# Course on Phase Equilibrium Thermodynamics
### By Professor Gargi Das
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### Indian Institute of Technology Kharagpur
### Lecture No 38
## Ideal solutions(Contd.)

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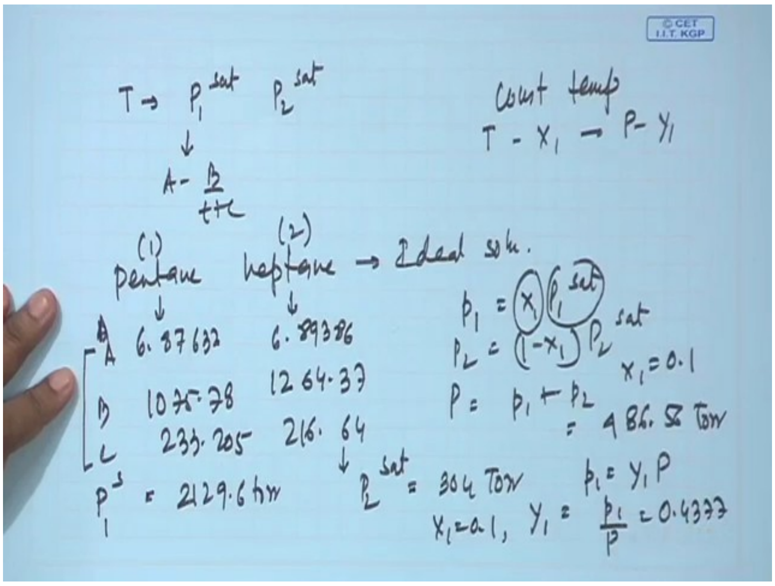

$T \rightarrow P_1^{sat} \quad P_2^{sat}$

$A - \frac{B}{t+c}$

Const temp

$T - x_1 \rightarrow P - y_1$

(1) pentane (2) heptane → Ideal soln.

| | pentane | heptane |
|---|---|---|
| A | 6.87632 | 6.89386 |
| B | 1075.78 | 1264.37 |
| C | 233.205 | 216.64 |

$P_1^{s} = 2129.6$ torr

$P_2^{sat} = 304$ Torr

$p_1 = x_1 P_1^{sat}$

$p_2 = (1-x_1) P_2^{sat}$

$x_1 = 0.1$

$P = p_1 + p_2 = 486.52$ Torr

$p_1 = y_1 P$

$x_1 = 0.1, \quad y_1 = \frac{p_1}{P} = 0.4377$

Well, so therefore as I have mentioned in the last class today we are going to discuss the phase diagrams for 2 component systems in equilibrium with one another in the vapor and the liquid phases, right? So first let us see about the situation when we do it under constant temperature, when we do it under constant temperature say we know T and we know X1, right? So from there we are required to find out P and we are required to find out y1.

So I had already given you the set of equations. So what are the set of equations that were given? Suppose you know T then you are in a position to find out P1 saturated P2 saturated, how you are supposed to find out P1 saturated and P2 saturated? Remember it was either the Clausius Clapeyron equation or the Antoine equation. Usually we use the Antoine's equation. What is the Antoine's equation?

Just to recollect this is equals to A minus B by t plus C. A, B, C they are constants characteristics of that particular compound. We will be taking up the specific example, say for example we take an example of say Pentane and Heptane we know that these are adjacent members of the homologous series. So therefore they form an ideal solution, right? And for this particular mixture I would we would like to generate a PXY diagram.

So the Antoine constants for Pentane they are given I think the problem is there at the end we or I will just give it to you. For pentane suppose it is pentane, for pentane A, B, C in case of pentane it is 6. 8 7 632 and B is 1075.78 and C is 233.205. For Heptane we find A is 6.89386 this (B) is 1264.37 this (C) is 216.64, right? So I know for pentane what are the Antoine constants? So from these Antoine constants I can find out P.

Suppose pentane is my component 1 say, right? This is component 1 this is component 2 because otherwise I have to write P pentane every time, so this is P1 saturated. Just calculate it out and see what you are going to get this is more or less just check it, it is possibly 2 21929.6 torr, In the same way for Heptane we can find out P2 saturated, what is it? 304torr, right the moment you know P1 saturated P2 saturated.

From Raoult's law what do you know? You know the partial pressure P1 is nothing but X1 P1 saturated assume a X1 you know P1 saturated you can find out P1, right? You know P2 it and find out 1 minus X1 P2 saturated, right? What else do you know? You know the total pressure P is equals to P1 plus P2. So therefore you can calculate it out say suppose for X1 equals to 0.1 I will just give you the value so you can check it up.

Your X1 equals to .1 you get more or less P equals to 486.56 torr, moment you know what is P, P equals to P1 plus P2. What is P1? P1 is nothing but equals to y1 P therefore from here you can find out the mole fraction in the vapor phase it is nothing but equals to P1 by P. So therefore we find out that for X1 equals to 0.1, y1 usually comes to as 0.4377, fine.

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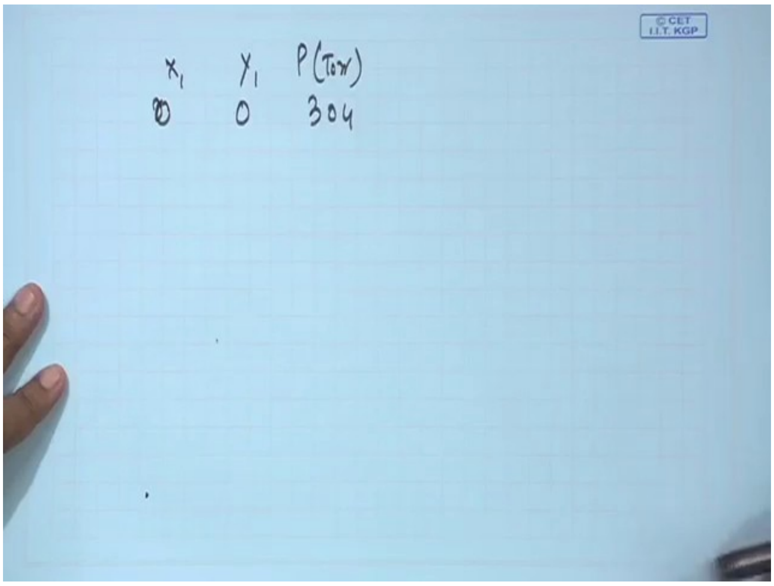

| $x_1$ | $y_1$ | P(Torr) |
|---|---|---|
| 0 | 0 | 304 |

So therefore in this particular way we can keep on assuming different X1 values and we can we can find out different P values, right? We can do it for example, so and this is 0 this is 0 and this is 304 torr, right?

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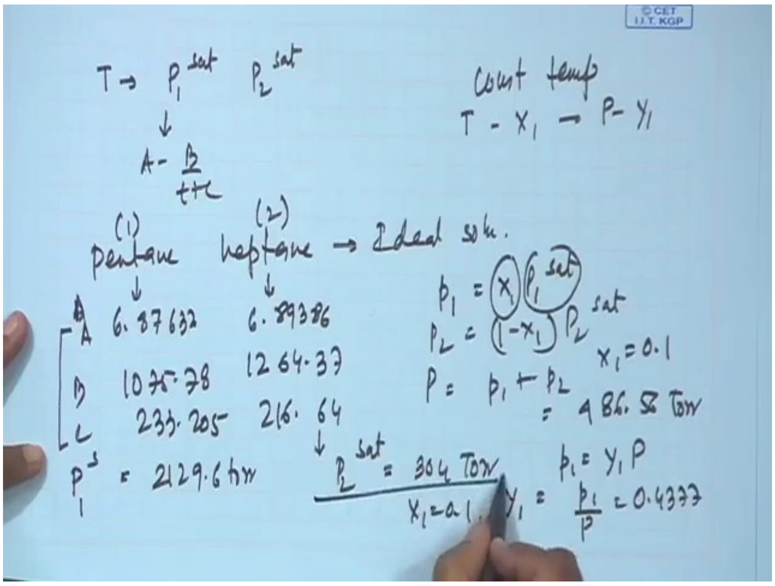

$T \to P_1^{sat}$ $P_2^{sat}$

$\downarrow$

$A - \frac{B}{t+c}$

Cont temp

$T - x_1 \to P - y_1$

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$P_1^s = 2129.6$ torr

$P_2^{sat} = 304$ Torr

$p_1 = x_1 P_1^{sat}$

$p_2 = (1-x_1) P_2^{sat}$

$x_1 = 0.1$

$P = p_1 + p_2$

$= 486.58$ Torr

$p_1 = y_1 P$

$x_1 = 0.1$, $y_1 = \frac{p_1}{P} = 0.4377$

Which is the vapor pressure of the, if you not this is the vapor pressure P2 saturated I believe this is P2 saturated.

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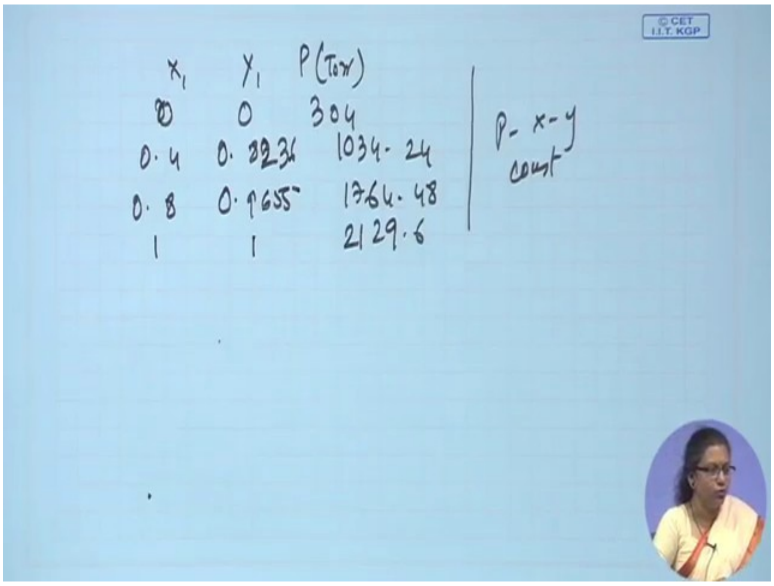

| $x_1$ | $y_1$ | P (Torr) |
|---|---|---|
| 0 | 0 | 304 |
| 0.4 | 0.8236 | 1034.24 |
| 0.8 | 0.9655 | 1764.48 |
| 1 | 1 | 2129.6 |

P - x - y

cont

Naturally when X1 equals to 0 then suppose I will just give you a few representative values for 0.4 it is 0.8236, this is 1034.24 then for 0.8 this is 0.9655 and this is1764.48 again for one what do you get? This y1 will also be equal to one and (2129.6) this is P1 saturated, right? So therefore in this way we can we can we can generate x, y P-x-y data at constant temperature and let us plot it. What sort of plot do you expect?

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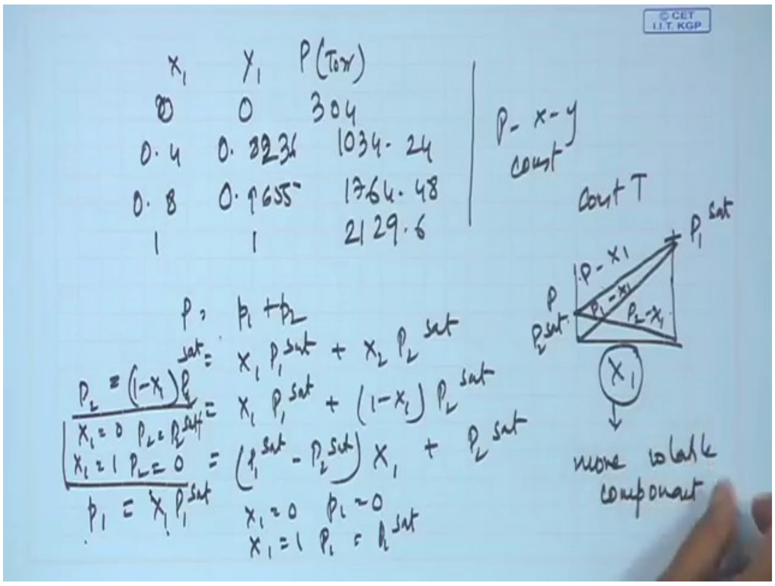

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| 0 | 0 | 304 |
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| 0.8 | 0.9655 | 1764.48 |
| 1 | 1 | 2129.6 |

P-x-y const

const T

$$P = p_1 + p_2 = x_1 P_1^{sat} + x_2 P_2^{sat} = x_1 P_1^{sat} + (1-x_1) P_2^{sat} = (P_1^{sat} - P_2^{sat}) x_1 + P_2^{sat}$$

$x_1 = 0$ $p_1 = 0$
$x_1 = 1$ $p_1 = P_1^{sat}$

$p_2 = (1-x_1) P_2^{sat}$
$x_1 = 0$ $p_2 = P_2^{sat}$
$x_1 = 1$ $p_2 = 0$

$p_1 = x_1 P_1^{sat}$

We find that suppose we plot P versus x, as I have already mentioned what is P equals to? It is P1 plus P2 we are just dealing with the same 2 or 3 equations and we are trying to do this. What is this? X1 P1 saturated plus X2 P2 saturated or in other word this is X1 P1 saturated plus 1 minus X1 P2 saturated or in other words this is equals to P1 saturated minus P2 saturated into X1 plus P2 saturated, what does this equation suggest?

This equation suggest that when you are plotting P versus X1 it should be a linear curve the linear curve should have P2 it starts from P2 saturated. Here we have already discussed P1 saturated here always remember that when we are talking about X1 we are always referring to the more volatile component this is something very important. So when we refer to the more volatile component naturally P1 saturated at constant temperature is higher than P2 saturated this happens at constant temperature.

So therefore we find P it varies from here to here and the variation of P versus X1 it has to be linear, right? And also if you find out the variation of P1, P1 is nothing but X1 P1 saturated. So therefore naturally if you are varying then in that case also we know that P1 versus X1 should be linear and at X1 equals to 0, P1 equals to 0 at X1 equals to 1, P1 equals to P1 saturated. So therefore this is the variation this is P versus X1 this is the variation of P1 versus X1.

What about P2? P2 we know this is 1 minus X1, P2 saturated. So for X1 equals to 0, P2 equals to P2 saturated. For X1 equals to 1, P2 equals to 0, right? So therefore this curve should be something of this sort, so this is P2 versus X1, fine. So therefore if you are plotting we find out that the partial pressure of component 1 the partial pressure of component 2 and the total pressure all these 3 they are linear functions of the mole fraction of the more volatile component there also linear functions of the mole fraction of the less volatile component.

If we would have taken the less volatile component we could have plotted X2 here than just the total nature of the curve would have been just inverted because this would have then been something of this sort that is only difference nothing else. So therefore we find that in the liquid phase the pressure versus mole fraction your curve that is linear.

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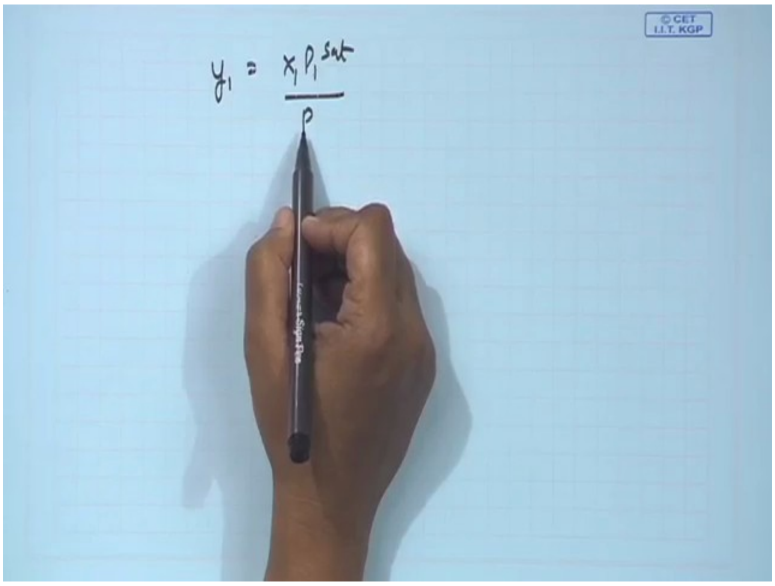

$$y_1 = \frac{x_1 P_1^{sat}}{P}$$

What about the vapor phase? In the vapor phase suppose we take then in that case what do we get? We get y1 this is equals to X1P1 saturated by P. So therefore we find that the relationship between y1 and P that is not linear, right?

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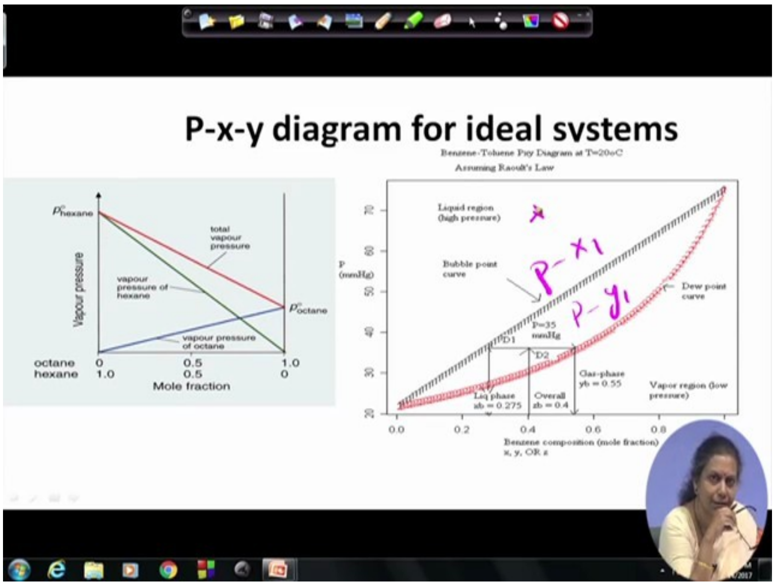

P-x-y diagram for ideal systems

So therefore we find that while the P versus X1 plot is linear the P versus y1 plot this is not linear this is something of this sort. So in this graphs now let us see we have plotted P versus X1 this is P versus X1 plot, this is P versus y1 plot, right? Now at very high pressure beyond this is a saturated vapor pressure curve beyond the saturation vapor pressure, what do we have? We have liquid, fine. We have liquid at high pressure this is sub-cooled liquid at high pressure, right?

So therefore suppose we have a liquid in the liquid region any particular point it can be denoted by, how many variables? In this particular case again in if you if you start to write C minus P plus 2, P is one, C is 2 so therefore F will be equals to 3.

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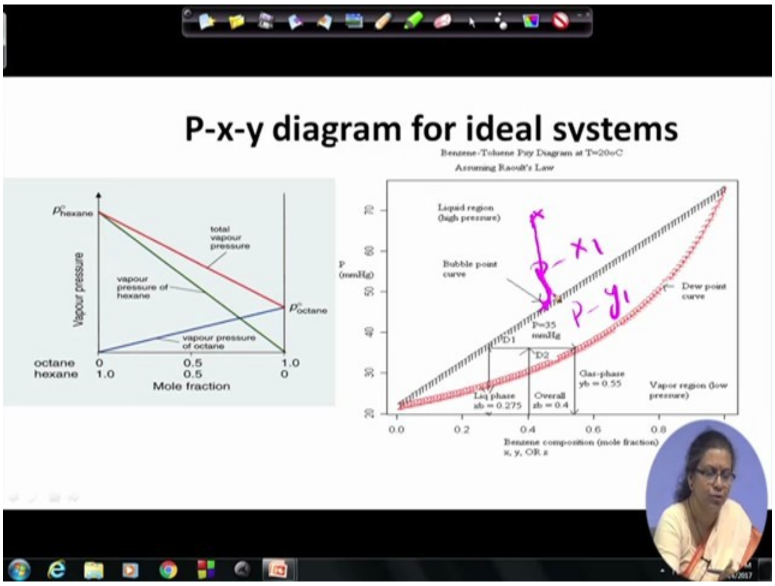

P-x-y diagram for ideal systems

So therefore in order to identify any point in the single phase liquid region we need at least 3 variables we need P, we need X1 and in this particular case the temperature is already constant. Now here if I start expanding the liquid mixture or rather at constant temperature. So when we start doing it at constant temperature when we are reducing the pressure we are basically following this vertical line, we keep on expanding we find the liquid keeps on getting expanded but it remains in the single phase region there is no change in composition.

Just a pressure over the liquid it keeps on getting lesser and lesser this continues till the liquid strikes the saturated liquid region when it strikes the saturated liquid region, what happens? The first vapor bubble appears and what is the composition of the vapor bubble? The vapor bubble is in equilibrium with the liquid phase. If it is in equilibrium with the liquid phase then it lies at constant temperature and pressure both the vapor and liquid are at constant temperature and pressure.

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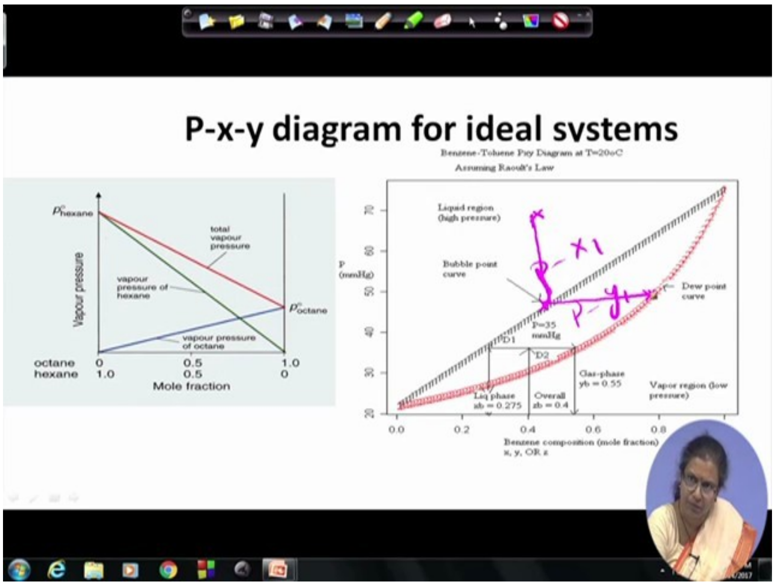

P-x-y diagram for ideal svstems

So naturally the vapor phase should have a composition on this particular horizontal line where it strikes the P versus y1 curve. So therefore the first vapor bubble which appears that will have a composition which lies on the horizontal line drawn from X1 where it cuts P versus y1 curve, agreed? So therefore and then again we keep on continuing our expansion process, when we start we keep on continuing the expansion process what do we find?

We find that from the single phase liquid region we have entered the 2 phase liquid vapor region this particular region which is bounded by the saturated liquid curve and the saturated vapor curve this is the zone of heterogeneous region where vapor and liquid both the mixture they exist, right? And remember one thing we are just going down a vertical line therefore the overall composition of the mixture is constant but this mixture after it crosses the saturated liquid line it separates out into a vapor phase and the liquid phase.

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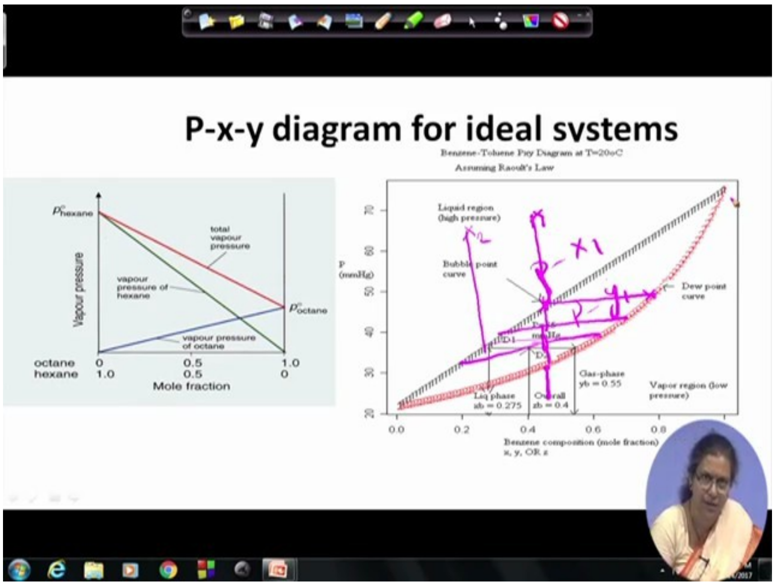

P-x-y diagram for ideal svstems

The composition of the liquid phase is given by the horizontal line from this point on the saturated liquid line and the corresponding vapor phase composition is given by the horizontal line extended to the saturated vapor curve, right?

So therefore we find that already overall composition it keeps on remaining constant as we go down and down but we find that the vapor composition and the liquid composition they keep on changing, right? This continues till we strike the saturated vapor curve, moment we strike the saturated vapor curve we find that the more or less the last drop of liquid has vaporized and then we enter the gas the single phase vapor region and again my composition in the vapor phase is the same as that of X1 this case I denote it with y1, right?

Though I had started with a composition of X1 in the liquid region I perform isothermal expansion and strike the saturated liquid region saturated liquid curve and after that I enter into the liquid vapor region it is important to remember that in the liquid vapor region the overall composition of the mixture remains constant quite naturally from conservation of mass but the proportion of liquid and vapor they keep on changing.

We find that the proportion of liquid and vapor it keeps on changing and while the proportion of liquid decreases the proportion of vapor it keeps on increasing, right? This continues while we are in the heterogeneous liquid vapor region and then once we cross the liquid vapor region we have entered the vapor region with overall composition as y. Now here I would like to mention that suppose I have started with one other point say X2 I would have continued in this particular point.

Here also when it strikes the saturated liquid region the vapor composition the composition of the first bubble which appears would have been given by this particular straight length, okay where it cuts the saturated vapor region. So therefore what do we find? We find that this entire saturated vapor curve it basically gives us the composition of the first bubble which appears when the saturated liquid is or it first converts to the vapor phase. So therefore this particular curve therefore is known as the bubble point curve.

In the same way suppose we would have started from here and we would have started compressing the vapor phase we will find that when the compressed vapor phase reaches the saturated vapor region the first drop of liquid the first dew which appears that would have a composition which would be given by the horizontal line from here when it crosses touches the saturated liquid region, right? So therefore we find that on saturated vapor curve we find that they all of them they give the composition of the first dew which points and whereas this gives us the composition of the first bubble which forms therefore the top one is known as the bubble Point curve the lower the saturated vapor curve is known as the dew point curve, right?

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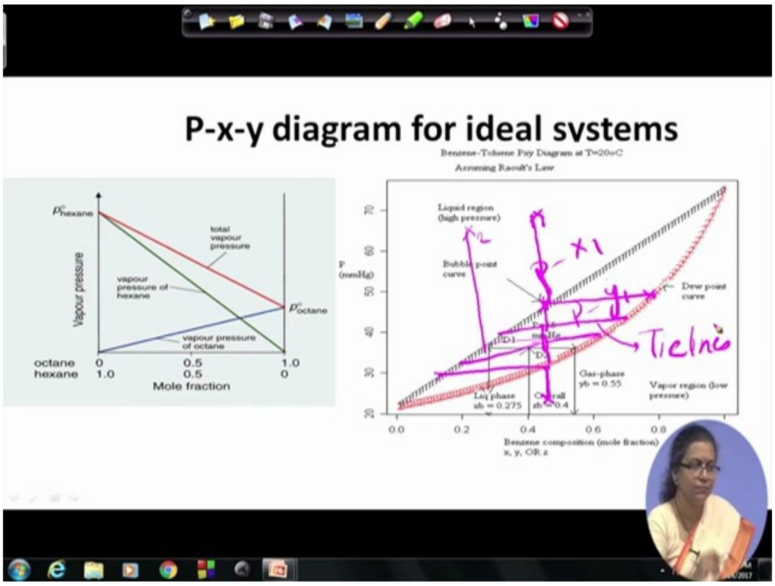

P-x-y diagram for ideal systems

And this particular horizontal line which we find which connects the liquid and vapor compositions in equilibrium these lines are known as tie lines, fine. So this was the Pxy diagram which we were discussing. Now very frequently we know that it is easier to maintain a constant pressure as compared to a constant temperature so therefore very frequently we are interested to generate Txy diagram as compared to Pxy diagrams.

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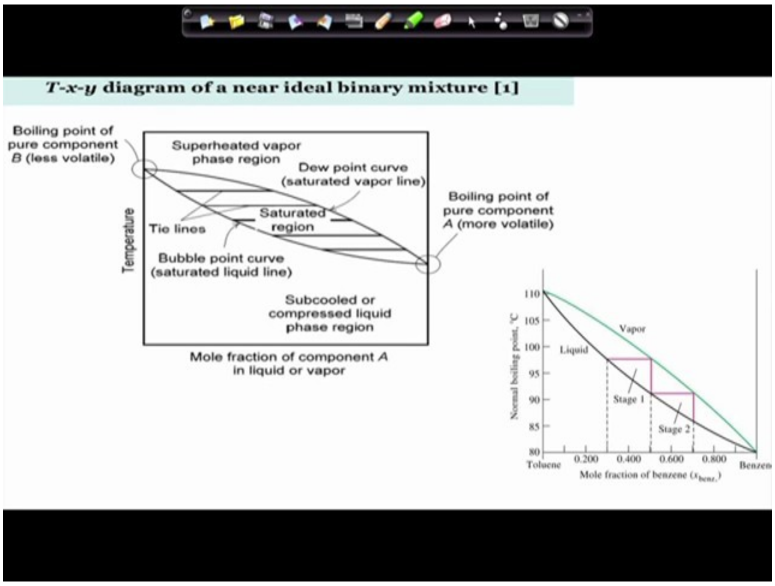

T-x-y diagram of a near ideal binary mixture [1]

So let us see at constant pressure, suppose we would like to generate a Txy diagram, how would it look like in this particular case?

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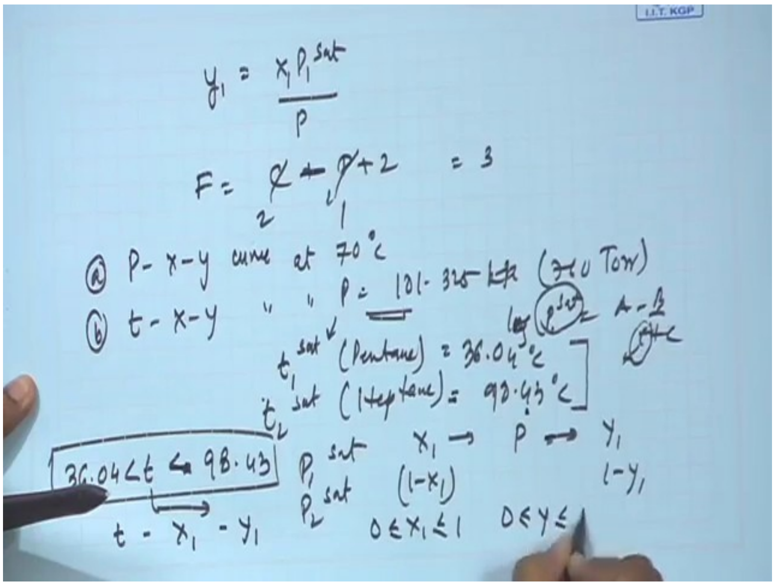

$$y_1 = \frac{x_1 P_1^{sat}}{P}$$

$$F = \underset{2}{\cancel{C}} - \underset{1}{\cancel{P}} + 2 = 3$$

ⓐ P - x - y curve at 70°C

ⓑ t - x - y " " P = 101.325 kPa (760 Torr)

$\log P^{sat} = A - \frac{B}{t + C}$

$t_1^{sat}$ (Pentane) = 36.04°C

$t_2^{sat}$ (Heptane) = 98.43°C

$\boxed{36.04 < t < 98.43}$

$t - x_1 - y_1$

$P_1^{sat}$ $\quad x_1 \rightarrow P \rightarrow y_1$

$P_2^{sat}$ $\quad (1-x_1) \qquad 1-y_1$

$0 \le x_1 \le 1 \qquad 0 \le y \le$

Now remember one thing for this particular case again let us start from the let us state previous problem, right? The previous problem was we were we were trying to find out we were trying to generate the Pxy curve at 70 degrees centigrade at that condition only I had given you P1 saturated etc.

The next problem suppose we try to generate the Txy curve at say P equals 101.325kpa or 760torq, fine. So in this particular case what do we know? We know the total pressure. Now corresponding to this pressure can we not find out the boiling point of component 1 which is nothing but pentane and the boiling point of component 2 which is nothing but Heptane, right? Now moment we can find out t1 saturated and t2 saturated, how do we find out?

Same Antoine's equation in the Antoine's equation we know that log P saturated equals to A minus A minus B by t plus c I have already written so you know this because this is the total pressure at this pressure you would like to find out the boiling point so you can very easily find this out. In this particular case you will find that the boiling point of pentane it is 36.04 degrees centigrade and that for Heptane it is 98.43 degrees centigrade, right?

Now it is very evident that the 2 phase region has to lie between these 2 temperatures, isn't it? So it has to lie between 36 to 98.43 degrees centigrade. So what we do? We choose temp any particular temperature between these 2. For that particular temperature say it is 36.4 it is greater and this is 98.43 choose the temperature here and then for that temperature we find out P1 saturated we find out P2 saturated once we can find out we choose one particular X1 and then we know one minus X1, from here what do we do?

We can find out the total pressure and then from there we can from total pressure we can find out y1, isn't it? Same way we can find out 1 minus y1 so this is the sequence in which the calculations proceed once we can do it then for each particular temperature that we have selected we can find out one particular x1 we can find out one particular y1 and where x1 it varies from 0 to 1 and y1 also corresponding y1 also varies from 0 to 1.

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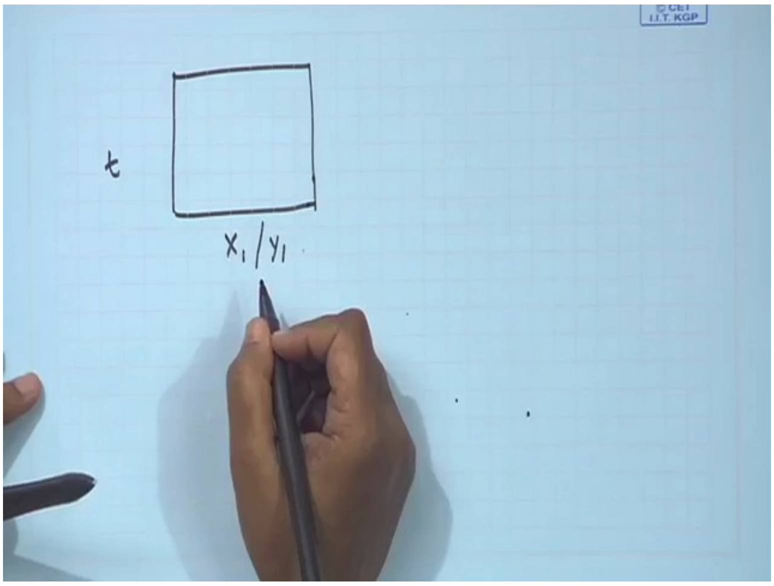

So therefore we can plot a txy plot also in this particular way where on the x axis we are we plot either X1 or y1 and we plot temperature here. This particular in this particular situation where X1 equals to 0 this should correspond to the boiling point of phase 2. Since phase 2 is the less volatile component so its boiling point will be higher so this is t say boiling point of this is component 1 component 2, right? And this should extend to the t boiling point of component 1 which is naturally it is more volatile it should be less, right?

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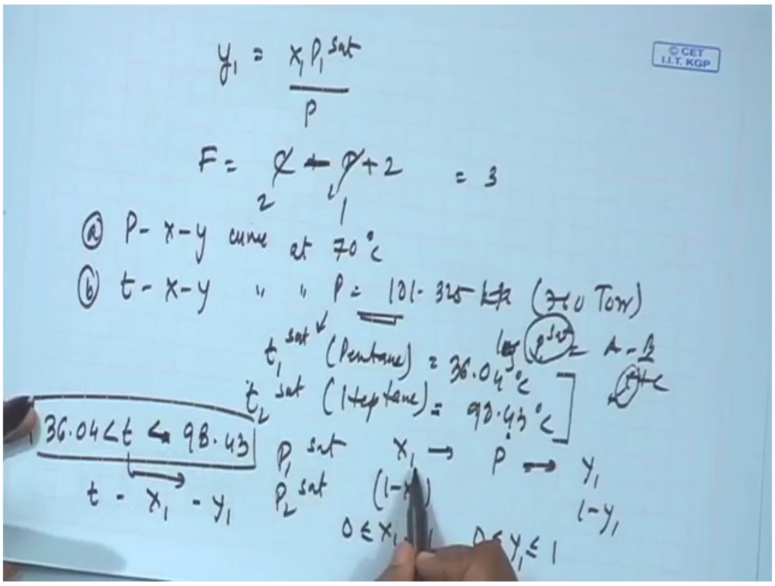

$y_1 = \frac{x_1 P_1^{sat}}{P}$

$F = \underset{2}{\cancel{C}} - \underset{1}{\cancel{\pi}} + 2 = 3$

ⓐ P - x - y curve at 70 °C

ⓑ t - x - y " " P = 101.325 kPa (760 Torr)

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$t_2^{sat}$ (Heptane) = 98.43 °C

$\boxed{36.04 < t < 98.43}$

$t - x_1 - y_1$

$P_1^{sat}$ $x_1 \to P \to y_1$

$P_2^{sat}$ $(1-x_1)$ $1-y_1$

$0 \le x_1 \le 1$ $0 \le y_1 \le 1$

And then and in this particular case we find that the relationship it is not linear the relationship is going to be non-linear because t it is related to X1 from X1 we P1 saturated from there we get X1. So therefore in this particular case the relation between t versus x1 or t versus y1 it is not linear.

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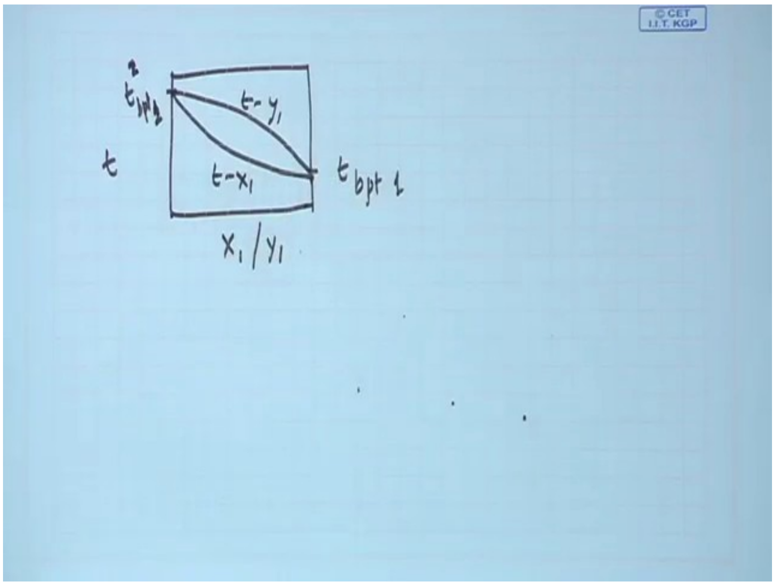

So more or less the type of curve which we get it is something of this sort, this is the t versus x1 curve this is the t versus y1 curve.

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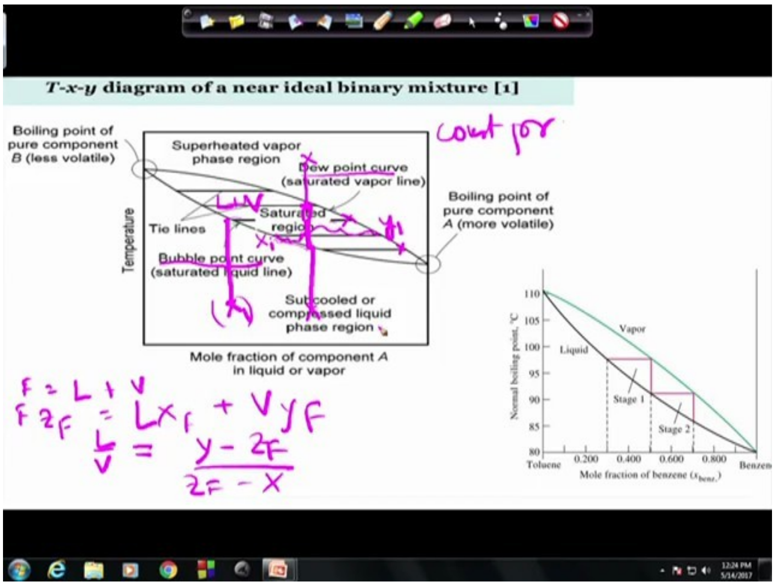

***T-x-y* diagram of a near ideal binary mixture [1]**

$F = L + V$

$F z_F = L x_F + V y_F$

$\frac{L}{V} = \frac{y - z_F}{z_F - x}$

I have shown this in this particular figure. Here also we proceed in the same way, at very low temperature what do we have? We have only the liquid region, suppose we have liquid at this particular composition X1 this is at a at some particular temperature and pressure in this sub-cooled liquid region we know that we have 3 variables we can vary the composition temperature pressure everything independent and for this particular case this has been drawn for a constant pressure conditions. So therefore we can vary t versus x1 and locate our any particular point in the sub-cooled liquid region.

From here what do I do? I start heating the liquid mixture at constant pressure, when I start heating at constant pressure what do I do? I am basically following this particular vertical line I follow this particular vertical line and then I touch this particular point in the saturated liquid curve, moment I touch this point what happens? The first bubble appears what is the composition of the bubble? Again it will be given by the horizontal tie line connecting this point to the saturated vapor curve. So this is the composition of the first bubble.

Suppose I would have started from this particular point again I would have isobarically heated it when the first bubble appears the composition would have been given by this particular point. So therefore what do I find we find that the this particular saturated liquid curve it is the locus of all the points where the first bubble appears or in other words this is known as the bubble Point curve as has been mentioned here, agreed?

Now once we cross the bubble Point, remember one more thing which I forgot to mention for pure components we have a boiling point, at the boiling point the liquid changes to the vapor phase the vapor condenses back to the liquid phase. For a true component mixture we do not have a definite boiling point of the mixture exceed point under a very specific condition which we will be discussing later on while for usually we find that the point from where the liquid starts vaporizing and the point from where the vapor starts condensing they are not the same point.

The vapor starts condensing when it when it first strikes the dew point curve the liquid starts vaporizing when it first touches the bubble Point curve and usually there is a good amount of difference as it is as you can see here between the dew point curve and the bubble Point curve the greater will be the difference when the boiling points between the 2 your component's will be more. Now this is very important while a pure liquid is characterized by a definite boiling point which is also the condensed the condensing point also but in this case the bubble Point and the dew point are not the same they are usually different.

For ideal solutions very interestingly when we go to an extreme state of ideality we find that these 2 points they coincide. So this is this is an ironical fact that more we move from ideality we find that that dew point curve or rather the dew point and the bubble Point of the 2 mixture they come closer and they coincide at one particular point which I can mention now but we will be discussing it later which is the point of isotropy where the liquid solution exhibit extreme deviation from ideality, right?

So therefore in this particular case then what do we get? Just in the same way we find that the saturated liquid line is the bubble Point curve, fine. Then now once we cross the bubble Point curve we have entered the liquid vapor region this is a heterogeneous liquid plus vapor region. Now when we are crossing this particular region we find that as we go to higher and higher temperature we find the amount of liquid that keeps on decreasing and the amount of vapor it keeps on increasing this keeps on happening, okay.

And the thing is, as when we are inside this liquid vapor region what do we find? The horizontal line which crosses the required composition and connects the bubble Point and the dew point curve these 2 extremes they give us the composition of the liquid phase and the vapor phase in equilibrium. Here we get the composition of the of the vapor phase which is in equilibrium with the liquid phase, right? So as we enter more and more into this region we find that the overall composition of the mixture remains same but X1 changes y1 changes and but at every point X1 is in equilibrium with y1.

And more interestingly we will find suppose we take up the the conservation of mass overall mass and component balance we find that the proportion of the liquid and vapor changes in the inverse ratio of the distances of the point from the dew point and the bubble Point curve, what do I mean? Suppose I take up the overall mass balance I know F the initial feed was equals to L plus v, F - I write it as ZF, why? Because it can be a liquid or it can be a vapor this is equals to LXF plus VyF, right?

So from here what do we get? From here I get L by V the proportion L is the moles of liquid form, V is the moles of vapor form keeping in mind that both of them add up to form the total volume of the feed which I have introduced. So from this substituting this here we get L by V is nothing but equals to y minus ZF by ZF minus X. So therefore what do I get? I get 2 things from the Tie lines I get the equilibrium values of the composition in the liquid phase and the vapor phase.

I also get the proportion of liquid and vapor which is formed from this particular feed they are in the inverse proportional to the distance of the Tie lines, what I mean is this particular distance it gives me the moles of liquid form and this particular distance gives me the moles of vapor form. So therefore as we move in we find that this distance decreases and this distance it increases. So therefore if I continue in this particular way what do we find?

That finally when we come here we have all vapor and this particular here we have all vapor and then we have no liquid, okay. And in the same way suppose we would have started from this particular point and if I would have condensed the vapor then in that case what would have I got? I would have found out that if I keep on decreasing the temperature of the vapor under isobaric conditions then we find moment the vapor it touches the saturated vapor curve the first dew appears and the composition of the dew is given by the Tie line drawn from this point to this point. So therefore this particular curve accordingly is the saturated vapor curve is known as the dew point curve, right? And again from here if I keep on reducing the temperature I enter into the liquid vapor region and in this particular way it continues.

So therefore here what do I find? We find that this that Txy diagram is characterized by a single phase region, a sub cool liquid region it is below the bubble Point curve it is characterized by a single phase superheated vapor region beyond the dew point curve and the liquid vapor region between the bubble Point curve and the dew point curve and we will find that while we are moving in the 2 phase region we find as we move from the bubble Point curve to the dew point curve we find the proportion of liquid decreases the proportion of vapor increases and finally we enter from a sub cooled liquid region to a saturated vapor region with the same overall composition of the mixture but in that heterogeneous region the compositions were different.

And using this we can explain the principle of fractional distillation which we will be doing in the next class, thank you very much.