Mass Transfer Operation I

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Module - 5
Distillation
Lecture - 1
Introduction to Distillation and Phase Diagrams

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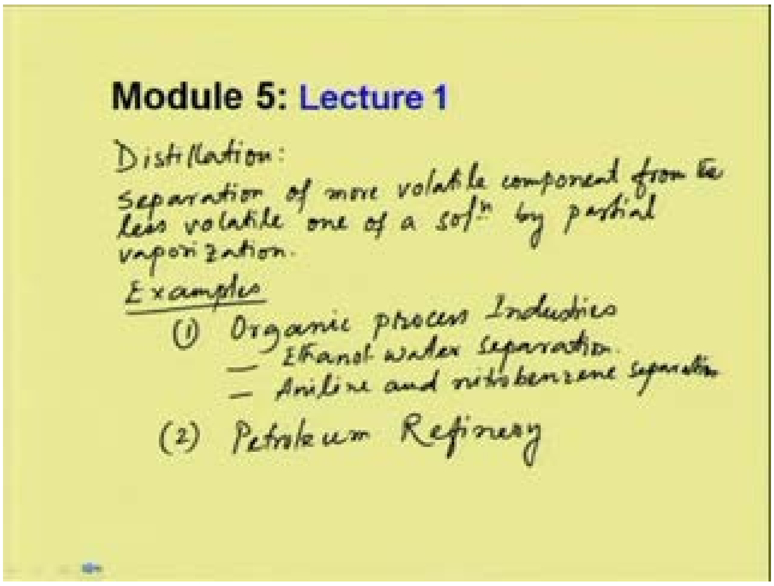

Module 5: Lecture 1

Distillation:
separation of more volatile component from the less volatile one of a sol^n by partial vaporization.

Examples
(1) Organic process Industries
– Ethanol water separation
– Aniline and nitrobenzene separation
(2) Petroleum Refinery

Welcome to the first lecture of module five. In this module, we will discuss distillation. Distillation is a method of separation of the more volatile component, separation of more volatile component from the less volatile one of a solution by partial vaporization. So, this partial vaporizations was done from the original solutions as another phase or the vapor phase is generated by partial vaporization, and then there is condensation of the vapor to get the desired product. This distillation is most widely used separation method for the liquid mixture. And the very common examples are organic process industries process industries like ethanol water separation, aniline and nitrobenzene separation. This is also most common in petroleum refinery petroleum refinery, and there are many other industries which uses the distillation as a process for separations of the liquid mixtures, where the liquid mixture contains the more volatile components and the less volatile components.

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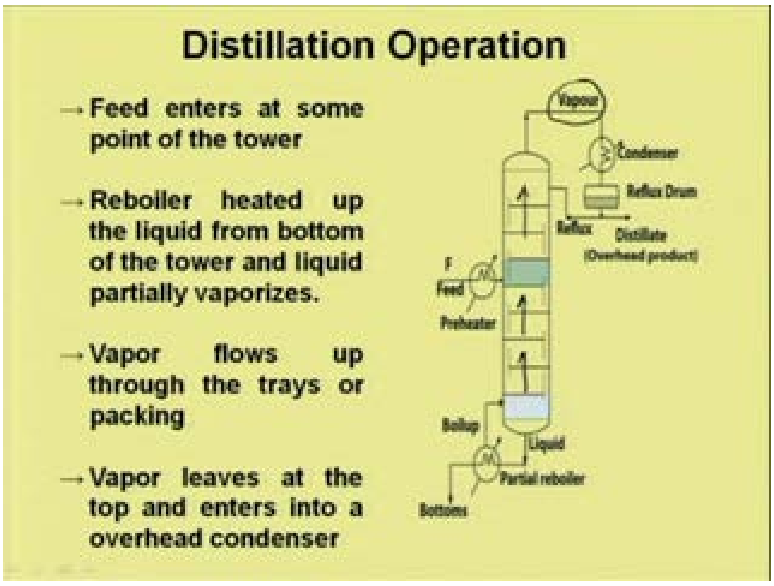

Distillation Operation

- 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 typical distillation column is look like this. This is a tray columns where the feed which is enter at some point on the tower in between that air either middle or at some points, and feed is preheated and then fit to the tower. There is a reboiler at the bottom of the tower which boils the liquid or it vaporizes the liquid partially and then the vapor flows up. So, vapor this goes off and then vapor leaves at the top vapor leaves at the top, and there is overhead condenser and then it reaches to the distributor. We call it reflux drum which separates the vapor and liquid mixture.

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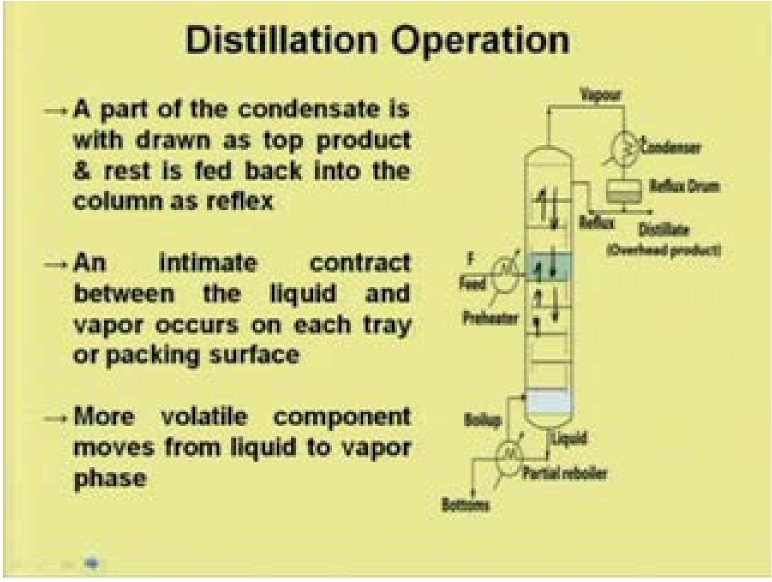

Distillation Operation

- A part of the condensate is with drawn as top product & rest is fed back into the column as reflex
- An intimate contract between the liquid and vapor occurs on each tray or packing surface
- More volatile component moves from liquid to vapor phase

A part of the condense heat from this reflux dram is recycled back at the top and rest is taken as the product. So, the liquid fall down or flow towards down and there is intimate contact between the vapor and the liquid on each tray. So, more volatile component moves from liquid in this process the more volatile component from the liquid phase to the transfer to the vapor phase.

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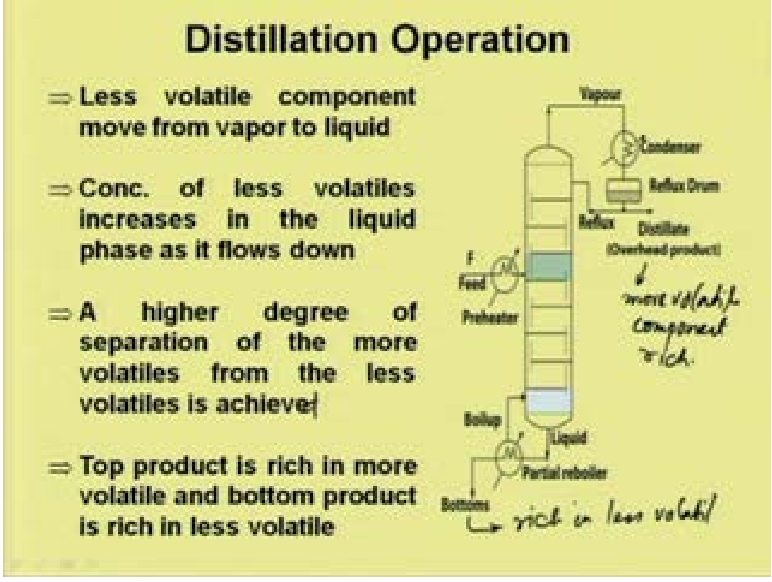

Distillation Operation

⇒ Less volatile component move from vapor to liquid

⇒ Conc. of less volatiles increases in the liquid phase as it flows down

⇒ A higher degree of separation of the more volatiles from the less volatiles is achieved

⇒ Top product is rich in more volatile and bottom product is rich in less volatile

And the less volatile components move from the vapor phase to the liquid phase. The concentration of the less volatile increases in the liquid as it flows towards down and the concentration of the more volatile increases in the vapor phase. So, a higher degree of separation of the more volatiles from the less volatile is achieved. The top product which we got over here as a overhead product is rich in more volatile component component rich, and the bottom product which is prompt as the bottoms is the rich in less volatile.

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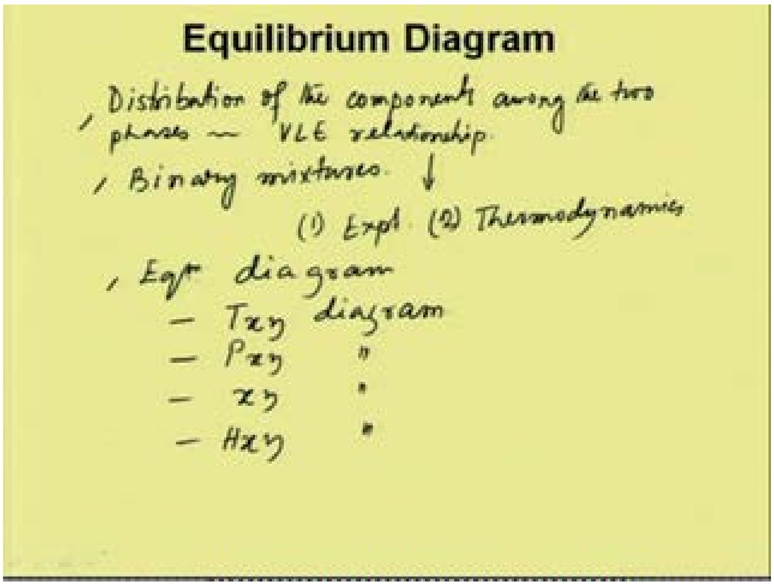

Equilibrium Diagram

✓ Distribution of the components among the two phases ~ VLE relationship

✓ Binary mixtures ↓

(1) Expt. (2) Thermodynamics

✓ Eqm diagram

— Txy diagram

— Pxy "

— xy "

— Hxy "

So, now the distillation process which is an equilibrium stage operation process it requires the vapor liquid equilibrium and physicochemical properties of the systems to solve this equilibrium stage operation. The distribution of the two components is governed by the vapor liquid equilibrium relationship, distribution of the components among the phases depends on the VLE vapor liquid equilibrium relationship.

So, here we will only consider the binary mixtures. So, this equilibrium data we can obtain from experiments, we can also obtain from thermodynamics. It is typically represented by the equilibrium diagram VLE data is represented by equilibrium diagram and they are like T x y diagram temperate mole fractions in the liquid phase and mole fraction in the vapor phase of the more volatile components. So, we call it T x y diagram or P x y diagram and the liquid and vapor compositions are related with the x y diagram and enthalpy mole fractions relationship is represented by enthalpy concentration diagram H x y diagram.

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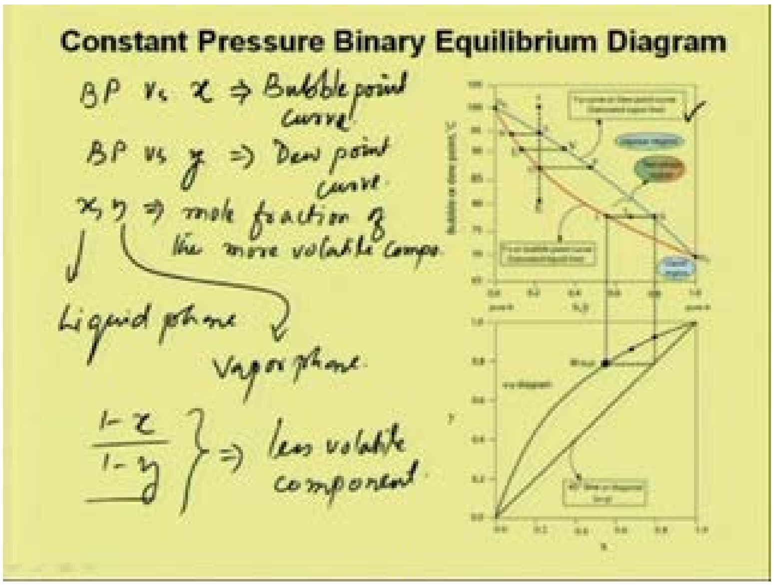

Constant Pressure Binary Equilibrium Diagram

BP vs x ⇒ Bubble point curve

BP vs y ⇒ Dew point curve.

x, y ⇒ mole fraction of the more volatile compo.

Liquid phase

Vapor phase.

1-x
1-y } ⇒ less volatile component

So, now we will consider T x y diagram. It is a constant pressure binary equilibrium diagram. Its boiling point is plotted versus liquid composition x is the liquid composition then we call it bubble point curve. Now if we plot boiling point versus y then it is dew point curve. A typical bubble point and dew point curve is plotted over here so the upper curve here this is the T y curve or the dew point curve that is each point on this curve represents the saturated vapor and the below line which is the T x or bubble point curve. So, here the composition x or y; these are represented in terms of the mole fractions, x, y represented in terms of the mole fraction of the more volatile component; x is in the liquid phase and y in the vapor phase. The less volatile component would be 1 minus x and 1 minus y.

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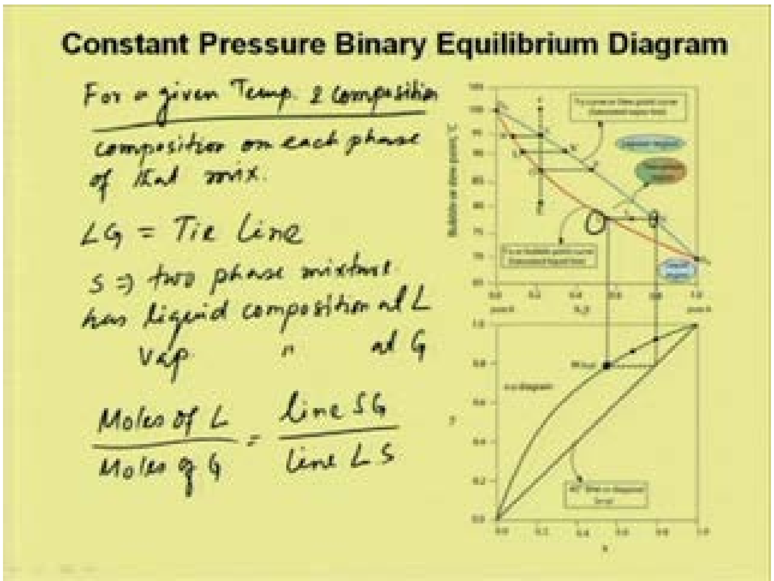

Constant Pressure Binary Equilibrium Diagram

For a given Temp. & composition

composition on each phase of that mix.

LG = Tie Line

S ⇒ two phase mixture
has liquid composition at L
Vap " at G

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

For any given temperature and composition for a given temperature and composition this curves tells us the composition of each phase of that mixture composition composition on each phase of that mixture. Suppose the point L over here this gives the equilibrium liquid phase composition T x and corresponding vapor phase composition at G and this line LG is known as the tie line. So, we can draw such an infinite number of tie lines in this region. And as I said the point on the lower curve represents the or at L represents the saturated liquid and points at G represents the saturated vapor. The region below this red line which is saturated liquid below that is known as the liquid region and above the blue line is represents the vapor region.

And the region between this two bubble point and dew point is known as the two phase region say a mixture point S on the tie line of LG represents the two phase mixture which has the liquid composition liquid composition at L. and vapor composition at G and the proportion can be obtained or the relatives amount can be obtained from the segment of these tie lines, segments S L and S G. Moles of L by moles of G we can write line S G by line L S.

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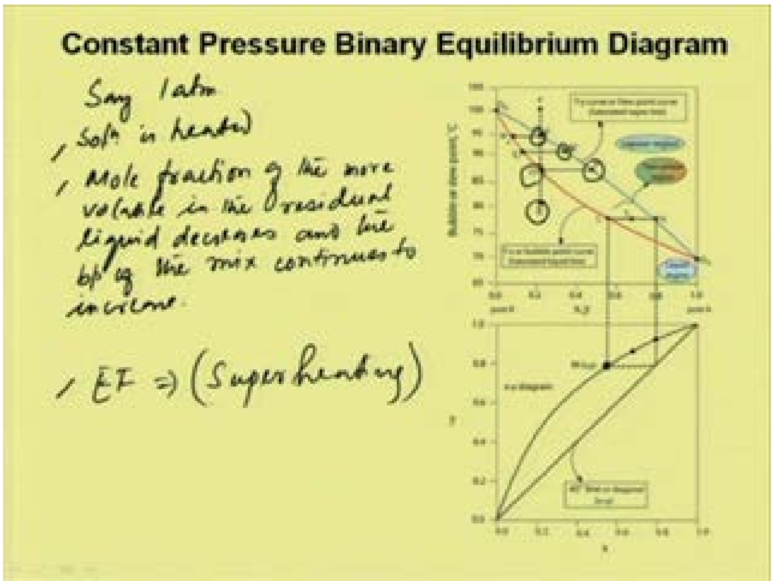

Constant Pressure Binary Equilibrium Diagram

Say 1atm

- Soln is heated
- Mole fraction of the more volatile in the residual liquid decreases and the bp of the mix continues to increase.
- EF ⇒ (Superheating)

Now if we consider a liquid at point E in a closed vessel and kept at constant pressure say one atmosphere. Now, if the solution is heated then the first drop of vapor will found at o and it has the composition at P, it will have the composition at P which is richer in mole volatile components. If we continue to heat it will follow E x line and the liquid line will follow o to u and it will give the vapor composition at b, but the compositions of the entire mass will still be remain as at E.

So, the mole fraction of the more volatile in the residual liquid decreases and the boiling point of the mixture continue to increase. The last drop of the vapor which is vaporizes at point x and has the composition and boiling point which is represented by w. When all the liquid is vaporized the vapor must have a composition equal to the initial E, initial liquid composition at E. Now, if no further heating is done then the final state of vapor is given by point x which is on the vertical line between from E to x. If we further heat this solution then the temperature will raise along the vertically through E F we call it super heating.

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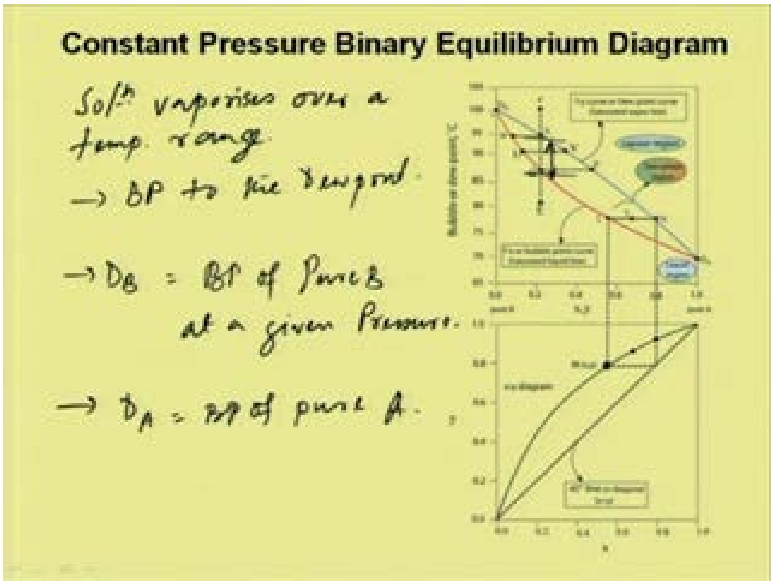

Constant Pressure Binary Equilibrium Diagram

Sol^n vaporises over a temp. range

→ BP to the Dewpoint.

→ D_B = BP of Pure B at a given Pressure.

→ D_A = BP of pure A.

So, in this case we can see the mixture is vaporized from the liquid to the vapor in the temperature region between o to x, this is the temperature region where the liquid is vaporized. Except pure substance the boiling point of a solution does not have any meaning because the solution solution vaporizes over a temperature range which is starting from bubble point to the dew point. The bubble and due points curves and meets point D B and at point D A, point D B represents the boiling point of pure B at a given pressure and point D A is the boiling point of pure A.

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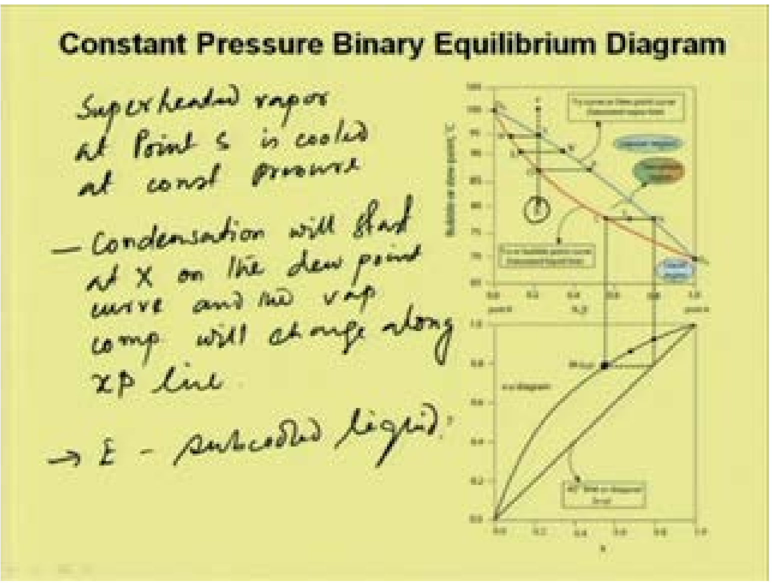

Constant Pressure Binary Equilibrium Diagram

Superheated vapor at Point S is cooled at const pressure

– Condensation will start at X on the dew point curve and the vap comp. will change along XP line

→ E - subcooled liquid.

Now, if some amount of super heated vapor say at point S super heated vapor at point S is cooled at constant pressure what will happen? It will follow the same path in the reverse directions for examples condensation condensation will start at X on the dew point curve and the vapor composition will change along x P line . So, when the inter vapor is condensed and then liquid is again cooled so it will reach the domain at E which is sub cooled.

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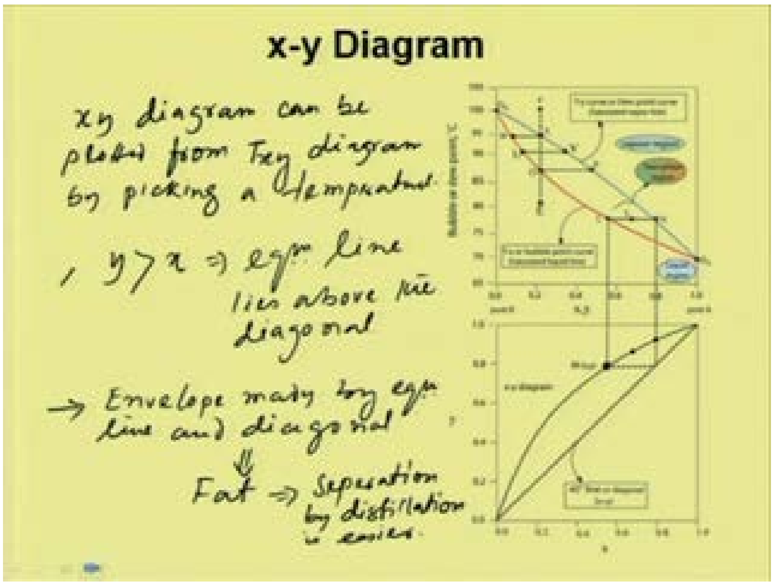

x-y Diagram

xy diagram can be plotted from Txy diagram by picking a temperature.

, y > x ⇒ eqm line lies above the diagonal

→ Envelope made by eqm line and diagonal
⇓
Fat ⇒ Separation by distillation is easier.

So, the equilibrium diagram for x y mole fractions is also plotted below the bubble point and dew point curve. So, this line represents the equilibrium curve x y diagram and below this is the 45 degree line or diagonal line where x is equal to y. So, the x y diagram can also be plotted from T x y diagram by picking a temperature and then corresponding y and x can be rate from this. The point A which is x y, on the x y curve represents to the tie line corresponding to the tie line LG on the T x y diagram. Since here y is greater than x the mole fractions of the more volatile component is more; the equilibrium line, line is lies above the diagonal. So, if the distance or the separations between the diagonal line and the equilibrium line is larger then separation is better. So, the envelope envelope made by equilibrium line, and diagonal this is fat then separation by distillation is easier.

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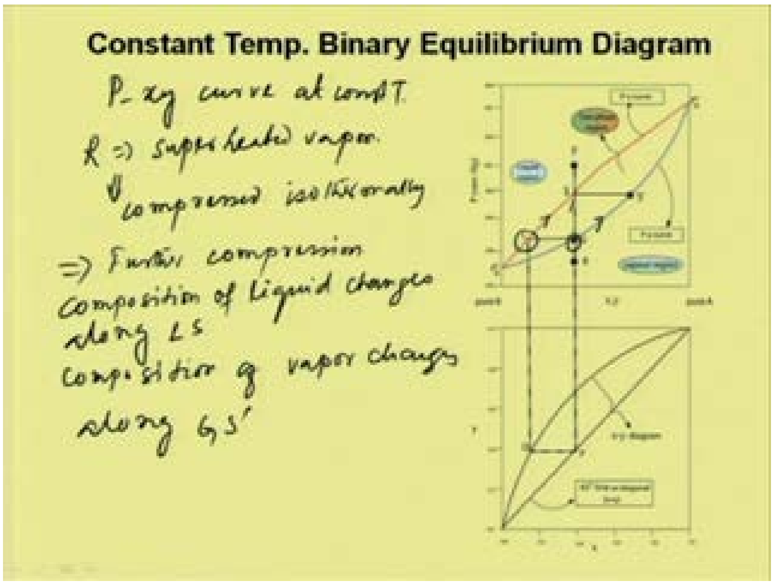

Constant Temp. Binary Equilibrium Diagram

P-xy curve at const T.
R ⇒ superheated vapor
⇓ compressed isothermally
⇒ Further compression
composition of liquid changes
along LS
composition of vapor changes
along GS'

Now, we will see the constant temperature binary equilibrium diagram. So, this is the plot where the total vapor pressure exerted by the solution at equilibrium depends on its composition. At a lower concentration of certain components the mixture will exert lower vapor pressure, the typical plot is so lower here where y axis represents P millimeter LG and this X is the mole fractions of more volatile components x and y, the horizontal line LG represents the tie line, the terminal points L and G; these are the liquid and vapor phase concentration of certain components and equilibrium of more volatile components and equilibrium. The region below this curve P x y curve, this is P x y curve at constant T below this blue line represents the vapor region, above this red line represents the liquid region and in between these two line represents the two phase region.

Suppose, if we consider a liquid in amount of vapor at location R super heated vapor at a given temperature now which compressed isothermally. The vapor will start condensing and it reaches the point at point G where the first drop of liquid will form at point G and will have composition at L. Now, if we further compress more vapor condenses and the composition of the accumulated condensed liquid changes along L S, the compositions of the liquid changes along L S the composition of the vapor changes along G S, composition of liquid changes along L S and composition of vapor changes along G S dash.

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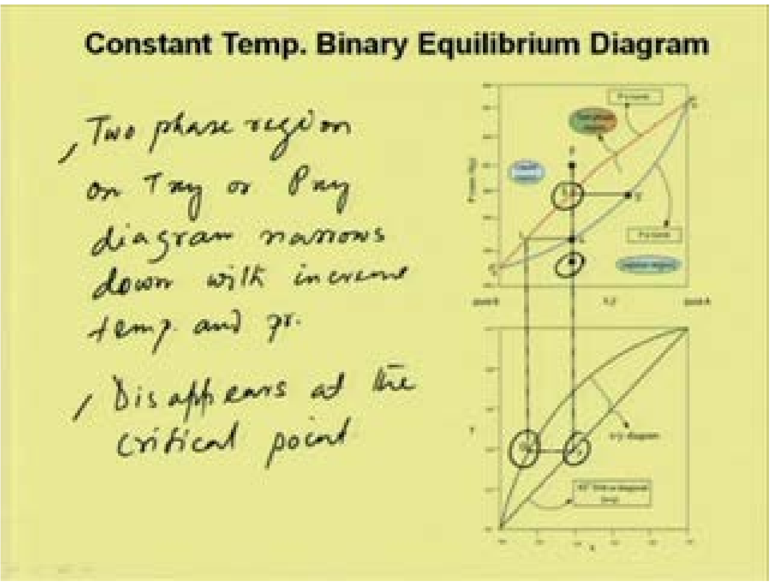

Constant Temp. Binary Equilibrium Diagram

/ Two phase region on Txy or Pxy diagram narrows down with increase temp. and pr.

/ Disappears at the critical point

Now, at a pressure corresponding to this point S the vapor condenses completely. Now the liquid composition will have the same composition of the original vapor which is at R, if the vapor pressure is raised further the liquid maybe considered sub cooled and it will follow the line through S F. The equilibrium composition to the tie line LG is represented by q P this is the equilibrium composition on the x y diagram, and the two phase region T x y or P x y this narrows down two phase region on T x y or P x y diagram narrows down with increase in temperature and pressure and disappears at the critical point.

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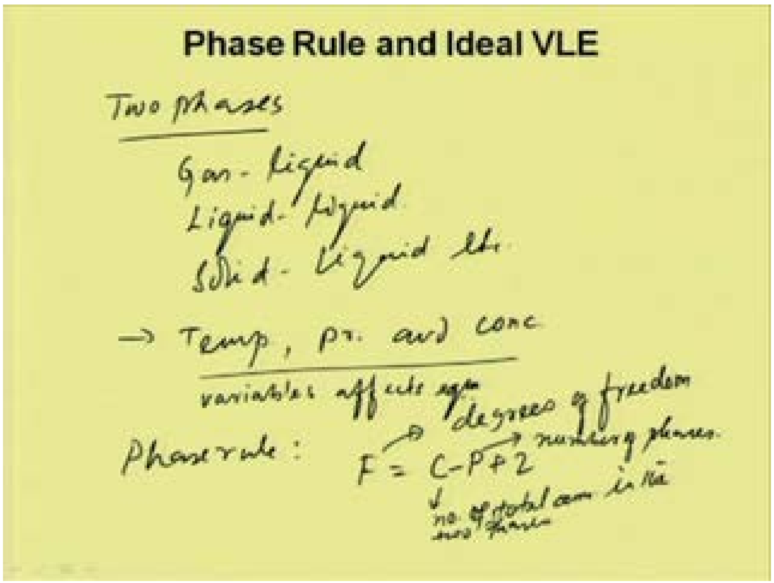

Phase Rule and Ideal VLE

Two phases

Gas - liquid
Liquid - liquid
Solid - liquid etc.

→ Temp, pr. and conc

variables affects equ

Phase rule: $F = C-P+2$

F → degrees of freedom
P → number of phases
C → no. of total com in the mix phases

Now, we will discuss phase rule and ideal V L E. If two phases are not in equilibrium then the transfer of mass from one phase to the other phase will be proportional to the driving force which is the departure from the equilibrium. In most of the cases which involves equilibrium two phases are generally involved this maybe two phase two phases gas liquid, liquid liquid, solid liquid and so on. The important variables which affects this equilibrium is the temperature pressure and concentration temperature, pressure and concentration parameters or variables affects equilibrium. The equilibrium between the phases for a given situation is restricted by phase rule and it states that F is equal to C minus P plus 2 where F is the number of variables or degrees of freedom F is the degrees of freedom freedom, C is the number of total components in the two phases number of total components in the two phases when there is no chemical reaction, and P is the number of phase number of phases.

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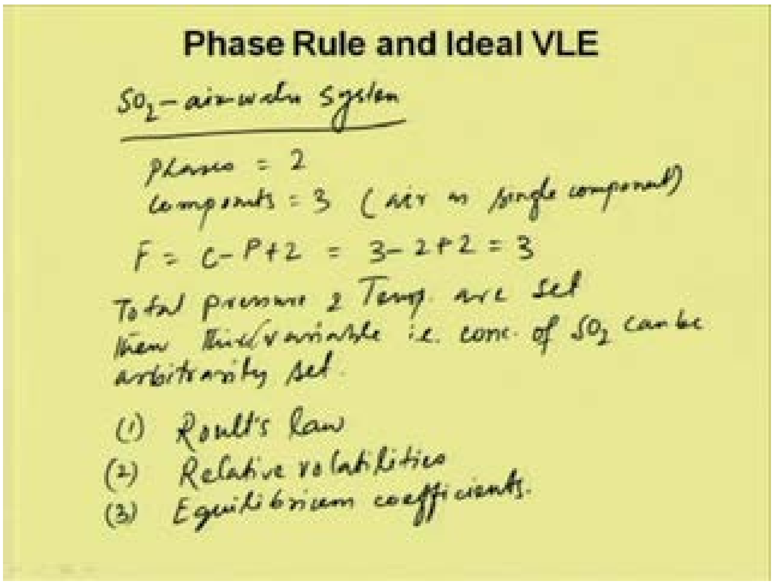

Phase Rule and Ideal VLE

SO_2 - air-water system

phases = 2
components = 3 (air as single component)

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

Total pressure & Temp. are set then third variable i.e. conc. of SO_2 can be arbitrarily set.

(1) Roult's law
(2) Relative volatilities
(3) Equilibrium coefficients.

So, if we consider a simple example of sulfur dioxide and air water system then phases are 2 components 3 and considering air as single component, then we can write F is equal to C minus P plus 2 which is 3 minus 2 plus 2 is equal to 3 this means that it has 3 variants or 3 degree of freedom. If the total pressure total pressure and temperature are set then the third variable, variable that is the concentration of sulfur dioxide can be arbitrarily arbitrarily arbitrarily set. So, the phase rule does not tell us the partial pressure in that equations with the selected mole fractions. So, the partial pressure must be determined experimentally. This thing can be simplified if we consider the ideal behavior or the ideal solutions; the 3 ways we can define or can be related one is Roult's law, second is relative volatility and third is equilibrium coefficients.

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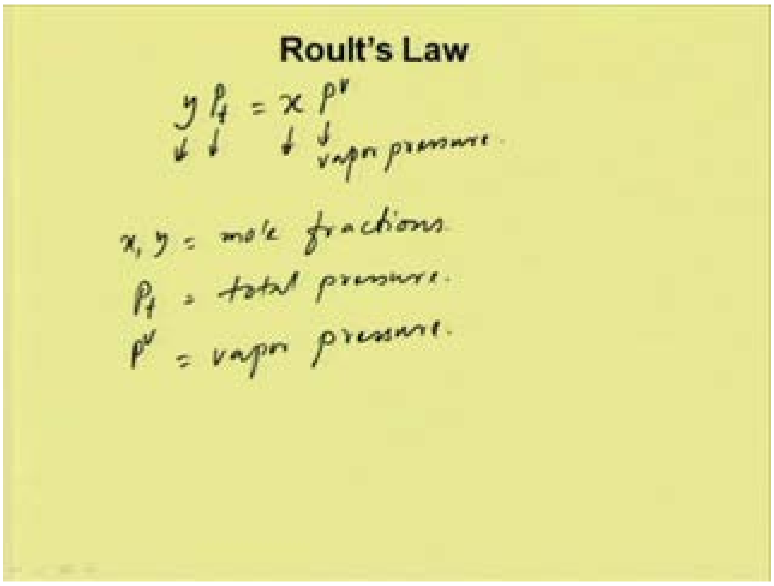

Roult's Law

$y\,P_t = x\,P^v$

$\downarrow \ \downarrow \quad \downarrow \ \downarrow$ vapor pressure.

x, y = mole fractions

P_t = total pressure.

P^v = vapor pressure.

The Roult's law relates with the vapor liquid compositions of a mixture to the pure component vapor pressure and system pressures. So, we can write y P t is equal to x P v where y is the mole fractions in the vapor phase, P t is the total pressure and x is the mole fractions in the liquid phase and P v is the vapor pressure.

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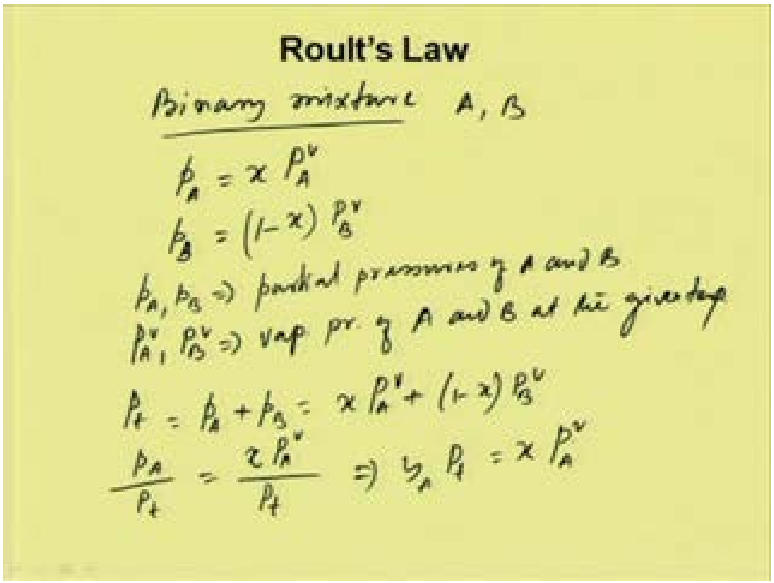

Roult's Law

Binary mixture A, B

$p_A = x\,P_A^v$

$p_B = (1-x)\,P_B^v$

$p_A, p_B \Rightarrow$ partial pressures of A and B

$P_A^v, P_B^v \Rightarrow$ vap pr. of A and B at the given temp

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

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

So, consider the binary mixture where say A and B we can write the partial pressure P A is equal to x into P A v and P B partial pressure of B we can write 1 minus x into P B v. So, P A and P B these are the partial pressures of partial pressures of A and B; P A v and P B v are the vapor pressure pressure of A and B at the given temperature. We can write P T is equal to P A plus P B is equal to x P A v plus 1 minus x P B v this will give P A by P t would be equal to x P A v by P t or we can write y A P t is equal to x P A v. This equations can be used to calculate the vapor liquid equilibrium data for an ideal binary mixture.

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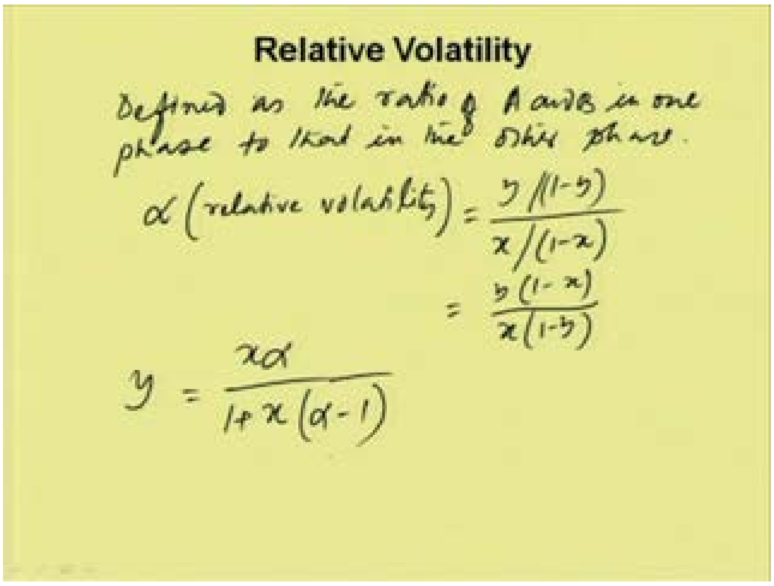

Relative Volatility

Defined as the ratio of A and B in one phase to that in the other phase.

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

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

Now, we will discuss the relative volatility. The greater the distance from the equilibrium curve and the diagonal curve the greater the difference in the liquid and vapor composition easier to separate by distillation. One numerical measure for this is the relative volatility; relative volatility is defined as the ratio ratio of A and B in one phase to that in the other phase. So, we can write alpha which is relative volatility can be written as y by 1 minus y divided by x by 1 minus x which we can write y into 1 minus x divided by x into 1 minus y. This can be rearranged and we can write y is equal to x alpha divided by 1 plus x into alpha minus 1.

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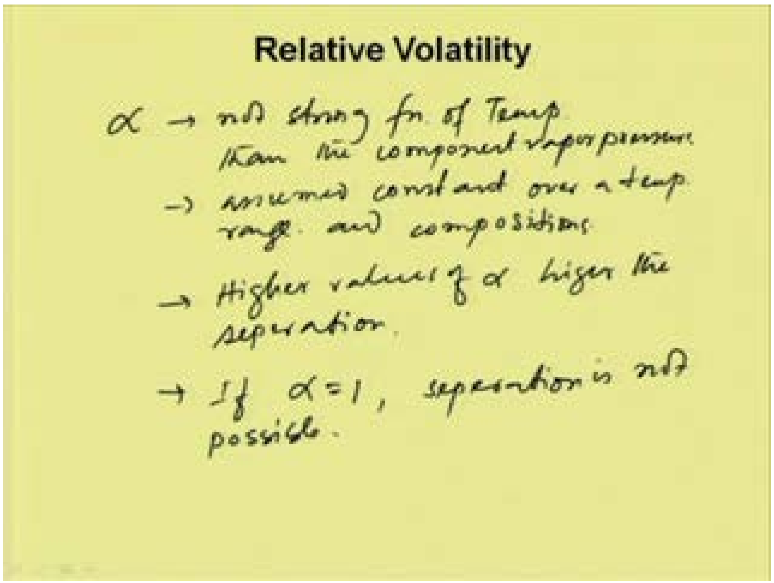

Relative Volatility

α → not strong fn. of Temp.
than the component vapor pressure

→ assumed constant over a temp. range and compositions

→ Higher values of α higer the separation.

→ If $\alpha = 1$, separation is not possible.

So, the relative volatility alpha is not strong function of of temperature than the component vapor pressure. So, it can be assumed constant over a temperature range, and composition. So, higher values of alpha higher the separation, if alpha is 1 then the separation is not possible, separation is not possible. In the next class we will discuss the examples on how to use relative volatility, and Roult's law to determine the T x y diagram.

Thank you.