Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
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Lecture No 37
Ideal solutions(Contd.)

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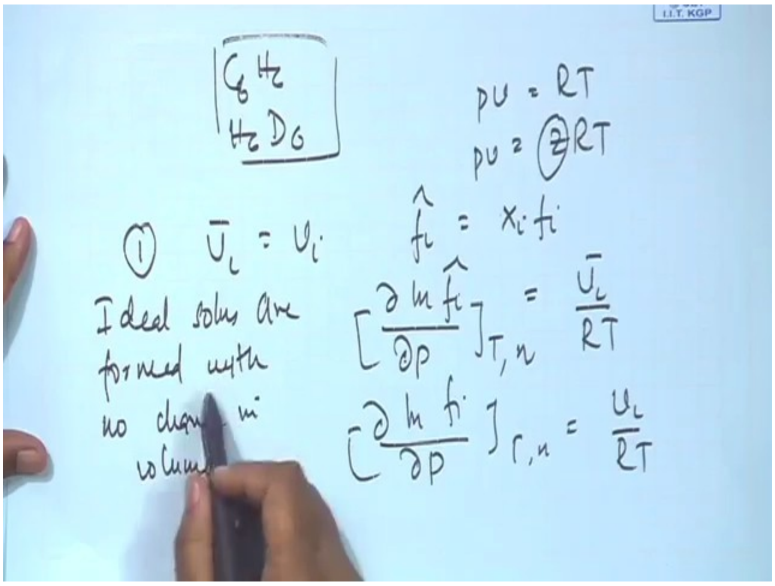

C_6H_6
C_6D_6

$pv = RT$

$pv = \textcircled{Z}RT$

① $\bar{v}_i = v_i$

Ideal solns are formed with no change in volume

$\hat{f}_i = x_i f_i$

$$\left[\frac{\partial \ln \hat{f}_i}{\partial p}\right]_{T,n} = \frac{\bar{v}_i}{RT}$$

$$\left[\frac{\partial \ln f_i}{\partial p}\right]_{T,n} = \frac{v_i}{RT}$$

Well, to come back to the properties of ideal solutions so therefore the first property we had already discussed in the last class where I told you that the ideal solutions are formed with no change in volume, right?

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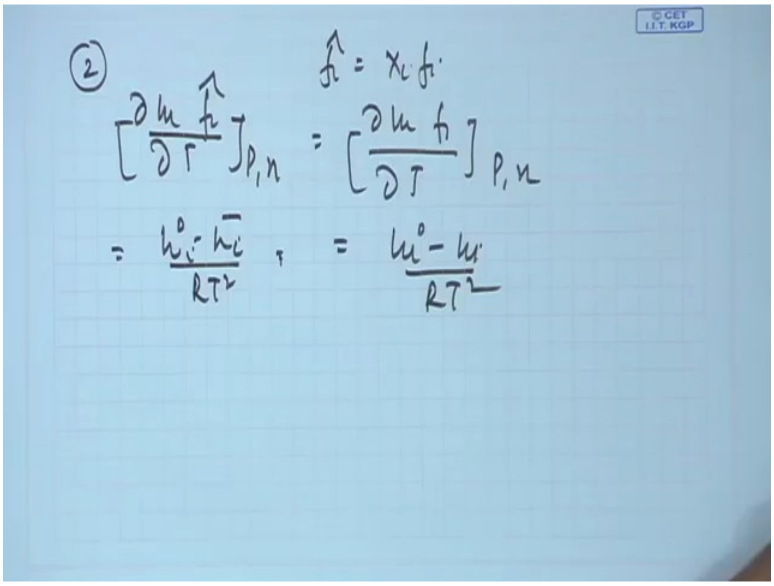

②

$\hat{f}_i = x_i f_i$

$$\left[\frac{\partial \ln \hat{f}_i}{\partial T}\right]_{P,n} = \left[\frac{\partial \ln f_i}{\partial T}\right]_{P,n}$$

$$= \frac{h_i^0 - \bar{h}_i}{RT^2}, \quad = \frac{h_i^0 - h_i}{RT^2}$$

Let us see what are the other properties? They will all come from the properties of fugacities that we have dealt with. I had already mentioned to you how fugacity changes with changes with temperature, right? So therefore in that particular case suppose we write it down what do we get del ln fi by del T at constant P this is nothing but equals to hi bar minus hi0 by RT square and what about this term also? If you refer to this is hi0 minus hi by RT square, right?

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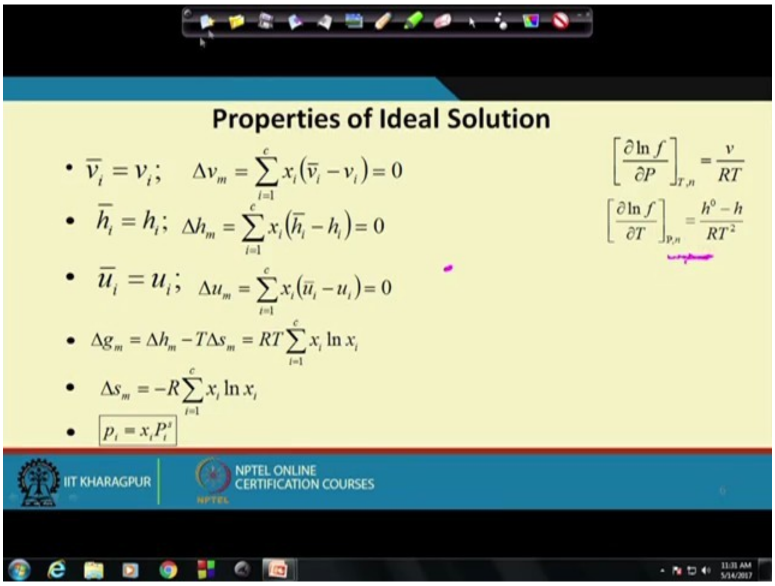

Properties of Ideal Solution

- $\bar{v}_i = v_i$; $\Delta v_m = \sum_{i=1}^{c} x_i(\bar{v}_i - v_i) = 0$
- $\bar{h}_i = h_i$; $\Delta h_m = \sum_{i=1}^{c} x_i(\bar{h}_i - h_i) = 0$
- $\bar{u}_i = u_i$; $\Delta u_m = \sum_{i=1}^{c} x_i(\bar{u}_i - u_i) = 0$
- $\Delta g_m = \Delta h_m - T\Delta s_m = RT\sum_{i=1}^{c} x_i \ln x_i$
- $\Delta s_m = -R\sum_{i=1}^{c} x_i \ln x_i$
- $\boxed{p_i = x_i P_i^s}$

$$\left[\frac{\partial \ln f}{\partial P}\right]_{T,n} = \frac{v}{RT}$$

$$\left[\frac{\partial \ln f}{\partial T}\right]_{P,n} = \frac{h^0 - h}{RT^2}$$

So therefore from this particular equation what do we get?

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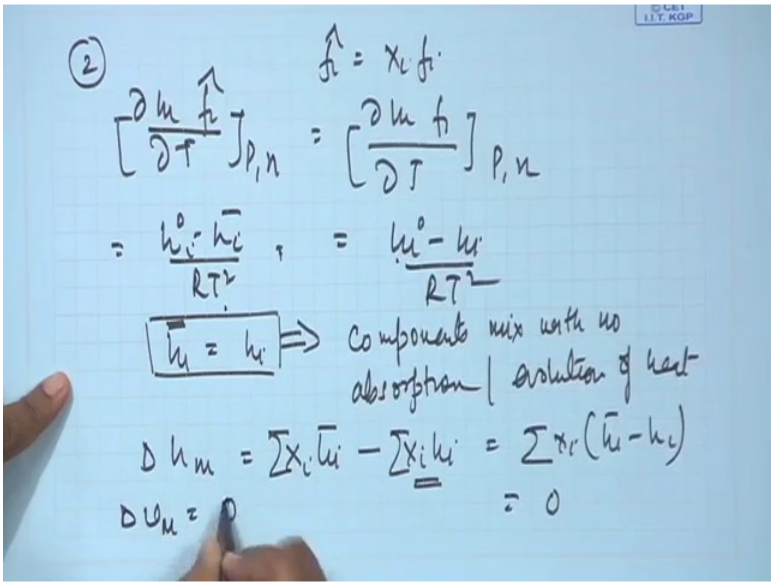

②

$$\hat{f}_i = x_i f_i$$

$$\left[\frac{\partial \ln \hat{f}_i}{\partial T}\right]_{P,n} = \left[\frac{\partial \ln f_i}{\partial T}\right]_{P,n}$$

$$= \frac{h_i^0 - \bar{h}_i}{RT^2}, \quad = \frac{h_i^0 - h_i}{RT^2}$$

$\boxed{\bar{h}_i = h_i} \Rightarrow$ Components mix with no absorption / evolution of heat

$$\Delta h_m = \sum x_i \bar{h}_i - \sum x_i h_i = \sum x_i(\bar{h}_i - h_i) = 0$$

$$\Delta u_m = 0$$

We get this, now from here what do we get? We find out that the partial molar enthalpy of component i is equals to the molar enthalpy of component i in other words which implies that the components mixed with no absorption or evolution of heat, they mix with no absorption or evolution of heat, right?

And that is quite expected, why? Because I have already mentioned that this is applicable when the interactions between unlike and like molecules are the same it automatically implies that when they are mixing there is no extra energy added or no extra energy evolved during this particular process. So therefore if this is correct then what about the molar enthalpy of mixing, what is the molar enthalpy of mixing? The molar enthalpy of the components after mixing minus the molar enthalpy of the component before mixing.

After mixing what is the molar enthalpy of the components this is Xihi bar Sigma and what were the molar enthalpy of the component? What was the enthalpy of the total enthalpy of the component when they were kept separate to each other that was Xihi the total proportion or rather for one mole of the mixture when the components were kept separately for each particular component this was the molar enthalpy taken together and after they mix the molar enthalpy changed to partial molar enthalpy so therefore the enthalpy of molar enthalpy change of mixing is given by this particular equation which can otherwise be written down as Xihi bar minus hi we know that these are equal so therefore the molar enthalpy of mixing is 0 in the same way just like we can also write down the molar sorry the molar volume change of mixing is also equal to 0.

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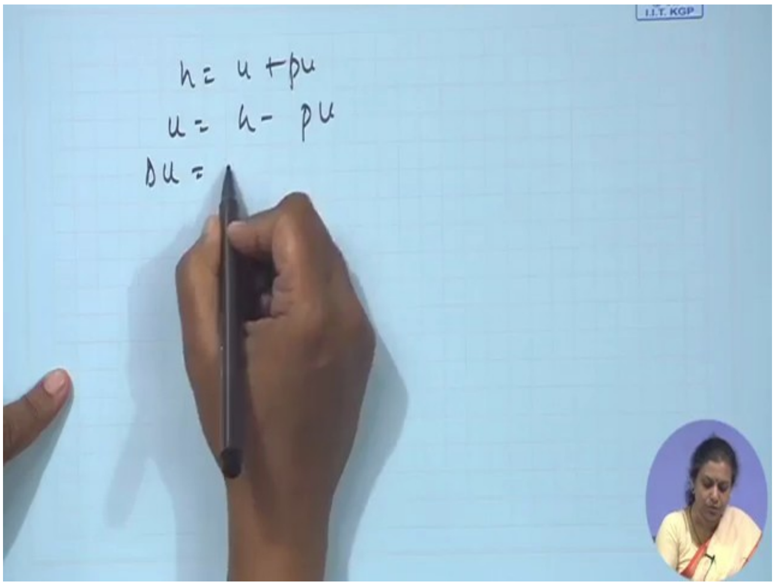

Now what do we know? We know h equals to u plus pv or in other words we know u equals to h minus pv or Delta u equals to delta h minus P delta v the whole thing is being carried out at constant pressure. So therefore in this particular case suppose I take that before mixing the or rather the if I take the molar internal energy change of mixing this should be equal to

Delta h mixing minus P delta v mixing already we have proved this equals to 0 this equals to 0 which automatically implies that delta um equals to 0.

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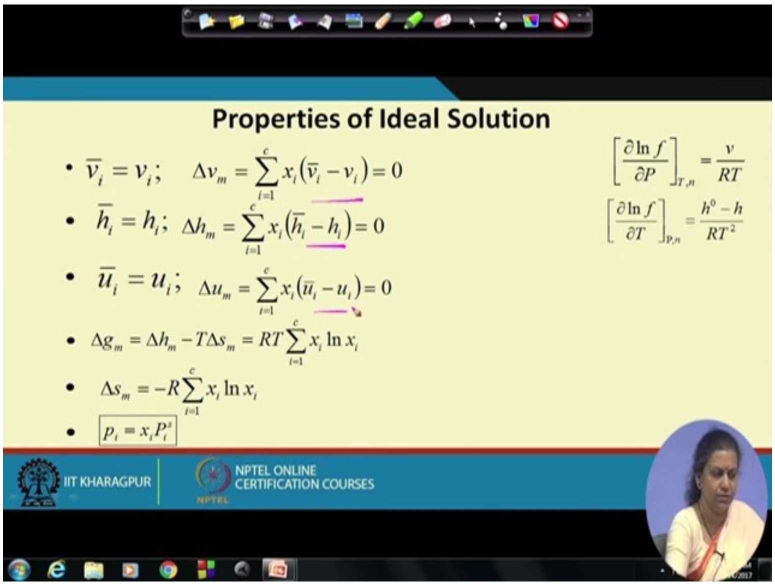

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- $\boxed{p_i = x_i P_i^s}$

$$\left[\frac{\partial \ln f}{\partial P}\right]_{T,n} = \frac{v}{RT}$$

$$\left[\frac{\partial \ln f}{\partial T}\right]_{P,n} = \frac{h^0 - h}{RT^2}$$

You can just notice that I have mentioned all these equations. So therefore we find, from here what do we find? We find that when ideal solutions are formed they are formed with no change in volume they are formed with no evolution and absorption of heat and no change in the internal energy of the solution quite naturally. What about the Gibbs free energy change of mixing? Does that also disappear or there is some Gibbs free energy change of mixing when the 2 components are mixing even when they form an ideal solution.

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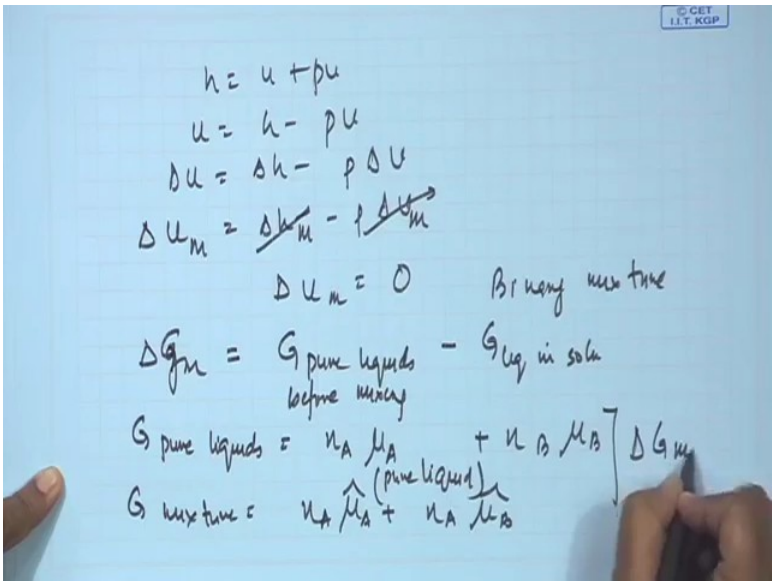

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$h = u + pv$

$u = h - pv$

$\Delta u = \Delta h - p\Delta v$

$\Delta u_M = \cancel{\Delta h_M} - \cancel{p\Delta v_M}$

$\Delta u_m = 0$ Binary mixture

$\Delta G_m = G_{\text{pure liquids before mixing}} - G_{\text{liq in soln}}$

$G_{\text{pure liquids}} = n_A \mu_A \,(\text{pure liquid}) + n_B \mu_B \Big] \Delta G_m$

$G_{\text{mixture}} = n_A \hat{\mu}_A + n_A \hat{\mu}_B$

Let us see what is Delta gm equals to this Delta gm this should be equal to suppose this is again suppose I take up the capital Gm, right? This will be equal to your G of pure liquids before mixing minus G of liquids in solution, right?

Now what is the G of pure liquids let us see? For the time being let us consider a binary mixture two components solution, okay. So therefore before mixing what was this? This was nA muA of pure liquid, so therefore I do not put anything just in case you get but for after this I am not going to write pure liquid plus nB muB, fine. What is G mixture after this A and B have been mixed? This will be nA muA again I would like to remind you that mu also has the same property of fugacity. So they are also shown by a cap here. So therefore in this particular case since I have written down G pure liquids I have written down G pure mixture. So therefore from here I should be in a position to find out Delta G mixture.

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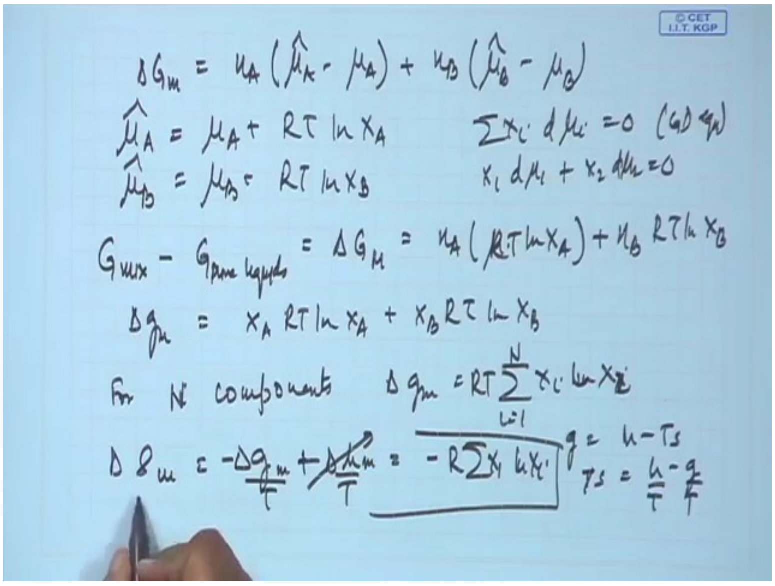

$$\Delta G_m = n_A(\hat{\mu}_A - \mu_A) + n_B(\hat{\mu}_B - \mu_B)$$

$$\hat{\mu}_A = \mu_A + RT \ln x_A \qquad \sum x_i \, d\mu_i = 0 \ (\text{GD eqn})$$

$$\hat{\mu}_B = \mu_B + RT \ln x_B \qquad x_1 \, d\mu_1 + x_2 \, d\mu_2 = 0$$

$$G_{mix} - G_{pure\ liquids} = \Delta G_M = n_A(RT \ln x_A) + n_B RT \ln x_B$$

$$\Delta g_m = x_A RT \ln x_A + x_B RT \ln x_B$$

For N components $\Delta g_m = RT \sum_{i=1}^{N} x_i \ln x_i$

$$\Delta s_m = -\frac{\Delta g_m}{T} + \cancel{\frac{\Delta h_m}{T}} = \boxed{-R \sum x_i \ln x_i} \qquad g = h - Ts \qquad Ts = \frac{h}{T} - \frac{g}{T}$$

Just subtracting what is Delta G mixture in this particular case you tell me? This is nothing but equal to nA muA bar minus muA plus nB muB bar minus muB, fine. Now you tell me how are this muA muA bar related to one another.

Is MuA bar not equal to muA plus RT ln XA, isn't it? Does this relationship hold or not? Again I would like to remind you from where did this relationship come, it came from the Gibbs Duhem equation, what was the Gibbs Duhem equation? What did I find out? If you remember xi dmu i equals to 0 this was Gibbs Duhem equation, right? So therefore in this particular case suppose I would like to integrate it from your Xi or in other words this is X1 d mu1 plus X2 dmu2 equals to 0. So therefore this comprises of component 1 this comprises of component 2.

Now suppose I integrate it from X1 equals to say one to that is the pure component to X1 equals to X1, suppose I perform that particular integration then we will find that this gives us your muA minus muA bar which is nothing but equals to RT ln XA. Same way we can write down muB is nothing but equal to muB plus RT ln XB, right? So therefore from here what do we know? We know that G mix minus G pure liquids which is nothing but equal to Delta GM this is nothing but equal to nA your RT ln XA plus nB RT ln XB.

So therefore what is the molar Gibbs free energy change of mixing this is nothing but XA RT ln XA plus XB RT ln XB. So therefore for N number of components, we can simply write Delta gm it is Sigma XI ln Xi RT i equals to 1 to N. If you recollect this is similar to the molar Gibbs free energy change of mixing for ideal gases as well, right? So we find that Delta gm is not equal to 0 if the components form an ideal solution.

So therefore if Delta gm is this, what about your Delta sm? The entropy change of mixing, we know Delta sm should be equal to Delta gm minus it is by T minus delta h by T, isn't it? We know g equals to h minus Ts so therefore Ts is nothing but equals to h minus g or in other words s equals to this. So this is going to be plus this is going to be minus, fine. We know this term your Delta hm 0 is 0. So therefore what is Delta sm? It is nothing but minus of Delta gm by T which gives you as in this particular case this gives you minus R sigma Xi ln Xi, right? And in this case I would like to tell you that since Xi is less than one Delta gm will always be negative if the solution has to be formed and again I would like to remind that we are dealing with solutions which are miscible in all proportions and again we know that Delta sm is greater than 0 for a solution to be formed these are with in line with what we have discussed till now.

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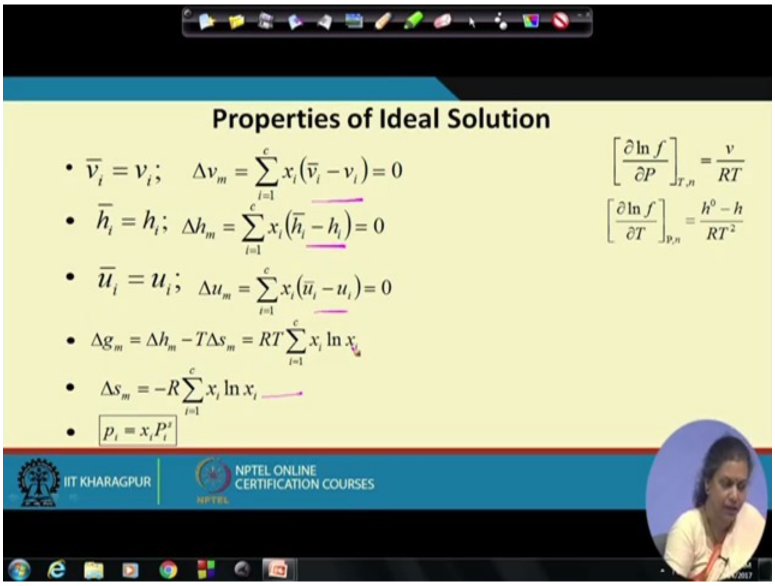

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$$\left[\frac{\partial \ln f}{\partial P}\right]_{T,n} = \frac{v}{RT}$$

$$\left[\frac{\partial \ln f}{\partial T}\right]_{P,n} = \frac{h^0 - h}{RT^2}$$

So therefore I have jotted down all the properties that I have mentioned and these are the properties of ideal solutions we find that the ideal solutions they are accompanied by no volume change of mixing, no absorption or evolution of heat, no change in internal energy but with an increase in the randomness of the solution and just because there is an increase in randomness of the solution that is why this the 2 components they mix spontaneously to form an ideal solution and it is this particular entropic effect which gives you a negative Gibbs free energy change of mixing due to which the solution mixes it is not due to the enthalpic effect it is due to the entropic effect.

Now therefore so suppose I give you a solution and I tell you to find out whether it is ideal or not we can definitely take we can measure the 2 volumes of the component that we are taking we mix them up and then we measure the volume of the solution from we find that there is no change in the volume of this solution we can assume that the solution is ideal but in this case there is something that you need to remember there are certain instances where we find that under specific composition the solution might behave ideally that in no way implies that the solution exhibits ideal behaviour over the entire range of composition.

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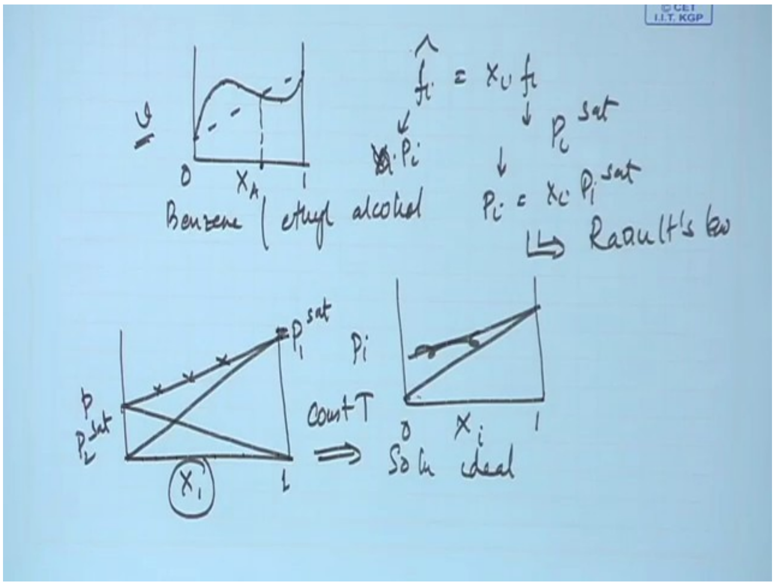

For example suppose say we find that, we take up a solution of say your benzene and ethyl alcohol, for this particular solution suppose we take this particular solution and we try to plot the molar volume as a function of say benzene, right? Where A is benzene, we find that for from 0 to one if we take the we more or less find that the graph it varies in this particular form we find that initially there is a increase in the the volume of the solution on mixing and then there is a decrease of the volume of solution on mixing and at one particular XA we find that the volume of mixing gives us 0.

Or in other words at one particular XA we find that there is no volume change on mixing the volume initially and after mixing are the same. So suppose we take up these 2 components and we try to see the volume change on mixing at this particular composition then automatically we think that the solution is ideal but it is not ideal it deviates from the Lewis fugacity rule but if you are testing it under one composition you might get P or you might get the wrong result.

Same thing can be applicable for enthalpy change as well and so therefore it is very important that when you are testing for ideality of a solution you perform the experiment over a large range of compositions, so that if it is valid over a large range of compositions then it is ideal or in other words the safest test for finding out is, if it is at low to moderate pressure then I have already mentioned that for low to moderate pressure, what is fi? fi is the fugacity of pure component i in the at the temperature and pressure of the mixture.

Suppose I am dealing with a liquid solution than for low to moderate pressure the poynting correction factor is 0 and the non-idealities due to the non-idealities of the gas phase that particular correction factor is also 0. So therefore fi it reduces to Pi saturated and under that condition what is this equal to? This is Xi into P or in other words, this is the partial pressure, isn't it? So for low to moderate pressure this reduces to Pi equals to Xi Pi saturated which as you all know this is nothing but the Raoults law, right?

So the safest thing is if you plot the partial pressure as a function of molar volume over the entire range of pressure and you see that you get a linear curve in this particular fashion then you know that the solution obeys ideal solution model. So therefore an ideal or a very safe test to test the ideality of solutions is not to test the volume change of mixing or the enthalpy change of mixing at very few mole fractions.

We can do it over a large range of mole fractions or else the safest thing is just find out the partial pressure and plot the partial pressure and you find the linear plot. In other words we will find that in fact suppose there are 2 components maybe component 1 and component 2 and then suppose we plot the partial pressure of both the components here. So for X1 what do we have? We find that when X1 equals to 1 then the partial pressure is equal to the pressure of the component; this is equals to P1 saturated.

And when X1 equals to 0 this is going to be P2 saturated, right? Now usually one is our more volatile component so therefore at constant temperature if I try to find out the X1 at if I keep on varying X1 and I try to find plot rather the partial pressure then I get a curve of something of this sort. For component 2 the curve will be something of this sort and therefore the total pressure in this particular case it varies from P2 saturated to P1 saturated in a linear fashion.

So the simplest way to do is what? You find out you mix 2 components in different proportions find out the total pressure over the mixture plot all the points and if you find that all the points more or less fall in a straight line which varies from P2 saturated at one end to

P1 saturated at other end then we know that the solution is ideal this is a sure test of ideal solution.

Well, so once we have understood an ideal solution and we have understood under what conditions ideal solutions are applicable? What is the next thing that we should do? We should find out ultimately we are dealing with phase equilibrium thermodynamics, so what we should do? We should find out the phase equilibrium relationships for ideal solutions in the vapor and the liquid phase. What do I mean? I mean suppose I have got the, a simplest solution a 2 component solution component a and component b say and they are there, there is a liquid solution in equilibrium with its vapor phase. So therefore component 1 and 2 they are present both in the liquid phase as well as in the vapor phase.

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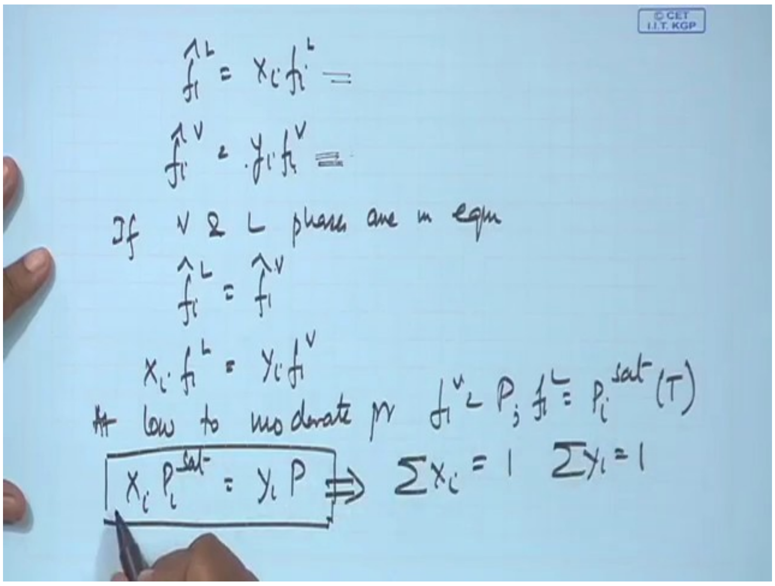

$\hat{f}_i^L = x_i f_i^L =$

$\hat{f}_i^V = y_i f_i^V =$

If V & L phases are in eqm

$\hat{f}_i^L = \hat{f}_i^V$

$x_i f_i^L = y_i f_i^V$

At low to moderate pr $f_i^V \approx P$; $f_i^L = P_i^{sat}(T)$

$\boxed{x_i P_i^{sat} = y_i P} \Rightarrow \sum x_i = 1 \quad \sum y_i = 1$

Now for the liquid phase suppose I say that in a liquid phase the solution is ideal then in that case I know fi liquid this is Xifi in the, I say that the vapor phase also exhibits the properties of an ideal solution or ideal mixture. So in the vapor phase what can I write? yifi this is L remember this is v. Again I remind the phases are given as subscripts the component numbers as superscripts, component number as subscripts and these are the partial molar properties these are the pure component properties, right?

So therefore in the liquid phase this is the equation, in the vapor phase this is the equation. If I assume that the vapor and the liquid phases are in equilibrium the vapor and liquid phases are in equilibrium, when is it possible? We know we have already framed the conditions of equilibrium for the 2phases in terms of fugacity we have already done. The fugacity of each component must be same in all the phases or in other words this should apply.

If we write it down in terms of pure components this particular function should apply at low to moderate pressures I have already mentioned at low to moderate pressure what happens? fi v equals to total pressure over the mixture, fi L is equal to the saturated vapor pressure of the pure component at the temperature of the mixture, so it is Pi saturated at the temperature of the mixture. So on substituting these, what do I get? I get at low to moderate pressure the equation for phase equilibrium reduces to this. This is the most important equation that we use for finding out the phase equilibrium problems and this along with the additional constraints that Sigma Xi should be equal to 1 and Sigma yi equals to 1 this whole set gives us the different phase equilibrium problems that we come across for 2 component systems of a 2 phase mixture, right?

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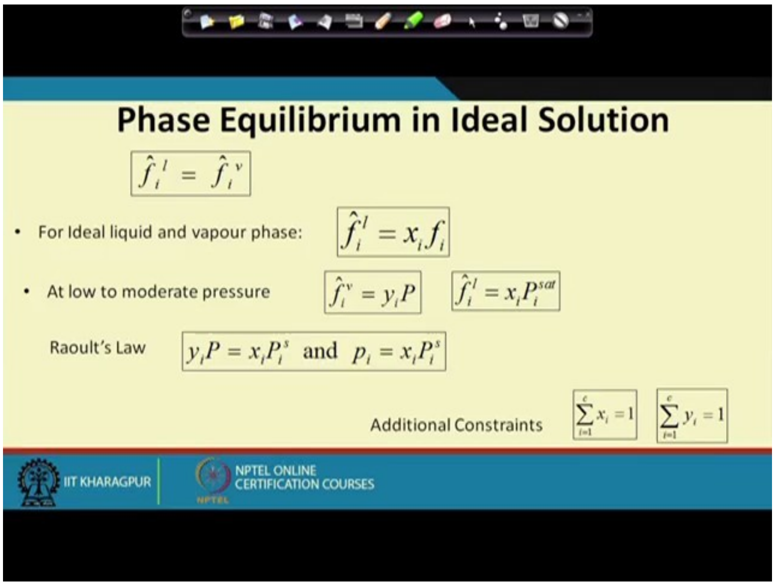

Phase Equilibrium in Ideal Solution

$$\boxed{\hat{f}_i^{\,l} = \hat{f}_i^{\,v}}$$

- For Ideal liquid and vapour phase: $\boxed{\hat{f}_i^{\,l} = x_i f_i}$
- At low to moderate pressure $\boxed{\hat{f}_i^{\,v} = y_i P}$ $\boxed{\hat{f}_i^{\,l} = x_i P_i^{sat}}$

Raoult's Law $\boxed{y_i P = x_i P_i^s \text{ and } p_i = x_i P_i^s}$

Additional Constraints $\boxed{\sum_{i=1}^{c} x_i = 1}$ $\boxed{\sum_{i=1}^{c} y_i = 1}$

So in this particular case therefore if it's2 component then what are the, what is F? What is the minimum number of, what is the degree of freedom in this particular case?

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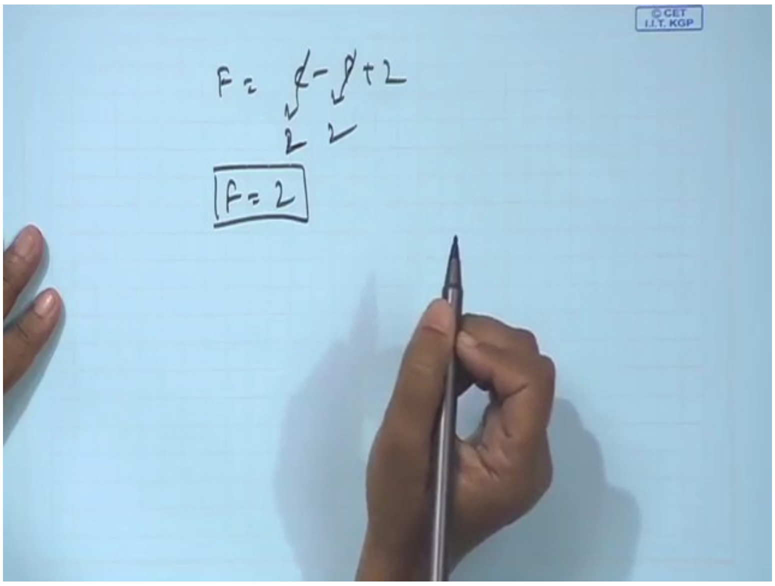

We know F equals to C minus P plus 2 this is 2 this is 2 so therefore F is also equal to 2, right? So therefore what are the total number of variables the temperature of the solution, the total pressure, the mole fractions in the liquid phase, mole fractions in the vapor phase.

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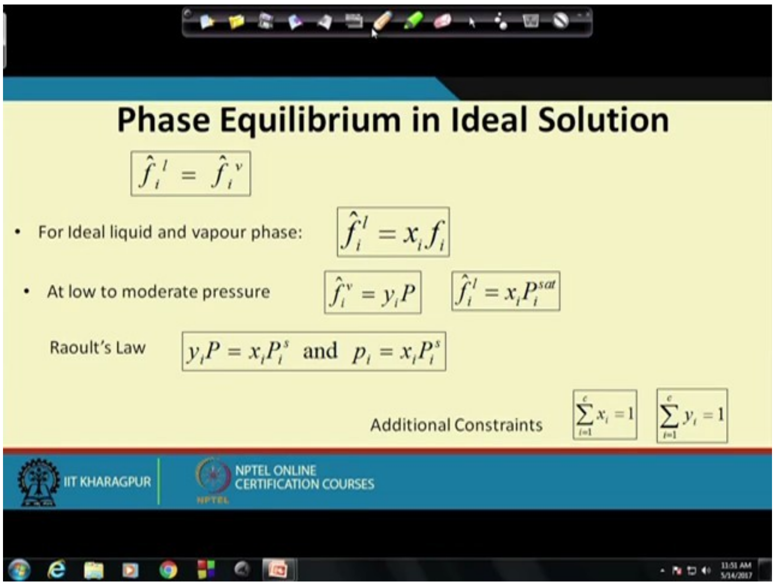

Phase Equilibrium in Ideal Solution

$\boxed{\hat{f}_i^{\,l} = \hat{f}_i^{\,v}}$

- For Ideal liquid and vapour phase: $\boxed{\hat{f}_i^{\,l} = x_i f_i}$
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Raoult's Law $\boxed{y_i P = x_i P_i^{s} \text{ and } p_i = x_i P_i^{s}}$

Additional Constraints $\boxed{\sum_{i=1}^{c} x_i = 1}$ $\boxed{\sum_{i=1}^{c} y_i = 1}$

And we know that x1 and x2 they are related by X2 equals to 1 minus X1 these 2 are related by y2 equals to 1 minus y2 these corresponds to this particular condition, right?

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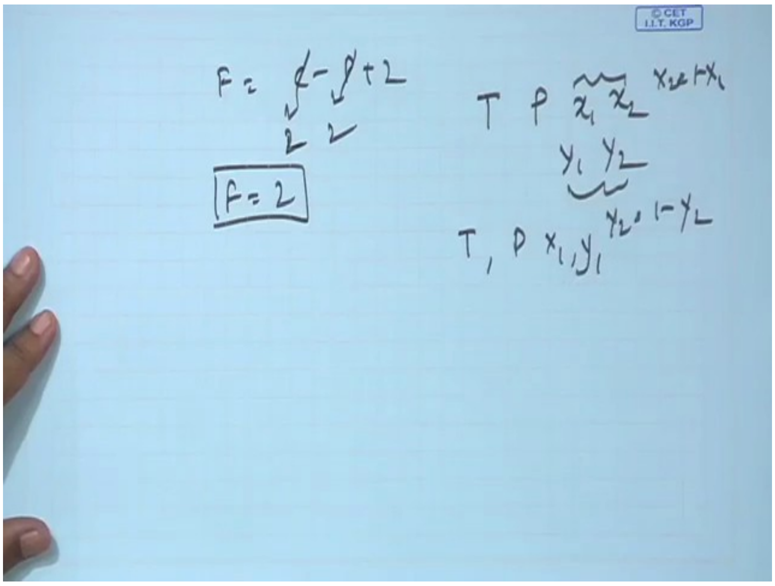

$$F = \underset{2}{c} - \underset{2}{p} + 2$$

$$\boxed{F = 2}$$

$$T \quad P \quad \overset{\sim}{x_1} \; \overset{\sim}{x_2} \quad x_2 = 1 - x_1$$

$$\underbrace{y_1 \; y_2} \quad y_2 = 1 - y_2$$

$$T, \; P \; x_1, y_1$$

So therefore these are related so therefore basically we have four variables out of these we know for a 2component system just 2 variables can be varied that will the other 2 automatically gets fixed up.

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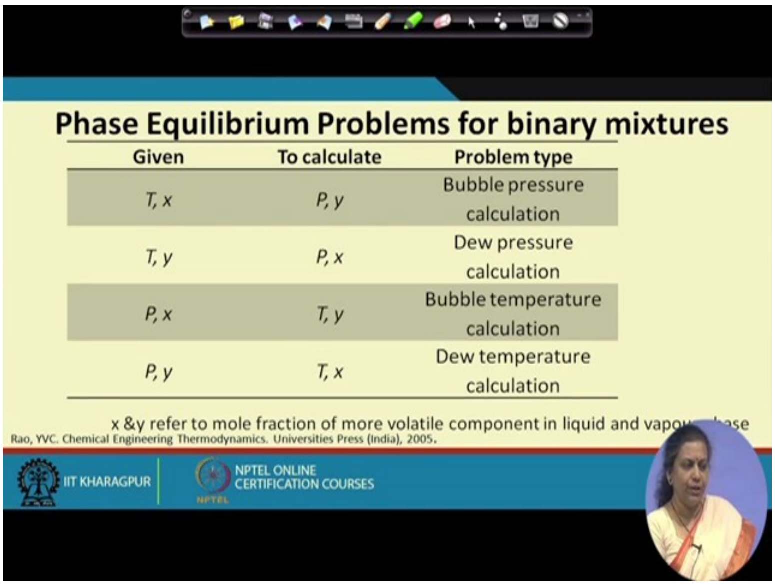

Phase Equilibrium Problems for binary mixtures

Given	To calculate	Problem type
T, x	P, y	Bubble pressure calculation
T, y	P, x	Dew pressure calculation
P, x	T, y	Bubble temperature calculation
P, y	T, x	Dew temperature calculation

x &y refer to mole fraction of more volatile component in liquid and vapour phase

Rao, YVC. Chemical Engineering Thermodynamics. Universities Press (India), 2005.

So what are the things that we can vary the different things which we can vary are, we can vary T and x. We can we have T and x we can vary P and y, we have T and y we can vary P and x and so on and so forth. So there therefore these are the 4 sets of things that we can vary and these are the 4 ways that we can vary the 2 variables and accordingly if we vary the 2 the other 2 has to be calculated accordingly. So before we do a number of problems the next thing which I would like to discuss are some phase diagrams for binary mixtures.

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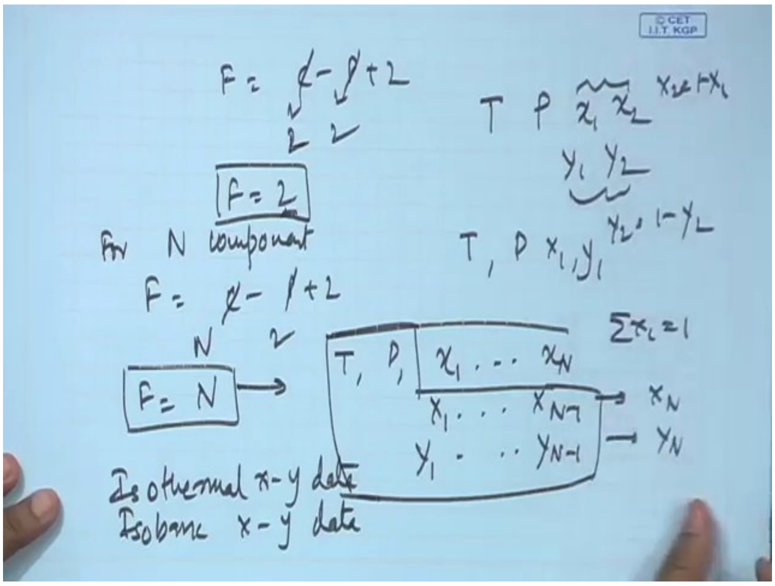

Well, before that it is important for you to note that for a binary mixture F was equal to 2. For n components n components what it becomes? F equals to C minus P plus 2 this is N this is 2 therefore F equals to N. So therefore for N number of components we find that the degrees of freedom is N and out of here we have T, P x1 to xN again bounded by the constraint of Sigma Xi equals to 1. So therefore X1 to XN minus 1 if I know then automatically I know XN and y1 to yN minus 1 which will automatically give me yN. So this is my range of variation out of which I can very just N number of components it can be the total N minus 1 composition's temperature, N minus 1 composition pressure or N minus 1 composition is in the vapor phase temperature, N minus 1 composition vapor phase at pressure.

So any of these permutation combinations are done usually they are done either at constant temperature or at constant pressure and accordingly we generate either isothermal xy data we will be doing a few problems or maybe isobaric xy data, right? And so therefore in the next class what we are going to do is, in the next class we are going to discuss the different phase diagrams primarily at constant temperature and constant pressure.

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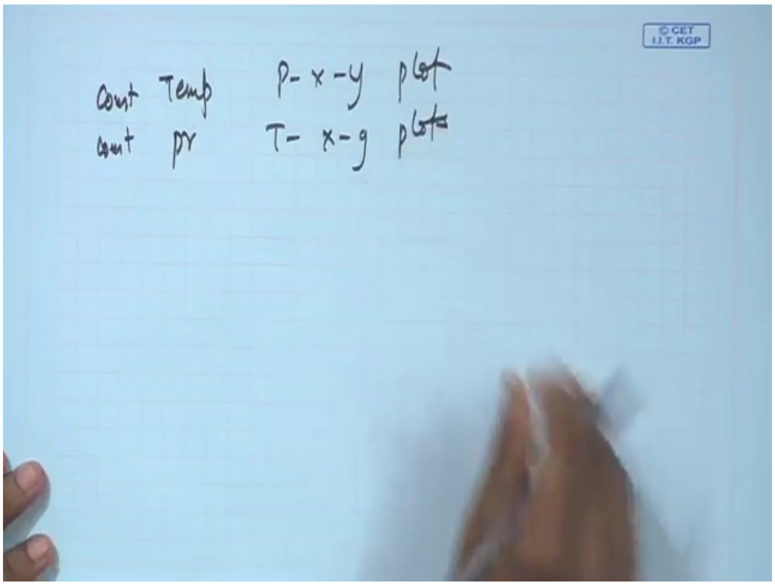

cont Temp P- x -y plot
cont pr T- x-y plots

At constant pressure temperature we generate the Pxy plot and at constant pressure we generate the Txy plots, we will be discussing these in the next class.