Course on Phase Equilibrium Thermodynamics
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Lecture No 40
Non Ideal solutions

Well, to continue with your discussions on solutions you will recall that in the last class we had discussed ideal solutions and there are several properties of ideal solutions that we said and for instance we had said that suppose we have for ideal solutions we had the things that we had shown for ideal solutions if you recall we had plotted the partial pressure versus partial pressure and the total pressure versus the mole fraction, right?

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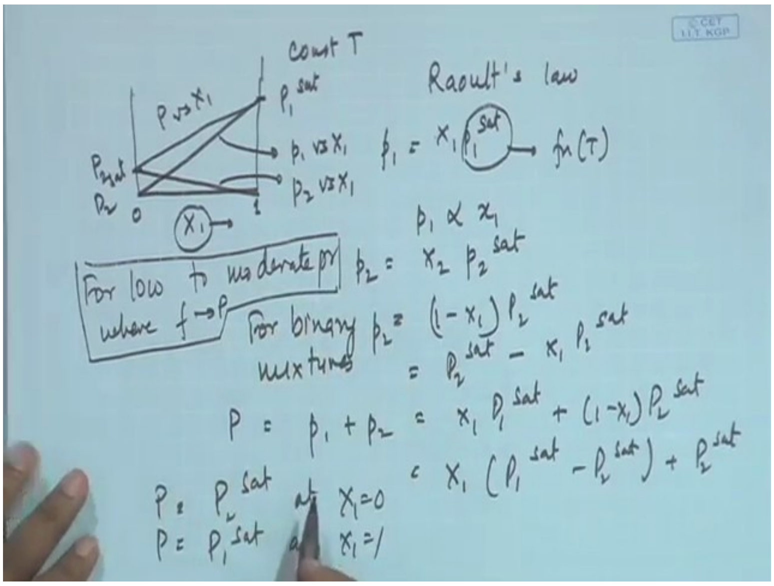

Raoult's law

$p_1 = x_1 \boxed{P_1^{sat}} \rightarrow fn(T)$

$p_1 \propto x_1$

For low to moderate pr where $f \rightarrow P$

$p_2 = x_2 P_2^{sat}$

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

$= P_2^{sat} - x_1 P_1^{sat}$

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

$= x_1 (P_1^{sat} - P_2^{sat}) + P_2^{sat}$

$P = P_2^{sat}$ at $x_1 = 0$

$P = P_1^{sat}$ at $x_1 = 1$

And what did we find? Please remember whenever we are plotting for this class this is not a standard convention for this class just to avoid any confusion we would like to plot the mole fraction of the more volatile component in the x-axis with that we plot the partial pressure of component 1, partial pressure of component 2 and the total pressure over the solutions. Now since this is a more volatile component, what do you expect?

Naturally the saturated vapor pressure of component 1 will be higher as compared to the saturated vapor pressure of component 2. So therefore we find that at X1 equals to 1, suppose this is P1 saturated then for X1 equals to 0 this is going to be say P2 saturated and we know that for ideal solutions what is the what is Raoult’s law for ideal solutions? Just to recollect that Raoults law is just the Lewis Randall rule for low to moderate pressure where the fugacity term can be replaced by pressure, right?

So the Raoult's law, if we write it down the Raoult's law for ideal solutions this was X1 P1 saturated this was equals to P1. So since we know that this particular P1 saturated this is nothing but the function of temperature and this particular plot, this is done under constant temperature conditions. So naturally P1 saturated becomes fixed as a result of which what do we find? We find that P1 is proportional to X1, right?

In the same way what is P2? This is nothing but equals to X2 P2 saturated, what is X2? Remember we are dealing with binary mixtures. So for binary mixtures P2 equals to 1 minus X1 into P2 saturated, so in this case also we know this is P2 saturated minus X1 P2 saturated. So in this case also we find that P2 it is inversely proportional to X1, right? So therefore if we plot say P1 as a function of X1, what do we expect?

We expect to get a linear plot like this, right? This plot is P1 versus X1 same way if you are plotting P2 versus X1, what do you expect? We expect to get a plot like this; this plot is P2 versus X1, all these things we have discussed in the last class, fine. And what is the total pressure P equals to? It is obviously P1 plus P2, what is it? It is X1 P1 saturated plus 1 minus X1 P2 saturated which gives you as X1 P1 minus P2 saturated plus P2 saturated, so what does it imply?

The curve of P versus X1 that should (ha) that should have an intercept of P2 saturated at X1 equals to 0 or in other words P equals to P2 saturated at X1 equals to 0. P equals to P1 saturated at X1 equals to 1. So therefore what does it imply? The P versus X curve should be a linear plot extending from P2 saturated to P1 saturated. So this was what we have obtained for an ideal solution if you recollect.

For again I would like to repeat that this whole thing was for low to moderate pressure where f can be replaced by the pressure term fine so therefore for this particular case we found out that this is the situation and this is the law which governs ideal solutions. Again I would like to repeat that we had already discussed that ideal solution model is applicable for solutions over a very rare narrow range of conditions if you recollect.

I had already mentioned the range of conditions for which ideal solution model is applicable and very frequently we come across as chemical engineers we come across solutions which are non-ideal and that can occur when the molecules are not similar in size, the intermolecular attraction between say aa and bb components it is not similar to the intermolecular attraction between ab components and so on and so forth this happens very frequently.

Now when this happens what do you expect? What are the things that you expect should happen? First thing is in that particular case can we directly write down just in this particular form.

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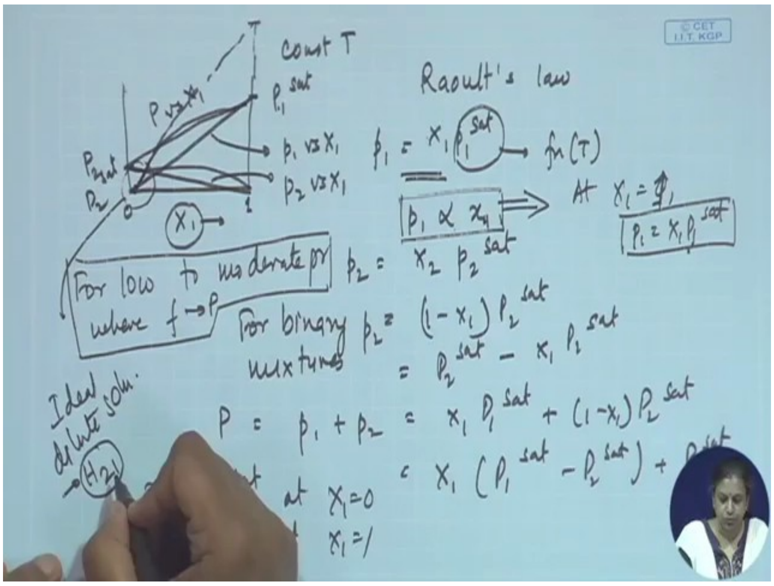

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$p_1 = x_1 P_1^{sat} \rightarrow fn(T)$

$\boxed{p_1 \propto x_1} \Rightarrow$ At $x_1 = 1$, $\boxed{p_1 = x_1 P_1^{sat}}$

$p_2 = x_2 P_2^{sat}$

For low to moderate pr where $f \rightarrow P$

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

$= P_2^{sat} - x_1 P_2^{sat}$

Ideal dilute soln.

H_2

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

$= x_1 (P_1^{sat} - P_2^{sat}) + P_2^{sat}$

at $x_1 = 0$

$x_1 = 1$

Can we write down this particular equation P1 is proportional to X1? This should not happen when it is in non-ideal solutions. So therefore what will happen? We find that there will be either the partial pressure will be greater than that calculated from the ideal solution model or it will be less than that calculated from the ideal solution model.

And remember one thing for every solution ideal or non-ideal at X1 equals to 0, we this particular equation is, at X1 equals to 1 when a component 1 is in excess we will always have P1 equals to X1 P1 saturated or in other case under that condition P1 always approaches P1 saturated. So far even for any non-ideal solution also for the excess component we find that the Raoult's law is applicable when the composition of the excess component approaches unity that is a universal truth that always happens.

So under ideal conditions also even if we have a negative or positive deviation from Raoult's law we will find that at the extreme cases under this particular condition Raoult's law will be applicable for component 1 it will also be applicable for component 2. I had also mentioned if you recollect that for very low concentrations under that condition also we will find P1 is proportional to X1 but under that condition as I told you the proportionality constant is not equal to the saturated vapor pressure of that particular component.

If if you if you extend this particular linear portion you will find that the intercept is at a different point as compared to P1 saturated and we had founded and we had told or rather we had termed this particular condition as an infinitely dilute ideal dilutes solution and for such ideal dilute solution we had found out that the proportionality constant it is equal to the Henry’s constant of component 2 in component 1 or vice versa.

So we have dealt with 2 types of ideal behaviours one was ideal solution where both the components obey Raoult's law when it is in excess quantity and ideal dilute solution this is particularly applicable for those particular components in solution which do not remain in the phase of the solution when it is in large excess, what do I mean? I mean say suppose carbon dioxide in water, what is the phase of the solution, liquid. Carbon dioxide when it is in much excess the solution does not remain in the liquid state. So therefore carbon dioxide does not remain in the phase of the solution and therefore for such situation we find that that ideal dilute solution is applicable for the solute part which is carbon dioxide and ideal solution model is applicable for the solvent part which is water in this case, right?

So therefore just like we have deviations from ideal solutions we will also have deviations from ideal dilute solutions the method of dealing with the deviation from ideality is the same for ideal solutions as well as for ideal dilute solutions, what do we observe?

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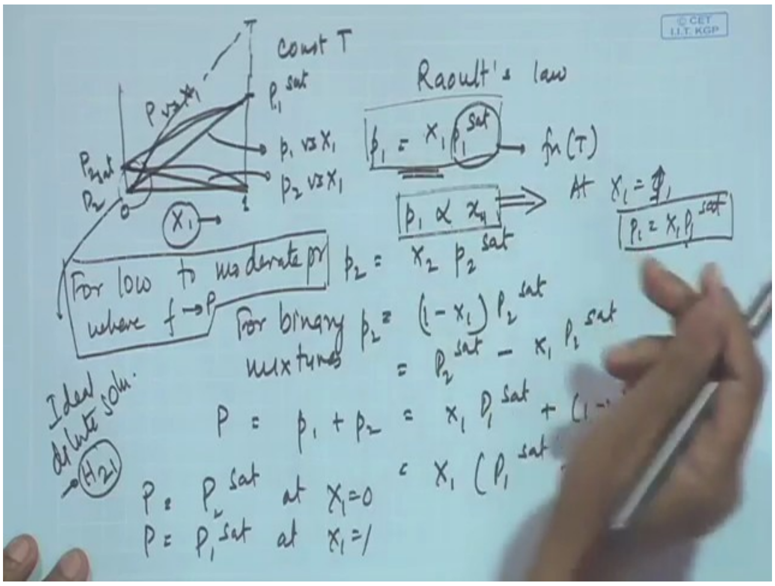

Raoult's law

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$= x_1 (P_1^{sat}$

$P = P_2^{sat}$ at $x_1 = 0$

$P = P_1^{sat}$ at $x_1 = 1$

We observe that the curve it deviates from ideality just as I have shown in a better representation here it deviates from ideality and it can either be positive deviation or it can be negative deviation. For positive deviation the total pressure calculated is greater than that which should have been obtained for Raoult's law, for negative deviation the total pressure is less than the sum of the partial pressures, right? Now how to account for this? You will again I will say that for Raoult's law this was the law which was applicable.

Now what to do for a non-ideal solution? For everything remember we again and again resort to ideal gas behaviour, why? Because it has got a sound theoretical basis in the Kinetic theory of gases, so for gases what do you do?

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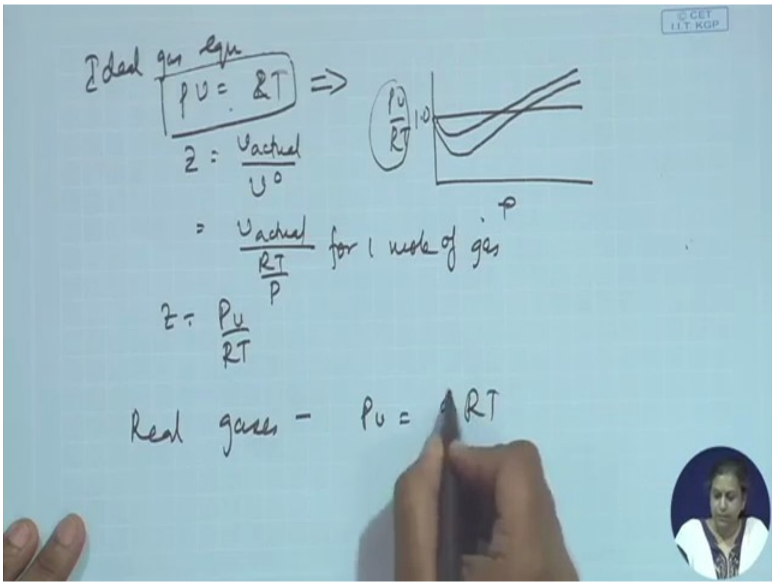

Ideal gas eqn

$\boxed{Pv = RT} \Rightarrow$

$z = \frac{v_{actual}}{v^0}$

$= \frac{v_{actual}}{\frac{RT}{P}}$ for 1 mole of gas

$z = \frac{Pv}{RT}$

Real gases - $Pv = \cdot RT$

We find that for gases we have a relationship like Pv equals to RT which implies, what does it implies? This implies that suppose we plot Pv by RT as a function of temperature say we should be getting a straight line at 1.0. For most of the situations what do we find? We find that usually the graph is something of this sort and it keeps on deviating from ideality in this particular way. So we find that Pv by RT it deviates from ideality, this is pressure it deviates from ideality at high pressure and at low-temperatures, all these isobars are for different temperature.

So what did we do? We found that the Pv by RT terms it deviates from ideality and therefore we had incorporated correction factor which is termed as the compressibility factor. What was the compressibility factor? It was the actual volume occupied by the gas divided by the ideal volume which we it would have occupied had it been ideal under the same conditions of temperature and pressure.

So what is this? This is nothing but v actual by RT by P for one mole of gas or in other words what is z equals to? This is nothing but Pv by RT for the real gas and therefore what did we do? This was the ideal gas equation, right? And for real gas what did we do? For real gases we just modified the equation by incorporating a correction factor z in this particular case.

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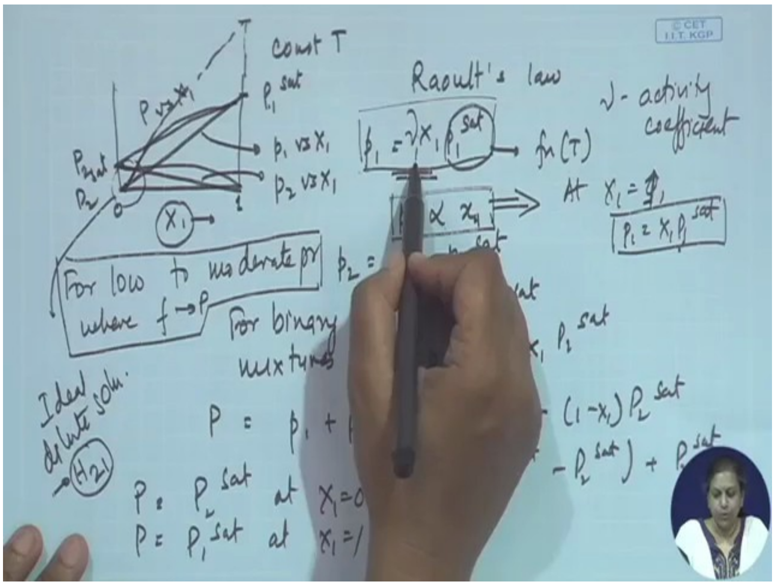

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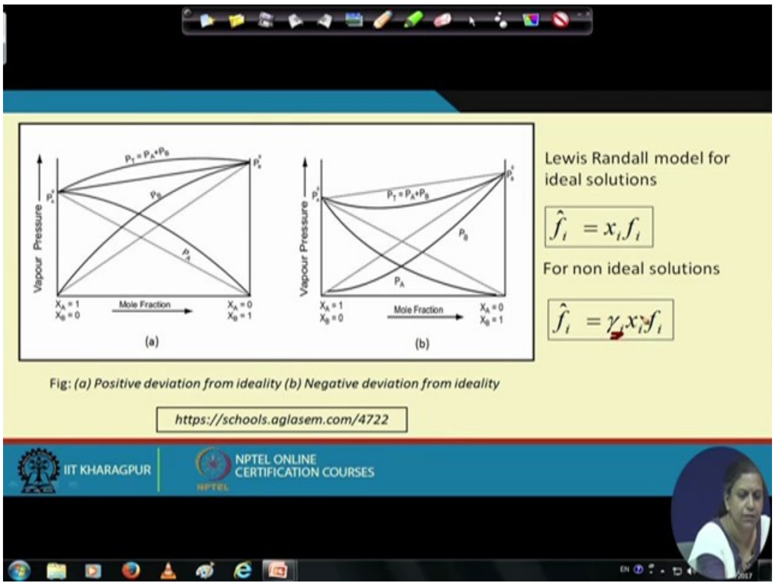

Lewis Randall model for ideal solutions

$\hat{f}_i = x_i f_i$

For non ideal solutions

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

Fig: (a) Positive deviation from ideality (b) Negative deviation from ideality

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In the similar way just take taking note from the ideal gas equations here also we try to do a similar thing, what is the similar thing? This is the case for ideal solution, so therefore when the solution is non-ideal what should happen? Very simply just to keep matter simple we can simply incorporate a correction factor here. The correction factor is conventionally defined by gamma and it is termed as the activity coefficient, right?

So therefore in order to account for non-ideal behaviour, what we do? We simply incorporate or modify the Raoult's law by incorporating a correction factor gamma and you will recollect that if you are dealing with higher pressures then in that case you will be modifying the fugacity expression by incorporating this particular correction factor this particular correction factor gamma. So therefore this is the way we try to do or rather we try to modify the ideal solution model which is pretty simple and can be obeyed by several solutions we try to modify it just by incorporating gamma.

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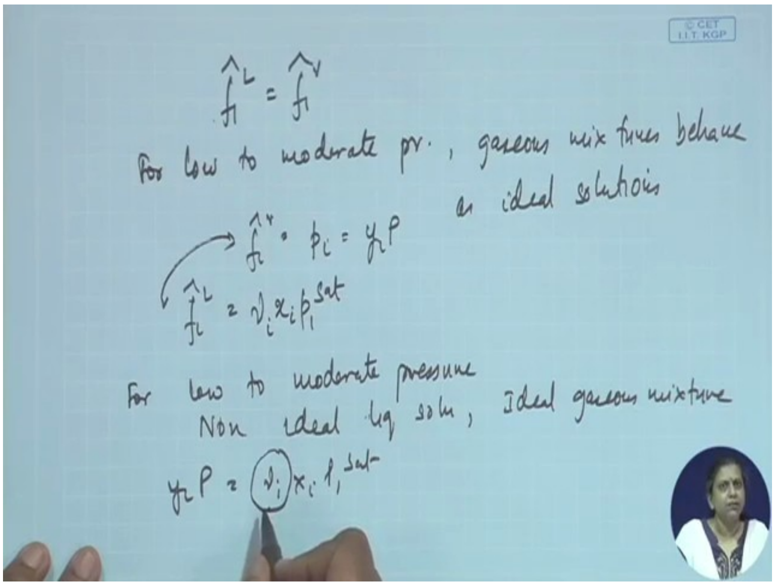

$\hat{f}_i^L = \hat{f}_i^V$

For low to moderate pr., gaseous mixtures behave as ideal solutions

$\hat{f}_i^V = p_i = y_i P$

$\hat{f}_i^L = \gamma_i x_i p_i^{sat}$

For low to moderate pressure
Non ideal liq soln, Ideal gaseous mixture

$y_i P = \boxed{\gamma_i} x_i p_i^{sat}$

So therefore now in this case what does my vapor liquid equilibrium become? The vapor liquid equilibrium if you recollect we had already told you that started with fiL for component 1 is equal to fiV. For low to moderate pressures usually remember for such conditions usually the gaseous mixtures behave as ideal solutions and that is quite a rational thing, why? Because the ideal solution model if you recollect it had its genesis from the Amagat's law of additive volumes which are obeyed by ideal mixture of real gases, right?

So therefore for most of the cases we can write fiV equals to Pi which is nothing but yiP, right? What is fiL equals to? Had the solution been ideal it would have been xiPi saturated since it is not ideal we will have a gamma i here. So therefore what happens for low to moderate pressure non-ideal liquid solution? And we usually have ideal gaseous mixture remember ideal gaseous mixture does not imply a mixture of ideal gases it implies a ideal mixture maybe of ideal gases or of real gases.

So for this case what will we have? We will be equating these 2 or rather we will be equating these 2 expressions, what do we get? We get yiP equals to gamma i Xi Pi saturated, agreed? So therefore we find out that if we really want to find out the vapor liquid equilibrium some this particular condition then we have to encounter an additional term gamma and if we can find out this particular additional term, in terms of some known measurable properties some known thermodynamic relationships then definitely we can use that particular equation here.

Once it is incorporated here then the calculations of vapor liquid equilibrium they come similar to the ideal solutions and I will just I will just recall that whatever different types of problems that we have dealt for the case of ideal solutions are applicable for non-ideal solutions there will be bubble pressure calculation, bubble temperature calculation, due pressure calculation and dew temperature calculations such as we had discussed Tx is Py has to be found out Ty is known Px has to be found out and so on and so forth just the way we had done.

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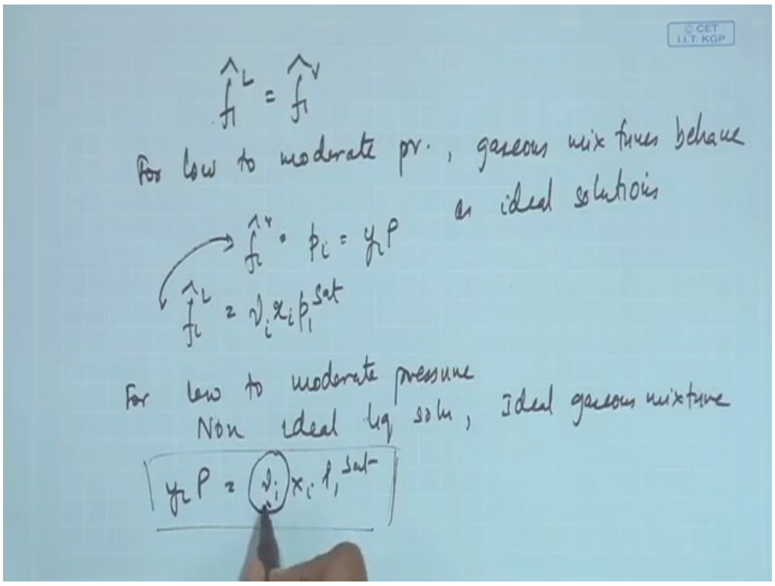

$$\hat{f}_i^L = \hat{f}_i^V$$

For low to moderate pr., gaseous mixtures behave as ideal solutions

$$\hat{f}_i^V \cdot p_i = y_i P$$

$$\hat{f}_i^L = \gamma_i x_i p_1^{sat}$$

For low to moderate pressure
Non ideal liq soln, Ideal gaseous mixture

$$\boxed{y_i P = \gamma_i x_i p_1^{sat}}$$

And for everything we have to start with referring this particular equation and the only hitch which we have here apart from whatever we had done for ideal solutions is calculation of this particular gamma this is the only new thing that we have incorporated in order to account for non-ideality in the liquid solutions equation. So now let us see how to find out Gamma in terms of known measurable parameters. What do you expect? Where with what parameters should gamma be related?

Let us analyze and find out, see what happened because the solution has shifted from ideal to non-ideal behaviour first thing which is happened is it does not obey Raoult's law. Let us jot down one by one what has happened, the first thing is again I will try to recover I try to emphasize that we are dealing with low to moderate pressure, why? Because repeatedly I am referring to Raoult's law not Lewis Randall solution or in other words I am referring to partial pressure, total pressure etc instead of fugacity that is the only reason. If you are going for higher pressure I will be talking about fugacity instead of pressure.

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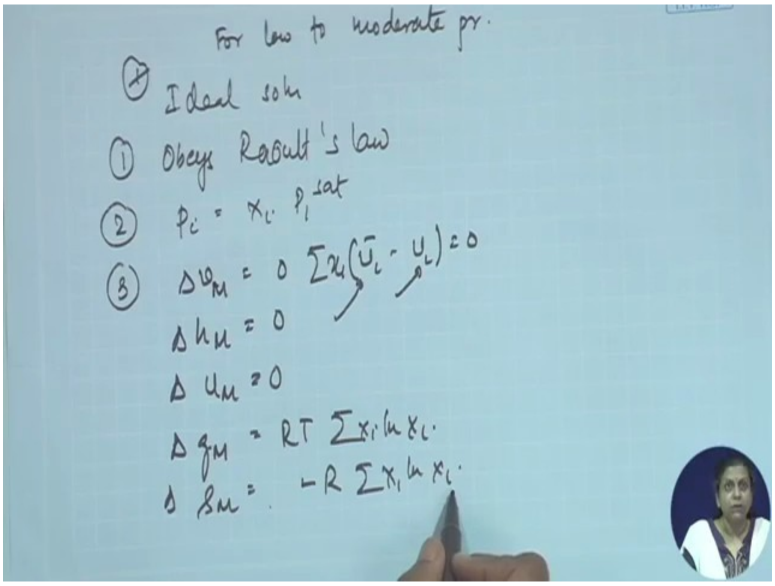

For low to moderate pr.

(*) Ideal soln

① Obeys Raoult's law

② $p_i = x_i P_i^{sat}$

③ $\Delta v_M = 0 \quad \sum x_i(\bar{v}_i - v_i) = 0$

$\Delta h_M = 0$

$\Delta u_M = 0$

$\Delta g_M = RT \sum x_i \ln x_i$

$\Delta s_M = -R \sum x_i \ln x_i$

So therefore for low to moderate pressure what are the things which happens if the solution was ideal, what would you have expected? Obeys Raoult's law, you agree with me. What was the second thing? Naturally if it obeys Raoult's law Pi equals to Xi Pi saturated. Third thing is if you remember we had found out some property changes of mixing. What did we tell under that condition? We had we had told you that delta v mixture was equals to 0.

Or in other words x sigma xi vi bar minus vi that was equal to 0 where if you recollect vi bar is the partial molar property of component i in solution. Since everything is in liquid so I am not putting this particular L superscript it is implied and this is the molar volume of the same component under the conditions of same temperature and same pressure as that of the solution. Similarly we had found out delta hM equals to 0 we had found out delta uM equals to 0, what else did we find out?

Delta gM was that equal to 0? If you recollect that was not equal to 0, we found out that Delta gM was sigma xi, Delta gM it was nothing but RT sigma xi ln xi and Delta sM this was equals to minus R sigma xi ln xi. We had derived all those things and I would also like to recollect if you remember that when we were dealing with mixing of ideal gases we found out that the entropy change was mixing was given by this particular equation when we had devised a reversible path for calculating the entropy change and we had calculated the entropy change for mixing of some ideal gases. So this was exactly the expression that we that we had obtained.

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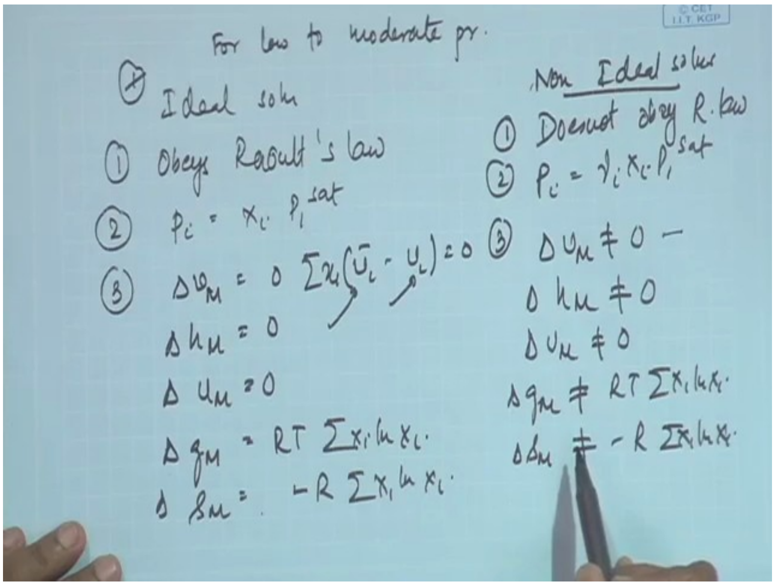

For low to moderate pr.

Ideal soln

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③ $\Delta v_M = 0$ $\sum x_i(\bar{v}_i - v_i) = 0$

$\Delta h_M = 0$

$\Delta u_M = 0$

$\Delta g_M = RT \sum x_i \ln x_i$

$\Delta s_M = -R \sum x_i \ln x_i$

Non Ideal soln

① Doesnot obey R. law

② $p_i = \gamma_i x_i P_i^{sat}$

③ $\Delta v_M \neq 0$

$\Delta h_M \neq 0$

$\Delta u_M \neq 0$

$\Delta g_M \neq RT \sum x_i \ln x_i$

$\Delta s_M \neq -R \sum x_i \ln x_i$

Now tell me one thing this whole thing was for ideal solutions. For non-ideal solutions what are the deviations that you would expect? Naturally first is does not obey Raoult's law, quite natural. As a result what do we have? Pi equals to gamma i xi Pi saturated and naturally what are the other things that you expect? Naturally in this particular case see the volume there was no volume change in mixing, why? Because definitely the molecular sizes and the shape were similar in the 2 components or in the N number of components which were there, so in this particular case when it is behaving in a non-ideal fashion naturally the molecular sizes and shapes should not be similar in that case, okay.

So therefore quite naturally Delta vM will not be equal to 0, expectedly Delta hM will not be equal to 0. Delta uM will not be equal to 0 similarly Delta gM will not be equal to this it is just the same thing if I write it down so none of these things should happen, right? What should happen then under that particular condition? That particular condition we find that the molecular sizes and shapes are not equal as I was telling so Delta vM is not equal 0.

Definitely the intermolecular interactions between molecules of component a and of component a and of solution ab are not the same. So naturally when they are mixing there will be either some absorption of heat or some rejection of heat. Quite naturally, so there will be some it will be accompanied by a heat of mixing that will not be equal to 0 and so on the other things follows. So what does it imply?

It implies, definitely it means that for real solutions there will be a nonzero component of the properties of mixing and this particular nonzero properties arise because the solution does not behave ideally, you get my point. If the solution would have behaved ideally then all these properties would have reduced to this they are not reducing to this just because the solution is real and not ideal. So therefore there has to be some amount of excess properties of all this particular extensive properties that we have written down and these excess properties are coming just because the solutions are real.

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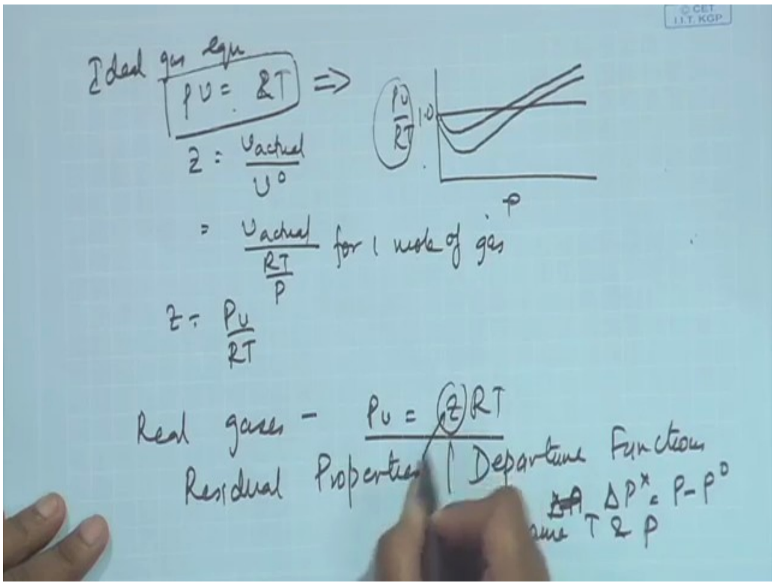

Again recollect the real gas and the ideal gas behaviour, for that particular case what did we say? We said just because the gas was not real, what came up? We had defined this equation and there had come up a series of residual properties or departure functions if you recollect and if you will also be recollecting that and they were they were shown by delta P star or delta M star whatever it is better whatever you wish you can you do can write it down.

These were the departure functions which were the actual properties minus the ideal gas properties at same temperature and pressure. And we found out that each of the residual properties are related to Z. Quite naturally because Z has been introduced to consider real gas behaviour and these residual properties have come up because the gas is real and not ideal. So therefore there should be some relationship between the residual properties and the compressibility factor and as a result of which we were we had tried to express each and every residual properties or departure functions whatever term you wish you can use in terms of the compressibility factor Z, right?

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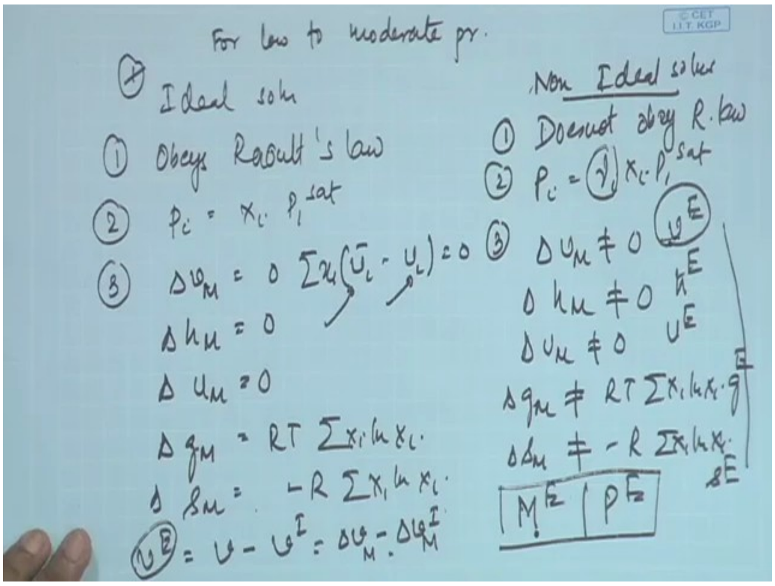

For low to moderate pr.

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$\Delta g_M = RT \sum x_i \ln x_i$

$\Delta s_M = -R \sum x_i \ln x_i$

$v^E = v - v^I = \Delta v_M - \Delta v_M^I$

Non Ideal soln

① Doesnot obey R. law

② $P_i = \gamma_i x_i P_i^{sat}$

③ $\Delta v_M \neq 0$ v^E

$\Delta h_M \neq 0$ h^E

$\Delta u_M \neq 0$ u^E

$\Delta g_M \neq RT \sum x_i \ln x_i$ g^E

$\Delta s_M \neq -R \sum x_i \ln x_i$ s^E

M^E | P^E

So therefore in a similar way is it, does it not occur to you that the behaviour of non-ideal solutions can be predicted or can be defined much more easily if we say that since the solution is not ideal since the solution is real so therefore it should have a set of excess properties defined as ME or PE in whatever way you wish to define the property of a solution. So therefore we find that just because it is real it should have a a set of excess properties.

It should have a excess volume v excess it should have h excess it should have u excess and similarly definitely it should have g excess it should have s excess, why does it have this excess property? Because the solution is not real so therefore how do we define v excess? Quite naturally should be the actual volume of the solution minus the volume of the solution had it been ideal, right?

And therefore or in other words it should be the volume change occurring in the solution due to mixing minus the volume change which would have occurred had the solution been ideal. We know that the volume change which occurs in ideal solution is 0, so naturally your excess properties nothing but the volume change on mixing, right? So this should also be i, so in the same way we should be able to define each and every of the excess properties that we have that rather each and every excess property of the extensive properties that we are dealing with and somehow we should there should be some relationship between Gamma and the set of excess properties and definitely that should give us some hint about estimation of gamma in terms of easily measurable properties, right?

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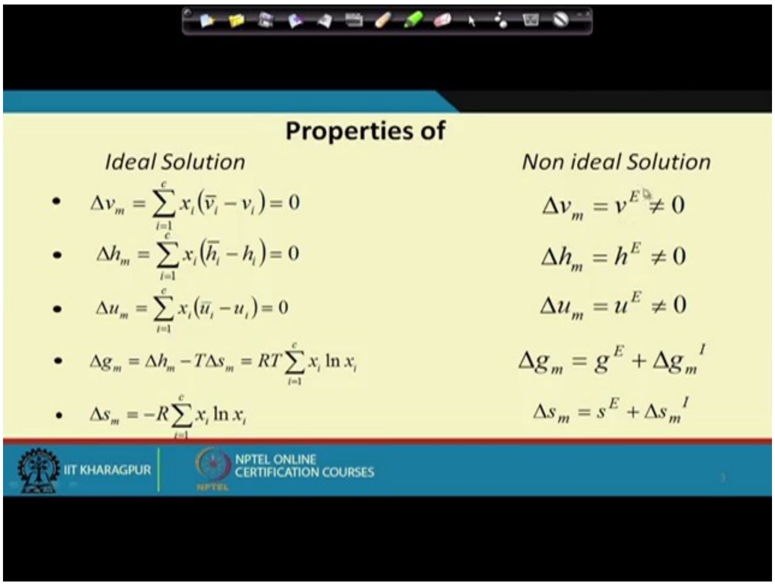

Properties of

Ideal Solution

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

Non ideal Solution

$\Delta v_m = v^E \neq 0$

$\Delta h_m = h^E \neq 0$

$\Delta u_m = u^E \neq 0$

$\Delta g_m = g^E + \Delta g_m{}^I$

$\Delta s_m = s^E + \Delta s_m{}^I$

So therefore what do we do now when we start dealing with non-ideal solutions? We have defined just to account for the non-ideality of the solution.

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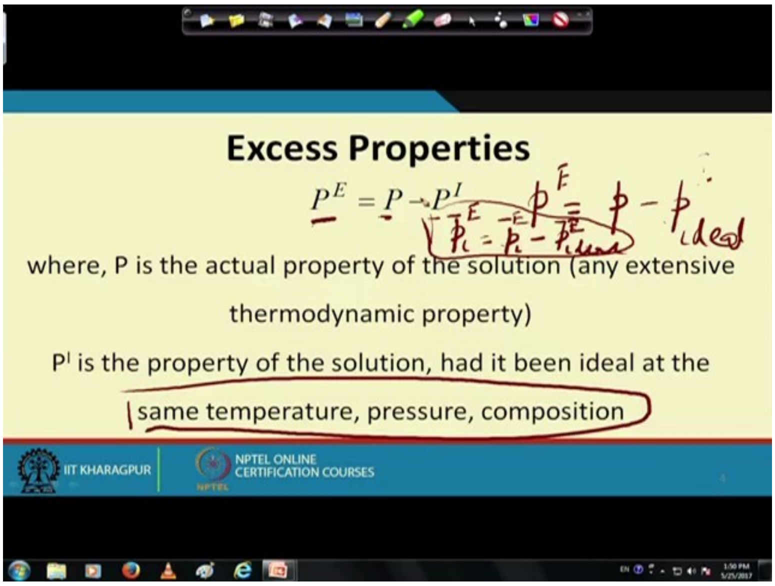

Excess Properties

$P^E = P - P^I$

$p^E = p - p_{ideal}$

$\bar{p}_i^E = \bar{p}_i - \bar{p}_{i\,ideal}$

where, P is the actual property of the solution (any extensive thermodynamic property)

P^I is the property of the solution, had it been ideal at the same temperature, pressure, composition

We have defined a set of excess properties, right? And we find out that these excess properties they arise just because the solution is not ideal. So therefore let us have a proper definition of these particular excess properties. How do we define these excess properties then? Naturally, if we define where any particular property with P, remembering that P should be referring to any extensive property.

So therefore and when we are denoting the property with the capital letter it refers to the total property and under that condition the excess property PE it it should have be it should be equal to the difference between the actual property of the solution minus the property which the solution would have, had it been ideal very important under the same conditions of temperature, pressure and composition and just like we have defined the total excess property definitely we should be in a position of defining a molar excess property as well, agreed?

We are dealing with solutions, so therefore for each component we should be in a position of defining partial molar this is the molar property minus the partial molar property of rather it is better if I write ideal solutions at i at the bottom. Let me write it down as I that will be better. So therefore this should be equal to P excess P bar excess under the ideal condition, right? This is P by, agreed? So therefore just like we have a total excess property we have a molar excess property and for each component we have a partial molar excess property which is the actual molar excess property, partial molar excess property of component i in solution minus the partial molar excess property of component i had the solution been ideal.

So what do we find? What have we done in the process can you tell me? In the process again unfortunately for you we have defined a set of another set of property list, this property list they are known as the excess properties and excess properties I repeat it is the difference between the actual property of the solution and the property which the solution has, had it been ideal under the same conditions of temperature, pressure, composition and remember one thing departure functions, excess properties etc they all refer to extensive properties, okay.

And therefore just like we have total excess properties or total departure functions for real gases we have a molar excess property we have a partial molar excess property. So in the next class what we do we try to express the excess properties or rather the activity coefficient in terms of excess properties and let us see for what comes out or whether we can find out activity coefficient in terms of easily measurable parameters.