

Chemical Engineering Thermodynamics
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Lecture 44: Gibbs-Duhem relations and its impacts on the activity

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Relation between a_i & f_i .

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

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

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

Relation: $RT \ln a_i = RT \ln f_i(T, P, \{x_i\}) - RT \ln f_i(T, P^*, \text{pure } i)$

Welcome back, in the last class we introduced a parameter called Activity which we said that is more relevant for the liquid phase instead of using fugacity. And the definition we put is here $RT \ln a_i$ is nothing but μ_i that means the component in the mixture minus chemical potential of the pure component in the same temperature and pressure.

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The image shows a digital whiteboard with handwritten mathematical equations. At the top, there are two terms: $+ \mu_i^I(T, P, p_{pure i})$ and $+ \mu_i^I(T, P, p_{pure i})$, both with a red diagonal line through them. Below these, the equation $[RT \ln f_i = \underline{\underline{\mu_i}} - \mu_i^I(T, P, p_{pure i})]$ is written. The next line is $RT \ln a_i = RT \ln f_i(T, P, x_i) - RT \ln f_i(T, P, p_{pure i})$. This is followed by $RT \ln a_i = RT \ln \frac{f_i(T, P, x_i)}{f_i(T, P, p_{pure i})}$. A large purple box contains the final equation: $a_i = \frac{f_i(T, P, x_i)}{f_i(T, P, p_{pure i})} = \gamma_i x_i$. At the bottom, the text "Activity is the ratio of fugacity" is written in cursive.

And this particular activity we try to now relate to the fugacity which we derived it to be a ratio of the fugacity of the component i in the mixture and the fugacity of the pure for example.

So activity is also defined in terms of the later on we said well activity can be also we can define in the similar sense as we have done for fugacity coefficient. We can also define activity coefficient which is nothing but a_i divided by x_i of that mixture which is nothing but a composition. And hence a_i can be written as simply $\gamma_i x_i$. So that was the definition which we talked about here.

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The whiteboard contains the following handwritten notes:

- IM $a_i^{IM} = x_i$
- $\therefore Q_i = \frac{f_i}{f_i^{IM}}$
- $a_i = \frac{f_i}{f_i^{IM}}$
- Activity coefficient - for a component - in a mix $\gamma_i = \frac{a_i}{x_i} = \frac{a_i}{a_i^{IM}} \Rightarrow a_i = x_i \gamma_i$
- IM $\gamma_i \rightarrow 1$ for all composition & for all component -
- $a_i^* = 1$ at $x_i \rightarrow 1$

So, this is something the definition of the activity coefficient where it is nothing but the activity divided by activity of that I mixture which is nothing but the composition.

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The whiteboard contains the following handwritten notes:

- $f_i(T, P, pure_i)$
- 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

So, this was something which we derived here and now the question is that we would like to use this activity for the liquid phase. So in today's lecture we will try to connect few dots we will try to understand the Gibbs-Duhem relations and his impact on the activity, that means how activity of let us say binary mixtures are connected, that is one part of it and the second part is that can we

come up with a model which we can use it for activity. So, something which we will try to develop such a model, for that we will define something called excess functions.

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Thermodynamic Relation between γ_i :

G-D Relⁿ $\sum n_i d\mu_i = 0$ at (T, P)

\downarrow
 $d \ln f_i$

$\sum n_i d \ln f_i = 0$

$f_i = n_i \gamma_i f_i^0$

$\sum n_i d \ln n_i + \sum n_i d \ln \gamma_i + \sum n_i d \ln f_i^0$
 \downarrow
const.

So, let me first start with the thermodynamic relation between gamma i that is activity coefficients. So, we will start with the Gibbs- Duhem relation here, we say it is that of course summation xi d mu I is equal to 0 at a given temperature and pressure. Now I can write this mu i in terms of fugacity I can write this as ni d ln fi is equal to 0 because d mu is nothing but d ln fi.

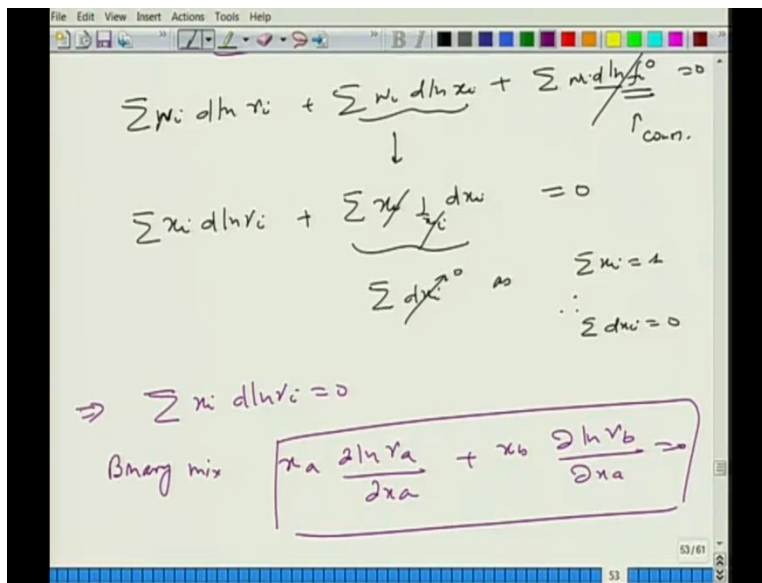
And here what I have mentioned here is basically number of moles I can write this in the capital one also but if I divide this by total number of moles it will be xi so I can keep it like xi if I preferred to do that but let me let me just stick to the number of moles here and I can use the capital ones also Ni or I can use the small one here. So let me use this capital here and then the next thing is that I have replaced d mu i by this and we got this expression.

Now fi relation with the gamma is here, fi is nothing but gamma i xi and this reference state which we are keeping at fi pure or we can keep it as fi 0. So if that is the case then I can write fi is equal to xi gamma i fi some reference state which usually is a pure or it could be when you have this let us say Henrys limit where we have to consider that for the case of the diluted solution.

But for a given temperature pressure even if you change a composition this is fixed because that is depends on the temperature or more or less we are saying that this is constant for a given temperature and pressure, even if you change the composition so this is x_i .

So now this is we can plug in this information here and now I have an information of this we can expand and we got $N_i d \ln \gamma_i$ plus $N_i d \ln x_i$ because I am replacing this plus summation $N_i d \ln f_i^0$. Now this is a constant remember that, for a given temperature and pressure, so the differential element that is going to be 0 and this whole thing should be equal to 0.

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$$\sum N_i d\mu_i = 0 \text{ at } (T, P) \text{ or, } \sum N_i d \ln f_i = 0$$

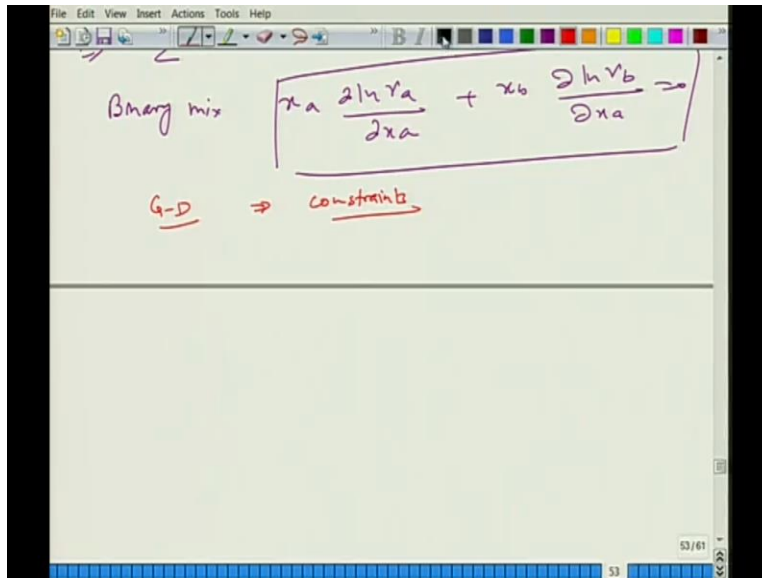
$$f_i = x_i \gamma_i f_i^0$$

$$\sum N_i d \ln \gamma_i + \sum N_i d \ln x_i + \sum N_i d \ln f_i^0 = 0$$

$$\sum x_i d \ln \gamma_i + \sum x_i \frac{1}{x_i} dx_i = 0 \quad \sum x_i = 1 \text{ hence, } \sum dx_i = 0$$

$$\sum x_i d \ln \gamma_i = 0$$

$$\text{Binary mixture: } \frac{x_a \partial \ln \gamma_a}{\partial x_a} + \frac{x_b \partial \ln \gamma_b}{\partial x_a} = 0$$

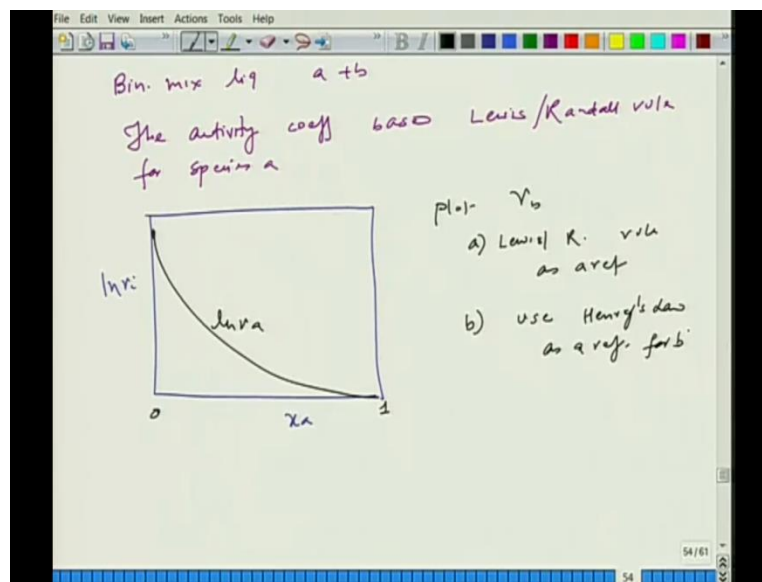
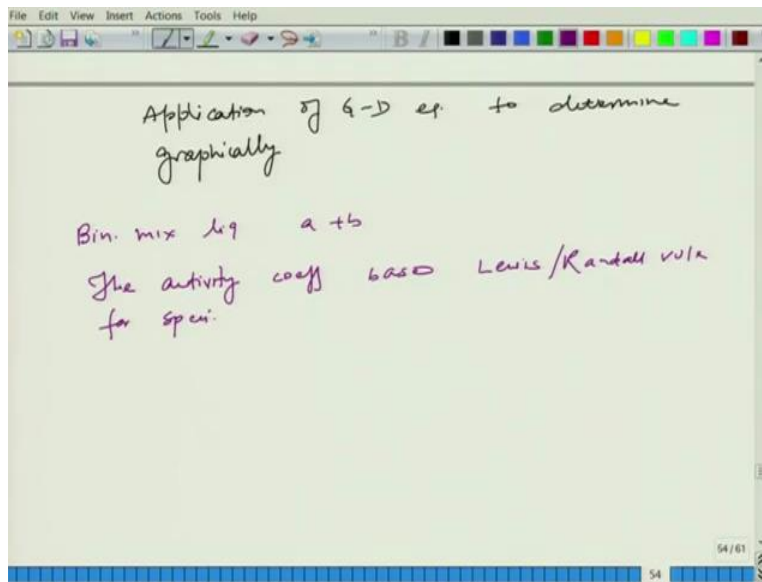


So, now we can now look at this part here so if we let us say differentiate this with N here capital total number N and we are talking about x_i , $d \ln x_i$. So this could be written as $N_i^{-1} x_i d x_i$ right and now if we differentiate this if we sorry divide this whole thing by capital N then I am going to get $x_i d \ln \gamma_i$ plus $x_i d \ln x_i$ is 1 by $x_i d x_i$ so this cancels out this must be equal to 0 . This term here summation $d x_i$ should be 0 as summation x_i is equal to 1 . Therefore, summation $d x_i$ should be 0 .

So this analysis yields the following expression that this implies that summation $x_i d \ln \gamma_i$ should be 0 . So for the binary mixture I can now write this as the following if I take it this as $x_a d \ln \gamma_a$ divided by $d x_a$ plus $x_b d \ln \gamma_b$ divided by $d x_a$ equals to 0 . I can also write $x_a d \ln \gamma_a$ plus $x_b d \ln \gamma_b$ but if we differentiate with respect to simply x_a then we can write it in this way. So this gives you a kind of a constraint or between or relation between the activity coefficients of different components in a given mixture. So let us try to make use of that.

So this is of course this is again a Gibbs-Duhem relation in the form of a gamma, right and it implies a, it provides you the constraints. So let me try to use this expression of Gibbs-Duhem relation which is based on now in gamma. So remember that earlier we have written the Gibbs-Duhem relations in terms with the chemical potential, then we change that to the fugacity and now we have a Gibbs-Duhem relation in terms of the activity coefficients which is relevant for the mixtures.

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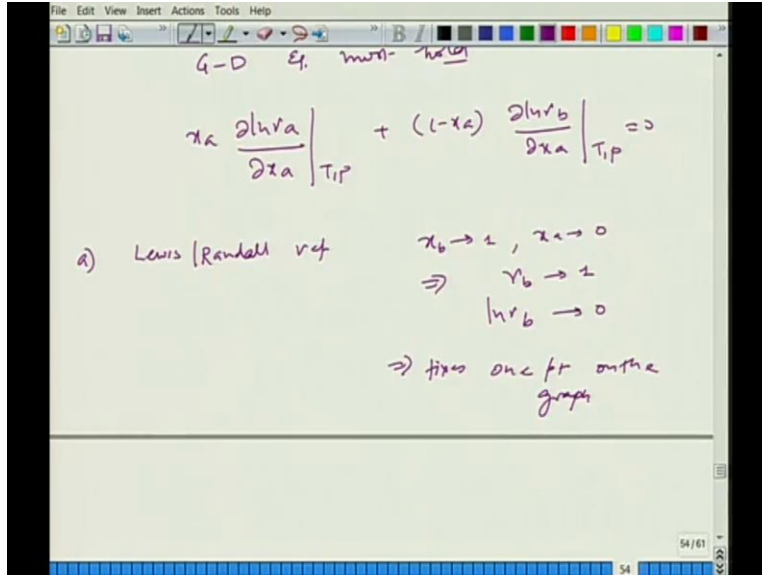


So let us take an example of an application of G-D equation to determine graphically. So consider so the question is that consider a binary mixture, binary mixture liquid phase. Let us say a plus b and what we are saying is that the activity coefficient is based on Lewis Randall rule for species a and it is being plotted as follows so you have been given that you have this activity coefficient for x_a is given like this.

So this is the $\ln \gamma_a$, it is based on Lewis Randall rule basically it is valid from 0 to 1 for x_a . So what we have been asked to do is to plot activity coefficient for b considering Lewis Randall

rule as a reference or the second part the first part is this the second part is to use Henry's law as a reference and again these are for component b.

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So here the Gibbs-Duhem relation comes very handy so let me first write it down and this will provide guidance because the G-D equation should hold must hold irrespective of whatever references you are taking here.

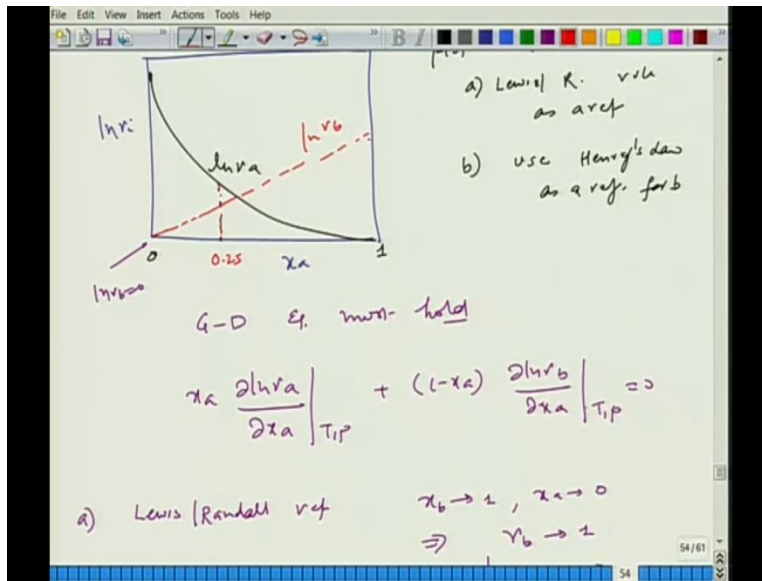
So this is $x_a d \ln \gamma_a$ divided by x_a at a given temperature and pressure and this is x_b which I can write now as $1 - x_a d \ln \gamma_b$ at a given temperature and pressure. So let us now little bit understand this now, if we look at this slope here at a given point the slope here is going to be negative right and since x_a is positive this is negative and this is positive which essentially means this must be positive, so that is something which we can come up with.

So, this gives you the constraints as far as the slope is concerned. Now if we have a slope at one point, we can actually figure it out. So, let us look at part one of this, for Lewis Randall reference species b when it approaches 1 that means when x_a approaches 0, the species the mixture will behave like an ideal gas. In such a case your γ_b should approach 1 or $\ln \gamma_b$ should approach 0. So, this particularly fixes one point on the graph.

$$\frac{x_a \partial \ln \gamma_a}{\partial x_a} \Big|_{T,P} + \frac{(1-x_a) \partial \ln \gamma_b}{\partial x_a} \Big|_{T,P} = 0$$

Lewis Randall vap. $x_b \rightarrow 1, x_a \rightarrow 0$ or, $\gamma_b \rightarrow 1 \ln \gamma_b \rightarrow 0$

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So it tells you very simple that $\ln b$ is 0 which essentially means that when x_a is equal to 0 this value here this must be here $\ln \gamma_b$ equal to 0. However based on this Gibbs-Duhem relation we know that this is something which is clearly this particular one is clearly positive which essentially means that your relation here should be something like this. So for example you can consider based on this relation you can consider very clearly that let us say you can find out x_a .

So if you have graphically information is available you can find let us say some value let us say 0.25, so given a 0.25 you know the slope here, that means this is the 0.75 so you can calculate this one. So for each points you can figure it out the slope and subsequently you can draw it like that but however I am just writing I am just drawing it just you know looking at the fact that this has to be slope should be positive and given that at the limiting conditions this must be 0, hence we should be able to find out something like this we should be $\ln \gamma_b$.

But more precisely you should be able to find for each point here and obtain the slope and use this relation to obtain the slope at each point and that way we can draw the lines also.

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b) Henry's law
 $\ln \gamma_b^{\text{Henry}}$ (Same as determined earlier)

$x_b \rightarrow 0 \Rightarrow x_a = 1$
 $\gamma_b^{\text{Henry}} \rightarrow 1$
 $\ln \gamma_b^{\text{Henry}} \rightarrow 0$

a) Lewis R. ref. as a ref. for b
 b) use Henry's law as a ref. for b

$G-D$ eq. must hold

$$x_a \left. \frac{\partial \ln \gamma_a}{\partial x_a} \right|_{T,P} + (1-x_a) \left. \frac{\partial \ln \gamma_b}{\partial x_a} \right|_{T,P} = 0$$

a) Lewis/Randall ref. $x_b \rightarrow 1, x_a \rightarrow 0 \Rightarrow \gamma_b \rightarrow 1$

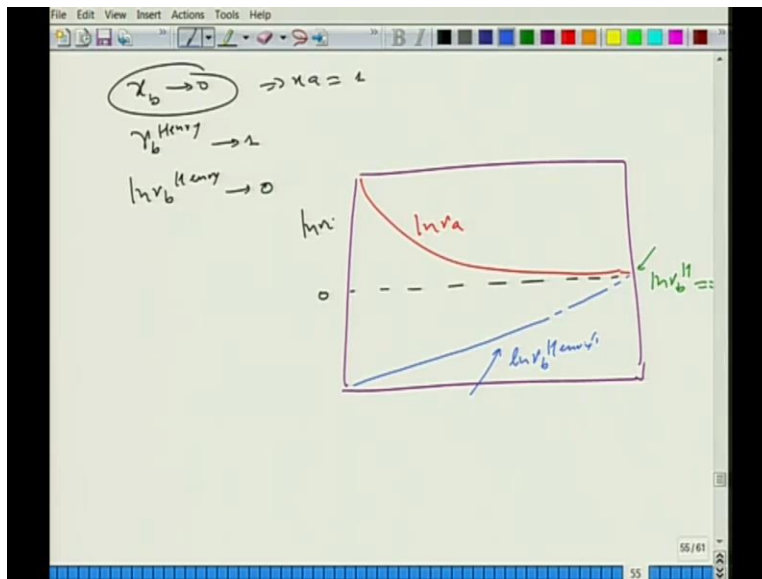
So, let us look at the case which is the case part b which is your Henry's law, now if you considering the reference state then again, the Gibbs-Duhem relation should be satisfied. Therefore, $\ln \gamma$ even if it is your Henry's law it should be same as that one you know same as 1 as determined in the first part earlier. So, slope has to be the same based on the Gibbs-Duhem relation.

So, slope is same here, so what we know is the slope is same but the point is that we do not know from where to start so we need some limiting condition. So that is why we start again looking at it that in the case of Henry's law your x when b goes to 0 then your γ_b Henry will start behaving

like an ideal solution and in that case this must be equal to 1 or in other words $\ln \gamma_b$ Henry, is a reference should be 0.

So which essentially means that x_b equals to 0 means x_a goes to 1 and in that case I should have something like this but if it is a positive, so here this point at this point your γ_b should be equal to 1 which essentially means $\ln \gamma_b$ should be equal to 0 but it is a positive the same slope.

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So this is only possible when the rest of the values should be negative, so in other words I will have the following graph for the case of Henry's law reference one. So I have this as 0 and $\ln \gamma_i$ and this is the one which is given to us, this is $\ln \gamma_a$. I am drawing little out of scale but I understand hope that I you are getting the point here.

So for the case of a Henry's reference I have here $\ln \gamma_b$ H that should be 0 and since the slope is same, so essentially I should be able to draw the following value here. So this is your $\ln \gamma_b$ H or Henry's.

Basically, telling you that if you take the reference the values are going to be different, the expressions are little bit though the slopes are same the values are in this case are going to be different. Now this is mainly due to the constraints which we have provided and this has helped us

to find out a typical behavior of the coefficient depending on what kind of the reference you are going to take.

Now one of the major challenges which we are going to face now is how do you calculate this gamma analytically and this is something which will become important. For example if you look at the philosophy of equation of state now equation of the state for the gas phase clearly depends on the parameters which try to relate to the molecules of the gases.

So some have attractive forces and because of that we bring we brought a, because of the size we brought b that is a wonder wall equation and then since wonder wall equation does not capture all of it we came up with a modification of the equation also. But what about the liquid phase, now can we connect gamma to again some interaction parameter between the molecules. So how do we go about it?

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Excess function

$$B^{Ex}(T, P, \{N_i\}) = B(T, P, \{N_i\}) - B^{IM}(T, P, \{N_i\})$$

Mixture properties

$$B^{Ex} = B - B^{IM} = \underbrace{B - \sum N_i B_i}_{\Delta B_{mix}} + \underbrace{\sum N_i B_i - B^{IM}}_{-\Delta B_{mix}^{IM}} = \Delta B_1^{Ex}$$

So let me first start with a another definition here which we call it as excess functions. So it is very useful as you will clearly see once we start working on it so is defined as the follows, B Excess at a given temperature and pressure is B T P N minus B of idle mixture at the same condition. So B excess is nothing but the difference with respect to the idle mixture the property and B could be any property. So B is a basically mixture property.

Now let me little bit extend this so I can write this B Excess this is B minus B idle mixture and then I can subtract and add the following which is $N_i B_i$ underscore which is a molar property and then we I am now adding the same thing and this specifically is nothing but ΔB_{mix} by definition and this is again it is going to be ΔB_{mix} for the idle mixture. So B Excess is nothing but the difference also in the ΔB_{mix} with respect to the idle mixture. So if you consider ΔB as a property then this is nothing but ΔB_{EX} mixture.

$$B^{EX}(T, P, \{N\}) = B(T, P, \{N\}) - B^{IM}(T, P, \{N\})$$

$$B^{EX} = B - B^{IM} = B - \sum N_i \underline{B}_i + \sum N_i \underline{B}_i - B^{IM}$$

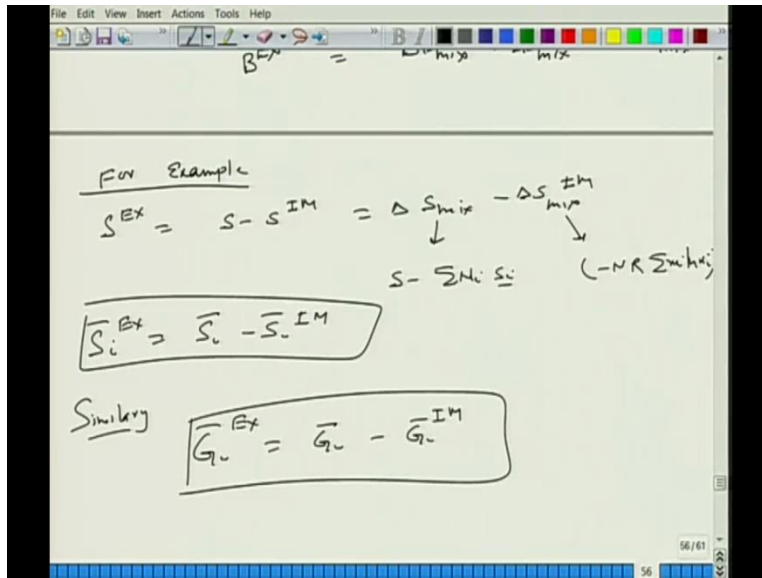
$$B^{EX} = \Delta B_{mix} - \Delta B_{mix}^{IM} = \Delta B_{EX}$$

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The image shows a digital whiteboard with handwritten notes. At the top, it says "Mixture properties, U, S, V, H, G ". Below this, the derivation is written:

$$B^{EX} = B - B^{IM} = \underbrace{B - \sum N_i \underline{B}_i}_{\Delta B_{mix}} + \underbrace{\sum N_i \underline{B}_i - B^{IM}}_{\Delta B_{mix}^{IM}} = \Delta B_{mix}^{EX}$$

The whiteboard interface includes a menu bar (File, Edit, View, Insert, Actions, Tools, Help), a toolbar with various drawing tools, and a status bar at the bottom showing "55 / 61".



So as I said the B could be any property mixture property this could be your U, S, V, H and G. Now for example for example S of Ex can be written as S minus S idle mixture and this nothing but delta S of mix minus delta S of mix idle mixture and this is of course you know this has nothing but S minus summation Ni molar S and this is nothing but your minus NR summation xi ln xi. So you can fill in the details, now this particular expression is an extensive property is a thermodynamic definition also.

So we can also extend this thing to partial molar property, we can also add it like this S of i Ex and we can prove that. Now similarly I can also show the G i Ex is G i bar minus G i idle mixture. So what I have defines as a B x is also extensible to partial molar properties. Alright, so this is by simple definition which we have written for the Excess property. Now what I am going to do is I am going to relate this thing to the Excess property to the activity. So these are two important part, let us go from there.

$$S^{EX} = S - S^{IM} = \Delta S_{mix} - \Delta S_{mix}^{IM}$$

$$\bar{S}_i^{EX} = \bar{S}_i - \bar{S}_i^{IM}$$

$$\text{Similarly, } \bar{G}_i^{EX} = \bar{G}_i - \bar{G}_i^{IM}$$

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Similarly $\overline{G}_i^E = \overline{G}_i - \overline{G}_i^{IM}$

Relation between excess free energy & activity

$$RT \ln \gamma_i x_i = \mu_i(T, P, \{x_i\}) - \mu_i(T, P, pure_i)$$
$$RT \ln \gamma_i + RT \ln x_i = \overline{G}_i - \mu_i(T, P, pure_i)$$

So let me gain go back to the definition of the activity coefficient and then subsequently we will see how to connect to the, this partial molar property. So this is to find out the relation between Excess function and activity. So let us start again with $RT \ln \gamma_i x_i$ that is activity, now that is by definition be $\mu_i(T, P, \{x_i\}) - \mu_i(T, P, pure_i)$. This can be written as $RT \ln \gamma_i + RT \ln x_i$ and this is nothing but the partial molar Gibbs free energy so this is nothing but $\gamma_i x_i$ and then we have this $\mu_i(T, P, pure_i)$.

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The image shows a whiteboard with handwritten mathematical equations. The top equation is $RT \ln \gamma_i x_i = \mu_i(T, P, \{x_i\}) - \mu_i(T, P, \text{pure } i)$. The second equation is $RT \ln \gamma_i + RT \ln x_i = \bar{G}_i - \mu_i(T, P, \text{pure } i)$. The third equation, starting with 'or', is $RT \ln \gamma_i = \bar{G}_i - \mu_i(T, P, \text{pure } i) - RT \ln x_i$. Below this, there is a bracketed term $-\left[\mu_i(T, P, \text{pure } i) + RT \ln x_i \right]$ which is equated to $\mu_i^{\text{IM}}(T, P, \{x_i\})$. An arrow points from the second equation to the third.

I take this part to here, I have an expression now which is $RT \ln \gamma_i$ is \bar{G}_i minus μ_i of T, P pure i minus $RT \ln x_i$. So we have got an expression which should be similar if you which should be familiar if you are able to see this expression. So recall that in mixture the chemical potential, there is a linear function of logarithmic value of composition where basically this is something which is what we have it now, there is a function μ_i plus $RT \ln x_i$.

So we should be now able to connect this thing to chemical potential of the component in ideal mixture in fact this is nothing but minus μ_i of pure which is a reference state plus $RT \ln \gamma_i$ plus $RT \ln x_i$ and this is nothing but your chemical potential of mixture at T, P x_i . So this is nothing but that so essentially what we have now is the following.

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$$\begin{aligned}
 \text{or } RT \ln \gamma_i &= \bar{G}_i - \mu_i(T, P, P_m, x_i) - RT \ln x_i \\
 &= \bar{G}_i - [\mu_i(T, P, P_m, x_i) + RT \ln x_i] \\
 &= \bar{G}_i - \mu_i^{IM}(T, P, P_m, x_i) \\
 &= \bar{G}_i - \bar{G}_i^{IM}(T, P, P_m, x_i)
 \end{aligned}$$

$$\text{or } RT \ln \gamma_i = \bar{G}_i - \bar{G}_i^{IM}$$

We have got an expression now or $RT \ln \gamma_i$ is nothing but \bar{G}_i minus μ_i of ideal mixture which is nothing but \bar{G}_i of ideal mixture of the same T, P, x_i . So this is your \bar{G}_i of ideal mixture, so this is the expression we have got from this exercise.

And what is this \bar{G}_i minus \bar{G}_i of ideal mixture, it is nothing but based on definition this is nothing but \bar{G}_i Excess.

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$$\begin{aligned}
 \text{or } RT \ln \gamma_i &= \bar{G}_i - \bar{G}_i^{IM} \\
 \Rightarrow RT \ln \gamma_i &= \bar{G}_i^{EX}
 \end{aligned}$$

Using general prop of partial molar prop

$$\bar{G}^{EX} = \sum x_i \bar{G}_i^{EX} = RT \sum x_i \ln \gamma_i$$

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

$$RT \ln \gamma_i + RT \ln x_i = \bar{G}_i - \mu_i(T, P, \text{pure } i)$$

$$RT \ln \gamma_i = \bar{G}_i - \mu_i(T, P, \text{pure } i) - RT \ln x_i - [\mu_i(T, P, \text{pure } i) + RT \ln x_i]$$

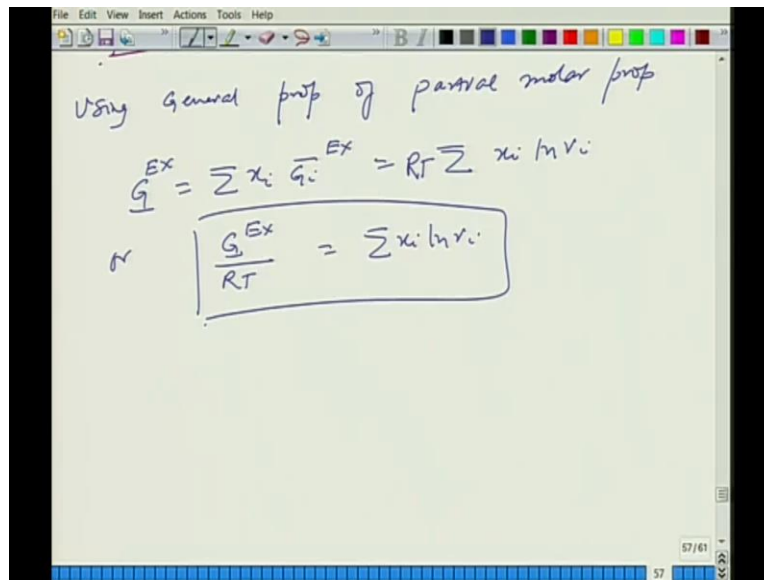
$$RT \ln \gamma_i = \bar{G}_i - \bar{G}_i^{IM}$$

$$RT \ln \gamma_i = \bar{G}_i^{EX}$$

Using general prop of partial molar prop

$$\underline{G}^{EX} = \sum x_i \bar{G}_i^{EX} = RT \sum x_i \ln \gamma_i$$

$$\frac{G^{EX}}{RT} = \sum x_i \ln \gamma_i$$



So this is the partial molar Gibbs free energy excess function of that and hence this I can write this is nothing but $RT \ln \gamma_i$ \bar{G}_i^{EX} . So we got a very beautiful function now, this is something which relates partial molar Gibbs free energy excess functions excess partial molar Gibbs free energy with the logarithmic value of the activity coefficient.

Now let me little bit extend this exercise and we can use the general using the general property of partial molar property, general property of partial molar properties which is the following that if you are talking about G then essentially I can write that N_i summation \bar{G}_i , that I can do that.

And now I am saying here is that G bar that is the small G and here I can replace this by x_i because I have divided by the N and here the G Excess is nothing but G Excess. So I have used the general property partial molar property to obtain the molar Gibbs free energy excess function and that is nothing but the summation x_i so the partial molar Gibbs free energy of excess function.

So using this formation now I can plug in here, this will tell you that G bar excess is nothing but summation $x_i \ln \gamma_i$ and this is $R T$ or you what you have is G bar Excess by $R T$ is G by G bar Excess divided By $R T$ is nothing but summation $x_i \ln \gamma_i$. So this is the expression which we got which connects the excess function of molar Gibbs free energy to the activity coefficients of components.

And now the question is what would be the relevant kind of functions of analytical forms of Gibbs free this particular excess function. I think this is something which we are going to discuss more in the next class so I will stop here and take it further in the next class. So, see you next time.