Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
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Indian Institute of Technology Kharagpur
Lecture No 36
Non Ideal solutions

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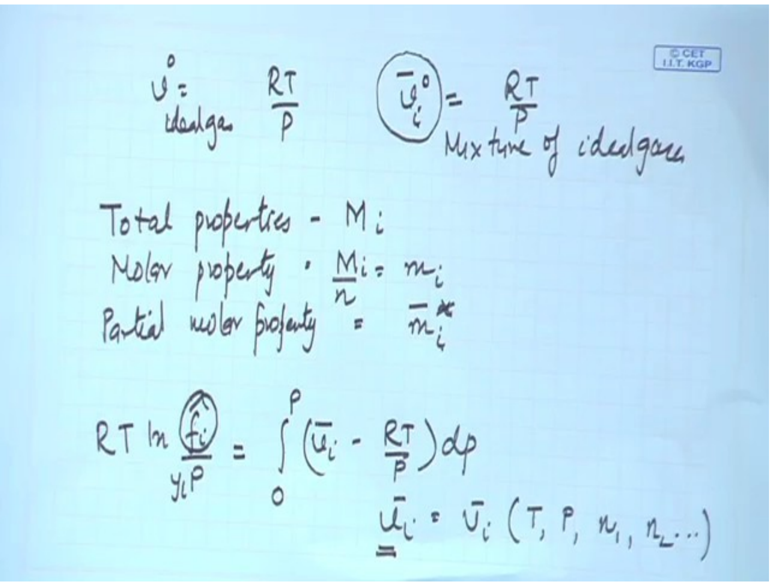

$v^{0}_{\text{idealgas}} = \frac{RT}{P}$ $\boxed{\bar{v}_i^{0}} = \frac{RT}{P}$

Mixture of idealgases

Total properties - M_i
Molar property : $\frac{M_i}{n} = m_i$
Partial molar property = $\bar{m}_i^{*}$

$$RT \ln \frac{\hat{f}_i}{y_i P} = \int_0^P \left(\bar{v}_i - \frac{RT}{P}\right) dp$$

$$\underline{\underline{\bar{v}_i}} = \bar{v}_i(T, P, n_1, n_2 \ldots)$$

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Well so to continue with your discussions, what did we observe in the last class? We observed that well to find out fugacity by using this particular equation, the equation I had already written down the equation, so we finding out fugacity by using this particular equation this was not at all very easy and so therefore this is the corrected this is the equation written properly. So therefore it was it was important to find out a simple model from which we can find out fi from known measurable parameters in terms of the composition.

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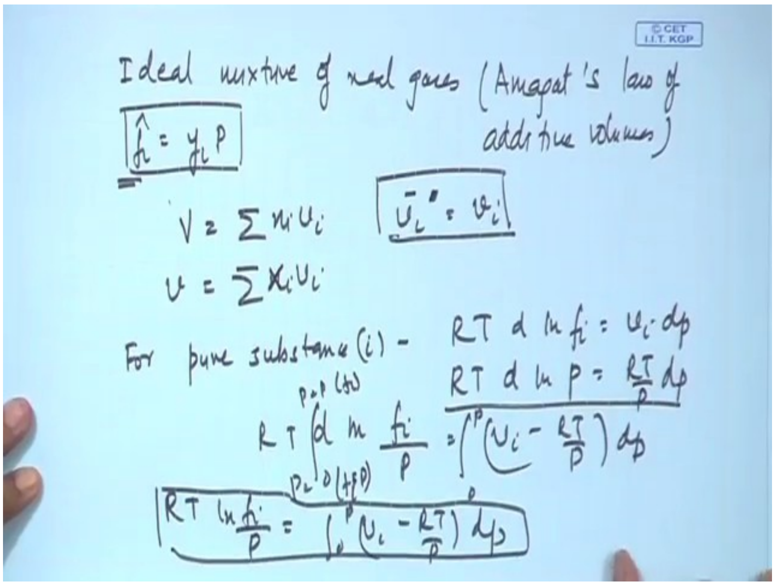

Ideal mixture of real gases (Amagat's law of additive volumes)

$$\boxed{\hat{f}_i = y_i P}$$

$$V = \sum n_i v_i \qquad \boxed{\bar{v}_i^0 = v_i}$$

$$v = \sum x_i v_i$$

For pure substance (i) - $RT\, d \ln f_i = v_i\, dp$

$$\underline{RT\, d \ln P = \frac{RT}{P}\, dp}$$

$$RT \int_{P=0\,(f=P)}^{P=P\,(f_i)} d \ln \frac{f_i}{P} = \int_0^P \left(v_i - \frac{RT}{P}\right) dp$$

$$\boxed{RT \ln \frac{f_i}{P} = \int_0^P \left(v_i - \frac{RT}{P}\right) dp}$$

So we found out that if we consider a mixture of ideal rather a yeah mixture of ideal gases then we know that fi bar is nothing but equals to yiP and this is too restrictive because it neglects the interaction between the molecules it tells us that that the interaction between the molecules is negligible which is quite restrictive particularly for dealing with liquid solutions. So then after that what we wanted to do we thought of doing let us go to an ideal mixture of real gases. Now what does this Amagat's law it suggests it basically suggests that the volumes can be added over the entire range of the volumes can be added over the entire range of pressure that we consider.

So therefore from here we know that the total volume of the mixture is nothing but equal to your nivi, okay. Or in other words we assume vi bar 0 equals to, it's not 0 it can be for a real gas that is equal to vi. So this on this particular bases we write down the total volume in terms of the molar volumes this Amagat's law of additive volume states or it states small v it it can be equal to xivi this is this is what it states.

Now suppose we use this particular assumptions or rather this particular consideration, let us see what is the expression of the partial molar fugacity that we get? Again we start from the very basics, suppose we have for a pure substance for a pure substance component i we can write it down as RT d ln fi the pure state so it is just a subscript nothing else this is equals to vidp and then in the ideal gas state it is P it is RT by P dp, right?

On subtracting what do we get? R T d ln fi by P equals to vi minus RT by P dp integral, sorry this integral and this is also integral, right? So therefore from there we get this integration is from P equals to 0 where fi equals to P to P equals to P where the value is fi, here the value of fi is equal to the total pressure, right? So therefore we get RT ln fi by P equals to integral 0 to P vi minus RT by P dp this is what we get for a pure substance, a pure component i.

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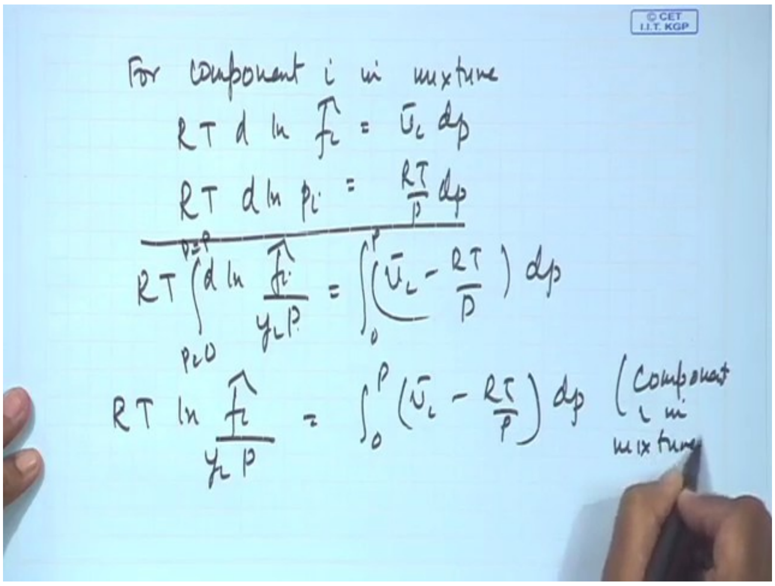

For component i in mixture

$$RT\, d \ln \hat{f}_i = \bar{v}_i\, dp$$

$$RT\, d \ln p_i = \frac{RT}{p}\, dp$$

$$RT \int_{p=0}^{p=P} d \ln \frac{\hat{f}_i}{y_i P} = \int_0^P \left(\bar{v}_i - \frac{RT}{p}\right) dp$$

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Now let us see what do we get for this same component i in mixture? For component i in mixture, what do we get you tell me? In this particular case this becomes R T d ln fi this is equals to vi bar dp and R T d ln Pi this is equals to RT by P dp, we know it. On subtraction what do we get? We get RT d ln fi by yiP is nothing but equals to vi bar minus RT by P dp if we integrate it again from P equals to 0 where fi bar equals to yi by P2P equals to P where fi bar equals to fi this side also 0 to P, what do we get? We get R T ln fi by yiP equals to integral 0 to P vi bar minus RT by P dp, this was for component i in mixture.

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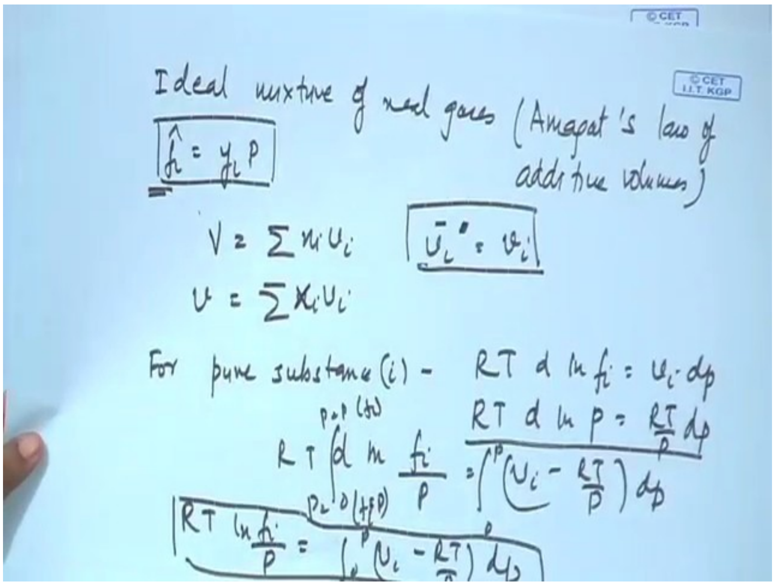

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$$\boxed{RT\ln\frac{f_i}{p} = \int_0^{p}\left(v_i - \frac{RT}{p}\right)dp}$$

And for the pure component i what do we get? I have just now derived for pure component i in the derivations i is here.

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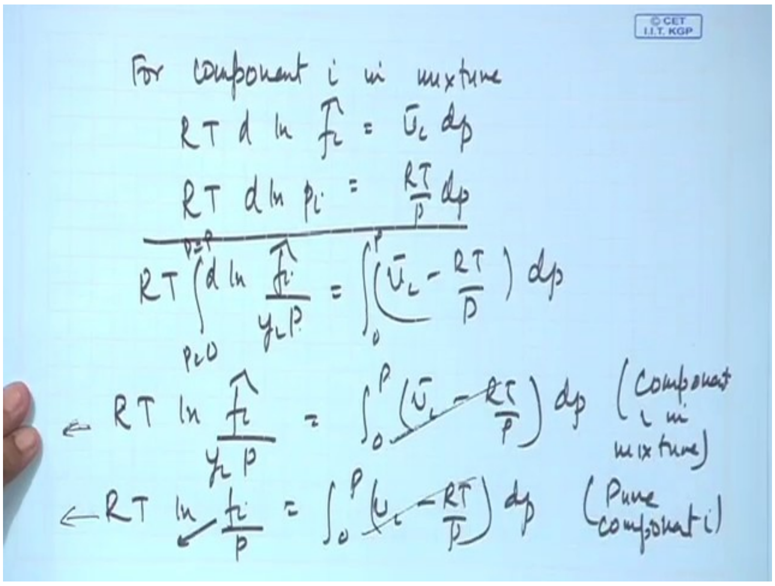

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$$\leftarrow RT\ln\frac{f_i}{P} = \int_0^{P}\left(v_i - \frac{RT}{P}\right)dp \quad \text{(Pure component i)}$$

So for the pure component i what do I get RT ln fi by P where fi this is vi minus RT by P dp and what is this fi equals to? This fi is the fugacity of pure component i, one thing we need to remember very well this fi bar fi everything is evaluated at the conditions of temperature and pressure remaining same. It for both the cases the pressure is P and the entire integration this and this have been done at constant temperature only when the pressure and temperature conditions of this equation and this equation are the same then we can combine the two.

Suppose this particular gas mixture it obeys Amagat’s law of additive volume than what was the Amagat’s law of additive volume I have already written down it's vi bar equals to vi. So therefore if it obeys the Amagat’s law of additive volume then this term and this term they cancel out.

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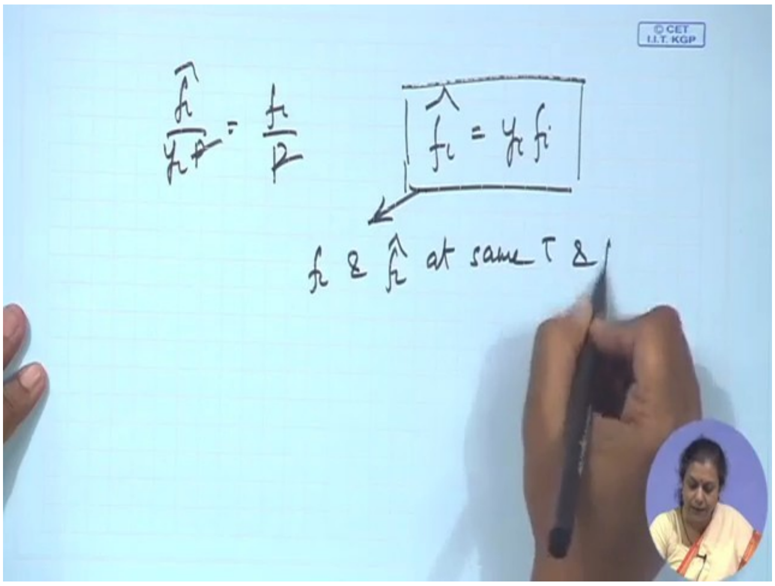

$$\frac{\hat{f}_i}{y_i P} = \frac{f_i}{P}$$

$$\boxed{\hat{f}_i = y_i f_i}$$

f_i & $\hat{f}_i$ at same T &

And then ultimately what do we get? We get on cancellation we get fi by yiP equals to fi by P or in other words the partial molar fugacity of component i in a mixture is nothing but equal to the mole fractions times the molar or rather the fugacity of component i in the pure state at the same temperature and pressure as that of the mixture. So therefore this is applicable we find this has been derived from Amagat’s law of additive volume this is applicable provided fi and fi bar at same T and P, right?

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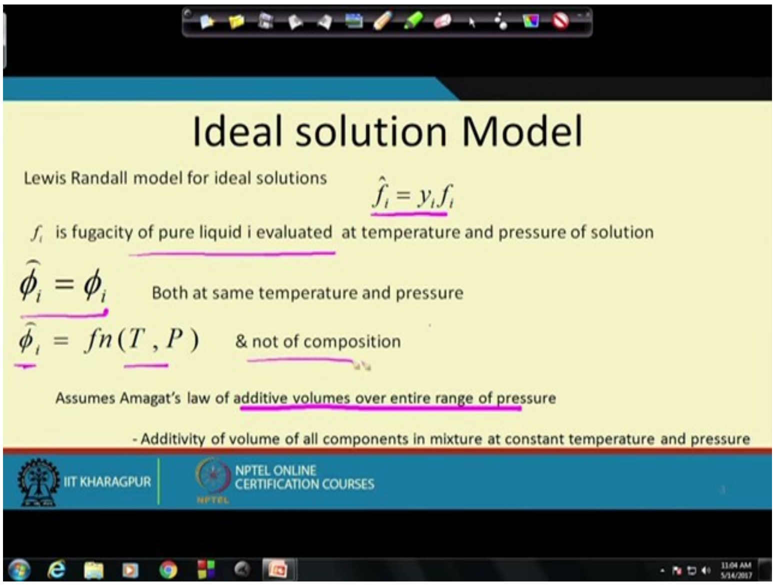

Ideal solution Model

Lewis Randall model for ideal solutions $\hat{f}_i = y_i f_i$

f_i is fugacity of pure liquid i evaluated at temperature and pressure of solution

$\hat{\phi}_i = \phi_i$ Both at same temperature and pressure

$\hat{\phi}_i = fn(T, P)$ & not of composition

Assumes Amagat's law of additive volumes over entire range of pressure

- Additivity of volume of all components in mixture at constant temperature and pressure

So therefore what is fi then in this particular case? I have written down the ideal solution model here, this is ideal solution model where what is fi equals to? Just remember it is fugacity of pure liquid i evaluated at temperature and pressure of solution. The only thing we need to know that this fi cap and fi are evaluated at the same conditions of temperature and pressure. Accordingly from this suppose I express fi bar by pi equals to fi bar and so therefore we know for the ideal solution model phi I phi i bar equals to phi i both being at the same temperature and pressure which automatically implies that the partial molar fugacity coefficient it is a function just of temperature and pressure it is not a function of composition which is quite restrictive assumption.

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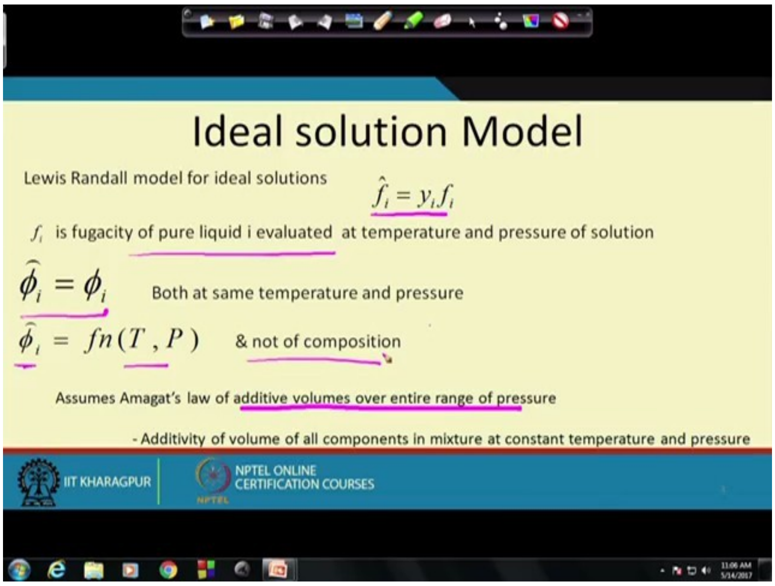

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Yet we find that from this particular restrictive assumption it is although it is restrictive it gives us a very simple equation a very simple model which tells us that the partial molar fugacity of component i in a mixture or in a solution is the mole fraction of that particular component in solution times the fugacity of that component in the pure state at the conditions of same temperature and pressure as that of the solution and finding out pure component and finding out your component fugacities in the in for a real gas for a liquid these I have already been discussed and those particular equations can be used to find out fi. Once we know fi we know the composition of the mixture of the solution we can find out fi bar. So therefore this particular rule for this particular law this was first suggested by Lewis M Randall and therefore it is known as the Lewis Randall model for ideal solutions.

Now here it is very important to note that it is less restrictive as compared to each of ideal gases, right? What does it assume? It is applicable when is, just try to understand it is applicable for a situation where the intermolecular attractions between unlike molecules are similar to the intermolecular attraction between like molecules. For example suppose I have a binary mixture most of my discussions will be in terms of binary mixture just because it is easier to conceive that and so that for a binary mixture there are say 2 components, component a and component b the Lewis Randall model will be applicable when the interactions between aa molecules and the interaction between bb molecules and the interaction between ab molecules are similar in nature, right?

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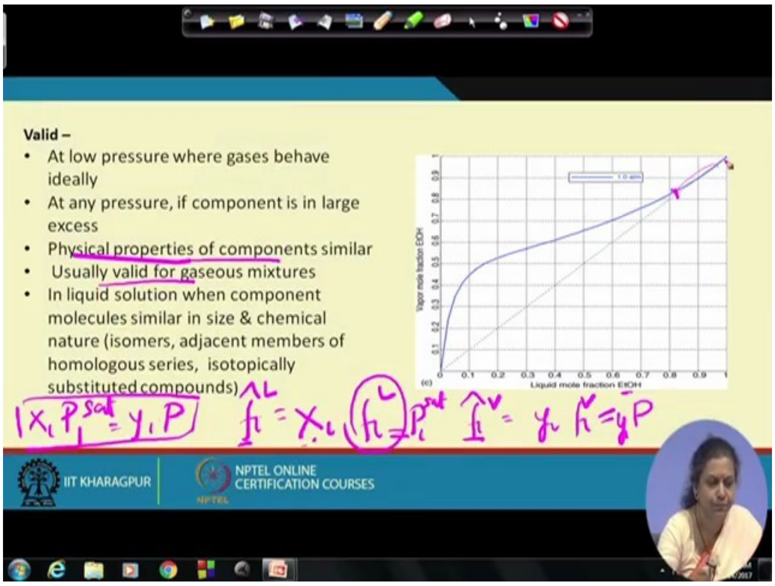

Valid –

- At low pressure where gases behave ideally
- At any pressure, if component is in large excess
- Physical properties of components similar
- Usually valid for gaseous mixtures
- In liquid solution when component molecules similar in size & chemical nature (isomers, adjacent members of homologous series, isotopically substituted compounds)

$\boxed{x_i P_i^{sat} = y_i P}$ $\hat{f}_i^L = x_i f_i^L = P_i^{sat}$ $\hat{f}_i^V = y_i f_i^V = y_i P$

So when does this happen? This can happen only for conditions this can happen under what conditions the first condition is when the physical properties of the components they are similar this is number 1, number 2 is when the chemical components they are also similar this is something very important and we know that, see whenever any component is in excess what happens? Suppose again a mixture of a and b they were large excess of a there we add some amount of a.

So therefore a feels at home in the environment of a there is very less b. So therefore whenever we find that at any particular pressure if the component is in large excess it obeys the Lewis Randall rule. We know that at low pressure gases behave ideally so they normally they obeyed the Amagat's law of additive volume. So for gases at low-pressure it is applicable usually it is valid for all gas mixtures and we find that at any pressure if the component is in large excess it obeys the Lewis Randall rule. This is evident from this particular figure where I have plotted the vapor mole fraction as function of the liquid mole fraction.

What do I find? We find that at, when the mole fraction of this particular component it's close to 1 we find that more or less, the Lewis Randall rule it is valid under this particular condition. For this particular case I can write down the fi bar this is equal to yi fi but let me remind you that this is done for a for a very low pressure. Now for low pressures what happens? For low pressures we know that fi it is equal to the total pressure of the component in the vapor phase, right?

So therefore if it is a vapor it is a pure component vapor then we know that this particular fiv is nothing but equal to the total pressure of the system. What about the liquid composition? In the liquid phase we have this fiL this will be equal to xi fi L. Now if you recall at low to moderate pressure what happens to this particular fiL this becomes when the poynting correction factor and the correction factor due to non-ideality of the of the gas, so the vapor phase is there it can be neglected this reduces to pi saturated, right? So therefore from here what do we get? Under equilibrium conditions we know fiL equals to fiv so for low to moderate pressures what do I get?

The equation becomes something like xiPi saturated equals to yi into P and I guess this equation, all of you already know you are aware of it you have been doing this from your school days this is nothing but the Raoult's law, right? So therefore under what conditions are these applicable? I repeat at low pressure for gases we behave ideally this is usually valid for gaseous mixtures it is valid for any pressure if the component is in large excess when we find that the component is in large excess then the linearity is maintained in this particular condition.

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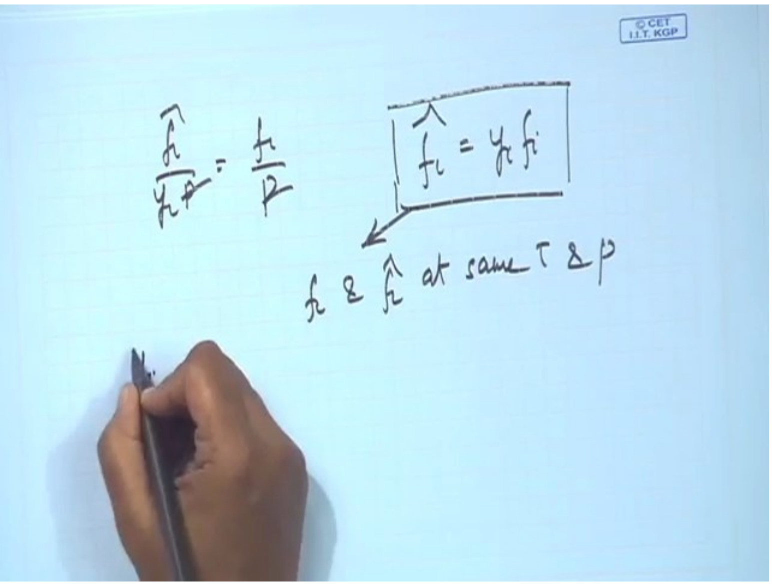

And we also notice for this particular condition we find that more or less the can write it down as your fi bar it is proportional to the composition of the mixture and we know that for when the when the component is in large excess for this particular portion more or less this particular proportionality constant this is equals to the fugacity of the pure component situation.

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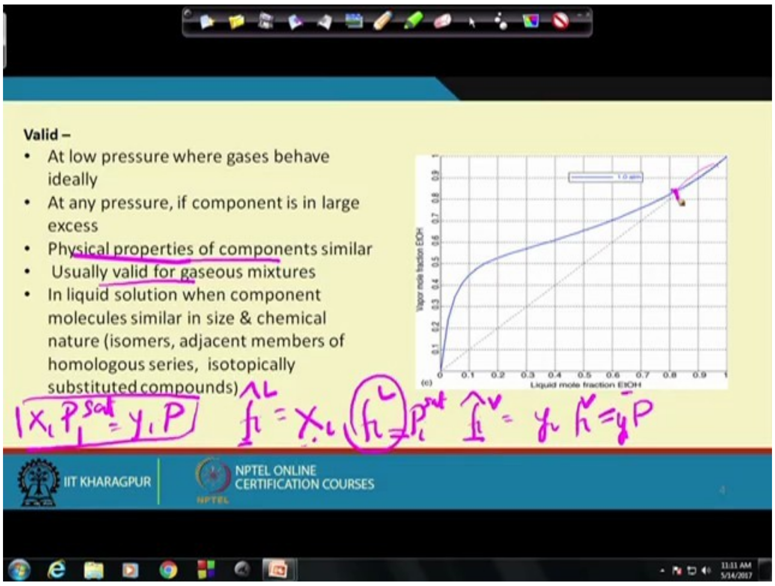

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Now before I proceed I would just like to bring your attention to another particular aspect of this graph, what do we observe? We observe that the graph it exhibits some sort of a deviation from Lewis Randall rule which we will be discussing later this is an, this shows that it exhibits non-ideal behaviour over a large range of composition we are not going to deal with it at the moment. At the moment we will just be dealing with the ideality portion. We find that it is ideal under this particular condition.

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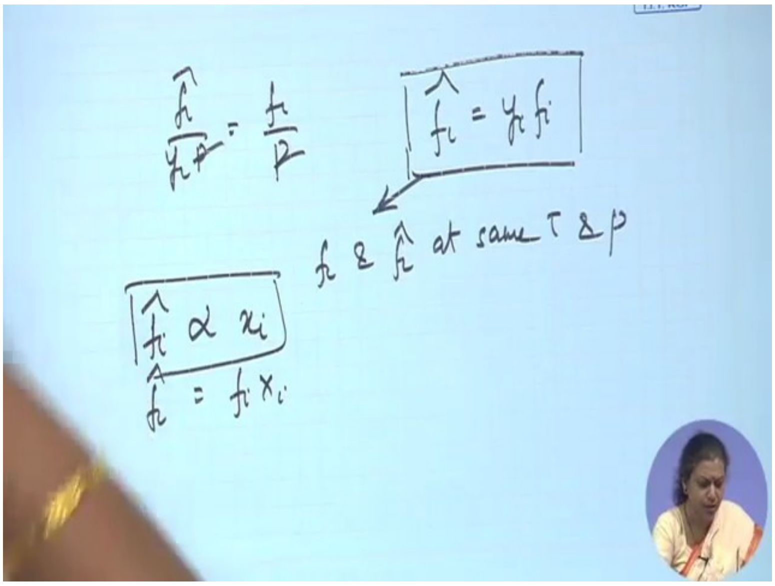


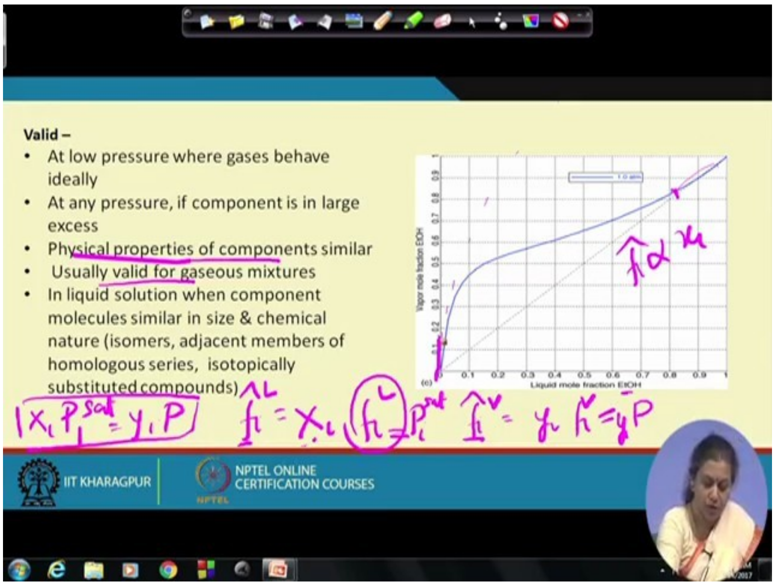
$\frac{\hat{f}}{y_i P} = \frac{f_i}{P}$ $\boxed{\hat{f}_i = y_i f_i}$

f_i & $\hat{f}_i$ at same T & P

$\boxed{\hat{f}_i \propto x_i}$

$\hat{f}_i = f_i x_i$

Here the relationship is linear and we know that this particular relation holds under that condition, right?



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So therefore for this particular condition we can write fi bar is proportional to xi, fine. Now let us notice the other extreme when the when the component is in very less amount. Just observe this portion we find that in this case the slope or the nature of the curve is completely different as compared to this case but if you slightly extrapolate this thing you will find that and if you keep on extrapolating this we find that in, at very low concentration that that when the concentration is almost equal to 0 under that condition also there is the linearity part holds.

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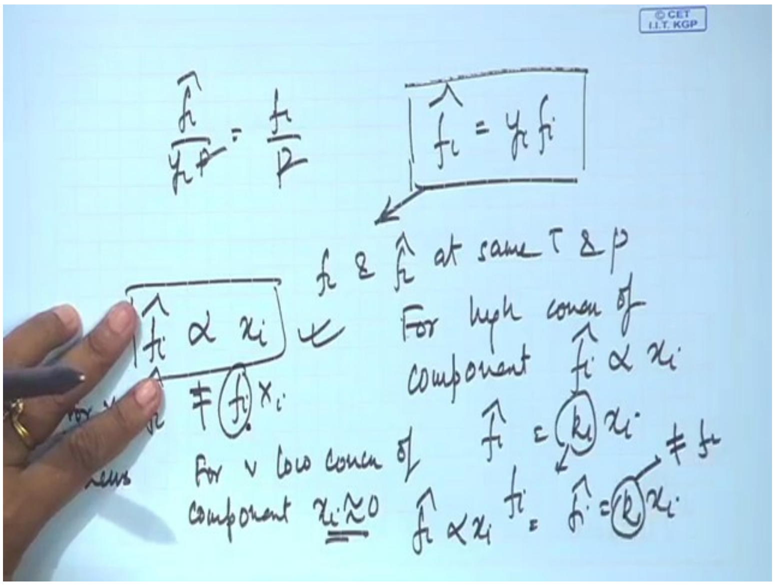

$\frac{\hat{f}_i}{y_i P} = \frac{f_i}{P}$ $\boxed{\hat{f}_i = y_i f_i}$

f_i & $\hat{f}_i$ at same T & P

$\boxed{\hat{f}_i \propto x_i}$ $\neq f_i x_i$

For high concn of component $\hat{f}_i \propto x_i$

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

For v low concn of component $x_i \approx 0$ $\hat{f} \propto x_i$ $\hat{f}_i = k_i x_i$

Or in other words this equation this equation holds under that case but for very low concentrations the linear the proportionality constant is not equal to the pure component fugacity at the temperature and pressure of the mixture. So therefore we know that for high concentration of component for high concentration of component f the partial molar fugacity is proportional to the mole fraction or fi bar equals to ki xi this ki is nothing but equal to the pure component fugacity.

We also know that for very low concentration of the component means a xi is almost equal to 0 under that condition also we find fi bar is proportional to xi but in this particular case or in other words fi bar equals to ki xi but in this particular case this ki is not equal to fi. On the other hand this is some other proportionality constant which is known as the Henry's constant or it gives the Henry's law for in infinitely dilute solution.

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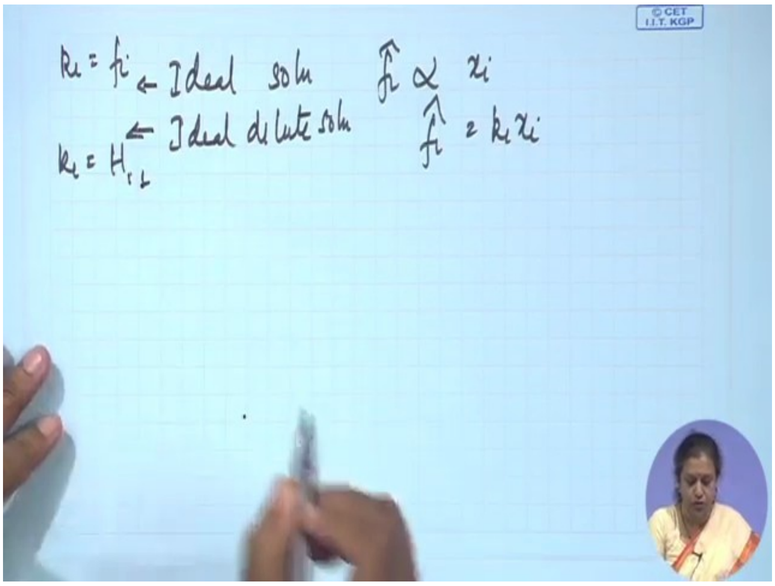

$k_i = f_i \leftarrow$ Ideal soln $\quad \hat{f_i} \propto x_i$

$\leftarrow$ Ideal dilute soln $\quad \hat{f_i} = k_i x_i$

$k_i = H_{i,L}$

So therefore we have the ideal solution which gives you and the ideal dilute solution for both the cases what do we have? fi bar is proportional to xi but for ideal solution or in other words fi bar equals to ki xi but for ideal solution ki equals to the pure component fugacity. For ideal dilute solution it is the Henry's constant of component i in the in the solvent. So this is something very important which I wanted to show you.

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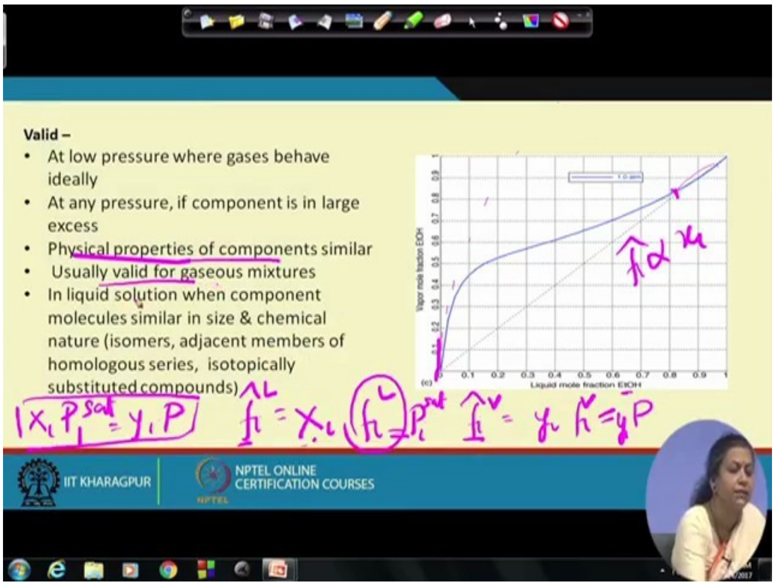

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$\hat{f} \propto x_1$

Well, what about the other thing? We found out then it is usually valid for gaseous mixtures as I have mentioned. It is rarely valid for liquid solutions because remember one thing what is the basis of the Lewis Randall rule the Amagat's law of additive volume. What is the basis of Amagat's law of additive volume? It assumes that the interactions between the molecules are same when it is in the pure state as well as in the solution this is quite applicable for gaseous mixtures where in any case the interactions are very weak. So therefore for gaseous mixtures very safely you can assume the Lewis Randall rule even if the gases are not ideal remember the basis is ideal mixture of real gases it is not an ideal mixture of ideal gases.

But for liquid solutions where the interactions are very important, for very few situations you will get that interactions between like molecules is similar to the interaction between the unlike molecules or in other words interactions between aa molecules and bb molecules will be different from the interaction between ab molecules for most of the cases of a binary solution of a and b, right?

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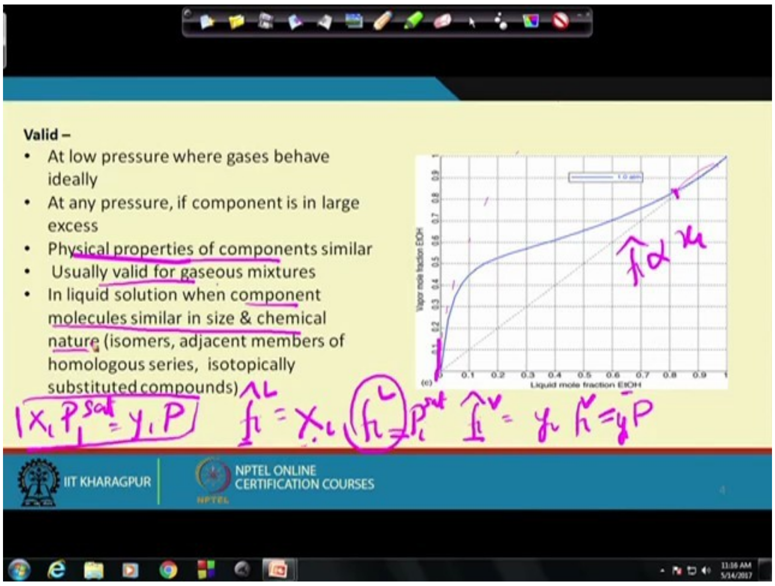

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$\hat{f} \propto x_i$

So therefore in this particular case we find that in liquid solutions Lewis Randall rule it is applicable when you find that the component molecules are similar in size and in chemical nature. For example isomers, adjacent members of a Homologues series for example benzene toluene mixture or heptane hexane for such mixtures it is applicable and also for isotopically substituted compounds.

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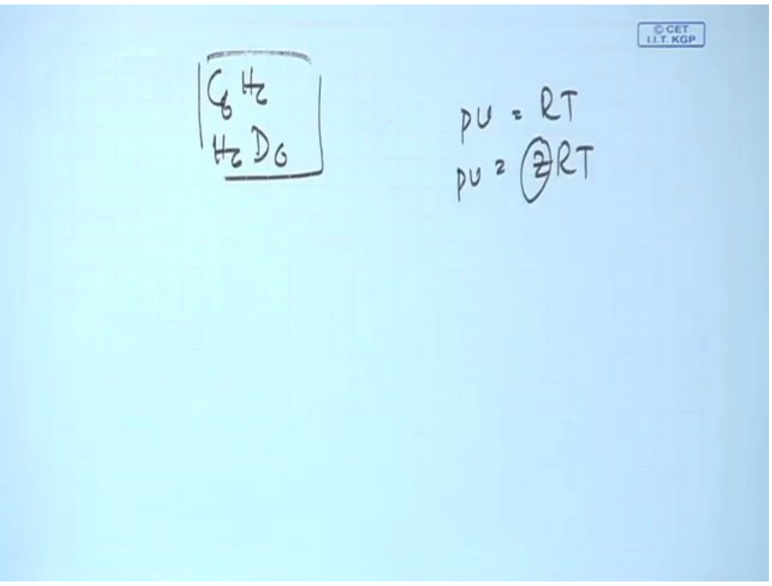

$\boxed{C_6H_6 \\ H_6D_6}$

$pv = RT$

$pv = \textcircled{z}RT$

For example suppose you have C_6H_6 H_6D_6 deuterium, so for such types of things only the ideal solution model is applicable for most of the cases it is not applicable but we need to remember just like ideal gases ideal gas equation it is not applicable for most of the cases yet we have it and when the gas deviates from ideality we have tried to incorporate some sort of a correction factor in order to incorporate the deviation from ideality.

We had incorporated the compressibility factor the normal ideal gas equation for one mole of the gas was this and for a real gas we suggested equation in this form where z is a correction to the to the ideal gas equation to take into account the real gas behaviour. In this particular case also knowing fully well that it may not be applicable for liquid solutions we consider the ideal solution model we are going to discuss the characteristics of ideal solution model and once we have understood ideal solution model we would try to see what are the corrections and in what way the corrections can be incorporated into the ideal solution model to account for the behaviour or to account for the non-ideal behaviour, right?

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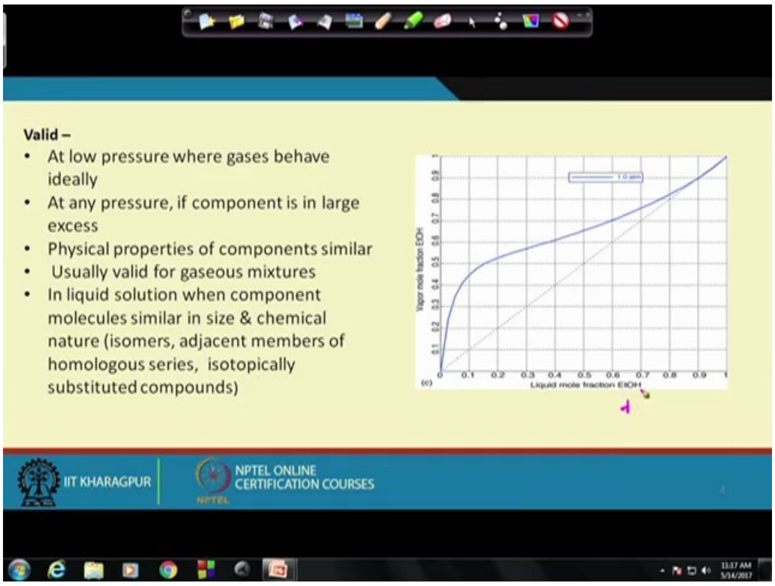

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So therefore let us discuss the properties of the ideal solutions before we proceed. So therefore what are the different ideal properties of ideal?

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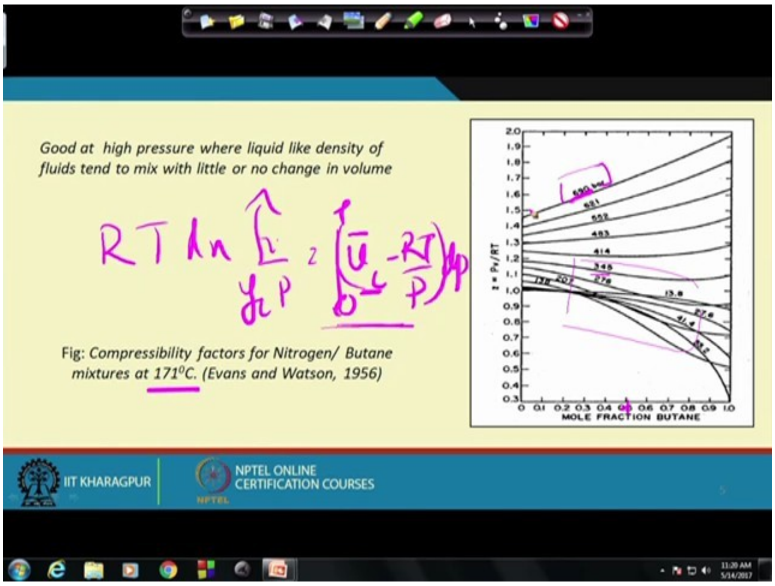

Good at high pressure where liquid like density of fluids tend to mix with little or no change in volume

$$RT \ln \frac{\hat{f}_i}{y_i P} = \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right) dp$$

Fig: Compressibility factors for Nitrogen/ Butane mixtures at 171°C. (Evans and Watson, 1956)

There is one interesting thing which I would like to say well, this is something very interesting that usually we feel that when the gas is at higher pressure where it exhibits liquid like density the fluids they tend to mix with little or no change in volume there is quite evident. So we are all always tempted to think that therefore when the gas is at high pressure then it should be opening Lewis Randall rule and therefore we can apply Lewis Randall rule for gases at high pressure.

Although at the first thought it seems to be probable or seems to be correct, at second thought we are reminded that this is not always correct, why? If we observe this graph what do we see this is a compressibility factor chart for Nitrogen Butane mixture at 171 degree centigrade, what do we find? That at 690bar more or less we find that it is a linear function. So therefore we are tempted to think that well at 690 bar we can use the Lewis rule because under is particular condition vi is linear function of mole fraction.

But we have we need to remember that the v is inside the integral. If you remember the equation is R T d ln fi by yi P which is equal to 0 to P vi bar minus RT by P dp this particular vi bar it is inside the integral sign, right? So therefore it is important that vi bar or the Amagat's law should not only be obeyed at 690 bar it should be obeyed from 0 pressure to 690 bar pressure. At 690 bar the Amagat's law is valid, right?

So therefore you can you might think at 690 bar we can use it but if you slightly come to lower and lower pressures you find that below 345 bar the linear variation or the additive property of volume is no longer applicable in this particular case. So therefore in this particular zone if you find in this particular zone we will find that the additive the additive property it fails completely but at the same time we need to remember that we want the additive property to be valid right from 0 pressure to 690 bar pressure.

So therefore just being applicable or just obeying the Amagat's law of additive volume at any pressure does not guarantee that that we can use the Lewis fugacity rule at that pressure because for using the Lewis fugacity rule we need to consider this particular integral where the volume is inside the integral sign and therefore the law of additive volume is required to be followed not only at the pressure of interest but over the entire range of pressure from 0 to the P. So therefore this has to be considered with caution.

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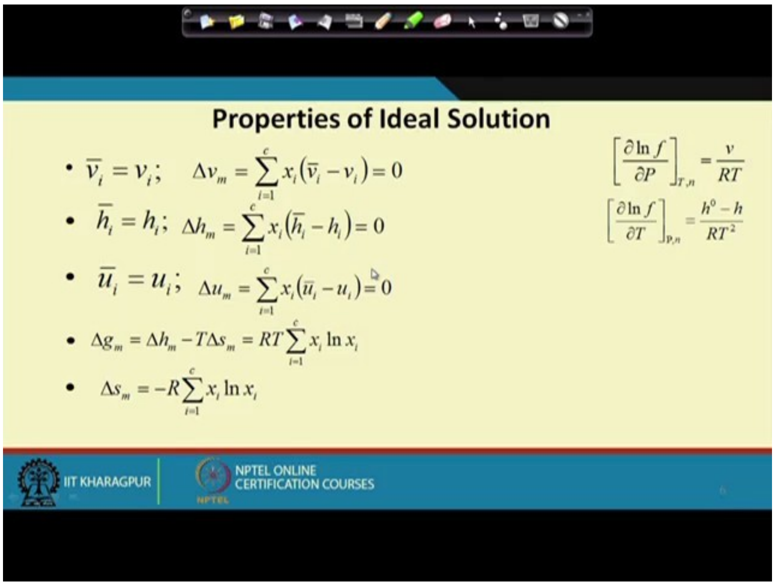

Properties of Ideal Solution

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

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

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

Well, so now let us come to the property of, what are the properties of ideal solutions? Let us see we have already assumed that it the mixture it satisfied the Amagat's law of additive volumes.

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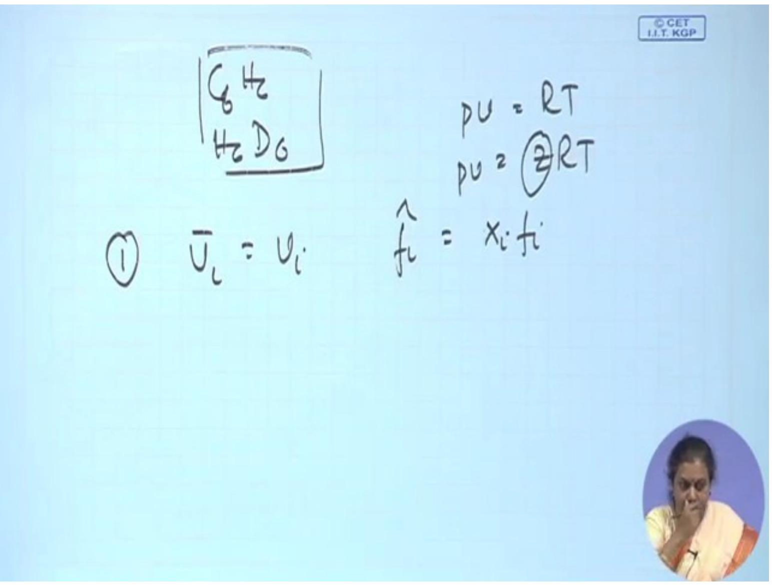

C_6H_6

H_6D_6

$pv = RT$

$pv = \circled{z}RT$

① $\bar{v}_i = v_i$

$\hat{f}_i = x_i f_i$

What is that particular law? It is vi bar equals to vi, fine. What is the Lewis fugacity rule? It is fi bar equals to Xi say fi, fine.

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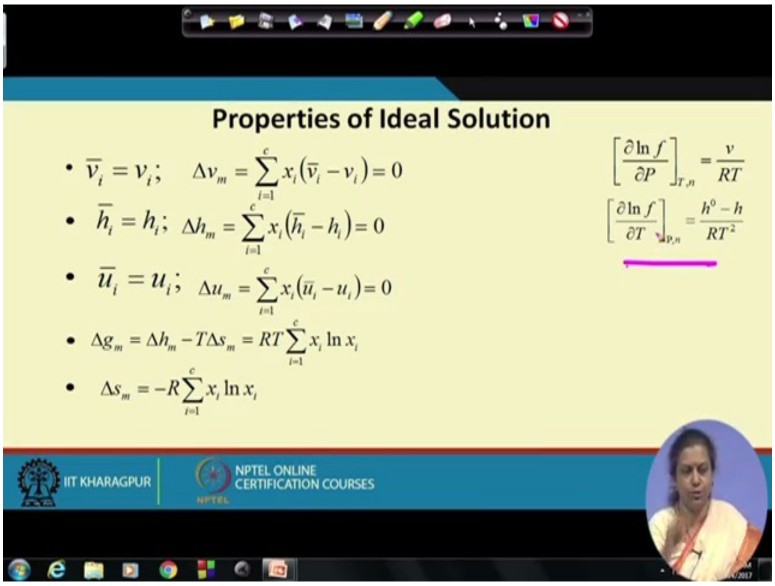

Properties of Ideal Solution

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

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

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

Now if you recall in the last class we had or maybe in few classes back we had tried to we had we had found out the variation of fugacity with pressure and the variation of fugacity with temperature.

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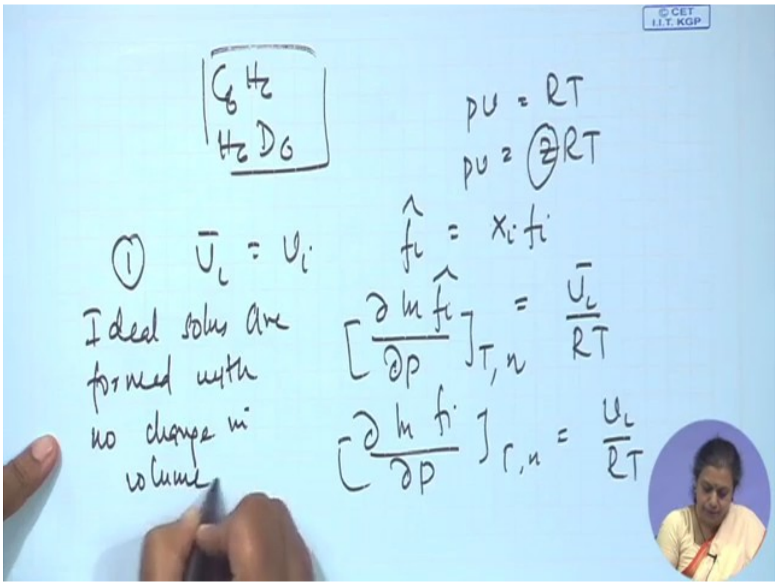

C_6H_6
C_6D_6

$pv = RT$

$pv = \boxed{z}RT$

① $\bar{v}_i = v_i$

Ideal solns are formed with no change in volume

$\hat{f}_i = x_i f_i$

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

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

There what did we found? We found out that del ln fi del P at constant T and total mixture this would be equal to vi bar by RT is same way from using this equation we can write down del ln fi del P at constant T, n this is nothing but equals to vi by RT, so we know that if vi bar equals to vi from where we got the equation. So therefore the first property is that ideal solutions are formed with no change in volume. So therefore there is no change in volume when ideal solutions are formed, right? What are the other properties? We will be discussing the other properties in the next class?