

Chemical Engineering Thermodynamics
Professor Jayant K. Singh
Department of Chemical Engineering
Indian Institute of Technology Kanpur
Lecture 43
Activity coefficient of Mixtures

Welcome back. In the last lecture we discuss about reference for liquids just like the way we have taken the reference for the gas phases as ideal gas, we said that well we can extend this analogy and the properties of the ideal mixtures we define it in the last lecture.

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- IG acts as a ref state for gas.
 Q: What we should take for solids & liq.

Ideal Mixture (also called Lewis mix)
 - Chemically similar nature

Prop of IM

- $$\Delta U_{mix}^{IM} = \Delta V_{mix}^{IM} = \Delta H_{mix}^{IM} = 0$$
- $$\bar{H}_i^{IM}(T, P, \{x\}) = \bar{H}_i(T, P, pure\ i)$$

$$\bar{V}_i^{IM}(T, P, \{x\}) = \bar{V}_i(T, P, pure\ i)$$
- $$\Delta S_{mix}^{IM} = -NR \sum x_i \ln x_i$$

$$\Delta G_{mix}^{IM} = NRT \sum x_i \ln x_i$$

(Similar to the ideal gas mixture)

$$\left. \frac{\partial \bar{G}_i^{IM}}{\partial P} \right|_{T, \{N\}} = \bar{V}_i^{IM} = \bar{V}_i^{IM}$$

Where essentially it is in line with what we have done for ideal gas mixtures. So, ideal mixtures or ideal solution properties can be written in a similar sense that Delta u, Delta V and Delta H is going to be 0 for the mixture and the partial molar properties are going to be molar properties that is something which we are extending it and they here essentially this is for the pure.

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The image shows a whiteboard with handwritten mathematical derivations for ideal mixtures. At the top, there is a header $V_c = (r, p, z, \dots)$. The main derivations are as follows:

$$3. \quad \Delta S_{mix}^{IM} = -NR \sum x_i \ln x_i$$

$$\Delta G_{mix}^{IM} = NRT \sum x_i \ln x_i$$

(Similar to the ideal gas mixture)

$$\left. \frac{\partial \bar{G}_i^{IM}}{\partial P} \right|_{T, \{N\}} = \bar{V}_i^{IM} = \underline{V}_i^{IM}$$

$$\frac{\partial (\bar{G}_i^{IM}/T)}{\partial T} = -\frac{\bar{H}_i^{IM}}{T^2} = -\frac{H_i^{IM}}{T^2}$$

The whiteboard also shows a menu bar (File, Edit, View, Insert, Actions, Tools, Help) and a toolbar with various drawing tools. The page number 46/55 is visible in the bottom right corner.

And then we use the similar kind of expressions which we have derived for ideal gas mixture, to the ideal mixtures or ideal solution which we are written for Delta S and Delta G. Then what we talked about is that you know how do you obtain the chemical potential difference between the pure component and that in the mixture and we showed that we can relate this to $RT \ln x_i$.

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$$\left. \frac{\partial \Delta G_{\text{mix}}^{\text{IM}}}{\partial n_i} \right|_{T, P, n_{j \neq i}} = \bar{G}_i - G_i$$

$$= \mu_i^{\text{IM}}(T, P, \{x_i\}) - \mu_i(T, P, p_{\text{pure}})$$

$$RT \ln x_i = \mu_i^{\text{IM}}(T, P, \{x_i\}) - \mu_i(T, P, p_{\text{pure}})$$

$$= RT \ln \frac{f_i^{\text{IM}}}{f_i^{\circ}}$$

$$f_i^{\text{IM}} = x_i f_i^{\circ} \quad *$$

And using the relation of chemical potential to fugacity, we showed that well $RT \ln x_i$ is nothing but $RT \ln f_i$ of ideal mixtures divided by fugacity of the reference phase here for the pure component. Now, this is where I put f_i is zero.

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$$= RT \ln \frac{f_i^{\text{IM}}}{f_i^{\circ}}$$

$$f_i^{\text{IM}} = x_i f_i^{\circ} \quad *$$

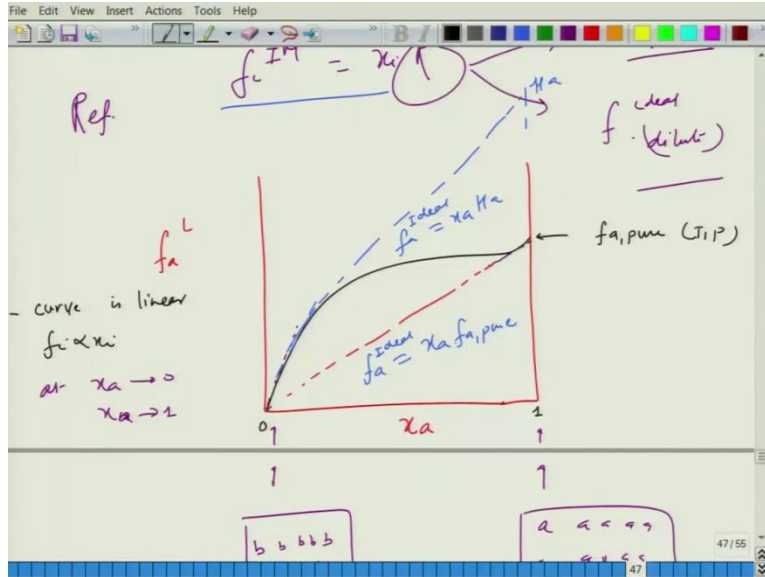
Ideal Soln / Mix : $\mu_i = \mu_i^{\circ} + RT \ln x_i$
 linear fn of $\log x$

* Identical to Lewis fugacity rule
 (\therefore all intermolecular forces are equal)

Using these two relations we said well fugacity of component I in an ideal mixture is proportional to the mole fraction with a constant here which is that of the fugacity of the reference state. Now, reference state we said well this we can take in the two ways depending on whether I is basically a solvent or a solid. For the solvent where all possible x are present, we will be considering

something like the Lewis-Randall rule where this f_i^0 would be that of the pure phase that means it will be a f_i pure.

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So, this was the case here f_a ideal corresponding to mixtures is going to be x_a that is a mole fraction multiplied by the reference state or a f_i^0 which is now in this case is f_a pure because all x_a exist from 0 to 1.

However, there would be some cases where the which would be relevant for solute which possibly may not exist in all composition from 0 to 1 in such case what we are going to consider is f_i ideal is proportional to x_a multiplied by something we call it H which is we call it Henry's constant and this is valid at extremely small concentration where x_a tends towards is 0.

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$b \ b \ b \ b$
 $b \ b \ b \ b$
 $a \ b \ b$
 $b \ a \ b$
 $b \ b$

$a \ a \ b \ c \ s$
 $c \ a \ s \ a$

i) $x_a \rightarrow 1$ pure species

$$f_a^o = f_a^{ideal} = f_{a, pure} \quad (\text{Lewis/Randall rule})$$

ii) $x_a \rightarrow 0$ another ref.

$$f_a^{ideal} = f_a^o = k_a \quad \text{Henry's law.}$$

Note

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$$f_a^{ideal} = f_a^o = k_a \quad \text{Henry's law.}$$

Note

a) If species a is defined by a Lewis-Randall reference
 → solvent-

b) a is defined by Henry's law
 - solute-

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So, that will be the case of the dilute condition and it is relevant for the solute, where the solute will be present in a very small amount in concentration. So, there are two cases, one is when x_a approaches 1 then we will be considering the reference the f_a is 0 here as simply f_a pure that will be your Lewis-Randall rule and other reference is the one which is relevant at the very low concentration of the component.

So, we do use this also sometimes where basically for example salt and some solute which are not even present in the complete range in such cases we prefer to use it. We will be trying to do some examples to illustrate this the differences in this reference in order to get more clarity but as of

now we are going to just put it like this and then we will move on to other aspects of that of this fugacity and the derivative of fugacity with respect to x and relating it to the pure component or Henry's constant. But as far as the clarities in terms of examples we will take it up in the subsequent lectures.

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Binary soln

$$\sum x_i d\bar{G}_i = 0 \Rightarrow x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad \text{at } T, P$$

$\therefore d\mu_i = RT d\ln f_i$

$$x_1 d\ln f_1 + x_2 d\ln f_2 = 0$$

divide by dx_1

$$x_1 \frac{d\ln f_1}{dx_1} + x_2 \frac{d\ln f_2}{dx_1} = 0 \quad \text{at } T, P$$

So, let me first consider in this today's lecture case where it is a binary solution and essentially, we know for the binary solution in general that Gibbs-Duhem relation or in general Gibbs-Duhem relation is going to be valid. So, essentially, I can write like Gibbs-Duhem relation as $x_i d\bar{G}_i$ or this is nothing but of course μ_i .

$$\text{Binary soln. } \sum x_i d\bar{G}_i = 0 \quad \text{or, } \quad x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad \text{at } T, P$$

$$d\mu_i = RT d\ln f_i$$

$$x_1 d\ln f_1 + x_2 d\ln f_2 = 0$$

$$\text{divide by } dx_1: \frac{x_1 d\ln f_1}{dx_1} + \frac{x_2 d\ln f_2}{dx_1} = 0 \quad \text{at } T, P$$

$$x_1 + x_2 = 1 \quad \text{or } \quad dx_2 = -dx_1$$

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The image shows a whiteboard with handwritten mathematical derivations. At the top, the equation $x_1 d \ln f_1 + x_2 d \ln f_2 = 0$ is written. Below it, the text "divide by dx_1 " is written, followed by the equation $x_1 \frac{d \ln f_1}{dx_1} + x_2 \frac{d \ln f_2}{dx_1} = 0$ with "at T, P" written to the right. Below this, the equation $x_1 + x_2 = 1$ or $dx_2 = -dx_1$ is written. The next line shows the rearranged equation: $x_1 \frac{d \ln f_1}{dx_1} = -x_2 \frac{d \ln f_2}{dx_1}$. Underneath, two terms are shown: $\frac{1}{f_1} \frac{df_1}{dx_1}$ and $\frac{1}{f_2} \frac{df_2}{dx_1}$, with arrows pointing from the terms in the equation above to these terms.

Now, considering is a binary mixture that means x_1 plus x_2 is equal to 1 or dx_2 is minus dx_1 . So, in that case we can write this expression here as $x_1 d \ln x_1$ therefore dx_1 is $x_2 d \ln f_2$ divided by dx_2 . So, this is something which I can write because if I bring take this term to the right-hand side it is going to be minus of that and since dx_1 is nothing but minus dx_2 .

So, this minus will cancel out and what we get is this expression. So, let me rearrange this expression now. So, if I rearrange this expression, I can write this as because $d \ln f_1$ is nothing but $\frac{1}{f_1} df_1$ and then you have this x_1 and x_2 . So, I can take this expression and this will be your $f_1 df_1$ by dx_1 . Similarly, this is going to be $f_2 df_2$ by dx_2 .

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$$\frac{df_1/dx_1}{f_1/x_1} = \frac{df_2/dx_2}{f_2/x_2}$$
 In the limit of $x_1 \rightarrow 1$, $x_2 \rightarrow 0$

$$\lim_{x_1 \rightarrow 1} \frac{df_1/dx_1}{f_1/x_1} = \lim_{x_2 \rightarrow 0} \frac{df_2/dx_2}{f_2/x_2}$$

$$\frac{1}{f_{1,pure}} \left(\frac{df_1}{dx_1} \right) \Big|_{x_1=1} = 1$$

$$\frac{df_1}{dx_1} = \frac{df_2}{dx_2}$$

$$\frac{f_1}{x_1} = \frac{f_2}{x_2}$$

In the limit of $x_1 \rightarrow 1$, $x_2 \rightarrow 0$

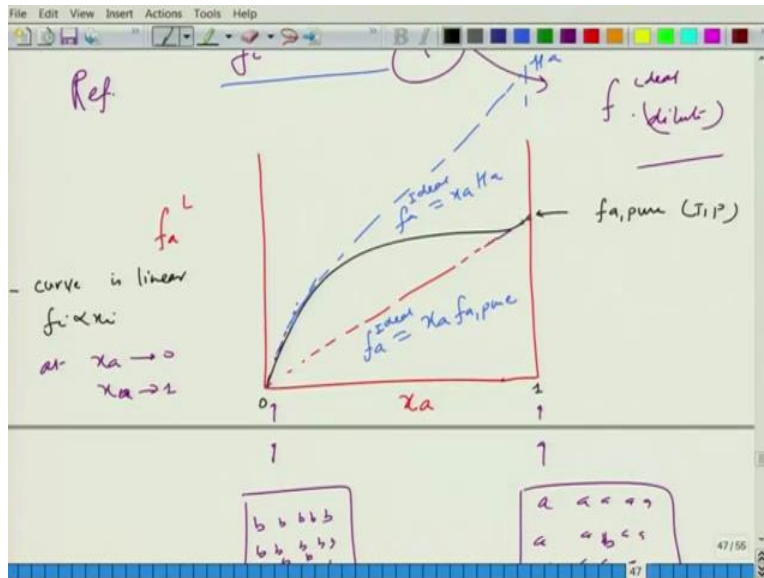
$$\lim_{x_1 \rightarrow 1} \frac{df_1}{dx_1} = \lim_{x_2 \rightarrow 0} \frac{df_2}{dx_2}$$

$$\frac{f_1}{x_1} = \frac{f_2}{x_2}$$

$$\frac{1}{f_{1,pure}} \left(\frac{df_1}{dx_1} \right) \Big|_{x_1=1} = 1$$

$$\frac{df_1}{dx_1} \Big|_{x_1=1} = f_{1,pure}$$

Expression of Lewis – Randall rule: $f_i^{ideal} = x_1 f_{1,pure}$



So, using this let me now get the expression here this would be your df_1 by dx_1 divided by f_1 by I take this here to the denominator x_1 this is going to be equal to df_2 by dx_2 f_2 by x_2 . So, where we are heading by doing this exercise. So, let me try to provide this information a bit here. So, if you look at let us go back again to look at a bit ahead.

So, what was this here. We showed that well the slope here is equal to f_a pure. Essentially that is a slope here or in other word you can also show that the slope here is essentially the Henry's constant and here is this f_a pure. So, how do you prove that? So, while this is something which we relate it in this form but we can also use this Gibbs-Duhem relation to get these expressions and that is what we are trying to do here.

So, we got this expression here from here how do you go to the next stage. So let us say now we put some limits. So, this is a expression which is true for all conditions for the binary mixture and in the limit of x_1 tending towards 1 or x_2 which tends towards zero if we put that limit to this expression then essentially I am going get a limit x_1 tending towards 1 df_1 by dx_1 divided by f_1 by x_1 .

And this is going to be limit x_2 because this is all x_2 df_2 by dx_2 f_2 by x_2 , x_2 goes to 0. In the limit of x_1 goes to f_1 , f_1 is going to be simply f pure and x_1 is of course 1. So, on the left-hand side what I am going to get is 1 by f_1 pure and then you have this df_1 by dx_1 in the limit of x_1 equal to 1.

And what about the right-hand side? Now, right hand side if you use this rule so if you differentiate this what you are going to get is the same term here and this will cancel each other and this is will lead to 1 here.

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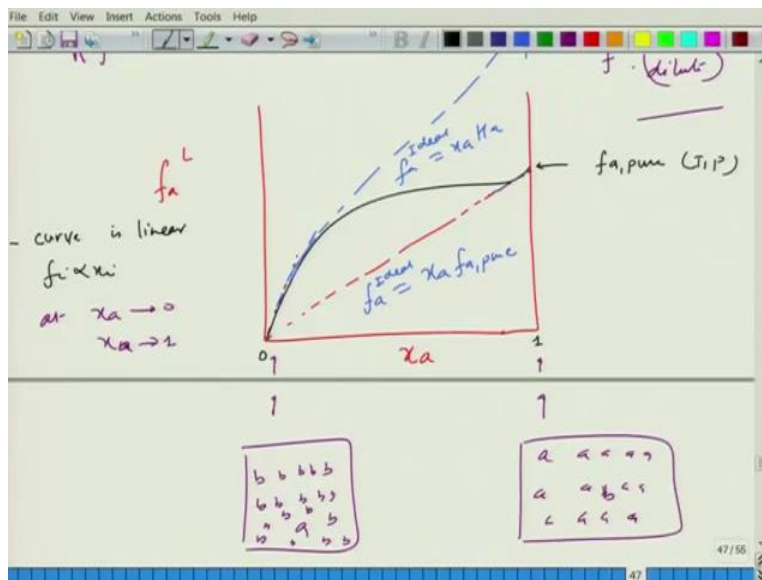
$$\lim_{x_1 \rightarrow 1} \frac{df_1/dx_1}{f_1/x_1} = \lim_{x_1 \rightarrow 1} \frac{df_1}{f_1}$$

$$\frac{1}{f_{1,pure}} \left(\frac{df_1}{dx_1} \right) \Big|_{x_1=1} = 1$$

$$\Rightarrow \boxed{\left. \frac{df_1}{dx_1} \right|_{x_1=1} = f_{1,pure}}$$

Expression of Lewis / Randall

$$\therefore f^I_{ideal} = x_1 f_{1,pure}$$

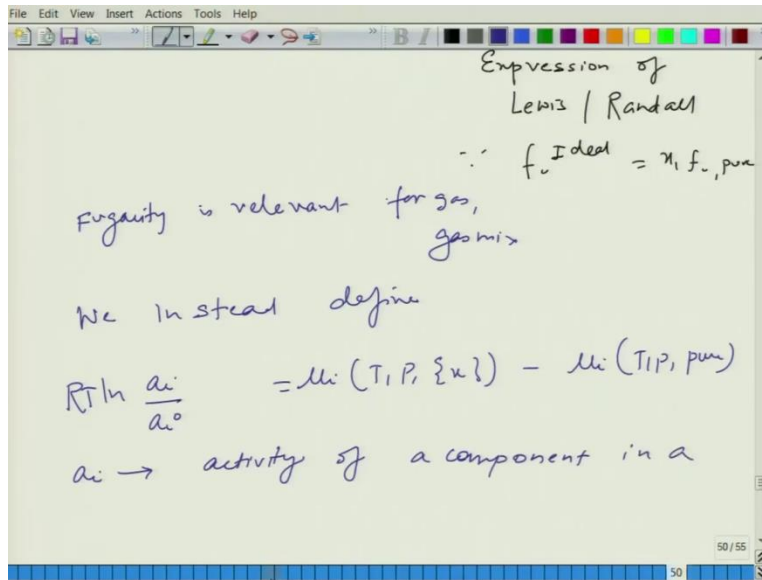


So, from this expression what we are going to get is this and essentially this all this implies that the slope of f_1 with respect to x_1 at x_1 equal to 1 is nothing but f_1 pure and that is something which we could clearly see from the ideal expression. That for the ideal solution, if you take the derivative of this with respect to x_a is nothing but f a pure.

And that is essentially the case of if you take it the real system and apply Gibbs-Duhem relation you obtain that relation particularly at x equal to 1. So, this is the basically the expression of Lewis-Randall. Where we have said that you know f_i ideal is nothing but $x_1 f_i$ pure. So, this is what exactly get and that means that basically when the composition x_1 tends towards 1 and when it approaches towards 1 the solution itself behaves like an ideal solution.

And that what is very clearly shown that because for an ideal solution the fugacity has to be proportional to composition and with the proportionality constant f_a pure so for the case of x_1 tending towards 1, f_i is nothing but the slope is nothing but therefore pure and that is what we could see that this is only feasible when the expression holds and that means at x equal to 1 this is nothing but ideal solution. So, we could prove it using that Gibbs-Duhem relations.

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Now, having said that I also made a remark that essentially fugacity is something which we often use for the gas phase and because its reference is usually the ideal gas, so what would be the right kind of parameter for the case of the solution. So, from that thoughts what we try to do is we try to define an another variable because as I mentioned here again the fugacity is more relevant for gases and mixtures.

So, with instead of this using fugacity for the liquid we still define a term which we use the same expression we said well is a $\mu_i(T, P, x)$ that difference of the chemical potential of a component i with respect to $\mu_i(T, P)$ for the pure case and we define this as $RT \ln a_i$ by a_i^0 . So, instead of fugacity we say activity. So, here a_i is nothing but the activity of a component in a mixture.

$$RT \ln \frac{a_i}{a_i^0} = \mu_i(T, P, \{x\}) - \mu_i(T, P, \text{pure}) \quad a_i \rightarrow \text{activity of a component in a mixture}$$

$$RT \ln a_i = \mu_i(T, P, \{x\}) - \mu_i(T, P, \text{pure})$$

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Unlike f_i , a_i^o is set to a pure member

$$\left. \begin{array}{l} a_i^o \rightarrow 1 \\ x_i \rightarrow 1 \end{array} \right\}$$

$$RT \ln a_i = \mu_i(T, P, \{x\}) - \mu_i(T, P, \text{pure})$$

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$$\frac{\partial \Delta G_{\text{mix}}^{IM}}{\partial N_i} \Big|_{T, P, N_{j \neq i}} = \bar{G}_i - \underline{G}_i$$

$$= \mu_i^{IM}(T, P, \{x\}) - \mu_i(T, P, \text{pure})$$

$$RT \ln x_i = \mu_i^{IM}(T, P, \{x\}) - \mu_i(T, P, \text{pure})$$

$$= RT \ln \frac{f_i^{IM}}{f_i^o}$$

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$$\frac{\partial \Delta G_{\text{mix}}^{IM}}{\partial N_i} \Big|_{T, P, N_{j \neq i}} = \bar{G}_i - \underline{G}_i = \mu_i^{IM}(T, P, \{x\}) - \mu_i(T, P, \text{pure})$$

$$RT \ln x_i = \mu_i^{IM}(T, P, \{x\}) - \mu_i(T, P, \text{pure } i) = RT \ln \frac{f_i^{IM}}{f_i^o}$$

$$a_i^{IM} = x_i$$

So, unlike fugacity we usually put a_i^0 is set to pure number. That means we are saying that a^0 usually we set to 1 which is basically for the case of a pure component limit x_i tending towards 1 which is what we are taking this as a reference. So, this would be the case where x_i tends towards 1.

So, that is a reference here which corresponds to the pure case here. So, thus we often write instead of what I have written earlier we often write $RT \ln a_i$ is simply $\mu_i(T, P, x)$ minus $\mu_i(T, P, \text{pure})$. Now, this is the definition here which we are going to use that.

Now, if you compare this particular definition of activity with respect to that what we have defined in for the case of ideal mixture then essentially the ideal mixture if you look at it again you could see that the chemical potential difference was connected to $RT \ln x_i$. So, this is the same thing but it is the $\ln x_i$. So, essentially for the ideal mixture the activity coefficient should be equal to composition.

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The image shows a digital whiteboard with handwritten notes. At the top left, it says "IM" and $a_i^{IM} = x_i$ is boxed. To the right, it shows $a_i = \frac{f_i}{f_i^0}$ with f_i^0 and f_i underlined. Below this, it says "activity coefficient - for a component - in a mix" and $\gamma_i = \frac{a_i}{x_i} = \frac{a_i}{a_i^{IM}}$. At the bottom, it says "IM $\gamma_i \rightarrow 1$ for all composition & for all component".

So, therefore for ideal mixture a_i for ideal mixture should be equal to the composition. But note that a_i is not a measure of a composition it is a measure of a chemical potential, because is the by definition we are relating to the chemical potential. Now, similar to the analogy of a fugacity

coefficient which we have used for when we discussed the gas phase is we are going to define the activity coefficient for a component in a mixture.

So, we are going to define the activity coefficient for a component in a mixture. The way we are going to define is that we will use the symbol called gamma i and this is going to be a_i divided by x_i . In the same way as we have done for fugacity coefficient where we said well fugacity coefficient is nothing but is the ratio of the pressure and the partial pressures. So, remember that ϕ_i was f_i by p_i or p_i was nothing but $y_i p$. So, in the same way we are going to define the gamma i as a_i which is the activity coefficient and the ratio of a_i with though that of ideal mixture.

So, in other word this is nothing but a_i divided by a_i ideal mixture correct. And so, say with the same way we have done that, here fugacity is f_i by f_i ideal which is nothing but $y_i p$. So, it tells you the deviation from the ideal mixture in some way because for a_{IM}, ideal mixture a_{IM} is nothing but x_i . So, which means that for ideal mixture gamma i has to be equal to 1 for all composition, for all components. So, for ideal mixture here gamma i is 1 for all composition and for all component.

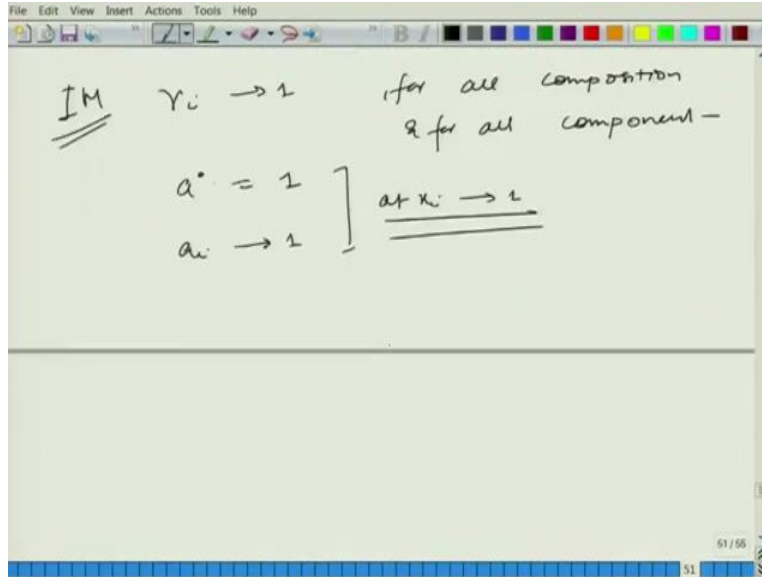
activity coefficient for a component in a mixture

$$\gamma_i = \frac{a_i}{x_i} = \frac{a_i}{a_i^{IM}}$$

IM: $\gamma_i \rightarrow 1$ for all composition and for all components

$$a^o = 1; a_i \rightarrow 1 \text{ at } x_i \rightarrow 1$$

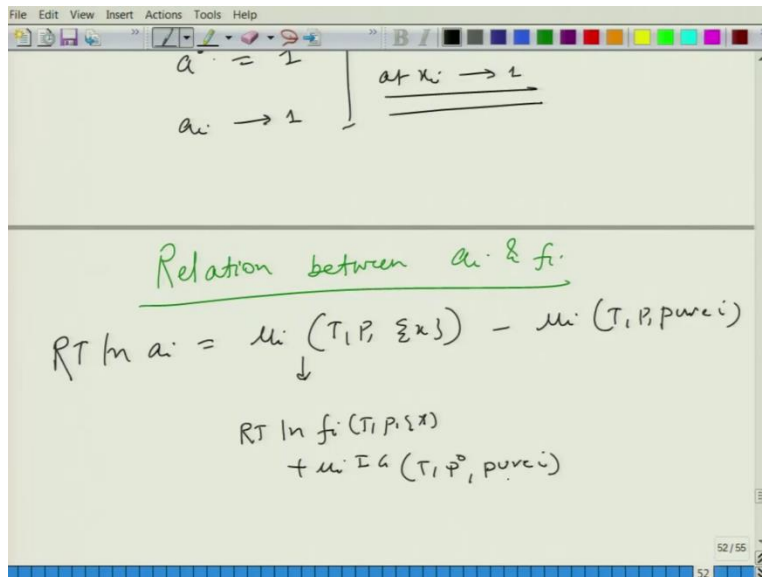
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Handwritten notes on slide 51. The text includes:

- IM $\gamma_i \rightarrow 1$ for all composition
- $a_i \rightarrow 1$ for all component -
- $a_i \rightarrow 1$] at $x_i \rightarrow 1$

Slide number: 51



Handwritten notes on slide 52. The text includes:

- $a_i \rightarrow 1$] at $x_i \rightarrow 1$
- $a_i \rightarrow 1$] at $x_i \rightarrow 1$
- Relation between a_i & f_i
- $RT \ln a_i = \mu_i(T, P, \{x_j\}) - \mu_i(T, P, pure i)$
- \downarrow
- $RT \ln f_i(T, P, \{x_j\}) + \mu_i^IG(T, P^0, pure i)$

Slide number: 52

Relation between a_i & f_i

$$RT \ln a_i = \mu_i(T, P, \{x_j\}) - \mu_i(T, P, \text{pure } i)$$

$$= \left[RT \ln f_i(T, P, \{x_j\}) + \mu_i^{\text{IG}}(T, P, \text{pure } i) \right] - \left[RT \ln f_i(T, P, \text{pure } i) + \mu_i^{\text{IG}}(T, P, \text{pure } i) \right]$$

$$RT \ln a_i = \underline{RT \ln f_i} - \mu_i^{\text{IG}}(T, P, \text{pure } i)$$

$$RT \ln a_i = RT \ln f_i(T, P, \{x_j\}) - RT \ln f_i(T, P, \text{pure } i)$$

Now, for the ideal mixture remember that since we have considered a zero is one which essentially means that if we are considering gamma equal to 1 then at x_i tending towards 1, I should get a_i because gamma tends towards 1, a_i is x_i and x_i also tends towards 1 and this condition then a_i should also tend towards 1 when you have this such a condition.

So, that is a definition of a_i which we talked about now how do you relate a_i to fugacity let us look at down because we have been talking about fugacity all the time when it related to the difference in the chemical potential even for the solution phase. Now, we had defined the activity coefficient and activity we would like to also relate this to the fugacity for the sake of completion of understanding. So, what is the relation between a_i and f_i .

So, let us look at it again by definition V is $RT \ln a_i$. So, that is going to be $\mu_i(T, P, \{x_j\})$ minus $\mu_i(T, P, \text{pure } i)$. Now, what I have to do is I have to use this expression and replace this in terms of the fugacity. Now, recall the definition of fugacity, fugacity was $RT \ln f_i$ was equal to μ_i minus that of the ideal gas that means the reference state there was an ideal gas so essentially this if you think about this, this was $RT \ln f_i + \mu_i^{\text{IG}}(T, P, \text{pure } i)$.

Because by definition, let me write it down the definition of $RT \ln f_i$ was so this is the definition $RT \ln f_i$ and considering $f_i = 1$ was nothing but μ_i , minus $\mu_i^{\text{IG}}(T, P, \text{pure } i)$ where p_0 and f_0 was connected. So, here this I am writing this as this because we are replacing μ_i by in terms of fugacity so it is going to be $RT \ln f_i$ plus this term.

So, this is the first term which we get and this the other term I also can use the same thing because now this is for the pure phase that means pure component in a liquid phase. So, I mean that is what we expect that is it has to be liquid. Now, let me write it here like this. So, this I can put it in the complete bracket and this again I can write it like this $RT \ln f_i$ this is a pure phase so it is going to be TP pure then you have this μ_i ideal gas again TP 0 pure.

Now, this is there is a negative sign and you have these four terms one, two and then you have negative sign there is another term and this term and this is within the bracket. Now, this term and this term can be cancelled, so what you have now is $RT \ln a_i$ is $RT \ln f_i$ TP x minus $RT \ln f_i$ TP pure of i.

(Refer Slide Time: 22:36)

The image shows a whiteboard with handwritten equations. The first equation is $RT \ln a_i = RT \ln f_i(T, P, x) - RT \ln f_i(T_i^0, p_{i, \text{pure}})$. The second equation is $RT \ln a_i = RT \ln \frac{f_i(T, P, x)}{f_i(T, P, \text{pure } i)}$. The third equation, enclosed in a box, is $a_i = \frac{f_i(T, P, x)}{f_i(T, P, \text{pure } i)} = \gamma_i x_i$.

So, this further can be simplified by taking this in the denominator. So, this is going to be the ratio of the fugacity of component i in the mixture and with respect to that in the pure phase. So, this is now $RT \ln a_i$. Now, if you use this if you consider the fact that a_i is by definition a_i is nothing but $x_i \gamma_i$ this is by definition.

Then I can relate this as because now this $RT \ln a_i$ is this essentially this also means that a_i is this ratio f_i TP x, f_i TP pure i and this is nothing but $\gamma_i x_i$. So, now we have a complete relation of activity or activity coefficient with this fugacity. So, this is basically the relation between the fugacity and activity.

Relationship between a_i and f_i

$$RT \ln a_i = \mu_i(T, P, \{x\}) - \mu_i(T, P, \text{pure } i)$$

$$RT \ln a_i = RT \ln f_i(T, P, \{x\}) - RT \ln f_i(T, P, \text{pure } i)$$

$$RT \ln a_i = RT \ln \frac{f_i(T, P, \{x\})}{f_i(T, P, \text{pure } i)}$$

$$a_i = \frac{f_i(T, P, \{x\})}{f_i(T, P, \text{pure } i)} = \gamma_i x_i$$

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The image shows a whiteboard with handwritten mathematical derivations. At the top, the text reads "Relationship between a_i and f_i ". The first equation is $RT \ln a_i = \mu_i(T, P, \{x\}) - \mu_i(T, P, \text{pure } i)$. The second equation is $RT \ln a_i = RT \ln f_i(T, P, \{x\}) - RT \ln f_i(T, P, \text{pure } i)$. The third equation is $RT \ln a_i = RT \ln \frac{f_i(T, P, \{x\})}{f_i(T, P, \text{pure } i)}$. The fourth equation is $a_i = \frac{f_i(T, P, \{x\})}{f_i(T, P, \text{pure } i)} = \gamma_i x_i$, which is enclosed in a purple box. Below the equations, a handwritten note states: "Activity is the ratio of fugacity of a component in a mixture to that of fugacity of the pure component at the same T & P". The whiteboard also shows a menu bar at the top with "File Edit View Insert Actions Tools Help" and a toolbar with various drawing tools. The bottom right corner of the whiteboard displays "52 / 55".

So, in words we can write this as that activity is the ratio of fugacity of a component in a mixture to that of fugacity of the pure component at the same temperature and pressure. Basically, it means the same aggregation whatever the state was we are considering the same conditions.

So, this way we could relate now the activity which is more appropriate for the solution phase to the fugacities but remember that many components in the solution may not exist in the pure liquid at temperature and pressure. So, for example they could be gases which are dissolved in solution and the gases may not be condensed at that particular room temperature for example if they are in a supercritical state.

So, in such case we usually do not arbitrate take this activity to such a condition, so we consider something called dilute solution and so forth and those kind of concept we are going to describe it

little more when we get a little bit of more understanding of the usage of the activity coefficient, activity and similarly for the Henry's law, Henry's constant.

So, something which we have to now spend little more time and that I am going to do that in a couple of more lectures today's lecture we are going to just focus on this which we just covered that and tomorrow's or next lecture we are going to extend this exercise and define another term which we call it access function and the reason is that now we will be talking about appropriate model for the liquid phase.

So, if you think about it the gas phase, we have a Van Der Waals equation of state, we have other equation of state which was very valuable or is valuable for obtaining such as fugacity coefficient. If you have information of volumetric data or the pressure explicit equation of state you can use that.

However, for the case of the liquid phase we do not often use this equation of state because those equation of states are not valid except for low pressure region. So, what would be the appropriate model in order to use for liquid phases, if you want to find out something like activity or activity coefficient. So, that is something which we are going to spend little more time in the next few lectures, hope to see you next time. That's it for today.