Mass Transfer Operations I

Prof. Bishnupada Mandal

Department of Chemical Engineering

Indian Institute of Technology, Guwahati

Module - 5

Distillation

Lecture - 2

Azeotropes and Enthalpy Concentration Diagrams

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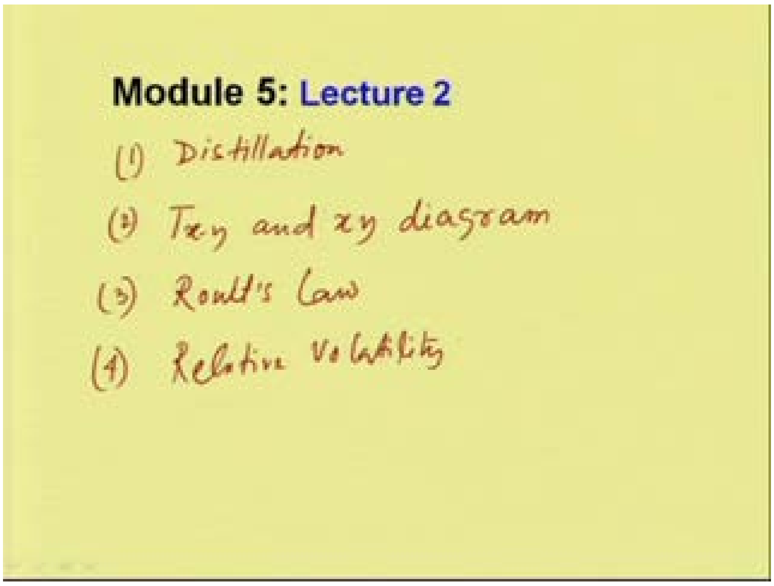

Module 5: Lecture 2

(1) Distillation

(2) Txy and xy diagram

(3) Roult's law

(4) Relative volatility

Welcome to the second lecture of module five. In the last lecture, we had a introduction on distillation, and then we discussed the equilibrium relationship T x y diagram, and x y diagram T x y and x y diagram. We have discussed the ideal relations like Roult's law, and we have also discussed the relative volatility.

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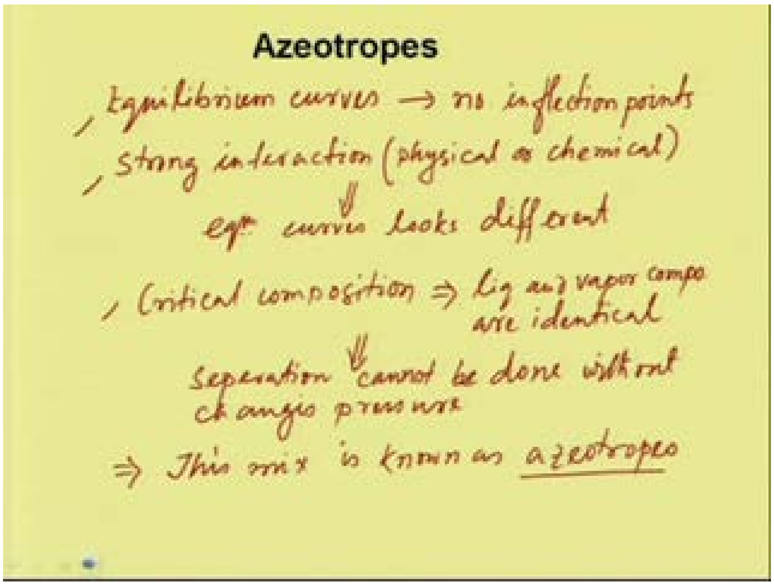

Azeotropes

/ Equilibrium curves → no inflection points

/ strong interaction (physical or chemical)

⇓

eqm curves looks different

/ Critical composition ⇒ liq and vapor compo are identical

⇓

separation cannot be done without changing pressure

⇒ This mix is known as azeotropes

In this lecture, we will discuss the deviation from ideality and the Azeotropes. The most of the cases in general the systems with equilibrium, we consider the equilibrium curves, equilibrium curves no inflection points. Now, if there is strong interaction - strong interaction physical or chemical, then the equilibrium curves looks different. In such a system, where there is a strong interaction, physical or chemical; there is a critical composition - critical composition where the liquid and vapor compositions are identical, liquid and vapor composition are identical.

In this case separation, separation cannot be done without changing pressure, and this mixture - mixture is known as Azeotropes. So, this critical mixture where the liquid and vapor compositions are same and they are known as the Azeotropes.

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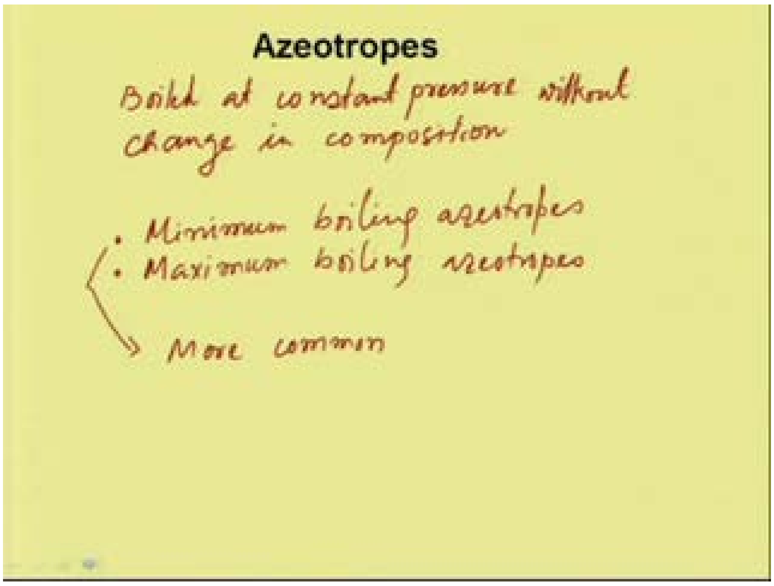

Azeotropes

Boiled at constant pressure without change in composition

- Minimum boiling azeotropes
- Maximum boiling azeotropes

More common

Azeotropes means it boils at constant pressure without change in composition, this is the azeotropic mixture. So, these Azeotropes have two different types; one is called minimum, minimum boiling Azeotropes, and second is maximum boiling Azeotropes; minimum boiling Azeotropes - this is more common.

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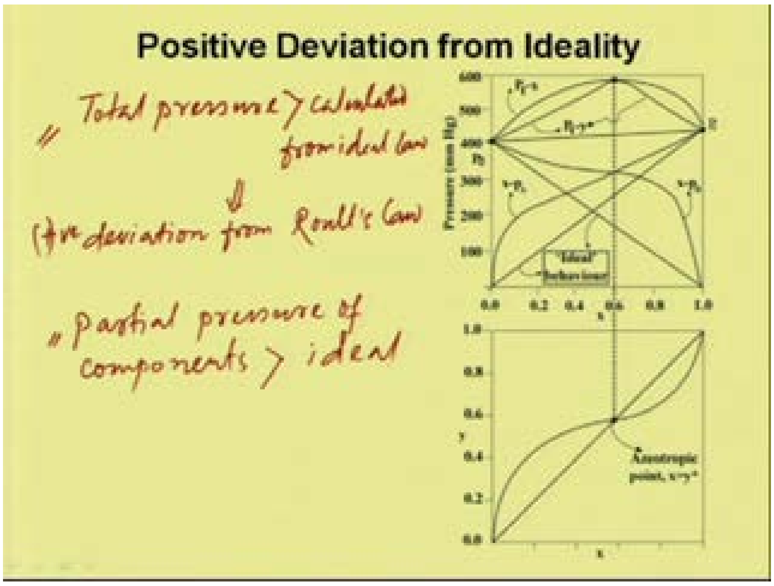

Positive Deviation from Ideality

// Total pressure > calculated from ideal law

⇓

(+ve) deviation from Raoult's law

// partial pressure of components > ideal

Now, we can see two types as we said one is minimum boiling Azeotropes, and another one is maximum boiling Azeotropes. Now, a mixture is total pressure - total pressure is greater than calculated from ideal law calculated from ideal law, then it shows the deviation, deviation from Roult’s law; that means, if it is greater then the deviation will be positive. So, positive deviation from Roult’s law, and the partial pressure partial pressure of components should be greater than than the ideal.

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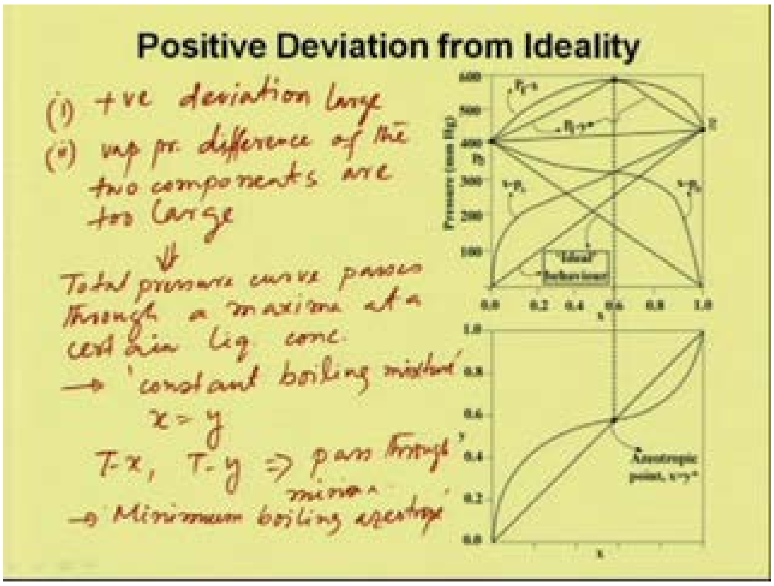

Positive Deviation from Ideality

(i) +ve deviation large
(ii) vap pr. difference of the two components are too large
⇓
Total pressure curve passes through a maxima at a certain liq conc.
→ 'constant boiling mixture'
$x = y$
T-x, T-y ⇒ pass through minima'
→ 'Minimum boiling azeotrope'

Now, if positive deviation deviation is large one, and second vapor pressure difference of the two components; components are too large. We can see the total pressure curve P T versus x and P T versus y, total pressure curves passes through a maxima at certain liquid composition. If this is happen? Total pressure curve pressure curve passes through a maxima at a certain liquid concentration. This liquid mixture at this location is known as the constant boiling mixture; constant, constant boiling mixture. As we can see at Azeotropic point where the total pressure curves concentration curve reaches a maxima, and the corresponding to the concentration of x is equal to y, x equal to y; if we plot T x or T y this should pass through minimum; that is why this mixture is known as the minimum boiling Azeotrope minimum boiling Azeotrope.

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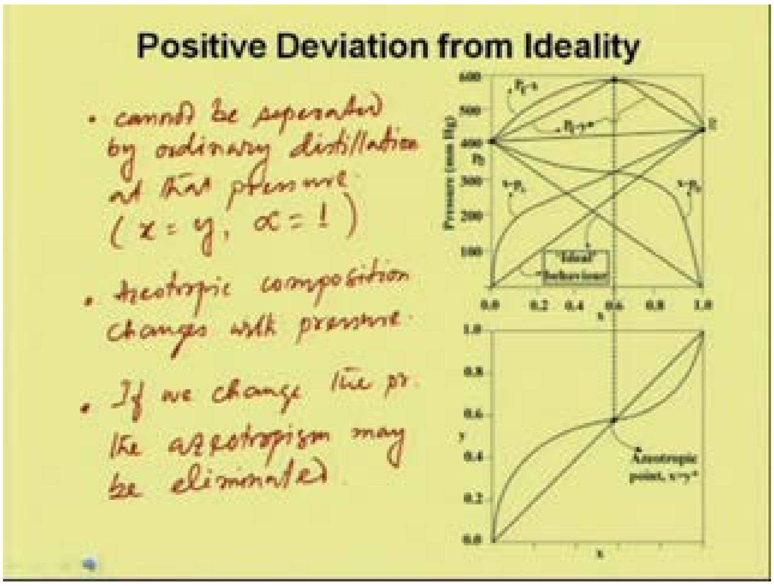

Positive Deviation from Ideality

- cannot be separated by ordinary distillation at that pressure ($x = y$, $\alpha = 1$)
- Azeotropic composition changes with pressure.
- If we change the pr. the azeotropism may be eliminated.

As we know at this composition a vapor composition will be same as the liquid composition, and it will boil at this constant temperature without change in composition. So, this type of mixture cannot be separated separated by ordinary distillation at that pressure.

So, here x will be equal to y and alpha the relative volatility will be 1, the Azeotropic composition, Azeotropic composition changes with pressure, in some cases if you change the pressure, pressure the Azeotropism may be eliminated, the Azeotropism may be eliminated. Now, this is positive deviation from ideality.

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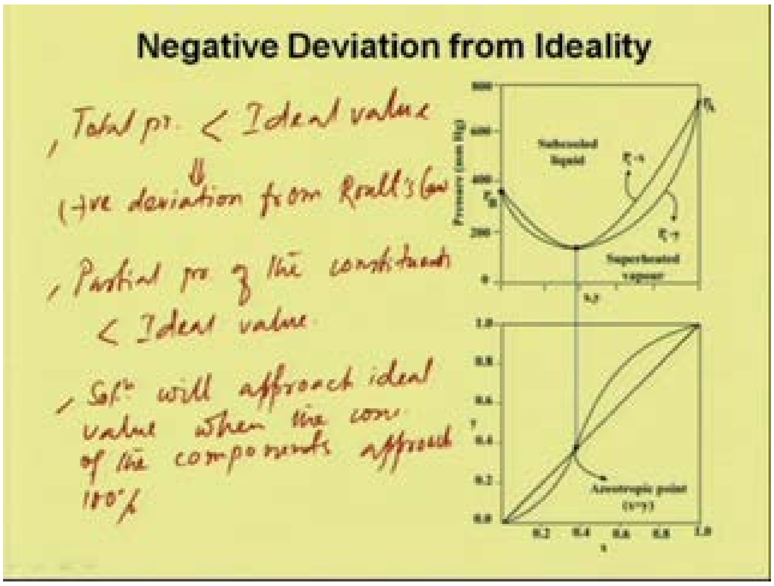

Negative Deviation from Ideality

- Total pr. < Ideal value
  ⇓
  (-)ve deviation from Roult's law
- Partial pr of the constituents < Ideal value
- Solⁿ will approach ideal value when the con of the components approach 100%

Now, in some cases when the total pressure calculated for a system, total pressure is less than the ideal value. So, this is known as the negative deviation negative deviation from Roult's law. And in this cases the partial pressure of the constituencies, partial pressure partial pressure of the constituencies would be less than the ideal value, and the solution will approach ideality, solution will approach ideal value when the concentration concentration of the component components approach 100 percent.

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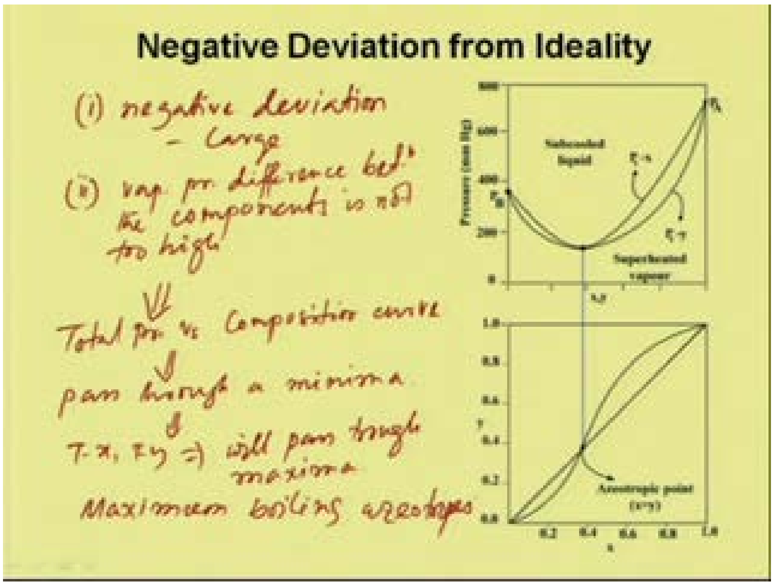

Negative Deviation from Ideality

(i) negative deviation - Large

(ii) vap. pr. difference betⁿ the components is not too high

⇓

Total pr vs Composition curve

⇓

pass through a minima

⇓

T-x, T-y ⇒ will pass trough maxima

Maximum boiling azeotropes

So, these are the Azeotropic point when negative deviation is large, negative deviation large and second is vapor pressure difference difference between the components is not too high. Then the total pressure curve total pressure pressure versus composition curve pass through a minimum, then the T x, T y curve will pass through a maximum. So, this is maximum boiling Azeotropes maximum boiling Azeotropes.

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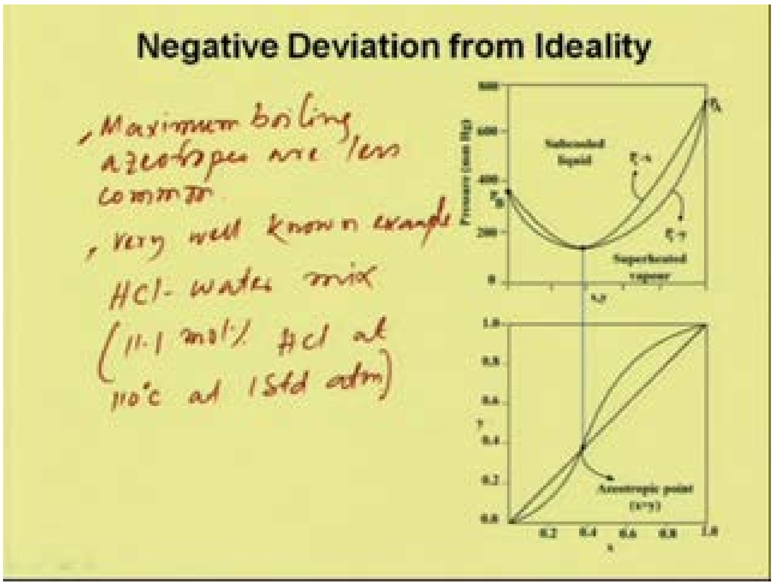

Negative Deviation from Ideality

, Maximum boiling azeotropes are less common

, very well known example HCl- water mix (11.1 mol% HCl at 110°C at 1 std atm)

So, maximum boiling Azeotropes as we said before maximum boiling Azeotropes Azeotropes are less common, very well known examples known example are the Hcl water mixture at 11.1 mole percent Hcl at 110 degree centigrade temperature at one std atmosphere standard atmosphere pressure.

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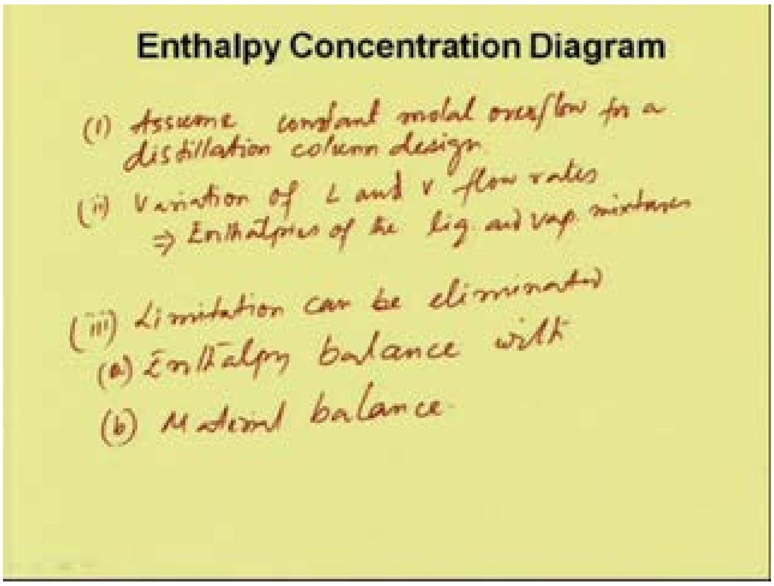

Enthalpy Concentration Diagram

(i) Assume constant molal overflow for a distillation column design.

(ii) Variation of L and V flow rates

⇒ Enthalpies of the liq. and vap. mixtures

(iii) Limitation can be eliminated

(a) Enthalpy balance with

(b) Material balance

So, now we will discuss another important equilibrium diagrams, which is required for the distillation calculations is the enthalpy concentration diagram. In general in a distillation calculation we assume constant constant molal over flow constant molal over flow for our distillation column design, but in a Hcl there is variation variation of liquid and vapor flow rates. And which is depends on the enthalpies of the liquid and vapor mixtures. So, the limitations can be eliminated, if we use enthalpy balance, balance with with the material balance.

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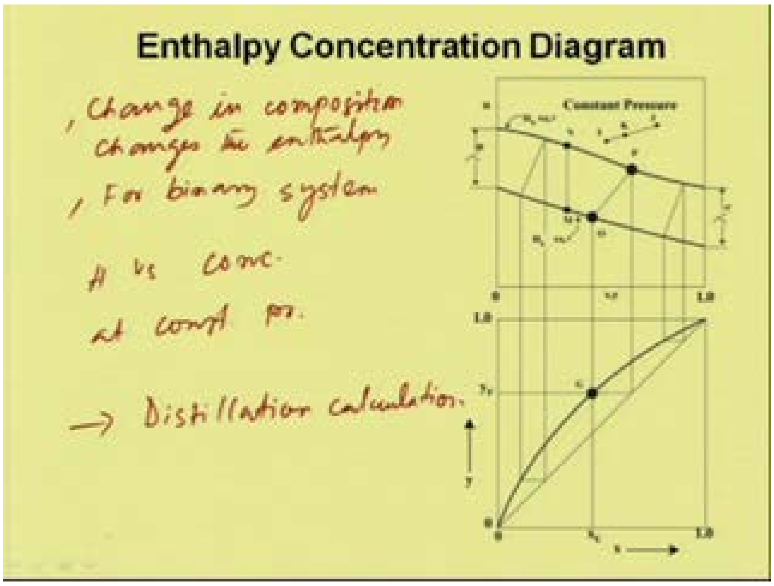

Enthalpy Concentration Diagram

, Change in composition changes the enthalpy

, For binary system

H vs conc.

at const pr.

→ Distillation calculation.

So, this is the typical enthalpy concentration diagram shown over here, and here as we know during distillation, during the change in phase, the change in compositions occurs change in composition, changes the enthalpy. So, this is the binary vapor liquid equilibria plots for binary system; it is plotted as enthalpy versus concentration at constant pressure, and this will be very much use full in distillation calculation.

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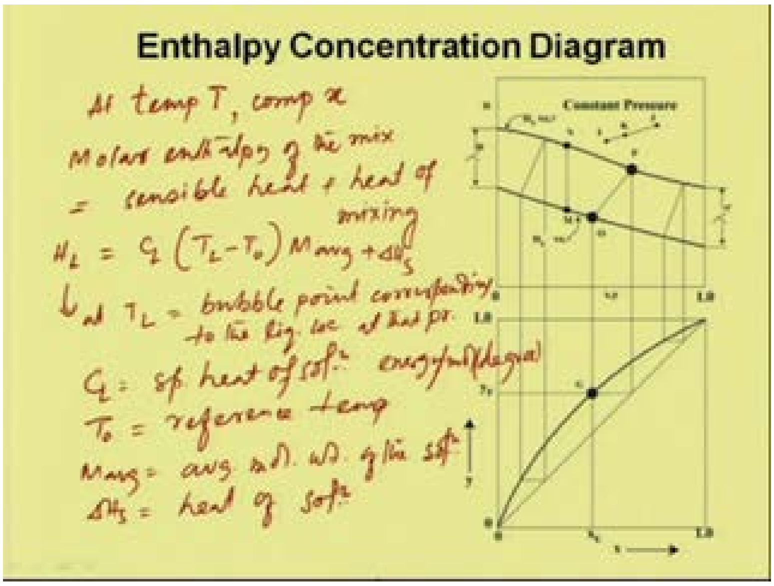

Enthalpy Concentration Diagram

At temp T, comp x

Molar enthalpy of the mix

= sensible heat + heat of mixing

$H_L = C_L (T_L - T_0) M_{avg} + \Delta H_S$

↳ at T_L = bubble point corresponding to the liq. conc. at that pr.

C_L = sp. heat of sol^n energy/(mol)(deg)

T_0 = reference temp

M_{avg} = avg. mol. wt. of the sol^n

ΔH_S = heat of sol^n

Now, suppose at a given temperature at temperature T and composition x. So, molar enthalpy enthalpy of the mixture would be equal to sensible heat plus heat of mixing, and this we can calculate using H L would be equal to C L into T L minus T naught M average plus delta H s, where H L is the molar enthalpy at T L. T L is the bubble point corresponding to the liquid concentration, bubble point corresponding to the liquid concentration at that pressure, C L is the specific heat of solution and this is energy per mole degree, T naught is the reference temperature, M average is the average molecular weight of the solution weight of the solution, and delta H s is the heat of solution heat of solution at the reference temperature T naught, and the concentration which is for the pure liquid components. So, delta H s is the heat of solutions.

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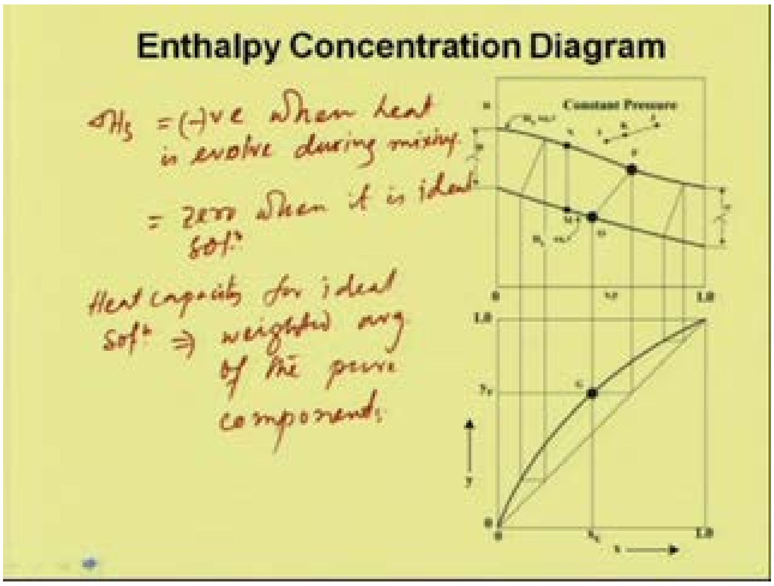

Enthalpy Concentration Diagram

ΔH_s = (−)ve when heat is evolve during mixing

= zero when it is ideal sol^n

Heat capacity for ideal sol^n ⇒ weighted avg of the pure components.

Now, this heat of solution, we can calculate or we can obtain from some literature data. Now, if delta H s will be negative when heat is evolved during mixing and value would be zero when it is ideal solution, the heat capacity in this case heat capacity for ideal solution would be the weightiest average average of the pure components.

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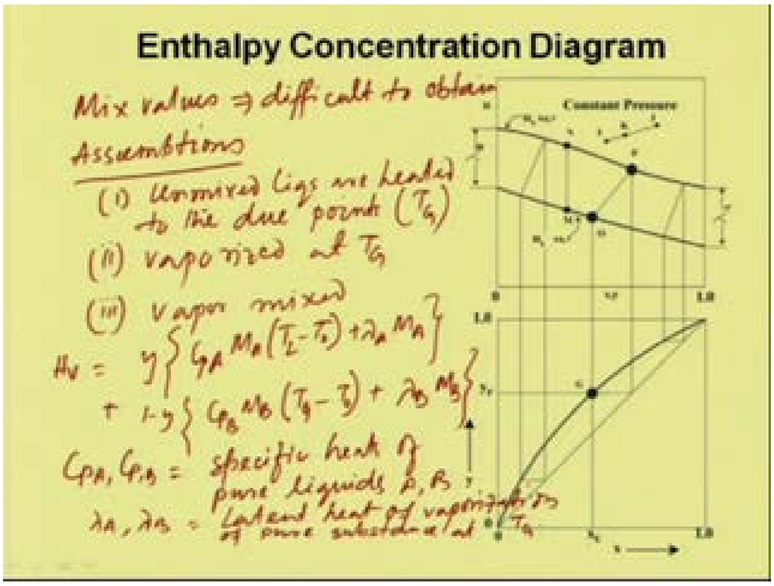

Enthalpy Concentration Diagram

Mix values ⇒ difficult to obtain

Assumptions

(i) Unmixed liqs are heated to the due point (T_G)

(ii) vaporized at T_G

(iii) vapor mixed

$$H_V = y\{C_{pA} M_A (T_L - T_0) + \lambda_A M_A\} + (1-y)\{C_{pB} M_B (T_G - T_0) + \lambda_B M_B\}$$

C_{pA}, C_{pB} = specific heat of pure liquids A, B

λ_A, λ_B = Latent heat of vaporization of pure substance at T_G

Now, it is very difficult to find out the mixture values, difficult to obtain if we assume we can get the approximate values assumptions, assume unmixed liquids mixed liquid are heated to the due points due points; that is T G, and second vaporized at T G and then vapor mixed. So, we can calculate H v would be equal to y into C P A M A T L minus T naught plus lambda A M A plus 1 minus y C P B M B T G minus T naught plus lambda B M B, where C P A and C P B - these are the specific heats of pure liquids A and B; and lambda A and lambda B these are the latin heat of vaporization of pure substance at T G, latin heat of vaporization of pure substance at T G; all these information will be use to construct this enthalpy concentration diagrams.

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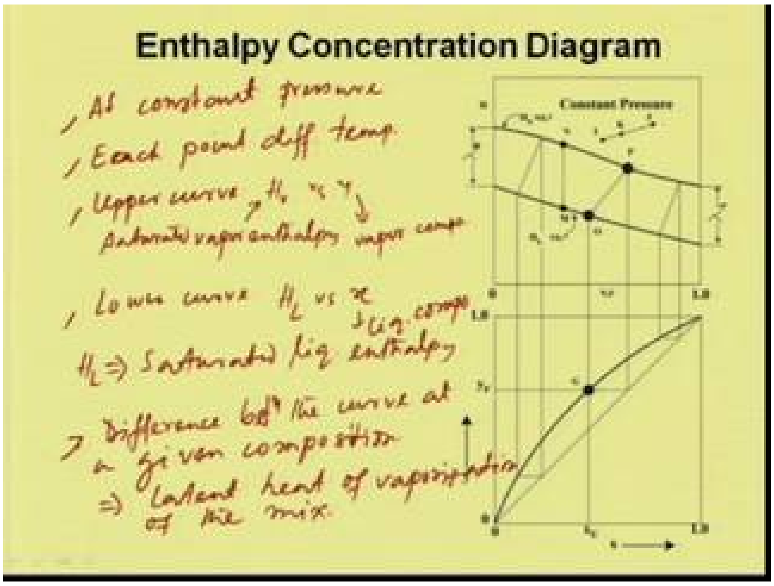

Enthalpy Concentration Diagram

- At constant pressure
- Each point diff temp
- Upper curve, H_v vs y
  saturated vapor enthalpy vapor comp
- Lower curve H_L vs x
  liq comp
  $H_L \Rightarrow$ Saturated liq enthalpy
- Difference b/w the curve at a given composition
  $\Rightarrow$ Latent heat of vaporization of the mix

So, the enthalpy concentration diagram is plotted at constant pressure at constant pressure, and each point on this enthalpy concentration diagrams, each point represents different temperature, and the upper curve this one H B y curve upper curve H B versus y, it is a plot of saturated vapor enthalpy saturated vapor enthalpy versus vapor composition. And the lower curve is the saturated liquid compositions curve H L versus x H L is the saturated liquid enthalpy - liquid enthalpy, and x is the liquid composition. Now, for any given composition the difference between these two curves at any points the difference between the two curves, difference between the curve at a given composition composition is the latent heat of vaporization of the mixture is known as the latent heat of vaporization of the mixture.

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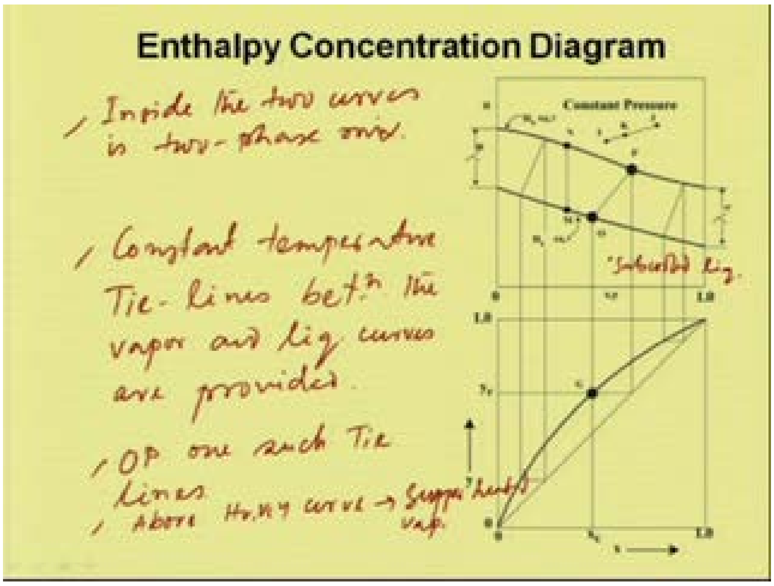

Enthalpy Concentration Diagram

- Inside the two curves is two-phase mix.
- Constant temperature Tie-lines betn the vapor and liq curves are provided.
- OP one such Tie lines
- Above Hv,y curve → Superheated vap.

Now, inside this two curves inside this naval of is a two phase mixture, inside the two curves two curves is two phase mixture, and sometimes between these two curves constant temperature tie lines temperature, constant temperature tie lines between the vapor and liquid curves are provided O and P one such tie lines O P one such tie lines.

Now, the mixture beyond this two points; one is above this h v y curve is the super heated vapor, and below this curve is the sub (( )) liquid. So, above h v versus y curve is the super heated vapor and below this line is a sub (( )) liquid, any point below this H L x curve. Now there is a direct relations between the H x y curve with the x y curve equilibrium diagram.

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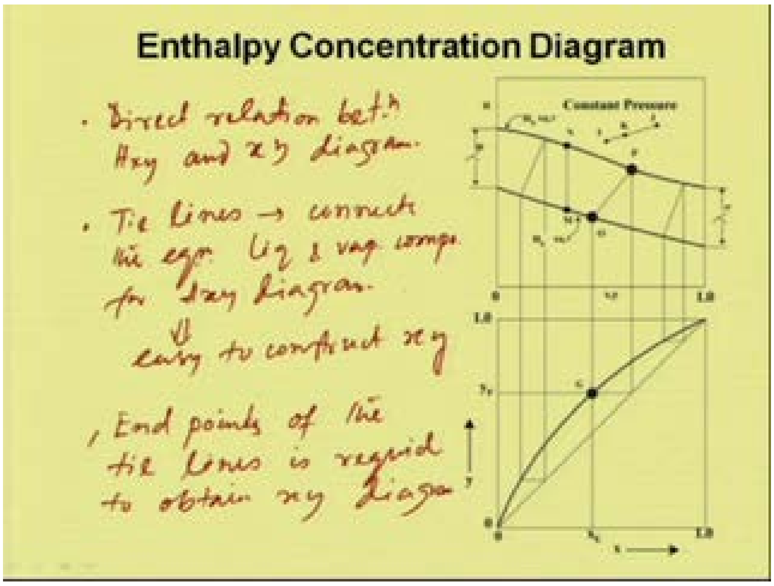

Enthalpy Concentration Diagram

- Direct relation betn Hxy and xy diagram.
- Tie lines → connects the eqm. liq & vap compo. for Hxy diagram.

  ⇓ easy to construct xy
- End points of the tie lines is reqd to obtain xy diagram

So, if we have enthalpy concentration relationship, we can have direct relation relation between H x y and x y diagrams, now if we have tie lines which connects connects the equilibrium liquid and vapor composition for H x y diagram, then it will be easy to construct x y diagram. So, only the end points of the tie lines end points of the tie lines is required to obtain x y diagram.

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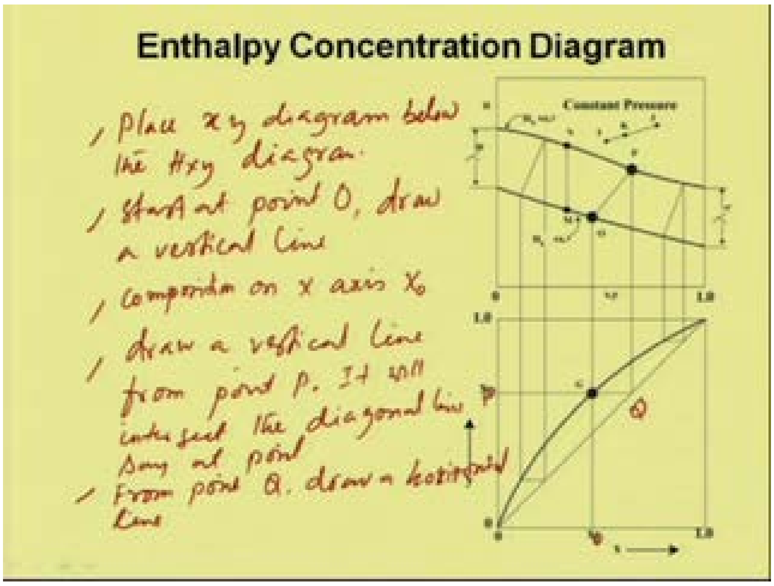

Enthalpy Concentration Diagram

- Place xy diagram below the Hxy diagram.
- Start at point O, draw a vertical line
- composition on x axis x_0
- draw a vertical line from point P. It will intersect the diagonal line along at point
- From point Q. draw a horizontal line

Now, let us see we have the equilibrium curve of H x y diagram, and point we will just place the x y diagram below the H x y diagram. Now, start at the liquid composition at point O start at point O, and draw a vertical line draw a vertical line. So, it will give the composition on the x axis composition on the x axis at X O will be X O composition on x axis would be on X O, and then draw a vertical line from the h v y curve draw a vertical line line from point p, it will intersect the diagonal line diagonal line say at point q, and from this point draw a horizontal line from point Q draw a horizontal line. So, it will crosses a point at point G. So, the composition of these will be y p. So, this the equilibrium point, similarly if we have other tie lines similar way we can plot and we will obtain the equilibrium curves.

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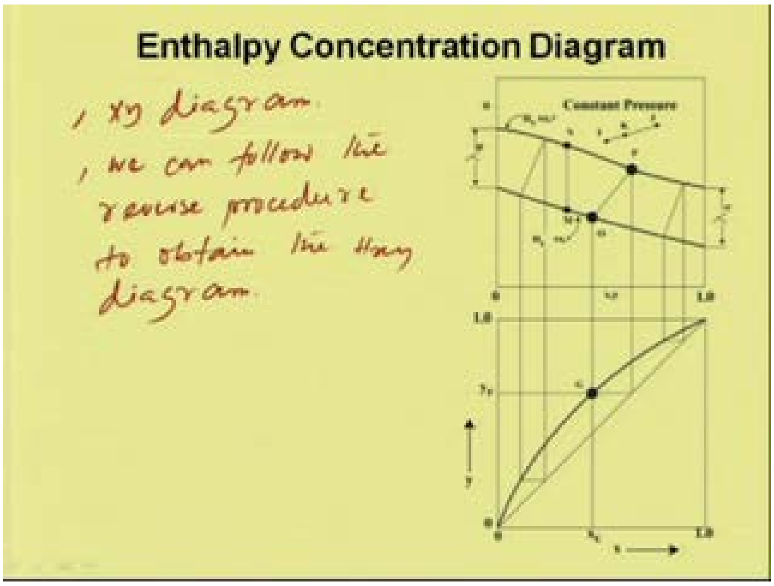

Enthalpy Concentration Diagram

, xy diagram

, we can follow the reverse procedure to obtain the Hxy diagram.

Similarly, if we have the equilibrium curve we can do in the reverse direction, we have the x y diagram then we can follow the reverse procedure to obtain the H x y diagram.

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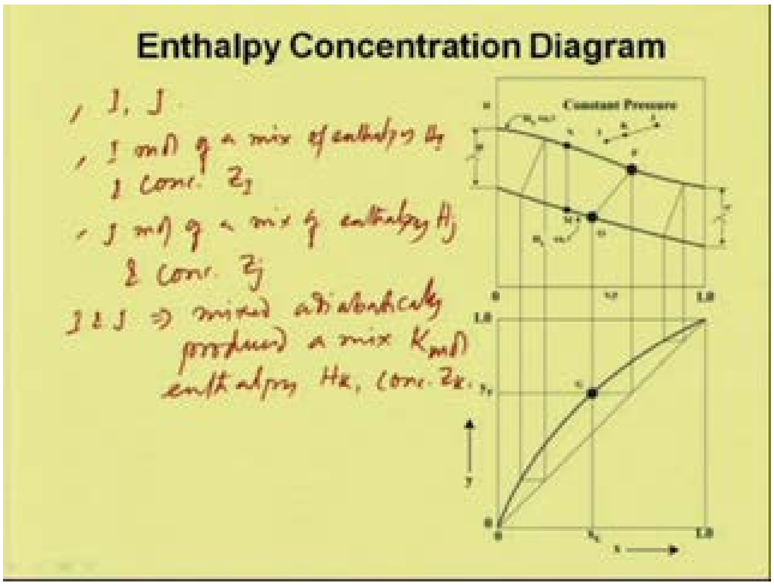

Enthalpy Concentration Diagram

- I, J
- I mol of a mix of enthalpy H_I & conc. Z_I
- J mol of a mix of enthalpy H_J & conc. Z_J

I & J ⇒ mixed adiabatically produced a mix K mol enthalpy H_K, conc. Z_K.

Now, let us take two solutions at I and two solutions I and J; I represents I mole of a mixture of enthalpy H I and concentration Z I, and J - J mole of a mixture of enthalpy H J and concentration Z J. Now, these solutions I and J mixed adiabatically, and produced a mixture K of enthalpy k mole of enthalpy H k and concentration Z k.

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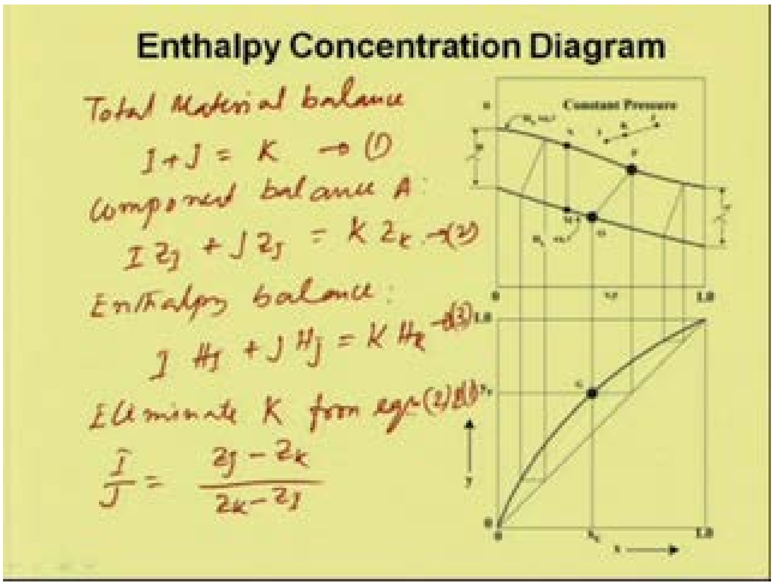

Enthalpy Concentration Diagram

Total Material balance

$$I + J = K \rightarrow (1)$$

Component balance A

$$I Z_I + J Z_J = K Z_K \rightarrow (2)$$

Enthalpy balance:

$$I H_I + J H_J = K H_K \rightarrow (3)$$

Eliminate K from eqn (2)(3)

$$\frac{I}{J} = \frac{Z_J - Z_K}{Z_K - Z_I}$$

Now, if we do the material balance total material balance I plus J would be equal to K equation one, then the component balance component A balance, so I Z I plus J Z J would be equal to K Z k enthalpy balance I, this is two - I H I plus J H J is equal to K H

k. Now, if you eliminate eliminate k from equation two and one, but we will obtain I by J would be equal to Z J minus Z k divided by Z k minus Z I.

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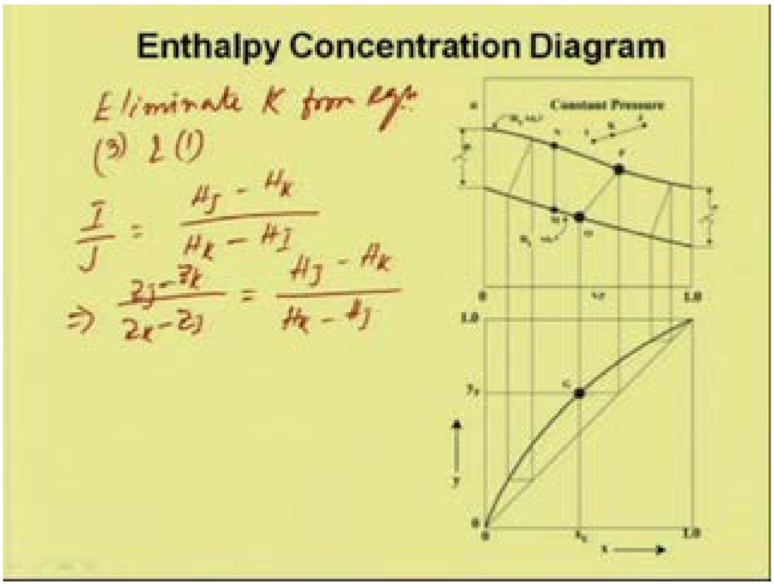

Enthalpy Concentration Diagram

Eliminate K from eqn. (3) & (1)

$$\frac{I}{J} = \frac{H_J - H_K}{H_K - H_I}$$

$$\Rightarrow \frac{Z_J - Z_K}{Z_K - Z_I} = \frac{H_J - H_K}{H_K - H_I}$$

Similarly, if we eliminate k from equation 3 and 1, we obtain I by J would be equal to H J minus H k divided by H k minus H I, we can write from these two relations Z J minus Z k divided by Z k minus Z I would be equal to H J minus H k divided by H k minus H I.

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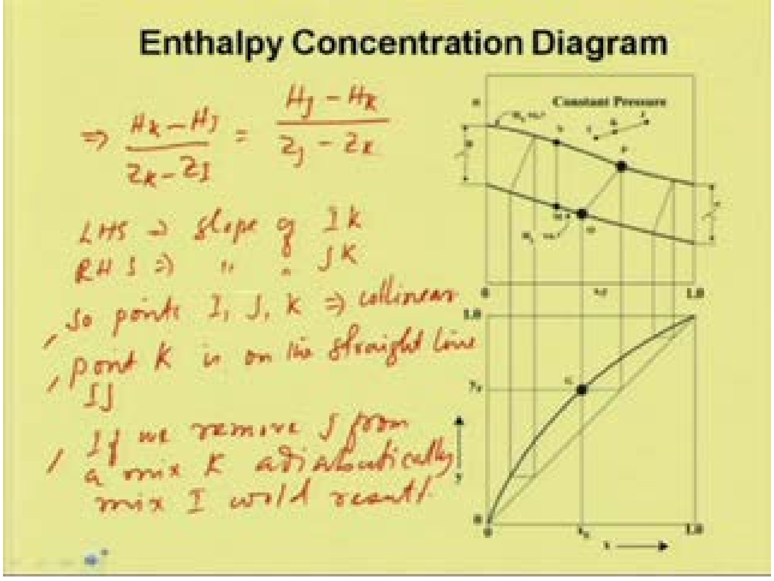

Enthalpy Concentration Diagram

$$\Rightarrow \frac{H_K - H_I}{Z_K - Z_I} = \frac{H_J - H_K}{Z_J - Z_K}$$

LHS ⇒ slope of IK
RHS ⇒ " " JK

/ So points I, J, K ⇒ collinear
/ Point K is on the straight line IJ
/ If we remove J from a mix K adiabatically mix I would result

So, now from this we can write H k minus H I divided by Z k minus Z I would be equal to H J minus H k divided by Z J minus Z k. So, left hand side it gives the slope of slope of I k line, and right hand side give the slope of J k section, and so points I, J, K; these are collinear. So, point; that means, point k is on the straight line I J; that means, if we remove if we remove J from a mixture K; adiabatically mixture I would result. Now, let us considered any points above the h v x curve say point C, and it will be use full if we conceder this in terms of the saturated vapor and saturated liquid.

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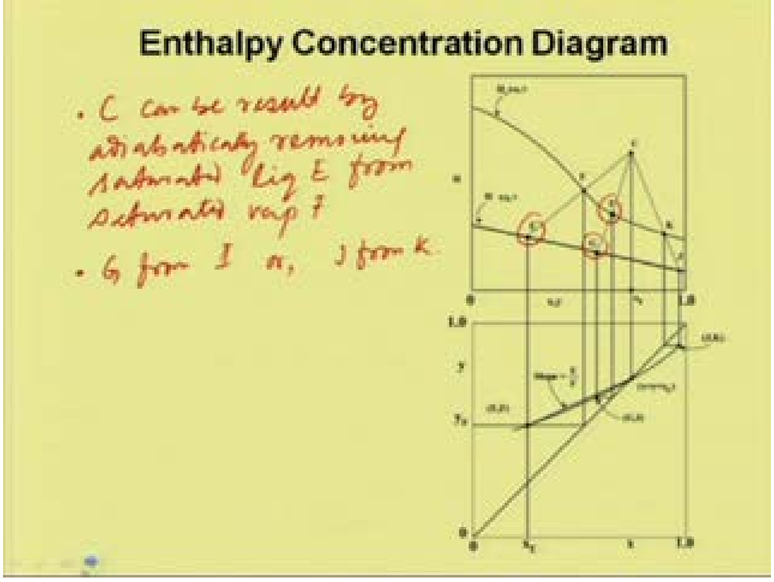

Enthalpy Concentration Diagram

- C can be result by adiabatically removing saturated liq E from saturated vap F
- G from I or, J from K

So, consider C can be result by adiabatically removing saturated liquid liquid; that is at point E from saturated vapor F and which is shown over here. This can also be considered removing adiabatically saturated liquid from G to G from I G from I or J from K, and any such combinations can be drawn and we can obtain C.

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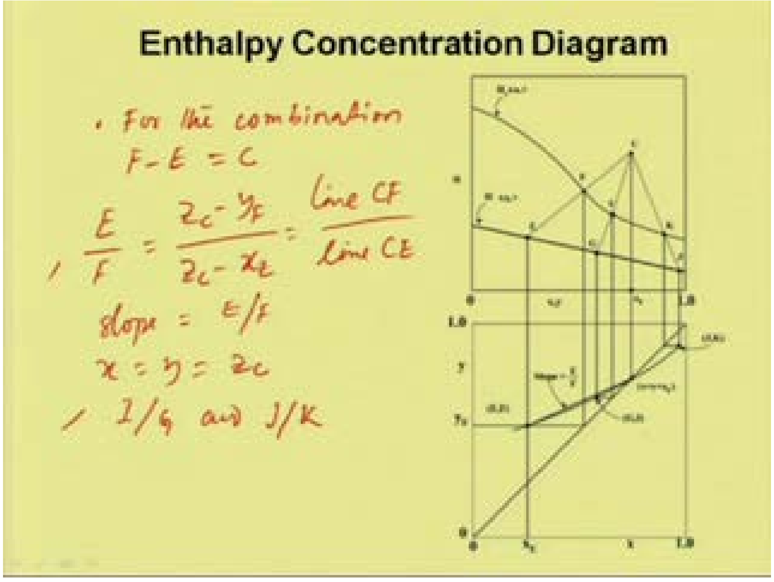

Enthalpy Concentration Diagram

- For the combination $F - E = C$

/ $\frac{E}{F} = \frac{z_C - y_F}{z_C - x_E} = \frac{\text{line CF}}{\text{line CE}}$

slope = E/F

$x = y = z_C$

/ I/G and J/K

Now, if we project all these lines, we can have the lower curve which is obtained over here at the bottom curve, now for any combination, for the combination F minus E equal to C, the material balance if we do E by F would be Z C minus y F by Z C minus x E. So, we can write line C F by line C E, this is the point with a slope of slope is E by F, and it is drawn on the x y diagram, and also it needs at point x is equal to y is equal to Z C on the x y diagram on the 45 degree line. Similarly, other plots can be done by I by G and J by K; this is also shown over here and this is drawn in the x y diagram.

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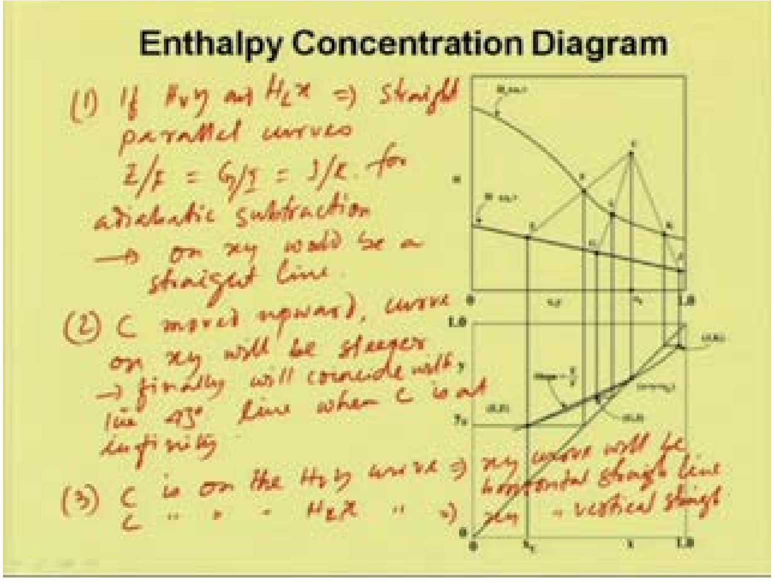

Enthalpy Concentration Diagram

(1) If $H_G y$ and $H_L x$ ⇒ straight parallel curves

$I/F = G/J = J/K$ for adiabatic subtraction

→ on xy would be a straight line

(2) C moves upward, curve on xy will be steeper

→ finally will coincide with the 45° line when C is at infinity

(3) C is on the $H_G y$ curve ⇒ xy curve will be horizontal straight line

C " " " $H_L x$ " ⇒ xy " vertical straight

Three important observations, we can see one is if H v y and H L x, these curves are straight lines, straight parallel curves, then the ratio E by F would be equal to G by I would be equal to J by K for adiabatic subtraction. Then the corresponding curve on x y would be a straight line.

Now, second point is that if we moved upward C moved upward, then the curve on x y will be steeper. Finally, will coincide with the 45 degree line, when C is at infinity; and third point we can see if C is on the H v y curve. Then we can see the x y curve will be horizontal straight line will be horizontal straight line, and C is on the H L x curve, then x y curve will be vertical straight line vertical straight line.

Thank you.