Advanced Thermodynamics
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Lecture – 19
Activity Coefficients and Thermodynamic Consistency

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is activity coefficients and thermodynamic consistency. Since it is a continuation of previous 2 lectures, what we have we will be having a kind of recapitulation of what we have seen in last 2 lectures.

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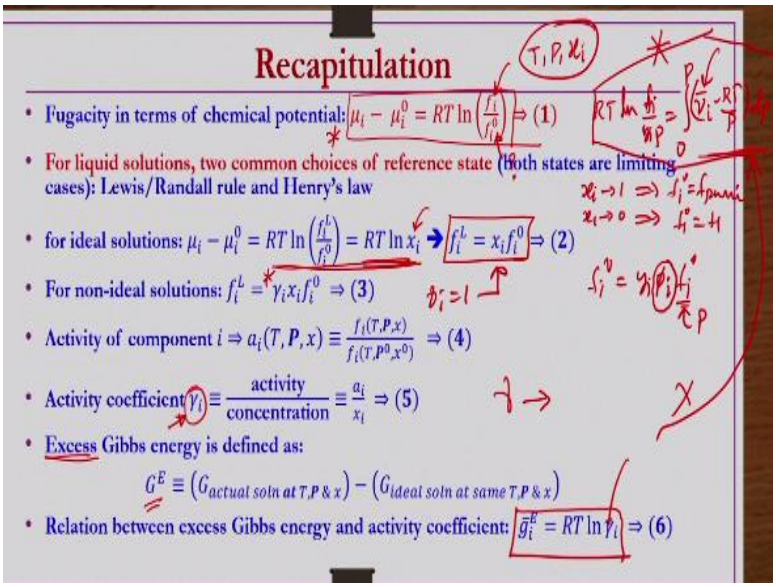

Fugacity in terms of chemical potential, we have already defined in one of the earliest lectures that $\mu_i - \mu_i^0 = RT \ln\left(\frac{f_i}{f_i^0}\right)$, f_i is the fugacity of component i in the mixture and then that is related to the temperature, pressure and then composition of the system, right? That is what it is, but this equation is useful only when this f_i^0 is known, right? Because from here once we have this volumetric data that using the volumetric data we can make a kind of relations like, something like as we have seen for the gaseous phase or $RT \ln\left(\frac{f_i}{y_i P}\right) = \int_0^P \left(\bar{v}i - \frac{RT}{P}\right) dP$.

This is what we have seen for a component i in a gaseous mixture and that gaseous mixture is having some kind of non-ideality and that non-ideality can be represented by fugacity coefficient $\frac{f_i}{y_i P}$, f_i is the fugacity, right? So, if you wanted to know this information, what is the non-ideality you should know this $\bar{v}_i$ so that you can get from the volumetric data of the system, okay? But in the process of deriving this equation, we have done several analysis and then we

realized that until and unless we have some kind of information about what is this f_i^0 reference state, at the reference state what is the fugacity of that component.

If you do not know this equation, you cannot further use and then for the ideal gas mixtures, we have taken this $f_i^0$is nothing but the partial pressure of that component in the mixture. If the gas is the kind of pure ideal gas, then this $f_i^0$is nothing but the total pressure of the system that is what we have taken as a kind of reference state because as long as the system is in the gaseous state, whatever is the non-linearity or non-ideality existing in the system, if the pressure reduces to the very small pressure that $P \rightarrow 0$ or close to the 0.

Then all gases behave as a kind of ideal gases where there are no interactions amongst the molecule of the system. So, that we have taken as a kind of reference state and then it is giving good results especially when comparing with the experimental results. But what happens in the case of liquids? In the case of liquids, we know that the liquids are existing because of the intermolecular interactions, intermolecular forces are binding together those molecules so that the condensed phase either in liquid or solid form and that can exist, right?

So, in the case of liquids, we cannot say that this reference state is a kind of state where there are no interactions. If we say that there are no interaction that means we are saying that there is no condensed phase, so that is not possible. So, what should be the appropriate reference state that we should use for the case of liquid solutions? That is one question and then another question is that can we use the same equation, this equation number 1 without any difficulty for condensed phase also?

We cannot use because of one reason, the reason is that the volumetric data required that has to be collected for the system from the case where the density is very low that is 0 density our ideal gas behavior level to the very high density or density of the condensed phase. Such wide range of density, covering such wide range of density obtaining volumetric data is not possible, it is a very tough job. So that is the reason we cannot use this equation as it is either. So, we have to appropriately develop alternative approach how to find out the non-ideality in the liquid system.

So, those 2 things we have done in the previous lecture, we are doing it kind of a recapitulation, right? So, we have seen that in the case of liquids, there are 2 extreme limits. The two limiting conditions are available as a kind of reference state, one is the reference state where you know the $x_i \rightarrow 1$ then fugacity of that particular component = the fugacity of pure component as it is existing pure component, right? So, because in the liquids we can say the liquid is ideal if the system is pure system.

In the case of liquids, non-ideality is coming because of the dissimilar or chemically different nature of the molecules that are present. Within the one system, if all molecules are of same nature then obviously their interactions are going to be same and then if the interactions are same then we can say that solution is the kind of ideal solution and for those ideal solution Δv_{mix} as well as ΔH_{mix} are going to be 0 that we know.

So, we have taken that when $x_i \rightarrow 1$ or close to 1, then whatever this f_i^0 is there is nothing but $f_{pure\ i}$, that is what we have taken, that is known as the Lewis Randall rule and then another case when this $x_i \rightarrow 0$ that is x_i is present in very small quantities kind of a dilute solutions then we take this f_i^0 is nothing but Henry's law constant which describes the solubility of this component i in the solvent or in the remaining component in which it is mixed. So, these are the 2 reference tests we have seen.

Then, from the analogous behavior like equation number 1 when we have written for gaseous system what we have written, this $\mu_i - \mu_i^0$ =RT ln $\left(\frac{f_i^v}{f_i^0}\right)$ = RT ln $\left(\frac{y_i \phi_i P}{P}\right)$ that is $y_i P$ we have written. So, analogous to that one if you write for the ideal solutions, then we get this information is nothing but RT ln x_i or $\Delta\mu$ is nothing but RT ln x_i. Analogous to the case whatever we have written for the mixture of ideal gases, there we got $\mu_i - \mu_i^0$ = RT ln $\left(\frac{y_i P}{P}\right)$that is RT ln y_i that is what we get.

So, analogously for ideal solutions, we should write RT ln x_i, x_i is the mole fraction of the component i, So, from these 2 quantities what we can write, $f_i^L = x_i f_i^0$. Now, if you take a Lewis Randall rule, then $f_i^0$is $f_{pure\ i}$. If you take the Henry's law as a kind of reference state, then f_i^0 is going to be H_i, okay? This is also we have seen. Then for obviously non-ideal

solutions what we have, we have the activity coefficient γ_i that is coming into the picture. In this expression $f_i^L = x_i f_i^0$ which is valid for only ideal solution.

If there is a non-ideality in this solution then that non-ideality has to be brought into the picture and as in the case of vapor phase, we have written $f_i^v = y_i \phi_i$ and then f_i^0 and f_i^0 we have taken kind of P in majority of the cases because ideal gas we are taken as a reference. So, this ϕ_i is indicating fugacity coefficient of component i in the vapor phase. So, accordingly this ϕ_i indicates the non-ideality of the vapor phase, non-ideality in the vapor phase due to this component that is what it indicates.

So, similarly if at all non-ideality is existing in the liquid phase in the liquid solutions. So that non-ideality has to be represented accordingly and that is γ_i, it is known as the activity coefficient. If $\gamma_i = 1$ then the solution is ideal solution then we have $f_i^L = x_i f_i^0$, okay? Now we have to ambiguity this how to make a kind of relation for γ_i, because ϕ_i this equation and then another two to three equations we have also developed.

So, those equations we can use and then we can get ϕ_i for the vapor phase but for γ_i such kind of equation we are not able to develop because developing volumetric data information for a system from low density to very high density, the range of liquid density value close to the liquid density value is very difficult. So, since we do not have volumetric data, we cannot use this equation. So, we have to find alternative approach what should be the things that we should use for this γ_i and then what should be the f_i^0. So f_i^0 is now clear. If it is $x_i \rightarrow 1$, then Lewis Randall law you can use as a kind of reference state.

If $x_i \rightarrow 0$, then Henry's law you can use it as a kind of reference state and then if the ideality is valid in the entire range of x_i from 0 to 1, then we can use so called Raoult's law as a kind of reference state or ideality defined with respect to Raoult's law that is what we can, that clarity is there but this clarity is not there, how to define γ_i, that also we have seen anyway. So, before defining the activity coefficient, what we have done? We have defined the activity of the component which is nothing but $\left(\frac{f_i}{f_i^0}\right)$, simply.

So, activity coefficient we have defined as activity divided by the concentration, some concentration measurement, let us say mole fraction. So, $\gamma_i = \frac{a_i}{x_i}$, this is also we have seen. Then in order to find out this information, this actually what it says γ_i activity coefficient it says the non-ideality in the liquid solution and the non-ideality is coming because of the foreign component is joining with the pure substance i something like that, right?

So, then the mixture is forming, so dissimilar chemical molecules are mixing together forming a solution, dissimilar interaction are there, so that dissimilar interactions are bringing non-ideality, right? So, that means before making a solution if the component is as a kind of ideal, so that maybe taken as a kind of ideal that may be taken as a kind of basis to define the non-ideality, so non-ideality if you write or if you define in terms of some thermodynamic property, let us say Gibbs energy, Gibbs energy under ideal conditions you know.

By adding some other component non-ideality is there. So, then whatever the Gibbs energy under the real conditions minus Gibbs energy under the ideal condition that should be giving how much non-ideality is coming into the picture and then that additional thing whatever is there in addition to the thermodynamic property under ideal conditions, whatever the additional property, additional thermodynamic property is there that we call as a kind of excess thermodynamic property.

Let us say excess Gibbs energy if you define G^E stands for excess Gibbs energy. So, $(G_{\text{actual soln at T,P \& x}}) - (G_{\text{ideal soln at same T,P \& x}})$ that is at the same temperature, pressure, and composition as in the case of mixture, okay? So, this is what we have seen and then in order to get some information about this one, we have already defined this one $\bar{g}_i^E = RT \ln\gamma_i$, this is what we have derived. We have derived in 2-3 different ways, okay?

So, now see this activity coefficient here we were not able to find out in a way that we found for the fugacity coefficient, we were not able to find out. So, then we have made a kind of alternative approach and the alternative approach that this activity coefficient is related to the excess Gibbs energy. Excess Gibbs energy using this form that is partial molar excess Gibbs energy = RT ln γ_i and γ_i stands for the activity coefficient of that component i in the real liquid solution, okay?

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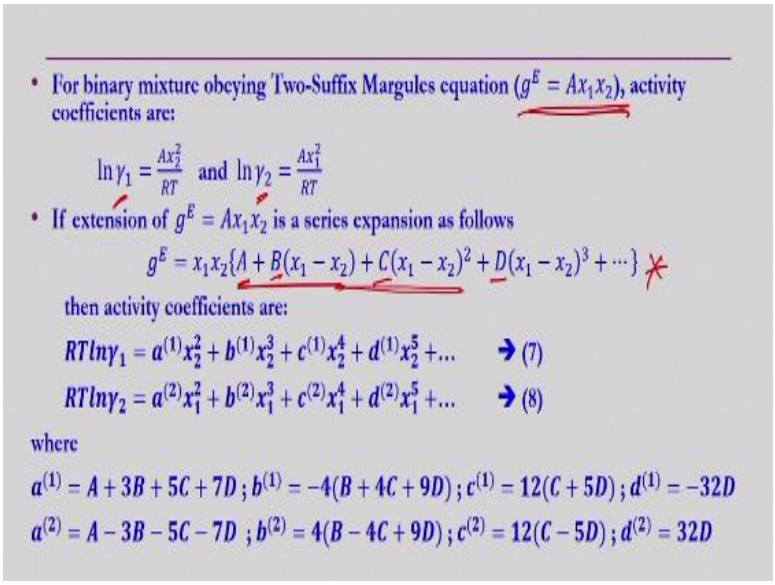

Then we have also seen for binary mixture obeying two-suffix Margules equation $g^E = Ax_1 x_2$. We have derived this activity coefficients as, $\ln \gamma_1 = \frac{Ax_2^2}{RT}$ and $\ln \gamma_2 = \frac{Ax_1^2}{RT}$. We have seen γ_1 is reported as a function of x_2 and then γ_2 is reported as function of x_1 because whatever the non-ideality is there that is because of the other component joining with the initial pure component. Let us say initially component 1 is pure so by adding second component or component 2, it has become non-ideal.

So, that is the reason whatever the non-ideality is there is written as a kind of function of a mole fraction of that second component joining this pure components and making that as a kind of a non-ideal solution, okay? And then we have seen these 2 coefficients are symmetric. That is they are, if $\ln \gamma_1$ versus x_1 if you plot and then similarly $\ln \gamma_2$ versus x_1 if you plot, you can see they are a kind of a mirror images of each other. So, if they are mirror images of each other then we can call them as a kind of symmetric coefficients.

This is for the second Margules equation, right? Let us say if you wanted to bring in more parameters then if you have a kind of extension of this second Margules equation or two-suffix Margules equation as a kind of series expansion in this form. When we have this $g^E = Ax_1 x_2$, this equation when we expand and then to include more parameters like B, C, D, etc., then corresponding activity coefficients $\ln \gamma_1$, $\ln \gamma_2$ we obtained as this, where this $a^{(1)}$, $b^{(1)}$, $c^{(1)}$, $d^{(1)}$ and then $a^{(2)}$, $b^{(2)}$, $c^{(2)}$, $d^{(2)}$ are given like this.

This A, B, C, D parameters are to be obtained from the experimental data at least for one component, you have to measure activity coefficient of that particular component with respect to the mole fraction and then plot the data and then do the curve fitting and get this A, B, C, D parameters, right? In this equation if you include only up to A, then it is two-suffix Margules equation. If you include the second part also that is B into x_1 minus x_2, then it is a three-suffix Margules equation.

If you include this part also, then it is four-suffix Margules equation and likewise we can have this solutions and then we can say here three-suffix and four-suffix Margules equation and other higher suffix Margules equations having a kind of activity coefficients which are asymmetric in the nature. So, till this point, we have seen. Now what we do? We make use of this Gibbs-Duhem equation and then try to obtain the activity coefficient of one component provided the activity coefficient of the other component is known in a binary mixture.

So, is it possible without doing experiment? That we are going to check. So, that would be the task of the today's lecture where we will be finding out activity of one component from the activity coefficient of other component in the binary mixture as well as we will be checking the thermodynamic consistency of a reported data, whether it is reliable, consistent or not, those things we are going to see.

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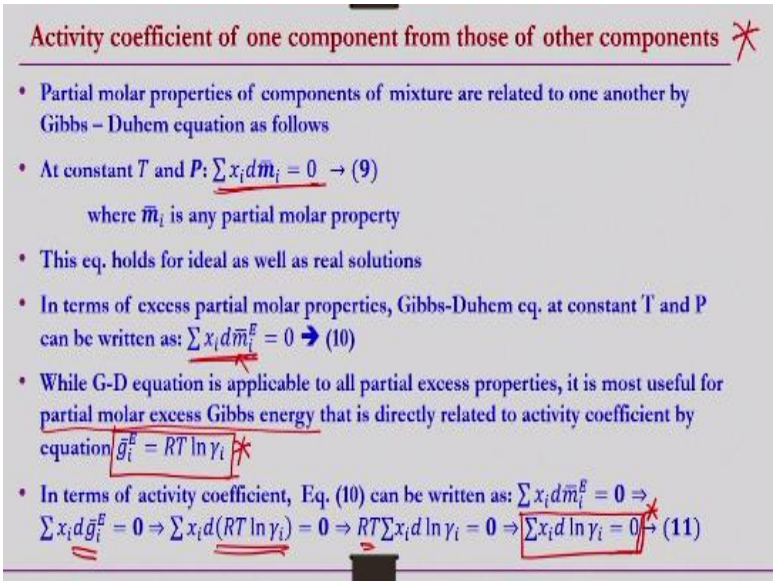

So, activity coefficient of one component from those of other components. We know that partial molar properties of components of mixture are related to one another by Gibbs-Duhem equation in this particular form. If the temperature and pressure are constant, then $\sum x_i d\bar{m}_i = 0$.

The $\bar{m}_i$ here is nothing but any partial molar property. The same equation whatever we have written it holds good both for ideal as well as the real solutions. If we write the same equation for the excess partial molar properties, then we will be having $\sum x_i \, d\bar{m}_i^{\,E} = 0$, right?

So, now if here $\bar{m}_i$ if I substitute $\bar{g}_i^{\,E}$, then what will happen? What equation we will get? Is that equation can be further used to fulfill our purpose or not that is what we see, right? While this G-D equation is applicable to all partial excess properties, it is most useful especially when it is applied to the partial molar excess Gibbs energy because that is directly related to the activity coefficient by this expression $\bar{g}_i^{\,E} = RT \ln \gamma_i$.

That means this equation if you use here in place of $\bar{m}_i^{\,E}$, if you substitute whatever $\bar{g}_i^{\,E} = RT \ln \gamma_i$, then you may be getting another expression which may be having $\sum x_i d \ln \gamma_i = 0$ as we do here. So, here in place of $\bar{m}_i^{\,E}$, I substituted $\bar{g}_i^{\,E}$ so that is d RT ln γ_i here, so RT is constant. So, $RT \sum x_i d \ln \gamma_i = 0$ that means $\sum x_i d \ln \gamma_i = 0$ this is what you get and this is another important equation especially as long as we are dealing with non-ideality in the liquid solutions in addition to this previous equation.

So, now this equation we will be using to find out the activity coefficient of one component from the data of the activity coefficient data of the other component in a binary system.

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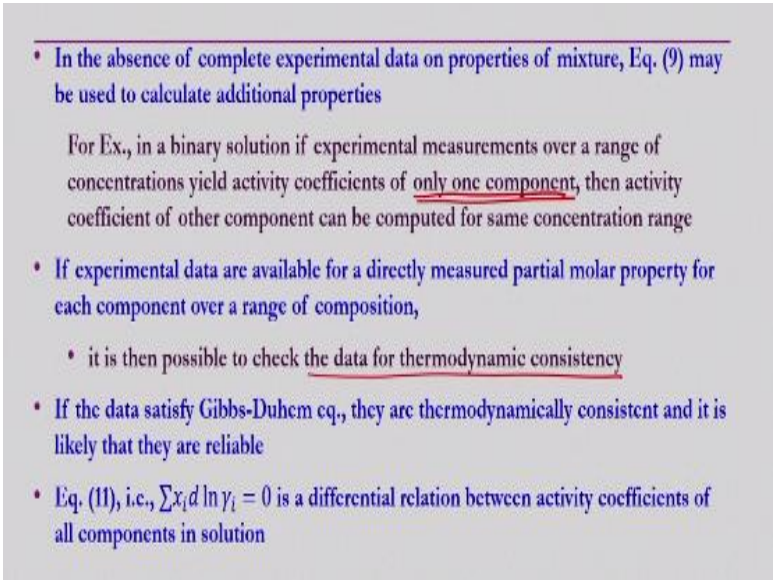

So, in the absence of complete experimental data on properties of mixture, equation 9 may be used to calculate additional properties. Example, in a binary solution if experimental

measurements over a range of concentration yield activity coefficients of only one component due to some difficulty. Let us say, you are not able to find out the activity coefficient of both the components experimentally but however, if you managed to obtain the activity coefficient of one component over the wide range of mole fraction or concentration of the species.

Then that information may be used to find out the activity coefficient of the other component using the equation $\sum x_i d \ln \gamma_i = 0$ under the same range of concentration range. So, if experimental data are available for a directly measured partial molar property for each component over a range of composition then it is possible to check whether the data is thermodynamically consistent or not and that is the other advantage of this same equation $\sum x_i d\ln \gamma_i = 0$, which is again coming from the Gibbs-Duhem equation or other form of the Gibbs-Duhem equation for this particular non-ideal liquid solutions case.

If the data satisfies Gibbs-Duhem equation, then we can say that the thermodynamically consistent data we obtained and it is likely that that data is going to be reliable. So, that is another important advantage of this equation. So, there are 2 important advantages of this equation. The first one is that and so if you have a binary system and then in the binary system if you find out the activity coefficient of only one component over a range of concentration variation, then the activity coefficient of other component you can find out that is one thing.

Another thing let us say if you have the data for activity coefficient of both the components so whether that data is reliable or not that you can check by crosschecking this Gibbs-Duhem equation $\sum x_i d \ln \gamma_i = 0$. If that data γ_i versus x_i satisfies this equation then we can say that data is thermodynamically consistent and if the data is thermodynamically consistent then we can say that data is likely to be reliable. There is no guarantee that data is going to be reliable if it is obeying the Gibbs-Duhem equation, but mostly it is going to be reliable that is what the other advantage.

But if the data is not obeying the Gibbs-Duhem equation then it is damn sure or confirm that the data is not reliable, right? So, if the Gibbs-Duhem equation is not obeyed by this activity coefficient which are obtained by experimental approach, if it does not satisfy the $\sum x_i d\ln \gamma_i=0$ then we can say that experimental data there is some kind of error and then that is not reliable

kind of thing. So, this equation is there, whatever this equation it is a differential relation between activity coefficients of all components in the solution.

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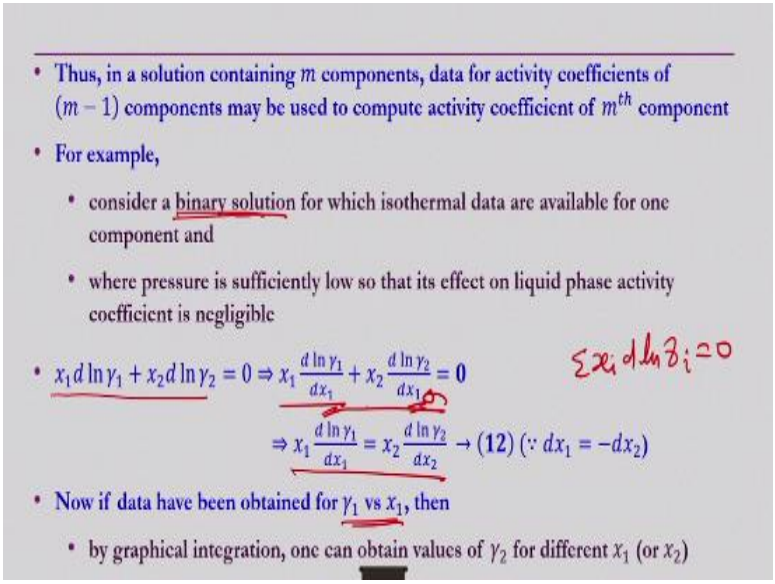

So, in other words in a system of m number of components if you know the activity coefficient of m minus 1 number of components, then m^{th} component activity coefficient you can find out using this equation $\sum x_i d \ln \gamma_i = 0$. For example, consider a binary solution for which isothermal data are available for one component and where the pressure is sufficiently low so that its effect on activity coefficient is negligible. Then, we have this equation $\sum x_i d \ln \gamma_i = 0$.

This if you write for the binary case because we are taking the binary case, right? Then we will be having $x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0$. If you write properly, it is $x_1 \frac{d\ln\gamma_1}{dx_1} + x_2 \frac{d\ln\gamma_2}{dx_1} = 0$. It should not be dx_2 because on differentiation both the terms has to be with the same that is what is meant by $d \ln \gamma_i$ okay? Now, this equation we can write if I write in place of dx_1 if I write dx_2 because $dx_1 + dx_2 = 0$ for a binary system. So, dx_1 I can write it as $- dx_2$.

So, I will be having $-x_2 \frac{d\ln\gamma_2}{dx_2}$ that I can take to the right hand side. Then I can have $x_1 \frac{d\ln\gamma_1}{dx_1} = x_2 \frac{d\ln\gamma_2}{dx_2}$, right? This is the other form. So, now here γ_1 versus x_1 data if you have then you can use some graphical approaches and then you can find out this γ_2 versus x_1 information, right? So, this is how we can use this equation, but, however, what we can do?

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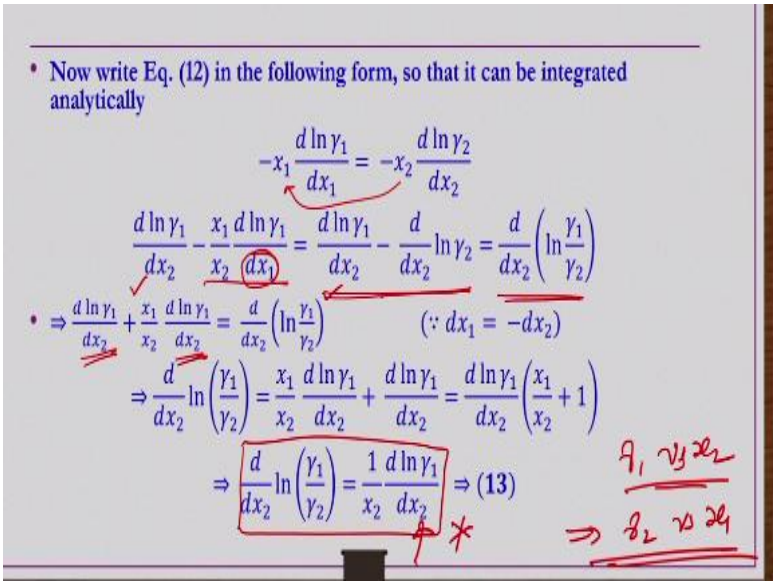

We can rewrite this equation in a different form, so that this equation can be analytically integrated easily without needing to do any graphical integration. So, that we do. So, the same equation what I have taken, I have multiplied by -1 either side and then in the next step what I have done, I have taken this x_2 to the left hand side and written $-\frac{x_1}{x_2}\frac{d\ln\gamma_1}{dx_1}$ and then right hand side $-\frac{d\ln\gamma_2}{dx_2}$ as it is. Then next step, I have added these two terms, this term either side that is $\frac{d\ln\gamma_2}{dx_2}$ I have added both sides.

So that what I can do, right hand side 2 terms I can combine them together and write it as $\frac{d}{dx_2}\ln\left(\frac{\gamma_1}{\gamma_2}\right)$, right? Then next step what I do? Here dx_1 I will be writing $-dx_2$ because the $dx_1 = -dx_2$ for a binary system. So, then I have $+\frac{x_1}{x_2}\frac{d\ln\gamma_1}{dx_2}$ and then remaining two terms as it is. So, now I have $\frac{d\ln\gamma_1}{dx_2}$ term both the terms in the left hand side, so that if I take common, then whatever the $\frac{x_1}{x_2} + 1$ that if I do LCM then I will be having $\frac{x_1+x_2}{x_2}$ that is $\frac{1}{x_2}$.

So, then what we will be having $\frac{1}{x_2}\frac{d\ln\gamma_1}{dx_2} = \frac{d}{dx_2}\ln\left(\frac{\gamma_1}{\gamma_2}\right)$ simply. So, let us say if you have γ_1 versus x_2 information is there, so you can get this $\frac{d\ln\gamma_1}{dx_2}$ information from here, substitute here, right? And then do some simplification. So, then you will be getting information γ_2 versus x_1 without any difficulty, okay? So, this is another form of the same equation which can be analytically integrated without any requirement of graphical integration.

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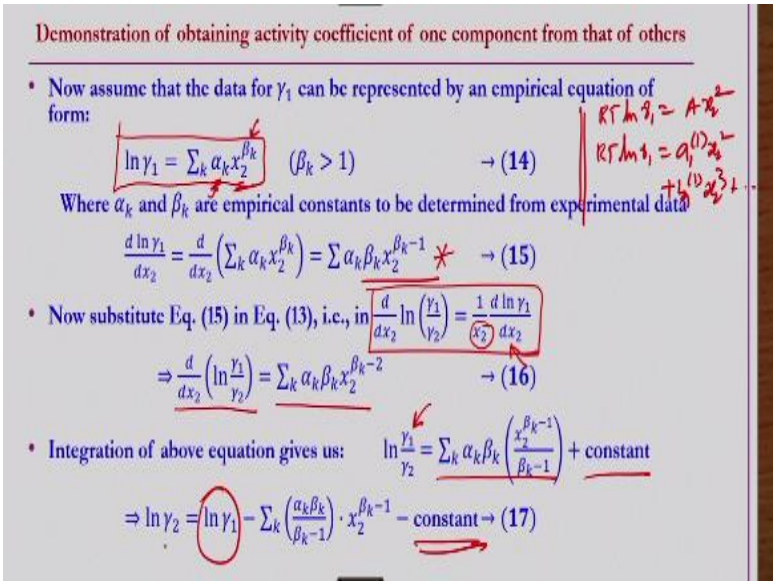

So, that we demonstrate now by taking an example. So, what we do? We assume that the data for γ_1 can be represented by an empirical equation of the form this one because why this form? We have seen this, let us say when we have a two-suffix Margules equation, we got RT ln $\gamma_1 = Ax_2^2$ then we have done the series expansion. So RT ln $\gamma_1 = a_1^{(1)}x_2^2 + b_1^{(1)}x_2^3$ and these kind of terms would be there, if you remember in one of the previous slides, okay? So that is the reason what we do?

We write like let us say sum x_2 power something and then it is multiplied by some constant, right? So how many terms should be there? So at least if it is two-suffix Margules equations are the simplest one that $\frac{g^E}{RT}$ = A x_1 x_2, that is the simplest one. If you take that form then we get Ax_2^2 as a kind of ln γ_1. So that means it should start with at least a $\beta_k \prec 1$ that is what we understand from here.

So that way we can have a generalized form, empirical form in this kind of analogous to this one because we have seen some of the g^E expression we have taken and then corresponding ln γ_1 and ln γ_2 expression when we have seen, they are having this kind of form that is the reason we have taken this form, okay? α_k is a constant, β_k is also constant, whereas the $\beta_k > 1$, α_k we cannot say anything. Let us say if it is two-suffix Margules equation, then α_k simply A, capital A, right, like that, okay?

So, now, where α_k and β_k obviously as we have been discussing they have to be found through the experimental data only, right? Empirical constant to be determined from experimental data,

okay? So, then if you do d by dx_2 of this equation both sides then you can have this expression that is $\frac{d\ln\gamma_1}{dx_2} = \sum_k \alpha_k$, α_k is constant, differentiation of $x_2^{\beta_k}$ with respect to x_2 is nothing but $\beta_k x_2^{\beta_k - 1}$, β suffix k minus 1, okay? This k is a kind of suffix for this α and β, right?

Now, this $\frac{d\ln\gamma_1}{dx_2}$ we will be substituting in this equation number 13 that is we just derived in this equation in place of $\frac{d\ln\gamma_1}{dx_2}$. If you use this expression then what we have $\sum_k \alpha_k \beta_k x_2^{\beta_k - 1}$ divided by this x_2 is there. So then we have $\frac{d}{dx_2} \ln\left(\frac{\gamma_1}{\gamma_2}\right)$ left hand side, right hand side we will be having $\sum_k \alpha_k \beta_k x_2^{\beta_k - 2}$, right? So now, this equation here we will be having this particular term, right?

After integration, we have $\left(\frac{x_2^{\beta_k - 1}}{\beta_k - 1}\right)$ + constant. When integrate this equation number 16, you will get this one, right? So, now we already know what ln γ_1 is. We have assumed $\ln\gamma_1 = \sum_k \alpha_k x_2^{\beta_k}$ that also we can substitute here. So, before substituting we can rearrange this equation $\ln\gamma_2 = \ln\gamma_1 - \sum_k \left(\frac{\alpha_k\beta_k}{\beta_k - 1}\right) . x_2^{\beta_k - 1}$ – constant, this is what we have, right? Now, we have to find out this constant, before finding out we will be substituting what is this one also.

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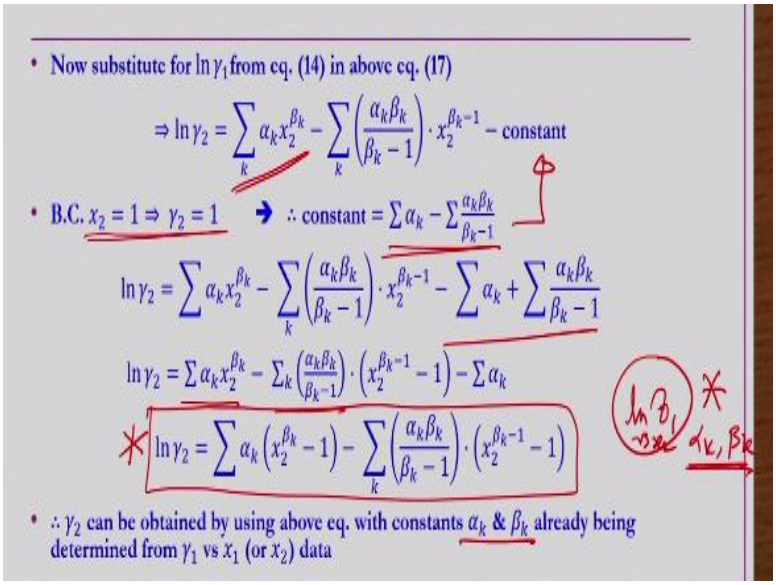

So, when we substitute ln γ_1 is nothing but this one. So we can have the boundary condition when x_2 = 1. It is a binary system, if x_2 = 1 that means component 2 is a pure component. Because x_2 = 1, so it is a pure component 2, component 1 is 0. So if in the liquid solution this component is pure component then obviously the activity coefficient should be equal to 1

because if the pure component, the solution is going to be ideal solution, okay? So, under that boundary condition, if you use that boundary condition here in the above equation, then you can get this constant as this one, right?

So, this constant you substitute back here and then simplify further by combining these $\left(\frac{\alpha_k \beta_k}{\beta_k - 1}\right)$ term as one term and then $\sum_k \alpha_k$ term as another term then we are having $\ln \gamma_2 = \sum_k \alpha_k \, x_2^{\beta_k - 1} - \left(\frac{\alpha_k \beta_k}{\beta_k - 1}\right).(x_2^{\beta_k - 1} - 1)$. So, now, you know $\ln \gamma_1$, you have found, right? Once you know this information which is having the constants α_k and β_k, so $\ln \gamma_1$ versus x_2 data that you get, try to get experimentally and then find out these constants.

So, then $\ln \gamma_2$ you can find out easily without worrying anything by simply using these constants here, fine? So, this is the one advantage. So, γ_2 can be obtained by using above equation with constants α_k and β_k which are already being determined from γ_1 versus x_1 or γ_1 versus x_2 data which has been found experimentally. So, this is the first advantage. Through the demonstration we have done.

We have taken a generalized case rather taking three-suffix Margules equation, four-suffix Margules equation or any other equation, we have taken a generalized form of $\ln \gamma_1$. That is $\ln \gamma_1 = \sum_k \alpha_k \, x_2^{\beta_k}$ that is what we have taken.

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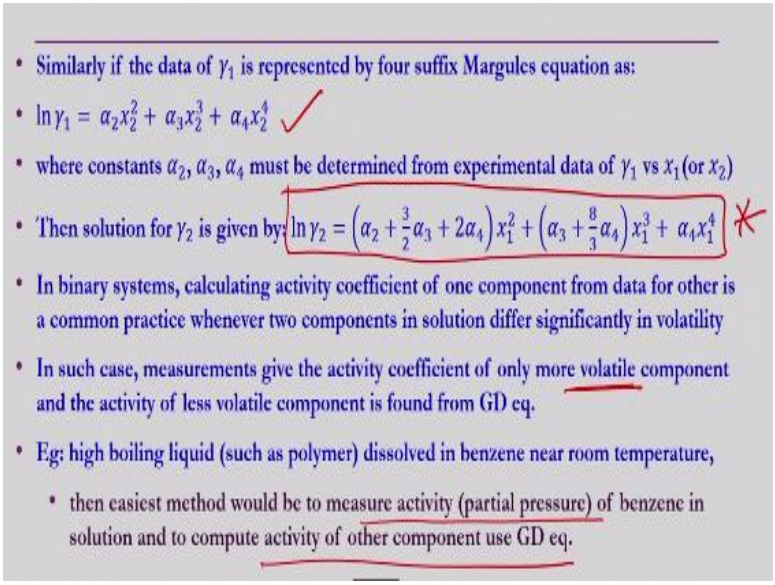

So, let us say if you have four-suffix Margules equation, right? If you have a four-suffix Margules equation then $\ln \gamma_1$ if you obtain, it will be having this form $\alpha_2 \, x_2^2 + \alpha_3 \, x_2^3 + \alpha_4 \, x_2^4$.

What is this α_2, what is this α_3, what is this α_4, we do not know, we have to find out experimentally. Let us assume experimentally you obtained γ_1 versus x_2 information. From that information when you have done the curve fitting then you found this α_2, α_3, and α_4.

So, that means they are known from the experimental conditions. Then using the previous approach that is using the equation $\sum x_i d \ln \gamma_i = 0$, when you use that equation and then apply this $\ln \gamma_1$, so then $\ln \gamma_2$ you can find out and then that $\ln \gamma_2$ is going to be this one. So, this simplification and calculations you can do because it is a simple mathematical simplification. So, you can get this $\ln \gamma_2$ if $\ln \gamma_1$ is given by this expression, right? Like this, you can do for any model of binary system.

If it is multi-component system or if m number of components are there, you have to find out m minus 1 number of components their activity coefficients, so m^{th} component you can find out. In binary system, calculating activity coefficient of one component from data for other is a common practice whenever two comprehensive solutions differ significantly in volatility. In such case, measurements give the activity coefficient of only more volatile component and the activity of the less volatile component is found from the G-D equation.

Because more volatile component, it is going to be in a lighter one and it is easier to go in the vapor phase let us say if you have vapor-liquid phase. So, then therefore, the more volatile component the fugacity may be, activity may be related to the partial pressure. So, it is easy to find out that one and then the non-volatile component is there, for that you can find out its activity coefficient using the Gibbs-Duhem equation because finding out the fugacity of highly non-volatile components experimentally is a bit difficult.

So, that is another advantage of this Gibbs-Duhem equation in terms of activity coefficients. So, example high boiling liquids such as polymers are dissolved in benzene near room temperature. Then the simplest way to find out that activity is that experimentally measure activity or the partial pressure of benzene which is quite easy to find out experimentally. Then compute the activity of other component that is a high polymer non-volatile component using the G-D. The activity of the other component you can find out using this Gibbs-Duhem equation, okay?

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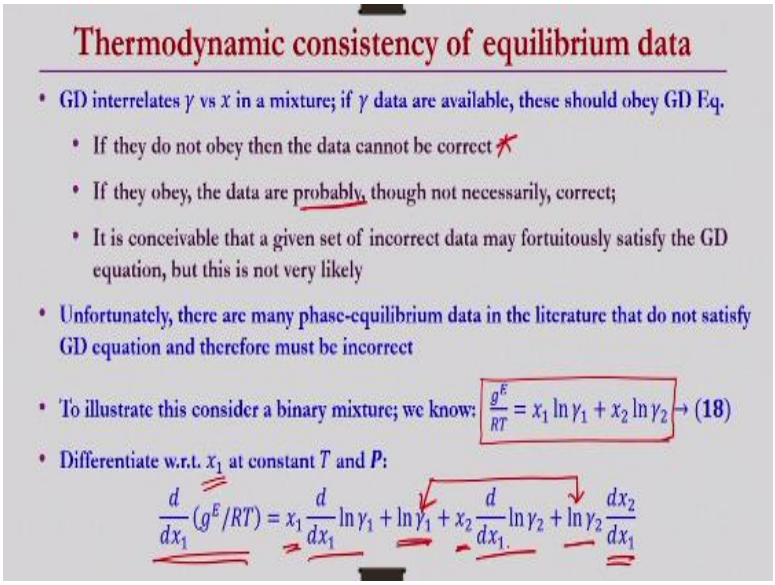

Now, thermodynamic consistency of equilibrium data, right? So, whatever the Gibbs-Duhem equation is there, how can we use it to check the thermodynamic consistency of the activity coefficient versus mole fraction data that is what, we are going to do now. G-D interrelates γ versus x in a mixture that means if γ data are available, this data should obey G-D equation. If they do not obey, then the data cannot be correct as I mentioned. If the experimentally obtained γ_i versus x_i information is obeying G-D equation then it is possible that the data is reliable, though it is not guaranteed.

But if it is not obeying G-D equation, then it is confirmed that the data is not reliable, data is inaccurate. There are some kind of problems in measuring this data experimentally, so one has to crosscheck. If they obey, the data are probably correct, but not necessarily correct, okay? This is one of the methods to make sure that the data is correct or not. If you cannot confirm whether the data is correct or not by G-D equation but at least you can confirm if the data is incorrect. If the data is incorrect, that is not going to satisfy the G-D equation here in this case.

For that it is conceivable that a given set of incorrect data may fortuitously satisfy the G-D equation but this is a very rare case in general and unfortunately there are many phase equilibrium data in the literature that do not satisfy G-D equation and therefore must be treated as incorrect data. To illustrate this particular thermodynamics consistency check, what we do? We take a binary mixture, for that g^E we write in this form $\frac{g^E}{RT} = x_1 \ln\gamma_1 + x_2 \ln\gamma_2$, we are doing for a binary system.

Now, this equation what we do? We differentiate with respect to x_1 at constant temperature and pressure, okay? Because these G-D equations whatever we are using for this purpose they are valid at constant temperature and pressure or whatever $\sum x_i$ dln $\gamma_i = 0$ that equation is valid obviously at constant temperature and pressure as we have seen. So, when we do this on left hand side $\frac{d}{dx_1}\left(\frac{g^E}{RT}\right)$ as it is, right hand side $x_1 \frac{d\ln\gamma_1}{dx_1} + \ln \gamma_1$ multiplied by 1 that is $\frac{dx_1}{dx_1}$ is 1 and then second term $x_2 \frac{d\ln\gamma_2}{dx_1} + \ln \gamma_2 \frac{dx_2}{dx_1}$.

So, this $\frac{dx_2}{dx_1}$ is nothing but -1. So, $\ln \gamma_1 - \ln \gamma_2$ I can write $\ln\left(\frac{\gamma_1}{\gamma_2}\right)$, right? And then in these 2 terms what I can write? This is in the form $x_1 \, d \ln \gamma_1 + x_2 \, d \ln \gamma_2$. So, according to Gibbs-Duhem equation, so this term should be 0.

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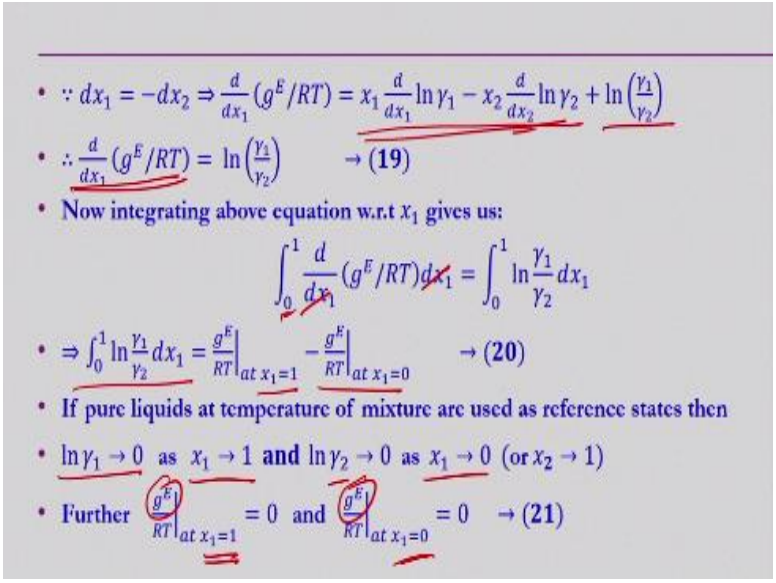

So, I have this $\ln\left(\frac{\gamma_1}{\gamma_2}\right)$ term and then other equation for simplicity I have written dx_2 here. So, when I write dx_2 here it will become minus. So Gibbs-Duhem equation, according to Gibbs-Duhem equation, this term is 0, that means $\frac{d}{dx_1}\left(\frac{g^E}{RT}\right)$ is nothing but $\ln\left(\frac{\gamma_1}{\gamma_2}\right)$, right? This integration is not complete unless you have the information about this one or this equation is not complete or cannot be used in a proper way to check the thermodynamic consistency unless you know the complete information in the left hand side.

For that purpose what we do now, we integrate it with respect to x_1 again. Then what we have, $\int_0^1 \frac{d}{dx_1}\left(\frac{g^E}{RT}\right)dx_1 = \int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1$. So, dx_1 x_1 is varying between 0 and 1. So limits are going to

be 0 to 1 either side. So dx_1, dx_1 is cancelled out. So, what we have $\ln\left(\frac{\gamma_1}{\gamma_2}\right)dx_1 = \left(\frac{g^E}{RT}\right)$ at $x_1 = 1$ $-\frac{g^E}{RT}$ at $x_1 = 0$. So it is a binary system, we are taking for the binary system for easiness. So binary system if pure liquid at temperatures of mixtures are used as reference states then what we have?

When $x_1 \rightarrow 1$ that means it is a pure component 1, so obviously it is pure component. So, pure liquid solution is always ideal. So, then γ_1 is 1, then $\ln \gamma_1$ is 0. Likewise, if the other limit $x_1 \rightarrow 0$. That means $x_1 \rightarrow 0$ that means $x_2 \rightarrow 1$ that means it is a pure component 2 again though it says other competent 2 but it is again pure component, so γ_2 is a kind of, I mean it should be 1 because it is ideal solution then $\ln \gamma_2$ should be 0, right? And other limiting condition at $x_1 = 1$ that means again pure component 1.

If it is pure component, then excess property should be 0. So $\frac{g^E}{RT}$ at $x_1 = 1$ should be 0. Likewise, at $x_1 = 0$ that means $x_2 = 1$. Again, it is a pure component. So again for the pure component g^E has to be 0. So, $\frac{g^E}{RT} = 0$. That means in the equation number 20, right hand side when you substitute either of these limits, $x_1 = 1$ or $x_1 = 0$, we are going to have 0 value. So, that means altogether we have right hand side zero value.

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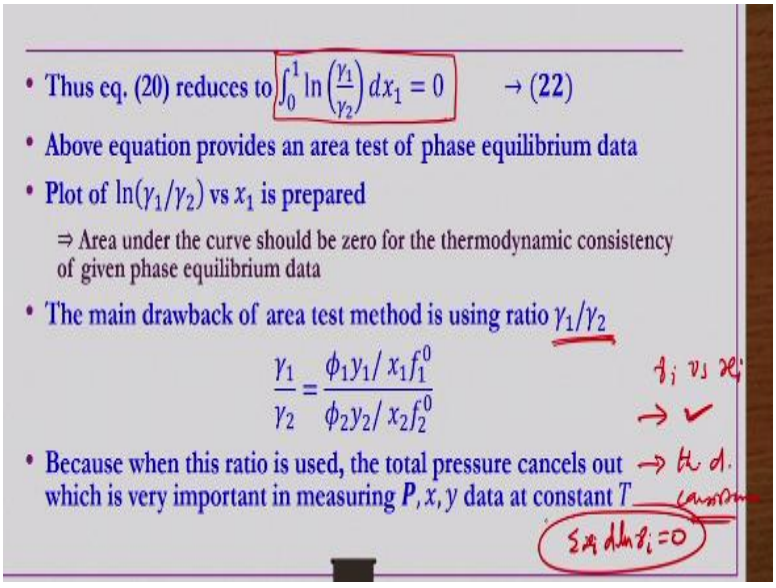

Finally, we get $\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0$. So that means you have experimentally γ_1, γ_2 information, you tabulate $\ln\left(\frac{\gamma_1}{\gamma_2}\right)$ versus x_1 and then you plot $\ln\left(\frac{\gamma_1}{\gamma_2}\right)$. When you plot $\ln\left(\frac{\gamma_1}{\gamma_2}\right)$ versus x_1, then

you will be having a curve and then if you find out the area under that curve, if it is 0 then we can say that the data is obeying the Gibbs-Duhem equation and it is thermodynamically consistent that is what you can say, okay?

That is the purpose of deriving this equation. So, if you wanted to check whether γ_i versus x_i information that experimentally found is reliable or not, thermodynamically consistent or not. So then you have to do this graphical integration and then find out the area under the curve. If the area under the curve is 0 then it is thermodynamically consistent. Above equation provides an area test of phase equilibrium data. Plot of $\ln\left(\frac{\gamma_1}{\gamma_2}\right)$ versus x_1 has to be prepared and then area under that curve if it is 0, then we can say the data is thermodynamically consistent.

Area under the curve should be 0 for the thermodynamic consistency of given phase equilibrium data, right? This is one of the method to check whether the data is reliable or not, but again it is also having a drawback. Main drawback is using this ratio $\frac{\gamma_1}{\gamma_2}$ for this testing because for phase equilibrium problem when you use the ratio $\frac{\gamma_1}{\gamma_2}$, what happens, the pressure terms cancel out. The pressure terms whatever the P is there, $\frac{\phi_1 y_1 P/x_1 f_1^0}{\phi_2 y_2 P/x_2 f_2^0}$, the P is cancelling out that is the major problem because pressure is having effect.

As long as the pressure is low to moderate then its effect and activity coefficient is negligible, so under such conditions anyway this method is reliable, right? But in general, any condensed phase that is the pressure is not necessarily be 0 always, under such conditions if the pressure is canceling out, the reliability is questionable because when this ratio is used, the total pressure cancels out which is very important in measuring P, x, y data at constant temperature, right?

So, that is what this is how we can use the γ_i versus x_i information like you know first one is the finding out the unknown activity coefficient of one component if you know the activity coefficient of other component in a binary system that you can do. The second one is that you can do, thermodynamic consistency check you can do, right? So, this is the other advantage of Gibbs-Duhem equation in the form of $\sum x_i d \ln \gamma_i = 0$.

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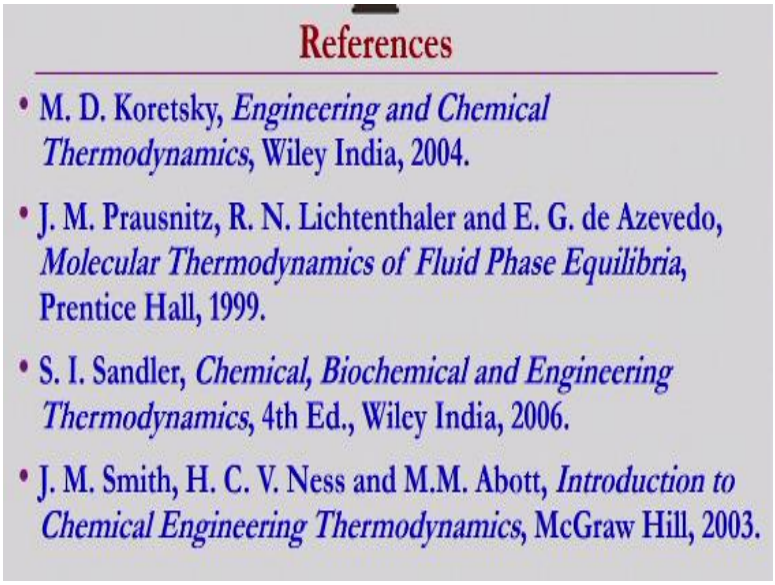

The references for this lecture are provided here. Engineering and Chemical Thermodynamics by Koretsky, Molecular Thermodynamics of Fluid Phase Equilibria by Prausnitz et al, Chemical Biochemical and Engineering Thermodynamics by Sandler; Introduction to Chemical Engineering Thermodynamics by Smith et al.

Thank you.