Course on Phase Equilibrium Thermodynamics
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Lecture No 50
Partial and complete immiscibility of liquid mixture

Well, so long we were dealing with liquid solutions where the both the components or the multi-component mixtures which we were considering they were miscible with each other over the entire range of composition. Now when they were miscible we found that they could exhibit ideal solution behavior, they could also exhibit nonideal solution behaviour, what happens, how to account for those things and they have been discussing and in the end discuss very peculiar counterintuitive phenomena the retrograde condensation which happens for binary and multi-component liquid solutions.

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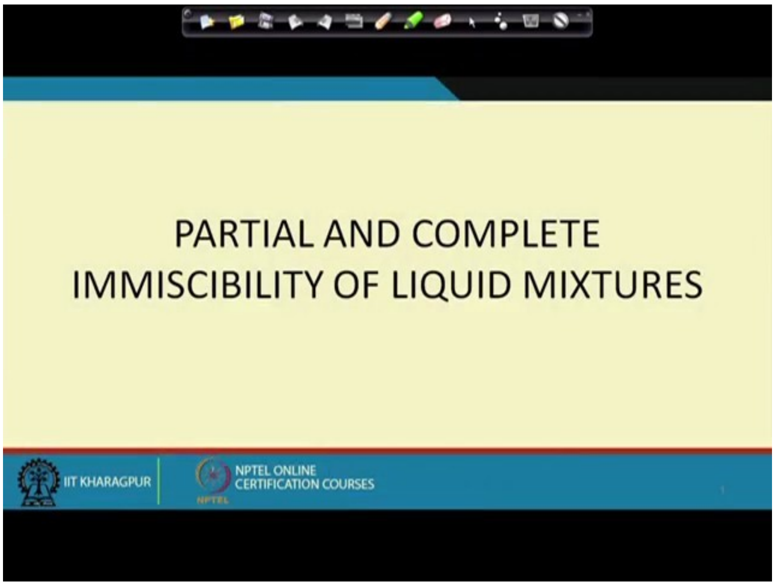

PARTIAL AND COMPLETE IMMISCIBILITY OF LIQUID MIXTURES

Well today we will be shifting to slightly different system, systems which are not miscible over the entire range of compositions. We will be dealing first with partially miscible systems where the solution or the components they are miscible over certain ranges of composition and they are immiscible over other range and then we will try to find out why liquids are miscible under certain conditions, they are not miscible under certain conditions, the phase diagrams for partially miscible systems and also the phase diagrams for completely miscible systems.

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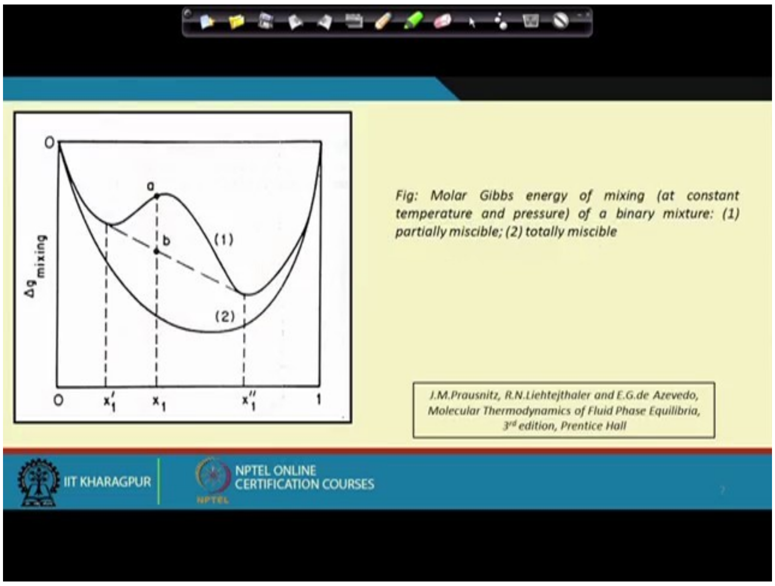

Fig: Molar Gibbs energy of mixing (at constant temperature and pressure) of a binary mixture: (1) partially miscible; (2) totally miscible

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

Now let us discuss a few salient features of it. First thing is why are components rather what happens due to which the components they do not mix with one another. Now we have already discussed while we were discussing the thermodynamic potentials we have already discussed that under constant temperature pressure conditions the, any particular system it will act such that Gibbs free energy minimizes in the course of the process.

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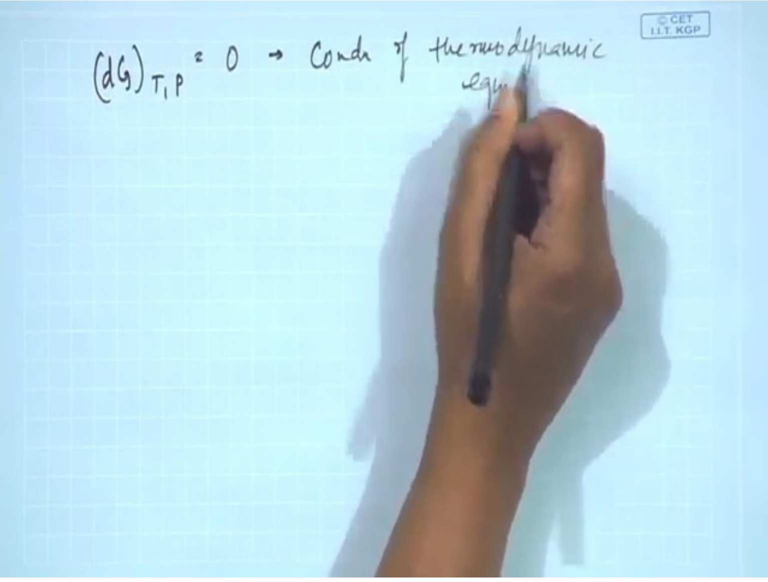

$(dG)_{T,P} = 0 \rightarrow$ Condn of thermodynamic equi

Or in other words mathematically if we put it we have seen that the condition of thermodynamic equilibrium under conditions of constant temperature and pressure is given by this particular equation, okay. And therefore it is quite evident that when there are 2 components which mix definitely they will be miscible if after mixing the Gibbs free energy of the solution is less as compared to the Gibbs free energy of the original components.

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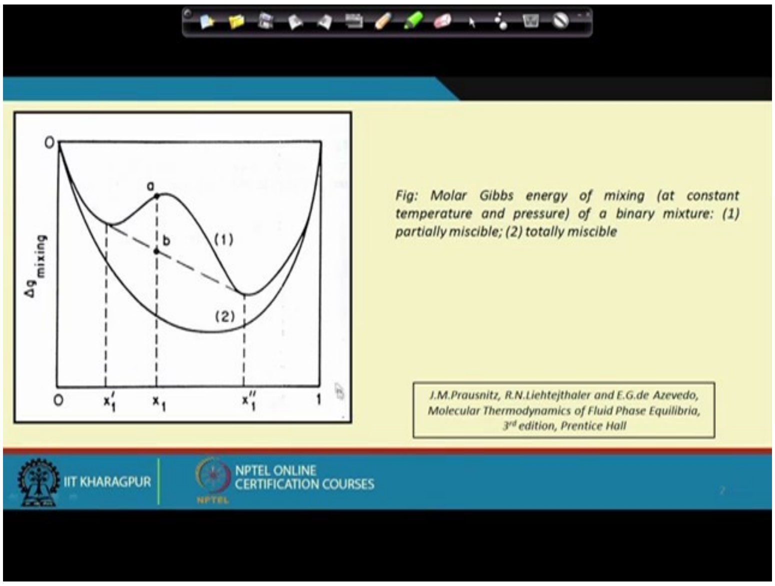

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For example this particular situation is given by curve 2 in this figure. In this particular curve we find that a single liquid phase will be obtained over the entire range of composition starting from X1 equals to 0 to X1 equals to 1.

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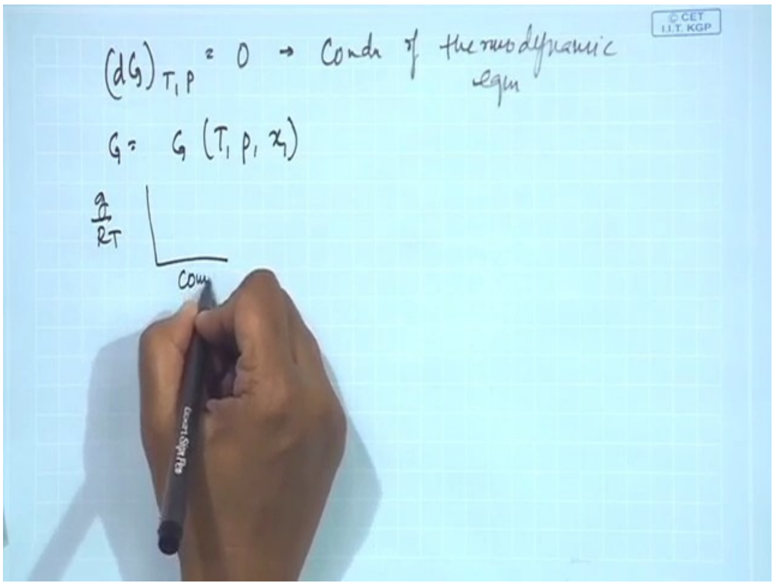

$(dG)_{T,P} = 0$ → Condn of thermodynamic eqm

$G = G(T, P, x_1)$

Now for such a binary system we find that Gibbs free energy it is a function of as we know it’s a function of temperature pressure and composition we have discussed the different relationships etc and for the system to be stable as I have already discussed (dG) T P has to be equal to

0. Now if we consider the dependence of g by RT over composition.

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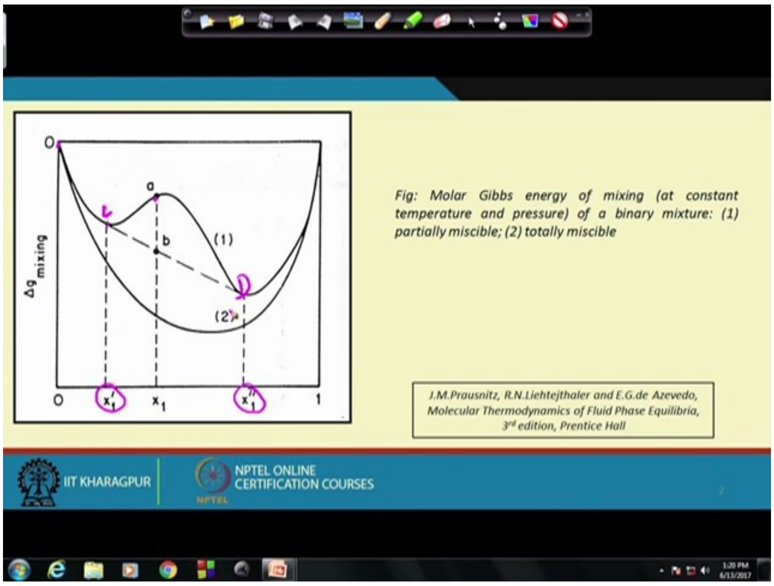

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Just the curve which I have shown in this particular figure and here we find that as I have already discussed for a completely miscible system the Gibbs free energy of mixing always reduces it is always less as compared to the Gibbs free energy of the individual components. Now under certain conditions if it happens that on mixing instead of following curve 2 the solution or rather the mixture it follows curve 1.

That means in curve 1 we find that over this particular portion starting from X1 equals to 0 to say X1 equals to X1 prime we find that there is a decrease in the Gibbs free energy change of mixing, okay. So over this particular range we know that the solution or rather the 2 components are miscible with one another but what about this particular portion which is accompanied by a hump in the curve.

In this portion we find that system it can attain the lower value of Gibbs free energy if instead of mixing with one another they remain as 2 separate components or 2 separate liquid solutions whose compositions will be given by X1 prime and X1 double prime. So naturally we find that the minimum value of G is not given by the solid curve but by the dotted line which joins the 2 points say point C and say point D.

So therefore the system it can attain the minimum Gibbs free energy if instead of a solution it exists as a mixture of 2 phases where the composition of the 2 phases will be given by X1 prime and X1 double prime respectively. So therefore any mixture which has an overall composition in this particular range it will not remain as a solution but it will break up into 2 liquid phases with the composition as I have mentioned. And therefore this is dictated by the condition of stability or the condition that the Gibbs free energy of a system has to decrease if a spontaneous reaction has to take place.

Now let us see what will be the vapor liquid equilibrium diagram for such a system we have already discussed the VLE diagram the Txy and Pxy diagrams for completely miscible systems and also the xy diagrams. Let us see what will be the vapor liquid equilibrium diagram under this condition? What is a system that we have here?

We have one vapor phase, one liquid phase and another liquid phase. Both the liquid phases they have some, suppose it is a binary mixture that means it comprises of 2 components then what do we have? In the vapor we will have both the components, in one liquid phase then will be a predominance of 1 component and a lower proportion of the other component and vice versa for the second liquid phase.

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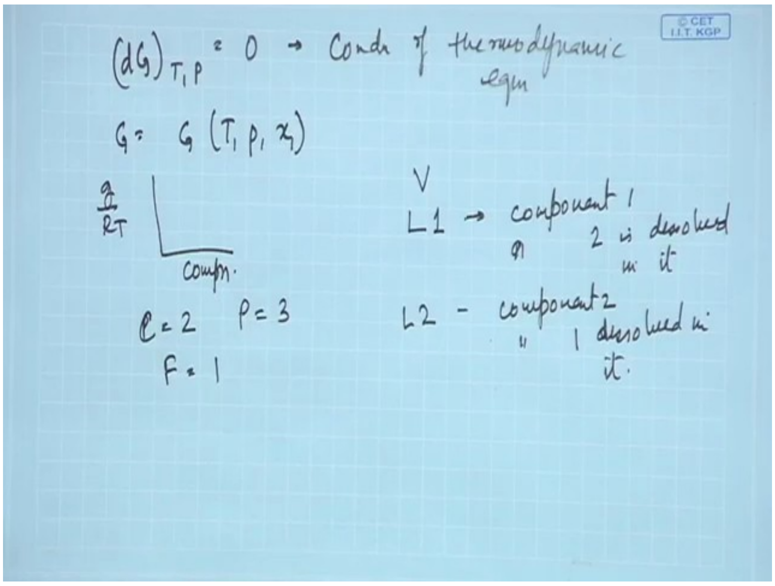

$(dG)_{T,P} = 0 \rightarrow$ Condn of thermodynamic eqm

$G = G(T, P, x_1)$

$\frac{g}{RT}$

Compn.

$C = 2 \quad P = 3$

$F = 1$

V

L1 → component 1
  " 2 is dissolved in it

L2 - component 2
  " 1 dissolved in it.

Or in other words we have a vapor phase, we have a liquid phase denoted by L1 which primarily comprises of component 1 where component 2 is dissolved in it and we have another liquid phase 2 which primarily comprises of component 2 and small amount of component 1 dissolved in it, right? So these are the 3 phases that we have unlike the 2 phase systems that we have been discussing so long.

So therefore if there are 3 phases, what is F in this particular case? When we know that for a binary system we know C equals to 2, we know P equals to 3, so therefore for all the 3 phases to coexist F has to be equal to 1. So therefore from here we can conclude that the 3 phases can coexist under one particular composition, temperature and pressure conditions.

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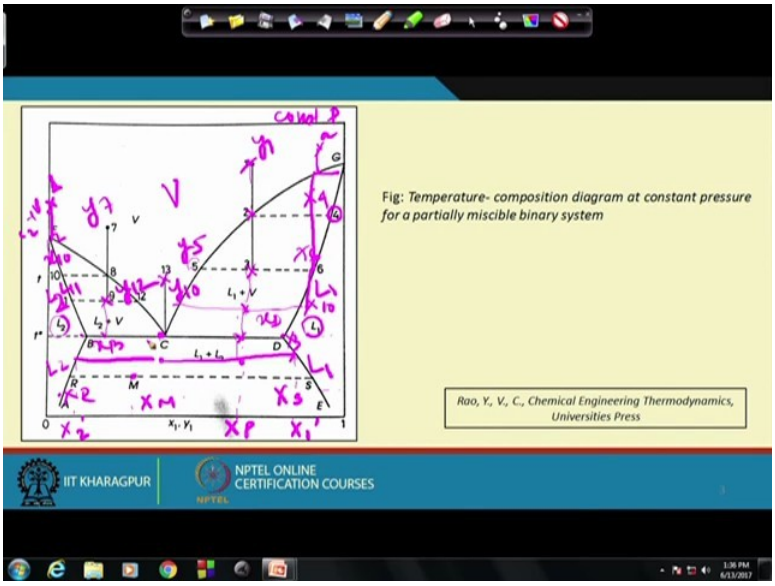

Fig: *Temperature- composition diagram at constant pressure for a partially miscible binary system*

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

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Under all other temperature, pressure, composition conditions either 2 of the 3 phases are going to be, there all the 3 phases cannot coexist. So let us see what is going to be the phase diagrams for such particular systems, we find for such systems as I have already mentioned that since F equals to 1 for the 3 phases to coexist, so we find that the 3 phases can coexist only under this particular condition which is denoted by C and this is a typical Txy diagram that we have drawn since it is at the Txy diagram this is drawn under constant pressure conditions and the point where the 3 phases can coexist that is given by the temperature T star at the constant pressure P.

Definitely T star will be different when we deal with different pressure conditions. Now what do we find here? We find here that the vapor of particular composition is in equilibrium with the liquid L1 whose composition will be given by xD and a liquid L2 whose composition will be given by xB above T star what do we find? Above T star we can either have only a vapor phase here.

We can have only L2 phase here and we can have L1 phase here or else we can also have a mixture of L1 plus the vapor phase L1 means predominantly component 1 with a small proportion of component 2 dissolved in it or they can have L2 and the vapor phase in equilibrium where L2 is predominantly component 2 with a small proportion of component 1 dissolved in it.

So this is a situation about T star below T star what can we have? Below T star either we can have one particular liquid solution which is L2 which is predominantly component 2 with small amount of component 1 dissolved or we can have a single liquid phase L1 which is component 1 with small amount of component 2 dissolved in it or we can have 2 separate liquid phases L1 and L2 where L1 comprises predominantly of component 1, L2 comprises predominantly of component 2 and depending upon the overall composition the compositions of the 2 liquid phases can be obtained from the horizontal Tie line or the intersection of the horizontal Tie line with the demarcation boundaries of L2 with L1 plus L 2 and L1 with L1 plus L 2, right?

So therefore if the composition is given by say Point M for the composition xM in this particular case we find that it separates out into L1 and L2 where L1 composition is given by XS and L2 composition is given by XR. Suppose instead of that we find that more or less the overall composition is given by say XP for example. So in this particular case what happens? we find that the system it exists as a liquid phase comprising of 2 liquid solutions where one solution L1 is given by a composition say this particular composition say X1 prime and L2 given by a which is denote or rather which has a composition of X2 prime.

Now for this particular same composition suppose we go for higher temperature, temperature higher then T star say at this particular point, here what do we have? We have the same overall composition but we have varied the temperature. We have only a vapor phase, right? From this vapor phase if you start reducing the temperature the overall composition remains the same.

And we find that the vapor it keeps on cooling till it reaches point 2. At point 2 the first drop of liquid appears or the first dew appears this is the dew point of the vapor mixture at a temperature T and an overall composition of XP. The dew which is formed has a composition corresponding to X4 or rather under this condition the dew which is formed it comprises of L1 which has a composition of X4.

Now with the same overall composition if we continue this cooling process, what are we going to have? We find that it follows the path 1 2 and 3 say in due course during the cooling process the mixture it reaches point 3 where it is separated into a vapor phase of composition y5 and a liquid phase of composition X6 we can keep on continuing this particular cooling process we find that on further cooling the composition of the vapor phase is given by say y10 and the liquid and the liquid composition say given by X10.

So therefore we find that as we continue this cooling process the vapor composition travels along GC while the liquid composition while there is just a 1 particular liquid which is in equilibrium with this particular vapor that liquid comprises of predominantly component 1 with small proportion of component 2 and its composition keeps on varying along GD as the cooling process continues and this continues till we reach the horizontal line given by CD at this point we find that the vapor phase completely disappears and it separates out into 2 liquid phases whose compositions are given by XB and XD.

A component liquid L1 with composition XD and a liquid L2 with composition XB, now if you still continue our cooling process we find that we will be again we will left with 2 liquids only and the compositions of the liquid will be varying along the curves ED and AB. Now this was when we started with a composition of vapor whose overall composition can be given by y1. Instead of that, if we start rather with a much lower vapor composition say we start at y7 and we continue the same particular cooling process at constant pressure, pressure is kept constant we continue the cooling process, what happens? The vapor keeps on getting cooled and it follows the paths given by 7, 8, 9, vertical line in this particular phase diagram, right?

Now in the cooling process when the vapor reaches points 8, what do we see? We find that the first dew appears this dew comprises of L2, okay. And the composition of L2 is given by X10 we continue the cooling process while we continue the cooling process with the overall composition remaining same we reach say point 9. Now under this condition the vapor composition is given by y12 while the liquid composition it is given by L11.

If we keep on the continuing this cooling process further, we find that the vapor composition travels along FC while it is in equilibrium with a single liquid comprising predominantly of component 2 and its composition varies along FB and finally when we touch this horizontal line BC we find that there is no amount of vapor left and the system which we are left with comprises of 2 liquid solutions the composition of one of them is given by XB and the composition of other is given by XD.

So therefore we will find that the which particular phase is going to exist or rather which phases are going to exist under constant pressure conditions it depends definitely on the temperature but also on the overall composition of the mixture that we have at hand. For example suppose we start at some particular point say F this is say point 1, right and we start cooling it, what do we find?

We find that as we continue the cooling process it follows the path say 1 2 and then it enters the 2 phase region and there we have L2 plus V. We continue the cooling region and we enter a single liquid phase which comprises predominantly of phase 2. So in this particular case the Txy behaviour is more or less similar to the behaviour of Txy that we have studied while dealing with nonideal and ideal solutions.

Same thing is going to happen if we if we deal with a very high overall composition of component 1. Say we have started with say small a, we start cooling it, we find that initially there is a vapor which is in equilibrium with the liquid phase. Now this continues and we have a liquid and vapor region where we find that the composition as we have already discussed composition on the vapor phase varies along GC composition of the liquid phase varies along GD.

Now this continues till we reach point 6, at point 6 the last vapor disappears off and the composition of the last vapor was given by y5. If we further continue the cooling process we find that we have not entered the 2 phase liquid region rather we have entered the single phase liquid region or we have entered the region of a single liquid solution. So therefore with this we find that it depends whether we are working at a range lower than T star then we will be having only liquid where we may have a single liquid phase in the composition lies in this range it may also have a single liquid phase of a different liquid if the composition lies in this range.

Or we may have a mixture of 2 liquids if the composition is given by curves AB and the composition lies between the zones of ABD and E. If you’re working at a temperature higher than T star then we may either have a single vapor phase. We may have a single L2 liquid we may have a single L1 liquid or we may have a mixture of L2 and vapor phase.

We may have a mixture of L1 plus vapor phase but only at this particular point we can have the 3 phases coexisting together. So therefore suppose we start with our initial composition at say 13 and we start cooling this particular mixture, what do we find? We find that there is a vapor phase, right? This vapor phase it keeps on getting cooled but it remains in the vapor phase and it continues the cooling process this keeps on happening till we come to the point C.

At C suddenly the entire vapor condenses and forms 2 liquid phases here. So therefore we find that the vapor liquid equilibrium for partially miscible systems comprising of 2 liquid phases and one vapor phase it has different zones of coexistence of the liquid and vapor there is one particular zone of coexistence of vapor and liquid L2, one particular zone of coexistence of vapor and liquid L1, one particular zone of coexistence for L1 plus L2 and just one point of coexistence of the 3 phases.

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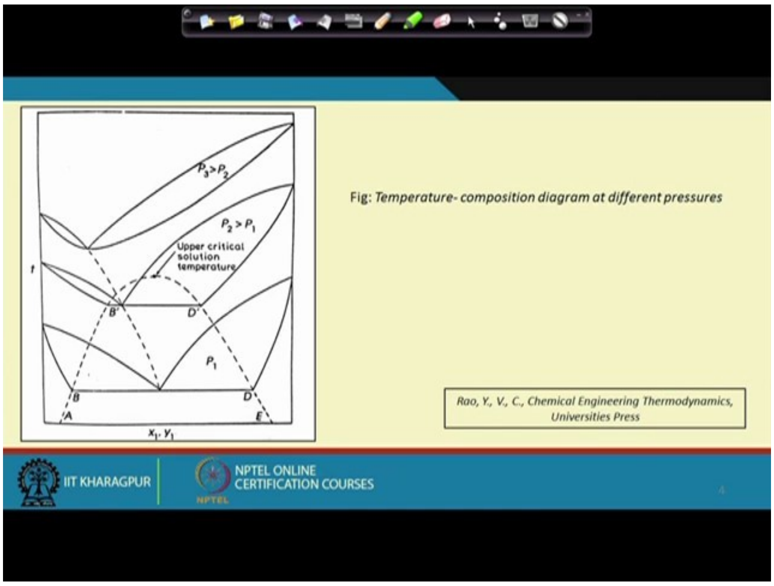

Fig: *Temperature- composition diagram at different pressures*

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

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Now suppose we have drawn it at one particular pressure, suppose we would like to repeat the experiments and see what happens if we are if we are drawing this Txy diagram at different pressures, what do we find if we go for higher and higher pressure? There are 2 things that we observe first thing is the T star which we have seen the T star it keeps on increasing as we increase the pressure or the 3 phase equilibrium temperature as it is called that increases as increase the pressure.

The other thing that we find we had observed if you notice the previous slide I will just show in the previous slide if you just notice the previous slide where we had drawn you will be finding that in this particular case AB and ED they are they slightly inclined towards one another which shows that the solubility of the phases increases with temperature.

As we increase the temperature greater amount of component 1 gets dissolved in L2 and a greater amount of component 2 gets dissolved in L1 as a result we find that when we are going for higher and higher pressure we find that these 2 curves AB and DE they start inclining towards one another more and more. As a result the horizontal line which marks the zone of existence of the 2 liquid phases that keeps on getting smaller and smaller till at one particular unique temperature it reduces to a point which is known as the critical solution temperature.

What happens beyond the critical solution temperature? We find that more or less the horizontal portion has disappeared and the Txy diagram resembles the diagrams or rather the phase diagram that we had developed for completely miscible substances with a minimum boiling point or it resembles the Txy diagram of a minimum boiling Azeotrope.

Now in this particular case since the solubility increases with temperature we find that there is a upper limit to the range of existence of the horizontal portion or the upper limit to the range of existence of the 2 immiscible liquid phases. Accordingly this is known as the upper critical solution temperature there are cases where we find that the solubility actually it decreases with pressure under that condition we have a lower critical solution temperature but let me tell you that is much less common, more common phenomena is solutions which exhibit upper critical solution temperature but we have lower critical solution temperature or rather solutions exhibiting lower critical solution temperature where there is hydrogen bonding for such cases there are also certain systems which I have written down where we find that they exhibit both the upper as well as a lower critical solution temperature. So this diagram it shows the phase stability in four binary liquid mixtures which exhibit increase in solubility with temperature decrease in solubility with temperature and also exhibit an upper and a lower critical solution temperature.

Well, there is one more thing that is quite interesting and I would like to mention it, the first thing is, so therefore what do we find? We find that the condition of instability of the binary liquid mixture it depends on 2 things firstly it depends upon the non-ideality of the solution and it also depends upon the temperature.

Now for the simplest case we find when gE is given by the one parameter equation or in other words when gE is given by the 2 suffix Margules equation for such cases we find that the consolute temperature this is given by the equation A by 2R the derivation is pretty simple but I will not be going into the details of this. Since there is some constraint of time also, so therefore we will find that the consulate temperature is given by A by 2R where the excess Gibbs free energy is given by the 2 suffix Margules equation.

And from this equation it appears that Tc should always be a maximum but in reality we know that it can be a maximum or minimum and although upper consolute solution temperatures are more common we do have lower consolute solution temperatures in mixtures where components form hydrogen bonds.

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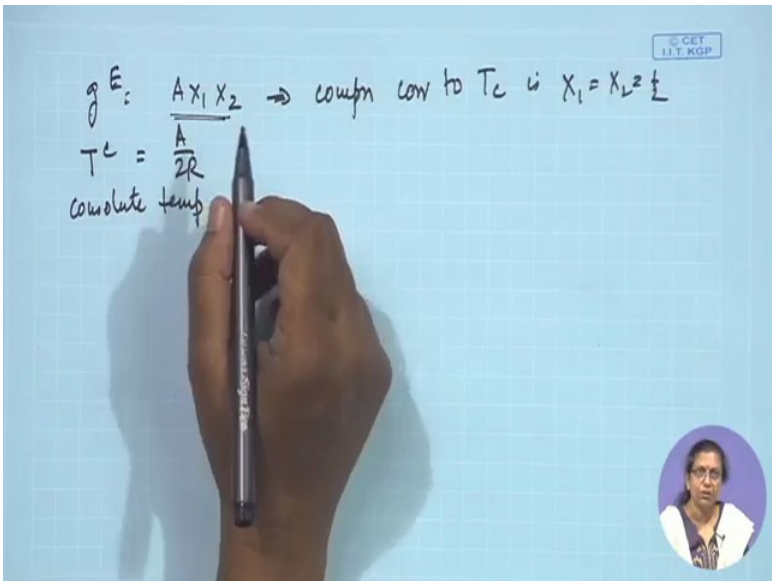

$g^E: \underline{A x_1 x_2} \Rightarrow$ compn corr to T_c is $x_1 = x_2 = \frac{1}{2}$

$T^c = \frac{A}{2R}$

consolute temp

And we also find that if gE is given by this equation then usually the composition corresponding to Tc is given by X1 equals to X2 equals to half but usually we find that gE is not given by such a symmetric distribution or gE is usually not so very symmetric with X1 and X2 and therefore the coordinates of the consulate point is often not at the composite midpoint. Well there is one more interesting thing that I would like to point out and we will be discussing it in the next class.