Course on Phase Equilibrium Thermodynamics
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Lecture No 51
Partial And Complete Immiscibility (Contd.)

Well, to continue with our discussions on partially miscible systems we had already discussed the phase diagram for miscible systems we also tried find out why certain systems are miscible under certain conditions and then immiscible under certain conditions but I would just like to elaborate slightly on this particularly I would like to discuss the effect of pressure on the zone of or the tendency of miscibility and immiscibility.

Just like I had discussed in the previous class 2 components are going to mix with one another provided this leads to a lowering of the Gibbs free energy of the system. If on mixing the Gibbs free energy of the system increases definitely the components will prefer to stay separated and only the Gibbs free energy decreases we are going to form a miscible solution, right?

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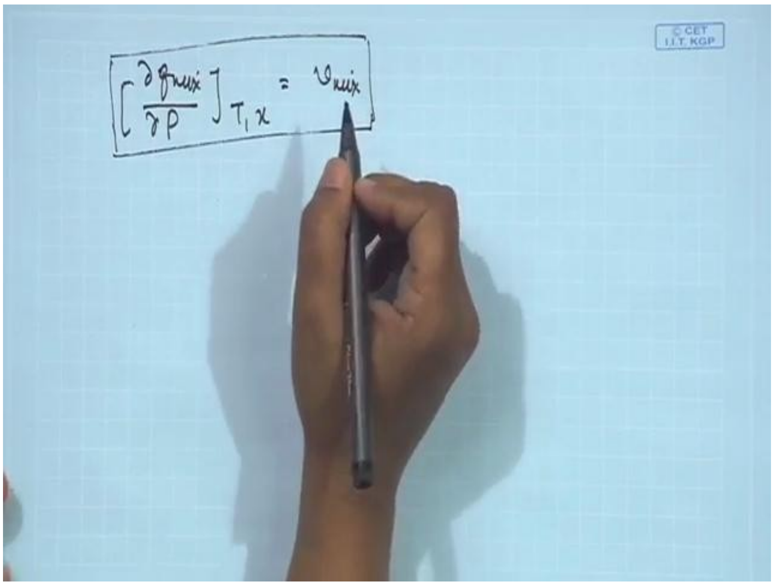

$$\boxed{\left[\frac{\partial g_{mix}}{\partial P}\right]_{T,x} = v_{mix}}$$

Now what decides whether the Gibbs free energy is going to increase or decrease when the 2 components are brought close or rather when they the 2 components are contacted with one another. If you recall what did we, we have already discussed that delg say delg mixture Del P at constant T and x, What was this? This was related to the volume of mixing if you remember, okay.

And this is the main equation which tells you that what is going to happen when the when the 2 components are brought close to one another. Now 2 components will be mixing as I have already mentioned provided delta g mix is less than 0 and del2 g mix Del x2 at constant temperature and pressure is greater than 0 for all x, only if this happens then only the 2 liquids are going to be miscible in all proportions.

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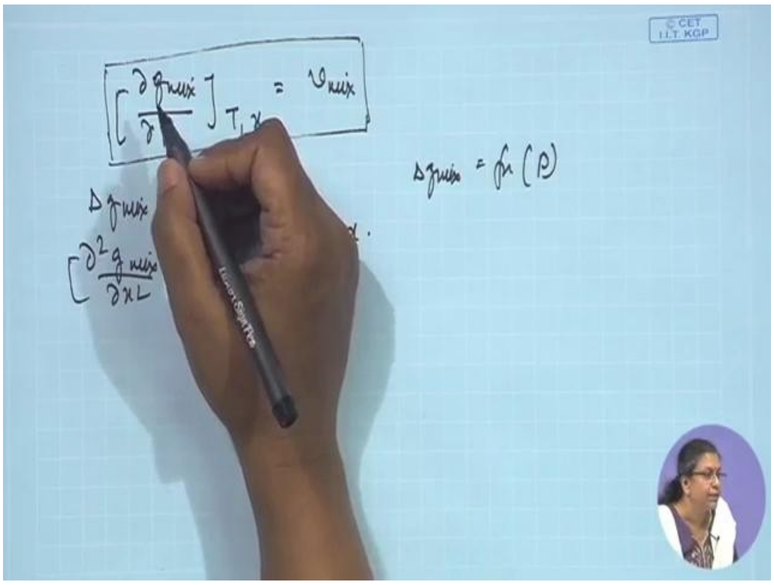

Now we know that Delta g mix it’s a function of pressure and therefore when we find that while increasing pressure it may lead to miscibility of the 2 components just like I had shown in this particular case it may also lead to immiscibility of the 2 components. So very naturally from this equation it is evident that that should depend upon the sign of V mix. Suppose we bring 2 components and mix them together and we find that V mix is actually greater than 0 then we know that when the 2 components are mixed and the variation of the g mixture with pressure is on to be positive, so at higher pressure we are going to get a positive value or a higher value g mix.

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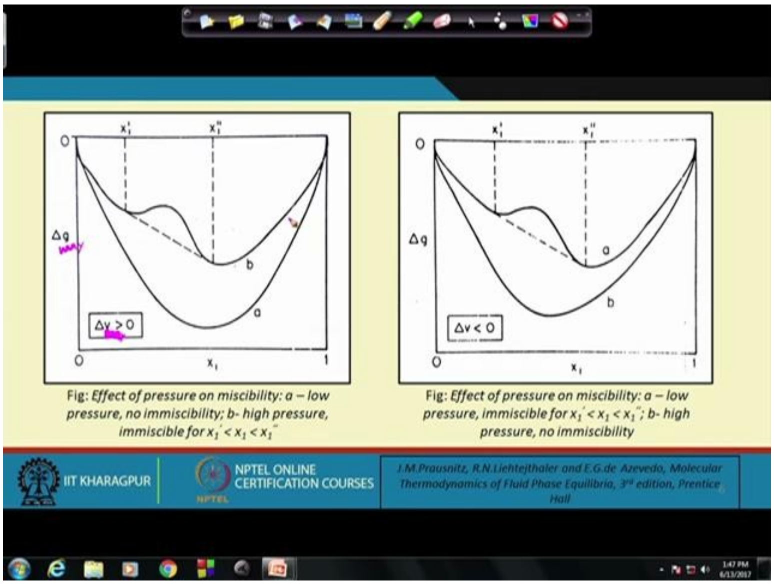

Fig: *Effect of pressure on miscibility: a – low pressure, no immiscibility; b- high pressure, immiscible for $x_1' < x_1 < x_1''$*

Fig: *Effect of pressure on miscibility: a – low pressure, immiscible for $x_1' < x_1 < x_1''$; b- high pressure, no immiscibility*

J.M.Prausnitz, R.N.Liehtejthaler and E.G.de Azevedo, Molecular Thermodynamics of Fluid Phase Equilibria, 3rd edition, Prentice Hall

So naturally when we are going at higher pressure a situation is going to arise when initially at a lower pressure it had formed initially at a lower pressure it was completely mixed and when we increase the pressure when delta V is delta V mix is greater than 0 this is a mixture Delta V and this is also g mixture. So therefore when Delta V is greater than 0 when we go for higher pressure we find that Delta g mix is actually increased and there is a hump as a result of which partial miscibility results and in this particular composition range given by X1 prime and X1 double prime the 2 components separate out into 2 liquid phases while they are miscible beyond X1 prime and beyond X1 double prime.

Similarly suppose we have one particular system which is immiscible at low at low pressures the curve which or rather the system which is given by the curve a denoting that Delta g mixture as a function of the composition, from this particle curve we find that there is partial miscibility between X1 prime and X1 double prime under the condition denoted by curve a and we know that for this case Delta V mixture is negative, is less than 0.

Now for such a case suppose we increase the pressure, what happens? Delta G mixture reduces and as a result we find that the solution or the system it was partially miscible at lower pressure but it becomes completely miscible at higher pressures. So therefore from such simple variations within we can very well understand that the qualitative affect of pressure on phase stability of binary liquid mixture it depends upon the magnitude as well as the sign of the volume change of mixing and therefore if you really want to perform quantitative calculations at some fixed temperature we need to have information of the variation of Delta v mixture with XP.

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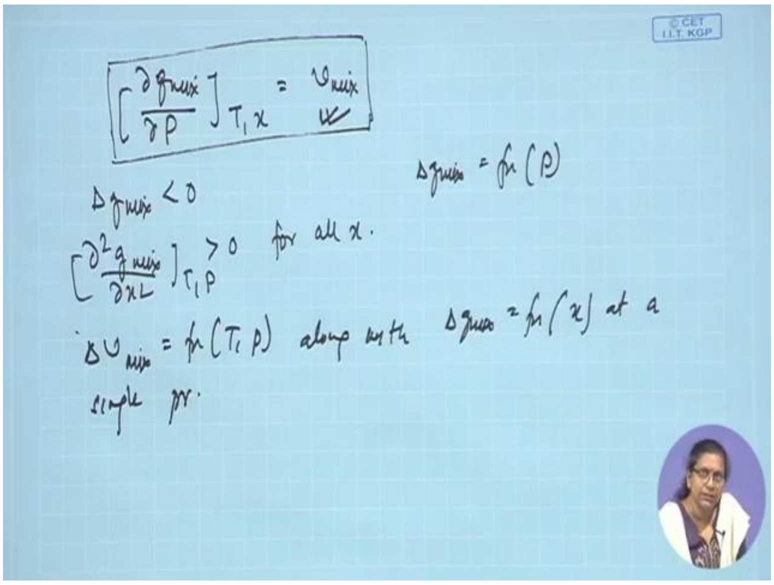

$$\boxed{\left[\frac{\partial g_{mix}}{\partial P}\right]_{T,x} = v_{mix}}$$

$\Delta g_{mix} = fn(P)$

$\Delta g_{mix} < 0$

$\left[\frac{\partial^2 g_{mix}}{\partial x^2}\right]_{T,P} > 0$ for all x.

$\Delta v_{mix} = fn(T, P)$ along with $\Delta g_{mix} = fn(x)$ at a single pr.

We need to have this particular information along with Delta g mixture as a function of x at a single pressure only if we have this data we can find out that under what conditions the 2 components will be mixing under what conditions the 2 components will not be mixing? They will be forming immiscible systems and if by increase of pressure we would land up into a miscible system or an immiscible system it all depends upon the sign and magnitude of the volume change of mixing of the 2 liquids.

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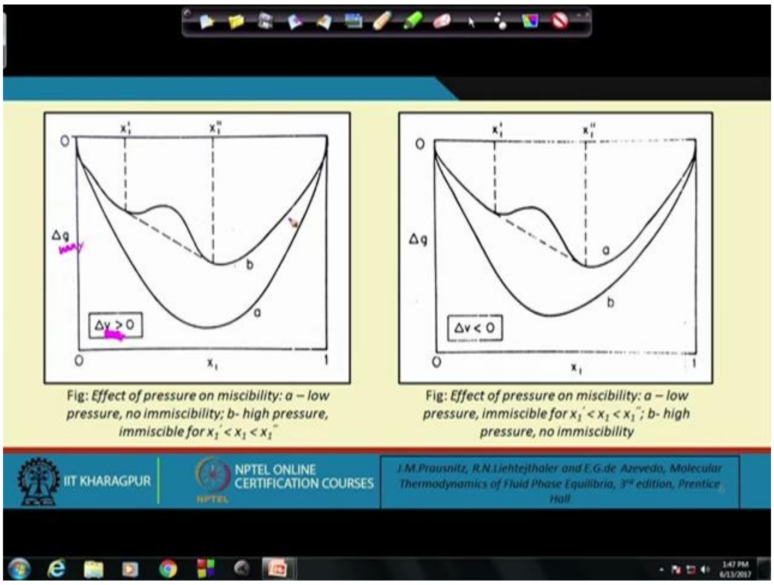

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Now let us go to the extreme of this particular situation we have been dealing with partially miscible systems we have been dealing with completely miscible systems. Now let us go to completely miscible systems, again under this condition I would like to remind you that in reality it’s very difficult to have a completely immiscible system. Such systems…

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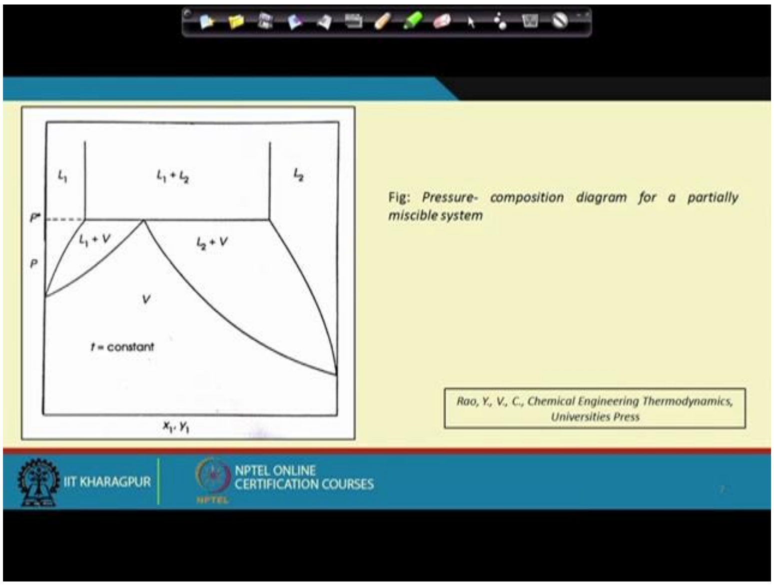

Fig: *Pressure- composition diagram for a partially miscible system*

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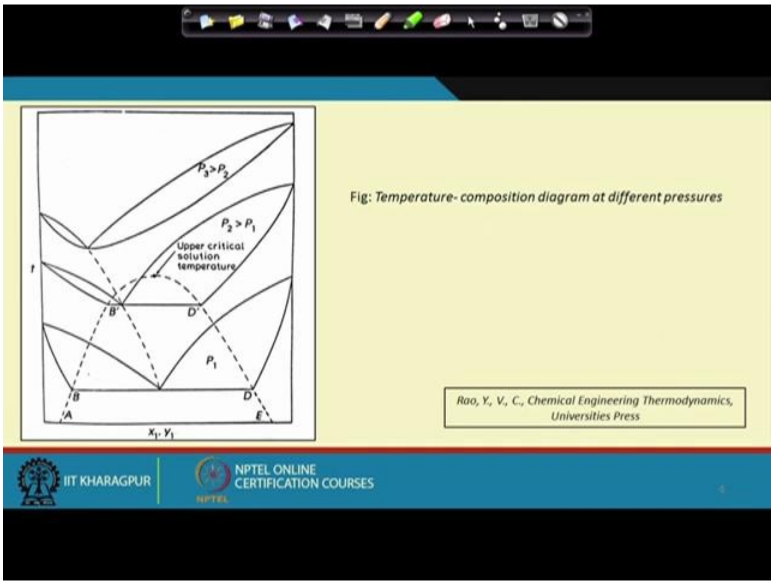

Fig: *Temperature- composition diagram at different pressures*

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Well, before that I would just like to mention that this is the corresponding Pxy diagram corresponding to the Txy diagram here. It’s interesting to note that while in the Txy diagram we found that the solubilities they were increasing with pressure. In this particular case the lines are more or less vertical which indicates that pressure insensitivity of liquid solubility which we already know.

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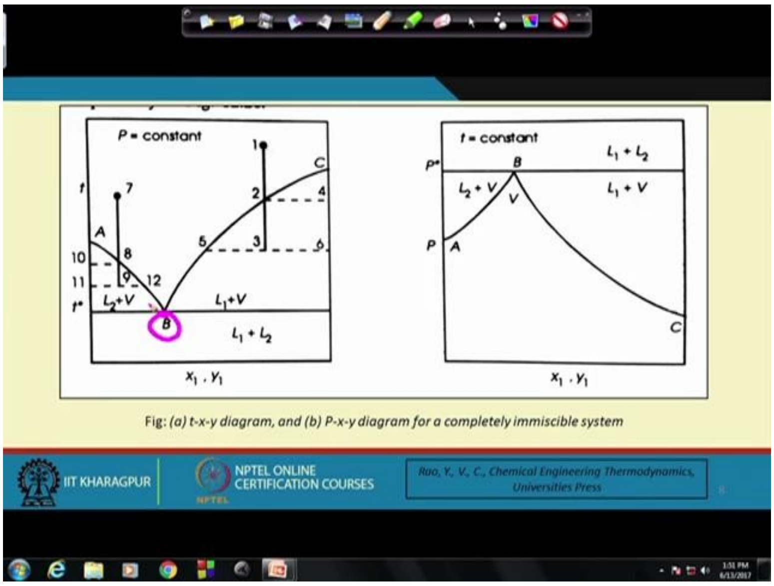

Fig: *(a) t-x-y diagram, and (b) P-x-y diagram for a completely immiscible system*

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Well, now to continue with our discussions with completely immiscible systems. Again as I was repeating at that time usually completely immiscible systems are not there in practice but they can be approached by several systems. So what should be the typical Txy and Pxy diagram in this condition? Again when there are completely immiscible systems we know that for 3 phases to coexist F equals to 1.

So therefore if we are drawing Pxy at a constant temperature or Txy at a constant pressure then there will be just one point where the 3 phases can coexist just like we have discussed in partially miscible systems, what is this point? If you observe these 2 curves this point is given by the point B, only here we have the 3 phases existing this is denoted as I have said by a 3 phase equilibrium temperature T star and a 3 phase equilibrium pressure P star, right?

Now other than this what happens to the other regions? Suppose we are operating at a temperature lower than the 3 phase equilibrium temperature, we do not have any vapour under this condition. We have to completely immiscible liquid systems if we're operating at temperature above T star we can have either a vapour phase or we can have the vapour in equilibrium with one of the liquids pure liquid, mind it. It's not a liquid solution.

In this case L1 means pure liquid L1 unlike the previous case where for partially miscible systems I had mentioned that L1 is a solution of 2 in 1. In this case L1 refers to pure liquid 1 or in other words depending upon the overall composition we can have a vapour phase in equilibrium with pure liquid L2. Now in this case also we find that suppose we start from state1 and we start cooling the vapour at constant temperature, what happens? Cooling continues.

And since it is a constant pressure cooling, so naturally it follows the vertical line say 1, 2, 3 as cooling proceeds the vapour comes or reaches the point 2. At 2 the first drop of liquid appears, what is this liquid? It is pure liquid L1 mind it, right? We continue the cooling process, we get greater and greater proportion of liquid L1 and the vapour composition it is given in this case by y5 we keep on continuing the cooling process further we find that the vapour composition varies along path CB and we get more and more of clear liquid L1.

And finally when we have touched this particular horizontal line the entire vapour has condensed to give us liquid L1 and the remaining portion is L2 which forms a separate layer, it does not mix with L1. On the contrary if we have a vapour of overall composition say y7 and we start cooling it we find that in this case also it follows a vertical line naturally constant pressure cooling and when it reaches point 8 the first dew of liquid which appears is pure liquid L2.

And if we continue the cooling process we get greater and greater proportion of liquid L2 and the vapour composition it keeps on decreasing along the path AB and finally when we continue the cooling process and rich this particular horizontal line say this horizontal line is JK, so when reaches this particular horizontal line we find that the entire vapour has disappeared and we get pure liquid L2 and definitely whatever component 1 was there in the vapour that condenses and separates out into a different liquid L1 and suppose we start rather we have the vapour of composition say yB and we continue the cooling process we find that we have only a single phase vapour region as long as the cooling continues then suddenly at the 3 phase equilibrium temperature entire vapour disappears and 2 liquids are formed, the proportion of the 2 liquids are same as the vapour or the same as the proportion of the 2 components in the vapour phase, right?

So therefore this is the phase diagram and since this is comparatively simple we can develop the mathematical equations which will be required in order to construct this particular phase diagrams, what are the things that we need? We need to first locate the point B and then we need to find out the locus of curves BC, the locus of curves AB and the horizontal line.

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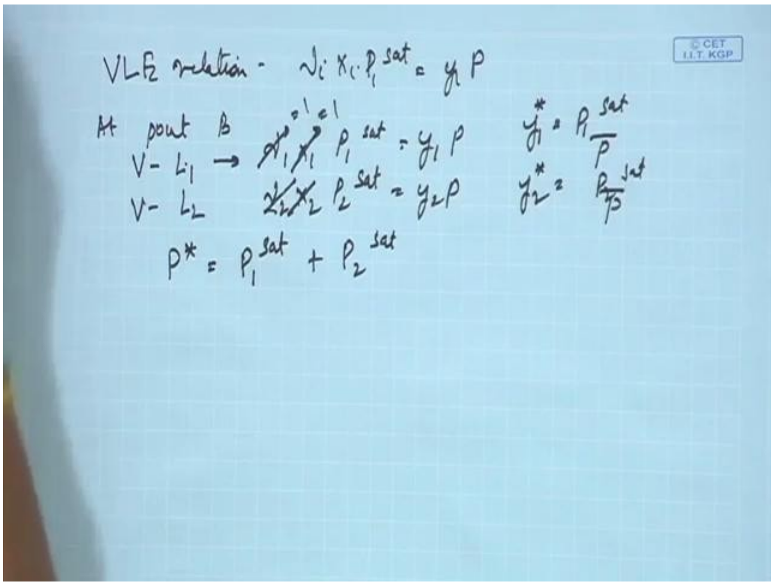

VLE relation - $\gamma_i x_i P_i^{sat} = y_i P$

At point B

V - L_1 $\rightarrow$ $\cancel{\gamma_1}^{=1} \cancel{x_1}^{=1} P_1^{sat} = y_1 P$ $\qquad y_1^* = \frac{P_1^{sat}}{P}$

V - L_2 $\qquad \cancel{\gamma_2} \cancel{x_2} P_2^{sat} = y_2 P$ $\qquad y_2^* = \frac{P_2^{sat}}{P}$

$P^* = P_1^{sat} + P_2^{sat}$

We assume for a time being that we are dealing with low pressure systems, for low pressure systems it's the standard VLE relation which we have written n number of times in our entire course is given by gamma i Xi the standard relation this is equals to yiP. Now if we apply this relation to the point B say, at point B, what is there? We find at point B vapour is in equilibrium with liquid L1 and vapour is in equilibrium with liquid L2.

So there will be 2 equilibrium relations, for the first case what will we have? For the first case it should be gamma1 X1 P1 saturated will be equal to y1P and again we remember that in this case X1 is equal to1 we have pure liquid. Since X1 equals to 1, naturally gamma1 will also be equal to one. So at point B, what is y1 equals to? It is P1 saturated by P.

Similarly at point B the equilibrium relationship governing the equilibrium of vapour and liquid L2, this is again going to be the same relationship with the same considerations which gives y2 is going to be P2 saturated by P and therefore once we know that the y1 star and y2 star at the 3 phase equilibrium temperature, we should be able to find out the P star under this condition which is nothing but equal to P1 saturated plus P2 saturated.

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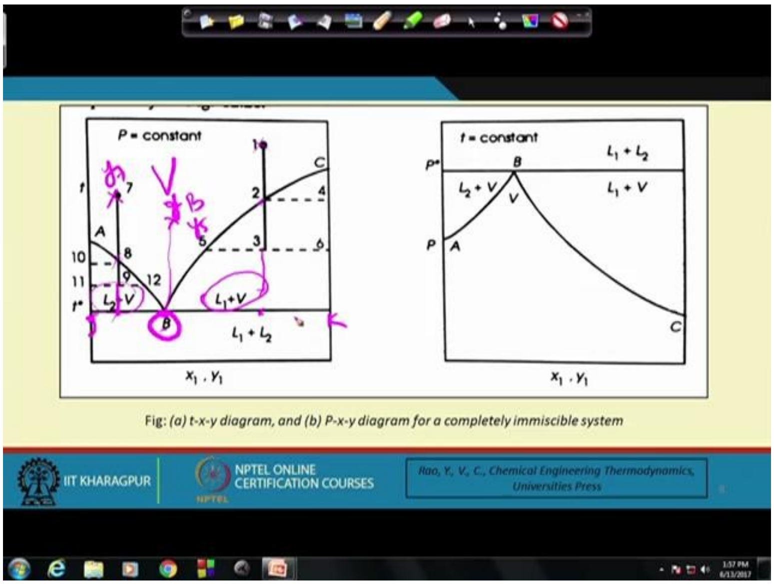

Fig: (a) t-x-y diagram, and (b) P-x-y diagram for a completely immiscible system

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And we observe one more interesting thing we find that at any particular specified pressure say for example this phase diagram is drawn at a constant pressure for such a case if 2 immiscible liquid phase is are in equilibrium with the vapour phase we find that the 3 phase equilibrium temperature will always be less than the saturation temperature of either liquids at that pressure, is it clear?

We will always find that TB will be lower than the equilibrium saturation temperature of liquid L2 and the equilibrium saturation temperature of liquid L1 this is always going to happen.

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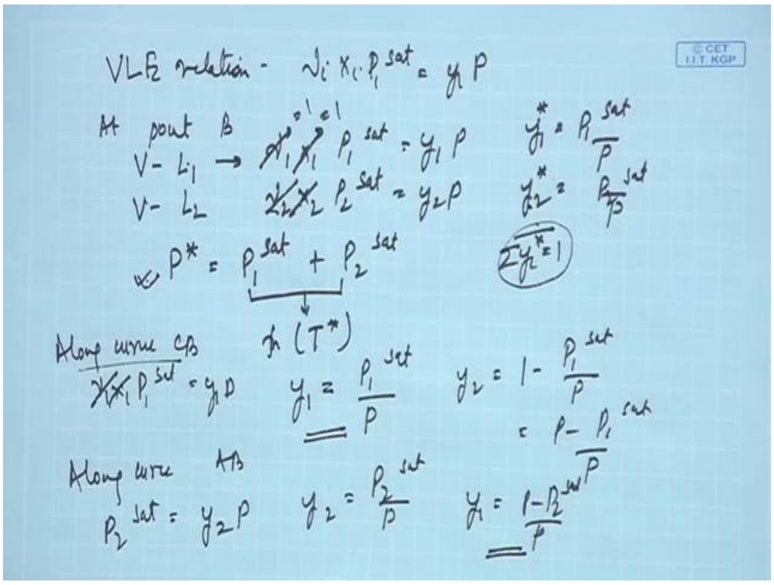

VLE relation - $\gamma_i x_i P_i^{sat} = y_i P$

At point B

V - L1 → $\overset{=1}{\cancel{\gamma_1}}\overset{=1}{\cancel{x_1}} P_1^{sat} = y_1 P$ $y_1^* = \frac{P_1^{sat}}{P}$

V - L2 $\cancel{\gamma_2}\cancel{x_2} P_2^{sat} = y_2 P$ $y_2^* = \frac{P_2^{sat}}{P}$

$P^* = \underbrace{P_1^{sat} + P_2^{sat}}_{f(T^*)}$ $\boxed{\Sigma y_i^* = 1}$

Along curve CB

$\cancel{\gamma_1}\cancel{x_1} P_1^{sat} = y_1 P$ $\underline{\underline{y_1 = \frac{P_1^{sat}}{P}}}$ $y_2 = 1 - \frac{P_1^{sat}}{P} = \frac{P - P_1^{sat}}{P}$

Along curve AB

$P_2^{sat} = y_2 P$ $y_2 = \frac{P_2^{sat}}{P}$ $\underline{\underline{y_1 = \frac{P-P_2^{sat}}{P}}}$

So therefore under this condition we have found out what is the composition of y1 star we have found out the composition of y2 star and we have also found out what should be P star under this condition. And this P1 Sat and P2 saturated they both of them they are functions of T star. So therefore we are in a position to locate point B.

Now suppose I would I would like to concentrate on this particular region. In this particular region L1 plus V what is the , we know that it’s pure liquid L1 for this region we just need to know the locus of this particular curve and we need to know the locus of this curve. Along this curve we do y1 is in equilibrium with pure liquid L1. So therefore for this curve can we not write down that again the again from the same equation these 2 cancel out, can we not write down that along curve CB, y1p is equals to P1 saturated.

Or in other words for this particular curve y1 will be given by P1 saturated by P and y2 will be given by 1 minus P1 saturated by P or in other words P minus P1 saturated by P, agreed? And what about curve AB? For this case again P2 saturated should be equal to y2P from where we know y2 should be equal to P2 saturated by P and y1 should be P minus P2 saturated by P. So therefore once we can locate the 3 phase equilibrium point, the P star, we can locate the T star because under that particular T star the P1 saturated and the P2 saturated that we get and the y1 star and the y2 star that we get, these 2 y1 y’s, Sigma yi star should be equal to one.

So therefore we can locate P star from the saturation pressures, we can locate or rather we can estimate the mole fractions of the 2 phases and once we find that the mole fractions sum up to

1, we know that our assumed temperature also corresponds to the 3 phase equilibrium temperature. So therefore from this we can find out or locate the point B.

Once we can locate the point B we can very easily find out the slopes of CB and AB, the slope of CB or the composition variation along CB is given by this particular equation and the composition variation along AB is given by this particular equation.

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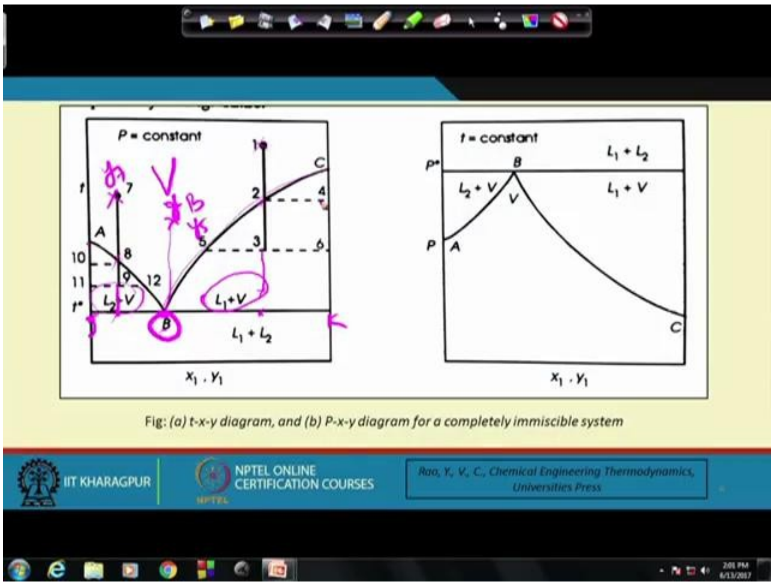

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So with these we can, it’s quite easy to construct the Txy and the Pxy diagram for completely miscible systems. Well, this completes the vapour liquid equilibrium discussions of different systems we have considered completely miscible, partially miscible and completely immiscible systems. We have among completely miscible systems we have considered ideal solutions and non-ideal solutions and we have also tried to find out how from pure common properties we are in a, we shall be in a position to find out the properties of the solutions and for both the liquid phase as well as the vapour phase.

In the next class we I will be giving you a short discussion on equilibrium studies or equilibrium considerations for other mass transfer processes. Since distillation is one of the most important mass transfer processes, so therefore thermodynamics primarily deals with the vapour liquid equilibrium rather of the vapour liquid equilibrium of different systems but definitely apart from distillation we also have to deal with other processes like absorption, adsorption etc.

As you read this processes you will be exposed into greater details regarding the equilibrium equations or the equilibrium considerations for this process but here I would just like to present a very brief discussion of the equilibrium considerations for other processes. So we do that in the next class and that is going to end up our course on phase equilibrium thermodynamics.