Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
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Lecture No 43
Non Ideal solutions (Contd.)

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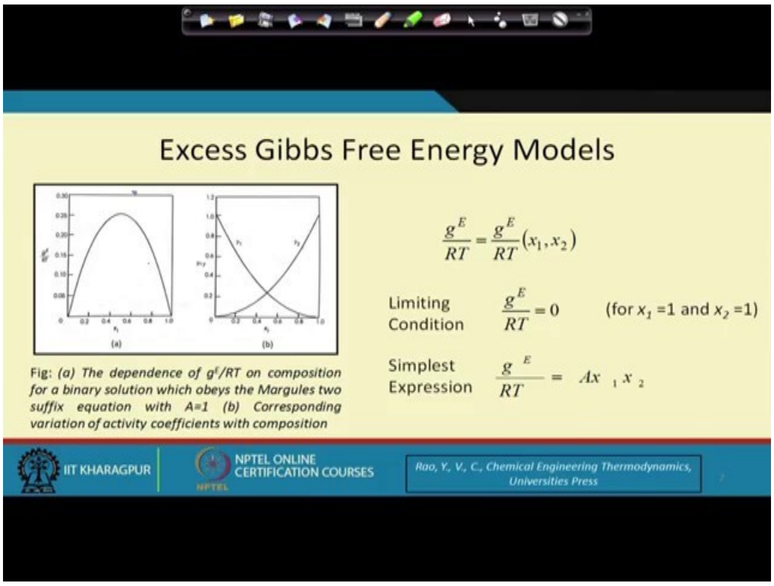

Excess Gibbs Free Energy Models

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

$$\frac{g^E}{RT} = \frac{g^E}{RT}(x_1, x_2)$$

Limiting Condition $\frac{g^E}{RT} = 0$ (for x_1 =1 and x_2 =1)

Simplest Expression $\frac{g^E}{RT} = Ax_1x_2$

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Well to continue with our discussions on non-ideal solutions where I had ended the last class was I had told you that usually since it is very difficult to have a proper equation of state to predict the behaviour of real solutions, so therefore usually the gammas they are predicted from empirical or semi-empirical equations and the simplest empirical equation which is used is known as the Margules 2 suffix equation which gives you g by RT in this particular form.

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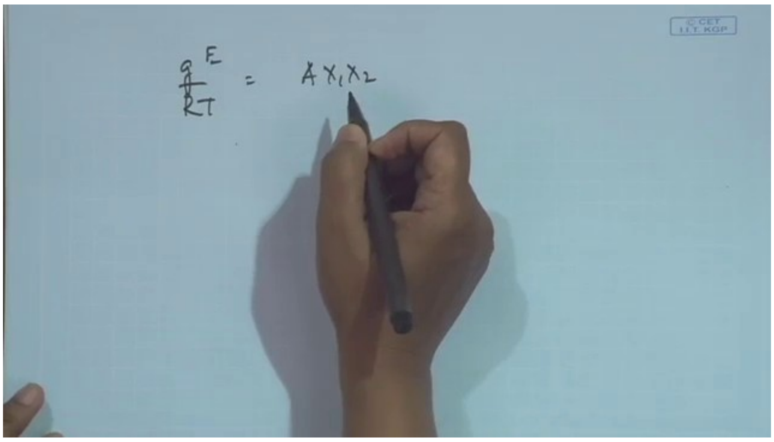

$$\frac{g^E}{RT} = AX_1X_2$$

And from there we find out that more or less my ln gamma 1 and ln gamma 2 they can be represented in this particular form gE by RT this is equals to A X1 X2 and from there if we are finding out ln gamma 1 which is nothing but gi bar E by RT which is del del N1 N1 plus N2 gE by RT and if you differentiate it you find that ln gamma 1 equals to AX 2 square similar way you can either differentiate it in terms of N2 and find out ln gamma2 or you can use the Gibbs Duhem equation once you know gamma 1 to find out gamma 2 the choice is yours you can do either of them and we find that ln gamma2 equal to AX1 square this in particular case.

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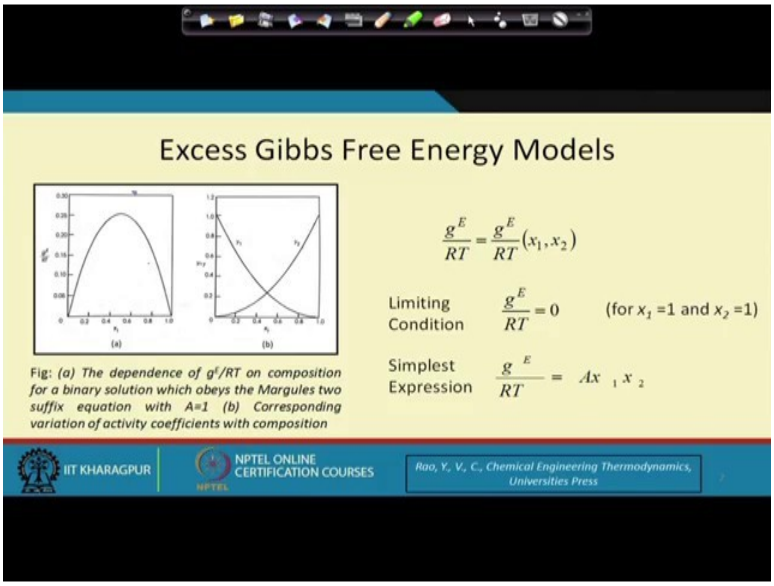

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And we have also depicted the curves of excess Gibbs free energy of a solution as a function of composition and also the ln gamma1 and ln gamma2 as a function of composition and I had already also mentioned in the last class that although the 2 suffix Margules equation it is good for very simple spherical molecules similar type of attractions etc but for most of the cases then we need to modify this particular equation in order to incorporate the non-ideal behaviour of solutions.

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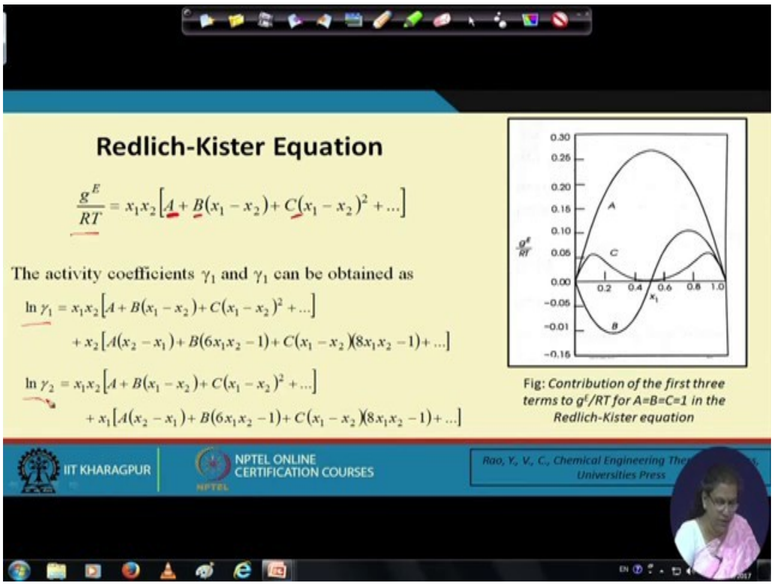

Redlich-Kister Equation

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

The activity coefficients γ_1 and γ_1 can be obtained as

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

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

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

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Now what are the different ways by which it is done? One particular way was proposed by Redlich and Kister, what they have done is they have they have simply extended the number of terms here if you observe. For this case if you observe that the first equation or the first-term it represents the 2 suffix Margules equation and the other terms they are they are just the series expansion in X1 minus X2 these are introduced if you observe closely you will find that it has got some similarity with the virial equation of state modifying the ideal gas equation and depending upon the complexity of the situation you can keep on increasing the number of terms in this particular case.

And in that way the number of parameters to be included in the model depends upon the complexity of the solution and if you observe these terms you find that the A it is symmetric in x just the A of the 2 suffix Margules equation, B if you observe B it is actually it is asymmetric in x and it tries to skew the parabola either to the left or to the right and if you observe the third term you will find it is again symmetric in x, what it tries to do? It tries to either sharpen the parabola or it tries to flatten the parabola.

So in this particular way the contribution of the first 3 terms ABC of the Redlich (ki) Kister equation is shown in this particular in this particular graph where we see that the first-term it is the contribution to excess Gibbs free energy due to 2 body interactions of molecules of unlike components and the second and third terms, these are the second and the third terms they refer to the 3 body interactions of unlike molecules, right?

And so therefore if we have expressed g by RT by this equation the activity coefficients can automatically be expressed in the in the way we have shown and from there we can express ln gamma 1 by gamma 2.

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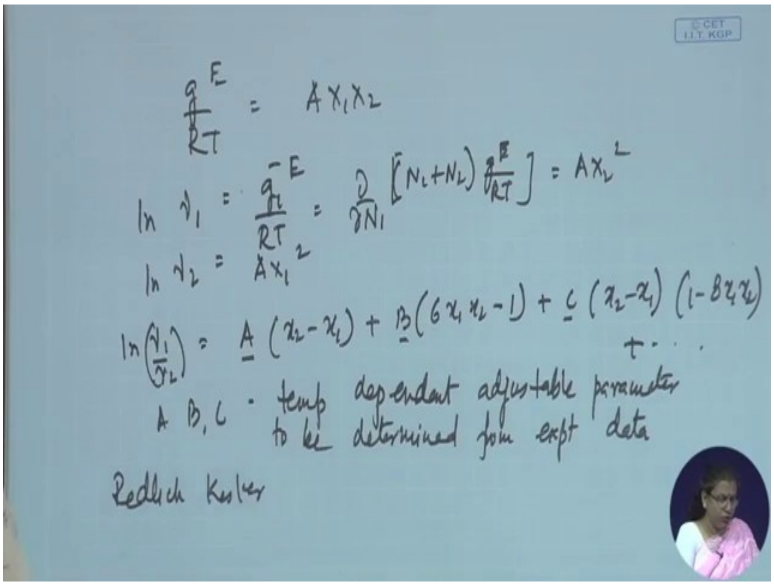

$$\frac{g^E}{RT} = A x_1 x_2$$

$$\ln \gamma_1 = \frac{\bar{g}_1^E}{RT} = \frac{\partial}{\partial N_1}\left[(N_1+N_2)\frac{g^E}{RT}\right] = A x_2^2$$

$$\ln \gamma_2 = A x_1^2$$

$$\ln\left(\frac{\gamma_1}{\gamma_2}\right) = \underline{A}(x_2 - x_1) + \underline{B}(6x_1x_2 - 1) + \underline{C}(x_2 - x_1)(1 - 8x_1x_2) + \cdots$$

A, B, C - temp dependent adjustable parameter to be determined from expt data

Redlich Kister

We can express this by dividing one with the other we can this ln gamma 1 and ln gamma 2 it can be expressed in this particular equation and we can we can we can subtract the 2 and we can find out how we can express ln gamma 1 and ln gamma 1 by ln gamma by 2 this can be expressed as A into x2 minus x1 plus B 6x1 x2 minus 1plus C x2 minus x1 into 1 minus 8 x1x2 plus so on and so forth and all these terms ABC they are temperature dependent adjustable parameters because we need to know that the composition dependence of gamma that should be a function of temperature and pressure. Since it is a liquid phase property it should not be a very significant function of pressure but it should be a significant function of temperature.

So therefore this ABC they are temperature dependent adjustable parameters to be determined from experimental data, right? So therefore we have some experimental data on the real liquid solution from which we can determine them and the number of terms which we need to include as I have already said that depends upon the complexity of the solution. So in that particular way we find that the Redlich Kister equation it is quite flexible.

And it can adequately represent the excess Gibbs free energy of the solution. We just need to include more and more terms if we have to make it more complex or rather when we have to deal with more complex situation.

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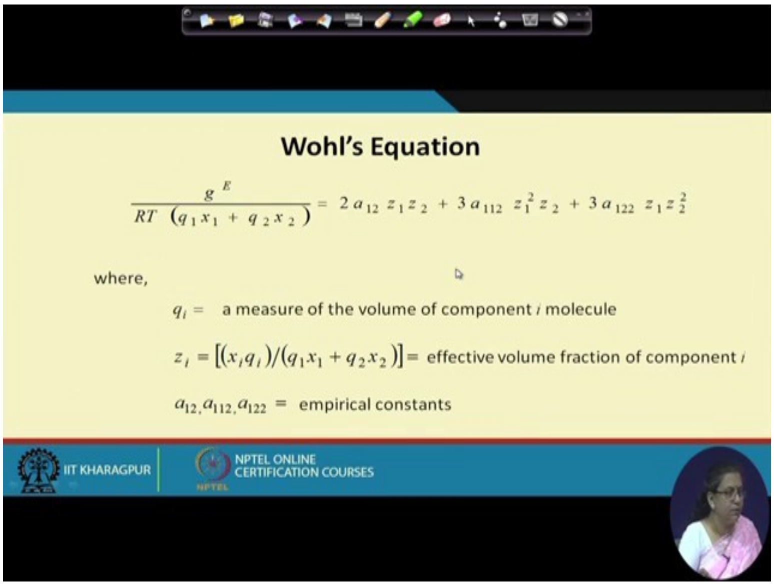

Wohl's Equation

$$\frac{g^E}{RT\ (q_1x_1 + q_2x_2)} = 2a_{12}\ z_1z_2 + 3a_{112}\ z_1^2z_2 + 3a_{122}\ z_1z_2^2$$

where,

q_i = a measure of the volume of component *i* molecule

$z_i = [(x_iq_i)/(q_1x_1 + q_2x_2)]$ = effective volume fraction of component *i*

a_{12}, a_{112}, a_{122} = empirical constants

Now there is one other way also apart from the Redlich Kister equation it is the Wohl's equation. These Wohl's equation also it takes into account the 2 body and the 3 body interactions and it gives us some type of rather it helps us to predict the excess Gibbs free energy of a binary liquid solution by taking into account the three body and the two body interactions between the like and unlike molecules as we have shown here this first-term takes into interaction the 2 body interactions and the subsequent terms they take into account the 3 body interactions in this particular case.

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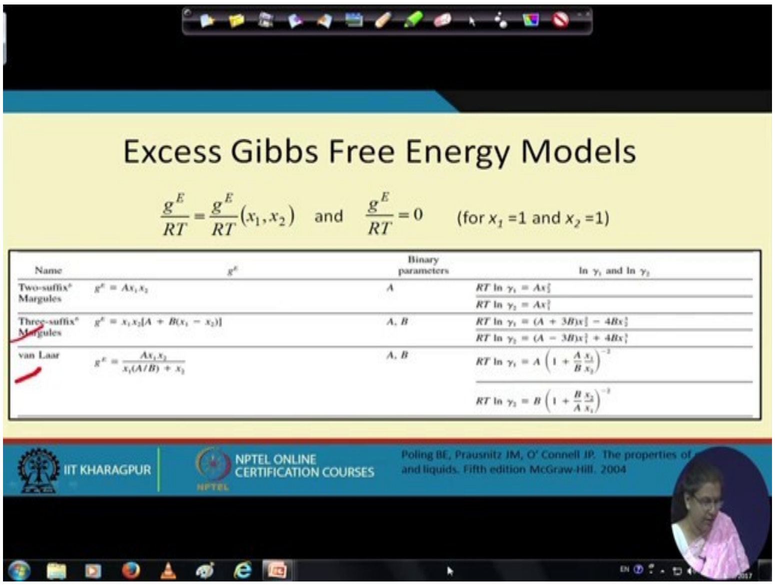

Excess Gibbs Free Energy Models

$$\frac{g^E}{RT} = \frac{g^E}{RT}(x_1, x_2) \quad \text{and} \quad \frac{g^E}{RT} = 0 \qquad (\text{for } x_1 = 1 \text{ and } x_2 = 1)$$

Name	g^E	Binary parameters	$\ln \gamma_1$ and $\ln \gamma_2$
Two-suffix* Margules	$g^E = Ax_1x_2$	A	$RT \ln \gamma_1 = Ax_2^2$
			$RT \ln \gamma_2 = Ax_1^2$
Three-suffix* Margules	$g^E = x_1x_2[A + B(x_1 - x_2)]$	A, B	$RT \ln \gamma_1 = (A + 3B)x_2^2 - 4Bx_2^3$
			$RT \ln \gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3$
van Laar	$g^E = \frac{Ax_1x_2}{x_1(A/B) + x_2}$	A, B	$RT \ln \gamma_1 = A\left(1 + \frac{A}{B}\frac{x_1}{x_2}\right)^{-2}$
			$RT \ln \gamma_2 = B\left(1 + \frac{B}{A}\frac{x_2}{x_1}\right)^{-2}$

Poling BE, Prausnitz JM, O' Connell JP. The properties of and liquids. Fifth edition McGraw-Hill. 2004

Now based on all this we find that several algebraic equations have been proposed to determine activity coefficients. Since from thermodynamics it's rather there is a sufficient guidance to formulate between gamma and x. So therefore large number of algebraic equations are proposed which satisfy Gibbs Duhem equation they are thermodynamically consistent and they are used or rather they are just a correction to the 2 suffix Margules equation in order to predict gamma under more non-ideal conditions.

For very less non-ideality 2 suffix Margules equation is fine when we have to go for much further or rather when there is greater amount of non-ideality we need little more equation the most generalized formulation to predict non-ideal behaviour is has been proposed by Redlich Kister and Wohl has also proposed and both of them they have considered 2 body 3 body interactions that they have tried to propose. That we find that apart from that if we use some algebraic equations which are basically empirical equations they do not have much thermodynamic foundation but they are (thermody) there found to be thermodynamically consistent number 1.

And they subscribe to the limiting condition which I have mentioned then in that case those equations they are usually used for finding out the activity coefficients the most common equations which will be important for this particular thermodynamic course are the 3 suffix Margules equation and the Van laar equation these 2 equations they are the most common equations where the Gibbs free energy excess Gibbs free energy model is given by these equations and the ln gamma1, gamma2 expressions are given from here.

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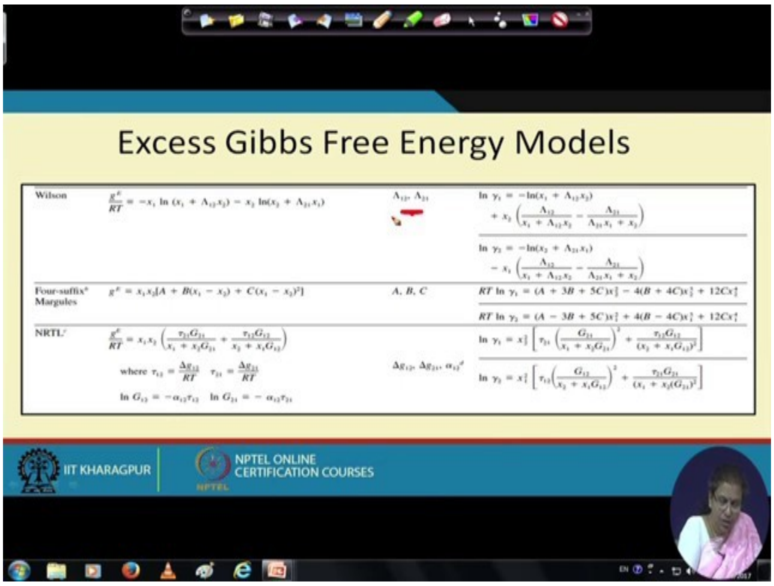

Excess Gibbs Free Energy Models

Wilson	$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1)$	$\Lambda_{12}, \Lambda_{21}$	$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$ $\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$
Four-suffix* Margules	$g^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$	A, B, C	$RT \ln \gamma_1 = (A + 3B + 5C)x_2^2 - 4(B + 4C)x_2^3 + 12Cx_2^4$ $RT \ln \gamma_2 = (A - 3B + 5C)x_1^2 + 4(B - 4C)x_1^3 + 12Cx_1^4$
NRTL'	$\frac{g^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right)$ where $\tau_{12} = \frac{\Delta g_{12}}{RT}$ $\tau_{21} = \frac{\Delta g_{21}}{RT}$ $\ln G_{12} = -\alpha_{12}\tau_{12}$ $\ln G_{21} = -\alpha_{12}\tau_{21}$	$\Delta g_{12}, \Delta g_{21}, \alpha_{12}{}^{d}$	$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right]$ $\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2(G_{21})^2}\right]$

Now apart from this we find that these equations they are fine but they do not incorporate the temperature dependence of gamma. So therefore in order to incorporate the temperature dependence of gamma we have some more equations which have been suggested for example Wilson equation is 1 where the adjustable parameters in this particular case the gamma sorry the lambda 1 to and the lambda 2 1 they are functions of temperature and we find that this particular equation the Wilson plot this is very good for mixtures where the components differ from each other in molecular size and interactions between the like and unlike molecules are different.

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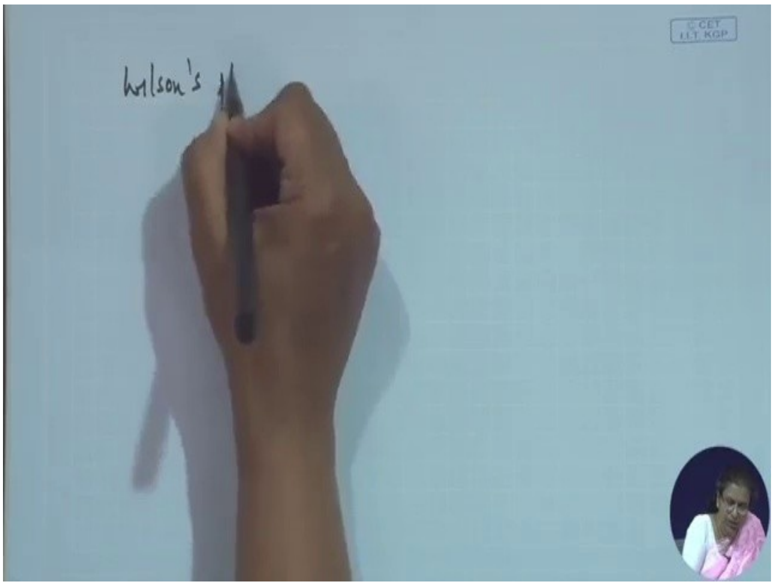

So we find that the Wilson's plot its I will just like to tell you that for this class the 2 suffix Margules equation that 3 suffix Margules equation as well as the Van laar equation are important, for the other equations you need not remember the equations but under what conditions those equations have been proposed that you need to remember because in future if you are supposed deal with non-ideal solutions it is important that you (ac) actually know that for which conditions which equation is applicable but along with that also remember that till today also several equations are being proposed to predict the excess Gibbs free energy and the activity coefficients of (Ide) sorry non-ideal solutions because it is very evident that suppose we are working with a mixture of hydrocarbons we find one equation is applicable definitely the same equation will not be applicable when you are working with aqueous solution of organic acids.

So naturally with each different compound or each different component of the solution newer and more and more different equations are necessary because all of them finally boil down to the intermolecular interactions and the molecular shapes and sizes which are different for the different cases, right?

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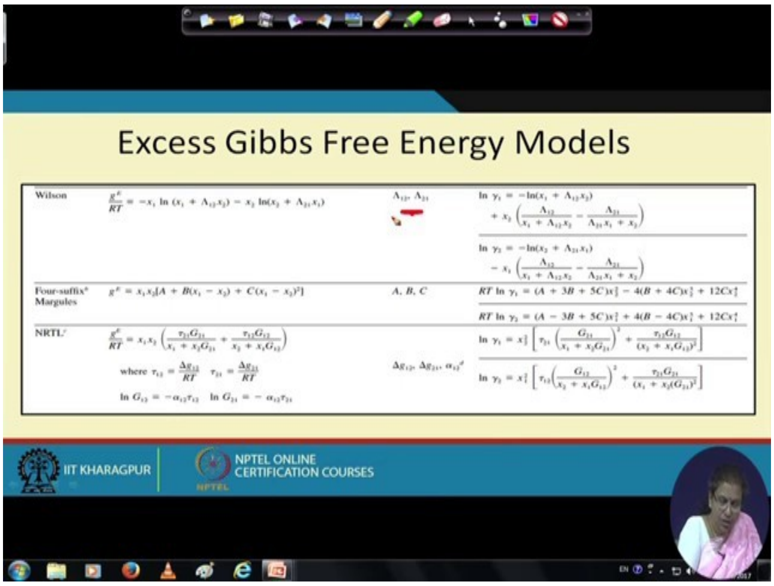

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Four-suffix* Margules	$g^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$	A, B, C	$RT\ln\gamma_1 = (A + 3B + 5C)x_2^2 - 4(B + 4C)x_2^3 + 12Cx_2^4$ $RT\ln\gamma_2 = (A - 3B + 5C)x_1^2 + 4(B - 4C)x_1^3 + 12Cx_1^4$
NRTL†	$\frac{g^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right)$ where $\tau_{12} = \frac{\Delta g_{12}}{RT}$ $\tau_{21} = \frac{\Delta g_{21}}{RT}$ $\ln G_{12} = -\alpha_{12}\tau_{12}$ $\ln G_{21} = -\alpha_{12}\tau_{21}$	$\Delta g_{12}, \Delta g_{21}, \alpha_{12}{}^{\ddagger}$	$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right]$ $\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right]$

But again I repeat I will just be discussing under what condition the more complex equations are applicable but for this particular class we will be dealing with just 3 equations the 2 suffix Margules equation, the 3 suffix Margules equation as well as the Van laar equation, fine. So for most of the cases which are required for you these 3 equations are fine but it is important to remember that they do not or rather they do not express the constants as temperature dependence. For them the same particular constants of the equations are applicable no matter or at what particular temperature and pressure conditions that we are working, fine. So therefore in order to incorporate the temperature (dep) dependence of activity coefficients we need to go for more and more complex equation.

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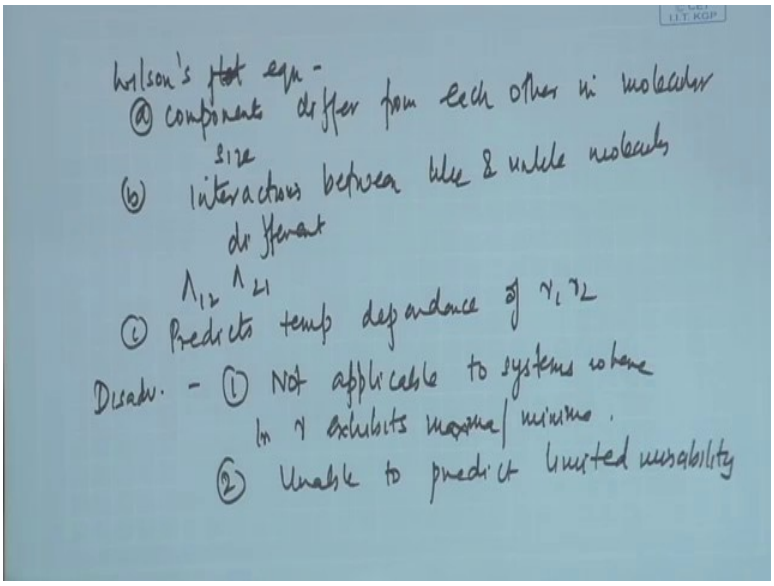

Wilson's ~~plot~~ eqn -

ⓐ components differ from each other in molecular size

ⓑ interactions between like & unlike molecules different

Λ_{12} Λ_{21}

ⓒ Predicts temp dependence of $\gamma_1 \gamma_2$

Disadv. - ① Not applicable to systems where $\ln \gamma$ exhibits maxima/minima.

② Unable to predict limited miscibility

One such equation is the Wilson equation which we where we find that the Wilson equation it is applicable for 2 conditions one is, the components differ from each other in molecular size and secondly interactions between like and unlike molecules are different, right? For these 2 conditions more or less they are applicable because the lambda 12 and lambda 21 they are related to the pure component molar volumes and characteristic energy differences etc.

So therefore the advantage is the third advantage is, it predicts temperature dependence of activity coefficients gamma1 and gamma2 and therefore these are developed through concentrations of molecular behaviour the only disadvantage which it has is, it is not applicable to systems where ln gamma exhibits maxima or minima this particular aspect we will be dealing separately after we have we have finished dealing with the normal situations. And it is also unable to predict limited miscibility these are the drawbacks of the Wilson plot.

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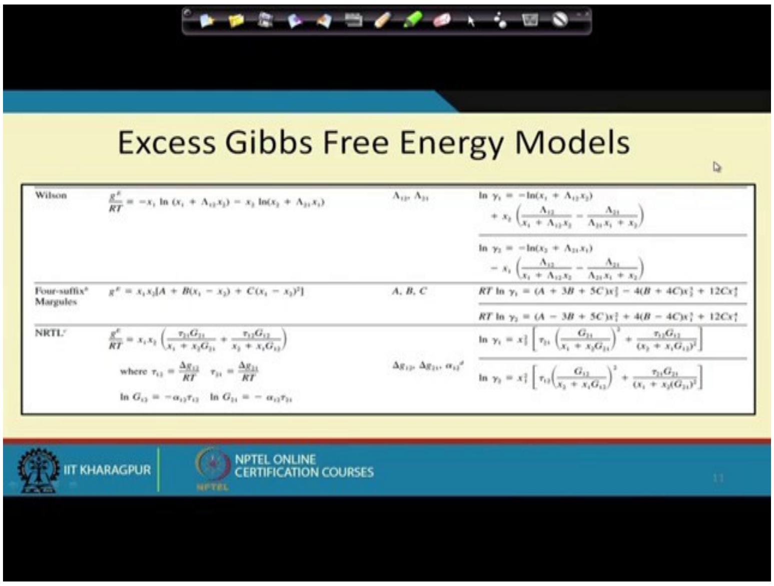

Excess Gibbs Free Energy Models

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			$\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$
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NRTL[c]	$\frac{g^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right)$ where $\tau_{12} = \frac{\Delta g_{12}}{RT}$ $\tau_{21} = \frac{\Delta g_{21}}{RT}$ $\ln G_{12} = -\alpha_{12}\tau_{12}$ $\ln G_{21} = -\alpha_{12}\tau_{21}$	$\Delta g_{12}, \Delta g_{21}, \alpha_{12}$[d]	$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right]$ $\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right]$

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Well, other than that what we have? We have a 4 suffix Margules equation which tries to modify further the 3 suffix equation by incorporating it's it’s basically a Redlich Kister equation which has 3 instead of 2 terms it is evident that we have a non-random two liquid equation the NRTL equation this is applicable to partial miscible and completely miscible systems and in this particular case also we find that here we do not have much advantage over the Van laar or the Margules equation for moderately non-ideal solution but it is it represents the excess Gibbs free energy of strongly non-ideal and partially miscible solutions quite satisfactory.

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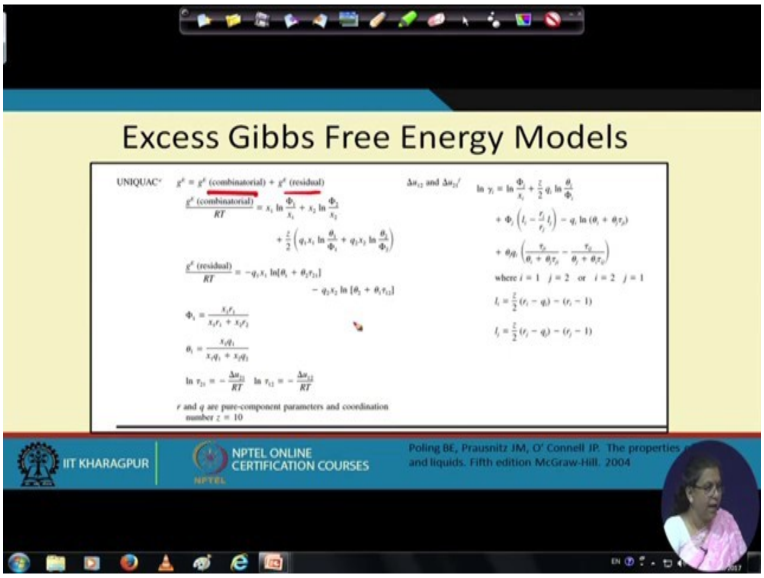

Excess Gibbs Free Energy Models

UNIQUAC[e]	$g^E = g^E\,(\text{combinatorial}) + g^E\,(\text{residual})$ $\frac{g^E\,(\text{combinatorial})}{RT} = x_1\ln\frac{\Phi_1}{x_1} + x_2\ln\frac{\Phi_2}{x_2} + \frac{z}{2}\left(q_1x_1\ln\frac{\theta_1}{\Phi_1} + q_2x_2\ln\frac{\theta_2}{\Phi_2}\right)$ $\frac{g^E\,(\text{residual})}{RT} = -q_1x_1\ln[\theta_1 + \theta_2\tau_{21}] - q_2x_2\ln[\theta_2 + \theta_1\tau_{12}]$ $\Phi_1 = \frac{x_1r_1}{x_1r_1 + x_2r_2}$ $\theta_1 = \frac{x_1q_1}{x_1q_1 + x_2q_2}$ $\ln\tau_{21} = -\frac{\Delta u_{21}}{RT}$ $\ln\tau_{12} = -\frac{\Delta u_{12}}{RT}$ r and q are pure-component parameters and coordination number $z = 10$	Δu_{12} and Δu_{21}[f]	$\ln\gamma_i = \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\Phi_i} + \Phi_j\left(l_i - \frac{r_i}{r_j}l_j\right) - q_i\ln(\theta_i + \theta_j\tau_{ji}) + \theta_jq_i\left(\frac{\tau_{ji}}{\theta_i + \theta_j\tau_{ji}} - \frac{\tau_{ij}}{\theta_j + \theta_i\tau_{ij}}\right)$ where $i = 1$ $j = 2$ or $i = 2$ $j = 1$ $l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$ $l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1)$

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Poling BE, Prausnitz JM, O' Connell JP. The properties of gases and liquids. Fifth edition McGraw-Hill. 2004

After that we find that apart from these there are some other equations also which are which have been proposed. For example we have the UNIQUAC which is nothing but the universal Quaci chemical equation and these equations we find that in fact they have been developed by Prusnitz and he was one of the contributors to this equation we find that they it primarily comprises of a combinatorial part and the residual part.

And we find that combinatorial part this accounts for the compositions the size and shape of the constituent molecules. So the combinatorial part it basically it comprises of pure component properties only and the residual part if you see that accounts for intermolecular forces and it contains 2 adjustable parameters.

And after that we find apart from the UNIQUAC equation it we there are also some other types of equations which have been proposed they are known as the group contribution method, what are these group contribution method? See if you assume that each particular component of the solution are made of individual molecules then there are huge number of molecules and then for each particular solution you have to find out the how the non-ideality is coming into picture? Other than that if you assume that each particular solution is made up of a number of radicals or number of groups of molecules and it is the contribution of the groups which lead to a non-ideality of the solutions then in that case we can have large number of solutions which have the same type of groups.

For example Methyl group can be present in a large number of liquids or maybe the acetate group can be present in a (la) acetic acid in a large number of acetate and we assume that the behaviour of these particular groups they are independent of the behaviour of the other molecules. Therefore in this particular case the advantage is if you know the group contribution for the group existing in one solution you can safely assume that this particular group contributes in a similar way when it is in a environment of some other type of molecules.

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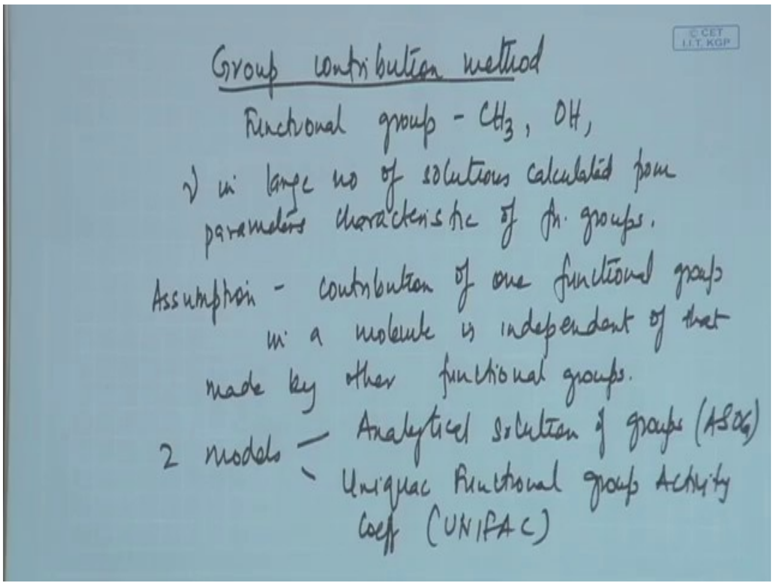

Group contribution method

Functional group - CH_3, OH,

γ in large no of solutions calculated from parameters characteristic of fn. groups.

Assumption - contribution of one functional group in a molecule is independent of that made by other functional groups.

2 models
- Analytical solution of groups (ASOG)
- Uniquac Functional group Activity coeff (UNIFAC)

So therefore the other way of finding out or evaluating the activity coefficient this is known as a group contribution method, right? Where we assume that each component it is made up of not only individual molecules but different functional groups like say the functional groups can be (func) each particular component of the solution are made up of functional groups like CH3,OH etc and then a solution of the component is treated actually as a solution of the groups.

And then the gamma i's they are determined by properties of the functional groups rather than the properties of the molecules. So this is the basic idea that we have several thousands of chemical compounds but there are very few functional groups constituting these compounds. So that the gamma in large number of solutions the basic idea is that the gamma in large number of solutions can be calculated from parameters characteristic of functional groups and the only assumption here is that it just assumes the only assumption here of the group contribution method is that contribution of 1 functional group in a molecule is independent of that made by other functional groups, right?

So therefore on this basis it expects that this makes our life little more simpler because if we know the contribution of 1 functional group in any molecule we can safely assume that the same contribution is made by the same functional group in a different molecule and there are 2 models which use this particular method one is the analytical solution of groups which is known as the ASOG and it is the Uniquac functional group activity coefficient or it is known as the UNIFAC.

So therefore I would not like to go into much details of these particular things. It is as important for you to remember that the large number of different algebraic equations, large number of models which have been proposed, the primary reason for the huge number of models are that it is very difficult to use one particular model for the wide range of solutions that we have considering the different shapes, sizes, orientation and the intermolecular interactions between the different molecules constituting the solutions and it is important to remember that may be one particular molecule it behaves in a in one particular way in an environment and behaves in a completely different way in a different environment.

So therefore depending upon the conditions different equations have been solved on the sorry have been proposed and when we find that the molecules are not (co) completely randomly mixed possibly due to hydrogen bonding etc then we go for the NRTL. When we find that gamma should be is not does not remain constant with temperature so in that case we have to we should go for Wilson plot etc but again I repeat that despite the large number of models which are present for your particular case you will be primarily concerned with 2 suffix Margules equation 3 suffix Margules equation and Van laar equation. So before I end this class I would like to discuss the estimation of gamma from using the 2 suffix is very simple, using the 3 suffix and the Van laar equation for that what we do we try to arrange the equation in such a form that it gives is very simple or rather the method of solution becomes very simple.

So I would like to discuss this particular method of solution before I end this class. So that if you are given some amount of data thermodynamic data say at a constant temperature usually the data given as X or Y or X and Y at either isothermal conditions or under isobaric conditions, right? And you are required to test the thermodynamic consistency of data or suppose you have data at one particular temperature or one particular pressure you are required to generate that the whole set of data or the whole set of gamma data for the solution with the compositions varying from almost 0 to or X1 varying from 0 to 1.These are generally the type of problems that you are supposed to deal with, right?

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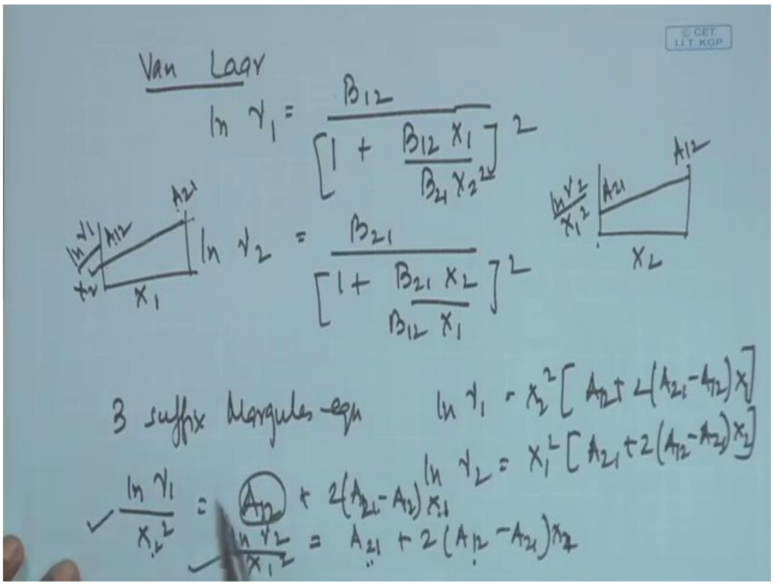

Van Laar

$$\ln\gamma_1 = \frac{B_{12}}{\left[1 + \frac{B_{12} x_1}{B_{21} x_2}\right]^2}$$

$$\ln\gamma_2 = \frac{B_{21}}{\left[1 + \frac{B_{21} x_2}{B_{12} x_1}\right]^2}$$

3 suffix Margules eqn $\ln\gamma_1 = x_2^2\left[A_{12} + 2(A_{21} - A_{12})x_1\right]$

$\ln\gamma_2 = x_1^2\left[A_{21} + 2(A_{12} - A_{21})x_2\right]$

✓ $\frac{\ln\gamma_1}{x_2^2} = \boxed{A_{12}} + 2(A_{21} - A_{12})x_1$

✓ $\frac{\ln\gamma_2}{x_1^2} = A_{21} + 2(A_{12} - A_{21})x_2$

So for that case what do we do? We are going to take up the Van laar equation and Margules equation and discuss the method of solution. So let us take up either of the equations and see in what way we can express it. For example suppose we are taking up the Van laar equation, what is the equation? If we write down the equation we will find ln gamma 1 is say suppose I have you can since they are constant you can express them in any particular way it can be AB it can be A12, A21 etc.

For my case what I do here is, I have expressed Van laar constants as B12, B21 and the 3 suffix Margules constants as A12, A21 just to differentiate that they belong to constants for different equations. So the Van laar equation is ln gamma 1 is 1 1 plus B12 X1 by B21 X2 whole square, right? ln gamma 2 this is nothing but B21 by 1 plus B21 X2 by B12 X1 whole square. Let me see the 3 suffix Margules equation ln gamma 1 X2 square into say A12 plus 2 into A21 minusA12 into X1.

ln gamma2 equals to X1 square A21 plus 2 into A12 minus A21 into X2, right? Now if you if you observe these 2 equations, what do you find? You find that for this equation if we write it down as ln gamma 1 by X2 square this becomes A12 plus 2 intoA21 minus A12 into X1. Similar way ln gamma 2 by X1 square this becomes equal to A21 plus 2 into A12 minus A21 into X2, sorry into X1. So therefore does it not imply that if I have plot of ln gamma 1 by X2 square versus X1 then in that case it should be a straight line and that particular straight line it should (ha) it should have a intercept of A12 at X1 equals to 0, fine.

So therefore from this particular straight-line I should be in a position to find out this. Similar way I can also plot ln gamma2 by X1 square as a function of X2 and I can also generate a straight line from this straight line from the intercepts at X2 equals to 0 and X2 equals to 1 I can find out A21 and A12, right? So in this particular case what do I find? That at X1 equals to 0 my intercept is A12 and at X1 equals to 1 my intercept is A21.

In this case we find that at X2 equals to 0 my intercept is A21, here my intercept is A12, agreed? So therefore we find out that from here is we have data at one particular temperature or pressure X X data and (gam) gamma versus X data then you can very well plot a straight line from the intercepts we can find out A12 A21. In a similar way we can also arrange this particular equation just observe this equation and try to find out in what way we can arrange this equation such that from such similar simple geometrical constructions we can find out the constants B21 and B12 we are going to discuss it in the next class before the next class try to think out, how we are going to express the Van laar equation? Such that we can have such similar (geom) such a simple geometric form from where just by construction or just by plotting one parameter against another we should be in a position of finding out the constants of the equation.

This is the first thing I want you to think, the second thing is suppose we are using gamma 1 and gamma 2 and plotting in this particular fashion then what do we find? This equation is going to give me one set of A12 A21 this graph is going to give me another set of A21 A12, how to combine the 2 and how to find out the average value that should be used? So with these 2 assignments for these 2 thoughts or rather these 2 topics for you to think I end this class we are going to discuss about this the next class, thank you very much.