Advanced Thermodynamics
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Lecture – 17
Liquid Mixtures and Excess Functions

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is liquid mixtures and excess functions. Till now, we have been discussing different aspects of fugacities, especially fugacities of gaseous mixtures when these gaseous mixtures obey the non-ideality. How the fugacity of that particular component can be estimated depending on the equation of state that has been used to describe the particular gas component or mixture of gaseous components, right? Those things we have seen, right?

Then we have also seen, what are the reasons for the non-ideality in the case of gaseous mixtures? So, what are those kinds of intermolecular forces that are causing some amount of non-ideality and then how to make use of those intermolecular forces in order to describe the non-ideality of the system and then from there how to get the fugacity of those non-ideal gaseous mixtures, those things we have seen till now in last few lectures, right? Now, we will be discussing fugacity of liquid mixtures, okay?

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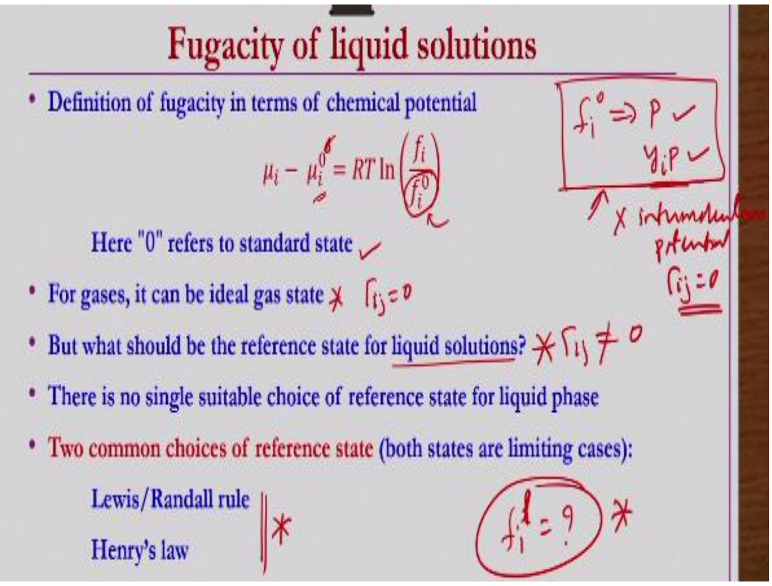

Fugacity of liquid solutions

- Definition of fugacity in terms of chemical potential

$$\mu_i - \mu_i^0 = RT \ln\left(\frac{f_i}{f_i^0}\right)$$

Here "0" refers to standard state ✓

- For gases, it can be ideal gas state ✗ $\Gamma_{ij}=0$
- But what should be the reference state for liquid solutions? $* \ \Gamma_{ij} \neq 0$
- There is no single suitable choice of reference state for liquid phase
- Two common choices of reference state (both states are limiting cases):

Lewis/Randall rule
Henry's law

$\boxed{f_i^0 \Rightarrow P \checkmark \quad y_iP \checkmark}$

✗ intermolecular potential $\Gamma_{ij}=0$

$f_i^l = ?$ *

So, definition of fugacity in terms of chemical potential that we have derived at the beginning of this course is that $\mu_i - \mu_i^0 = RT \ln\left(\frac{f_i}{f_i^0}\right)$, right? f_i is the fugacity of that particular component in the mixture, f_i^0 is the fugacity of that particular component under certain specified reference states or μ_i^0 is the chemical potential at the reference standard state, okay? This superscript not stands for reference state that is what we have seen, and then this equation is useful only when we have the information about this f_i^0.

So, for this in order to know this f_i^0, what we need to have, we need to have a kind of some reference state, right? So, that reference state cannot be taken as blindly. So, what we have taken in the case of gaseous mixture? We know that for the gaseous mixture, if $P \rightarrow 0$, the gaseous mixture reduces to the ideal gas mixture. If it is a pure component, then also when $P \rightarrow 0$, the pure gas component reduces to ideal gas, okay?

So, that condition we have taken as a kind of reference and then that reference standard state that we have taken $f_i^0 = P$ if it is a pure component that is the total pressure of the system and then it is $y_i P$ that is the partial pressure if it is a kind of mixture of gases. That is what we have taken reference state, right? And then here this ideal gas behavior that is what we have taken as a kind of reference state in the case of gaseous component. So that what it tells that there is no intermolecular interactions or intermolecular potential whatever γ_{ij} those things we have seen that is 0 for the ideal gas behavior, right?

But that reference state we cannot take in the case of liquid mixtures because the liquid mixture or any condensed phase is existing because of the presence of intermolecular forces. These intermolecular forces are binding the molecules together to form a kind of condensed phase. So, we cannot take a kind of limiting condition, low intermolecular potential as a kind of limiting condition or as a kind of reference state for the case of liquid solutions, right?

Until and unless you have some information about this f_i^0, you cannot move forward to get more information about the fugacity of liquid mixtures especially if these liquid mixtures are non-ideal, okay? So, now those things we are going to see. First what we do? We define ideal solutions in the context or in analogous way to the ideal gases and then we find out what is this f_i^0 for ideal solutions and then is it only one reference state possible like in case of gaseous mixture or more than one reference states are possible.

Those things we see for this liquid solution and then we try to get more details about the microscopic details like you know, how this non-ideality in the liquid phase may be related to the temperature, pressure and composition of that particular system. Those details we see and then we develop corresponding mathematical relations. So, here this not refers to the standard state, for gases it can be ideal gas state as we have already seen several cases in previous few lectures but what should be the reference state for the liquid solutions.

Because if you take the ideal gas state you are saying that intermolecular potential is 0 but in the case of liquid solutions you cannot say that intermolecular potential is 0. So, then obviously this particular reference state, ideal gas reference state whatever we have taken that we cannot apply for the liquid solutions and then there is no single suitable choice of reference state for liquid phase, right? So, what are those choices are available? Why not one single suitable choice of reference state is there for liquid phase?

Why there are more than one reference states are available, those things we have to see, okay? So, in general there are 2 common reference states that is one is known as the Lewis Randall rule or the ideal behavior with reference to the Lewis Randall rule and then ideal behavior with reference to the Henry's law, okay? So, these details also we are going to see before getting information about what is f_i^l, fugacity of the component i in a liquid mixture, right? So, before going into these details, we need to understand all these ideal solutions and then what are the reference states.

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Ideal gas versus ideal solution

- For liquids, one cannot extrapolate (ideal gas law) to state that there are no intermolecular interactions
- Because presence of intermolecular forces makes condensed phase (liquid/solid) to exist
- On macroscopic level, a solution is ideal when all mixing rules are same as for an ideal gas, i.e., $\underline{\Delta v_{mix}^{ideal} = 0 \ \& \ \Delta h_{mix}^{ideal} = 0}$
- Although concept of an ideal solution developed in analogy to an ideal gas, there are a few following interesting differences
- A pure gas can be non-ideal gas but a pure liquid cannot be non-ideal solution because
  - all intermolecular forces in a pure liquid are same
- Increase in pressure leads to deviation from ideal gas behavior whereas deviation from ideal solution are caused due to changes in composition because
  - non-ideal behavior results primarily from chemical differences of species in a mixture even at low pressures

So, ideal gas versus ideal solutions. What we do? We define ideal solution analogous to the ideal gas behavior. What we have in ideal gas behavior? In ideal gas behavior we say that there is no intermolecular interaction amongst the molecules of the gas whatever we have taken if it is ideal gas or intermolecular potential is 0 that is what we say but in the case of ideal solutions. There are definitely intermolecular interactions because of that one only indeed the solution condensed phase there in the liquid form or solid form it is possible.

So, we cannot say there is no intermolecular potential but what we can say, we can say that if the intermolecular interactions are same or inter molecular potentials are same for a given component then we can say that particular component is a kind of ideal component, okay? Because we cannot say there is no intermolecular interaction there is definitely intermolecular interactions. So, what we can say? If these intermolecular interactions are same for all the molecules that are present in the system, then we can say that that particular liquid system is a kind of ideal liquid solution, okay?

For liquids one cannot extrapolate ideal gas law to state that there are no intermolecular interactions because presence of intermolecular forces makes this condensed phase to exist and on macroscopic level we can say a solution is ideal when all mixing rules are same as for an ideal gas. For ideal gas, what we have, $\Delta\ \mathrm{v}_{\mathrm{mix}}^{ideal}$ should be 0 and then $\Delta\ \mathrm{h}_{\mathrm{mix}}^{ideal}$ should also be 0 that is what we have seen. If these two principles are also applicable for liquid solution then we can say those liquid solutions are also ideal liquid solutions, right?

Now, though this ideal solution we are defining by taking ideal gas as a kind of reference, there are a few differences. What are those differences that is what we see now, right? In the case of gases, if gas is a pure gas then also non-ideality is possible, right? In the case of gases, non-ideality is there because of increasing the pressure. When increases the pressure, the intermolecular interactions increases and there comes into the picture non-ideality, right?

But in the case of liquid solutions, if the component is pure or the liquid component is pure then all interactions are same. So, let us say if you have a component A and then let us designate the molecules of that component A like a a a like this. So, then for this molecule, there are interactions and all these interactions are a-a interactions that is, all interactions are same. So, that means if you have a kind of pure liquid, then it will always be a kind of ideal solution because ideal solution says all the intermolecular interactions are same, right?

And if in a system if all the molecules are of the same substance, pure substance then obviously all of their interactions would be same, whatever may be the pressure, low pressure or high pressure, whatever may be the pressure range as long as that phase exists in a kind of liquid phase, all interactions would be same. So, then that pure liquid will always be ideal whereas a pure gas cannot be ideal always whether the pure gas or mixture of gas it can be ideal only at the low pressure. So, that is one of the differences.

The first difference is this one, a pure gas can be nonideal gas but a pure liquid cannot be nonideal solution because if intermolecular forces are same, then we say that particular liquid solution as a kind of ideal liquid solution, right? So, if the liquid is pure liquid obviously all the intermolecular forces would be same, so then a pure liquid will always be ideal liquid whereas a pure gas cannot be ideal always. A gas can be ideal only under the case of $P \rightarrow 0$ or low pressure conditions, okay?

In the case of gases, increasing pressure leads to the deviation from the ideal gas behavior because when you increase the pressure the intermolecular interaction increases, the molecules come closer to each other and then there will be interactions, and then depending on the nature of the interactions, different types of non-ideality may come into the picture for the case of gases and those non-idealities may be represented by different equation of state, those things we have seen.

But in the case of liquids it is not true because in the case of liquids whatever the non-ideality is there that is coming because of the dissimilarity of the chemical nature of substance. That is, if you have a kind of A component, A component which is having a molecules, so as long as this A is pure, all the interactions are same. Whether you increase the pressure or decrease the pressure, it is not going to affect as long as this particular A component is in the liquid phase, right?

But it can become non-ideal provided if you add some other component B. Let us say if you add some other component B then there will be a kind of b-b molecules will be there and there will be a kind of interactions a-a interactions, b-b interactions, and then a-b interactions.

Depending on the composition and depending on the nature of these interactions, you know the non-ideality may be coming into the picture. That is because of the change in composition non-ideality is coming into the picture in the case of the solutions, okay, right?

Then sometimes even this a-b interactions, a-a interactions are like interaction, b-b interactions are also known as the like interactions, a-b interactions are known as the unlike interaction or the interaction between 2 different molecules, okay? So, 2 different molecules does not mean that they always need to be different from a-a interactions and b-b interactions. That means, even if there is a kind of solution, it is possible that this depending on the nature of the species, chemical nature of these molecules if the a-b interactions are also similar to either a-a interactions or b-b interaction.

So then under such conditions this solution may also have a kind of some ideality under certain limiting conditions, something like $x_i \rightarrow 0$ or $x_i \rightarrow 1$ under those limiting conditions. Those things we will also see now anyway. So, increase in pressure leads to deviation from ideal gas behavior whereas deviation from ideal solution are caused due to changes in composition because non-ideal behavior results primarily from chemical differences of species in a mixture even at low pressure provided that phase is in a kind of liquid phase, provided that phase is a liquid phase.

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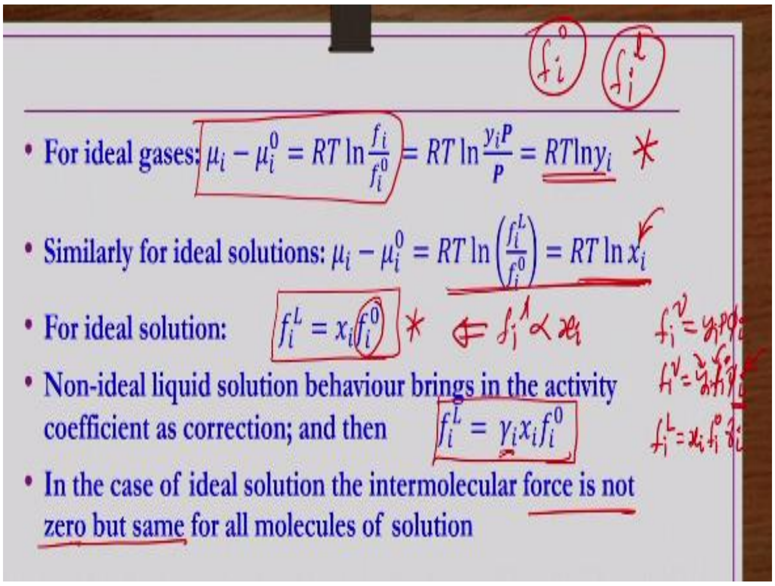

f_i^0 f_i^l

- For ideal gases: $\boxed{\mu_i - \mu_i^0 = RT\ln\frac{f_i}{f_i^0}} = RT\ln\frac{y_iP}{P} = \underline{RT\ln y_i}$ *
- Similarly for ideal solutions: $\mu_i - \mu_i^0 = RT\ln\left(\frac{f_i^L}{f_i^0}\right) = RT\ln x_i$
- For ideal solution: $\boxed{f_i^L = x_i f_i^0}$ * $\Leftarrow f_i^l \propto x_i$
- Non-ideal liquid solution behaviour brings in the activity coefficient as correction; and then $\boxed{f_i^L = \gamma_i x_i f_i^0}$
- In the case of ideal solution the intermolecular force is not zero but same for all molecules of solution

$f_i^v = y_i P\phi$

$f_i^v = y_i f_i$

$f_i^L = x_i f_i^0$

So, now we have to define what is this fugacity of component i in the liquid phase. We have defined, what this f_i^0 is or the possible reference states we are going to see more definitions anyway, right? So, now we have to define this f_i^l analogous to the case of ideal gases. So, μ$_i$ $-\mu_i^0$ =RT ln $\left(\frac{f_i}{f_i^0}\right)$ =RT ln y$_i$, this is what we have already seen if the gaseous mixture is a kind of ideal gas mixture. Now, if you have a ideal liquid solution, then similarly, what we can have? We have this relation μ$_i$ $-\mu_i^0$ =RT ln $\left(\frac{f_i}{f_i^0}\right)$.

Then superscript l we are using to distinguish for the liquid phase. This is same whether it is condensed phase or gaseous phase, this relation is same, it is not going to change, okay? But only thing that whether it is appropriate to use or not that depends on the case to case and then depends on the data availability. Those things we will see anyway, right? So, this is same. So here also for the ideal gases up to this part is same, right? So, now if the gaseous ideal gas then this difference is nothing but RT ln y$_i$.

So, similarly analogously if you wanted to define for the ideal solutions, this difference that is μ$_i$ $-\mu_i^0$ you should define it as RT ln x$_i$ where x$_i$ is nothing but the mole fraction of that particular component i in the liquid solution, right? So, that means what we can write from here, we can write that f_i^l is nothing but by equating these two, we can write f_i^l is nothing but x$_i$ f_i^0, this is what we can write. So, now, here this f_i^0 is at certain reference standard state. This equation is useful only when we know what is this f_i^0, okay? That we see anyway by taking different reference state.

So, this is for the ideal solution. If the liquid solution is ideal then f_i^l = x$_i$ f_i^0 or we can say f_i^l is proportional to x$_i$ if it is ideal solution, linear relationship is there and then that proportionality constant is f_i^0 for the time being. It can be different also depending on what reference state are we taking, right? So, non-ideality in the system or the non-ideal liquid solution behavior brings in the activity coefficient as correction, like you know f_i^v in the vapour phase or the gaseous phase what we have y$_i$ P ϕ$_i$.

This is what we are having or you know if you have not defined as a kind of any reference state, then you have y$_i$ f_i^0 ϕ$_i$ this is what you have for the vapour phase. So, this composition is there and then at certain reference state what is f$_i$? f_i^0 that is there, so additionally this fugacity coefficient ϕ$_i$ is there in the case of gases or vapour mixtures. So, analogously if you write for the liquid states, then it should be in place of y$_i$ it should be x$_i$ and then f_i^0 some reference state.

At some reference state what is the fugacity that we do not know, we are writing f_i^0 and then non-ideality in the vapor phase is brought into the picture in terms of this ϕ_i. So, now, here the same thing non-ideality in the liquid phase is brought into the picture by this activity coefficient γ_i. So, $f_i^l = \gamma_i x_i f_i^0$. So, this γ_i whatever is there that is known as the activity coefficient. It brings in the non-ideality in the system or it brings in the effect of non-ideality in the system, okay?

Whatever the non-ideality is there in that system that can be mathematically represented or related to the fugacity through this activity coefficient γ_i, right? So, as we have seen in the case of ideal solution, the intermolecular force is not 0 but same for all molecules of solutions, right? So, this is the difference between ideal gas and then ideal solution. Ideal gas we are saying there are no intermolecular forces at all.

In the ideal solution, we are saying there are intermolecular forces, indeed there exist intermolecular forces that is the reason this condensed phase is existing. But we can say this liquid or solution phase as a kind of ideal if these intermolecular forces are same in a given system, okay?

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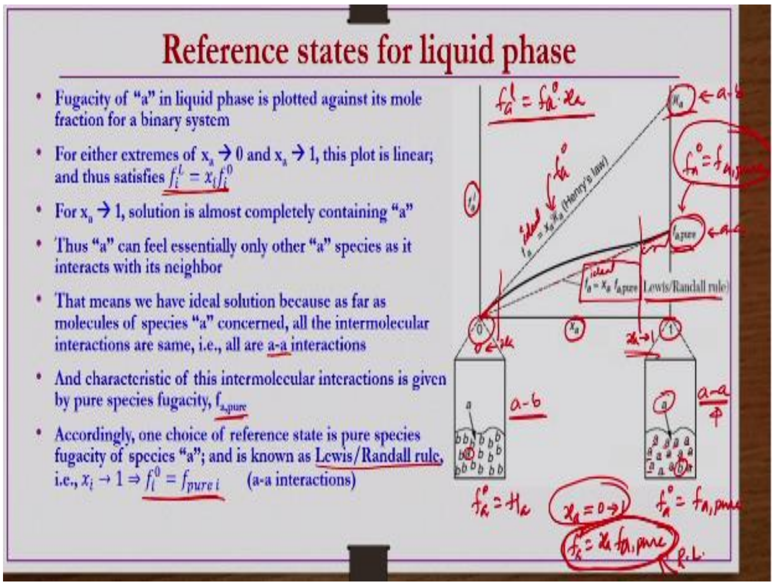

Reference states for liquid phase

- Fugacity of "a" in liquid phase is plotted against its mole fraction for a binary system
- For either extremes of $x_a \rightarrow 0$ and $x_a \rightarrow 1$, this plot is linear; and thus satisfies $\underline{f_i^l = x_i f_i^0}$
- For $x_a \rightarrow 1$, solution is almost completely containing "a"
- Thus "a" can feel essentially only other "a" species as it interacts with its neighbor
- That means we have ideal solution because as far as molecules of species "a" concerned, all the intermolecular interactions are same, i.e., all are a-a interactions
- And characteristic of this intermolecular interactions is given by pure species fugacity, $f_{a,pure}$
- Accordingly, one choice of reference state is pure species fugacity of species "a"; and is known as Lewis/Randall rule, i.e., $x_i \rightarrow 1 \Rightarrow \underline{f_i^0 = f_{pure\, i}}$ (a-a interactions)

So, now reference states for the liquid phase, okay? So, now what we do? Before going into the details of reference state, we take a binary mixture of component A and then component B. This A is having molecules a-a molecules and then B is having b-b molecules like this, what we do? This liquid mixture A and B we take then we experimentally measure the fugacity of component A in this liquid mixture and then for different composition this fugacity of liquid mixture, this fugacity of A in the liquid mixture we measure and that information that is f_a^l versus x_a we plot experimentally whatever the information is there.

Let us say that information is having this particular nature. This f_a^l versus x_a if you plot experimental information whatever is there, that is having this solid curve like this, right? And then two limits of x_a are 0 and then 1. We can see f_a^l versus x_a is non-linear because there is a kind of non-ideality. If at all it is ideal, then we should have this f_a^l = some reference state f_i, now component A, f_a^0 x_a, this form we should have if it is ideal solution but it is not ideal. So that is the reason we are having non-ideal nature of the curve like this, right?

So, now, what we do? We take the either extremes of x_a. Let us start with $x_a \rightarrow 1$. Then what we have, we have in this system only a-a molecules are there because $x_a \rightarrow 1$ that means it is almost pure component 1, right? Only few b molecules are there and they are negligible compared to the "a" molecule. So, any a molecule if you take, with reference to this a molecule what it sees in its neighborhood, it will see only a-a molecules, right? Because they are only majorly dominating.

So, under such conditions, what we will have? We will be having a-a interactions and in all these a-a interactions are equal, right? So, that means when $x_a \rightarrow 1$, then $x_b \rightarrow 0$. So, $x_a \rightarrow 1$ that means a kind of pure component 1 or pure component A, right? If the liquid component is pure component then obviously it is ideal component. So, that is the reason in the limit close to $x_a \rightarrow 1$, we can see a kind of a linear behavior is there, right? So, that means obviously whatever this reference state f_a^0 is there that should be $f_{\text{pure a}}$ or $f_{\text{a,pure}}$ anyway you can write it.

So, this is one of the reference states, right, okay? And now, this particular case where $x_a \rightarrow 1$, mostly "a" interactions are there, all those interactions are same. So, then we have a kind of ideal behavior in the limit $x_a \rightarrow 1$. So, this, under this is one boundary condition or one limiting condition of x_a because $x_a \rightarrow 0$ to 1, right? So, whatever this $x_a \rightarrow 1$ then fugacity of that particular component should be equals to fugacity of pure component. So, that means f_a^0 you can take $f_{\text{a,pure 1}}$ or $f_{\text{pure a}}$ that is what you can see, right?

So, that is one reference state and this is known as the Lewis Randall rule, right? And then whatever this line is there, this limit $x_a \rightarrow 1$, this straight line if you extend further, so you have this particular line. Then you can say $f^{ideal} = f_a^{ideal} = x_a\ f_{a,pure}$. Or the fugacity of pure component A multiplied by x_a should be equals to f_a^{ideal} if you define Lewis Randall rule as a kind of reference state, then you will have this one, okay? Other limitation is $x_a \rightarrow 0$.

That means, “a” is present in very small quantities, you can see here now, a is present in very small quantities in b that is a dilute solution of a, right? Now, here you can see with reference to a, we are doing all these things with reference to a, so with reference to a, it will see only a-b interaction, right? So, it will have only a-b interaction. So, all these a-b interactions are also equal similar with reference to a. So, under such condition also it is ideal. Ideal in the sense all the interactions should be same or intermolecular forces should be same.

So, intermolecular forces now we are representing qualitatively in terms of interactions. So, in the case of Lewis Randall law, all interactions are same but those interactions are a-a, in the case of other limitation $x_a \rightarrow 0$, all interactions are again same. But those interactions are a-b interactions. So, under this limitation also, we can have for certain range a kind of ideal behavior that is the reason here again we have a kind of a linear curve for the range when $x_a \rightarrow 0$, right? And this case, whatever the $f_a^{ideal}$is there, so that can be referred or defined with respect to Henry's law as a kind of reference state.

Henry’s law can be taken as a kind of reference state and under such conditions whatever the f_i^0or f_a^0 is there in this case is nothing but H_a that is Henry's law constant. So, now we have 2 reference states for a liquid solution when $x_a \rightarrow 1$, whatever the f_a^0 is nothing but $f_{pure\ a}$ or $f_{a,pure}$ and then another limiting condition $x_a \rightarrow 0$ where we can have f_a^0 =Henry’s law constant H_a, right? So, there may be a case, indeed there should be a case where the reference state may be valid for the entire range of x_a from 0 to 1, right?

So, then under such conditions this f_a^0 should be $x_a\ f_{pure\ a}$ or $f_{a,pure}$, this is what we have and this is known as Raoult’s law. So, if the solution is ideal in the entire range of mole fraction of a from 0 to 1, then that ideality may be defined with respect to the Raoult law where f_a is nothing but $x_a\ f_{a,pure}$ and in many case $f_{a,pure}$ is taken as the P_a^{sat}or the saturation pressure of that component a that way it has been taken. So, now we can see different reference states are possible in the case of liquid phase, okay?

So, now what we have? We see detail of these things that is a kind of notes everything is given here, right? Fugacity of a in liquid phase is plotted against its mole fraction for a binary system here, for either extreme say that is $x_a \rightarrow 0$ and the $x_a \rightarrow 1$, this plot is linear, we can see here, right? So as we have seen, and now we can see when $x_a \rightarrow 1$ under the Lewis Randall case, this $f_{a,pure}$ is a kind of reference state, whereas kind of $x_a \rightarrow 0$, then this H_a that Henry's constant or Henry's law.

According to Henry's law whatever the Henry's constant H_a is there that should be a kind of reference state or f_a^0 in the case, right? Now we can see here $f_{a,pure}$ is much small, whereas H_a is much large, what does it mean? If you see the fugacity as a kind of tendency to escape, right? And then join with other molecules or get into the other phases that is what it roughly means by, right? So, if the tendency is more, so then it is easily escaping and then going and joining with other molecules or other species or into the other phase is also possible, right?

So, under such conditions, we can say that the non-ideality is very high, it is easily going in and joining with the other molecules. If tendency is low that means it is having strong binding with its own molecules and then it is not going to escape from this phase and then joining to the other phase or other species, right? So, smaller fugacity, that means stronger interactions, stronger like interaction and then molecules try to be together themselves in their ideal state, in their own state as a kind of ideal state, right?

So, if the tendency is high that means let us say in the case of second case where $x_a \rightarrow 0$**,** the a molecules are very few and then it is not possible for it to stay with the b molecules comfortably, so it will try to escape, its tendency to escape for from the mixture of ab would be high that is the reason H_a is high. Whereas the other extreme $x_a \rightarrow 1$ or with reference to a molecules, all the molecules are a molecules kind of thing. So, it is having good binding with a molecule.

So, it does not want to move from its own a molecules in the vicinity to the surrounding other molecules or escaping from this liquid phase and then going and joining to the other molecules. So, that is the reason $f_{a,pure}$ is low, right? So, that means $f_{a,pure}$ is low that means here the like interactions are very strong. If H_a is low that means here unlike interactions are going to have a kind of or going to define the ideality and then the same molecules are having higher tendency to escape from the solution, okay? But in either of the extremes what we have, f_i^l = x_i f_i^0 that is linear plot is there.

That means if the plot between f_i^l and x_i is linear, then we can say that the mixture is an ideal liquid mixture, okay? For $x_a \rightarrow 1$, solution is almost completely containing a, thus a can feel essentially only other a species as it interacts with its neighbor. That means, we have ideal solution because as far as molecules of species a concerned all the intermolecular interactions are same, that is all are a-a interactions and characteristics of this intermolecular interaction is given by pure species fugacity $f_{a,pure}$.

So, under such conditions, f_a^0 is nothing but $f_{a,pure}$. So, accordingly one choice of reference state is pure species fugacity of species a and is known as Lewis Randall rule and that is $x_i \rightarrow 1$, f_i^0 $=f_{pure\ i}$, where a-a interactions are dominating or all interactions are aa kind of interactions and they are similar interactions.

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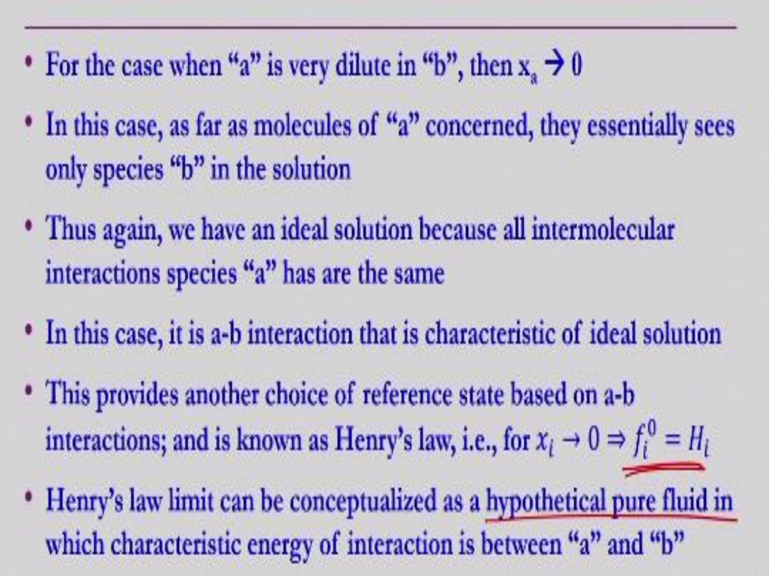

- For the case when “a” is very dilute in “b”, then $x_a \rightarrow 0$
- In this case, as far as molecules of “a” concerned, they essentially sees only species “b” in the solution
- Thus again, we have an ideal solution because all intermolecular interactions species “a” has are the same
- In this case, it is a-b interaction that is characteristic of ideal solution
- This provides another choice of reference state based on a-b interactions; and is known as Henry’s law, i.e., for $x_i \rightarrow 0 \Rightarrow f_i^0 = H_i$
- Henry’s law limit can be conceptualized as a hypothetical pure fluid in which characteristic energy of interaction is between “a” and “b”

For the case when “a” is very dilute in b, then what we say $x_a \rightarrow 0$ because a is very small in b. In this case, as far as molecules of a concerned they essentially see only species b in the solution. Thus again we have an ideal solution because all intermolecular interactions species “a” has are the same again. But in this case these interactions are a-b interaction that is the characteristic of ideal solution and the limit of $x_a \rightarrow 0$ unlike in the case of $x_a \rightarrow 1$ it is a-a interactions.

Whether it is a-a interactions or a-b interaction it should be same, then we can say it is ideal solution. So, in the case of $x_a \rightarrow 0$, it is a-b interaction that are there and then if they are all same, especially with respect to a. This provides another choice of reference state based on a-b interaction and is known as the Henry's law. So, that is for the $x_i \rightarrow 0$, $f_i^0 = H_i$, H_i is nothing but the Henry's law constant for that component i in a solvent, whichever solvent you we have taken, so in this case solvent is b.

Henry's law limit can be conceptualized as a hypothetical pure fluid in which characteristic energy of interactions is between a and b molecules only.

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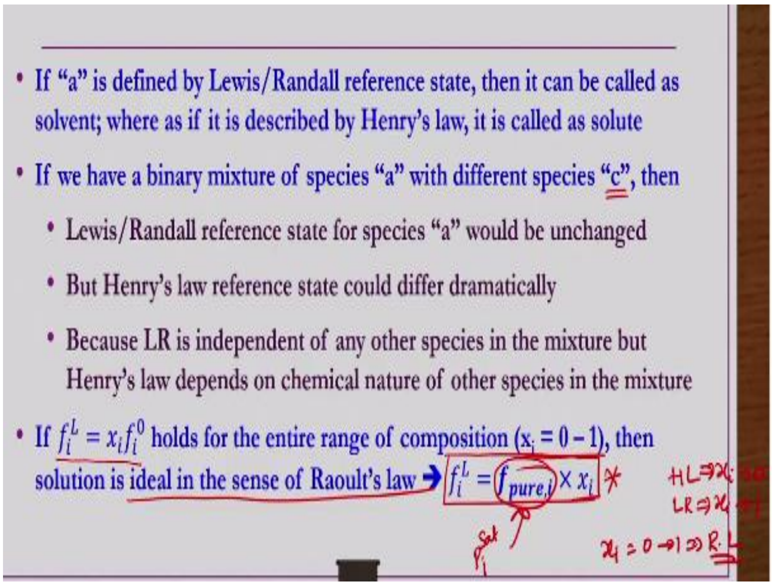

- If "a" is defined by Lewis/Randall reference state, then it can be called as solvent; where as if it is described by Henry's law, it is called as solute
- If we have a binary mixture of species "a" with different species "c", then
  - Lewis/Randall reference state for species "a" would be unchanged
  - But Henry's law reference state could differ dramatically
  - Because LR is independent of any other species in the mixture but Henry's law depends on chemical nature of other species in the mixture
- If $f_i^L = x_i f_i^0$ holds for the entire range of composition ($x_i = 0 - 1$), then solution is ideal in the sense of Raoult's law ➔ $\boxed{f_i^L = f_{pure,i} \times x_i}$ *

So, now if a is defined by Lewis Randall reference state then it can be called as a kind of solvent because Lewis Randall reference state that means pure component fugacity we are taking, pure component fugacity we are taking as a reference that means x_i is going to be close to 1. So, here in the case of this one it is x_a, $x_a \rightarrow 1$ that means it is all pure solvent a is there, there is no b at all, but with respect to Henry's law if you take, this a is present in only small quantities as a solute in b solvent, right? So, that is the difference.

If "a" is defined by Lewis Randall reference state, then it called as a kind of solvent whereas if it is described by Henry's law, the same "a" is called as a kind of solute because it is present in very minute small quantities, $x_a \rightarrow 0$, it is not exactly 0, $x_a \rightarrow 0$, small quantities. So, if we have a binary mixture of species a with different species c, then what will happen? So, the example that we have seen for the binary mixture of a and b. Now again, we take a binary mixture but a and c, right? So then reference states how would they change?

So, $x_a \rightarrow 1$, it is pure a almost, whether the other component which is present in very small quantities, if it is b or c, it does not make difference. It does not make any difference, so that Lewis Randall reference state is going to remain same that is f_i^0 is going to be $f_{pure\ i}$, right? But in the case of $x_a \rightarrow 0$, so it is now $x_a \rightarrow 0$ that means Henry's law is a kind of reference state. So, then under such conditions what happens, this a is present in very small quantities, very small quantities and then it is going to be mixed with some other solvent c because now the binary mixture is a and c.

Previously, the binary mixture was a and b. So, in the case of a and c solution, which is defined using the Henry's law, so this whatever the f_i^0 is going to be very different compared to the previous case because what Henry's law says, it defines about the solubility of a specific solute in a solvent. So, now solvent is changing though the solute is remaining. So, depending on the solubility of the solute a in b and then depending on the solubility of solute a in c, this reference state would dramatically change.

If the solubility of a in b and c is almost same then this may remain same, there is no guarantee that the solubility of solute a is going to be same in 2 different solvents. So, this Henry’s law reference state is not going to be same if you change the solvent or if you change the second component of the binary mixture, whereas Lewis Randall reference state is going to be same because whatever the $x_a \rightarrow 1$, it sees only $x_a \rightarrow 1$, what is the remaining small amount that does not make any difference, so it is going to be $f_{a,pure\ i}$ or $f_{a,pure}$ or $f_{pure\ i}$, okay?

So that is what we see now here. So, if you have a binary mixture of a and c then Lewis Randall reference state for species a would be unchanged obviously because of this reason but Henry's law reference state could differ dramatically because it depends on the solubility of a and b and then solubility of a and c. So, in general, solubility of one solute in 2 different solvents may not be same, so it may differ dramatically.

Because LR is independent of any other species in the mixture but Henry's law depends on the chemical nature of other species in the mixture in which the solute a is going to be dissolved to form a kind of a liquid solution. So that means further another step if $f_i^l = x_i f_i^0$ holds for the entire range of composition that is from x_i varying from 0 to 1 that is for the entire range then the solution is ideal in the sense of Raoult's law where we have a f_i^l = $f_{pure,i}$ x_i, right?

So, this Henry's law is applicable when $x_i \rightarrow 0$ and then Lewis Randall rule is applicable when $x_i \rightarrow 1$ but the ideal behavior is there for the entire range of x_i changing from 0 to 1 then this Raoult's law is going to be a kind of reference state and then for that case, this f_i^l is defined as $f_{pure\ i}$ x_i and then for majority of the cases, $f_{pure\ i}$ is defined as P_i^{sat} or saturation pressure of that component i, this $f_{pure\ i}$ is mostly defined or taken as P_i^{sat} or saturation pressure of that i^th component, okay?

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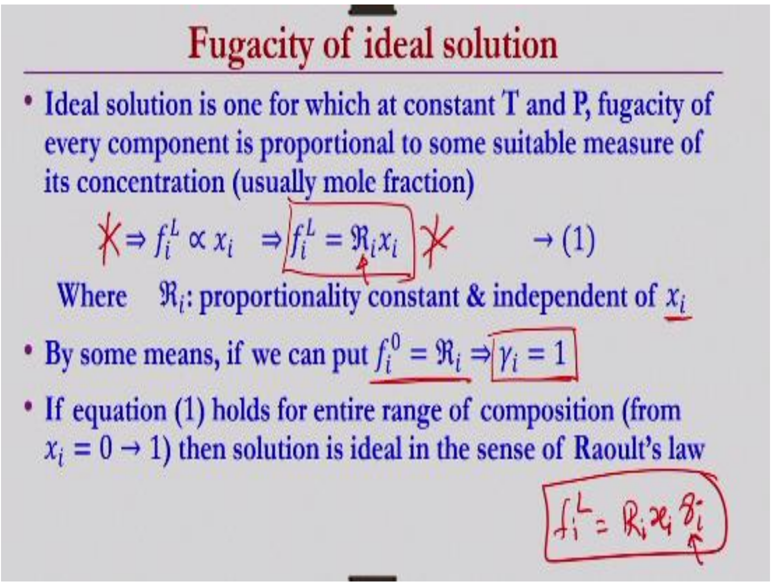

Fugacity of ideal solution

- Ideal solution is one for which at constant T and P, fugacity of every component is proportional to some suitable measure of its concentration (usually mole fraction)

$$\Rightarrow f_i^L \propto x_i \quad \Rightarrow \boxed{f_i^L = \Re_i x_i} \qquad \rightarrow (1)$$

Where $\Re_i$: proportionality constant & independent of $\underline{x_i}$

- By some means, if we can put $\underline{f_i^0 = \Re_i} \Rightarrow \boxed{\gamma_i = 1}$
- If equation (1) holds for entire range of composition (from $x_i = 0 \rightarrow 1$) then solution is ideal in the sense of Raoult's law

$$\boxed{f_i^L = R_i x_i \gamma_i}$$

Now we see fugacity of ideal solution, okay? So, we have seen a few basic details of ideal solution that are required in order to get into the fugacity of liquid solution. So, before going into the details of fugacity of non-ideal solutions, we start with fugacity of ideal solution, right? Ideal solution is one for which at constant temperature and pressure, fugacity of every component is proportional to some suitable measure of its concentration, usually mole fraction that is what we have seen.

So, that means f_i^l is proportional to x_i, that we can write f_i^l = some constant $\Re_i$ x_i and then this $\Re_i$ is going to change depending on the reference state which reference state we are going to take. If you take $x_i \rightarrow 0$, then it should be H_i, and then if you take $x_i \rightarrow 1$, then it should be $f_{pure\ i}$ that is what we have seen. So, this $\Re_i$ is a proportionality constant and it is independent of mole fraction or composition, okay?

So by some means if we can put a $f_i^0 = \Re_i$, then we can say γ_i =1, that means the ideal behavior γ_i or the activity coefficient should be 1. If the solution is ideal solution, then this γ_i has to be 1, similarly like if the gases mixture is ideal gas mixture then fugacity ϕ_i should be equals to 1 that is how we have defined for the gaseous mixture. The similar way for the liquid mixture also γ_i should be equals to 1 if the solution is ideal liquid solution.

So, this equation one holds for the entire range of composition from $x_i = 0$ to 1 then the solution is ideal in the sense of Raoult's law. Remember this definition is true for the ideal liquid solution only. This equation number 1 is true only for the ideal liquid solution only. If the liquid solution is non-ideal, then we have f_i^L = some constant $\Re_i$ x_i then γ_i, that activity coefficient γ is known as the activity coefficient that will come into the picture.

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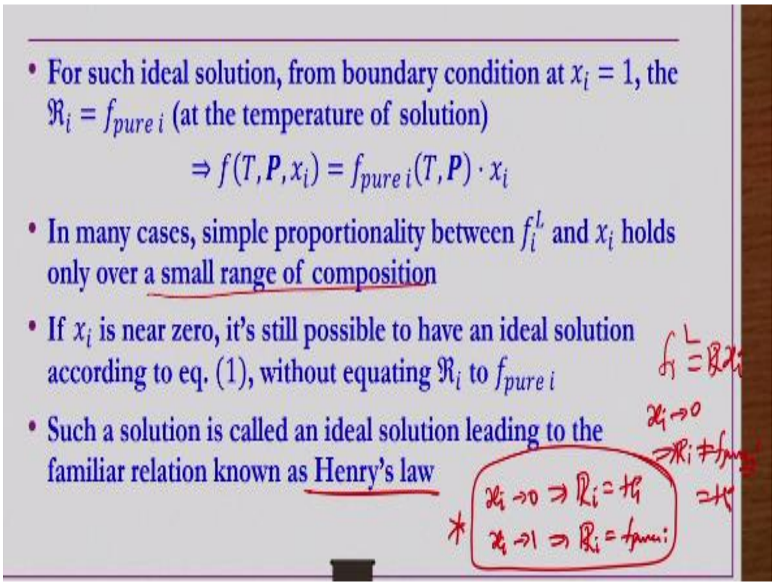

- For such ideal solution, from boundary condition at $x_i = 1$, the $\Re_i = f_{pure\,i}$ (at the temperature of solution)

$$\Rightarrow f(T,P,x_i) = f_{pure\,i}(T,P) \cdot x_i$$

- In many cases, simple proportionality between f_i^L and x_i holds only over a small range of composition
- If x_i is near zero, it's still possible to have an ideal solution according to eq. (1), without equating $\Re_i$ to $f_{pure\,i}$
- Such a solution is called an ideal solution leading to the familiar relation known as Henry's law

$f_i^L = \Re x_i$

$x_i \to 0$

$\Rightarrow \Re_i \neq f_{pure\,i}$

$= H_i$

$$* \boxed{\begin{array}{l} x_i \to 0 \Rightarrow \Re_i = H_i \\ x_i \to 1 \Rightarrow \Re_i = f_{pure\,i} \end{array}}$$

For such ideal solution from boundary condition at x_i is equals to1 then $\Re_i = f_{pure\,i}$ at the same temperature of solution as we have already discussed previously. Then we can write, $f(T,P, x_i) = f_{pure\,i}(T,P). x_i$ and then in many cases simple proportionality between f_i^L and x_i holds over a small range of composition in general, right?

So, if x_i is near 0, then it is still possible to have an ideal solution according to equation number 1 whatever that $f_i^v = \Re_i$ x_i but if $x_i \to 0$ then you do not need to write $\Re_i = f_{pure\,i}$, but you have some other constant H_i, according to Henry's law. Such a solution is called as ideal solution leading to the familiar relation known as the Henry's law, okay? So in the case of $x_i \to 0$, this constant $\Re_i = H_i$. In the case of $x_i \to 1$ this constant $\Re_i$ is nothing but $f_{pure\,i}$.

The previous one we have discussed for only binary mixture a and b, now we are writing the same relation for generalized case where it can be any number of components.

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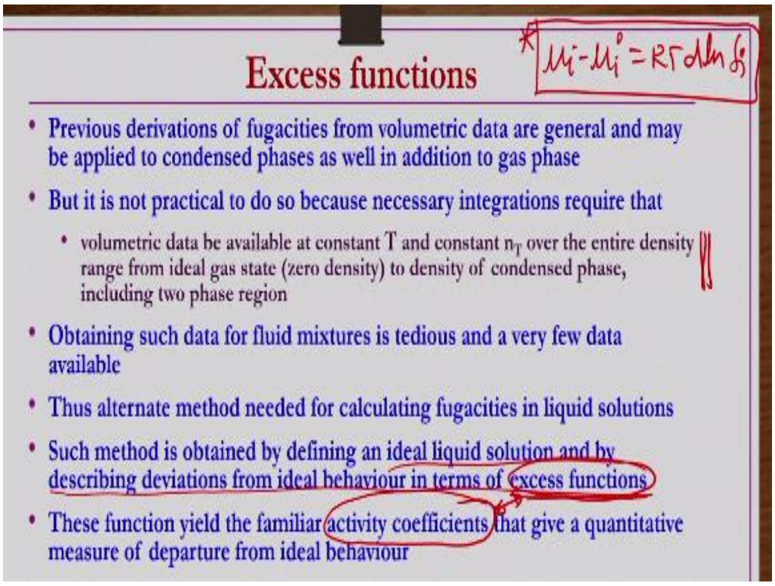

Excess functions

$\mu_i - \mu_i^0 = RT d \ln f_i$

- Previous derivations of fugacities from volumetric data are general and may be applied to condensed phases as well in addition to gas phase
- But it is not practical to do so because necessary integrations require that
  - volumetric data be available at constant T and constant n_T over the entire density range from ideal gas state (zero density) to density of condensed phase, including two phase region
- Obtaining such data for fluid mixtures is tedious and a very few data available
- Thus alternate method needed for calculating fugacities in liquid solutions
- Such method is obtained by defining an ideal liquid solution and by describing deviations from ideal behaviour in terms of excess functions
- These function yield the familiar activity coefficients that give a quantitative measure of departure from ideal behaviour

So, now we see excess functions, what are these excess functions? Why should we define this excess function in order to discuss the non-ideality of liquid mixtures that is what we are going to see now? Whatever the previous derivations are there that is $\mu_i - \mu_i^0 = RT\ d \ln f_i$ this information we have derived in the beginning of the course, right? This information, this equation is defined irrespective of the phase which phase are we dealing with. So it is valid for all the phases, gaseous phase, liquid phase, and solid phases also, right?

So, these derivations of fugacities from volumetric data are general and may be applied to condensed phase as well in addition to the gas phase but however, though this equation we have used successfully for the case of gaseous mixtures, we may not be able to use this expression for the condensed phase or liquid mixtures because it is not practical to do because necessary integrations require that this volumetric data should be available at constant temperature and then constant composition.

But over the entire density range from ideal gas state that is 0 density range to the density of condensed phase including 2 phase region if at all there is a two phase region existing. So, this information is required actually, okay? So and obtaining such data for fluid mixtures is very tedious and a very few data only available in the literature. Because of this reason, this equation we cannot use directly for the case of liquid solution. So, there must be an alternative approach for calculating fugacities in liquid solutions, right?

One such method is obtained by defining an ideal liquid solution and by describing deviation from ideal behavior in terms of excess functions, okay? Excess functions, what does it mean by? Like you know thermodynamic property of real solution - the thermodynamic property of the ideal system at the same temperature, pressure, and composition that is in excess to the ideal solution conditions whatever the thermodynamic property in excess to the ideal phase, ideal liquid solution conditions but at the same temperature pressure composition.

So, this may be helpful in getting the required activity coefficient. So, this excess function may provide us required activity coefficient that describe the non-ideality in the liquid solutions, okay? So, how it is going to be useful? How this excess function is going to be useful to develop this activity coefficient relation for the case of liquid solution that is what we are going to see now.

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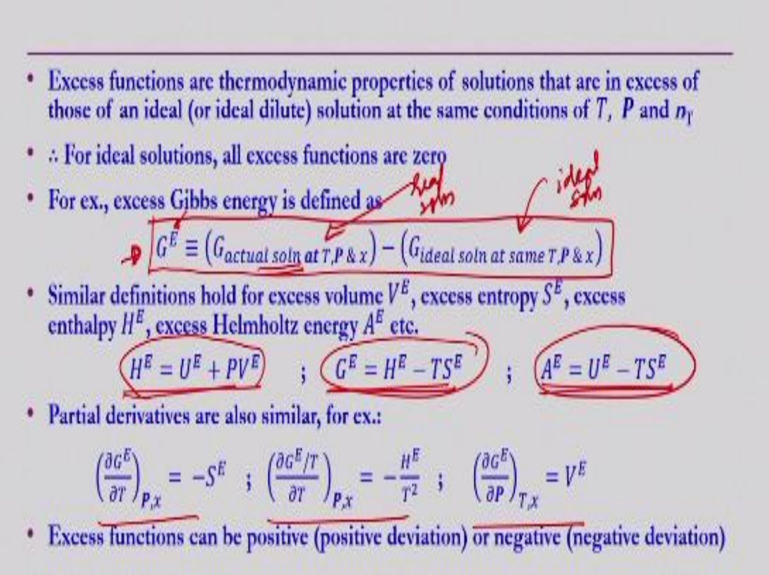

- Excess functions are thermodynamic properties of solutions that are in excess of those of an ideal (or ideal dilute) solution at the same conditions of T, P and n_T
- $\therefore$ For ideal solutions, all excess functions are zero
- For ex., excess Gibbs energy is defined as

Real soln

ideal soln

$$G^E \equiv (G_{\text{actual soln at } T,P\,\&\,x}) - (G_{\text{ideal soln at same } T,P\,\&\,x})$$

- Similar definitions hold for excess volume V^E, excess entropy S^E, excess enthalpy H^E, excess Helmholtz energy A^E etc.

$$H^E = U^E + PV^E \quad ; \quad G^E = H^E - TS^E \quad ; \quad A^E = U^E - TS^E$$

- Partial derivatives are also similar, for ex.:

$$\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -S^E \quad ; \quad \left(\frac{\partial G^E/T}{\partial T}\right)_{P,x} = -\frac{H^E}{T^2} \quad ; \quad \left(\frac{\partial G^E}{\partial P}\right)_{T,x} = V^E$$

- Excess functions can be positive (positive deviation) or negative (negative deviation)

So, excess functions are thermodynamic properties of solution that are in excess of those of an ideal solution or ideal dilute solution at the same conditions of temperature, pressure and composition. That means for ideal solutions all excess functions are 0. Excess function is nothing but for example excess Gibbs energy, if you define excess Gibbs energy the superscript E stands for excess. This excess Gibbs energy, total Gibbs energy $G^E \equiv (G_{\text{actual soln at T,P \& x}}) - (G_{\text{ideal soln at same T,P \& x}})$ as of the actual solution.

So, this second part in the RHS refers to the ideal solution but at the same temperature, pressure and composition and then this is for the real solution or actual solution, okay? If you take this difference whatever excess is there that is known as the excess thermodynamic property. Here in this case we have defined for the Gibbs energy. If it is 0 that means system is ideal because whatever the property and the real conditions are there, they are same as the property under the ideal condition.

So, that excess property is going to be 0. So, that means for ideal solutions, all excess functions are 0. Similar definitions hold for the excess volume, excess entropy, excess enthalpy, etc., these relations in general we are having for thermodynamic properties they are also valid for excess thermodynamic properties as well, right? And then partial derivatives are also similar for this excess function for examples defined like this, okay? So, excess functions can be positive deviation or negative deviation.

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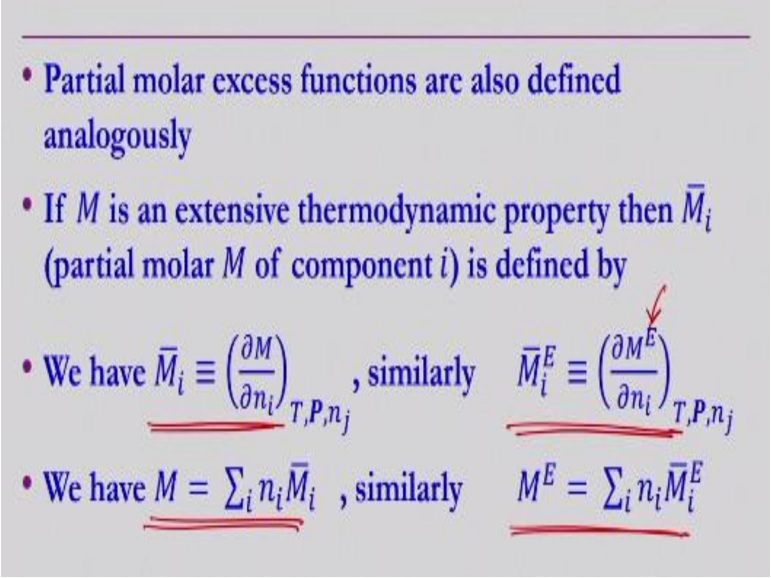

- Partial molar excess functions are also defined analogously
- If M is an extensive thermodynamic property then $\bar{M}_i$ (partial molar M of component i) is defined by
- We have $\underline{\bar{M}_i \equiv \left(\frac{\partial M}{\partial n_i}\right)}_{T,P,n_j}$, similarly $\underline{\bar{M}_i^E \equiv \left(\frac{\partial M^E}{\partial n_i}\right)}_{T,P,n_j}$
- We have $\underline{M = \sum_i n_i \bar{M}_i}$, similarly $\underline{M^E = \sum_i n_i \bar{M}_i^E}$

So, partial excess functions are also defined analogously. Let us say if M is an extensive thermodynamic property, then $\bar{M}_i$we have defined like this. So, similarly $\bar{M}_i^{\,E}$ we can define like this, only thing that here no we are using M^E, excess extensive property M and then M $=\sum_i n_i\ \bar{M}_i$ we have in general. So, in terms of excess properties if you have, we can have M^E $=\sum_i n_i\ \bar{M}_i^{\,E}$, so analogously we can define these properties without any difficulty for the case of excess functions as well.

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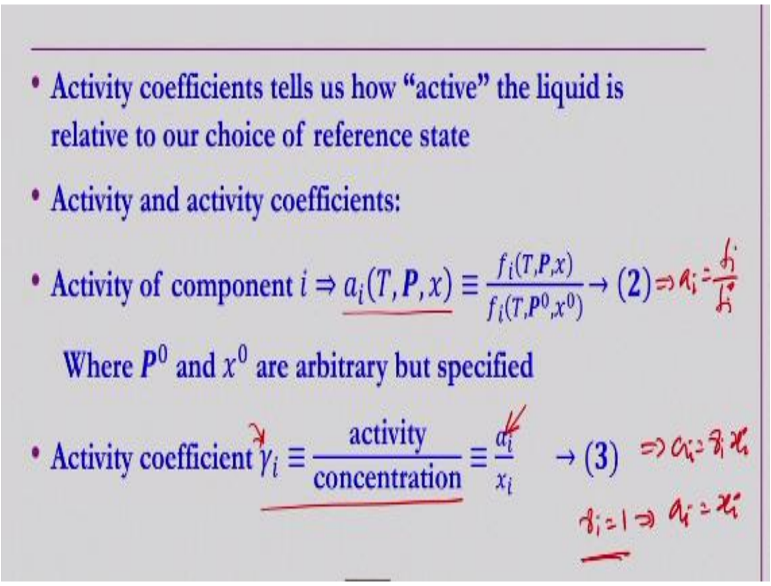

- Activity coefficients tells us how "active" the liquid is relative to our choice of reference state
- Activity and activity coefficients:
- Activity of component $i \Rightarrow \underline{a_i(T,P,x)} \equiv \frac{f_i(T,P,x)}{f_i(T,P^0,x^0)} \rightarrow (2) \Rightarrow a_i = \frac{f_i}{f_i^0}$

  Where P^0 and x^0 are arbitrary but specified
- Activity coefficient $\gamma_i \equiv \underline{\frac{\text{activity}}{\text{concentration}}} \equiv \frac{a_i}{x_i} \rightarrow (3) \Rightarrow a_i = \gamma_i x_i$

  $\underline{\gamma_i = 1} \Rightarrow a_i = x_i$

Activity coefficient tells us how active the liquid is relative to our choice of reference state and then activity and activity coefficient if you want to define, so the activity of component i $a_i(T, P, x)$ is equivalently defined as ratio between f_i and then f_i^0, $\frac{f_i(T,P,x)}{f_i^0(T,P^0,x^0)}$. So, that is P^0 and x^0 are arbitrary but specified pressure and specified composition. Then activity coefficient γ_i is defined as activity divided by the concentration this a_i is the activity and then γ_i is the activity coefficient.

So, now from here what we are having, $a_i = \frac{f_i}{f_i^0}$, and then from here $a_i = \gamma_i x_i$ that is what we are having. So, that means if the system is ideal then what we can say a_i is nothing but x_i that is activity of that particular component = the mole fraction of that particular component provided that solution is ideal, okay?

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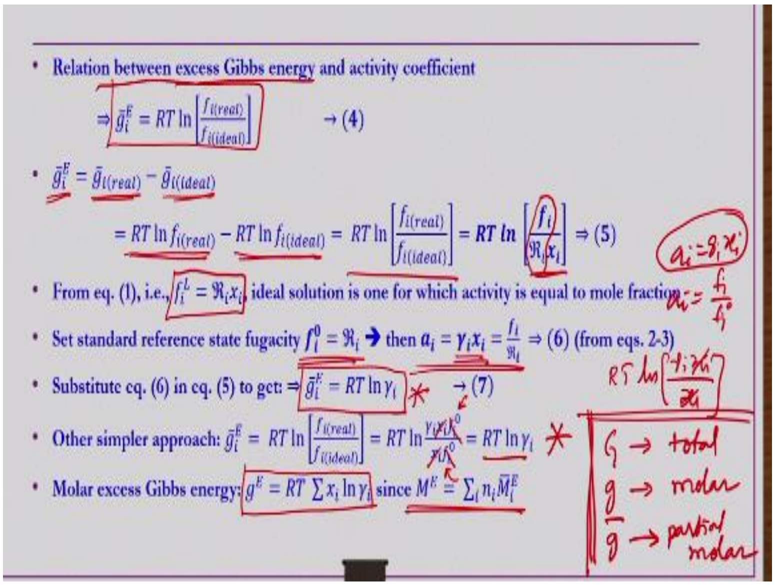

- Relation between excess Gibbs energy and activity coefficient

$$\Rightarrow \boxed{\bar{g}_i^E = RT \ln\left[\frac{f_{i(real)}}{f_{i(ideal)}}\right]} \qquad \rightarrow (4)$$

- $\bar{g}_i^E = \bar{g}_{i(real)} - \bar{g}_{i(ideal)}$

$$= RT \ln f_{i(real)} - RT \ln f_{i(ideal)} = RT \ln\left[\frac{f_{i(real)}}{f_{i(ideal)}}\right] = RT \ln\left[\frac{f_i}{\Re_i x_i}\right] \Rightarrow (5)$$

- From eq. (1), i.e., $\boxed{f_i^L = \Re_i x_i}$ ideal solution is one for which activity is equal to mole fraction
- Set standard reference state fugacity $f_i^0 = \Re_i$ ➔ then $a_i = \gamma_i x_i = \frac{f_i}{\Re_i} \Rightarrow (6)$ (from eqs. 2-3)
- Substitute eq. (6) in eq. (5) to get: $\Rightarrow \boxed{\bar{g}_i^E = RT \ln \gamma_i}$ * $\rightarrow (7)$
- Other simpler approach: $\bar{g}_i^E = RT \ln\left[\frac{f_{i(real)}}{f_{i(ideal)}}\right] = RT \ln \frac{\gamma_i \cancel{x_i} \cancel{f_i^0}}{\cancel{x_i} \cancel{f_i^0}} = RT \ln \gamma_i$ *
- Molar excess Gibbs energy: $\boxed{g^E = RT \sum x_i \ln \gamma_i}$ since $M^E = \sum_i n_i \bar{M}_i^E$

$a_i = \gamma_i x_i$

$a_i = \frac{f_i}{f_i^0}$

$RT \ln\left[\frac{\gamma_i x_i}{x_i}\right]$

$G \rightarrow$ total

$g \rightarrow$ molar

$\bar{g} \rightarrow$ partial molar

This is going to be useful here in order to define the relation between excess Gibbs energy and activity coefficient, okay? Now, we try to develop relation between excess Gibbs energy and activity coefficient. So, first we have to write excess Gibbs energy but what we do excess partial molar Gibbs energy we are writing, right? Excess partial molar Gibbs energy is nothing but partial molar Gibbs energy of that component i under the real conditions - partial molar Gibbs energy of the same component under the ideal condition at the same temperature, pressure and composition as of the real solution, right?

So, then this $\bar{g}_i$we know that it is nothing but RT ln $f_{i(real)}$ by the definition, already we have defined previously and then $\bar{g}_{i(ideal)}$ should be RT ln $f_{i(ideal)}$. That means we can write $\bar{g}_i{}^E$ is nothing but RT ln $\frac{f_i}{f_{i(ideal)}}$. That means, let us say if you take some $\Re_i$ as a kind of reference state then $\bar{g}_i{}^E$ is nothing but RT ln $\frac{f_i}{\Re_i x_i}$, this is what we have, right? Just now, we have seen this $a_i = \gamma_i x_i$ and then we have also seen that $a_i = \frac{f_i}{f_i^0}$, right?

Let us say if you have this ideal behavior, then $f_i^L = \Re_i R_i x_i$ linear relation should be there and this if you take this ideal solution is one for which activity = the molar fraction that we have seen already. If ideal solution, then activity coefficient =1, so then activity is nothing but molar fraction of that particular component, right? Then set standard state $f_i^0 = \Re_i$, then what we can have? We can have $a_i = \frac{f_i}{\Re_i}$. Now, this in place of $\frac{f_i}{\Re_i}$ here if you substitute $\gamma_i x_i$, then what we have, we have RT ln $\gamma_i \frac{x_i}{x_i}$, so, this x_i x_i is canceled out, so then we can have RT ln γ_i.

So, that is $\bar{g}_i$ = RT ln γ_i. So, this is the most important relation that we wanted to develop. Because now if you know the excess partial molar Gibbs energy of component i, you can find out its activity coefficient γ_i. If the activity coefficient is known then you can establish the non-ideality in the liquid phase as well. So, this is going to be very much essential and this relation must be remembered for long term, right? So, the same thing we can develop very simple way.

So, we have this one, this relation, so that is $\bar{g}_i$ =RT ln $\frac{f_{i(real)}}{f_{i(ideal)}}$, $f_{i(real)}$ is nothing but γ_i x_i f_i^0, what is this reference state, let us not worry about it, and then $f_{i(ideal)}$ is nothing but x_i f_i^0, again what is this reference state, whether LR or Henry's law or Raoult's law let us not worry. So, then here again x_i x_i, f_i^0 f_i^0 are cancelled out, so you have RT ln γ_i, the same relation we can get, this is the simpler way to get this same relation. That is $\bar{g}_i^E$ =RT ln γ_i this is going to be very essential for next few lectures as long as we are going to deal with this liquid mixtures.

So, molar excess Gibbs energy g^E is nothing but RT $\sum x_i$ ln γ_i because we have this $M^E = \sum_i n_i \bar{M}_i^E$. So, here x_i if you write n_i by n_T, that n_T if you take to the left hand side, so n_T g^E that will become G^E. Remember our notations are same as we have been following in the entire course. Capital letters, total properties we are taking; small letters we are taking for the molar properties; small letters with bar we are taking for partial molar properties. In the case here now, g^E I have written because we are discussing Gibbs energy, the same notations we are following here.

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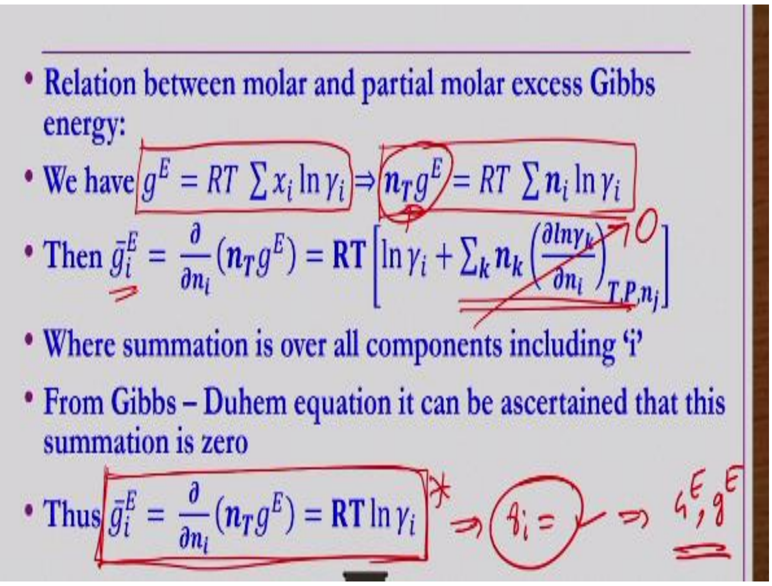

- Relation between molar and partial molar excess Gibbs energy:
- We have $g^E = RT \sum x_i \ln \gamma_i \Rightarrow n_T g^E = RT \sum n_i \ln \gamma_i$
- Then $\bar{g}_i^E = \frac{\partial}{\partial n_i}(n_T g^E) = \mathrm{RT}\left[\ln \gamma_i + \sum_k n_k \left(\frac{\partial \ln \gamma_k}{\partial n_i}\right)_{T,P,n_j}\right]$ $\to 0$
- Where summation is over all components including 'i'
- From Gibbs – Duhem equation it can be ascertained that this summation is zero
- Thus $\bar{g}_i^E = \frac{\partial}{\partial n_i}(n_T g^E) = \mathrm{RT} \ln \gamma_i$ * $\Rightarrow g_i = \Rightarrow G^E, g^E$

So, relation between molar and partial molar excess Gibbs energy we can have it as we have this g^E =RT $\sum x_i$ ln γ_i. So, that means x_i if I write n_i by n_T, so n_T if I take to the left hand side n_T g^E =RT $\sum n_i$ ln γ_i. So, $\bar{g}_i^E$ if you wanted to know you how to differentiate this left hand side with respect to n_i. That if you do $\frac{\partial}{\partial n_i}$ (n_T g^E) is nothing but $\bar{g}_i$. So, that is you will get RT ln γ_i $\frac{\partial}{\partial n_i}(n_i)$ is 1 here, so ln γ_i only you will be having + $\sum n_k \left(\frac{\partial ln\gamma_k}{\partial n_i}\right)_{T,P,n_j}$ for all remaining components generalized we are writing.

Then from Gibbs-Duhem equation we can find it out this summation which includes for the component i also is going to be 0. So, that means again we have this expression $\bar{g}_i$ =RT ln γ_i, different ways of getting the same expression we are trying to get this things, right? So, this is going to be important, this is what we have developed. This expression now we will be taking as a kind of basis for developing next discussions in coming lecture. So, this $\bar{g}_i^E$ =RT ln γ_i, so from here you can get the γ_i.

So, that means if you know the Gibbs energy, excess Gibbs energy or molar excess Gibbs energy if you know, then you can calculate this γ_i and then once you have the γ_i, you can establish the non-ideality in the system, this is what we are going to do in the next coming up couple of lectures.

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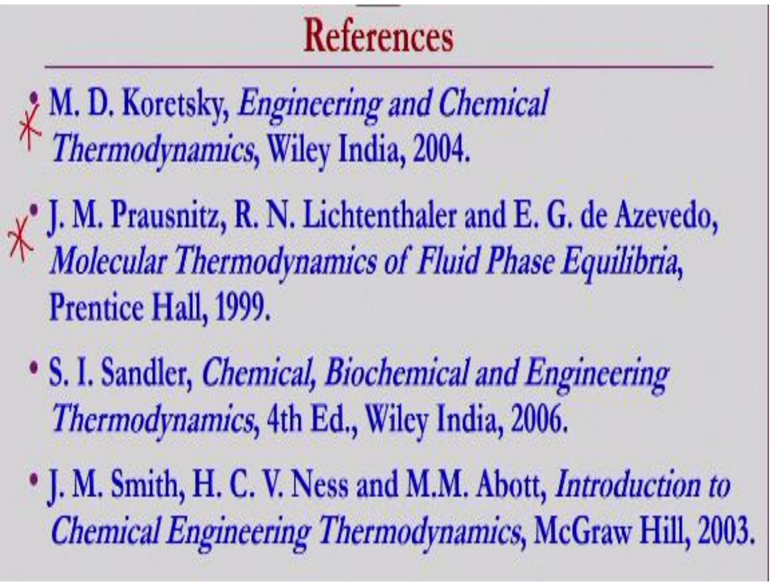

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So, the references for this particular lecture are given here. Engineering and Chemical Thermodynamics by Koretsky; Molecular Thermodynamics of Fluid Phase Equilibria by

Prausnitz et al; Chemical Biochemical and Engineering Thermodynamics by Sandler; and Introduction to Chemical Engineering Thermodynamics by Smith et al. So, most of the lectures that we have discussed are taken from these 2 reference books, Koretsky and Prausnitz et al.

Thank you.