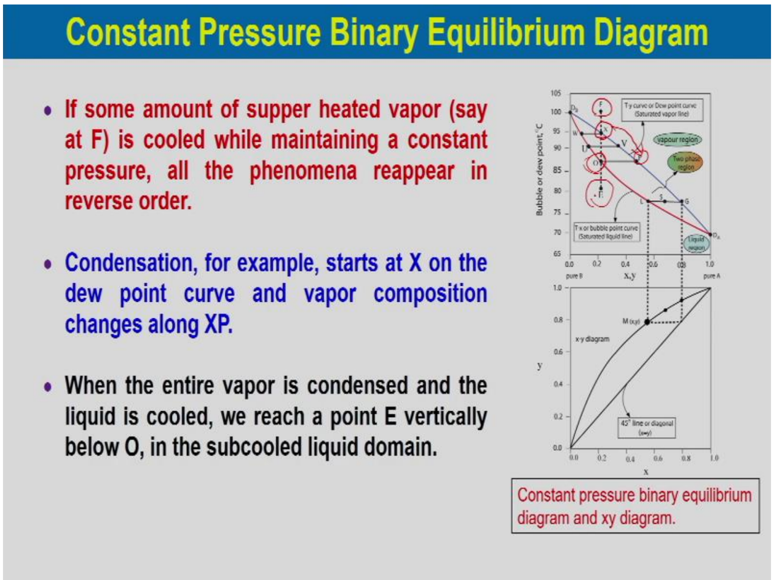

Constant Pressure Binary Equilibrium Diagram

- If some amount of supper heated vapor (say at F) is cooled while maintaining a constant pressure, all the phenomena reappear in reverse order.
- Condensation, for example, starts at X on the dew point curve and vapor composition changes along XP.
- When the entire vapor is condensed and the liquid is cooled, we reach a point E vertically below O, in the subcooled liquid domain.

Constant pressure binary equilibrium diagram and xy diagram.

So, now if some amount of superheated vapor say at point F which is taken over here is cooled while maintaining a constant pressure, all the phenomena reappear in the reverse order. So, earlier we have heated taking a liquid at this point E and then it is vaporized and then heated to the its condition at F which is superheated vapor. Now if we just cool down this superheated vapor keeping the pressure constant, then the phenomena which appear during the vaporization will reappear during the condensation in the reverse order.

So, condensation for example starts at X at this location on the dew point curve and the vapor composition changes along XP. So, composition will change from X to XP. When the entire vapor is condensed and the liquid is cooled, we reach a point E vertically below O. So, it will be the final composition when all the vapors it will be condensed and the composition will given by O and further cooling it will reach to point E vertically which is called as sub cooled liquid. So, E is a sub cooled liquid.

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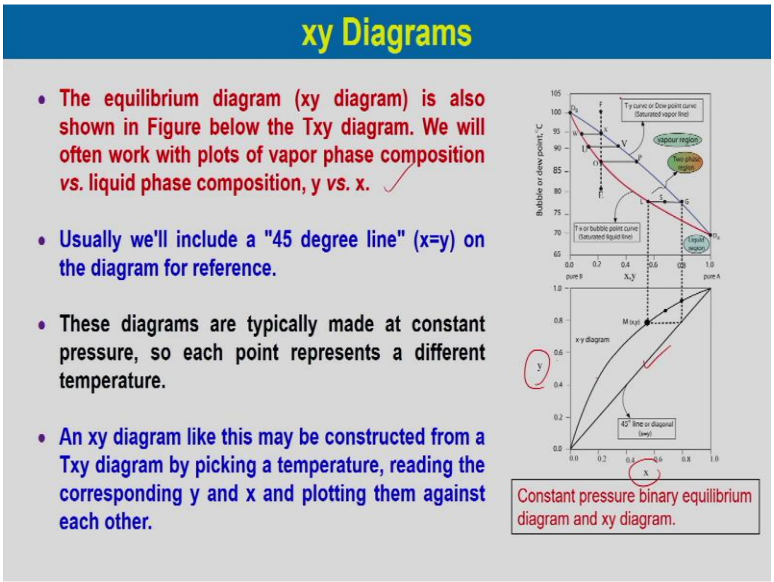

xy Diagrams

- The equilibrium diagram (xy diagram) is also shown in Figure below the Txy diagram. We will often work with plots of vapor phase composition *vs.* liquid phase composition, y *vs.* x.
- Usually we'll include a "45 degree line" (x=y) on the diagram for reference.
- These diagrams are typically made at constant pressure, so each point represents a different temperature.
- An xy diagram like this may be constructed from a Txy diagram by picking a temperature, reading the corresponding y and x and plotting them against each other.

Constant pressure binary equilibrium diagram and xy diagram.

Now, we will discuss about the xy diagrams which is shown over here at the bottom of this line of the Txy diagram. The equilibrium diagram which is called xy diagram is also shown in this figure below the Txy diagram and we will often work with plots of a vapor phase composition versus the liquid phase composition that is y versus x. So, usually we will include a 45 degree line that is in the xy diagram this is y and this is x, this is the 45 degree diagonal and that is at x is equal to y, in this xy diagram that is for the reference. So, this is for reference the 45 degree diagonal is for the reference.

These diagrams are typically made at constant pressure. So, each point represents a different temperature. So, each point on the equilibrium curve represents a different temperatures. An xy diagram like this may be constructed from Txy diagram by picking a temperature, reading the corresponding y and x and plotting them against each other. So, if we have the Txy diagram, we can pick up a particular temperature and then we can read from this at the temperature what is the vapor and liquid composition and from that we can plot the xy diagram.

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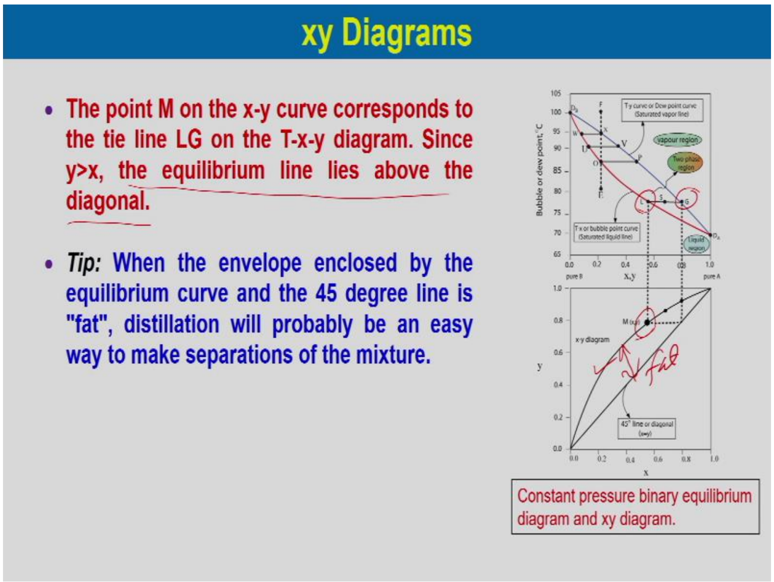

xy Diagrams

- The point M on the x-y curve corresponds to the tie line LG on the T-x-y diagram. Since y>x, the equilibrium line lies above the diagonal.
- *Tip:* When the envelope enclosed by the equilibrium curve and the 45 degree line is "fat", distillation will probably be an easy way to make separations of the mixture.

Constant pressure binary equilibrium diagram and xy diagram.

The point M, you can see over here which is xy point on the x y curve correspond to the tie line LG. So, this is L and this is G and this point M is called the tie line which is corresponding to the LG line. Since y greater than x, the equilibrium line lies above the diagonal. Because, diagonal x is equal to y, if y is greater than x then it will lie above the diagonal line; so, it is above the diagonal equilibrium line so, this is the equilibrium line.

Now, tip is that when the envelope enclosed by the equilibrium curve and the 45 degree line is fat distillation will probably be an easy way to make the separation of the mixture. So, if we have a larger distance from the 45 degree diagonal to the equilibrium curve, if this is fact, then as it is far from the 45 degree diagonal the equilibrium line the separation of the component mixture would be much easier by distillation.

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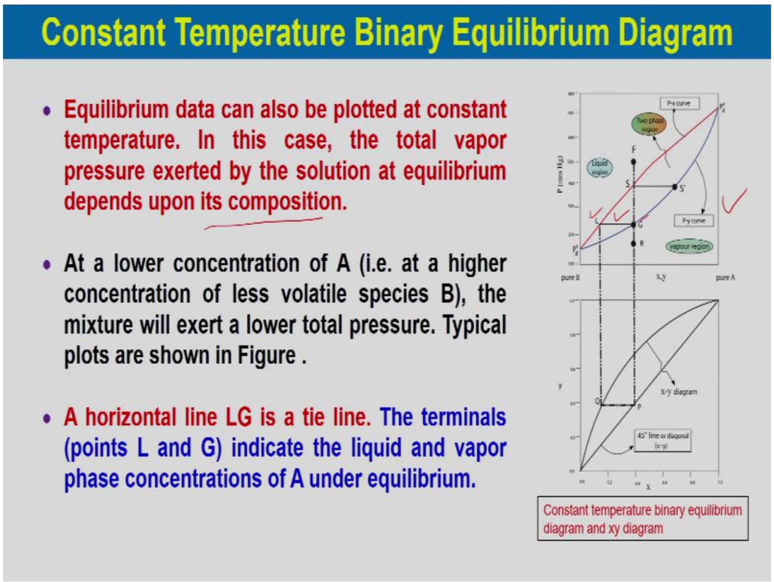

Constant Temperature Binary Equilibrium Diagram

- Equilibrium data can also be plotted at constant temperature. In this case, the total vapor pressure exerted by the solution at equilibrium depends upon its composition.
- At a lower concentration of A (i.e. at a higher concentration of less volatile species B), the mixture will exert a lower total pressure. Typical plots are shown in Figure .
- A horizontal line LG is a tie line. The terminals (points L and G) indicate the liquid and vapor phase concentrations of A under equilibrium.

Constant temperature binary equilibrium diagram and xy diagram

Now, we will discuss about the constant temperature binary equilibrium diagram. Equilibrium data can also be plotted at constant temperature. In this case the total pressure exerted by the solution at equilibrium depend upon its composition. So, a lower concentration of A that is at a higher concentration of less volatile species B, the mixture will exert a lower total pressure typical plots are shown in this figure. So, over here, so this is Pxy diagram at constant temperature.

So, as we said at a lower concentration of A that is at higher concentration of less volatile component B, the mixture will exert lower total pressure. So, you could see P-x curve that is total pressure versus x or total pressure versus y curve know they will be you can see over here, the when we have a more volatile component very less. So, the system pressure will be low, total pressure will be low because it will exert lower vapor pressure. A horizontal line LG is a tie line which is shown over here LG and this line is the tie line, the terminal points L and G indicates the liquid and vapor phase concentration of A under equilibrium.

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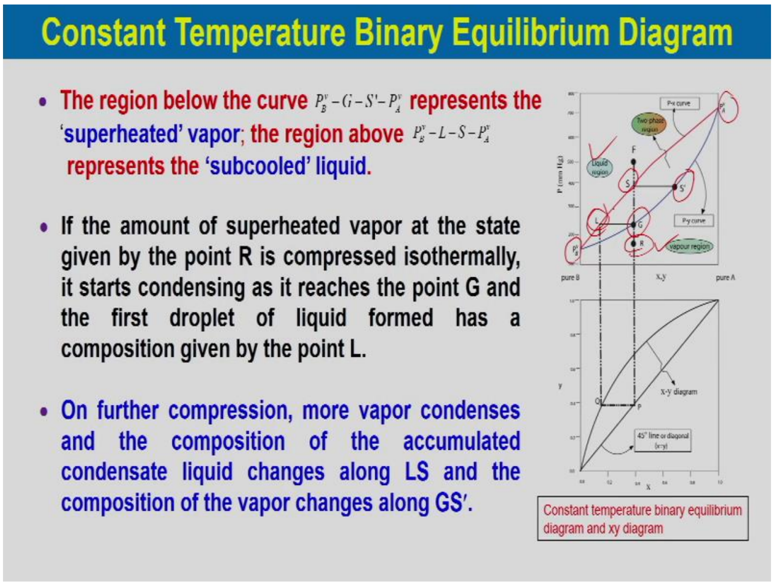

Constant Temperature Binary Equilibrium Diagram

- The region below the curve $P_B^v - G - S' - P_A^v$ represents the 'superheated' vapor; the region above $P_B^v - L - S - P_A^v$ represents the 'subcooled' liquid.
- If the amount of superheated vapor at the state given by the point R is compressed isothermally, it starts condensing as it reaches the point G and the first droplet of liquid formed has a composition given by the point L.
- On further compression, more vapor condenses and the composition of the accumulated condensate liquid changes along LS and the composition of the vapor changes along GS′.

Constant temperature binary equilibrium diagram and xy diagram

Now, the region below in this case that is P B V, these points G S dash and P A B. So, below this plot represents the superheated vapor and above this P B V L S and P A V represents the sub cooled liquid. So, above these regions is the sub cooled liquid. So, this is liquid region and this is the vapor region. Now if the amount of superheated vapor at the state given by the point R, so which is over here this is superheated vapor and is compressed isothermally at a constant temperature, it is compressed. So, its pressure will change, it starts condensing at is reaches at point G. So, the first drop of the liquid will form when it reaches point G corresponding to its liquid composition L.

Now on further compression, more vapor will condense and the composition of the accumulated condensates liquid changes along the LS line. So, its composition of the liquid phase will change and it will increase and it will go along the S. So, it will follow along LS and the composition of the vapor changes along the GS dash.

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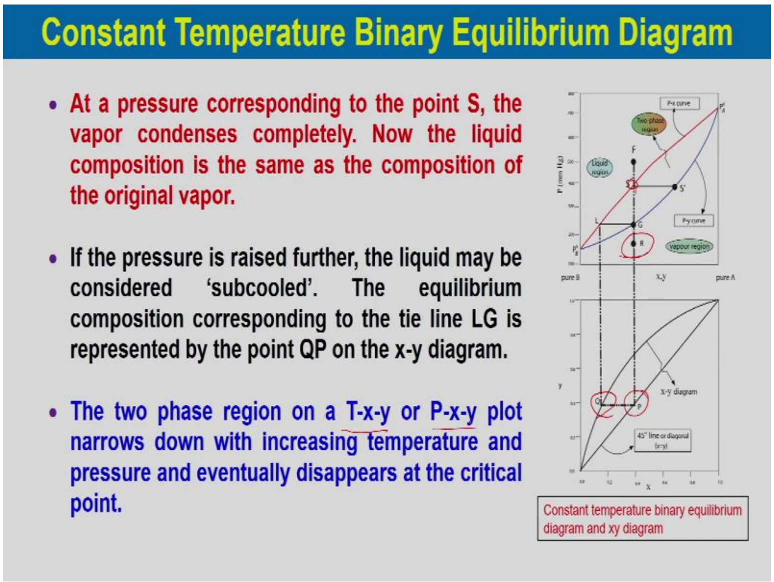

Constant Temperature Binary Equilibrium Diagram

- At a pressure corresponding to the point S, the vapor condenses completely. Now the liquid composition is the same as the composition of the original vapor.
- If the pressure is raised further, the liquid may be considered 'subcooled'. The equilibrium composition corresponding to the tie line LG is represented by the point QP on the x-y diagram.
- The two phase region on a T-x-y or P-x-y plot narrows down with increasing temperature and pressure and eventually disappears at the critical point.

Constant temperature binary equilibrium diagram and xy diagram

At a pressure corresponding to the point S, the vapor condenses completely. So, you can see like here it if you go vertically, so all the vapor corresponding to this point at this pressure will completely condensate. Now, the liquid composition is the same as that of the original vapor composition that is over here. So, it will be the same composition if the pressure is further raised the liquid may be considered sub cooled the equilibrium composition to the tie line. LG is represented by point QP, this is the equilibrium composition on the xy diagram and if we further increase the pressure, it will be sub cooled liquid.

The two phase region on Txy or Pxy as we have discussed earlier Txy diagram or in this Pxy diagram plot in this case narrows down with increasing the temperature and pressure and eventually disappear at the critical point.

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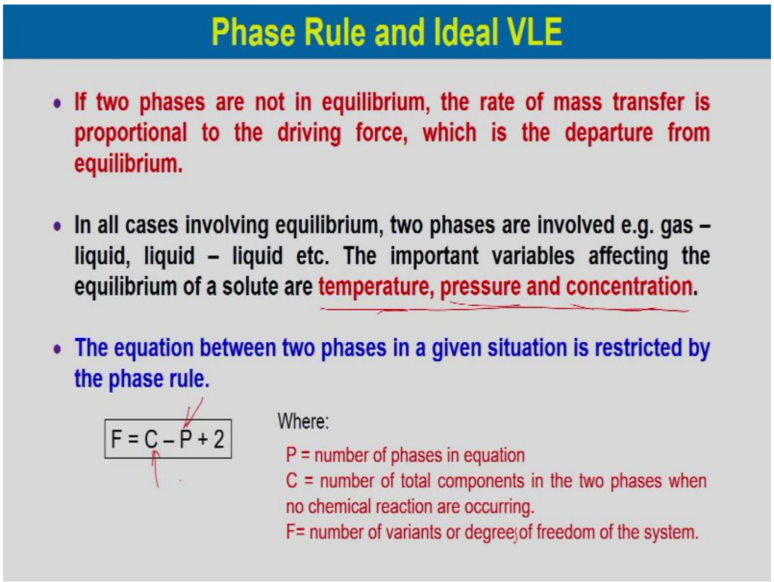

Phase Rule and Ideal VLE

- If two phases are not in equilibrium, the rate of mass transfer is proportional to the driving force, which is the departure from equilibrium.
- In all cases involving equilibrium, two phases are involved e.g. gas – liquid, liquid – liquid etc. The important variables affecting the equilibrium of a solute are temperature, pressure and concentration.
- The equation between two phases in a given situation is restricted by the phase rule.

$$\boxed{F = C - P + 2}$$

Where:

P = number of phases in equation
C = number of total components in the two phases when no chemical reaction are occurring.
F= number of variants or degree of freedom of the system.

Now, we will discuss phase rule and ideal VLE. So, if two phases are not in equilibrium, the rate of mass transfer is proportional to the driving force which is the departure from the equilibrium. In all cases it involves the equilibrium. Two phases are involved for example, gas liquid or liquid-liquid and so on. The important variables which affect the equilibrium of a solute depends on the temperature, pressure and concentration. For all cases where there would be equilibrium between the phases. So, it involves the important parameters which will affect the equilibrium composition of a particular solute on these three parameters that is temperature, pressure and concentration.

The equation between the two phases in a given situation is restricted by phase rule. So, as we know that is F is equal to C minus P plus 2. In this case P is the number of phases in this equation. So, number of phases P, C is the total number of components in the two phases where no chemical reactions are occurring. So, C is the number of components present when there is no chemical reaction and F is the number of variant or degrees of freedom of the system; so, F is the degrees of freedom.

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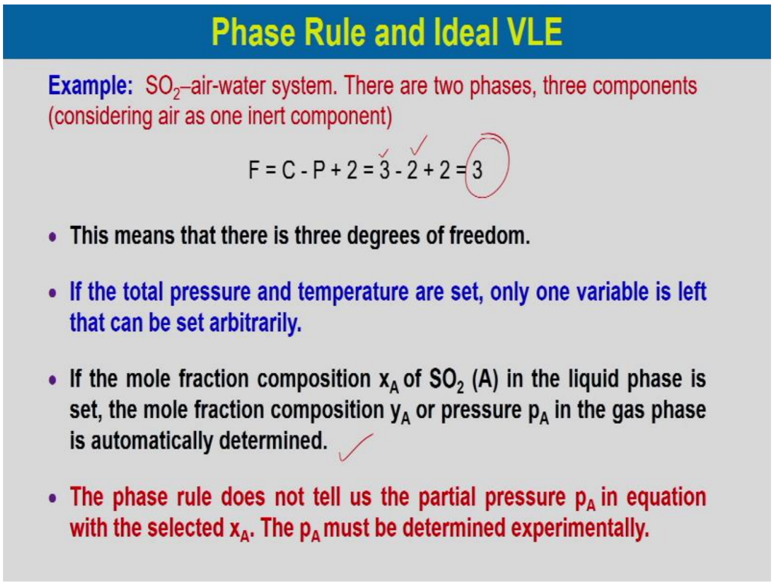

Phase Rule and Ideal VLE

Example: SO_2–air-water system. There are two phases, three components (considering air as one inert component)

$$F = C - P + 2 = 3 - 2 + 2 = 3$$

- This means that there is three degrees of freedom.
- If the total pressure and temperature are set, only one variable is left that can be set arbitrarily.
- If the mole fraction composition x_A of SO_2 (A) in the liquid phase is set, the mole fraction composition y_A or pressure p_A in the gas phase is automatically determined.
- The phase rule does not tell us the partial pressure p_A in equation with the selected x_A. The p_A must be determined experimentally.

Now, consider an example sulphur dioxide air water system. So, we can see that there are two phases. One is the gas phase which will have sulphur dioxide in air and in the liquid phase which is water three components sulphur dioxide and water and then we can consider air as a single component considering an inert, no component or assuming an inert component.

So, if we apply the phase rule in this case, we can see that F would be equal to C minus P plus 2. So, here no component is 3 phases, 2 phases plus 2. So, you could see that it will lead to the degrees of freedom 3. So, that means that there are three degrees of freedom. Now if the total pressure and temperature are set, only one variable is left that can be set arbitrarily.

So, if the mole fraction composition of X A of sulphur dioxide in the liquid phase is set, the mole fraction composition of Y A that is a partial pressure, P A in the gas phase is automatically determined. The phase rule does not tell us the partial pressure P A in equation with the selected X A. The partial pressure must be determined experimentally.

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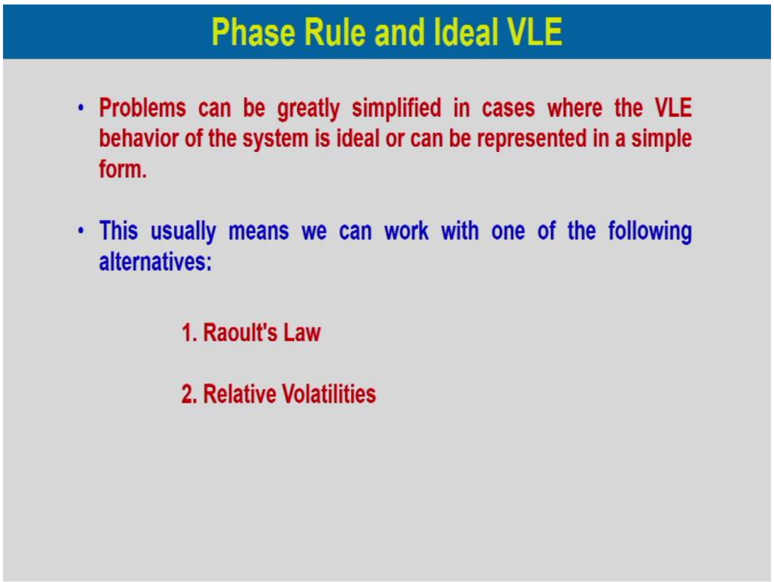

Phase Rule and Ideal VLE

- Problems can be greatly simplified in cases where the VLE behavior of the system is ideal or can be represented in a simple form.
- This usually means we can work with one of the following alternatives:

  1. Raoult's Law
  2. Relative Volatilities

Now, this problem can be greatly simplified in cases where the VLE behaviour of the system is ideal or can be represented in a simple form like, this is usually no means we can work with one of the following alternatives that is, either we can use Raoult's law or we can use Relative Volatility. So, either of these two can work to simplify solving these problems.

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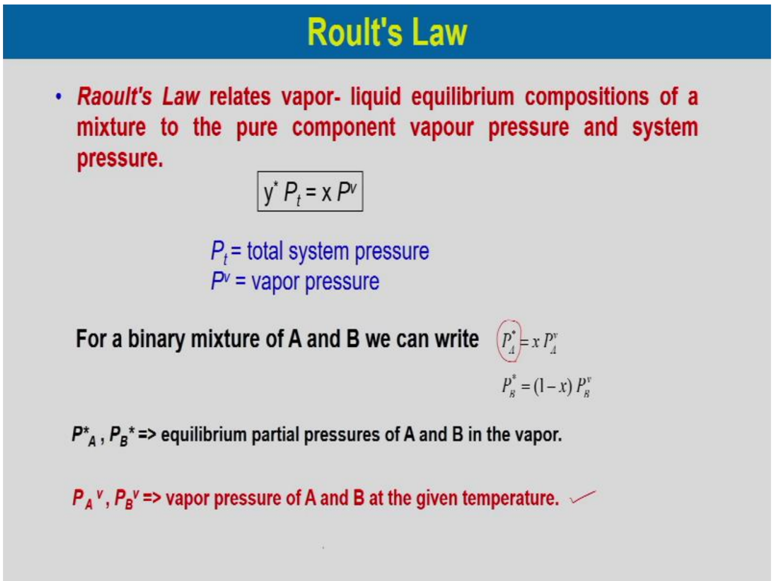

Roult's Law

- *Raoult's Law* relates vapor- liquid equilibrium compositions of a mixture to the pure component vapour pressure and system pressure.

$$\boxed{y^* P_t = x P^v}$$

P_t = total system pressure
P^v = vapor pressure

For a binary mixture of A and B we can write $P_A^* = x P_A^v$

$$P_B^* = (1-x) P_B^v$$

P^*_A , $P_B{}^*$ => equilibrium partial pressures of A and B in the vapor.

$P_A{}^v$, $P_B{}^v$ => vapor pressure of A and B at the given temperature.

Now, Raoults law as you have already learnt, Raoults law relates vapor liquid equilibrium composition of a mixture to the pure component vapor pressure and the system pressure. So, basically y star into P t would be equal to x into P V. That means, the P t over here is the total pressure system pressure and P V is the vapor pressure. So, for a binary mixture if we considered A and B, then we can write P A star is equal to x into P A V. So, partial pressure of A would be equal to x P A V and P B star would be equal to 1 minus x P B V. Now if we just substitute in this case P A star and P A, P B star are the equilibrium partial pressure of component A and B in the vapor and P A V and P B V vapor pressure of A and B at a given temperature.

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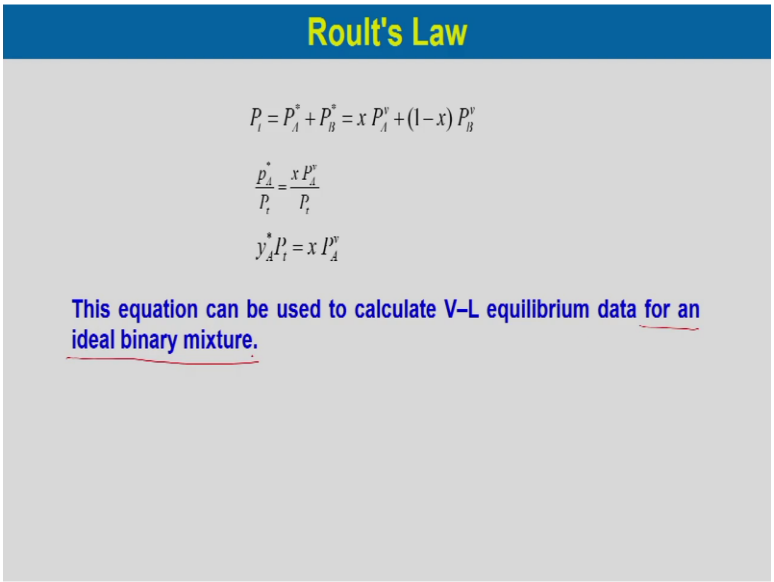

Roult's Law

$$P_t = P_A^* + P_B^* = x\,P_A^v + (1-x)\,P_B^v$$

$$\frac{p_A^*}{P_t} = \frac{x\,P_A^v}{P_t}$$

$$y_A^* P_t = x\,P_A^v$$

This equation can be used to calculate V–L equilibrium data for an ideal binary mixture.

So, we can write the total pressure is equal to the partial pressure of A plus partial pressure of B. Now if we just add them x P A V plus 1 minus x P B V, then we will have P A star by P t would be equal to x, P A V by P T and hence, we can write y A star P t would be equal to x P A V. So, the Raoults law equation can be used to calculate the vapor liquid equilibrium data for ideal binary mixture. So, please remember that, this is only applicable for ideal binary mixture.

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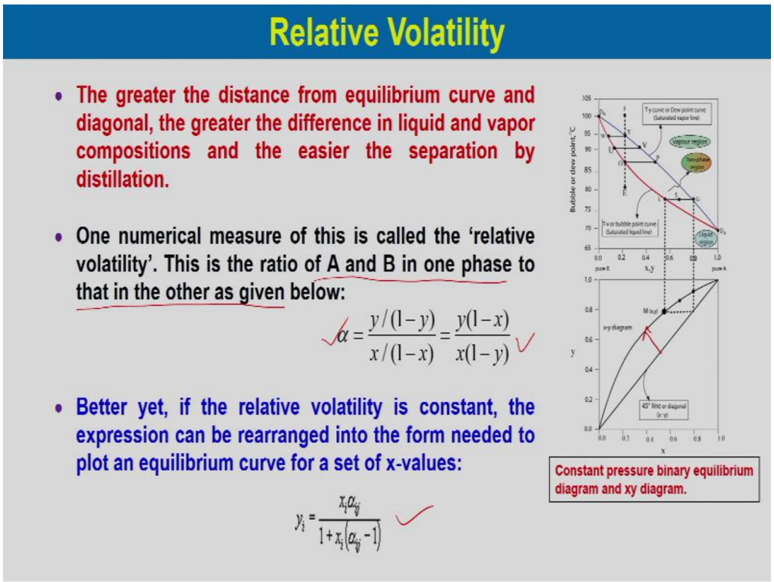

Relative Volatility

- The greater the distance from equilibrium curve and diagonal, the greater the difference in liquid and vapor compositions and the easier the separation by distillation.
- One numerical measure of this is called the 'relative volatility'. This is the ratio of A and B in one phase to that in the other as given below:

$$\alpha = \frac{y/(1-y)}{x/(1-x)} = \frac{y(1-x)}{x(1-y)}$$

- Better yet, if the relative volatility is constant, the expression can be rearranged into the form needed to plot an equilibrium curve for a set of x-values:

$$y_i = \frac{x_i\alpha_{ij}}{1+x_i(\alpha_{ij}-1)}$$

Constant pressure binary equilibrium diagram and xy diagram.

Now, we will discuss the relative volatility. The greater the distance from the equilibrium curve and the diagonal, the greater the difference in the liquid and vapor composition and easier the separation by distillation. This is already we have said from the diagonal, greater is the distance of the equilibrium curve from the diagonal that will be easier for the separation by distillation. So, one of the numerical measure to see the easiness of the separation is called the relative volatility and this is the ratio of A and B in one phase to that in the other phase which can be represented by alpha is equal to y divided by 1 minus y divided by x divided by 1 minus x.

So, that is ratio of y A by B in one phase divided by ratio of A and B in the other phase that is over here. So, this will be equal to y into 1 minus x divided by x into 1 minus y. Now, if the relative volatility is constant, this alpha is constant the expression can be rearranged into the form needed to plot an equilibrium curve for a set of x values. So, we can write y i would be equal to x i alpha i j; alpha i j is the relative volatility of A with respect to B divided by 1 plus x i into alpha i j minus 1. So, with this we can assume a particular value of x and we can calculate the values of y knowing the values of relative volatility alpha.

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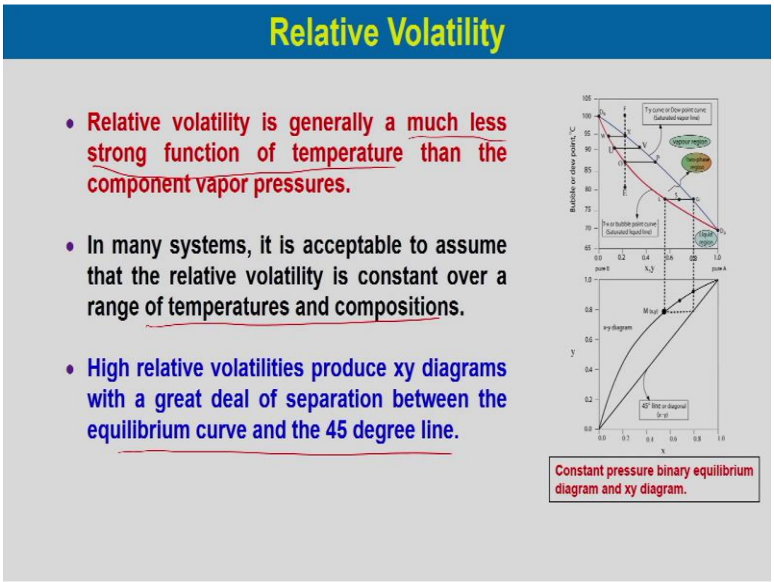

Relative Volatility

- Relative volatility is generally a much less strong function of temperature than the component vapor pressures.
- In many systems, it is acceptable to assume that the relative volatility is constant over a range of temperatures and compositions.
- High relative volatilities produce xy diagrams with a great deal of separation between the equilibrium curve and the 45 degree line.

Constant pressure binary equilibrium diagram and xy diagram.

Relative volatility is generally a much less stronger function of temperature than the component vapor pressure. It is much less stronger function with respect to temperature. So in many systems, it is acceptable to assume that the relative volatility is constant over a range of temperature and composition. High relative volatility produced xy diagram with a great deal of separation between the equilibrium curve and the 45 degree diagonal. So, as the values of relative volatility is higher, it will tell about the departure from the 45 degree line and to the equilibrium line.

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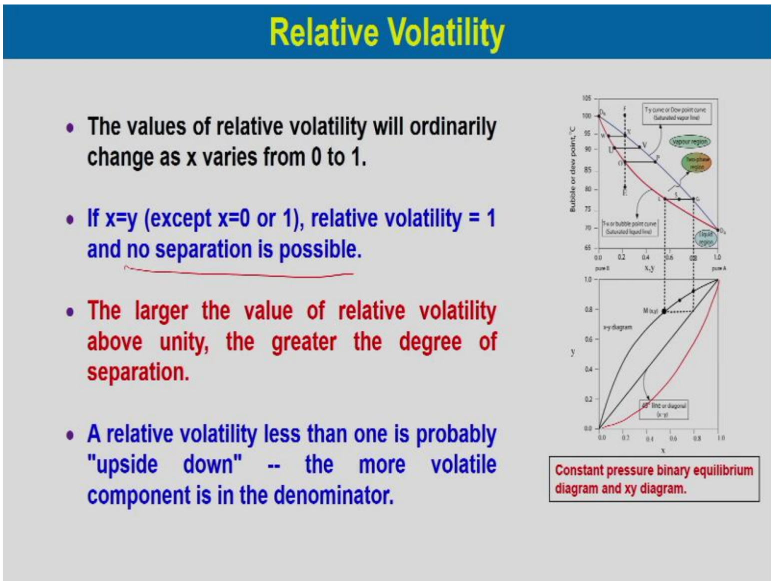

Relative Volatility

- The values of relative volatility will ordinarily change as x varies from 0 to 1.
- If x=y (except x=0 or 1), relative volatility = 1 and no separation is possible.
- The larger the value of relative volatility above unity, the greater the degree of separation.
- A relative volatility less than one is probably "upside down" -- the more volatile component is in the denominator.

Constant pressure binary equilibrium diagram and xy diagram.

The values of relative volatility will ordinarily change as x varies from 0 to 1. If x is equal to y except x is equal to 0 or 1, relative volatility would be equal to 1. When x is equal to y, then if you put in relative volatility equation so, the alpha would be equal to 1 when x is equal to y, that means no separation is possible. The larger the value of relative volatility above unity, the greater the degree of separation. So, a relative volatility which is less than 1 is probably the upside down. So, that would be on this side, the more volatile component is in the denominator. So, which is not know case of the separation by distillation. So, we generally look for relative volatility more than 1.

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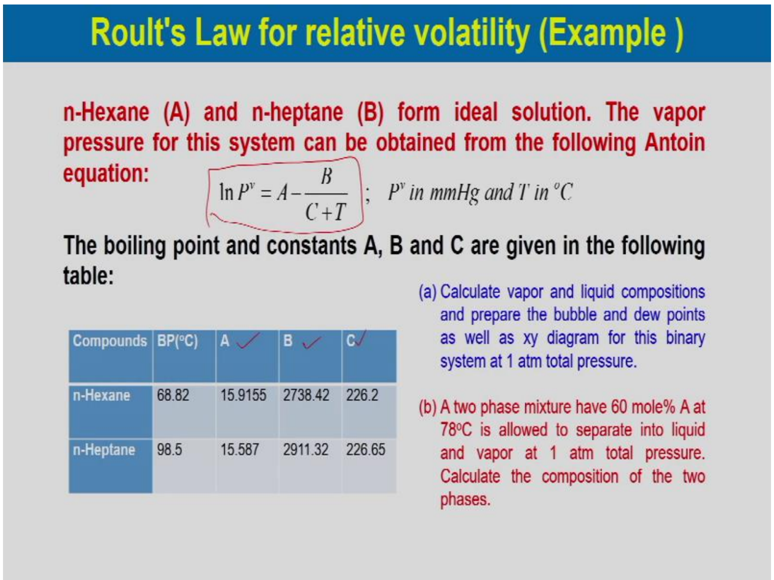

Roult's Law for relative volatility (Example)

n-Hexane (A) and n-heptane (B) form ideal solution. The vapor pressure for this system can be obtained from the following Antoin equation:

$$\boxed{\ln P^v = A - \frac{B}{C+T}}\ ; \quad P^v \text{ in mmHg and } T \text{ in } ^\circ C$$

The boiling point and constants A, B and C are given in the following table:

Compounds	BP(°C)	A ✓	B ✓	C✓
n-Hexane	68.82	15.9155	2738.42	226.2
n-Heptane	98.5	15.587	2911.32	226.65

(a) Calculate vapor and liquid compositions and prepare the bubble and dew points as well as xy diagram for this binary system at 1 atm total pressure.

(b) A two phase mixture have 60 mole% A at 78°C is allowed to separate into liquid and vapor at 1 atm total pressure. Calculate the composition of the two phases.

So, now let us take an example for using the Raoults law for relative volatility to solve the problem n-Hexane which is considered component A and n-Heptane considered component B from the ideal solution. The vapor pressure for this system can be obtained from the Antoin equation. this is the Antoin equation ln P V is equal to A minus B by C plus T and P V is in millimeter Hg and P is in degree centigrade.

Now, the boiling point and constants of A and B and C which is given in the Antoin equations are given in this following tables, n-Hexane boiling points 68.83, n-Heptane and 98.5 and A, B and C the constants for this Antoin equations is given. Now we need to calculate vapor and liquid composition and prepare the bubble and dew point as well as xy diagram for this binary system at one atmosphere total pressure. So, that is the first problem and the second one is a two phase mixture having 60 mole percent of A at 78 degrees centigrade is allowed to separate into the liquid and vapor at one atmosphere pressure, total pressure. We need to calculate the composition of the two phases.

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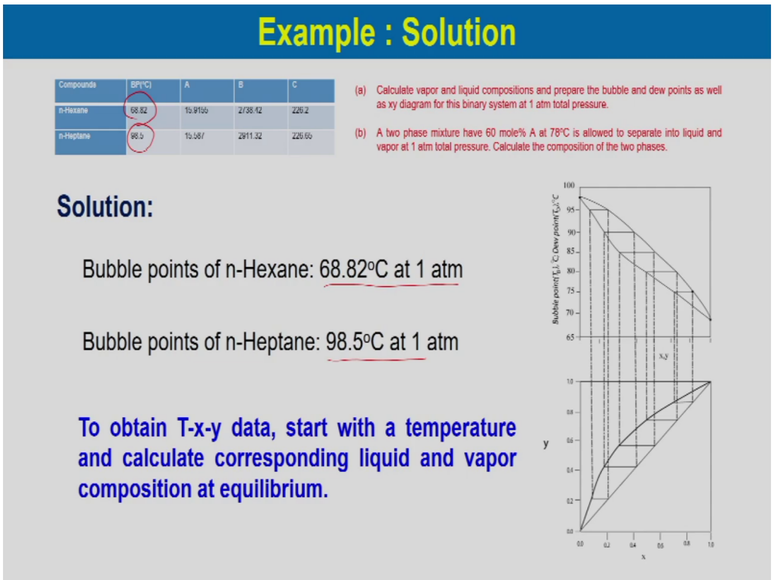

Example : Solution

Compounds	BP(°C)	A	B	C
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(a) Calculate vapor and liquid compositions and prepare the bubble and dew points as well as xy diagram for this binary system at 1 atm total pressure.

(b) A two phase mixture have 60 mole% A at 78°C is allowed to separate into liquid and vapor at 1 atm total pressure. Calculate the composition of the two phases.

Solution:

Bubble points of n-Hexane: 68.82°C at 1 atm

Bubble points of n-Heptane: 98.5°C at 1 atm

To obtain T-x-y data, start with a temperature and calculate corresponding liquid and vapor composition at equilibrium.

Now, bubble point of n-Hexane is given which is over here. So, 67.82 at one atmosphere pressure, bubble point of n-Heptane that is 98.5 degree centigrade at one atmosphere which is given over here. This is the typical curve we need to obtain. So, we will discuss this to obtain this curve Txy data. Start with the temperature and calculate the corresponding liquid and vapor composition at equilibrium.

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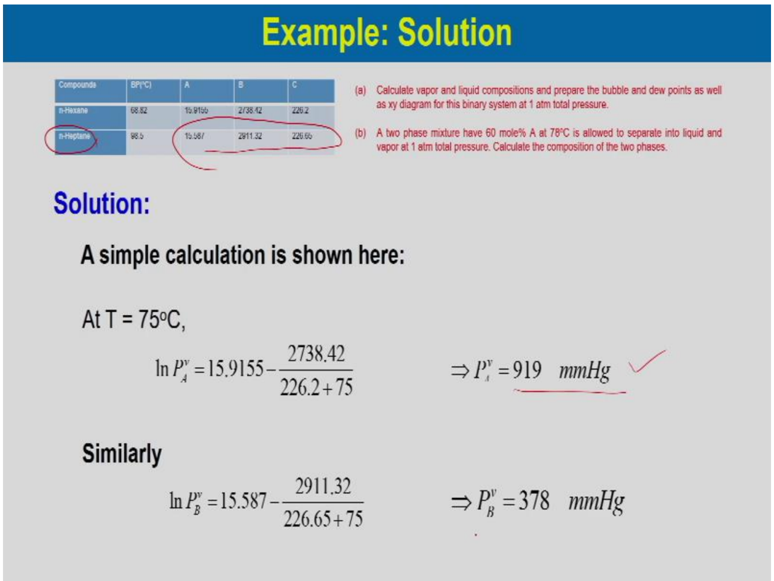

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(b) A two phase mixture have 60 mole% A at 78°C is allowed to separate into liquid and vapor at 1 atm total pressure. Calculate the composition of the two phases.

Solution:

A simple calculation is shown here:

At T = 75°C,

$$\ln P_A^v = 15.9155 - \frac{2738.42}{226.2+75} \quad \Rightarrow P_A^v = 919 \quad mmHg$$

Similarly

$$\ln P_B^v = 15.587 - \frac{2911.32}{226.65+75} \quad \Rightarrow P_B^v = 378 \quad mmHg$$

So, we have to start at a particular temperature a simple calculation is shown over here. Now, consider at T is equal to 75 degree centigrade which is any point between 68 And 98, ln P A V is after substituting this parameter A, B and C in this equation, we can calculate P A V is equal to 919 millimeter Hg. And similarly, we can do for component B which is this one component B ln P B V would be using these parameters over here given at this table we can calculate vapor pressure of component B which is 378 millimeter Hg.

A is the more volatile components because it is at the same temperature has a mole vapor pressure and B is the less volatile component has a less vapor pressure. We have calculated the vapor pressure at a particular temperature.

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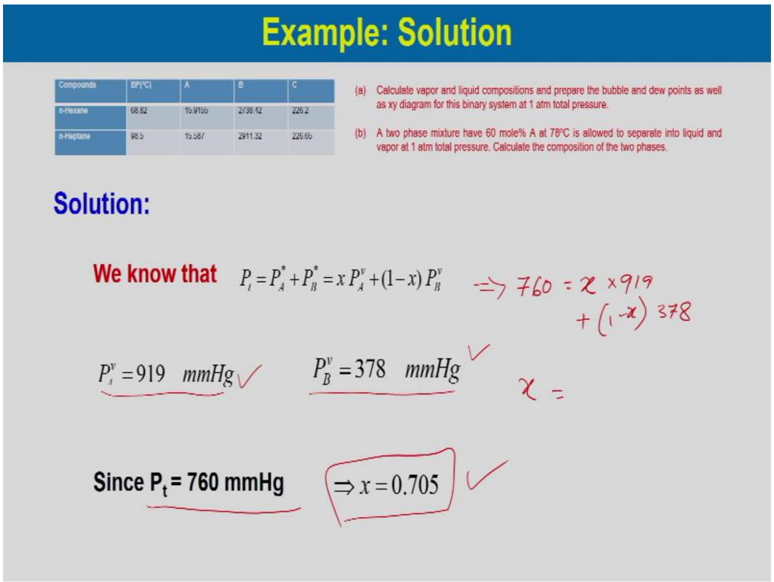

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(b) A two phase mixture have 60 mole% A at 78°C is allowed to separate into liquid and vapor at 1 atm total pressure. Calculate the composition of the two phases.

Solution:

We know that $P_t = P_A^* + P_B^* = x P_A^v + (1-x) P_B^v$ $\Rightarrow 760 = x \times 919 + (1-x)\, 378$

$P_A^v = 919 \quad mmHg$ ✓ $P_B^v = 378 \quad mmHg$ ✓ $x =$

Since $P_t = 760$ mmHg $\boxed{\Rightarrow x = 0.705}$ ✓

Now, we know that P t is PA star plus P B star would be equal to x P A V plus 1 minus x P B V. So, P A V we have obtained already and P B V we also we have obtained earlier and P t is 760 millimeter Hg which is given at one atmosphere pressure. So, if we substitute over here from this equation, we can write 760 would be equal to x into 919 plus 1 minus x into 378. Now if you solve this for x which would obtain 0.705. So, we can calculate x at this temperature and at this pressure condition.

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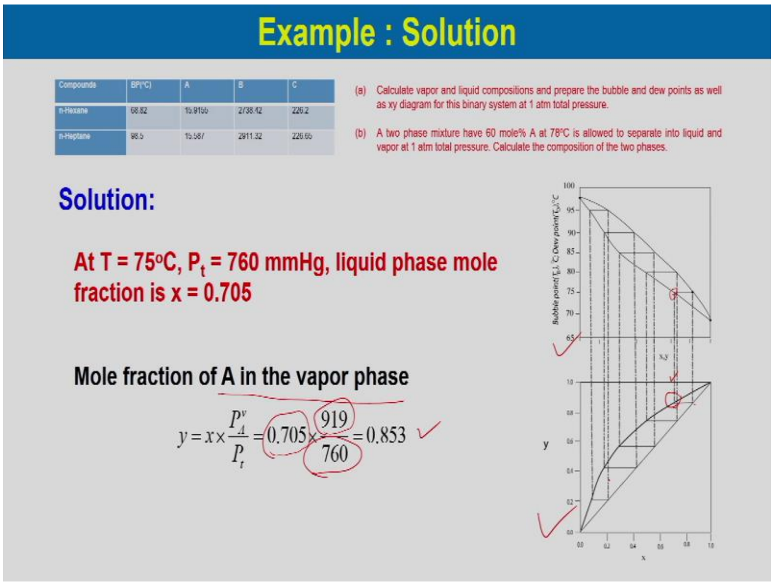

Example : Solution

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(b) A two phase mixture have 60 mole% A at 78°C is allowed to separate into liquid and vapor at 1 atm total pressure. Calculate the composition of the two phases.

Solution:

At T = 75°C, P_t = 760 mmHg, liquid phase mole fraction is x = 0.705

Mole fraction of A in the vapor phase

$$y = x \times \frac{P_A^v}{P_t} = 0.705 \times \frac{919}{760} = 0.853$$

Now, at T is equal to 75 degree centigrade P t is the total pressure, the liquid phase mole fraction x is known to us. The mole fraction of A in the vapor phase we can calculate that is y would be equal to x into P A V by P t. So, we use the known Raoult’s law and we can calculate y is equal to x into P A V by P t. So, x we have calculated 0.705 P A V is 919, P t is the total pressure so, we can calculate y 0.853. So, using the different temperature starting in this range from know 68.82 to 98.5, in similar fashion we can obtain the x and y data and the vapor pressure for both the components.

So, then if you plot we will obtain the Txy diagram like this and also the xy diagram over here so, which is shown below. So, T xy and xy plot we can obtain or simply if you have a Txy plot and we have the tie line we just come down vertically to the 45 degree diagonal and then, plot a horizontal line and also from this tie line from this point draw a vertical line. So, this vertical line and the horizontal line where it intersects gives the point of equilibrium points. This way either if we have Txy plot, we can draw the equilibrium curve know xy plot at the bottom or if you have xy plot in a similar fashion we can just draw the tie line and obtain the Txy diagram.

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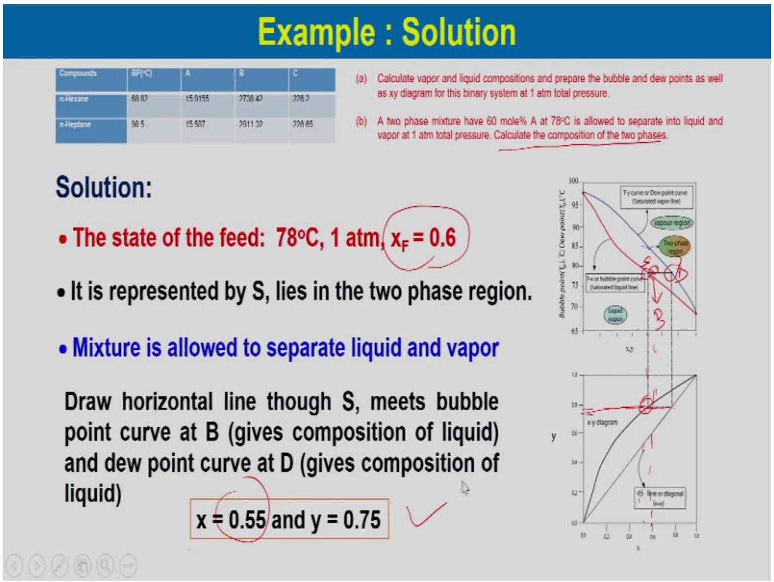

Example : Solution

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(a) Calculate vapor and liquid compositions and prepare the bubble and dew points as well as xy diagram for this binary system at 1 atm total pressure.

(b) A two phase mixture have 60 mole% A at 78°C is allowed to separate into liquid and vapor at 1 atm total pressure. Calculate the composition of the two phases.

Solution:

- The state of the feed: 78°C, 1 atm, $x_F = 0.6$
- It is represented by S, lies in the two phase region.
- Mixture is allowed to separate liquid and vapor

Draw horizontal line though S, meets bubble point curve at B (gives composition of liquid) and dew point curve at D (gives composition of liquid)

$x = 0.55$ and $y = 0.75$

Now the second problem is a two phased mixture having 60 mole percent of A at 78 degree centigrade is allowed to separate into liquid and vapor at one atmosphere total pressure.

Now we need to calculate the composition of the two phases. The state of the feed is set 78 degree centigrade, 1 atmosphere, x F is 0.6. It is represented by S, lies in the two phase region. So, if we look into over here this is the point where this is say point S is the two phase region so, 0.6 if you come down over here vertically, so it represents know 0.6.

So, this point S is it in the two phase region and mixture is allowed to separate liquid and vapor. Now, draw a horizontal line through S and it will meet the bubble point curve at B; so, that is point over here. So, this is point B and it will also meet at a dew point curve B here. From this you can obtain know you just come down vertically to the 45 degree diagonal and then, go horizontally and then, from the point B draw a vertical line and it will meet at a certain point on the equilibrium line and this will give you values of x which is 0.5 and correspondingly the value of y you will get 0.75.

So, this way we can solve this type of problem using Raoult's laws so to composition of the vapor and liquid phase for a particular mixture. So, thank you for hearing this lecture and we will continue our discussion on Fundamentals of the Distillation in the next class as well.