Course on Phase Equilibrium Thermodynamics
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Lecture No 48
Thermodynamic consistency test of VLE data

Well, hello everybody so long you must have a lot of dose about nonideal solutions activity coefficients, how to find out activity coefficients, Azeotropes, K factors, van laar, Margules and Wilson and NRTL lot of things. Just it's important for you to remember that for the purpose of this particular course you just need to remember the 2 suffix Margules equation and you need to know how to solve problems using the 3 suffix Margules equation and the van laar equation.

In your assignments and in your tests the basic equations for ln gammas will be provided and so that you can proceed but you need to know how to do problems just the way I have done the problems in the last class. Now before ending the last class what did I say? I said that it's very important for you to know that when you are dealing with the experimental data that you're dealing with thermodynamically consistent data.

What does thermodynamics consistency of any data mean? It means that the data obeys Gibbs Duhem equation for any partial molar property or for any partial molar excess property. It's important for you to remember that if any particular thermodynamic data it does not obey Gibbs Duhem equation it is definitely incorrect but when it obeys Gibbs Duhem equation there is no guarantee that it is completely correct.

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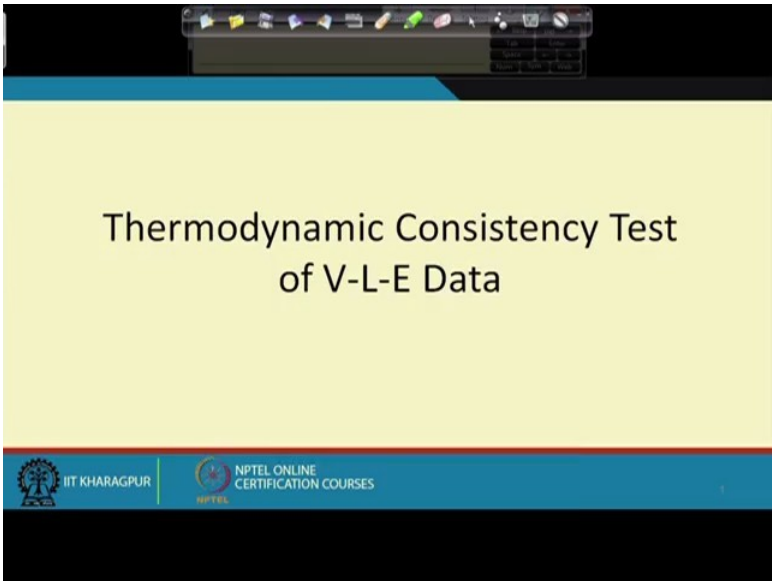

Thermodynamic Consistency Test of V-L-E Data

But it can often happen that by a fortunate cancellation of errors we find that the particular quantity it obeys or rather it obeys the Gibbs Duhem equation under that condition we can use the data it can be considered to be reliable for or thermodynamic purposes but it is not correct such a case is unlikely but it cannot be ruled out completely therefore we are not dealing with thermodynamic correctness of data we're just trying to find out how we are going to ensure that the data are thermodynamically consistent?

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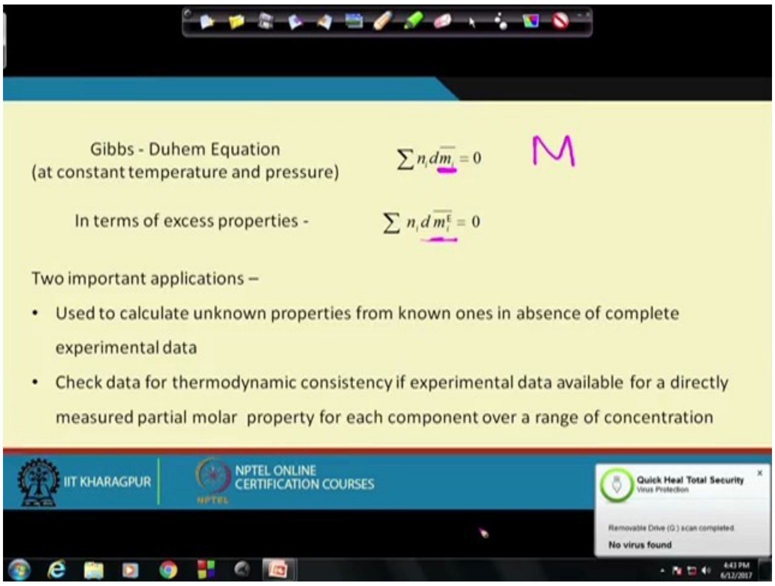

Gibbs - Duhem Equation
(at constant temperature and pressure) $\sum n_i d\underline{\overline{m_i}} = 0$ M

In terms of excess properties - $\sum n_i d\underline{\overline{m_i^E}} = 0$

Two important applications –

- Used to calculate unknown properties from known ones in absence of complete experimental data
- Check data for thermodynamic consistency if experimental data available for a directly measured partial molar property for each component over a range of concentration

Our main guide is the Gibbs Duhem equation, what is the Gibbs Duhem equation let us see? All of us we know that Gibbs Duhem equation it can be written in terms of any particular partial property where we know this mi bar refers to any particular partial molar property for the extensive property M. Now we know that the same equation can be written in terms of molar partial molar excess property as well.

And we know that this equation it has got 2 very important applications which we have already discussed in our previous classes, the first important application is that suppose we do not have the complete thermodynamic data then in that case suppose we have data for one suppose we are dealing with C number of components we have say the activity coefficients for C minus 1 components we can find out the activity coefficient for the cth component using the Gibbs Duhem equation this we have already discussed.

The other important thing is, suppose we have data over the entire range of composition then in that case we can use the data to find out if the experimental data which is available for any particular directly measured partial property whether it is thermodynamically consistent or not, how do we go about doing this?

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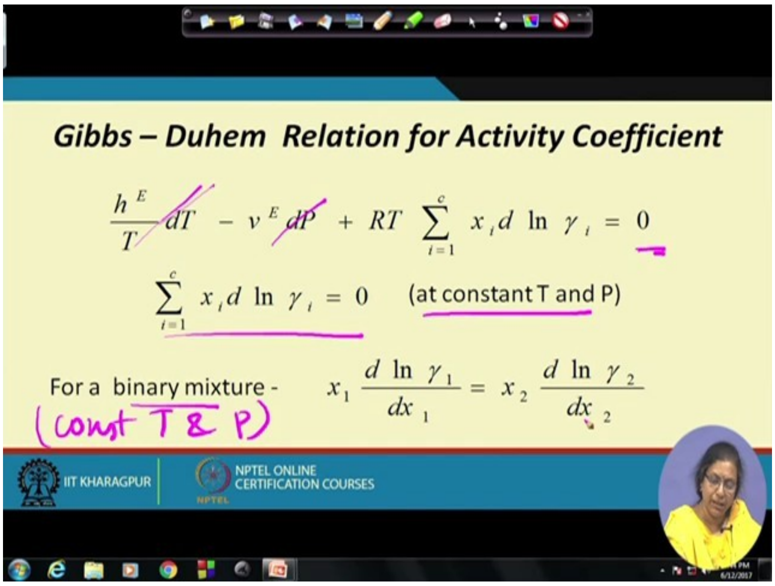

Gibbs – Duhem Relation for Activity Coefficient

$$\frac{h^E}{T}\cancel{dT} - v^E\cancel{dP} + RT\sum_{i=1}^{c} x_i\, d\ln\gamma_i = 0$$

$$\sum_{i=1}^{c} x_i\, d\ln\gamma_i = 0 \quad \text{(at constant T and P)}$$

For a binary mixture - $x_1\dfrac{d\ln\gamma_1}{dx_1} = x_2\dfrac{d\ln\gamma_2}{dx_2}$

(const T & P)

So what is the Gibbs Duhem equation? We have already derived this particular equation and we know that this is the generalized Gibbs Duhem equation, right? And usually I have already mentioned that at constant temperature and pressure this particular term cancels out this particular term these 2 cancels out as we get this particular equation.

And for our practical purpose we find that mostly we will be dealing with the equation for binary mixture. So for a binary mixture under condition of constant temperature and pressure the equation reduces to this particular form. And we now therefore that is if we have the complete VLE data what you mean by the term complete VLE data?

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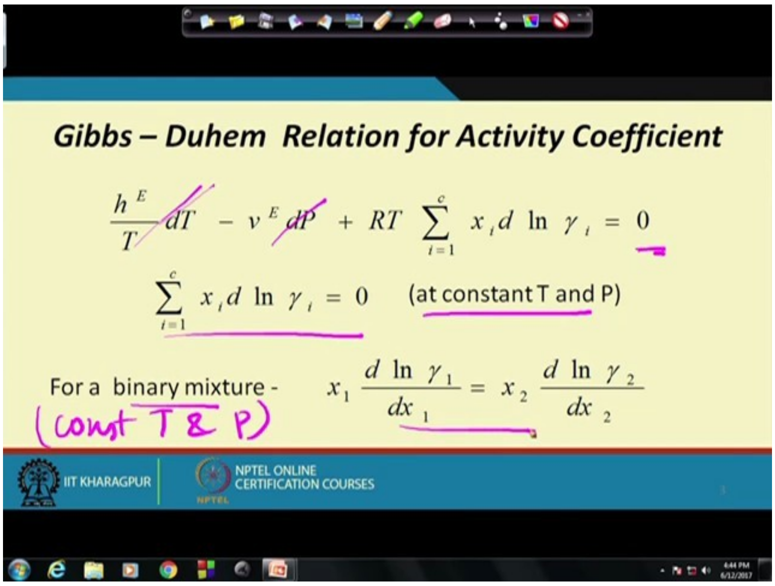

Gibbs – Duhem Relation for Activity Coefficient

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For a binary mixture - $x_1\frac{d\ln\gamma_1}{dx_1} = x_2\frac{d\ln\gamma_2}{dx_2}$

(const T & P)

It means you have data on P, T, x1 and y1 if you have the complete VLE data then for a binary system that we can use this equation to find out whether the data is consistent or not.

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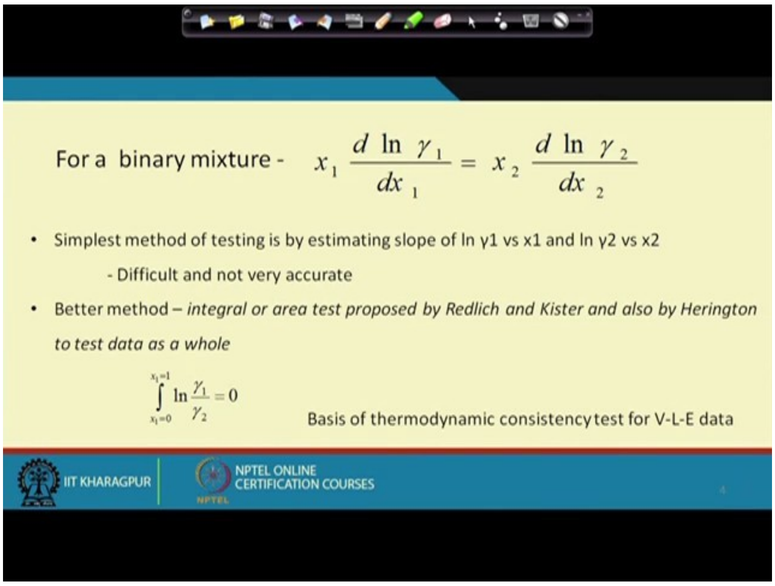

For a binary mixture - $x_1\frac{d\ln\gamma_1}{dx_1} = x_2\frac{d\ln\gamma_2}{dx_2}$

- Simplest method of testing is by estimating slope of ln γ1 vs x1 and ln γ2 vs x2
  - Difficult and not very accurate
- Better method – *integral or area test proposed by Redlich and Kister and also by Herington to test data as a whole*

$$\int_{x_1=0}^{x_1=1} \ln\frac{\gamma_1}{\gamma_2} = 0$$

Basis of thermodynamic consistency test for V-L-E data

Now just by looking at this equation can you tell me how we can use this equation to find out the thermodynamic data? What is the simplest method? Just by looking at the equation it is very evident that you're x1 d ln gamma 1 by dx1 is equal to x2d ln gamma 2 by dx2, so what does it suggest?

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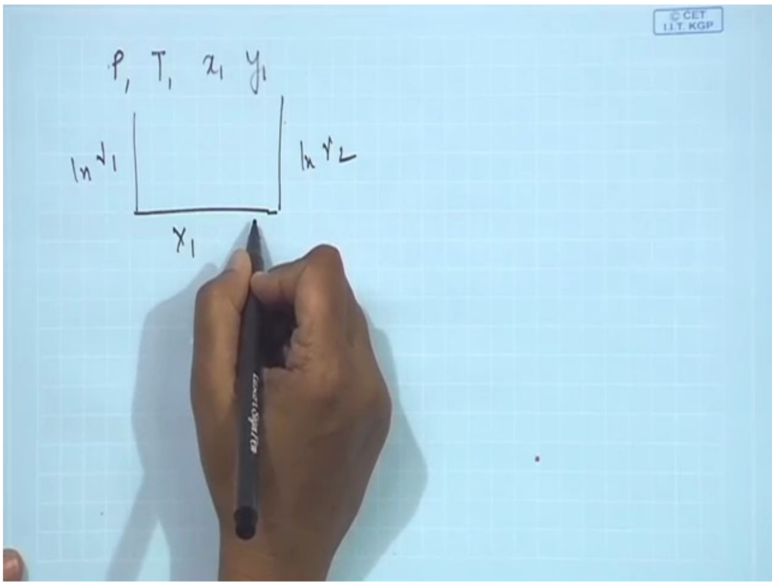

It suggests that if you're having a plot of say ln gamma 1 versus x1 and if you're having a plot of say ln gamma 2 versus X1 then in that case suppose we are having this particular plot, right? This is 0 this is 1and at X1 equals to 1 your ln gamma1 that becomes equal to 0, right, say suppose? And this is a ln gamma2, so this is one particular method which is evident from here you select a number of points here and once you select a number of points you can draw tangents and you can find out the slopes at each and every point.

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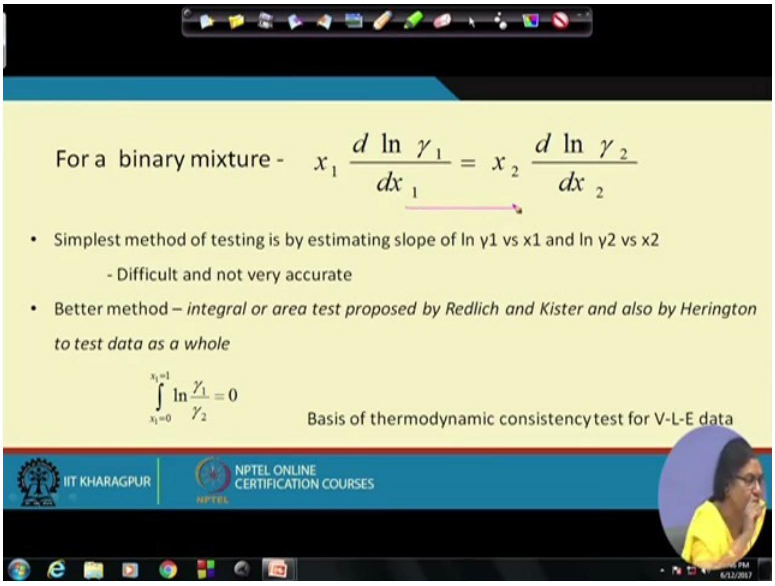

For a binary mixture - $x_1 \frac{d \ln \gamma_1}{dx_1} = x_2 \frac{d \ln \gamma_2}{dx_2}$

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$$\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2} = 0$$

Basis of thermodynamic consistency test for V-L-E data

For the same compositions you can find out the slopes of ln gamma 2 versus X2 as well and then once can find out the slopes then you can use this particular equation to find whether the data is thermodynamically consistent or not. This particular technique it looks to be pretty accurate and it also appears to be quite simple at least theoretically it appears to be quite simple.

But there are 2 things which you need to remember firstly finding out slopes in this particular way it’s not very easy and second thing is that the experimental data they will inevitably be having some amount of scatter, so therefore it’s not so easy and feasible to find out slopes at different particular points very accurately and then to check up whether the equation whether this particular equation is going to be valid or not.

So therefore usually this equation it is used for some very serious errors in the data for example you can just plot ln gamma1 as the function of x1 ln gamma2 as a function of x2 and find out whether both the slopes of positive or not or else if you know that ln gamma1 versus x1 is horizontal at any composition you can just check that whether at that composition ln gamma 2 versus X1 is horizontal as well.

Just these gross checks can be done from this particular slope technique but in order to check the thermodynamic consistency of data we find that a better method is the integral area test or the integral test or the area test which was proposed by Redlich and Kister and also by Herington independently the test the data as a whole.

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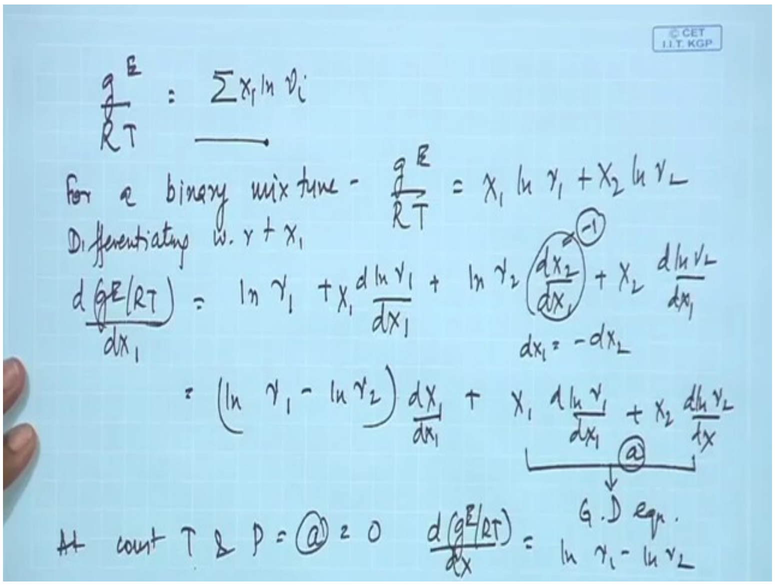

$$\frac{g^E}{RT} = \sum x_i \ln \gamma_i$$

For a binary mixture - $\frac{g^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$

Differentiating w. r. t. x_1

$$\frac{d(g^E/RT)}{dx_1} = \ln \gamma_1 + x_1 \frac{d \ln \gamma_1}{dx_1} + \ln \gamma_2 \overset{-1}{\left(\frac{dx_2}{dx_1}\right)} + x_2 \frac{d \ln \gamma_2}{dx_1}$$

$dx_1 = -dx_2$

$$= (\ln \gamma_1 - \ln \gamma_2) \frac{dx_1}{dx_1} + \underbrace{x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx}}_{ⓐ \downarrow \text{ G.D eqn.}}$$

At const T & P = ⓐ = 0 $\quad \frac{d(g^E/RT)}{dx} = \ln \gamma_1 - \ln \gamma_2$

Let us see what this integral of the area test is and how it works? So therefore for this, what we do? We write down the basic equation which relates molar Gibbs free energy to activity coefficient. What was that particular equation if you remember? We have been using this equation since the time we have introduced nonideal solutions.

So for a binary mixture what happens to this equation? This also we have done a large number of times. If you observe you will find that for that we do not use a large number of equations but we used the same equations in different forms to serve our purposes like for example this equation we have been using very frequently and in different forms may be for binary mixtures, for multi-component mixtures we use this.

So for a binary mixture what do we get? This equation reduces to X1ln gamma1 plus X2 ln gamma 2 if you differentiate this particular equation, say with respect to X1 what do we get? We get d gE by RT dX1 this should be equal to ln gamma1 plus d ln gamma1 dX1 plus ln gamma 2 dX2 dX1 plus X2 d ln gamma2 dX1, what is this term?

We know dX1 equals to minus dX2 therefore this term is nothing but minus 1. So from here what do we get? We get ln gamma1 minus ln gamma 2 into dX1 plus X1 d ln gamma1 dX1 plus X2 d ln gamma2 dX2, what is this? This is one of the terms of the Gibbs Duhem equation. What is this? At constant temperature and pressure we get that this particular term equals to, this suppose I write this term as a then this a term becomes equal to 0 provided we are working at constant temperature under isothermal isobaric conditions.

So therefore we know that for this particular condition we find d gE by RT dX1 this is dX1 by dX1 this is equals to ln gamma1 minus ln gamma2.

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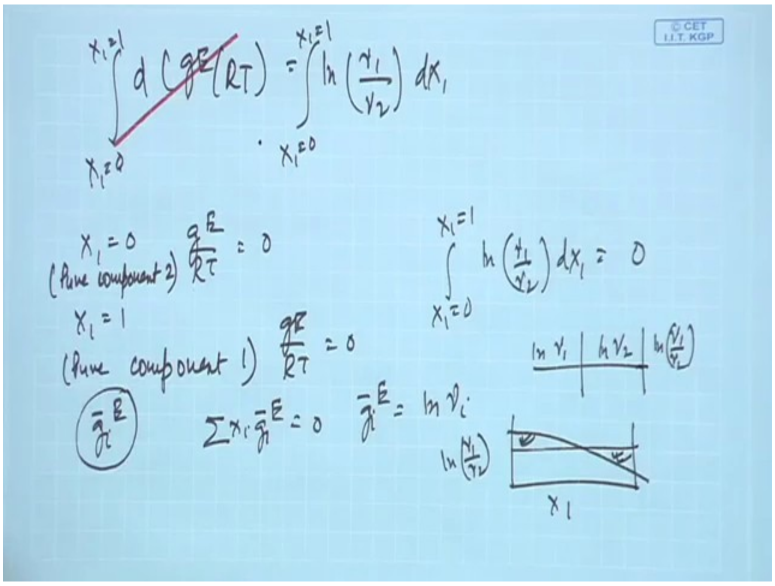

$$\int_{x_1=0}^{x_1=1} \cancel{d\left(g^E/RT\right)} = \int_{x_1=0}^{x_1=1} \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1$$

$x_1 = 0$ (Pure component 2) $\frac{g^E}{RT} = 0$

$x_1 = 1$ (Pure component 1) $\frac{g^E}{RT} = 0$

$$\int_{x_1=0}^{x_1=1} \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0$$

$\ln\gamma_1$	$\ln\gamma_2$	$\ln\left(\frac{\gamma_1}{\gamma_2}\right)$

$\bar{g}_i^E$ $\quad \sum x_i \bar{g}_i^E = 0 \quad \bar{g}_i^E = \ln\gamma_i$

Or else what can we write this down as? We can write this down as d gE by RT equals to ln gamma1 by gamma 2 of dX1. Now we can integrate this particular equation, isn't it? We can integrate this particular equation say from X1 equals to 0 to X1 equals to 1. Here also we integrate it from X1 equals to 0 to X1 equals to 1. What do we know? We know that at X1 equals to 0 we have pure component X2.

So naturally when we have pure component X2 gE by RT becomes equal to 0. At X1 equals to 1 what do we have? We have pure component 1, isn't it? When we have pure here we have pure component2. When we have pure component 1, naturally under that case also gE by RT becomes equals to 0. So therefore what is the fate of the left hand side of the equation?

The left inside of the equation when we are integrating it from 0 to 1 this term it disappears off, right? So therefore what do we find? We find that X1 equals to 0 to X1 equals to 1 ln gamma1 by gamma 2 dX1 this should be equal to 0 for gamma1 and gamma 2 data to be thermodynamically consistent, isn't it?

And so therefore this is what it is the area test and remember one thing we can and perform the area test for any particular partial molar property but the most relevant partial molar property is the partial molar Gibbs free energy which is given as gi bar E this is the most relevant property and therefore the Gibbs Duhem equation expressed in this particular term is most important since we know that gi bar E is related to the activity coefficients and it's very important to find out whether the activity coefficients are thermodynamically consistent or not.

And this can be found out if we have gamma1 and gamma 2 values that we can find out ln gamma1 for each case we can find out the ln gamma2 for this case and then we can find out ln gamma1 by gamma2 for each case and then we can plot ln gamma1 by gamma 2 as a function of X1 and we can more or less we get something of this sort the find out the area above this area below this and then we find whether the areas are equal or not.

Accordingly we can conclude whether the data that we have it is thermodynamically consistent or not.

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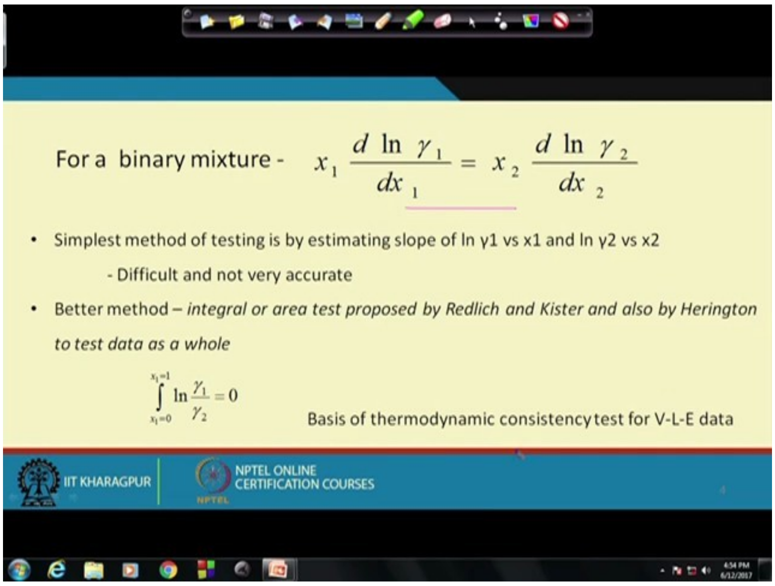

For a binary mixture - $x_1 \frac{d \ln \gamma_1}{dx_1} = x_2 \frac{d \ln \gamma_2}{dx_2}$

- Simplest method of testing is by estimating slope of ln γ1 vs x1 and ln γ2 vs x2
  - Difficult and not very accurate
- Better method – *integral or area test proposed by Redlich and Kister and also by Herington to test data as a whole*

$$\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2} = 0$$

Basis of thermodynamic consistency test for V-L-E data

So therefore with this it is quite evident that the basis for testing thermodynamic consistency of VL E data is given by this particular equation.

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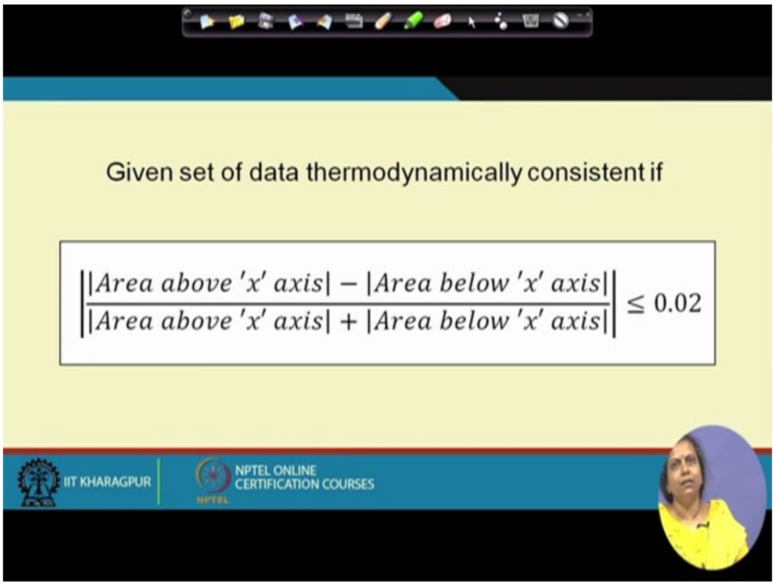

Given set of data thermodynamically consistent if

$$\left|\frac{|Area\ above\ 'x'\ axis| - |Area\ below\ 'x'\ axis|}{|Area\ above\ 'x'\ axis| + |Area\ below\ 'x'\ axis|}\right| \le 0.02$$

And we also know that we are dealing with experimental data. Now since we are dealing with experimental data, so therefore it can always happen that due to experimental uncertainties we will definitely not get the area to be exactly equal to 0. So therefore keeping this in mind normally it is thought that the area above the x axis minus the area below the x axis divided by the total area has to be less than equal to 2percent.

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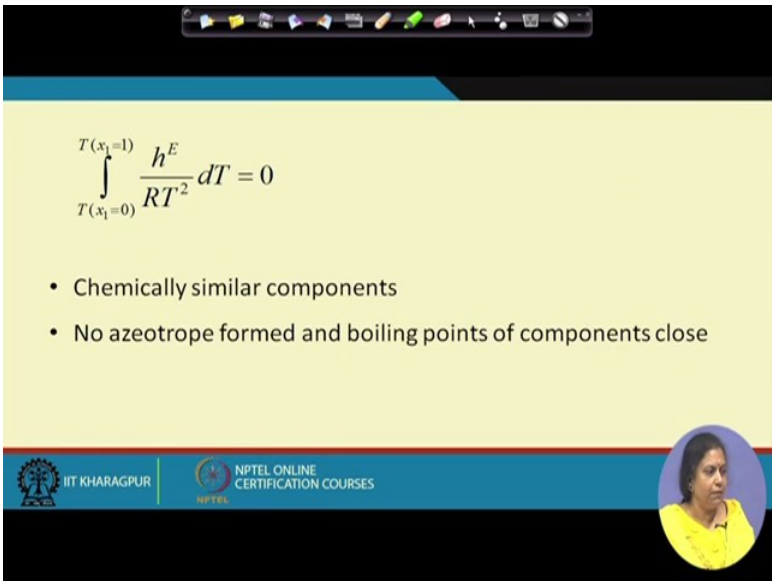

$$\int_{T(x_1=0)}^{T(x_1=1)} \frac{h^E}{RT^2} dT = 0$$

- Chemically similar components
- No azeotrope formed and boiling points of components close

So this is generally the situation which is which we get. Now there are certain things till this much is sufficient for this class but while you're using some particular technique to find out thermodynamic consistency it is also important for you to remember the drawbacks of this particular technique.

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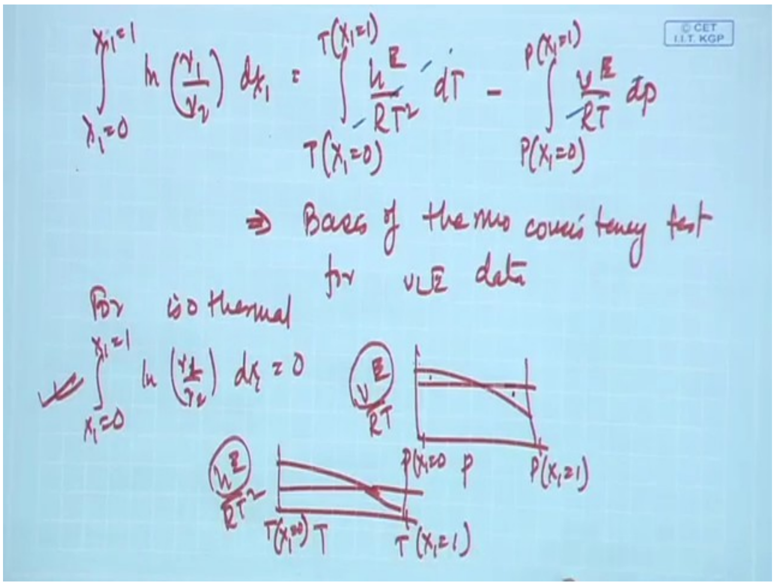

$$\int_{x_1=0}^{x_1=1} \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = \int_{T(x_1=0)}^{T(x_1=1)} \frac{h^E}{RT^2} dT - \int_{P(x_1=0)}^{P(x_1=1)} \frac{v^E}{RT} dp$$

⇒ Basis of thermo consistency test for VLE data

For isothermal

$$\int_{x_1=0}^{x_1=1} \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0$$

Now in this particular technique what do we do? We have firstly we have assumed constant temperature and pressure, suppose we do not assume constant temperature and pressure then the total equation then we actually start with the Gibbs Duhem equation Then once we start with the generalized Gibbs Duhem equation, I will just write down the generalized equation the actual equation it should be X1 equals to 0 to X1 equals to 1 ln gamma1 by gamma 2 dX1 this should be equal to actually hE by RT square dT ranging from the temperature at X1 equals to 0 to the temperature at X1 equals to 1 minus vE by RT dP while pressure the corresponding pressure at X1 equals to 1 to X1 equals to 0, this is the generalized equation at constant temperature and pressures since both these terms they disappear off. Therefore we can take this to be equal to 0 but actually this forms the basis of thermodynamic consistency test for VLE data.

We know that for isothermal cases, what happens? The first term it disappears off, right? For isothermal cases we know that this term should disappear off and we know that for low pressure cases this term should disappear off. So therefore for isothermal low-pressure VLE data the thermodynamic consistency test is given by gamma1 by gamma 2 dX1 equals to 0. So if experimental data satisfy this then we are happy but remember one thing if we are dealing with rigorous testing, then in that case what we should be doing?

We should be plotting vE by RT as a function of P and then we should we should be finding out the area here we should also be plotting hE by RT square as a function of T where T it ranges from T at X1 equals to 0 to T at X1 equals to 1. Here it should range for P at X1 equals to 0 to P at X1 equals to 1 and then we should be finding out these particular data and then we should be comparing and then only we can say that really the data is thermodynamically consistent.

But generally what happens? We do not have sufficient data on the excess property of volume and the excess property of the hE as a result of which what we do? We generally assume these to be 0 and for the purpose of your undergraduate class this equation is sufficient for you.

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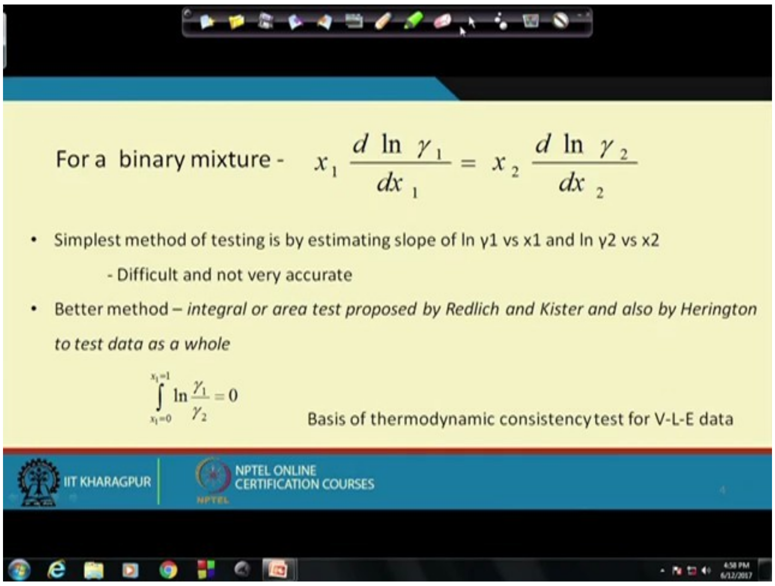

For a binary mixture - $x_1 \frac{d \ln \gamma_1}{dx_1} = x_2 \frac{d \ln \gamma_2}{dx_2}$

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Basis of thermodynamic consistency test for V-L-E data

Now when do we have this equal to 0 can you tell me? We have this equal to 0, naturally when your excess volume is 0 or in other words the molecules of the 2 components they are similar in size. Only under that condition we can have v equals to 0.

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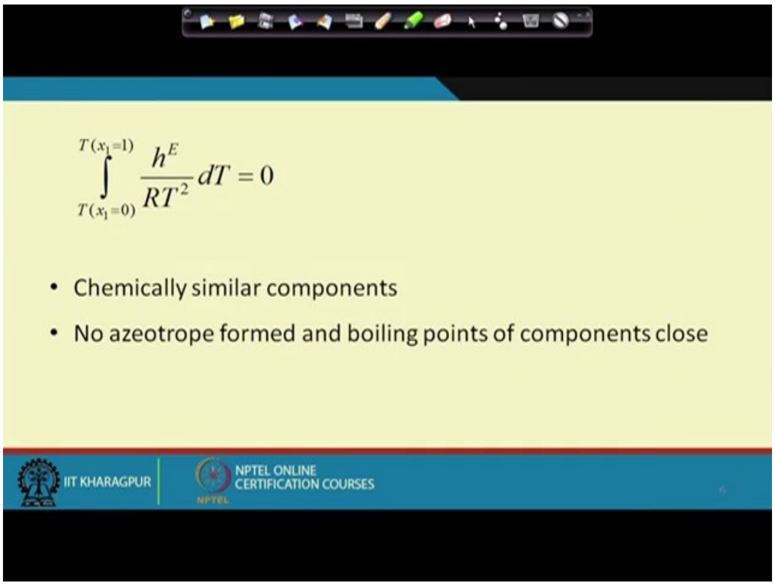

$$\int_{T(x_1=0)}^{T(x_1=1)} \frac{h^E}{RT^2} dT = 0$$

- Chemically similar components
- No azeotrope formed and boiling points of components close

Can you tell me under what condition we have hE equals to 0? Naturally when we mix the 2 components and there is no enthalpy generation, when will it happen? Firstly when the 2 components are chemically similar and there are no Azeotropes formation and the boiling points of the components are also close to one another. Under that condition we're going to have this case.

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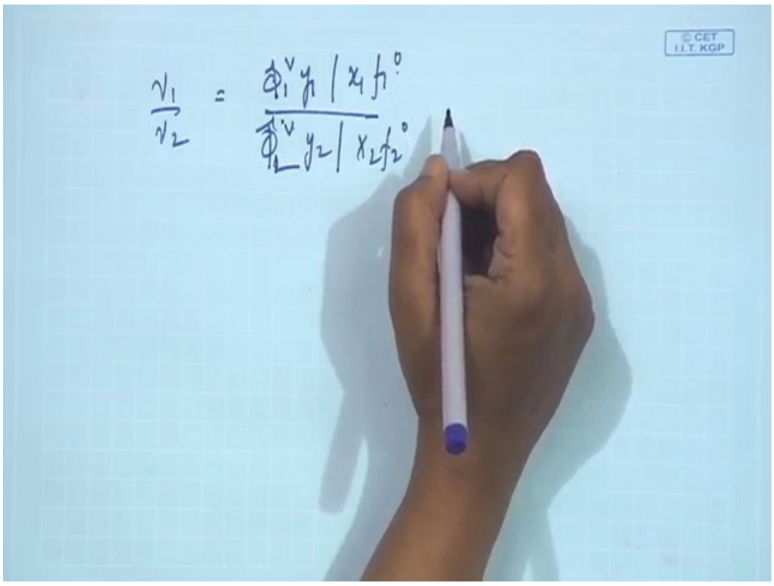

$$\frac{\gamma_1}{\gamma_2} = \frac{\phi_1^v y_1 / x_1 f_1^0}{\phi_2^v y_2 / x_2 f_2^0}$$

But under all other conditions it is very difficult to assume this particularly it is important for you to remember that when we are dealing with gamma 1 by gamma 2 actually what are we doing just try to understand, this is given by x1f1 0 by phi2 v y2 by x2f2 0. Therefore what are we doing?

We are actually cancelling out the pressure term and that is the term which is very important because that can be measured very accurately and it's very easy to know the total pressure conditions. So therefore when we are doing this area test we are actually cancelling out the pressure term and that is the main limitation of this test and therefore if we have to do it accurately the way I was telling we have 3 data we have for isothermal data we can vary Pxy we should be varying we should be generating data on Pxy and on Py as well as on Px.

And then we from the 2 data which should be finding out the third compare that with the experimental value only under that condition we will be convinced that the data are thermodynamically consistent but for your purpose it is sufficient for you to remember that if you plot ln gamma1 by gamma 2 versus X1 and find the area to be 0 your purpose is served again say that the data is thermodynamically consistent.

If you recall that we have done a large number of problems in the last class regarding finding or generating Pxy data Txy data etc. Now it's very important for you to test whether those data were thermodynamically consistent or not. So we have we are taking up one particular problem from the set of problems that we had.

If you remember that in this particular problem you had already calculate it gamma1 gamma 2 and so therefore from this particular data it's very easy for you to calculate ln gamma1 by gamma 2, right?

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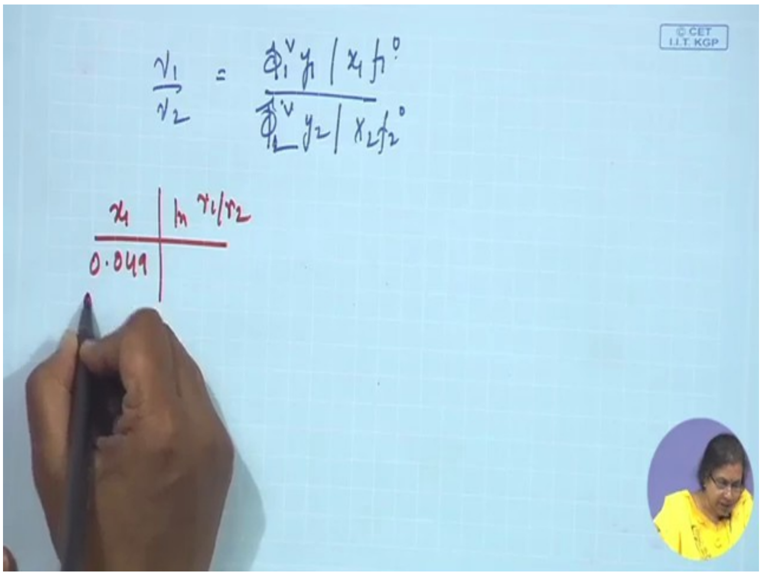

$$\frac{\gamma_1}{\gamma_2} = \frac{\Phi_1^v y_1 / x_1 f_1^\circ}{\Phi_2^v y_2 / x_2 f_2^\circ}$$

x_1	$\ln \gamma_1/\gamma_2$
0.049	

So I will be writing down the corresponding ln gamma1 by gamma 2 in this particular case. If you remember the data were 0.297, 0.447, 0.5650, 0.650 and am going to write a good number of data's, so that you can check up whether you have done it correctly or not. X1 0.926, 0.945 the corresponding ln gamma1 by gamma2, gamma 1 and gamma 2 we had already calculated in the last class.

So therefore you can calculate this 0.2234 this was minus 0.415, minus 0.2245 then it was minus 0.3496, minus 0.4668, minus 0.6396 this was minus 0.6908 and minus 0.7056.

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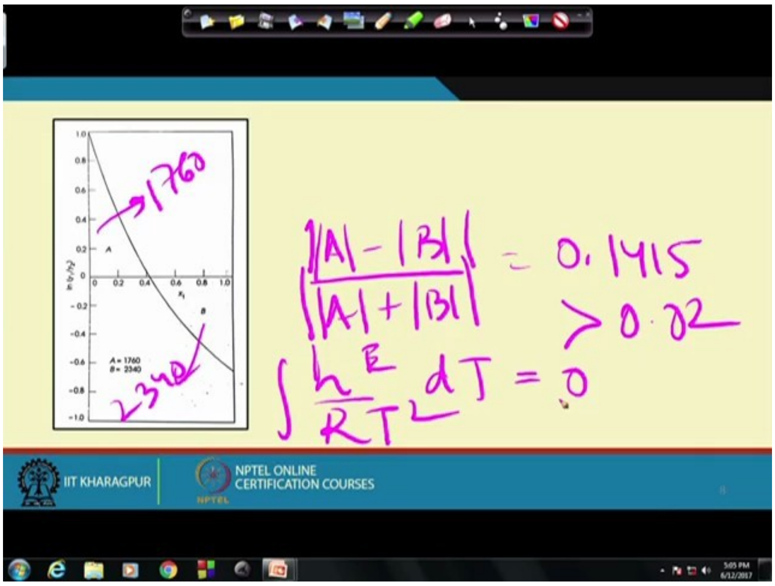

$$\frac{||A|-|B||}{||A|+|B||} = 0.1415$$

$$> 0.02$$

$$\int \frac{h^E}{RT^2} dT = 0$$

So with these, what you can do? You can plot ln gamma1 by gamma 2 versus X1, right? And we find that in this case the area about the x-axis this particular portion this area it corresponds to 1760 whereas this part of the area it corresponds to 2340 at as it is written. So therefore if you subject it to the criteria that we had that area above X minus the area X divided by the total area then we find that in this particular case your A minus B by A plus B this gives you as 0.1415 which is definitely greater than 0.021.

So with this, what do you conclude you find out that in this case the data is not thermodynamically consistent we had wasted a good amount of time in finding out the data and in using the 2 suffix Margules and the van laar equation but in reality the data was not thermodynamically consistent at least from the fragmentary thing that you have done you it appears that it is not thermodynamically consistent.

But it is very difficult for us to conclude it in such a simple fashion because for this particular case you are required to find out in this case the hE by RT square, right? hE dT by RT square just as I had said and this has to be found out and this has to be its required to verify whether this is equal to 0 or not.

If you find that this is equal to 0 then only we can conclusively say that area test or the it shows that the data is not thermodynamically consistent otherwise it is very difficult for us to predict this and so therefore this possibly highlights the limitations of the area test to test the thermodynamic consistency of data and it is important for us to remember that the assumptions of excess volume energy of mixing as well as the excess enthalpy change of mixing is also always not very accurate, right?

But anyhow it’s very important for us to remember that even though ln gamma1 by gamma2 as the area test has got some limitations there are some very important applications or rather are there some very important implications of this particular term ln gamma1 by gamma 2.

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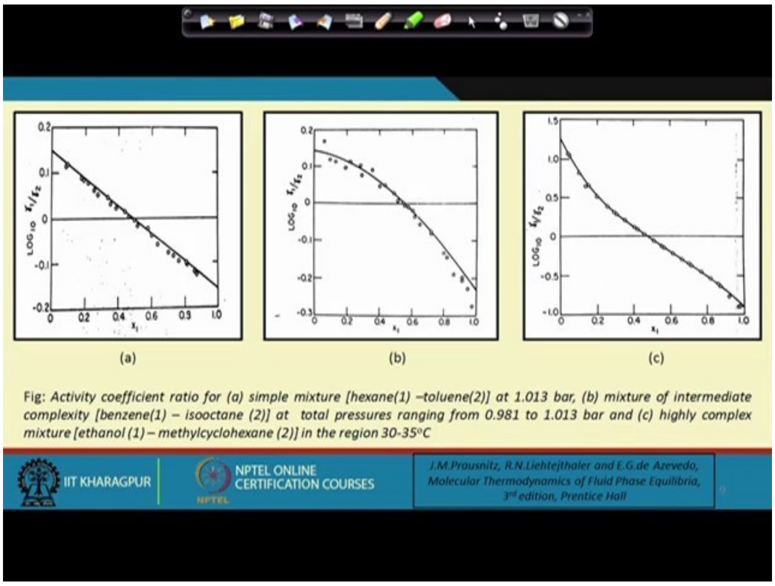

(a) (b) (c)

Fig: *Activity coefficient ratio for (a) simple mixture [hexane(1) –toluene(2)] at 1.013 bar, (b) mixture of intermediate complexity [benzene(1) – isooctane (2)] at total pressures ranging from 0.981 to 1.013 bar and (c) highly complex mixture [ethanol (1) – methylcyclohexane (2)] in the region 30-35°C*

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Let us see what are the important or rather what are the interesting things which we which this particular term ln gamma1 by gamma 2 has? We find that this is a very effective parameter in defining the different types of mixtures into simple, more complex and most complex solutions, how? Suppose we plot ln gamma1 by gamma 2 as a function of X1, we find that suppose for simple mixtures like say hexane and toluene in this very lowercase we find that it is more or less a straight line and we immediately say that this particular solution at the pressure condition it is straight line.

On the other hand suppose we plot the law gamma1 by gamma 2 versus X1, for benzene isooctane we find that in this case it is curved. It is interesting to note that for both the cases we have been dealing with one particular aliphatic hydrocarbon one particular aromatic hydrocarbon despite that we found that in this case we had obtained a linear curve this case we have obtained a curved solution.

And this can be attributed to the difference in the sizes of the molecules constituting benzene and isooctane and hexane and toluene while the molecules are similar in size while for hexane and toluene there is much difference between the sizes for benzene and isooctane. So although we are dealing with similar type of similar type of components we find that the graphs of ln gamma 1 by gamma 2 versus X1 are not the same while hexane toluene confirms to simple solutions.

We find that benzene isooctane it does not confirm to simple solutions under this particular pressure condition and interestingly when we go for some other mixtures we find that it’s not only that it is curved there is also a point of inflection, for example in the case of ethanol Methylcyclohexane, now what does this complex it imply?

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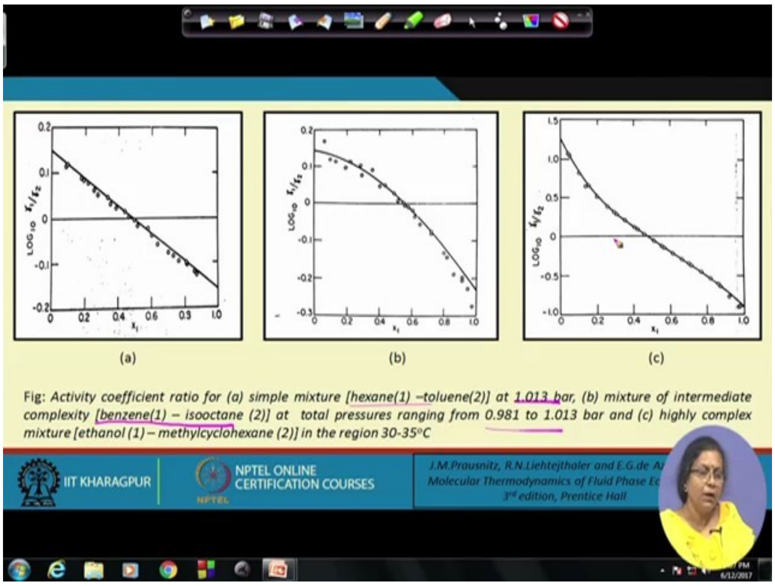

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From the graphs when we know that this equation is simple, this is more complex, this is most complex how do we use this information? We use this information if you recollect that we had we had referred to the Redlich Kister equation which was an extension of the 2 suffix Margules equation it simply added more number of terms and by that we could have a much more realistic expression or equation to express gE by RT as a function of compositions.

Now from this equation we will find that we can we can find out ln gamma1 by gamma 2 and from there we can find out ln gamma1 by gamma 2. So if you compare this expression as well as the graphs here, what do we see?

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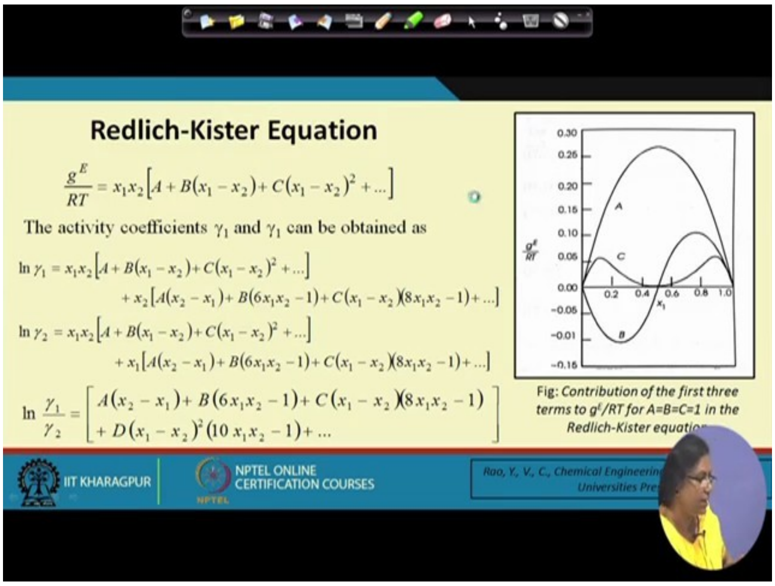

Redlich-Kister Equation

$$\frac{g^E}{RT} = x_1x_2\left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots\right]$$

The activity coefficients γ_1 and γ_1 can be obtained as

$$\ln \gamma_1 = x_1x_2\left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots\right]$$
$$+ x_2\left[A(x_2 - x_1) + B(6x_1x_2 - 1) + C(x_1 - x_2)(8x_1x_2 - 1) + \ldots\right]$$

$$\ln \gamma_2 = x_1x_2\left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots\right]$$
$$+ x_1\left[A(x_2 - x_1) + B(6x_1x_2 - 1) + C(x_1 - x_2)(8x_1x_2 - 1) + \ldots\right]$$

$$\ln \frac{\gamma_1}{\gamma_2} = \begin{bmatrix} A(x_2 - x_1) + B(6x_1x_2 - 1) + C(x_1 - x_2)(8x_1x_2 - 1) \\ + D(x_1 - x_2)^2(10\,x_1x_2 - 1) + \ldots \end{bmatrix}$$

Fig: *Contribution of the first three terms to g^E/RT for A=B=C=1 in the Redlich-Kister equatio*

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If we compare this particular equation as well as the curves here we find that for the first curve it is sufficient to use just one particular term in ln gamma 1 by gamma 2. So therefore the first curve represents those solutions which can be accurately predicted by 2 suffix Margules equation. For the second case we find that for this particular case we have to include the first and second case for the first and the second terms.

And we find that for the last case which is the most complex or highly complex mixtures an accurate prediction can be obtained if we if we include the first 4 terms in this case. So therefore we find that ln gamma1 and gamma 2 is water good amount of or rather it has got a very good amount of importance in classifying mixtures as simple, more complex and most complex but at the same time it is important to remember that this classification is more or less arbitrary because there can be solutions which may due to fortunate cancellations of errors again which may be predicted by one or 2 parameters but actually in reality they are much more complex.

A typical example of this is the mixtures of 2 alcohols say methanol and ethanol we find that very frequently they can be well predicted by just using one or 2 parameters or the Redlich Kister equation but in reality they are much more complex due to hydrogen bonding.

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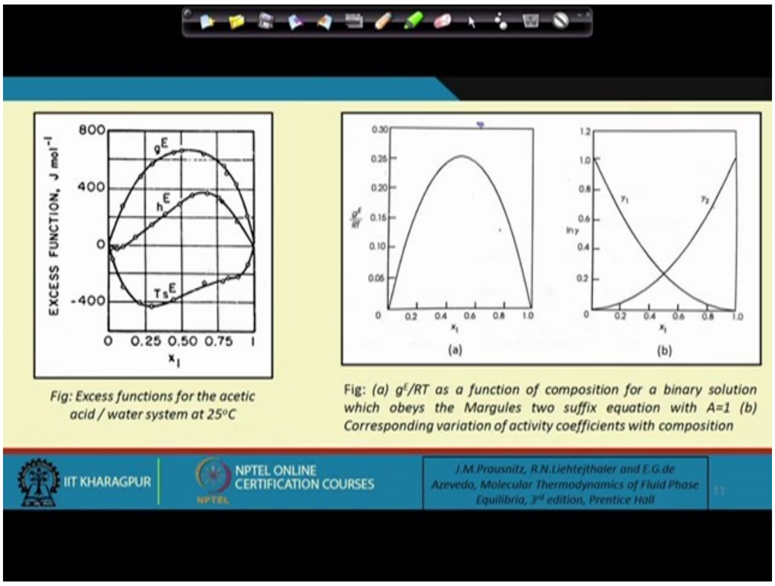

Fig: Excess functions for the acetic acid / water system at 25°C

(a)

(b)

Fig: *(a) g^E/RT as a function of composition for a binary solution which obeys the Margules two suffix equation with A=1 (b) Corresponding variation of activity coefficients with composition*

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Another very interesting example we can find in the case of acetic acid and water. If you observe the excess Gibbs free energy curve as a function of composition you find that it resembles the 2 parameter Margules equation therefore you will be tempted to say that acetic acid water it forms a simple solution but when you are when you go compare the hE curve and the TsE curve immediately it shows in reality it is a complex mixture and the similarity of the excess Gibbs free energy curve with the 2 suffix Margules equation is obtained just due to a fortunate cancellation of errors.

So therefore with this I conclude this class and before ending I would like to mention that most of the solutions that we deal in chemical engineering solutions of non-electrolytes they can very well be predicted by including 2 to 3 parameters in the Redlich Kister equation. So therefore most of them they are solutions of intermediate complexity. So with that I would like to emphasize that we had discussed the area test for discussing thermodynamic consistency of experimental data and I had also discussed the limitations of the area test it is very important to remember that it is applicable only when your gamma1 gamma2 they do not vary remarkably with temperature and pressure and for most of the cases for a much more rigorous testing we need to calculate or rather we need to consider the excess volume change and the excess enthalpy change of mixing of the solutions.

And apart from that I also discussed the other importance of ln gamma1 by gamma 2 this particular parameter it is not only used for finding out the thermodynamic consistency of data is also used for classifying data or rather classifying solutions are simple, complex and more complex and they give us an idea regarding the number of parameters of the Redlich Kister equation which should be included in order to predict the VLE data of that particular mixture.

And again I would like to emphasize that this is quite arbitrary although it is it is generally used it is quite arbitrary for several particular solutions like say acetic acid water methanol ethanol etc and it can give some misleading results due to fortunate cancellations of errors. Now with this we say we are going to finish our topics of solutions both ideal and nonideal. So far we have been dealing with completely miscible systems we are going to discuss some more interesting aspects of VLE in the next class, thank you very much.