

Mass Transfer Operations -I
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Lecture - 27

Distillation in Non-ideal Systems and concept of Enthalpy-Concentration Diagram

Welcome to the second lecture of module 5 of Mass Transfer Operation. In this module, we are discussing distillation process. So, before going to this lecture, let us have small recap of our previous lecture. In our previous lecture we mainly consider few things, one is we had introduction to distillation, introduction to distillation.

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Module 5: Lecture 2

Last Lecture

- Introduction to Distillation
- Constant Pressure Binary Equ Diagram (P_{xy})
- $x-y$ Diagram
- Constant Temp. Binary Equ. Diagram (T_{xy})
- Raoult's Law
- Relative Volatility

This Lecture

- Deviation from Ideality
- Azeotropes
- Enthalpy-Concentration Diagram

The second thing we consider is constant pressure binary equilibrium diagram; constant pressure binary equilibrium diagram and we call it $P \times y$ diagram. The second thing we have considered each $x-y$ diagram and then we have discussed constant temperature binary equilibrium diagram $T \times y$ diagram, we have also discussed **Raoult's law** and then we have discussed relative volatility. In this lecture we will mainly consider deviation from ideality under which we have mainly we will mainly discuss know azeotropes and finally, we will discuss enthalpy concentration diagram.

So, all this fundamentals would be very much important and relevant while we go for the designing of the plate columns or packed columns for distillation using different methods. So, if you for ideal cases ideal gas and ideal liquid, we will consider one

method in case of deviation from non ideality then we need to have the energy balance equation and enthalpy concentration diagram would be important to design the distillation tower.

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Deviation from Ideality and Azeotropes

Non-Ideal Systems

- In cases where the VLE cannot be treated as ideal, more rigorous models based on multicomponent thermodynamics are required.
- We won't worry about these for a while.

Azeotropes

- Most of the time, we deal with systems where the equilibrium curves have no inflection points.
- If there are strong physical or chemical interactions between components, diagrams may look different.

So, non ideal systems deviation from ideality and azeotropes, we will start with first we will consider non ideal systems. So, this is the case where the v l e vapour liquid equilibria cannot be treated as ideal; that means, we need to have more rigorous models based on multicomponent thermodynamics, which are required for the calculation of the vapour liquid equilibrium. So, we will not to worry about this for a while, we will now discuss about the deviation from ideality and the azeotropes. In most of the time we deal with the systems where the equilibrium curves have no inflection points that is for ideal cases. So, the equilibrium curve does not show any inflection point.

If there are strong physical or chemical interaction between the components diagram may look different. So, we will see under the different interactions how the diagram changes its behaviour or its pattern.

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Deviation from Ideality and Azeotropes

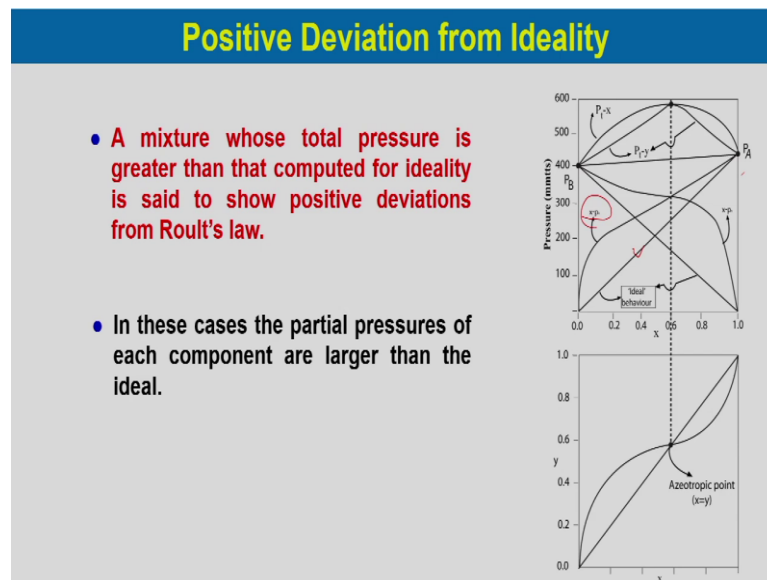
- In some such systems, there is a critical composition where the liquid and vapor compositions are identical. Once this composition is reached, separation cannot continue without changing pressure. These mixtures are called azeotropes.
- Composition of the vapor produced from an azeotrope is the same as the liquid, so an azeotrope can be boiled at constant pressure without changing composition
- Azeotropes will have minimum or maximum boiling points.
- Minimum boilers are more common.

In some such systems there is a critical composition, where the liquid and vapour composition are identical. Once this composition is reached separation cannot continue without changing the pressure these mixtures are called azeotopes. So, composition of the vapour produced from an azeotrope is the same as that of liquid. So, an azeotrope can be boiled at constant pressure without changing composition.

So, if we take any azeotropic composition and even if we boil it at a particular pressure, it will not change its composition. As we have seen in case of ideal systems, if we heat of some liquid it forms the first drop of vapour and then as long as it reaches its boiling point, then it more vapours forms from the liquid at that constant pressure the temperature changes and composition changes. So, in case of azeotropes it does not change the composition at constant pressure even if we feed the solution for a longer time.

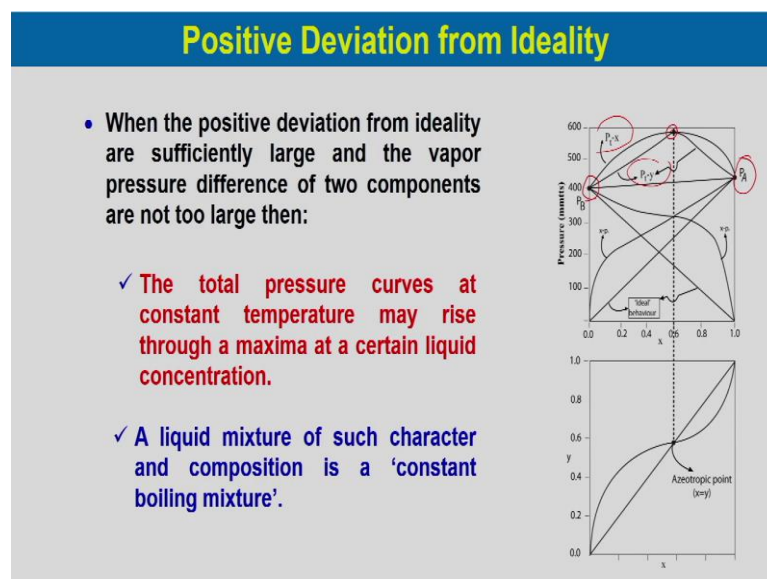
So, azeotropes will have minimum or maximum boiling points. In general the minimum boilers are more common. So, minimum boiling points of the azeotropic mixture or more common than the maximum boiling azeotropes.

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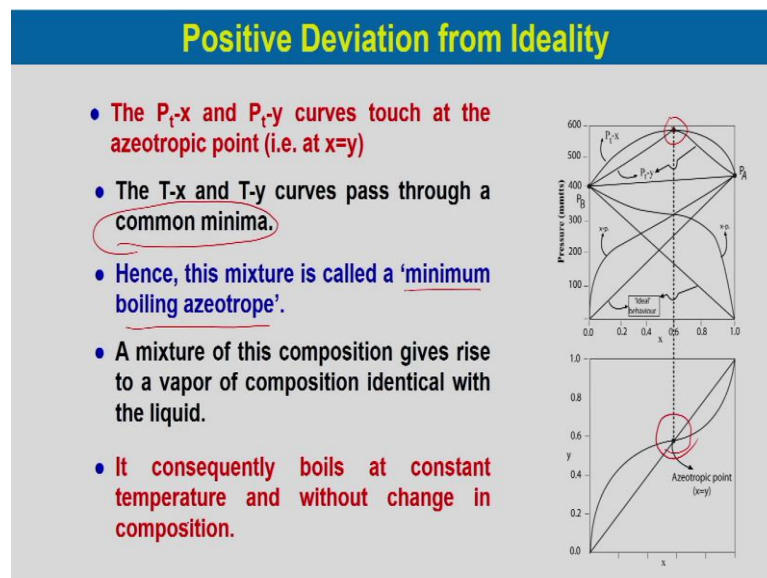
A mixture whose total pressure is greater than computed from Raoult's law is set to show positive deviation from Raoult's law. So, if you look into over here in this figure, you can see that this is the ideal behaviour of 45 degree diagonal over here, which the partial pressure and the mole fraction changes linearly as for Raoult's law. So, if we see the total pressure curve x and P_t curve it deviates from this ideal behaviour positive deviation, then it is summed as the non ideal systems. In this case the partial pressure of each component are larger than the ideal.

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So, when the positive deviation from ideality are sufficiently large and the vapour pressure difference of the two components are not too large, you can see over here the vapour pressure of component B over here and vapour pressure of component A is over here. So, there is a very little change of their vapour pressure then the total pressure curve at constant temperature may rise at a certain liquid composition. So, you can see the total pressure and mole fraction curve $P_t x$ and $P_t y$ both reaches a maxima here. A liquid mixture of this characters having the maximum inflection point for the P_t and mole fraction. So, a total pressure and mole fraction curve is a constant boiling mixture at this condition.

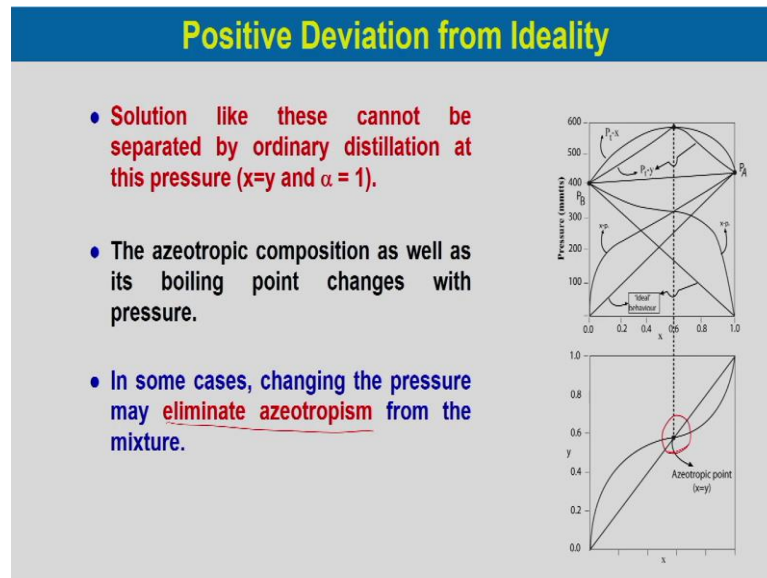
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That $P_t x$ and $P_t y$ curves touches at a azeotropic point, which is this is the azeotropic point and its composition corresponding to the $x y$ curve is over here that is x is equal to y on the 45 degree diagonal of the $x y$ curve.

In this case if we look into the T x and T y curve temperature concentration curve T x y curve that would pass through a common minima. So, since there is a T x y curve. So, which a common minima; that means, this type of mixture is known as the minimum boiling azeotrope hence this mixture is called a minimum boiling azeotropes. A mixture of this composition gives rise to a vapour of composition identical with the liquid that is called azeotropic mixture it consequently boils at constant temperature and without change in composition.

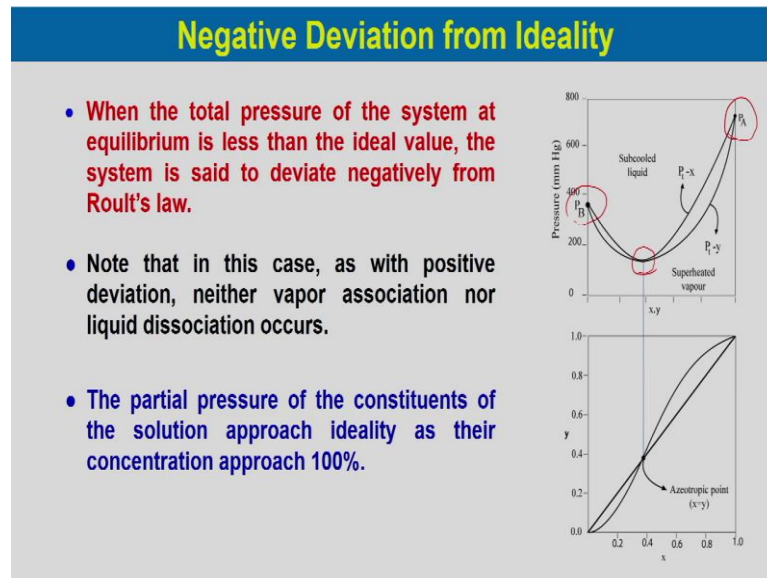
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Solution like this cannot be separated by ordinary distillation at this pressure. Because at this pressure x is equal to y and relative volatility α is 1 that is why it lies on the 45 degree diagonal. Since the relative volatility is 1. So, this cannot be separated under these conditions without changing the pressure the azeotropic composition as well as boiling point changes with pressure. So, composition will change and also its boiling point will change as we change the pressure. In some cases changing the pressure sometimes eliminate the azeotropism from the mixture.

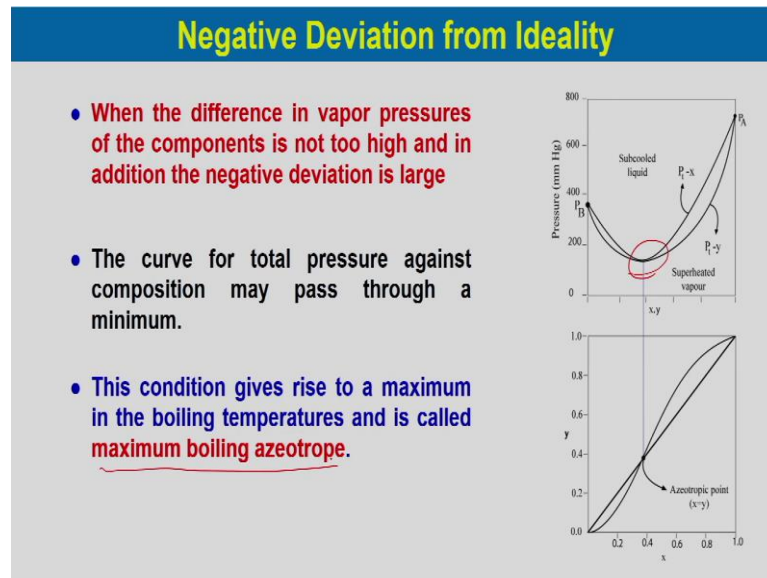
So, we have discussed positive deviation from ideality and we have seen that the pressure and concentration diagram reaches a maximum at a certain composition and if we look into this composition we look for $T \times y$ diagram, there is a common minima. So, this type of mixture we called minimum boiling azeotropes. Now we will look into the negative deviation from ideality.

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When the total pressure of the system at equilibrium is less than the ideal value, the system is set to deviate negatively from Raoult's law. So, note that in this case as with positive deviation neither vapour association nor liquid dissociation occurs. So, the partial pressure of the constituents of the solution approach ideality as their concentration approach 100 percent. So, you can see over here in this figure the pressure versus mole fraction diagram it reaches a common minima at this point and the y axis over here at P B is the 100 percent component B and also in this axis at this point the component is pure A. So, this is 100 percent A and this is 100 percent B. So, the partial pressure of the constituent of the solution approach ideality as their concentration approach 100 percent.

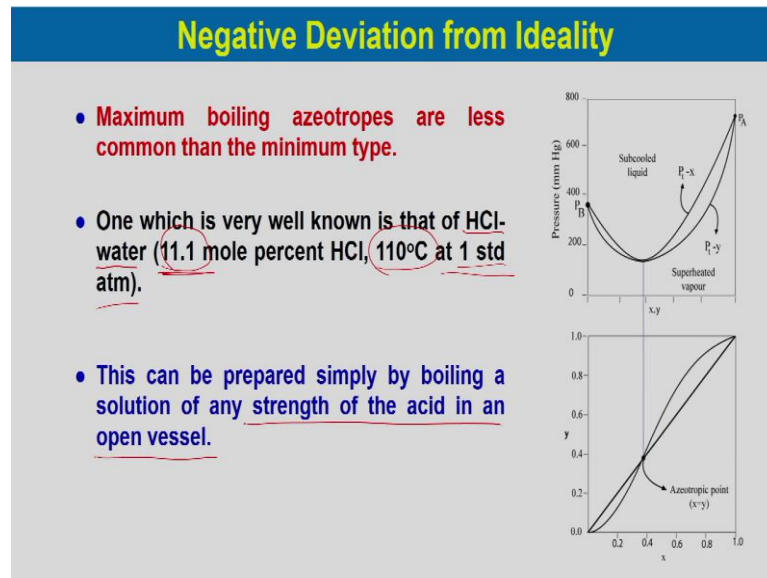
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When the difference in vapour pressure of the component is not too high and in addition the negative deviation is large, the curve for total pressure against composition may pass through a minima as we have shown you earlier. So, it passes through a common minima the total pressure and mole fraction curve or total pre pressure composition curve it passes through a common minima. So, in this case if we look into the $P \times y$ diagram this composition will pass at a common maxima.

So, the condition gives rise to a maximum in the boiling temperature and is called maximum boiling azeotrope. So, this type of behaviour which is negative deviation from ideality, in this case the total pressure and the composition curve such a common minima and $T \times y$ diagram shows a maxima that is why it is called maximum boiling azeotropes. As we have already said before that the maximum boiling azeotropes are less common than the minimum type.

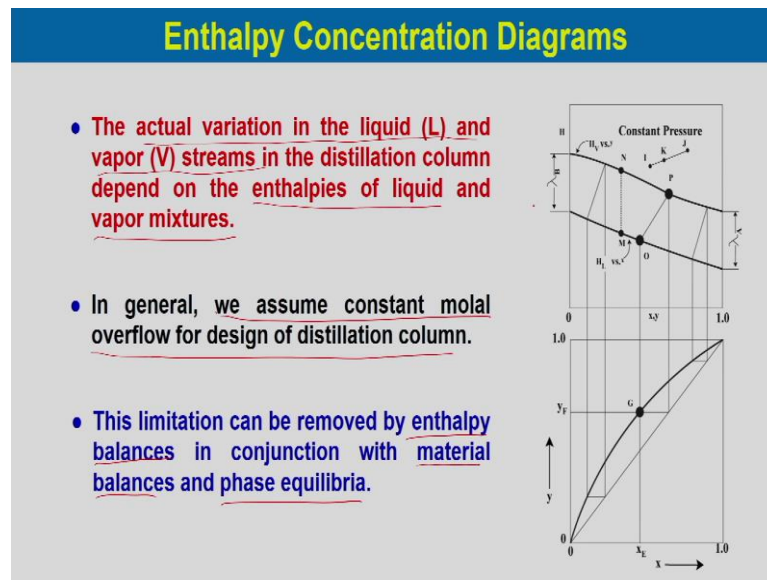
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One which is very well known is that of hydrochloric acid water system. So, in case of hydrochloric acid and water system are the mole percent of hydrochloric acid is 11.1 mole percent and at 110 degree centigrade temperature at one atmosphere pressure this shows the azeotropic mixture and is a maximum boiling azeotropes. And this can be prepared by simply no boiling a solution of any strength of acid in an open vessel.

So, if we take any concentration of hydrochloric acid in aqua solution and then if we just in open vessel if you boil it and it reaches a particular composition at a 11.1 mole percent HCl at 110 degree centigrade and since it is open vessel. So, it will maintain the atmospheric pressure and then the composition will not change after this. So, we will have the azeotropic mixture.

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Now, we will discuss about the enthalpy concentration diagram the actual variation in the liquid and the vapour streams in the distillation column depend on the enthalpies of the liquid and vapour mixtures. So, the liquid flows or the variation of the flows into the column the liquid and vapour steam in the distillation column, these will depend on the enthalpies of the liquid and the vapour mixtures. In general we assume constant molal overflow for design of distillation column; that means, no throughout the column either it is a tray column or packed column throughout the column, the molal flow rate or the molar flow rate of gas as well as liquid does not change from one tray to the other or from one location to the other location in case of the packed towers.

So, this limitation we can remove by enthalpy balance in conjunction with the material balance and phase equilibria. So, if we consider enthalpy balance equation along with the material balance equation and phase equilibria as we have done in case of the constant molal overflow, then we need not to worry about it can considered the variation of the liquid and vapour flows in the column to design the distillation process or distillation column for a particular process for a particular separation. This part you can see this is a typical no enthalpy concentration diagram.

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Enthalpy Concentration Diagrams

- A change in composition of a phase during distillation is accompanied by a change in its enthalpy.
- Binary vapor-liquid equilibria can be plotted as enthalpy vs concentration at constant pressure.
- This is known as enthalpy-concentration diagram and useful for distillation calculation.

A change in composition of a phase during distillation is accompanied by a change in enthalpy. So, binary vapour liquid equilibria can be plotted as enthalpy versus concentration at constant pressure. So, this is a enthalpy concentration diagram at constant pressure. And that is why it is known as enthalpy concentration diagram and it is no very much useful for the distillation calculation.

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Enthalpy Concentration Diagrams

- At a given temperature T and concentration of liquid (x_L) the molar enthalpy of the mixture include both sensible heat and heat of mixing the components and can be calculated from the following equation:

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

Where

- H_L = molar enthalpy of solution at temperature T_L ; for saturated liquid T_L is the bubble point corresponding to the liquid concentration at the prevailing pressure.
- T_0 = reference temperature
- M_{avg} = average molecular weight of the solution
- ΔH_s = heat of solution at the reference temperature T_0 and the prevailing concentration referred to the pure liquid components, energy/mol solution

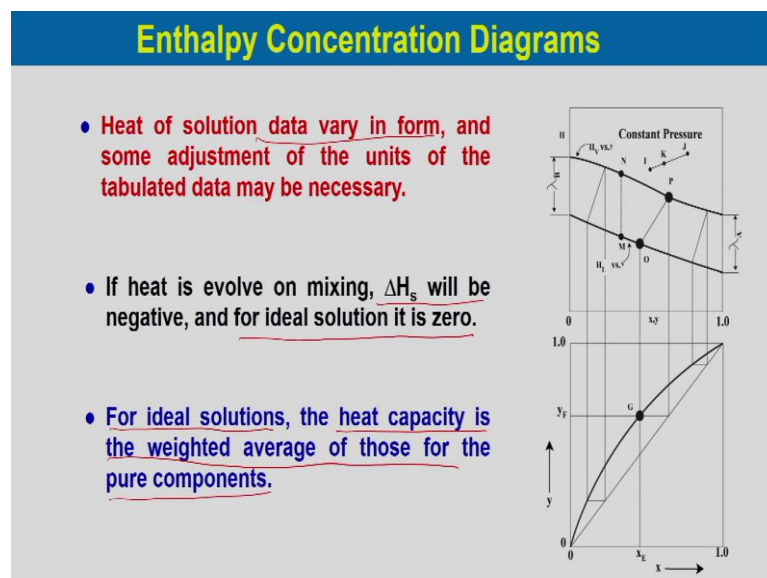
Now, at a given temperature T and concentration of liquid x , the molar enthalpy of the mixture will include the sensible heat and the heat of mixing of the components. So, any

given temperature and the concentration of the liquid x , the molar enthalpy of the mixture if you want to calculate, it will also include both sensible heat and the heat of mixing of the components.

So, this can be calculated from the following equations where H_L would be equal to C_L into the temperature gradient T_L minus T_{naught} into average molecular weight plus ΔH_s . Here H_L is the molar enthalpy of solution at temperature T_L . For saturated liquid this T_L is the bubble point corresponding to the liquid concentration at the particular pressure.

So, H_L is the molar enthalpy at a temperature T_L and for if it is a saturated liquid, this T_L would be the bubble point temperature corresponding to the liquid concentration at the reserved at that particular pressure. T_{naught} over here is the reference temperature and M average is the average molecular weight of the solution ΔH_s is the heat of solution at the reference temperature T_{naught} and the prevailing concentration, which is referred to the pure liquid components and its units is energy per mole solution. So, energy per mole solution; so, this is ΔH_s heat of solution this is the molar enthalpy which is based on the sensible heat and heat of mixing. So, this is sensible heat and this is heat of mixing.

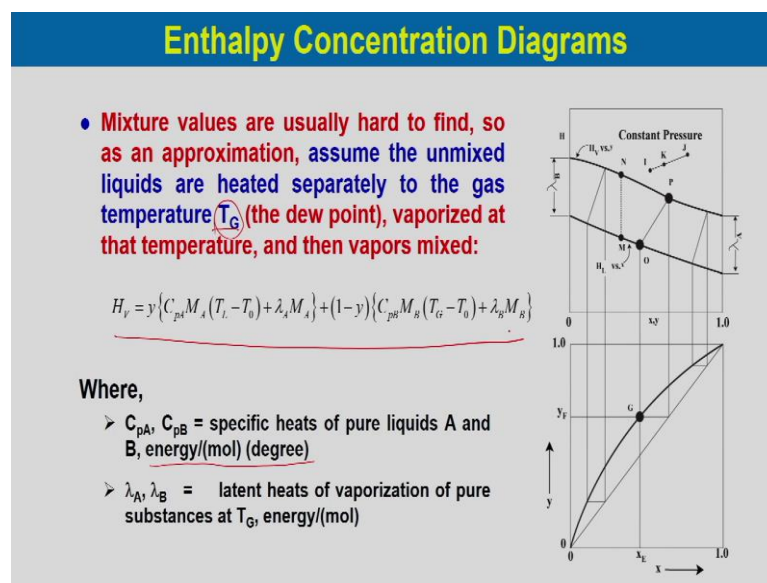
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Now, heat of solution data which vary in form and some adjustment of the units of the tabulated data may be necessary. So, it varies in different forms and variation of the

units. So, or adjustment of the unit of the data available may be necessary in some cases. If heat is evolved on mixing ΔH_s will be negative. So, heat is evolved that is exothermic in nature, then ΔH_s would be negative and for ideal solution it is considered ΔH_s would be equal to 0. Now for ideal solutions the heat capacity is the weighted average of those for the pure components. If we consider ideal solution the heat capacity is the weighted average of those for the pure component. So, this will be calculated from the weighted average of the pure component for the calculation of the heat capacity if we consider the ideal solution.

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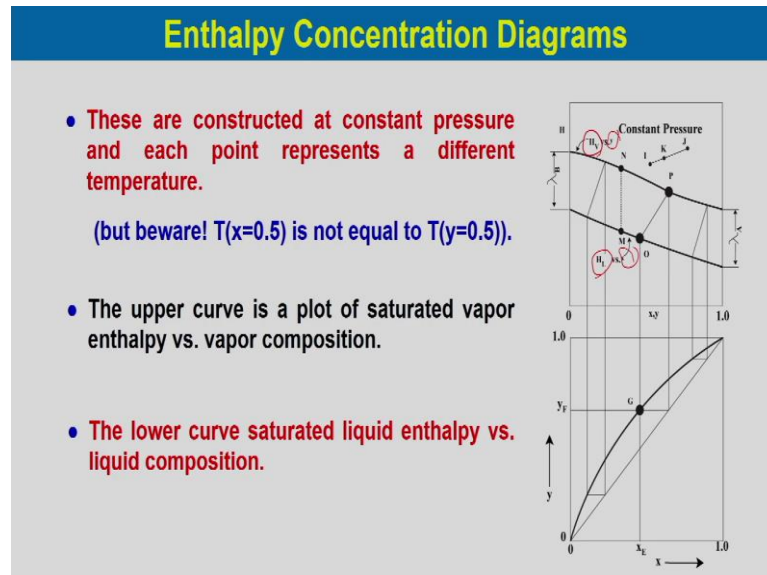


Now, for mixture we usually find very difficult to obtain this mixture values. So, an approximation that is we consider assume the unmixed liquids are heated separately to the gas temperature T_G and this is the dew point temperature then vaporized at that temperature and then the vapour mixed.

So, for the mixture, how we find out the values? Now we assume the unmixed liquids are heated separately to the gas temperature T_G at their dew point. And then the vapour which is generated is mixed at the temperature and then we can calculate H_v would be equal to y into $C_{pA} M_A T_L$ minus T_{naught} plus $\lambda_A M_A$ plus 1 minus y into $C_{pB} M_B$ into temperature gradient T_G minus T_{naught} plus $\lambda_B M_B$. So, here C_{pA} and C_{pB} are the specific heat of pure liquid A and B in energy per mole degree and λ_A and λ_B are the latent heat of vaporization of pure substance at T_G

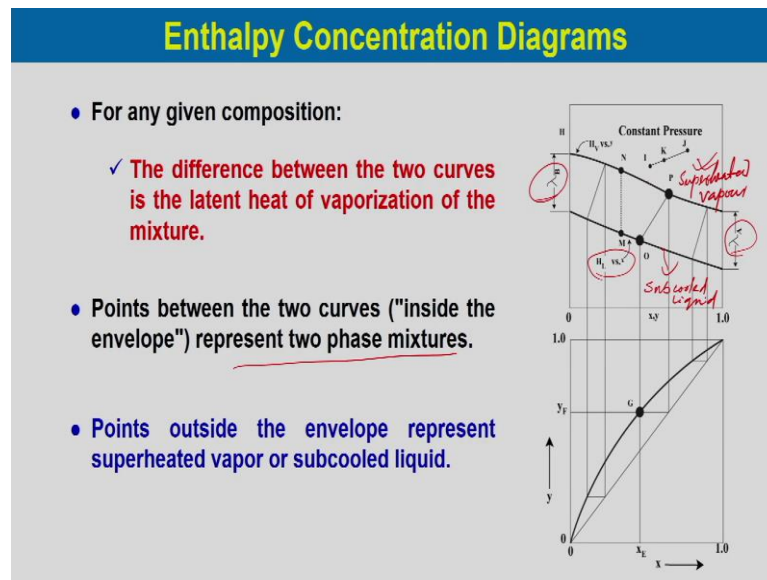
energy per mole. So, the other no terms which are already no mentioned in our earlier expression, which has the usual significance and so, this way we can calculate H_v .

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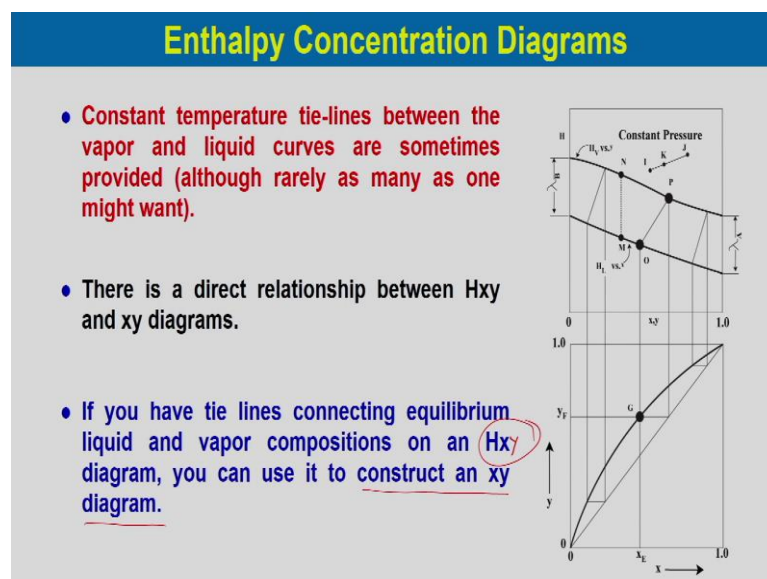
Enthalpy concentration diagrams are no constructed at constant pressure and at each point represent a different temperature, but we understand that T at x is equal to 0.5 is not equal to T at y is equal to 0.5 the upper curve over here in this enthalpy concentration diagram is a plot of saturated vapour enthalpy versus the vapour composition. So, vapour composition is small y and the enthalpy of the saturated vapour is represented by H_v . So, the upper curve here represents the plot of saturated vapour enthalpy versus the vapour composition, and the lower curve is the saturated liquid H_L versus the liquid mole fraction or liquid composition.

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Now, for any given composition the difference between the two curves from this curves to this curves, the difference between this two curves is the latent heat of vaporization it is shown over here λ_B and λ_A . So, the difference between these two curves is the latent heat of vaporization of the mixture. Points between the two curves inside the envelope represents two phase mixture and points outside the envelope represent if it is above this envelope that is above the H_v vs y curve, this portion this represents the superheated vapour and region below this curve, that is below the H_L vs x curve is the sub cooled liquid. So, this is sub cooled liquid and this is superheated vapour region.

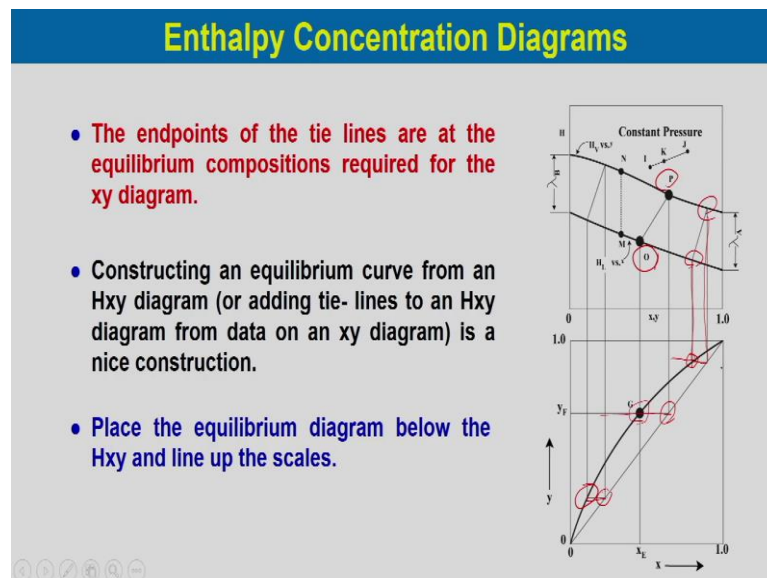
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Constant temperature tie lines between the vapour and liquid curves are sometimes provided although really as many as one might want. So, the tie lines you can always draw as many as possible between these two curves. There is a direct relationship between H vs y and x vs y diagrams as we have seen before the relationship between the p vs x vs y and the x vs y diagram. So, similar to that there is a direct relation between the H vs y and x vs y diagrams. So, if you have tie lines connecting equilibrium liquid and the vapour composition on an H vs y diagram you can use it to construct an x vs y diagram. So, it is H vs y diagram.

So, if you have tie lines which connects the equilibrium liquid and vapour composition in the H vs y diagram, you can use that data to construct x vs y diagram.

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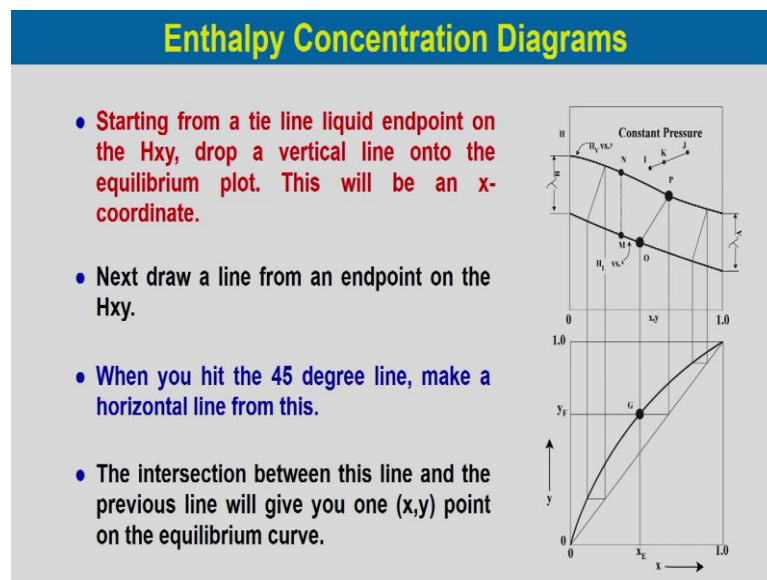
The end points of the tie lines are at the equilibrium compositions required for x vs y diagram. So, you can see over here say constructing an equilibrium curve from an x vs H vs y diagram or adding tie lines to an H vs y diagram from the data on an x vs y diagram is a nice construction that is why place the equilibrium diagram below the H vs y and line up the scales.

That means, if you have the tie lines and in the H vs y diagram suppose point O and point P here. So, you just draw a vertical line on the x vs y diagram with their 45 degree diagonal you have a point over here, and then you draw a vertical line from the O and also from

this point which intersect on the 45 degree diagonal draw a horizontal line that is this one, and this meets at a point G.

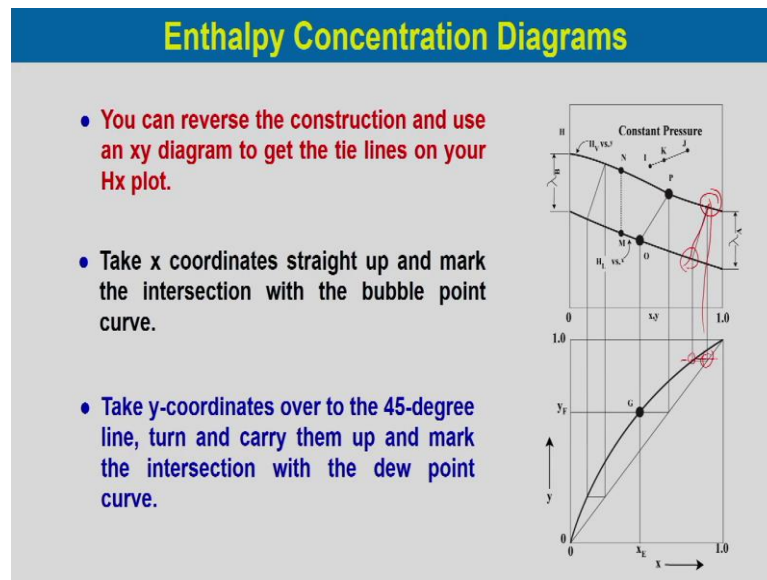
So, this point is the equilibrium point on the x y diagram similar to that if you take any other point say over here and over on the tie line, and draw the vertical line and then draw the horizontal line, draw the vertical line from here the intersecting point would be the equilibrium point. So, you can draw as many as you want no from here you can go here this is one and you can draw the equilibrium curve. Similar to this if you have the equilibrium data you can also draw the H x y diagram with the values of the equilibrium data on the x y diagram.

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As we have already discussed starting from a tie line liquid end points on the H x y drop a vertical line on to the equilibrium plot, this will be an x coordinate. Next draw a line from an end point on the H x y, when you heat the 45 degree line make a horizontal line from this and the intersection between the line and the previous line will give you one x y point on the equilibrium curve this way you can draw the equilibrium line.

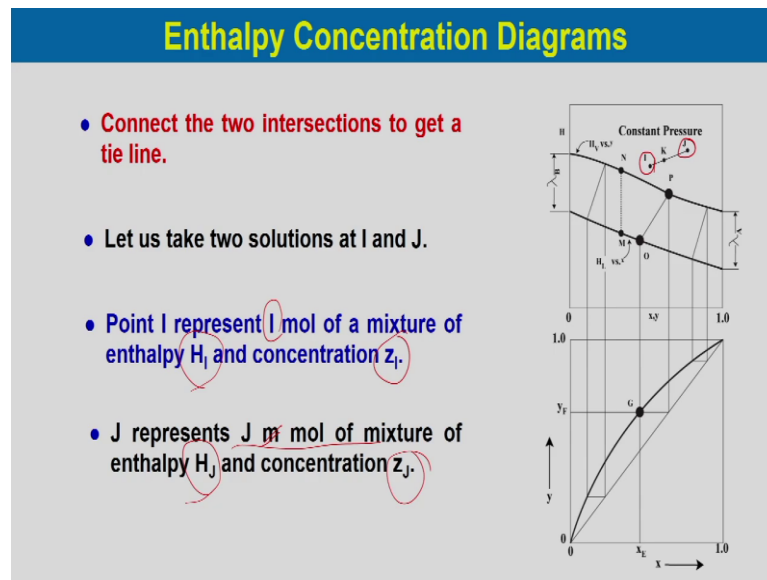
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You can reverse the construction and use any x y diagram to get the tie lines on your H x plot. The x coordinates straight up and mark the intersection with the bubble point curve, they take any y coordinate over the 45 degree line turn and carry them off and mark the intersection with the dew point curve.

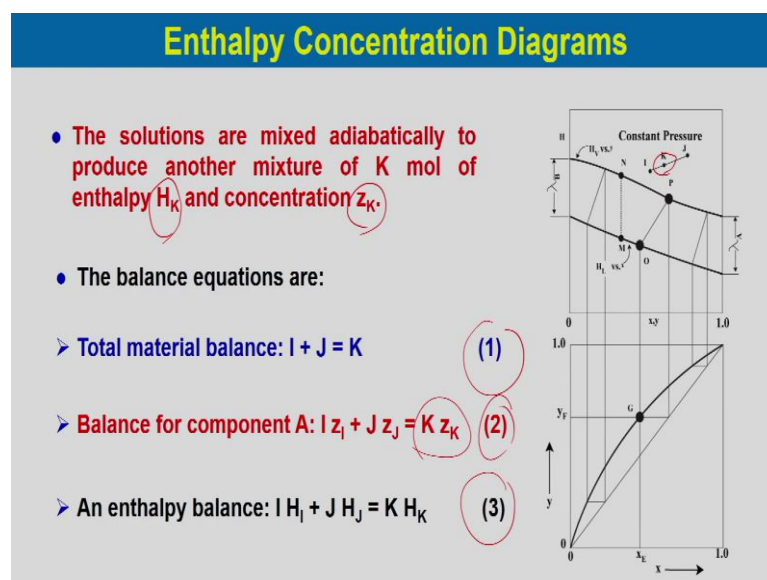
So, you have in the H x y diagram, you have dew point curve as well as no bubble point curve and you have equilibrium curve you just reverse the construction here from the equilibrium point you go to the vertically and which will intersect the bubble point curve and then from the take a horizontal line from this intersection point go vertically which will meet in the bubble point curve and connect them. So, you will get tie lines and you have multiple tie lines you can draw on the H x y diagram.

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So, now let us take no two solutions at I and J. So, which is shown over here I and J two points and point I represents I mol of mixture of enthalpy H I and the concentration z I point J represents J mol of mixture of enthalpy H J and concentration z J. So, I point represents I mol of mixture and having the enthalpy H I and concentration z I and point J which represents J mol of the mixture having the enthalpy of H J and z J.

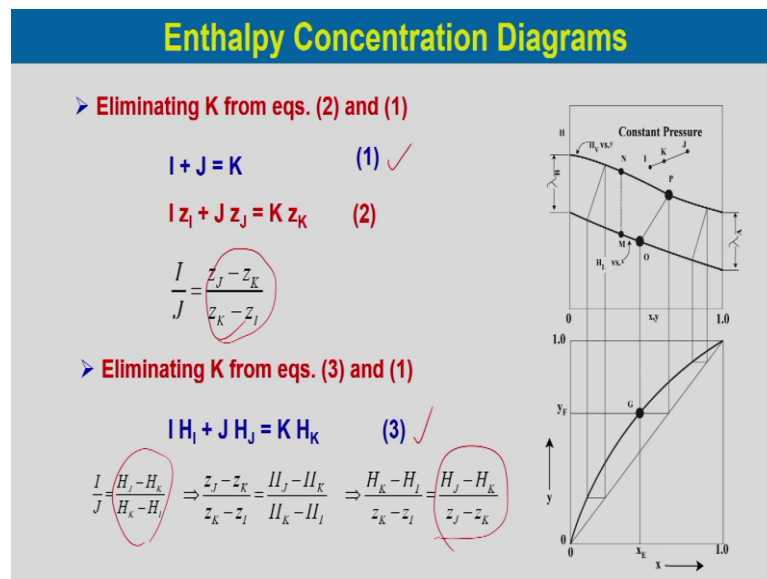
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Now, the solutions are mixed adiabatically to produce another mixture of K. So, which is shown over here this is a mixture which is produced by mixing I and J adiabatically and

having the total K moles of enthalpy H K and concentration z K; so, H K and z K. Now if we do the balance equation this would be total material balance would be I plus J they are mixing and making a total of K moles balance for component a if we do I into z I then I moles into the composition of the I K a it is z I. So, I z I plus J z J would be equal to K into z K. Now if you do the enthalpy balance it would be I H I plus J into H J would be equal to K into H K. So, equation 1 2 3 are the three balance equations which we can write material balance, component balance and enthalpy balance.

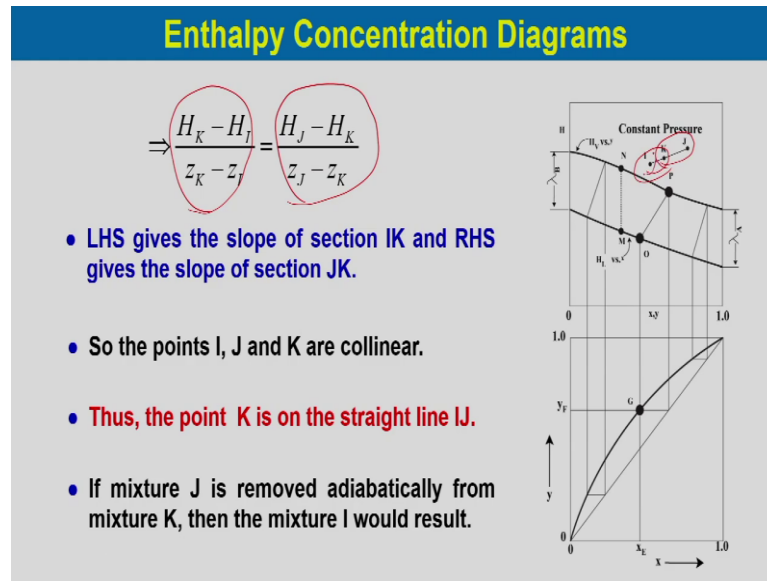
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Now, if we eliminate K from equation 2 and 1. So, this is equation 1 and this equation 2 and if we eliminate K from these two equations we would obtain I by J would be equal to z J minus z K divided by z K minus z I. Now if you eliminate K from equation 3 and 1. So, if you consider equation 3 and equation 1 and if we eliminate K we will obtain I by J would be equal to H J minus H K divided by H K minus H I from here we can write z J minus z K because these two are no same because I by J.

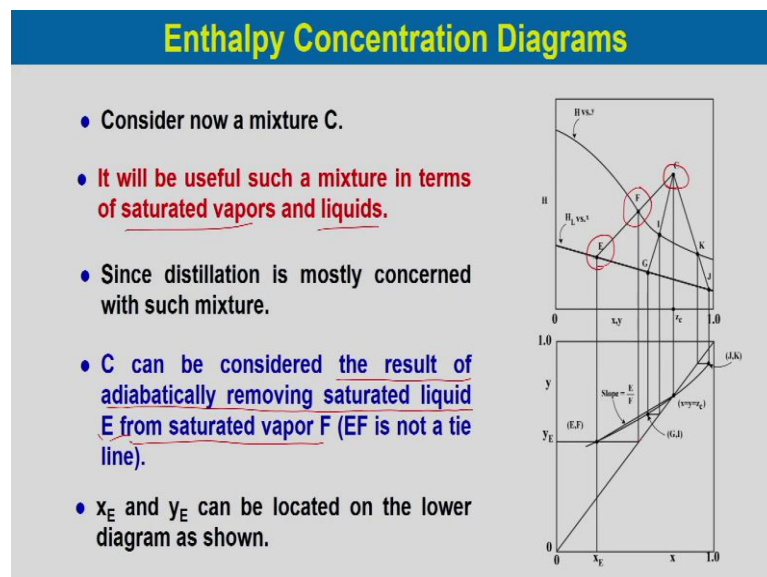
So, we can equate them. So, we will obtain z J minus z K divided by z K minus z I would be equal to H J minus H K divided by H K minus H I and then if you just rearrange we will have H K minus H I divided by z K minus z I would be equal to H J minus H K divided by z J minus z K.

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So, the left hand side in this equation is the slope of the section IK. So, from slope of this section IK is H_K minus H_I divided by Z_K minus Z_I and the other right hand side this one is the slope of the section J K. So, the slope of the section J K is H_J minus H_K divided by z_J minus z_K . So, the points IJ and K are collinear that means, the point K is on the straight line IJ. So, this K points would be collinear and it is on that line only straight line. This means that if a mixture J is removed adiabatically from a mixture K then the mixture I would result. So, if we can remove adiabatically J from a mixture K then we would obtain I.

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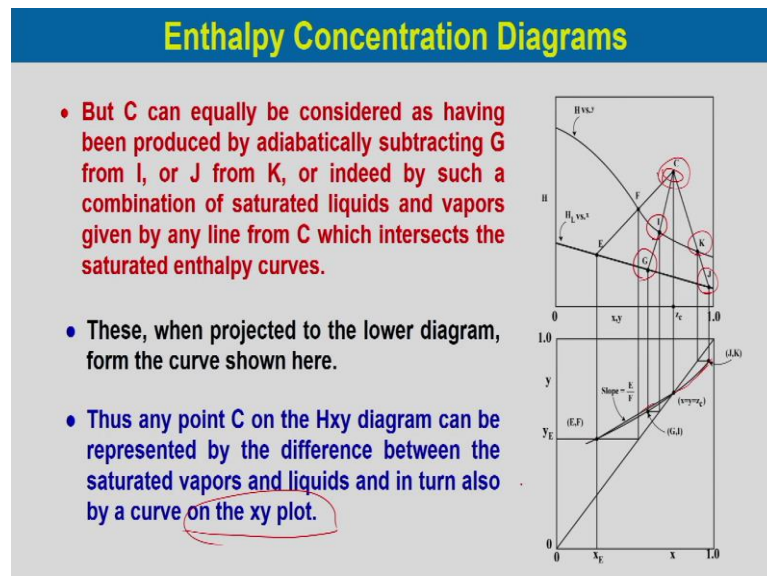


Now, if we consider another mixture say C over here. It will be useful such a mixture in terms of saturated vapours and liquid. Since distillation is mostly concerned with such mixture. So, it would be very much useful in terms of the saturated vapour or saturated liquid the mixture of that if the C point we can consider that way. C can be considered the result of adiabatically removing saturated liquid E from saturated vapour F.

C can be considered the result of adiabatically removing saturated liquid E that is here from saturated vapour F. So, EF is not a tie line. So, here this EF is not a tie line. So, do not confuse with the tie line over here, we have considered any point c and like earlier case as we have seen that point IJK are collinear in nature and if we remove adiabatically J from K we can obtain the composition at I similar way if this considered point C this could be considered adiabatically removing e from f and we would obtain the composition at C.

So, x_E and y_E can be located on the lower diagram as shown. So, we can come up over here from this point vertically over here and then we can go horizontally and then we can come from this point vertically, we can obtain the composition here which is corresponding to y_E and x_E the composition corresponding to E.

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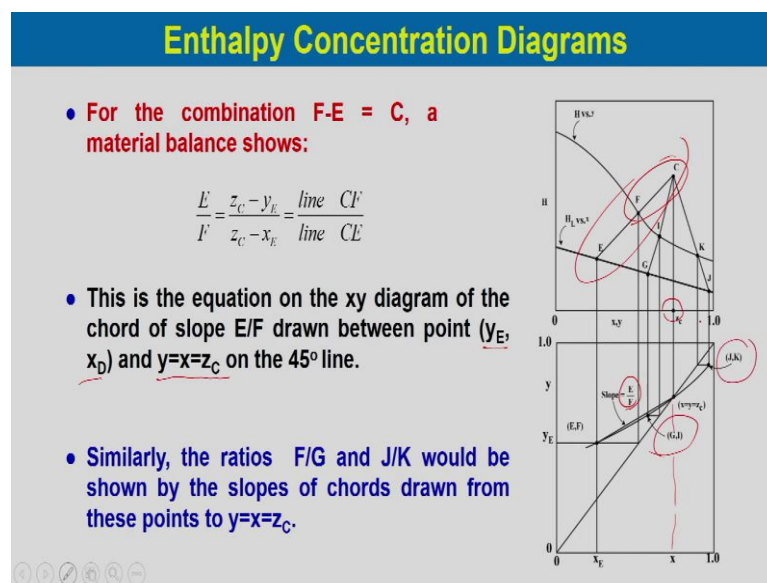


But this C can equally be considered as having been produced by adiabatically subtracting G this any point G from I and we would obtain this point C or it can be also considered adiabatically removing J from K and we would obtain the composition C. So,

by this way any such combination of saturated liquids and vapour given by any line from C which intersects the saturated vapour and saturated liquid curve.

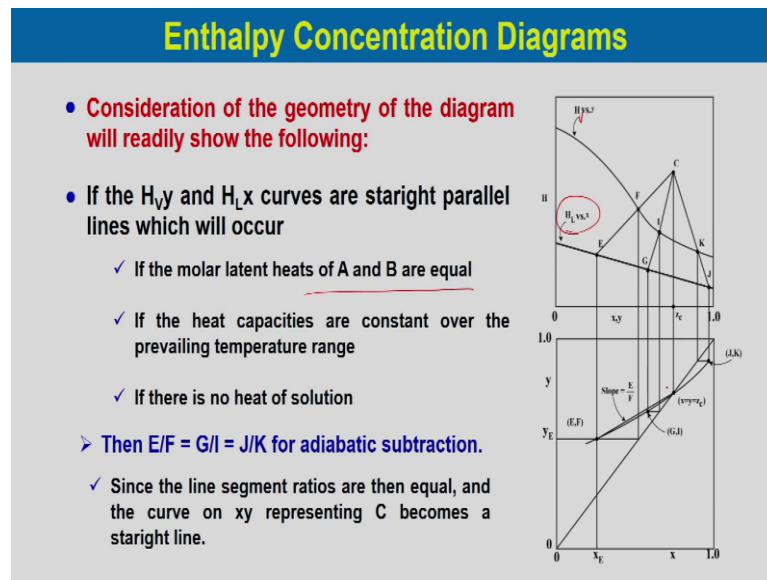
So, an enthalpy curves that would give this mixture this when projected to the lower diagram from the curve shown over here. You can see now if you if we plot it would show the curve like this on the lower diagram thus any point C on the H x y diagram can be represented by the difference between the saturated vapour and liquids and intern also by a curve on the x y plot. So, also we can plot in the x y curve over here.

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Now, for the combination F minus E is equal to C a material balance if you do, it will be E by F would be equal to z C minus y E divided by z C minus x E would be equal to line CF this one divided by line CE or line. This is the equation of the x y diagram of the chord of slope EF which is shown over here slope EF drawn between the point no y E and x D. So, this is we are no between the point this is drawn between the point y E x D and y is equal to x is equal to z C. So, this is z C this point and that is on the 45 degree diagonal similarly the ratios F by G and J by K would be shown by the slopes of the chords drawn from these points to y is equal to x is equal to z C. So, you can see the other chord feature drawn over here.

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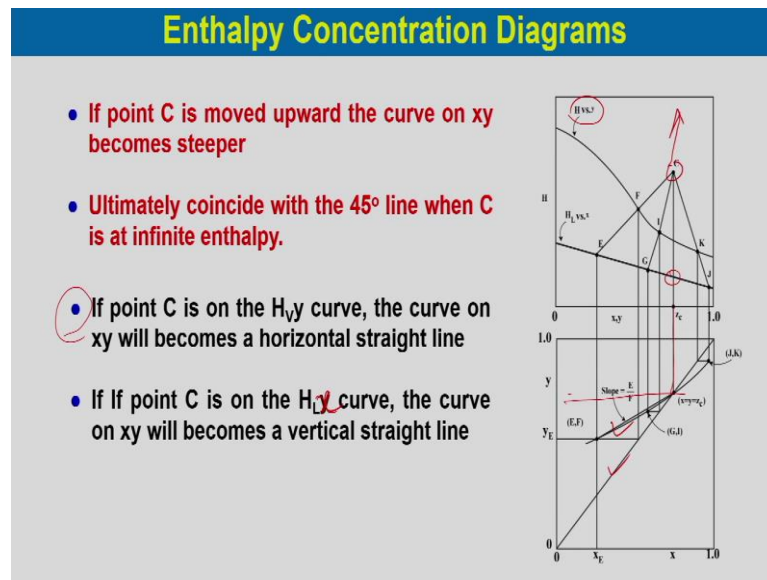


Now, if we considered the geometry of this diagram, which would readily show the following if the $H_v y$ and $H_L x$ curves are straight parallel lines which would occur when the molar latent heat of A and B are equal. So, this two curves this is $H_v y$ or $H_G y$ and $H_L x$ curves would be straight parallel line and if the molar latent heats of A and B are equal if the heat capacities are constant over the prevailing temperature range.

So, these two things are required to satisfy that the enthalpy constant the dew point curve on the enthalpy concentration diagram and the boiling and point curve on the enthalpy concentration diagram would be straight and parallel and if also there is no heat of solution. Then E/F would be equal to G/I would be equal to J/K for adiabatic subtraction. So, these will be all equal.

Since the line segments ratios are than equal and the curve on the xy representing C becomes a straight line.

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So, instead of this curve chord you will get a straight line. If the points C is moved upward the curve on x y becomes steeper. So, as you take it off upward direction as long as possible slope of the curve would become steeper and ultimately it will coincide with the 45 degree diagonal. So, when this point C would be taken to the infinite enthalpy. If point C is on the $H_v y$ curve the curve on the x y will become a horizontal straight line.

If point C is on the $H_L x$ curve, the curve on x y would become a vertical straight line. So, these two points please do remember that if C is on this curve, $H_v x$ curve then the curve on the x y become a horizontal line and any point C curve is on the line on the $H_L x$ point this is $H_L x$ curve, the curve will be a vertical straight line.

From this geometry we can understand the behaviour of the enthalpy concentration diagram and how to draw the tie line from the x y diagram and also if we have $H_x y$ diagram how we can plot the x y diagram and the concept from the geometry of the enthalpy concentration diagram. So, with this we will conclude our discussion on this second lecture and thank you for attending this lecture and we will continue our discussion of distillation process in the next lecture.