Chemical Engineering Thermodynamics
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Lecture 45
Excess Gibbs Free Energy Models

Welcome back. In the last class we introduced a function called excess function which is something which we discussed that is going to be relevant for the liquid phase, so the definition was very simple it is nothing but is difference of the any property with respect to the property in the ideal mixture and this could be any property as I said U, S, V, H.

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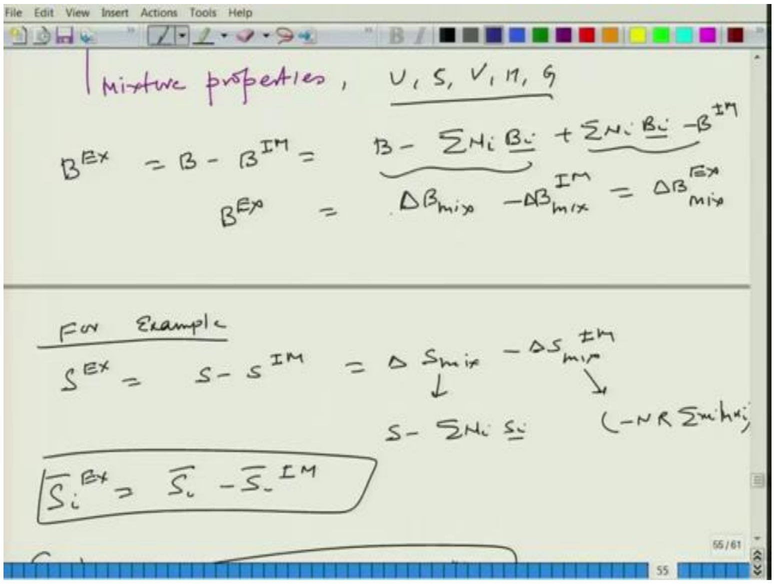


Mixture properties, $\underline{U, S, V, H, G}$

$$B^{EX} = B - B^{IM} = \underbrace{B - \sum x_i \underline{B_i}} + \underbrace{\sum x_i \underline{B_i} - B^{IM}}$$

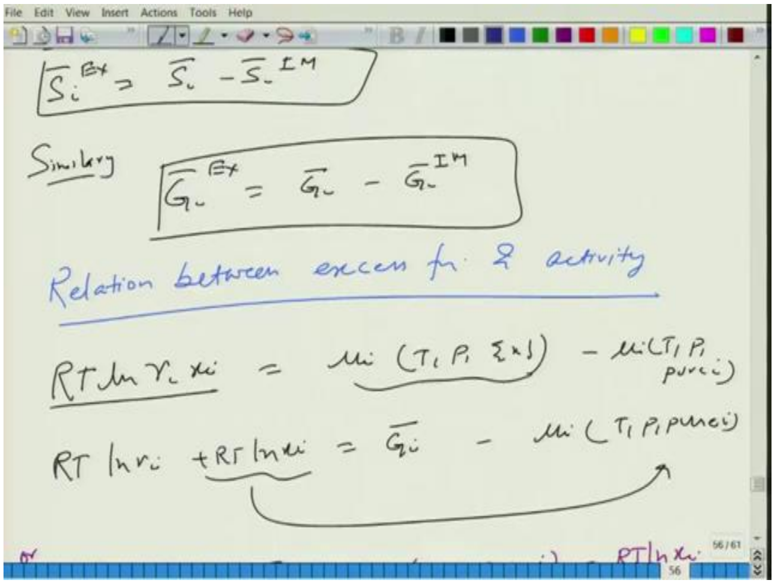
$$B^{EX} = \Delta B_{mix} - \Delta B^{IM}_{mix} = \Delta B^{EX}_{mix}$$

For Example

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

$$\Delta S_{mix} \downarrow S - \sum x_i \underline{S_i} \qquad \Delta S^{IM}_{mix} \searrow (-NR \sum x_i \ln x_i$$

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



$$\boxed{\overline{S}_i^{Ex} = \overline{S}_i - \overline{S}_i^{IM}}$$

Similarly

$$\boxed{\overline{G}_i^{Ex} = \overline{G}_i - \overline{G}_i^{IM}}$$

Relation between excess fn. & activity

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

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

or $\quad - RT\ln x_i$

So, we said that well a B excess or in general can be defined as B minus B ideal mixture and this further can be shown that this is nothing but the Delta B mix minus Delta B mix ideal and this further can be extended for partial molar properties because being an extensive property you can use that and the definition of excess that is the difference of the property with respect to that in the ideal mixture can further extended to partial molar properties, so that is how we defined Gi bar excess and then we showed that Gi bar excess is nothing but is related to activity coefficient as RTln gamma I.

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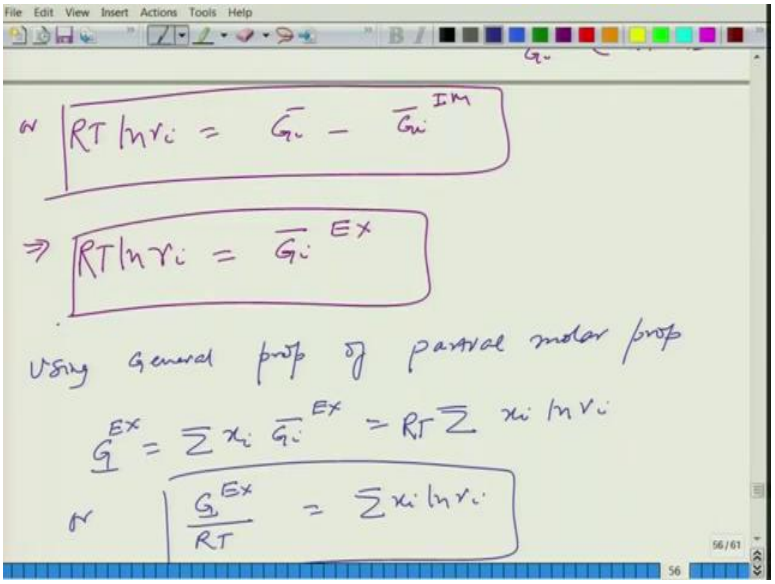


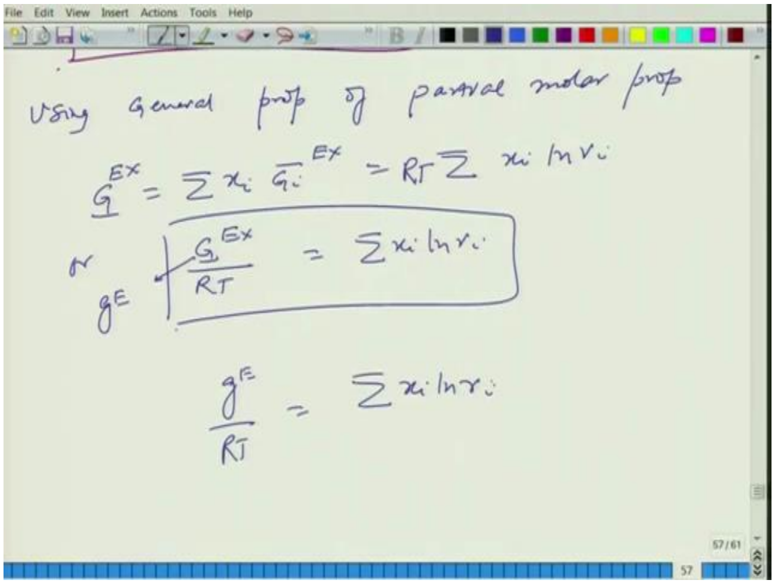
or $\boxed{RT\ln\gamma_i = \overline{G}_i - \overline{G}_i^{IM}}$

$\Rightarrow \boxed{RT\ln\gamma_i = \overline{G}_i^{Ex}}$

Using general prop of partial molar prop

$$\underline{G}^{Ex} = \sum x_i \overline{G}_i^{Ex} = RT\sum x_i\ln\gamma_i$$

or $\boxed{\dfrac{\underline{G}^{Ex}}{RT} = \sum x_i\ln\gamma_i}$



Using General prop of partial molar prop

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

or $g^E \rightarrow \boxed{\frac{G^{EX}}{RT} = \sum x_i \ln \gamma_i}$

$$\frac{g^E}{RT} = \sum x_i \ln \gamma_i$$

So, this is something which connects the it is rather the general property of the partial molar property excess function and this is something which will become very relevant. So, this further can be simplified in this form that is what we came up with in expression that because Gi excess if you weight it by the composition and sum it up it will become simply a molar Gibbs excess function.

So, this is something which we came up with that well G bar all this can be something like a small g excess. So, I can write this as G of E by RT and this is your summation Xi ln gamma i.

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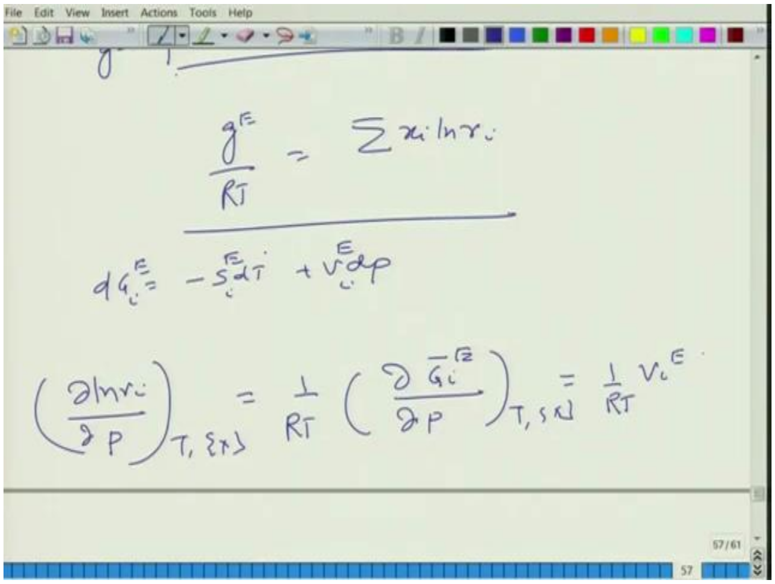
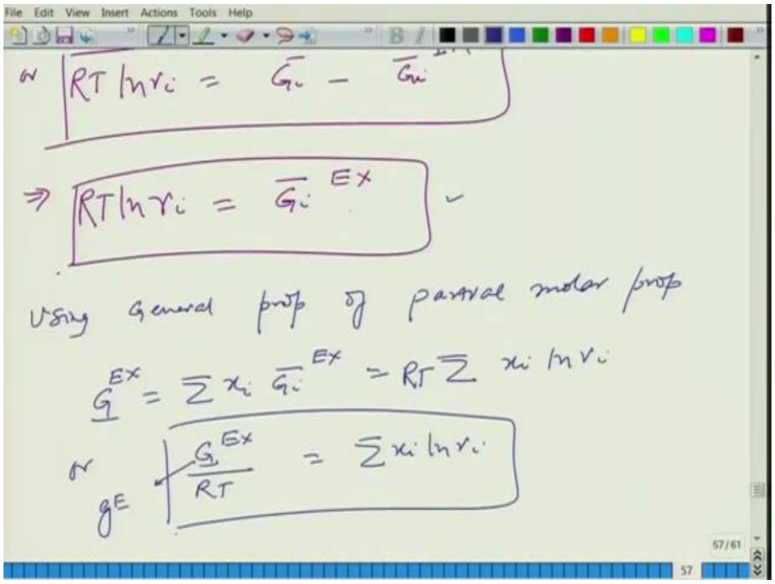


$$\frac{g^E}{RT} = \sum x_i \ln \gamma_i$$

$$d\bar{G}_i^E = -\bar{S}_i^E dT + \bar{V}_i^E dP$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,\{x\}} = \frac{1}{RT}\left(\frac{\partial \bar{G}_i^E}{\partial P}\right)_{T,\{x\}} = \frac{1}{RT} \bar{V}_i^E$$



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

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

Using General prop of partial molar prop

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

$$\text{or} \quad g^E \quad \boxed{\frac{\underline{G}^{EX}}{RT} = \sum x_i \ln \gamma_i}$$

Now, we can relate this thing to various different properties as we know that your DG is minus SDT plus VDP since this thermodynamic function also holds excess functions so I can simply write excess here and if you want to make it i here we can simply write as i this is also fine.

Now, with this I should be able to connect the derivative of this which would be your let us say Del Ln gamma i by Del P at a given temperature and composition can be written as here. So, if you take use Gi power excess so this is nothing but RT Ln gamma H so if you take a differentiation of this with respect to the pressure you are simply a saying that this is nothing but 1 by RT Del of Gi bar excess by Del PTX.

So, this is directly from this expression. Now, if I use the thermodynamic definition of the Gibbs free energy because if you take the partial differentiation of this with respect to P we are going to get VI excess at a constant temperature so I can write this as 1 by RT or excess here.

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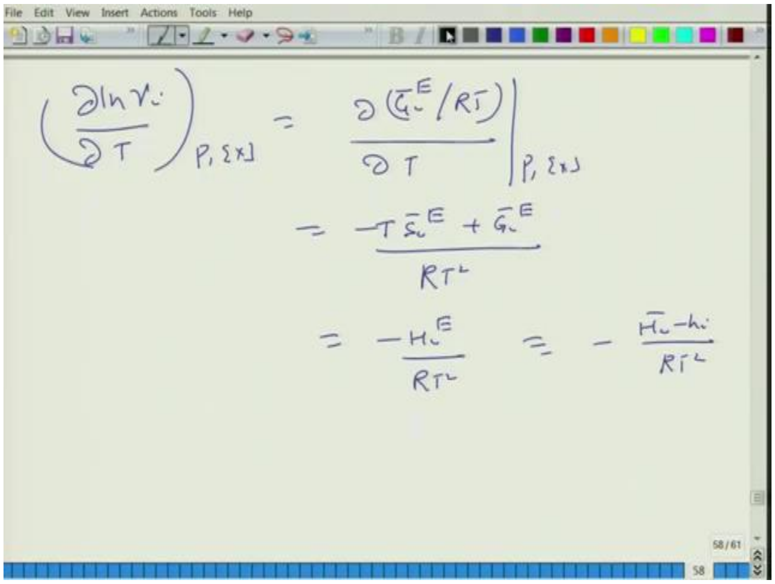


$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\{x\}} = \frac{\partial(\bar{G}_i^E/RT)}{\partial T}\bigg|_{P,\{x\}}$$

$$= \frac{-T\bar{S}_i^E + \bar{G}_i^E}{RT^2}$$

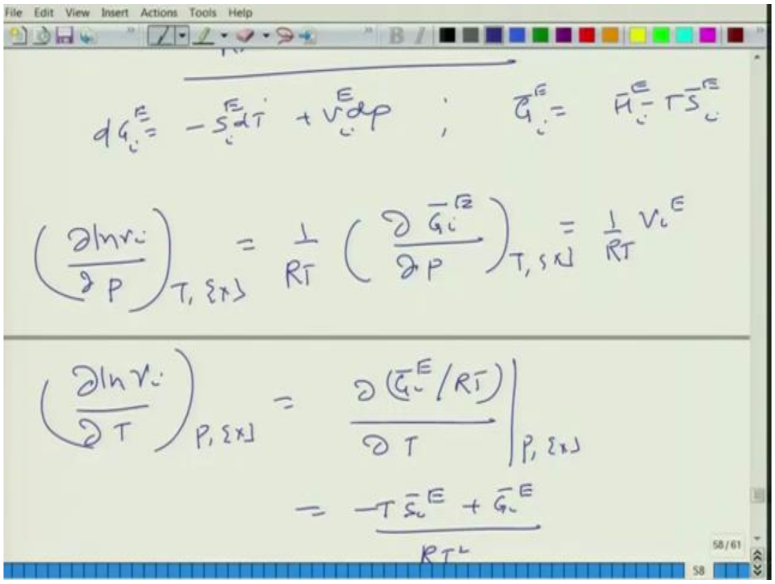
$$= \frac{-H_i^E}{RT^2} = -\frac{\bar{H}_i - h_i}{RT^2}$$

$$\frac{g^E}{RT} = \sum x_i \ln\gamma_i$$

$$dG_i^E = -S_i^E\,dT + v_i^E\,dP$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,\{x\}} = \frac{1}{RT}\left(\frac{\partial \bar{G_\iota}^E}{\partial P}\right)_{T,\{x\}} = \frac{1}{RT}V_i^E$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\{x\}} = \frac{\partial\left(\frac{\overline{G_\iota^E}}{RT}\right)}{\partial T}|_{P,\{x\}} = -\frac{T\bar{S_\iota}^E + \bar{G_\iota}^E}{RT^2} = -\frac{H_i^E}{RT^2} = -\frac{\overline{H_\iota} - h_i}{RT^2}$$

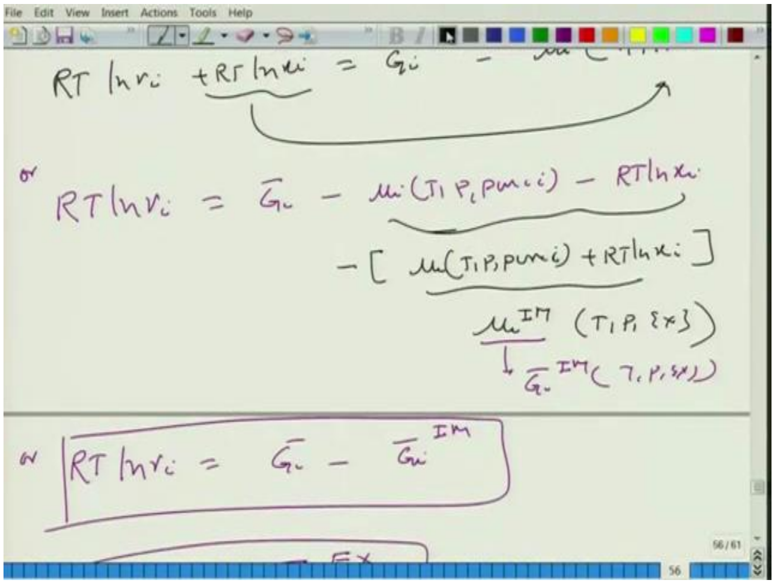


$$dG_i^E = -S_i^E\,dT + V_i^E\,dp \;; \qquad \bar{G}_i^E = \bar{H}_i^E - T\bar{S}_i^E$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,\{x\}} = \frac{1}{RT}\left(\frac{\partial \bar{G}_i^E}{\partial P}\right)_{T,\{x\}} = \frac{1}{RT} V_i^E$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\{x\}} = \left.\frac{\partial(\bar{G}_i^E/RT)}{\partial T}\right|_{P,\{x\}}$$

$$= \frac{-T\bar{S}_i^E + \bar{G}_i^E}{RT^2}$$



$$RT\ln\gamma_i + RT\ln x_i = G_i - \mu_i(\ldots$$

or

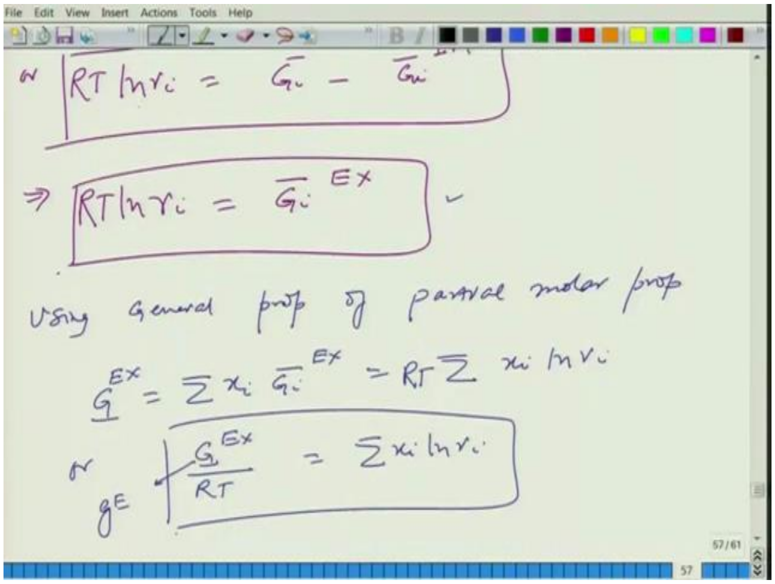
$$RT\ln\gamma_i = \bar{G}_i - \underbrace{\mu_i(T,P,\text{pure } i) - RT\ln x_i}$$

$$- \Big[\underbrace{\mu_i(T,P,\text{pure } i) + RT\ln x_i}_{\mu_i^{IM}(T,P,\{x\})}\Big]$$

$$\mu_i^{IM}(T,P,\{x\}) \rightarrow \bar{G}_i^{IM}(T,P,\{x\})$$

or

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



or $\boxed{RT \ln \gamma_i = \bar{G}_i - \bar{G}_i}$

$\Rightarrow \boxed{RT \ln \gamma_i = \bar{G}_i^{Ex}}$ ✓

Using general prop of partial molar prop

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

$$\text{or } \; g^E \; \boxed{\frac{G^{Ex}}{RT} = \sum x_i \ln \gamma_i}$$

So, this is something which we can show here. Similarly, I can also consider the case where we would like to have a partial differentiation with respect to temperature at a constant pressure and this you can show as the following here again I can write this as Del Gi excess by RT by Del T and since we have; so here the RT came in the denominator because it was a case of differentiating with respect to the pressure but here we are differentiating with respect to temperature and hence we kept it together as a part of it because Ln gamma is nothing but this and this is at a pressure and composition.

Now, using this function or using this definition here, I can show this as follows because I can also write by definition that G is nothing but H minus TS and we can say the G excess is H excess, T excess and also, we can write it like this. So, this way we have the definition here of Gi excess also, so we can also write this as in terms of excess this is extensible to partial molar properties. So, with this I can now simplify the expression as the following without going into the details of it plus Gi excess so if you take the differentiation you are going to get this.

So, this is going to be Gi partial differentiation of this and this RT square will come out like this and then you make use of these expressions which is here, so you can show that you are going to get this expression and this from the definition is nothing but minus Hi Ex by RT square which is nothing but minus of Hi bar with respect to the pure molar property of the component i and hence I can write it in this way.

$$dG_i^E = -S_i^E dT + v_i^E dP \; ; \quad \overline{G_\iota}^E = \overline{H_\iota}^E - T\overline{S_\iota}^E$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,\{x\}} = \frac{1}{RT}\left(\frac{\partial \overline{G_\iota}^{E}}{\partial P}\right)_{T,\{x\}} = \frac{1}{RT}V_I^E$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\{x\}} = \frac{\partial\left(\frac{\overline{G_I^E}}{RT}\right)}{\partial T}|_{P,\{x\}} = -\frac{T\overline{S_\iota^E} + \overline{G_\iota^E}}{RT^2}$$

So, essentially what we connected here is that the partial differentiation of this ln gamma i with respect to the pressure and the temperature are connected to excess property or excess molar property of you know the system of component i, so this is how we connect that. Now, we also mentioned about Gibbs-Duhem relations in when it came to the fugacity part, now here also we can extend this expression and we can connect this activity coefficient should satisfy Gibbs-Duhem relation so that will come out to be another important criteria.

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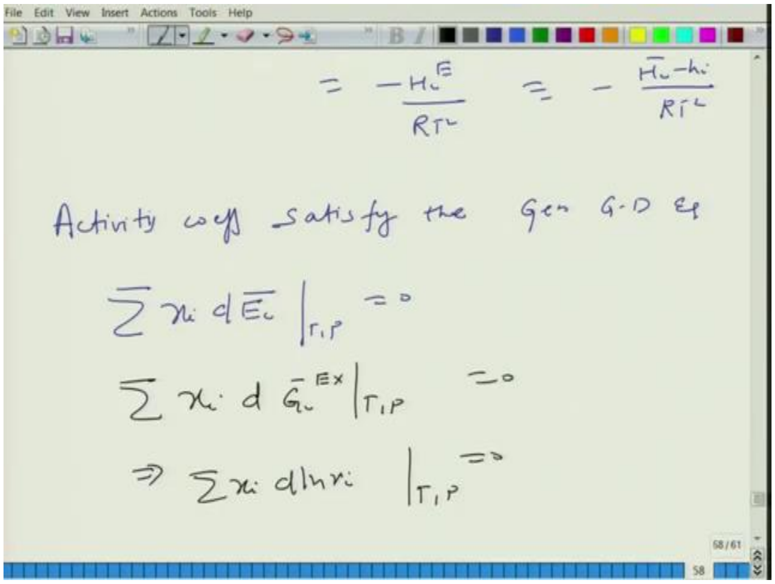

$$= -\frac{H_i^E}{RT^2} = -\frac{\bar{H_i} - h_i}{RT^2}$$

Activity coeff satisfy the Gen G-D Eq

$$\sum x_i\, d\bar{E_i}\Big|_{T,P} = 0$$

$$\sum x_i\, d\,\bar{G_i}^{Ex}\Big|_{T,P} = 0$$

$$\Rightarrow \sum x_i\, d\ln \gamma_i\Big|_{T,P} = 0$$

So, let us look at it, so this activity coefficient which we have defined should satisfy the general Gibbs-Duhem equation which is nothing but summation Xi dE I, E is a thermodynamic potential and this can be replaced by let us say G and this has to be equal to zero and this one can show that the this is easily extensible for the following case where I can write this as simply Ex at temperature at T and P or in other word I can write this as summation Xi D Ln gamma i at temperature T and P and this must be equal to 0.

$$\sum x_i d\overline{E_\iota}|_{T,P} = 0$$

$$\sum x_i d\overline{G_i}^{EX}|_{T,P} = 0$$

$$or, \qquad \sum x_i dln\gamma_i|_{T,P} = 0$$

So, with this you have a condition of Gibbs-Duhem relation. Let us check or use this information to understand how do you verify the data if you have the data of activity coefficient so let us say for binary mixtures or multiple component mixture so how do you check that. So, you will be using this constraint in order to verify the consistency of the data.

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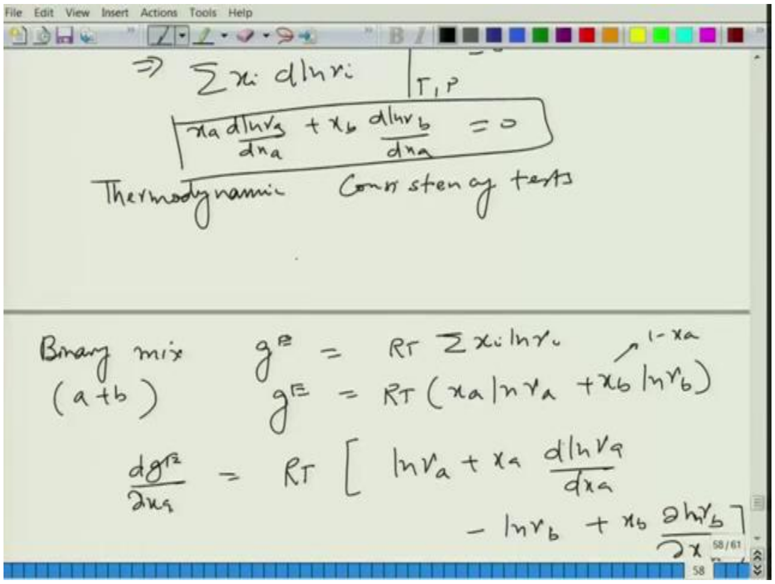


$$\Rightarrow \sum x_i \, d\ln\gamma_i \Big|_{T,P}$$

$$\boxed{x_a \frac{d\ln\gamma_a}{dx_a} + x_b \frac{d\ln\gamma_b}{dx_a} = 0}$$

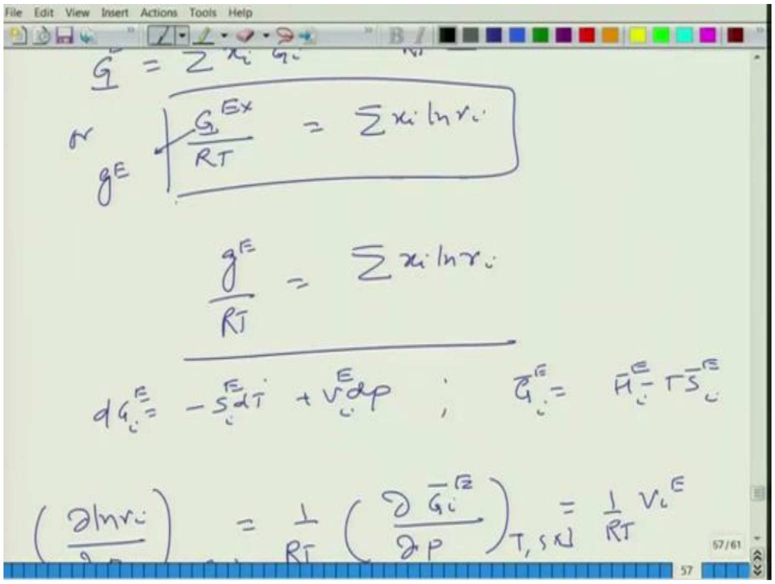
Thermodynamic Consistency tests

Binary mix (a+b)

$$g^E = RT \sum x_i \ln\gamma_i$$

$$g^E = RT\left(x_a \ln\gamma_a + \overset{1-x_a}{x_b} \ln\gamma_b\right)$$

$$\frac{dg^E}{\partial x_a} = RT\left[\ln\gamma_a + x_a \frac{d\ln\gamma_a}{dx_a} - \ln\gamma_b + x_b \frac{\partial\ln\gamma_b}{\partial x}\right]$$



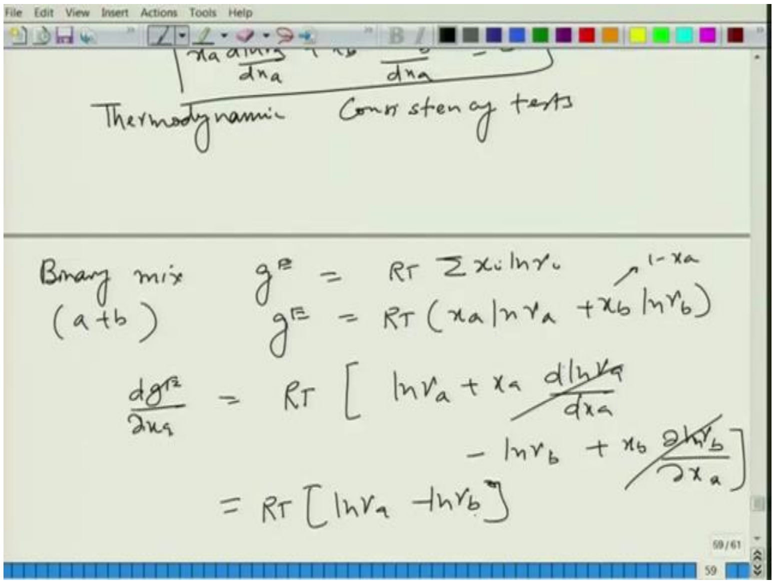
$$\underline{G} = \sum x_i G_i$$

or $g^E \leftarrow$ $\boxed{\frac{G^{Ex}}{RT} = \sum x_i \ln\gamma_i}$

$$\frac{g^E}{RT} = \sum x_i \ln\gamma_i$$

$$dG_i^E = -S_i^E dT + V_i^E dP \quad ; \quad \bar{G}_i^E = \bar{H}_i^E - T\bar{S}_i^E$$

$$\left(\frac{\partial \ln\gamma_i}{\partial P}\right) = \frac{1}{RT}\left(\frac{\partial \bar{G}_i^E}{\partial P}\right)_{T,x_i} = \frac{1}{RT} V_i^E$$



Thermodynamic Consistency tests

Binary mix $(a+b)$

$$g^E = RT \sum x_i \ln\gamma_i$$

$$g^E = RT\left(x_a \ln\gamma_a + \overset{1-x_a}{x_b} \ln\gamma_b\right)$$

$$\frac{dg^E}{\partial x_a} = RT\left[\ln\gamma_a + \cancel{x_a \frac{d\ln\gamma_a}{dx_a}} - \ln\gamma_b + \cancel{x_b \frac{\partial \ln\gamma_b}{\partial x_a}}\right]$$

$$= RT\left[\ln\gamma_a - \ln\gamma_b\right]$$

So, in order to demonstrate that we can consider a binary mixture. So, let us consider binary mixture. So, in that case if we are considering G excess here which is going to be the RT summation Xi Ln gamma i, so this is for the binary mixture and what do you want to show is that how that this Gibbs-Duhem relation should be satisfy hence in order to check the thermodynamic consistency of the data certain relations will evolved and we would like to evolve that relation.

Let us look at it again particularly this is a binary mixture, so I can write this as Xa, let us say you have A and B mixture, ln gamma A plus XB ln gamma B. So, this is by definition we of the expression which we have got here. So, I am using this expression that excess molar Gibbs free energy is related to the function or to the expression RT multiplied by summation Xi ln gamma i and for the binary mixture I can write it like this.

So, now at this point what I can do is I can take the differentiation of with respect to Xa, so if you do that I get the expression RT ln gamma A plus Xad ln gamma a by DXA and since this Xa and this Xb is nothing but 1 minus Xa and hence if I do take a differentiation of this term with respect to Xa, I am going to get minus ln gamma P plus Xb del ln gamma B by Xa. So, I have an expression here.

Now, this term here tells you the following that if you take let us say if you take this and differentiate with respect to Xa for the binary mixture this would mean that XaD ln gamma A dxb plus Xb D ln gamma B by Dx. So, if you take a just a differentiation with respect to B or divided by D Xa you are going to get this expression like this.

Similarly, if you do the same thing for B you are going to get again another expression but it will be D ln gamma A divided by D Xb. Now, with this information this term has to go to 0 and what remains is the following is RT ln gamma a minus RT ln gamma B. So, you see gamma is activity coefficients if A and B.

$$Binary\ mixture\ (a+b):\ g^E = RT\sum x_i ln\gamma_i$$

$$g^E = RT(x_a \ln\gamma_a + x_b \ln\gamma_b)$$

$$\frac{\partial g^E}{\partial x_a} = RT[\ln\gamma_a + \frac{x_a dln\gamma_a}{dx_a} - \ln\gamma_b + \frac{x_b \partial ln\gamma_b}{\partial x_a}]$$

$$= RT[\ln\gamma_a - \ln\gamma_b]$$

$$dg^E = RTln\frac{\gamma_a}{\gamma_b}dx_a$$

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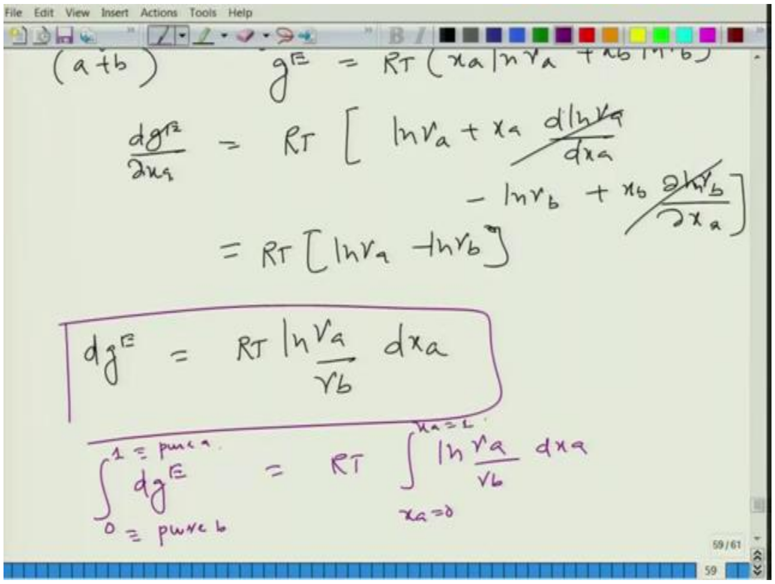

$$(a+b) \qquad g^E = RT(x_a \ln\gamma_a + x_b \ln\gamma_b)$$

$$\frac{dg^E}{\partial x_a} = RT[\ln\gamma_a + x_a \cancel{\frac{d\ln\gamma_a}{dx_a}} - \ln\gamma_b + x_b \cancel{\frac{\partial\ln\gamma_b}{\partial x_a}}]$$

$$= RT[\ln\gamma_a - \ln\gamma_b]$$

$$\boxed{dg^E = RT\ln\frac{\gamma_a}{\gamma_b}dx_a}$$

$$\int_{0\ \equiv\ pure\ b}^{1\ \equiv\ pure\ a} dg^E = RT\int_{x_a=0}^{x_a=1} \ln\frac{\gamma_a}{\gamma_b}dx_a$$

Now, what we can do is we can integrate this, so I can have D of G of e as RT ln gamma a by gamma B D X of a. So, I have an expression now if I integrate this, so it will be from let us say 0 because if I taking X of A is 0 is corresponds to pure B and here is 1 when Xa is equal to 1 it corresponds to pure a and then you have this RT ln gamma A by gamma B D Xa. So, what would be this function this is something which you can consider or you can even eventually you can find it out by looking at just the left-hand side.

So, left hand side you have a function or you have a variable Dg excess and since G is a thermodynamic function so it just depends on the end points. So, if you look at the end points because it depends on the straight point and hence the end points are the relevant here. Now, the end points are the pure states.

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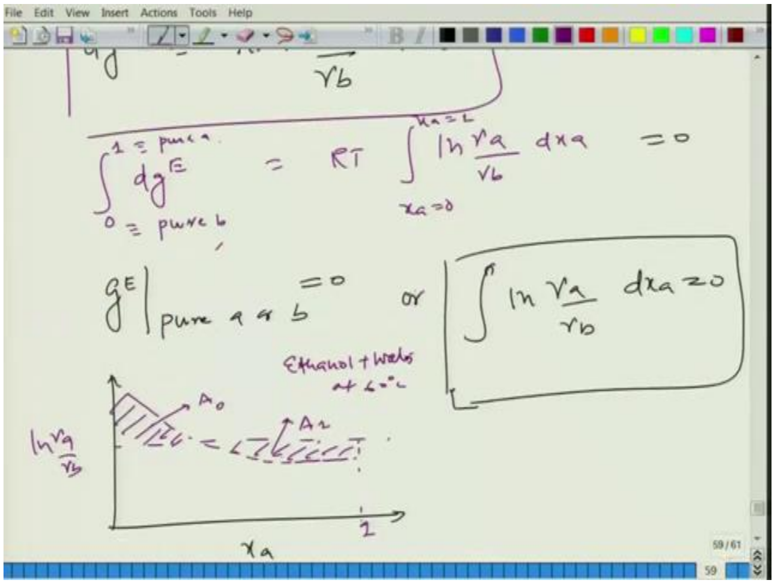


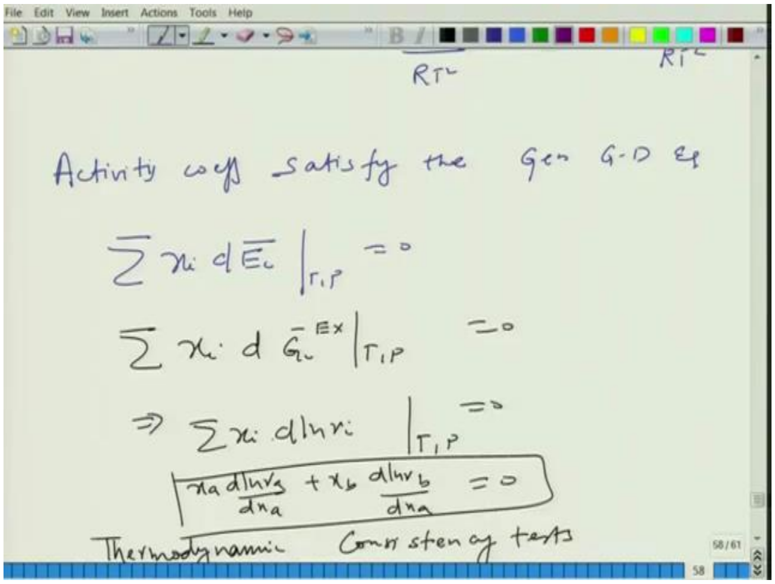
$$\gamma_b$$

$$\int_{0 \,\equiv\, \text{pure } b}^{1 \,\equiv\, \text{pure } a} dg^E = RT \int_{x_a=0}^{x_a=1} \ln \frac{\gamma_a}{\gamma_b}\, dx_a = 0$$

$$g^E \Big|_{\text{pure } a \text{ or } b} = 0 \quad \text{or} \quad \boxed{\int \ln \frac{\gamma_a}{\gamma_b}\, dx_a = 0}$$

$$\int_0^1 dg^E = RT \int_{x_a=0}^{x_a=1} \ln \frac{\gamma_a}{\gamma_b} dx_a = 0$$

$$g^E|_{pure\ a\ or\ b} = 0 \quad or, \qquad \int \ln \frac{\gamma_a}{\gamma_b} dx_a = 0$$



$$RT \qquad RT$$

Activity coeffs satisfy the Gen G-D eq

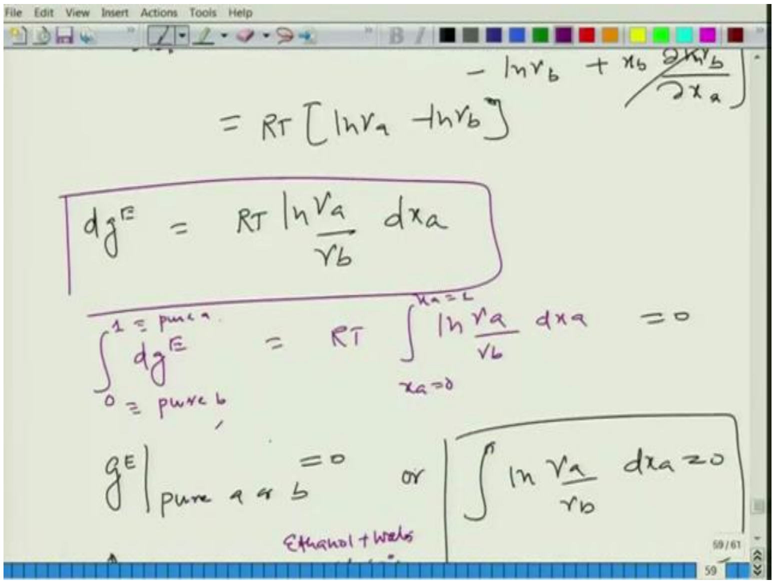
$$\sum x_i \, d\bar{E}_i \Big|_{T,P} = 0$$

$$\sum x_i \, d\bar{G}_i^{EX} \Big|_{T,P} = 0$$

$$\Rightarrow \sum x_i \, d\ln\gamma_i \Big|_{T,P} = 0$$

$$\boxed{x_a \frac{d\ln\gamma_a}{dx_a} + x_b \frac{d\ln\gamma_b}{dx_a} = 0}$$

Thermodynamic Consistency tests



$$- \ln\gamma_b + x_b \frac{\partial \ln\gamma_b}{\partial x_a} \Big]$$

$$= RT\left[\ln\gamma_a - \ln\gamma_b\right]$$

$$\boxed{dg^E = RT \ln\frac{\gamma_a}{\gamma_b}\, dx_a}$$

$$\int_{0\,=\,\text{pure } b}^{1\,=\,\text{pure } a} dg^E = RT \int_{x_a=0}^{x_a=1} \ln\frac{\gamma_a}{\gamma_b}\, dx_a = 0$$

$$g^E\Big|_{\text{pure } a \text{ or } b} = 0 \quad \text{or} \quad \boxed{\int \ln\frac{\gamma_a}{\gamma_b}\, dx_a = 0}$$

Ethanol + Water

So, you have G excess of the pure and the G excess of the pure A and pure B which must be if it is a pure a or b this must be equal to 0. So, with this the left-hand side must be equal to 0, that means this term must be equal to 0 or in other word integral of gamma logarithmic value of gamma a by gamma b this must be equal to 0. So, this is a very important expression eventually because this is something which we can use to check our determinations, our calculations of this activity coefficient and then we can check whether the data which we have used in order to evaluate that eventually is consistent or not.

So, consistency would become at the end valuable because you can test the data and this is often used for example if you consider let us say from 0 to 1 and then let us say this is Xa and this could be an example for let us say ethanol plus water at some temperature because we are fixing the temperature. So, a typical value of this log of gamma a by gamma b would be something like this that it will be till 1 which means that area under this and this must be equal to 0, that is why sorry area under this and this must be a of let us say area of this is let us say 1 and 2, so area under this and this must be equal to 0 must be same and hence this integral should lead to 0.

So, I hope that it becomes clear that the reason for us to do this analysis first is to consider the fact that the Gibbs-Duhem should satisfy this gives you a constraint on the logarithmic value of gamma or activity coefficient. Now, using that we can come up with a specific consistency test and that came out to be for binary mixture this, for ternary and others the things will be the expressions are going to be different but for binary this is the expression which it comes out to be.

Now, as we have discussed about the fugacity that a fugacity coefficient for that matter can be evaluated if you have a very good equation of state and then we said well if you are interested to find out let us say activity which is more suitable for liquid phase you need to also come up with the appropriate models which represents the interaction parameters or the behavior of the fluid or the liquid phase.

Now, this gamma ln gamma i is basically related to G E and hence the question is that can we come up with a suitable model for excess Gibbs free energy? And that is something which now we are going to look into that because if you have the model and a suitable model you can you can make use of to obtain this gamma that is activity coefficients and then relate that with respect to the ideal mixtures and so forth.

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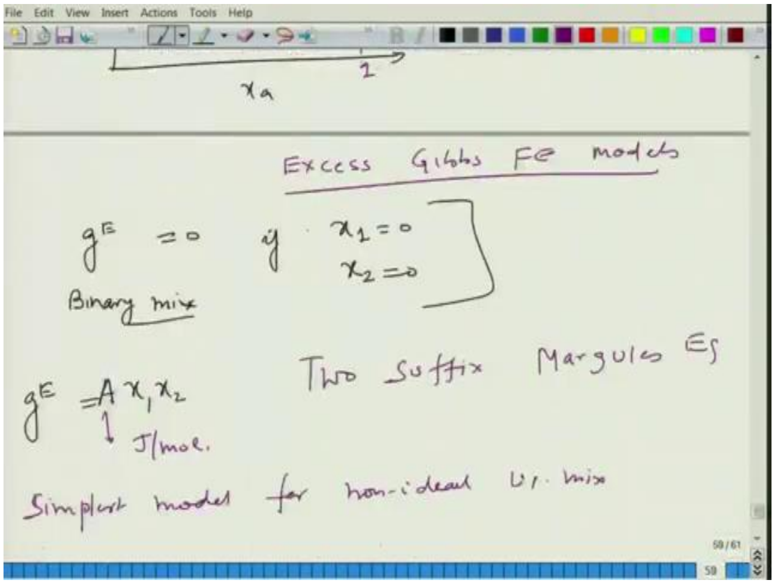

Excess Gibbs FE models

$g^E = 0$ if $x_1 = 0$
$x_2 = 0$

Binary mix

$g^E = A x_1 x_2$

J/mol.

Two suffix Margules Eq

Simplest model for non-ideal l.q. mix

$$g^E = 0 \ \ if \ x_1 = 0; x_2 = 0$$

$$g^E = A x_1 x_2$$

So, let us now focus on this Excess Gibbs Free Energy Model which would be relevant for us for calculating later the vapor liquid equilibria for where the vapor phase will be model using the fugacities and the liquid phase will be model using these activities. So, hence it becomes relevant to find out a suitable model for us for representing the liquid mixtures.

So, if you look at G of E it must satisfy certain conditions, so let us take an example of a binary mixture. So, for the binary mixture G excess for the pure case are going to be 0. So, anyway this G excess has to be 0 if it is a pure. So, there are two criteria or two conditions or limiting case which we have to consider that G excess should be 0 if X1 is 0 or X2 is 0.

So, this is something which we can write it that G excess is 0 if X1 is 0 or X2 is 0 or we can use the a and b also. Now, assuming that you are using this Refer Lewis-Randall Refer state for both the component that means both the component exist in the 0 to 1 case. So, this must tell of course the other condition is that energy excess must satisfy the Gibbs-Duhem relation that something is there already. So, the question is given this constraint or something which we know which will have which will be the case as far as the thermodynamic definitions goes what would be the simplest model which satisfy these conditions?

So, if you look into that you have this X1 equal to 0, X2 equal to 0 the simplest model which satisfy this condition would be A times some; A is constant multiplied by X1 and X2. So, if we can consider this then this would be our simplest model where you have one constant and so and two suffixes, so essentially this is something which we call as two suffix Margules equation due to Margules.

And here because composition is there so the A is nothing but the unit of A is nothing but joules per mole, the same as the G is here. So, this was the simplest model which will represent non ideality of the liquid mixtures, that is something which is something which we are trying to we will work on more.

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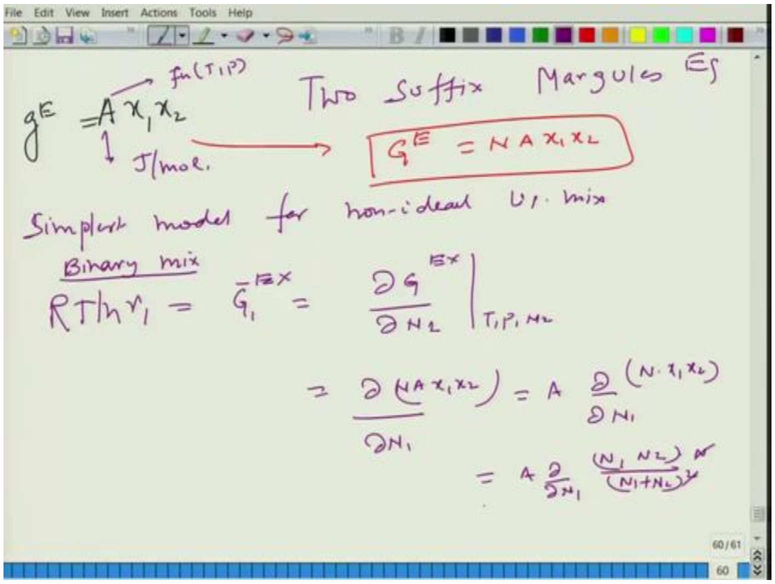


Two suffix Margules Eq

$g^E = A x_1 x_2$ $\xrightarrow{}$ fn(T, P)

J/mol. $\longrightarrow$ $\boxed{G^E = N A x_1 x_2}$

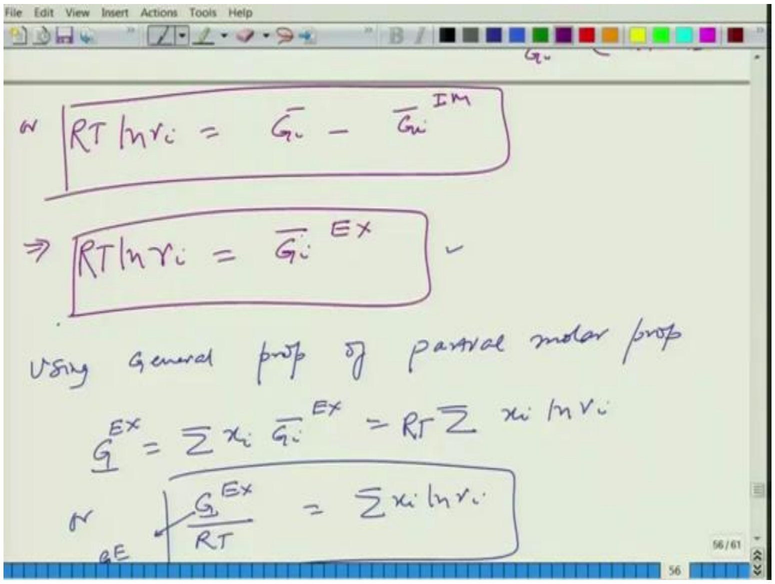
Simplest model for non-ideal U/. mix

Binary mix

$$RT \ln \gamma_1 = \bar{G}_1^{EX} = \left.\frac{\partial G^{EX}}{\partial N_2}\right|_{T, P, N_2}$$

$$= \frac{\partial (N A x_1 x_2)}{\partial N_1} = A \frac{\partial}{\partial N_1} (N \cdot x_1 x_2)$$

$$= A \frac{\partial}{\partial N_1} \frac{(N_1 N_2) N}{(N_1 + N_2)^2}$$



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

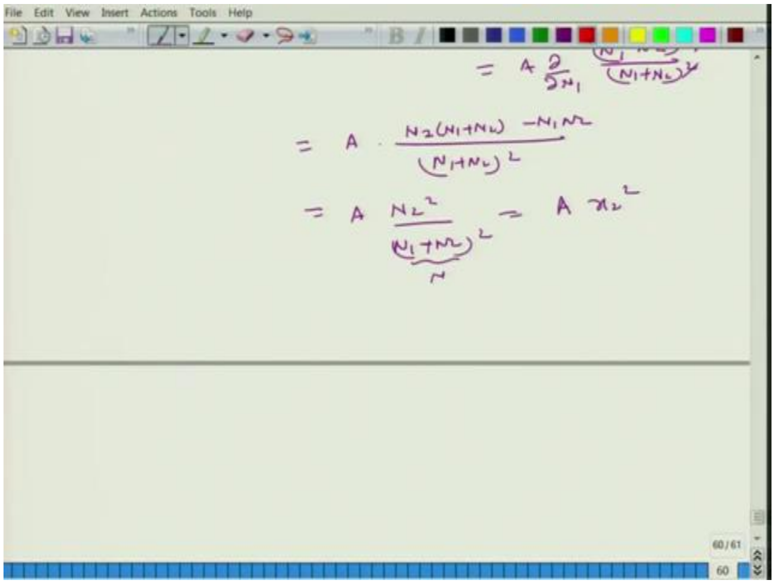
$\Rightarrow$ $\boxed{RT \ln \gamma_i = \bar{G}_i^{EX}}$ ✓

Using General prop of partial molar prop

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

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

g^E



$$= A \frac{\partial}{\partial N_1} \frac{N_1 \quad}{(N_1+N_2)^2}$$

$$= A \cdot \frac{N_2(N_1+N_2) - N_1 N_2}{(N_1+N_2)^2}$$

$$= A \frac{N_2^2}{\underbrace{(N_1+N_2)}_{N}^2} = A x_2^2$$

So let us consider this, this is a simplest model for non-ideal mixture, liquid mixture. So, this is the simplest model. So, one of the important things is A, so we will talk about this A, how do you get the A but let me now first try to connect this expression or the model to the activity coefficients. So, let us use this expression so the activity coefficient we know is related to the partial molar Gibbs free energy excess of that function. So, in other word, I need to use the definition RT ln gamma 1 if you look back here the definition will be clear again, so the way we are writing is the following RT ln gamma is Gi Ex Gi by Ex.

So, you need to find out Gi Ex here, so if it is 1 then you have to talk about G1 bar Ex. So, this is nothing but del G Ex by N1, keeping the temperature, pressure and N2 constant, so this is let us say for the binary mixture. Now, I can write this as del by if you look at it here the model which you are going to consider is G so essentially here this also means that G of Ex is N times A X1 X2. This is also indicated because this is a per mole or molar property so I can write this as and this can be because A is independent of composition, A only depends on temperature and pressure.

So, A is a function of temperature or pressure. So, I can take this A out del by del N1 and X1, X2. Now, this I can further simplify A del by del N1, N1 N2 by N1 plus N2 square multiplied by N here so this cancels out because they are two component N1 plus N2 is N. Now, if you further simplify this is going to be A times N2, N1 plus N2 minus N1 N2 and this is N1 plus N2 square and this further can be written as A N2 square by N1 plus N2 square now which this is nothing but N and hence I can write this as A X2 square.

$$G^E = NAx_1x_2$$

$$Binary\ mixture:\quad RTln\gamma_1 = \overline{G_1}^{EX} = \frac{\partial G^{EX}}{\partial N_1}|_{T,P,N_2} = \frac{\partial (NAx_1x_2)}{\partial N_1}$$

$$= \frac{A\partial (Nx_1x_2)}{\partial N_1} = \frac{A\partial}{\partial N_1}\left(\frac{(N_1N_2)N}{(N_1+N_2)^2}\right)$$

$$= A\ \frac{N_2(N_1+N_2) - N_1N_2}{(N_1+N_2)^2} = \frac{AN_2^2}{(N_1+N_2)^2} = Ax_2^2$$

$$RTln\gamma_1 = Ax_2^2$$

$$Similarly,\qquad RTln\gamma_2 = Ax_1^2$$

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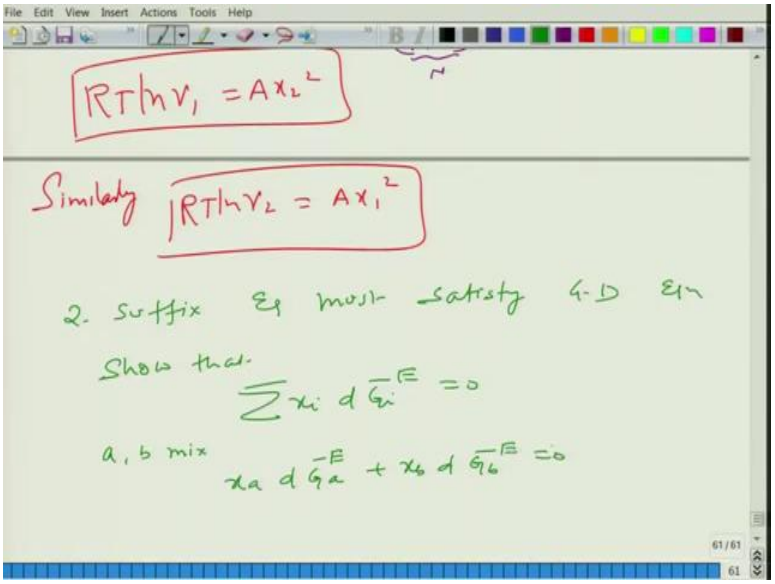


$\boxed{RT\ln\gamma_1 = Ax_2^2}$

Similarly $\boxed{RT\ln\gamma_2 = Ax_1^2}$

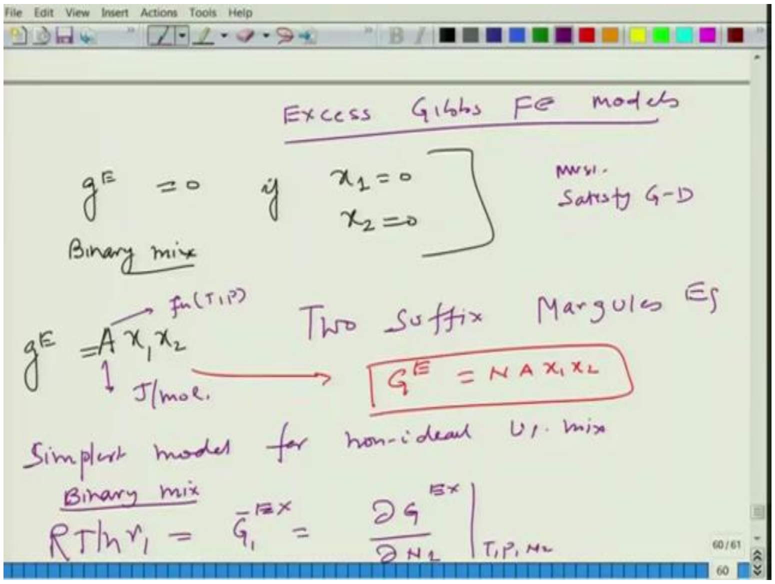
2. Suffix Eq must satisfy G-D Eqn

Show that

$\sum x_i\, d\,\overline{G_i}^E = 0$

a, b mix

$x_a\, d\,\overline{G_a}^E + x_b\, d\,\overline{G_b}^E = 0$



Excess Gibbs FE models

$g^E = 0$ if $x_1 = 0$, $x_2 = 0$ — must satisfy G-D

Binary mix

$g^E = A x_1 x_2$ — A: fn(T, P), J/mol.

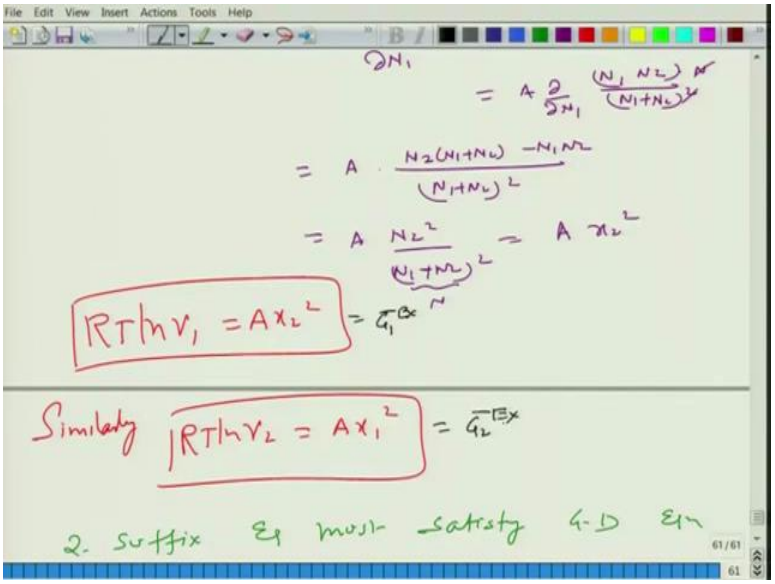
Two Suffix Margules Eq

$$\xrightarrow{} \boxed{G^E = N A x_1 x_2}$$

Simplest model for non-ideal V/. mix

Binary mix

$$RT \ln \gamma_1 = \bar{G}_1^{EX} = \frac{\partial G^{EX}}{\partial N_2}\Big|_{T,P,N_2}$$



∂N_1

$$= A \frac{\partial}{\partial N_1} \frac{(N_1 N_2) N}{(N_1+N_2)^2}$$

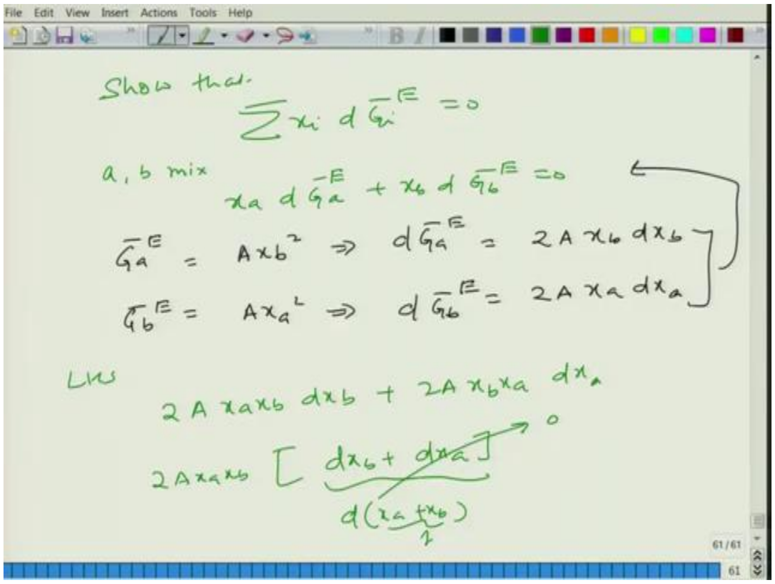
$$= A \cdot \frac{N_2(N_1+N_2) - N_1 N_2}{(N_1+N_2)^2}$$

$$= A \frac{N_2^2}{\underbrace{(N_1+N_2)^2}_{N}} = A x_2^2$$

$$\boxed{RT \ln \gamma_1 = A x_2^2} = \bar{G}_1^{EX}$$

Similarly $\boxed{RT \ln \gamma_2 = A x_1^2} = \bar{G}_2^{EX}$

2. Suffix Eq must satisfy G-D Eqn



Show that.

$$\sum x_i \, d\bar{G}_i^E = 0$$

a, b mix

$$x_a \, d\bar{G}_a^E + x_b \, d\bar{G}_b^E = 0$$

$$\bar{G}_a^E = A x_b^2 \Rightarrow d\bar{G}_a^E = 2A x_b \, dx_b$$

$$\bar{G}_b^E = A x_a^2 \Rightarrow d\bar{G}_b^E = 2A x_a \, dx_a$$

LHS

$$2A x_a x_b \, dx_b + 2A x_b x_a \, dx_a$$

$$2A x_a x_b \left[\underbrace{dx_b + dx_a}_{d(\underbrace{x_a + x_b}_{1})} \right] \rightarrow 0$$

So, you have a relation now which tells you that this RT ln gamma 1 is A X2 square. Similarly, you can show that RT ln gamma 2 is A X1 square. Now, this is because of the fact that we are considered G Ex as the one constant or two suffix Margules equation so if you change that model the relations are going to change but this is a simplest model which satisfy the limiting conditions.

Now, the question is how do you get this A? So, A can be fitted to the experimental data for the given binary function, A is typically a function of temperature or pressure, it does not depend on the composition but A basically gives you the idea of how particles are interacting.

So, let us little bit look into this expect of that, so I am going to spend little more time on this understanding of component this parameter A but this particular thing which we mentioned here if you look at it here, we mentioned this to expect, first is that this is a limiting condition, the other thing is that this must also satisfy the Gibbs-Duhem relation. So, must satisfy G-D relation.

So, let us first look into that and then we will discuss a little bit of you know the concept of A and how A is related to interactions trend but the first I am going to just show that using this relation or using this model to two suffix Margules equation this should satisfy the Gibbs-Duhem equation.

So, let us check that for the case of the binary mixture, so which essentially means show that summation Xi Dgi should be equal to 0. So, for the case of a mixture, so let us say is a and b mixture this means that I can write this as dGa excess plus Xb okay.

So, now you can find out the values of that, so value of this Ga bar excess, so Ga bar excess by definition is A Xb square and Gb bar excess is A X square that is what we obtain it. So, this is nothing but G1 bar excess. Similarly, this is nothing but G2 bar excess. So, with this information you can obtain d of Ga excess which is nothing but 2 times A Xb dXb and this means that Gb excess is 2 times A Xa dXb.

Now, if you use this in this equation, you obtain the following that you have 2 Xa Xb dXb plus 2 A again Xb Xa dXb so we just look at the left-hand side here. So, this is now 2 A Xa Xb which is a common and d Xb plus so this has to be A so dXb plus dXa. So, now this here is nothing but dXa plus Xb which is 1 and hence this must be equal to 0 that means left hand side is equal to 0 which means that this expression or two suffix equation leading to this expression of RT ln gamma is equal to Ax 1 square this satisfies the Gibbs-Duhem relation.

$$\sum x_i d\overline{G_i}^E = 0$$

$$a, b\ mixture: \quad x_a d\overline{G_a}^E + x_b d\overline{G_b}^E = 0$$

$$\overline{G_a}^E = Ax_b^2 \quad or, \quad d\overline{G_a}^E = 2Ax_b dx_b$$

$$\overline{G_b}^E = Ax_a^2 \quad or, \quad d\overline{G_b}^E = 2Ax_a dx_a$$

$$LHS: \quad 2Ax_a x_b dx_b + 2Ax_b x_a dx_a$$

$$2Ax_a x_b[\, dx_b + dx_a] \ \rightarrow \ 2Ax_a x_b d(x_a + x_b) \rightarrow 0$$

$$LHS = 0$$

So, this particular is something which can be used for explaining the behavior of fluid mixtures and though is a very simple model but it is useful in many cases and we will talk about this more in detail at this point that something which we will, so we will discuss about the A parameter in the next class and as well as some examples to illustrate the advantage of taking such models and issues related to such models also. So, that would be the end of today’s class, I will see you next time.