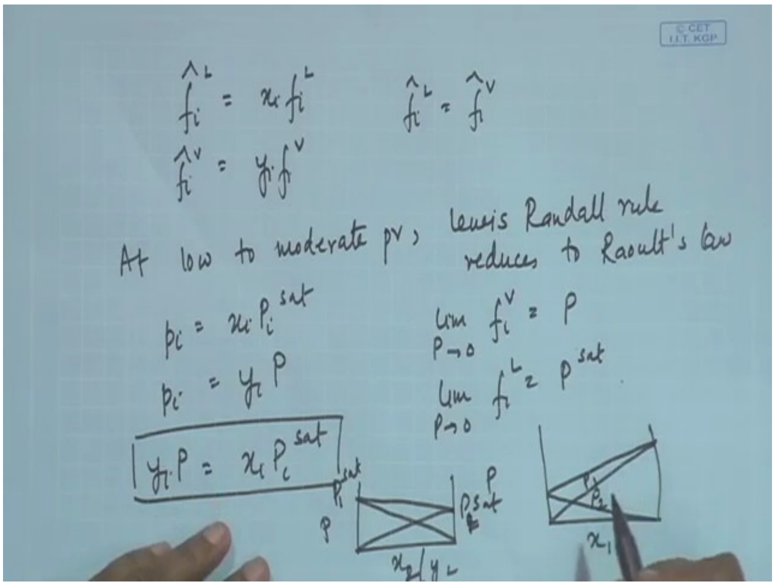
Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture No 42
Non Ideal Solutions(Contd.)

Well to continue with our discussions on nonideal solutions before I proceed to for today's class I would just have a short recap of what we have already done. Just taking into consideration the fact that nonideal solutions are quite complex means when students first deal with them they often get confused with the different sorts of terminologies one extra set of properties that have come up. So I will have a quick recap of what I have already taught in the last class and then we proceed further.

What did we do? Initially when I started solutions I dealt with ideal solutions. I would like to mention I have dealt with 2 types of solutions one was ideal solution one was ideal dilute solutions. Most of my discussions are limited and will be limited to ideal solution and maybe at sometimes I will touch upon ideal dilute solutions.

(Refer Slide Time: 2:00)



$\hat{f}_i^L = x_i f_i^L$ $\qquad \hat{f}_i^L = \hat{f}_i^V$

$\hat{f}_i^V = y_i f^V$

At low to moderate P's, Lewis Randall rule reduces to Raoult's law

$p_i = x_i P_i^{sat}$ $\qquad \lim_{P \to 0} f_i^V = P$

$p_i = y_i P$ $\qquad \lim_{P \to 0} f_i^L = P^{sat}$

$\boxed{y_i P = x_i P_i^{sat}}$

And there what did we find again as a recapitulation we found out that more or less Lewis Randall rule is applicable for ideal solutions where we get that the partial fugacity of component i in a solution it can be a vapor mixture, it can be a liquid solution doesn't matter the law is the same this is equal to xifi if this refers to a liquid solution it can be denoted by a superscript L and if it is a vapor solution than it can be represented by a superscript V, right?

And we found out that under equilibrium conditions fiL equals to fiV, so long our situation was fine and then we found out that the situation becomes simpler at low to moderate pressure, why? Because under those conditions we found out that the Lewis Randall rule it reduces to Raoult's law as a result what do we find? We find that the f's can be replaced by P's the pressure terms. As a result of which we find that for low to moderate pressure it becomes Pi equals to xi Pi saturated and in this case Pi equals to yiP, okay.

Recalling that for the vapor phase at low to moderate pressure or in other words limiting P tends to 0 f of pure component of the vapor phase this is the total pressure if you recollect and for the liquid phase what did we derive? We derived for the liquid phase this was equal to P saturated and then there was some other correction terms taking into account the corrections would account for the non-ideality of the vapor phase as well as the compression of the liquid from the saturated pressure to the pressure of interest which was incorporated in an exponential term of an termed as the poynting correction factor, right?

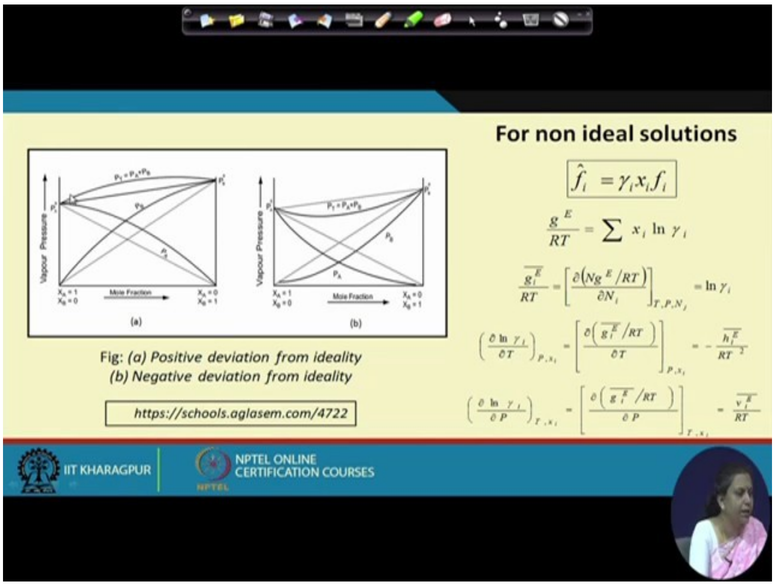
So therefore for low to moderate pressure this was the situation and this is the rule according to which we can write down we can combine the 2 and we can write it down in this particular form for an ideal solution. Then we went for a nonideal solution and according to this we also found out that if we plot pressure versus x1 then in that case what do we expect? We get the total pressure curve as something of this the P2 versus x1 curve like this and the P1 versus x1 curve in this particular fashion. We found that all the 3 they are linear because partial pressure of component 1 partial pressure of component 2 as well as the total pressure all of them vary linearly with the mole fraction of either of the component.

It's important to remember that when we are plotting these phase diagrams we are always plotting the mole fraction of the more volatile component in the x-axis it can be the mole fraction of the more volatile component in the liquid phase or in the vapor phase but just by convention we try to maintain the fact or rather maintain the practice that we will be plotting the more volatile component composition in the x-axis.

You will often come across problems maybe I can also give you can get such problems in the textbooks which you are referring and you'll find that in those problems often we find that the less volatile component composition is used to plot in the X axis. It's interesting to remember that the curve remains same only when we are plotting the less volatile component quite natural its vapor pressure will be less. As a result of which under that condition what are we going to get?

For that condition if it is x2 or y2 then in that case we will be getting something like this. The curve will just change because it is important to remember that the less volatile component will have a lower vapor pressure as compared to the more volatile component this is the only thing which is going to happen, right?

(Refer Slide Time: 6:27)



For non ideal solutions

$$\boxed{\hat{f}_i = \gamma_i x_i f_i}$$

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

$$\frac{\overline{g_i^E}}{RT} = \left[\frac{\partial \left(Ng^E/RT\right)}{\partial N_i}\right]_{T,P,N_j} = \ln \gamma_i$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,x_i} = \left[\frac{\partial \left(\overline{g_i^E}/RT\right)}{\partial T}\right]_{P,x_i} = -\frac{\overline{h_i^E}}{RT^2}$$

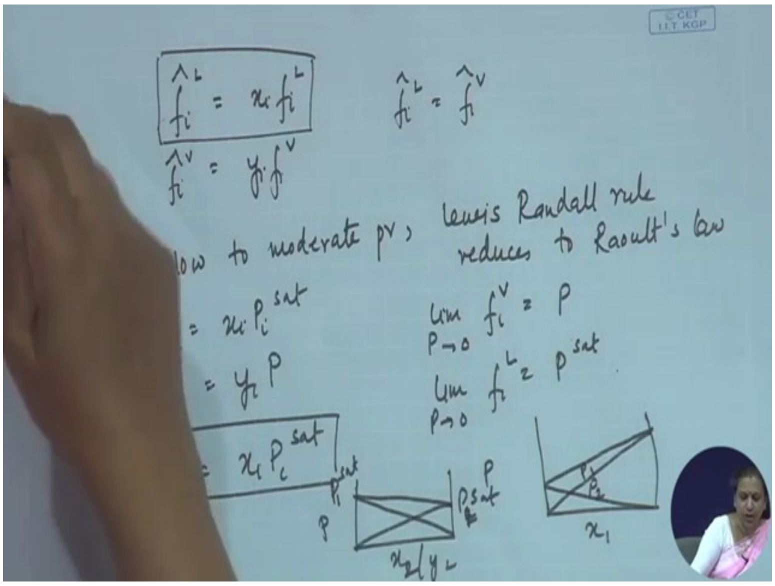
$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x_i} = \left[\frac{\partial \left(\overline{g_i^E}/RT\right)}{\partial P}\right]_{T,x_i} = \frac{\overline{v_i^E}}{RT}$$

Fig: *(a) Positive deviation from ideality*
(b) Negative deviation from ideality

https://schools.aglasem.com/4722

After this what we did? We went to nonideal solutions and in nonideal solutions what did we find? We found out that in nonideal solutions there can be either positive deviations from ideality or there can be negative deviation from ideality, okay. When we have a positive deviation from ideality the total pressure calculated is greater than that calculated from Raoult's law when there is a negative deviation from ideality the total pressure calculated at any particular composition is less than that predicted from Raoult's law.

(Refer Slide Time: 7:10)



$$\boxed{\hat{f}_i^L = x_i f_i^L} \qquad \hat{f}_i^L = \hat{f}_i^V$$

$$\hat{f}_i^V = y_i f^V$$

low to moderate pr, Lewis Randall rule reduces to Raoult's law

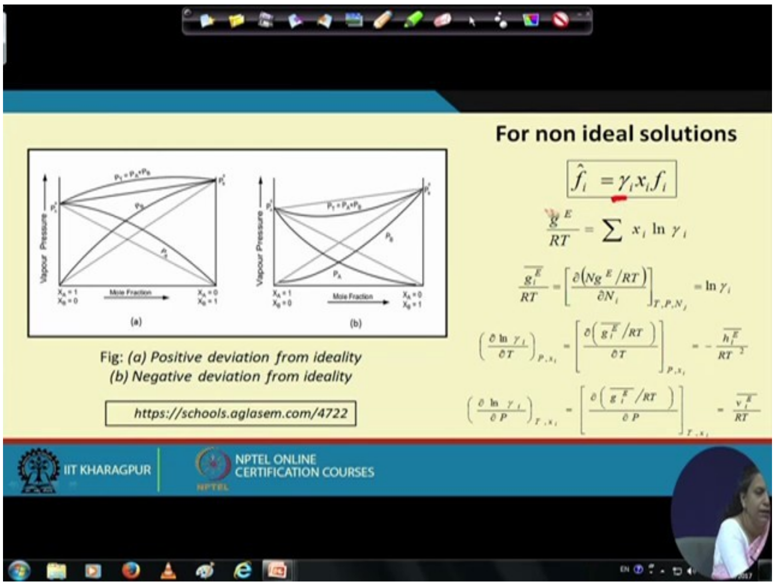
$$= x_i P_i^{sat} \qquad \lim_{P \to 0} f_i^V = P$$

$$= y_i P \qquad \lim_{P \to 0} f_i^L = P^{sat}$$

$$\boxed{= x_i P_i^{sat}}$$

As a result it was felt necessary to modify the equation which we had derived this equation or this equation for ideal solutions in order to incorporate nonideal behaviour.

(Refer Slide Time: 7:22)



For non ideal solutions

Fig: *(a) Positive deviation from ideality*
(b) Negative deviation from ideality

https://schools.aglasem.com/4722

$$\boxed{\hat{f}_i = \gamma_i x_i f_i}$$

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

$$\frac{\overline{g_i^E}}{RT} = \left[\frac{\partial (N g^E / RT)}{\partial N_i}\right]_{T,P,N_j} = \ln \gamma_i$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,x_i} = \left[\frac{\partial \left(\overline{g_i^E}/RT\right)}{\partial T}\right]_{P,x_i} = -\frac{\overline{h_i^E}}{RT^2}$$

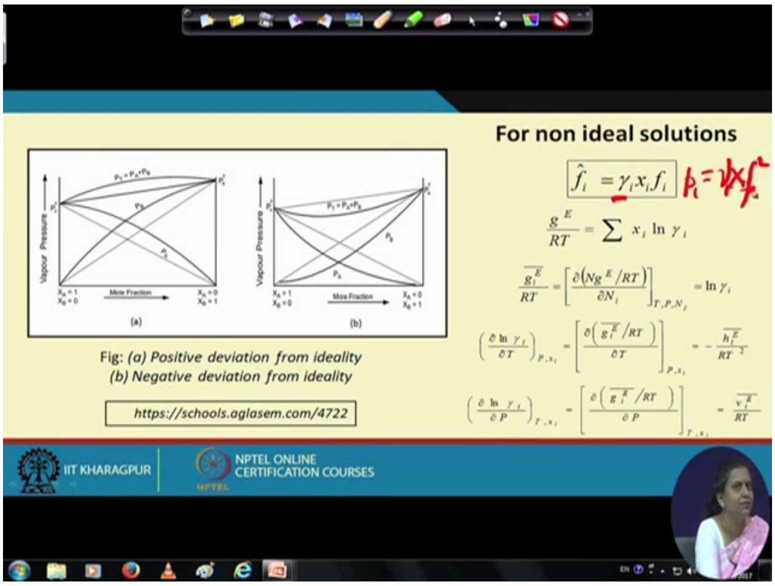
$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x_i} = \left[\frac{\partial \left(\overline{g_i^E}/RT\right)}{\partial P}\right]_{T,x_i} = \frac{\overline{v_i^E}}{RT}$$

IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

And this was done by introducing a term yi in the by introducing a term gamma i in the equation of Lewis Randall equation.

(Refer Slide Time: 7:42)



For non ideal solutions

$$\boxed{\hat{f}_i = \underline{\gamma_i} x_i f_i} \quad p_i = \gamma x f^L$$

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

$$\frac{\overline{g_i^E}}{RT} = \left[\frac{\partial (N g^E / RT)}{\partial N_i}\right]_{T,P,N_j} = \ln \gamma_i$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,x_i} = \left[\frac{\partial \left(\overline{g_i^E}/RT\right)}{\partial T}\right]_{P,x_i} = -\frac{\overline{h_i^E}}{RT^2}$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x_i} = \left[\frac{\partial \left(\overline{g_i^E}/RT\right)}{\partial P}\right]_{T,x_i} = \frac{\overline{v_i^E}}{RT}$$

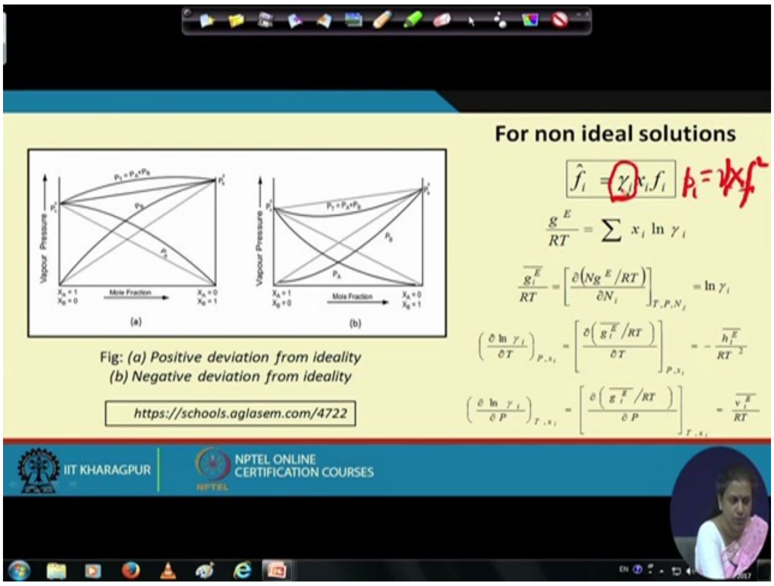
Fig: *(a) Positive deviation from ideality*
(b) Negative deviation from ideality

https://schools.aglasem.com/4722

IIT KHARAGPUR
NPTEL ONLINE CERTIFICATION COURSES

And for low to moderate pressure what happen? The equation reduces to Pi equals to gamma I Xifi liquid if it is a liquid phase and it is also important to remember that mostly non-ideality they exist in liquid solutions, gaseous mixtures are usually ideal, why? Because the Lewis Randall rule is based on Amagat's law of additive volumes which I have mentioned several times in my previous classes.

(Refer Slide Time: 8:09)



For non ideal solutions

$$\boxed{\hat{f}_i = \boxed{\gamma_i} x_i f_i} \quad p_i = \gamma x f^L$$

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

$$\frac{\overline{g_i^E}}{RT} = \left[\frac{\partial (N g^E / RT)}{\partial N_i}\right]_{T,P,N_j} = \ln \gamma_i$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,x_i} = \left[\frac{\partial \left(\overline{g_i^E}/RT\right)}{\partial T}\right]_{P,x_i} = -\frac{\overline{h_i^E}}{RT^2}$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x_i} = \left[\frac{\partial \left(\overline{g_i^E}/RT\right)}{\partial P}\right]_{T,x_i} = \frac{\overline{v_i^E}}{RT}$$

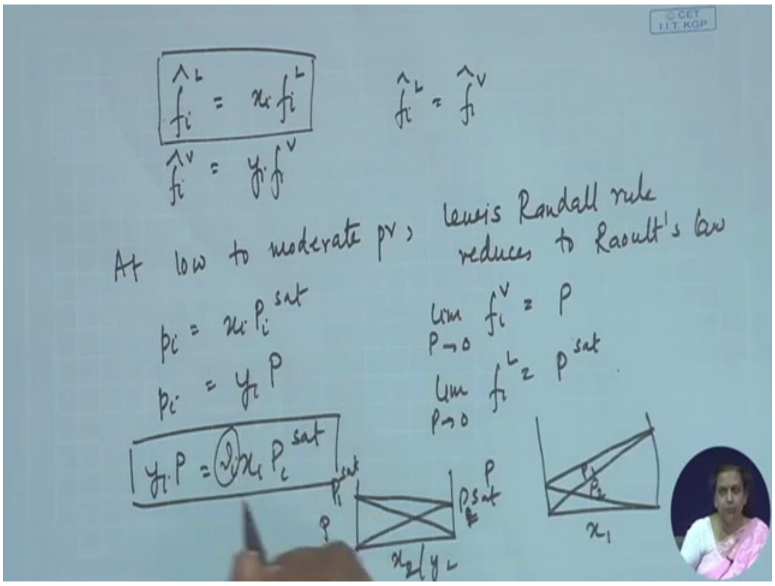
Fig: *(a) Positive deviation from ideality*
(b) Negative deviation from ideality

https://schools.aglasem.com/4722

IIT KHARAGPUR
NPTEL ONLINE CERTIFICATION COURSES

So therefore for non-ideal solutions we find that - thee non-ideality is taken care of by introducing this particular activity coefficient in the Lewis Randall rule and we found out that once can find out gamma i then the vle behaviour of nonideal solutions and ideal solutions are naturally the same.

(Refer Slide Time: 8:30)



$\boxed{\hat{f}_i^L = x_i f_i^L}$ $\hat{f}_i^L = \hat{f}_i^V$

$\hat{f}_i^V = y_i f^V$

At low to moderate pr, Lewis Randall rule reduces to Raoult's law

$p_i = x_i P_i^{sat}$

$p_i = y_i P$

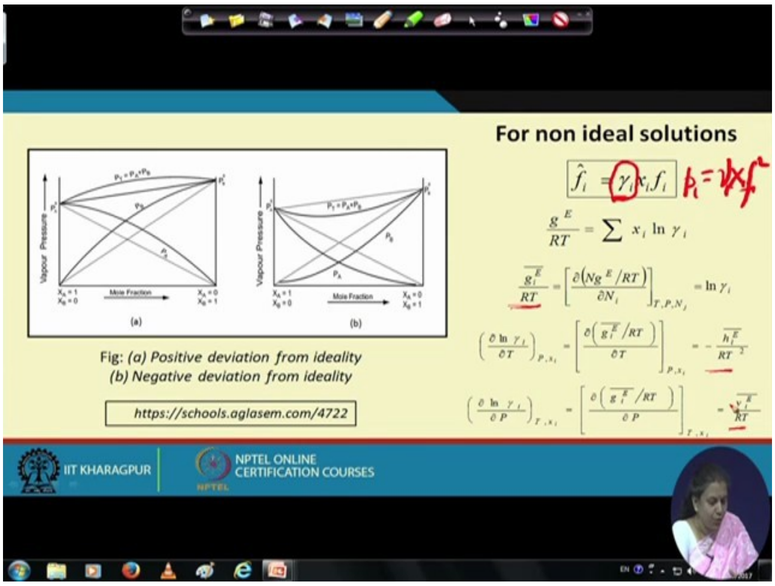
$\boxed{y_i P = \gamma_i x_i P_i^{sat}}$

$\lim_{P \to 0} f_i^V = P$

$\lim_{P \to 0} f_i^L = P^{sat}$

The only difference is that in this particular equation we will be having a gamma i here there is no other change. So therefore we have introduced one other property of component i when it is in solution. So the next interest was to express Gamma i in terms of known parameters or in terms of parameters which we have already discussed.

(Refer Slide Time: 9:00)



For non ideal solutions

$\boxed{\hat{f}_i = \gamma_i x_i f_i}$ $f_i = \gamma x f^L$

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

$$\frac{\overline{g_i^E}}{RT} = \left[\frac{\partial (Ng^E/RT)}{\partial N_i}\right]_{T,P,N_j} = \ln \gamma_i$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,x_i} = \left[\frac{\partial \left(\overline{g_i^E}/RT\right)}{\partial T}\right]_{P,x_i} = -\frac{\overline{h_i^E}}{RT^2}$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x_i} = \left[\frac{\partial \left(\overline{g_i^E}/RT\right)}{\partial P}\right]_{T,x_i} = \frac{\overline{v_i^E}}{RT}$$

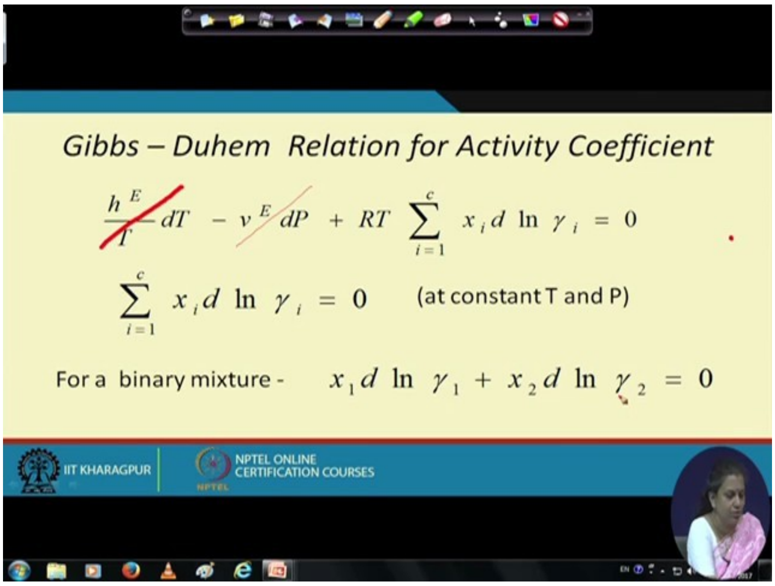
Fig: *(a) Positive deviation from ideality*
(b) Negative deviation from ideality

https://schools.aglasem.com/4722

In the last class we have made those particular derivations and we found out that the ln of gamma i it is nothing but equal to the partial molar excess Gibbs free energy of component i in solution, right? You also found out that the variation of gamma i with temperature can be related to the partial molar excess enthalpy of component i in solution and its variation with pressure can be related to the partial molar excess volume of the component i in solution.

So this was what we had derived in the last class and after this, what we did was we derived the Gibbs Duhem equation in terms of activity coefficient and I stopped there mentioning that particularly for binary solution the Gibbs Duhem equation gives us large number of important information.

(Refer Slide Time: 9:59)



Gibbs – Duhem Relation for Activity Coefficient

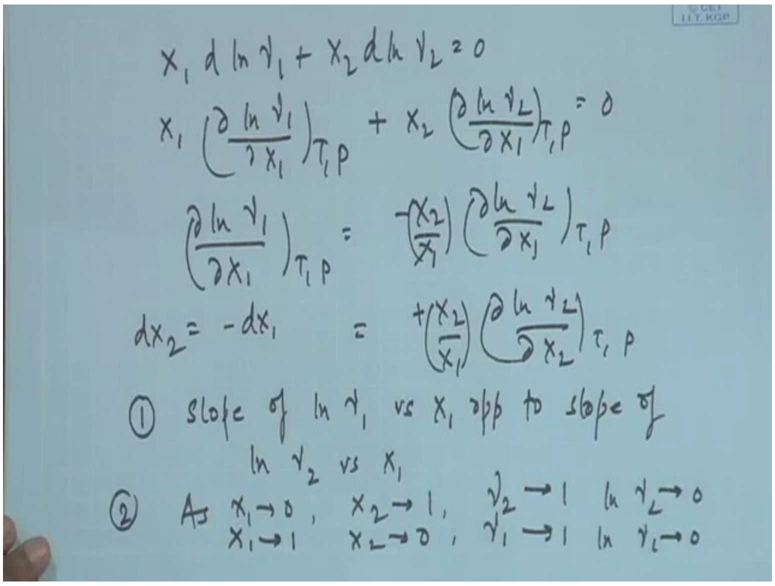
$$\cancel{\frac{h^E}{T}}dT - v^E \cancel{dP} + RT\sum_{i=1}^{c} x_i d\ln\gamma_i = 0$$

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

For a binary mixture - $x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0$

So let us start from that particular point and see what are the important information’s that we have, okay. So therefore I believe I had derived rather we have derived this particular generalized equation Gibbs Duhem equation in terms of activity coefficient and this was the equation which we had derived and in this particular equation at constant temperature and pressure naturally this becomes 0 this becomes 0 and this is the Gibbs Duhem equation which for a binary mixture reduces to this.

(Refer Slide Time: 11:03)



$$x_1\, d\ln\gamma_1 + x_2\, d\ln\gamma_2 = 0$$

$$x_1\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln\gamma_2}{\partial x_1}\right)_{T,P} = 0$$

$$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} = -\left(\frac{x_2}{x_1}\right)\left(\frac{\partial \ln\gamma_2}{\partial x_1}\right)_{T,P}$$

$$dx_2 = -dx_1 \qquad = +\left(\frac{x_2}{x_1}\right)\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)_{T,P}$$

① Slope of $\ln\gamma_1$ vs x_1 opp to slope of $\ln\gamma_2$ vs x_1

② As $x_1 \to 0$, $x_2 \to 1$, $\gamma_2 \to 1$ $\ln\gamma_2 \to 0$
$x_1 \to 1$ $x_2 \to 0$, $\gamma_1 \to 1$ $\ln\gamma_1 \to 0$

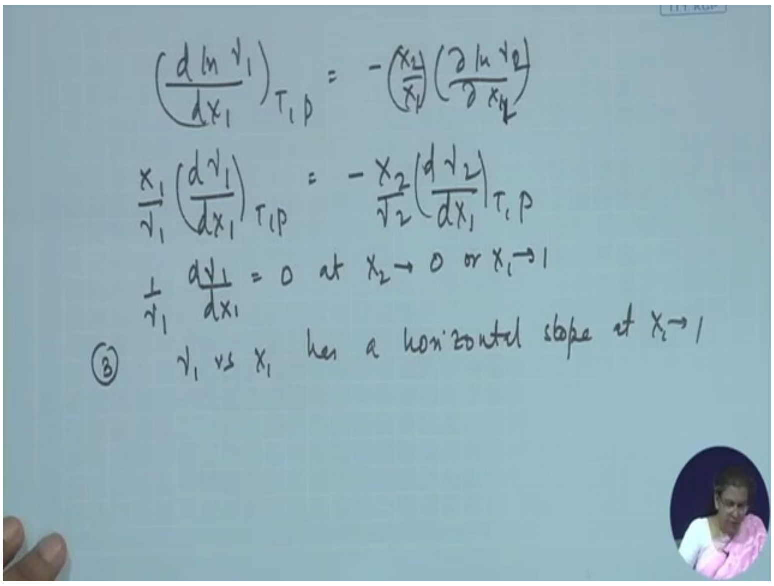
Now let us see what important information we can get from this equation? Say for instance if I write it down as, I will just write down and derive it once more X1 d ln gamma1 plus X2 d ln gamma 2 equals to 0, can we not write it down as X1 del ln gamma 1 del X1 at constant temperature, pressure plus X2 del ln gamma 2 del X1 at constant temperature, pressure this is equal to 0.

Or in other words del ln gamma1 del X1, is this not equal to minus X2 by X1 del ln gamma2 del X1 at constant T, P. We know that since it is a binary mixture d X2 equals to minus dX1. So this can be written down as minus X2 by X1 del ln gamma2 del X2 at constant temperature and pressure automatically what do we see? We see that the first thing is slope of ln gamma1 versus X1 is just opposite to the slope of ln gamma2 versus X1 this is the first thing that we see here right number 1.

Number 2, can we write down this particular equation? So let me write down the first thing is slope of ln gamma 1 versus X1 opposite to slope of ln gamma2 versus X1. What is the next thing that we know from here? We know that as X1 tends to 0, what happens you tell me? X1 tends to 0 means X2 tends to 1. Naturally under that condition what happens? Your gamma 2 tends to 1 and ln gamma 2 tends to 0.

So therefore what do we see? We see that when we are plotting gamma 2 versus X1 then at X1 equals to 0 the gamma 2 becomes equal to one and similarly we also see at X1 tends to 1 or X2 tends to 0, what happens? Gamma 1 tends to 1 and ln gamma 1 tends to 0, quite natural whichever component is in excess it's natural that Gama 1 tends to 1 at X1 tends to 1 and gamma 2 tends to 1 at X2 tends to 1, fine.

(Refer Slide Time: 13:40)



$$\left(\frac{d \ln \gamma_1}{dx_1}\right)_{T,P} = -\left(\frac{x_2}{x_1}\right)\left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)$$

$$\frac{x_1}{\gamma_1}\left(\frac{d\gamma_1}{dx_1}\right)_{T,P} = -\frac{x_2}{\gamma_2}\left(\frac{d\gamma_2}{dx_1}\right)_{T,P}$$

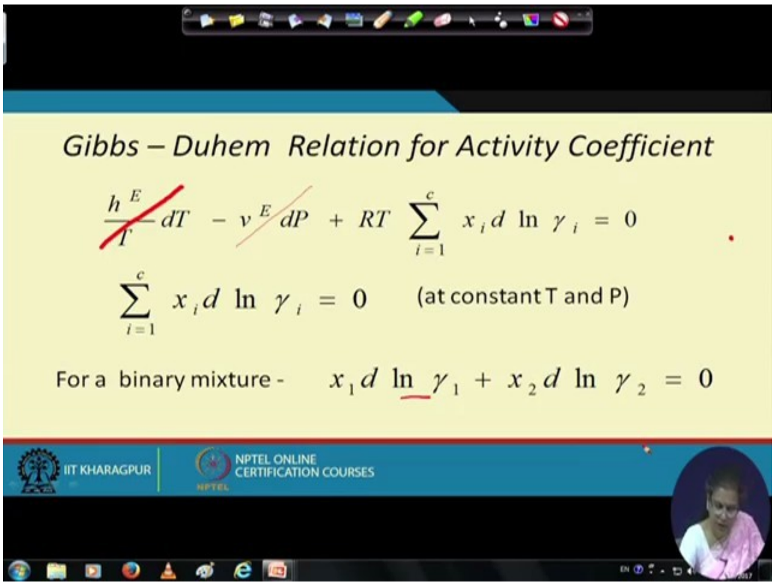
$$\frac{1}{\gamma_1}\frac{d\gamma_1}{dx_1} = 0 \text{ at } x_2 \to 0 \text{ or } x_1 \to 1$$

③ γ_1 vs x_1 has a horizontal slope at $x_1 \to 1$

What is the other thing that that we can observe from here? Just observe and see from the equation which I have written down. The equation implies that, let me write down the equation d ln gamma 1 d X1 constant T, P this is equals to minus X2 by X1 del ln gamma 1 del X1, right? Now or in other words if I write it down in this way also X1, can I not write it down as X1 by gamma 1 d gamma1 d X1, is this not equal to minus X2 by gamma 2, d gamma 2 d X1, can I not write it in this particular form?

I can write it down or else I can also write it down as, in this form also I can write it down that 1 by gamma1 d gamma1 d X1, is this not? Because what happens, is this not equal to 0 at X2 tends to 0 or X1 tends to 1, what does this imply? It implies gamma1 versus X1 has a horizontal slope at X1 tends to 1, fine. So therefore there are 3 observations which we find from here.

(Refer Slide Time: 15:29)



Gibbs – Duhem Relation for Activity Coefficient

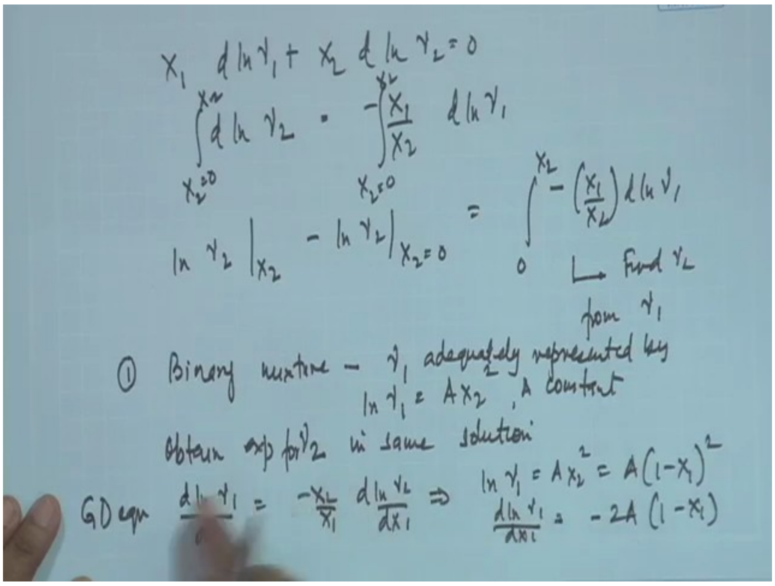
$$\cancel{\frac{h^E}{T}dT} - \cancel{v^E dP} + RT\sum_{i=1}^{c} x_i d\ln\gamma_i = 0$$

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

For a binary mixture - $x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0$

What are the 3 observations? The first thing if we observe the equation this particular equation, what do you find number 1 is gamma 1 and gamma 2 they are not independent of one another. So therefore they are more or less related to composition in this particular fashion.

(Refer Slide Time: 15:44)



$$x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0$$

$$\int_{x_2=0}^{x_2} d\ln\gamma_2 = -\int_{x_2=0}^{x_2}\frac{x_1}{x_2}d\ln\gamma_1$$

$$\ln\gamma_2\Big|_{x_2} - \ln\gamma_2\Big|_{x_2=0} = \int_0^{x_2} -\left(\frac{x_1}{x_2}\right)d\ln\gamma_1$$

↳ Find γ_2 from γ_1

① Binary mixture – γ_1 adequately represented by $\ln\gamma_1 = Ax_2^2$, A constant

Obtain exp for γ_2 in same solution

GD eqn $\frac{d\ln\gamma_1}{dx_1} = -\frac{x_2}{x_1}\frac{d\ln\gamma_2}{dx_1} \Rightarrow$ $\ln\gamma_1 = Ax_2^2 = A(1-x_1)^2$

$$\frac{d\ln\gamma_1}{dx_1} = -2A(1-x_1)$$

Next is that if we know one we will be in a position to find the other in what particular way we will be doing a problem and finding this out that suppose we know one say X1 d ln gamma 1 plus X2 d ln gamma 2 equals to 0. So suppose I know gamma 1 I would like to find out gamma 2. So what is this d ln gamma2 minus X1 by X2 d ln gamma1, right? Now I would like to find out gamma 2 at some particular composition X2.

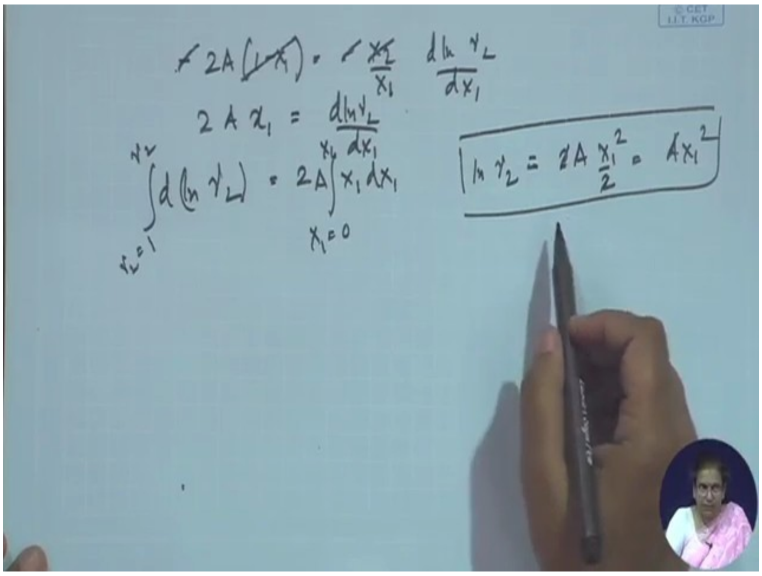
Starting from X2 equals to 0 and here this also X2 equals to 0 to X2. So therefore ln gamma 2 at X2 minus ln gamma 2 at X2 equals to 0 is nothing but 0 to X2 minus X1 by X2 d ln gamma 1. So therefore suppose I know gamma1 or gamma1 variation with X1 then we can find gamma 2 gamma 1 this is number 1. Suppose we take up a problem in this respect, say for instance I take up a problem I know that in a binary mixture say suppose the problem is that I have got a binary mixture, right?

In the binary mixture I know gamma1 is represented by an equation as ln gamma1 equals to AX2 square, where A is a constant, fine. I would like to find out or I would like to express obtain expression for gamma 2 in the same solution. So therefore I have a binary mixture of component 1 and 2 gamma1 adequately represented adequately represented by this particular equation where A is a constant obtain expression for gamma 2 of component2 in the same solution, how do we think we should be proceeding for this?

Just if you if you look at this particular equation we can we can very well find it out from here. We know that d ln gamma1 we already know that d ln gamma 1 dX1 this is equals to minus X2 by X1 d ln gamma 2 dX1, right? This is nothing but as I have mentioned this is Gibbs Duhem equation. So from here what do we know? We know ln gamma1 it's given it's already AX2 square which can be written down as A into 1 minus X1 whole square, right?

So therefore in that case what is d ln gamma1 d X1 equals to? It is minus 2A into 1 minus X1, agreed? So therefore I know this particular term, right? So what is d ln gamma2 by dX1 we can simply substitute this here and we can find it out.

(Refer Slide Time: 19:09)



$$\cancel{-}2A(\cancel{1-x_1}) = \cancel{-}\frac{\cancel{x_2}}{x_1}\frac{d\ln\gamma_2}{dx_1}$$

$$2Ax_1 = \frac{d\ln\gamma_2}{dx_1}$$

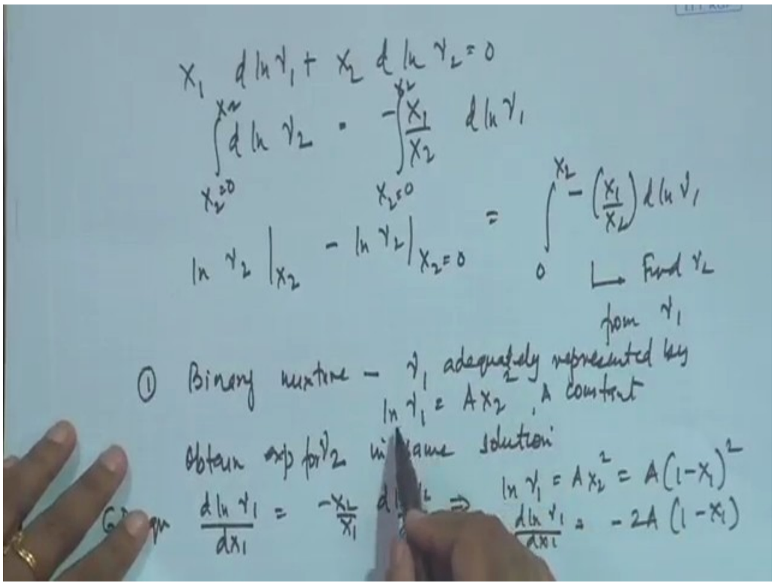
$$\int_{\gamma_2=1}^{\gamma_2} d(\ln\gamma_2) = 2A\int_{x_1=0}^{x_1} x_1\,dx_1$$

$$\boxed{\ln\gamma_2 = \cancel{2}A\frac{x_1^2}{2} = Ax_1^2}$$

So therefore this reduces to minus 2A into 1 minus X1 equals to minus X2 by X1 d ln gamma2 d X1, this is nothing but X2 this is also X2 here it is minus here also it's a minus, so the minuses they cancel out, what do I get? I get 2A x1 is nothing but d ln gamma2 d X1, agreed? So I would like to find out an expression for gamma 2. So we know d ln gamma 2 is nothing but 2A X1d X1, fine. We will be performing the integration from X1 equals to 0 to X1 equals to X1, right? And we know that at X1 equals to 0, what is the value of gamma 2? X1 equals to 0 means X2 equals to 1 and therefore at X2 equals to 1 Gamma 2 has to be equal to 1. So therefore this is going to extend from ln gamma 2 has to be 0. So therefore this has to extend from gamma 2 equals to 1 to gamma 2.

As a result of which if you perform this integration what do we get? We get ln gamma2 this is nothing but 2 into A X1 square by 2 which is nothing but equal to AX1 square. We find that we will be dealing more with these with such type of equations.

(Refer Slide Time: 20:23)



$$x_1\, d\ln\gamma_1 + x_2\, d\ln\gamma_2 = 0$$

$$\int_{x_2=0}^{x_2} d\ln\gamma_2 = -\int_{x_2=0}^{x_2} \frac{x_1}{x_2}\, d\ln\gamma_1$$

$$\ln\gamma_2\Big|_{x_2} - \ln\gamma_2\Big|_{x_2=0} = \int_0^{x_2} -\left(\frac{x_1}{x_2}\right) d\ln\gamma_1$$

↳ Find γ_2 from γ_1

① Binary mixture – γ_1 adequately represented by $\ln\gamma_1 = Ax_2^2$, A constant

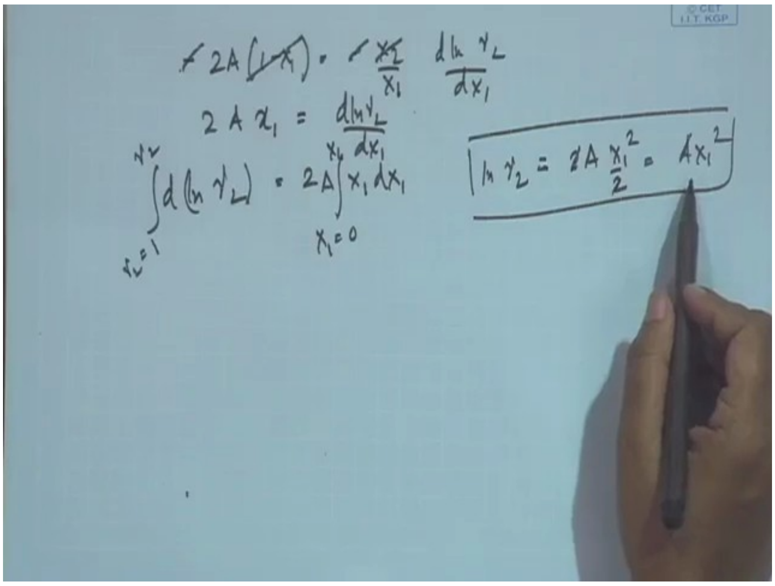
Obtain exp for γ_2 in same solution

$$\ln\gamma_1 = Ax_2^2 = A(1-x_1)^2$$

G[illegible] $\frac{d\ln\gamma_1}{dx_1} = -\frac{x_2}{x_1}\, d$ [illegible] $\Rightarrow \frac{d\ln\gamma_1}{dx_1} = -2A(1-x_1)$

We find that more or less then in that case your variation of ln gamma1 with composition

(Refer Slide Time: 20:28)



$$-2A\cancel{(1-x_1)} = -\frac{\cancel{x_2}}{x_1}\frac{d\ln\gamma_2}{dx_1}$$

$$2A x_1 = \frac{d\ln\gamma_2}{dx_1}$$

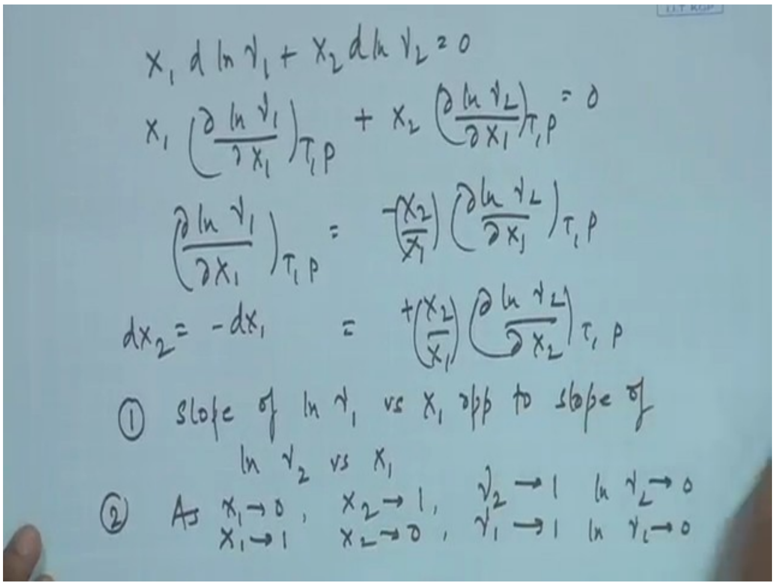
$$\int_{\gamma_2=1}^{\gamma_2} d(\ln\gamma_2) = 2A\int_{x_1=0}^{x_1} x_1\,dx_1$$

$$\boxed{\ln\gamma_2 = 2A\frac{x_1^2}{2} = Ax_1^2}$$

and ln gamma 2 with composition they are more or less symmetric to one another, agreed? So therefore just imagine I had started from or rather I had the expression of gamma variation with composition for any 1 component in a binary mixture and we found out since we knew Gibbs Duhem equation using the equation we could find out the variation of the activity coefficient of the other component as a function of composition.

So in this particular way this is just one very typical example can take up a lot of examples and you will find that for most of the situations if you know the gamma variation for 1 component in whatever be the functional form you can find out the gamma variation for the other component this is for a binary mixture if it is just like what I had repeated in the last class. If I if I'm dealing with multi-component mixture then if I know the gammas for the n minus 1 component I can find the gamma for the nth component using the Gibbs Duhem equation. So this is the first thing which is very important.

(Refer Slide Time: 21:41)



$x_1\, d\ln\gamma_1 + x_2\, d\ln\gamma_2 = 0$

$x_1\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln\gamma_2}{\partial x_1}\right)_{T,P} = 0$

$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} = -\left(\frac{x_2}{x_1}\right)\left(\frac{\partial \ln\gamma_2}{\partial x_1}\right)_{T,P}$

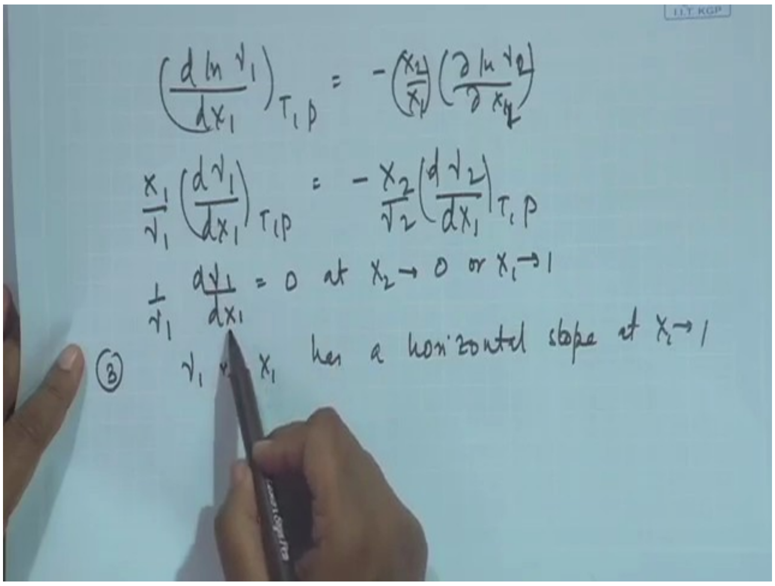
$dx_2 = -dx_1 \qquad = +\left(\frac{x_2}{x_1}\right)\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)_{T,P}$

① slope of $\ln\gamma_1$ vs x_1 opp to slope of $\ln\gamma_2$ vs x_1

② As $x_1 \to 0$, $x_2 \to 1$, $\gamma_2 \to 1$ $\ln\gamma_2 \to 0$
$x_1 \to 1$ $x_2 \to 0$, $\gamma_1 \to 1$ $\ln\gamma_1 \to 0$

The next thing as I have already mentioned the next thing is when we know that gamma 1 tends to tends to 1 at X1 tends to 1. So therefore we know that at X1 tends to 1, suppose I would like to plot gamma or gamma1 as a function of X1, what do I know? That at X1 equals to 1 gamma1 also has to be 1, right? Suppose we start and suppose say there is a positive deviation from Raoult's law, so therefore the equation should be something of this sort.Similarly for gamma 2 the equation should be something of this sort.

(Refer Slide Time: 22:19)



$\left(\frac{d\ln\gamma_1}{dx_1}\right)_{T,P} = -\left(\frac{x_2}{x_1}\right)\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)$

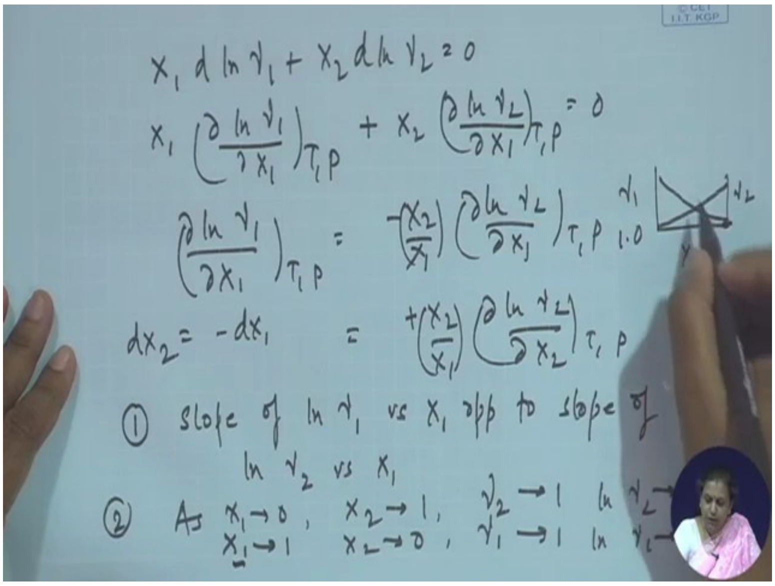
$\frac{x_1}{\gamma_1}\left(\frac{d\gamma_1}{dx_1}\right)_{T,P} = -\frac{x_2}{\gamma_2}\left(\frac{d\gamma_2}{dx_1}\right)_{T,P}$

$\frac{1}{\gamma_1}\frac{d\gamma_1}{dx_1} = 0$ at $x_2 \to 0$ or $x_1 \to 1$

③ γ_1 vs x_1 has a horizontal slope at $x_1 \to 1$

What is the other thing that I know? The other thing which I know is that at X1 equals to 1 year d gamma1d X1 the slope 0 or in other words the curve should be horizontal.

(Refer Slide Time: 22:27)



$x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 = 0$

$x_1\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln\gamma_2}{\partial x_1}\right)_{T,P} = 0$

$\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} = -\left(\frac{x_2}{x_1}\right)\left(\frac{\partial \ln\gamma_2}{\partial x_1}\right)_{T,P}$

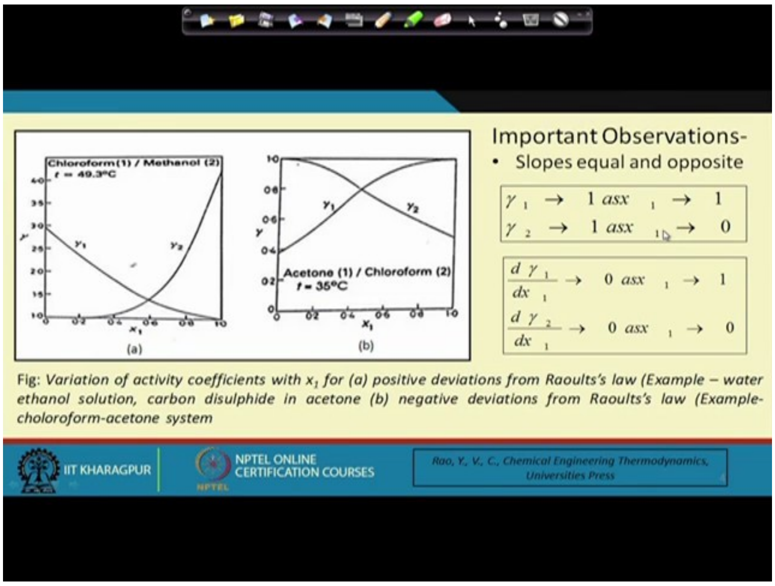
$dx_2 = -dx_1 \qquad = +\left(\frac{x_2}{x_1}\right)\left(\frac{\partial \ln\gamma_2}{\partial x_2}\right)_{T,P}$

① slope of $\ln\gamma_1$ vs x_1 opp to slope of $\ln\gamma_2$ vs x_1

② As $x_1 \to 0$, $x_2 \to 1$, $\gamma_2 \to 1$ $\ln\gamma_2 \to$
$x_1 \to 1$ $x_2 \to 0$, $\gamma_1 \to 1$ $\ln\gamma_1 \to$

Or in other words we know that at this particular point when we are plotting gamma 1 the gamma 1 has to be 1 at X1 equals to 1 and the curve has to be horizontal at this particular point the same applies for gamma2 at X1 equals to 0, right?

(Refer Slide Time: 22:54)



Important Observations-

- Slopes equal and opposite

$\gamma_1 \to 1$ as $x_1 \to 1$

$\gamma_2 \to 1$ as $x_1 \to 0$

$\frac{d\gamma_1}{dx_1} \to 0$ as $x_1 \to 1$

$\frac{d\gamma_2}{dx_1} \to 0$ as $x_1 \to 0$

Fig: *Variation of activity coefficients with x_1 for (a) positive deviations from Raoults's law (Example – water ethanol solution, carbon disulphide in acetone (b) negative deviations from Raoults's law (Example- choloroform-acetone system*

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES

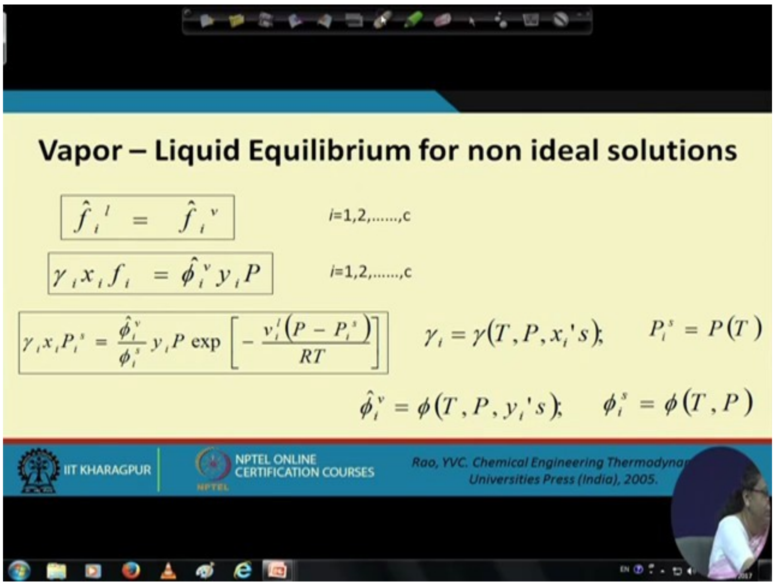
Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

So therefore these are some of the important information which the Gibbs Duhem equation provides to us, right? So I had already mentioned I have also shown the plots gamma variations with composition if you observe this particular thing as I have told you gamma1 tends to 1 as X1 tends to 1, this is true whether we have a negative variation from deviation from Raoult's law or a positive deviation from Raoult's law.

That we have a positive deviation the value of gamma is greater than one, so therefore we find that at X1 equals to 1 gamma1 is equal to one. In this case also as X1 equals to 1 gamma1 equals to 1 number 1. Number 2 the slope is horizontal here for gamma1 horizontal here for gamma 2. Here also the slope is horizontal here for gamma 2 the slope is horizontal here for gamma 1.

So therefore these are the 3 important this was the first observation which we had slopes equal and opposite the second observation was this and the third observation is this. And the fourth thing I have already mentioned I have done a problem and shown you that how gamma 1 or rather how, if you know gamma variation of 1 component with composition how the gamma variation of the other component can be found out.

(Refer Slide Time: 24:26)



Vapor – Liquid Equilibrium for non ideal solutions

$$\boxed{\hat{f}_i^{\,l} = \hat{f}_i^{\,v}} \qquad i=1,2,\ldots\ldots,c$$

$$\boxed{\gamma_i x_i f_i = \hat{\phi}_i^{\,v} y_i P} \qquad i=1,2,\ldots\ldots,c$$

$$\boxed{\gamma_i x_i P_i^{\,s} = \frac{\hat{\phi}_i^{\,v}}{\phi_i^{\,s}} y_i P \exp\left[-\frac{v_i^l\left(P - P_i^{\,s}\right)}{RT}\right]} \qquad \gamma_i = \gamma(T, P, x_i\text{'s}); \qquad P_i^{\,s} = P(T)$$

$$\hat{\phi}_i^{\,v} = \phi(T, P, y_i\text{'s}); \qquad \phi_i^{\,s} = \phi(T, P)$$

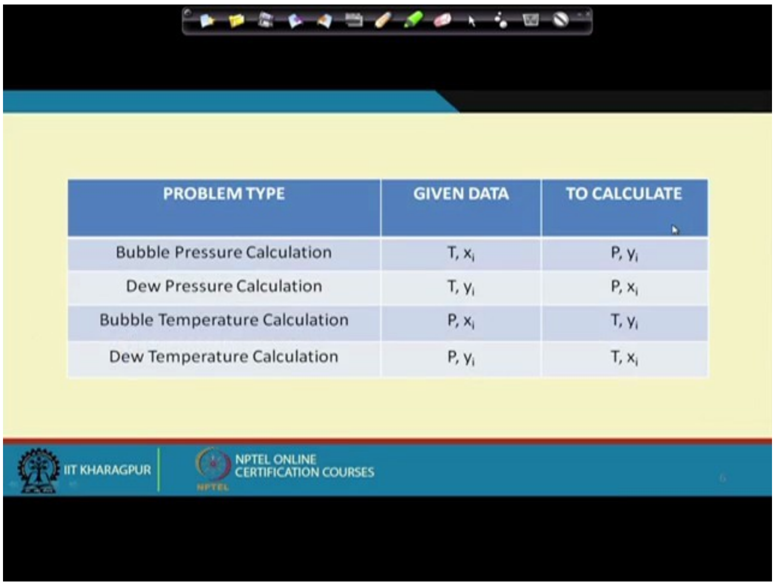
IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES

Rao, YVC. Chemical Engineering Thermodyna
Universities Press (India), 2005.

So therefore with this I think we have discussed sufficiently regarding the importance of gamma, now we have to go for finding out and we know that that this also I have repeated we know that once we can find out gamma then we will be able to tackle the vapor liquid equilibrium data and gamma as we know it is a function of temperature, pressure, the liquid phase composition very importantly which is not mentioned here it is also a function of the vapor phase composition.

Because the gamma has to be obtained from this particular equation which deals with both the liquid phase as well as the vapor phase. It is important to remember that although gamma is a property of the liquid solution in order to find it out we need to have data on both the liquid phase as well as the vapor phase composition.

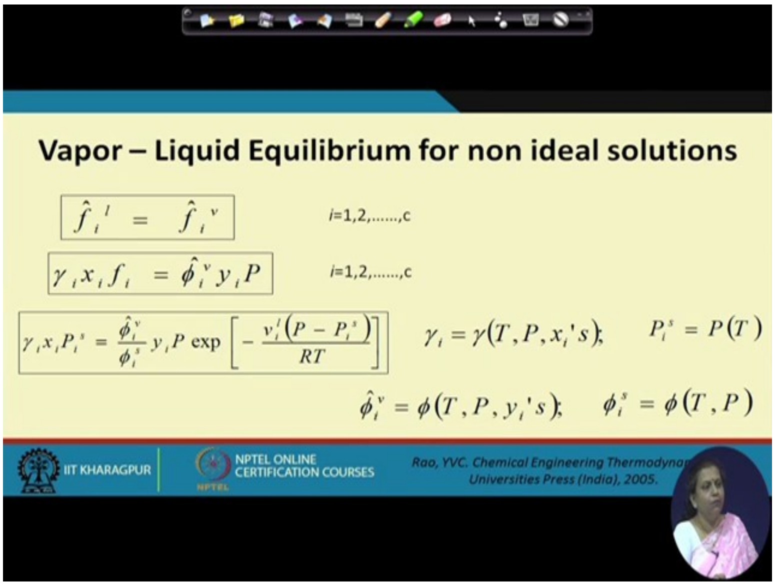
(Refer Slide Time: 25:11)



PROBLEM TYPE	GIVEN DATA	TO CALCULATE
Bubble Pressure Calculation	T, x_i	P, y_i
Dew Pressure Calculation	T, y_i	P, x_i
Bubble Temperature Calculation	P, x_i	T, y_i
Dew Temperature Calculation	P, y_i	T, x_i

Now how to find out gamma? What are the different normal ways of finding out gamma, right? So usually what we do is, the problem types yesterday also I have told you that these are the different problem types and whatever problems are given these are the equations which have to be used to solve them.

(Refer Slide Time: 25:31)



Vapor – Liquid Equilibrium for non ideal solutions

$$\boxed{\hat{f}_i^{\,l} = \hat{f}_i^{\,v}} \qquad i=1,2,\ldots\ldots,c$$

$$\boxed{\gamma_i x_i f_i = \hat{\phi}_i^{\,v} y_i P} \qquad i=1,2,\ldots\ldots,c$$

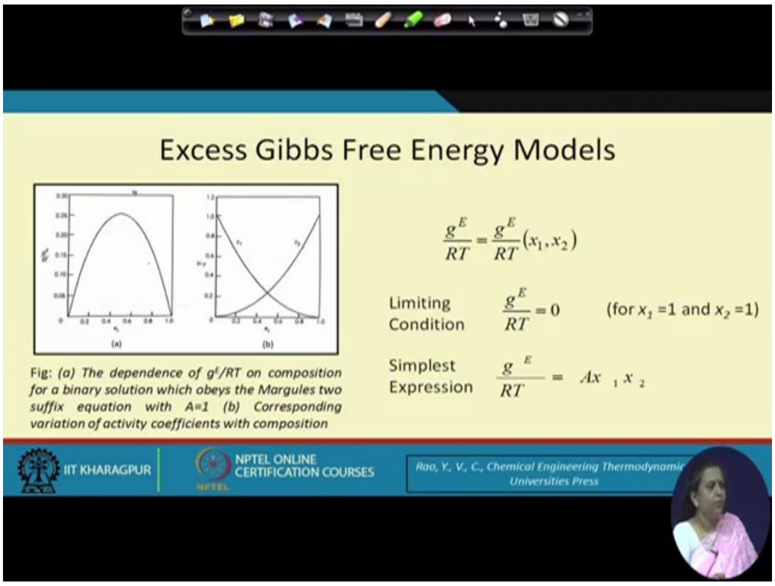
$$\boxed{\gamma_i x_i P_i^{\,s} = \frac{\hat{\phi}_i^{\,v}}{\phi_i^{\,s}} y_i P \exp\left[-\frac{v_i^l\left(P - P_i^{\,s}\right)}{RT}\right]} \qquad \gamma_i = \gamma\left(T, P, x_i's\right); \qquad P_i^{\,s} = P(T)$$

$$\hat{\phi}_i^{\,v} = \phi\left(T, P, y_i's\right); \qquad \phi_i^{\,s} = \phi\left(T, P\right)$$

Rao, YVC. Chemical Engineering Thermodyna Universities Press (India), 2005.

We have already done this for ideal solutions the extra thing which needs to be done here is to incorporate the or rather is to know how to calculate gamma from known input parameters.

(Refer Slide Time: 25:34)



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

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | *Rao, Y., V., C., Chemical Engineering Thermodynamic Universities Press*

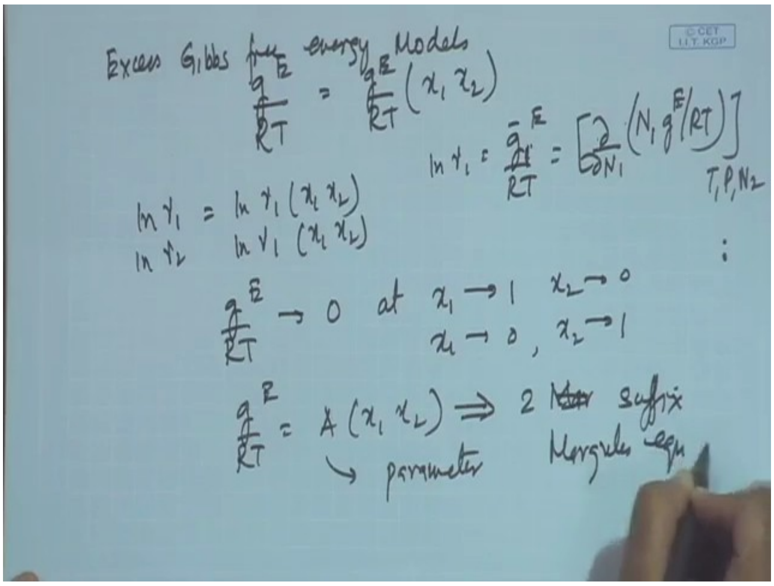
So well the thing which is usually done is that see it’s mostly gamma data it’s very difficult to find out how a real solution actually behaves or rather how gamma in the real solution can be related to the properties of the real solution, why? Because see for a real solution when it is deviating from ideality why it happens. Firstly the size and shape of the molecules can be different, so as a result of which there is a non-vanishing volume of mixing.

Second thing is the intermolecular interactions as I have said their different for the like pairs and the unlike pairs. So therefore actually if we have to find out a particular model in order to predict gamma from the liquid phase compositions then in that case it makes a very good knowledge of the intermolecular potential etc and this is not very easy. So therefore usually the things which are done are either a semi-empirical or empirical correlations are used.

Well, and these empirical correlations they are developed from experimental data. Now whenever you’re developing any empirical correlations from experimental data we need to remember certain things, what are those certain things? The first thing is that it must subscribe to certain limiting conditions number 1. Number 2 is that more or less whenever we have proposed something from experiments it is very important to test whether it is thermodynamically consistent and that we will be discussing later it will be done with the help of Gibbs Duhem equation.

Now let us see what is the easiest model which can be proposed which subscribe to the limiting conditions of a real solution and can be thought of describing the real solution behaviour or it can be related to the composition in the real solution. Usually these particular models or the equations which are proposed they are proposed from or rather they usually express the excess Gibbs free energy of the solution in terms of composition.

(Refer Slide Time: 28:08)



What I mean to say is, that in this particular case what we do is we usually instead of directly expressing ln gamma1or ln gamma 2 as a function of x1 x2 usually what we prefer to do is, we would prefer to express Gibbs free energy as a function of x1 x2 once this can be expressed we know that ln gamma 1 is nothing but g1 bar E by RT and this can very well be found out by expressing your del del N1 of N1 gE by RT at constant temperature, pressure and N2, right?

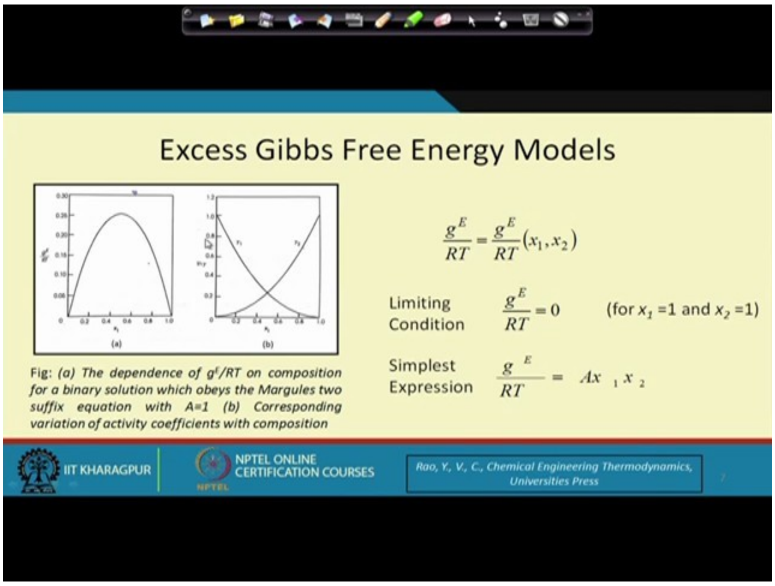
So usually we try to express or rather we try to find out activity coefficient from some particular models which are known as excess Gibbs free energy models which express excess Gibbs free energy of the solution as a function of its composition, why we do it? Because we really do not know that or rather it is not very convenient to find out the limiting situation or limiting condition for ln gamma1 and ln gamma 2.

We just know that ln gamma1 must be equal to 0 at X1 equals to 1 this is the only thing that we know ln gamma 2 must be equal to 0 at X1 equals to or rather at X2 equals to 1 this is only thing that is just one limiting condition. On the other hand when we're dealing with excess Gibbs free energy models what do we know? We know that the excess Gibbs free energy should disappear both at both when either of the component is in excess.

Or in other words the limiting condition in this particular case is this tends to 0 at X1 tends to 1 at X1 tends to 0 or in other words X2 tends to 1 under both these conditions. So therefore the simplest expression which expresses the excess Gibbs free energy in terms of composition should become equal to 0 either when X1 becomes equal to 0 or when X2 becomes equals to 0. So therefore what can be the simplest expression?

Simplest expression can just be this a product of the compositions where A is parameter which has to be determined experimentally and this particular equation this is the simplest Gibbs free energy model this particular expression it is known as 2 suffix Margules equation.

(Refer Slide Time: 31:14)



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

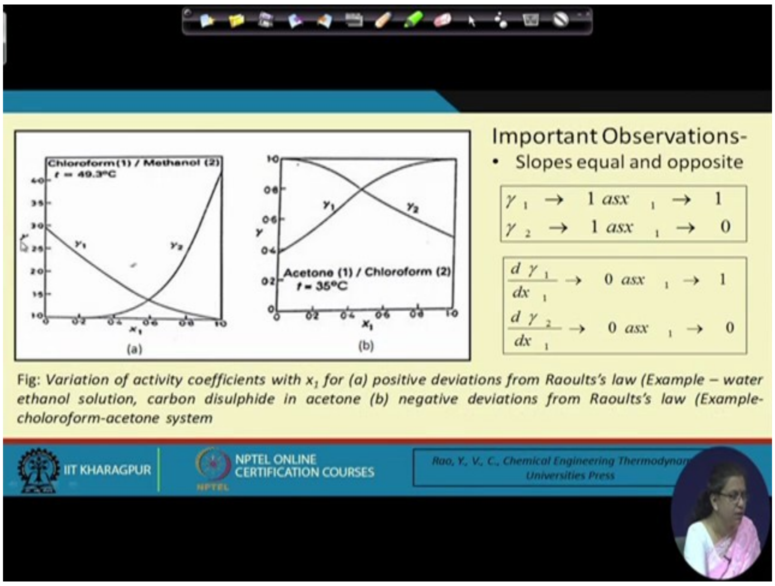
IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

And here I have shown you that for this particular condition what should be the characteristic of the Gibbs free energy the excess Gibbs free energy as a function of composition and the characteristics of ln gamma as a function of composition. If you observe you find that in this particle figure we find that g by RT it is symmetric about 0.5, why? Because we have taken A equals to 1 in this particular case, right?

(Refer Slide Time: 31:50)



Important Observations-

- Slopes equal and opposite

$$\gamma_1 \to 1 \text{ as } x_1 \to 1$$
$$\gamma_2 \to 1 \text{ as } x_1 \to 0$$

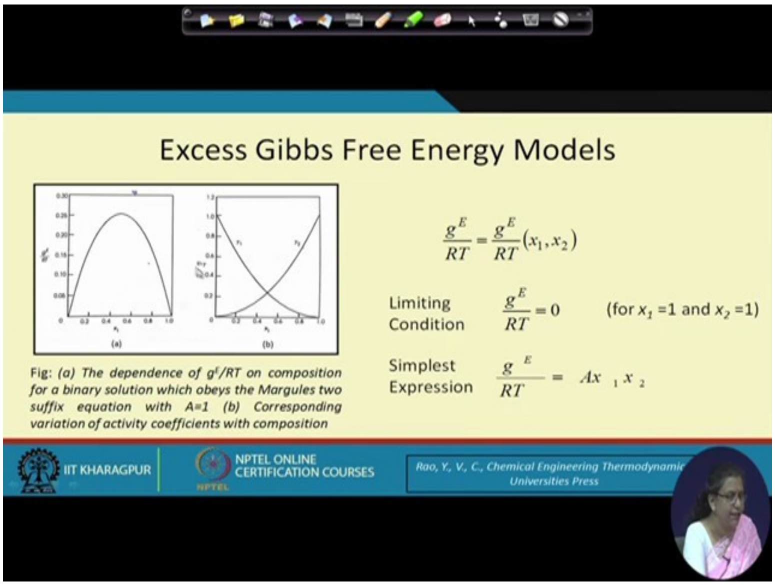
$$\frac{d\gamma_1}{dx_1} \to 0 \text{ as } x_1 \to 1$$
$$\frac{d\gamma_2}{dx_1} \to 0 \text{ as } x_1 \to 0$$

Fig: *Variation of activity coefficients with x_1 for (a) positive deviations from Raoults's law (Example – water ethanol solution, carbon disulphide in acetone (b) negative deviations from Raoults's law (Example-choloroform-acetone system*

Rao, Y., V., C., Chemical Engineering Thermodynam
Universities Press

And this shows the corresponding variation of gamma1 and gamma 2 as a function of composition, just note the difference with the previous curves which I have shown you the previous curves it was just gamma versus X1 as a result of which we have obtained curves of this sort.

(Refer Slide Time: 31:58)



Excess Gibbs Free Energy Models

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

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

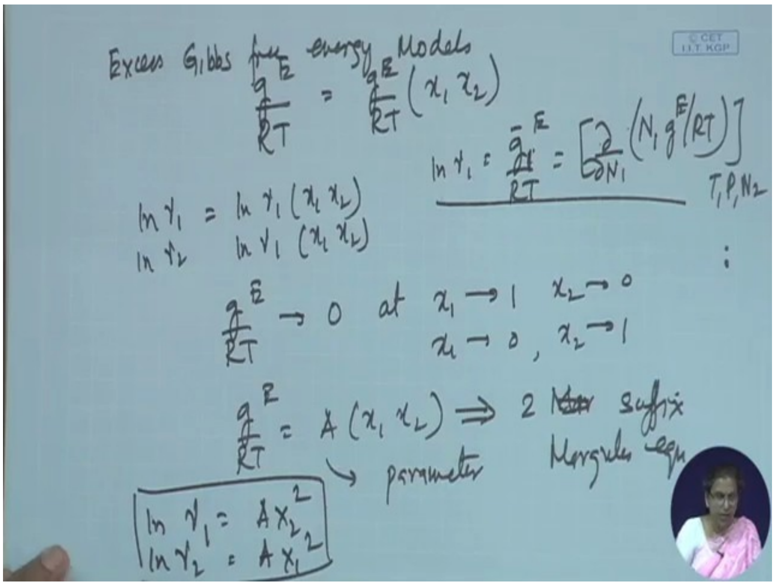
Simplest Expression $\frac{g^E}{RT} = Ax_1x_2$

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*

Rao, Y., V., C., Chemical Engineering Thermodynamic
Universities Press

In this particular case it is ln gamma versus X1, so therefore we find that ln gamma reduces to 0 at X2 equals to 1, ln gamma reduces to 0 at X1 equals to 1, right? So therefore we find that the simplest equations which can be used in order to find out the excess Gibbs free energy is nothing but the simplest expression is a product of the 2 compositions.

(Refer Slide Time: 32:35)



Excess Gibbs free energy Models

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

$$\ln\gamma_1 = \frac{\bar{g}_1^E}{RT} = \left[\frac{\partial}{\partial N_1}(N_1 g^E/RT)\right]_{T,P,N_2}$$

$$\ln\gamma_1 = \ln\gamma_1(x_1 x_2)$$

$$\ln\gamma_2 \quad \ln\gamma_1(x_1 x_2)$$

$$\frac{g^E}{RT} \to 0 \text{ at } x_1 \to 1 \quad x_2 \to 0$$

$$x_1 \to 0, \quad x_2 \to 1$$

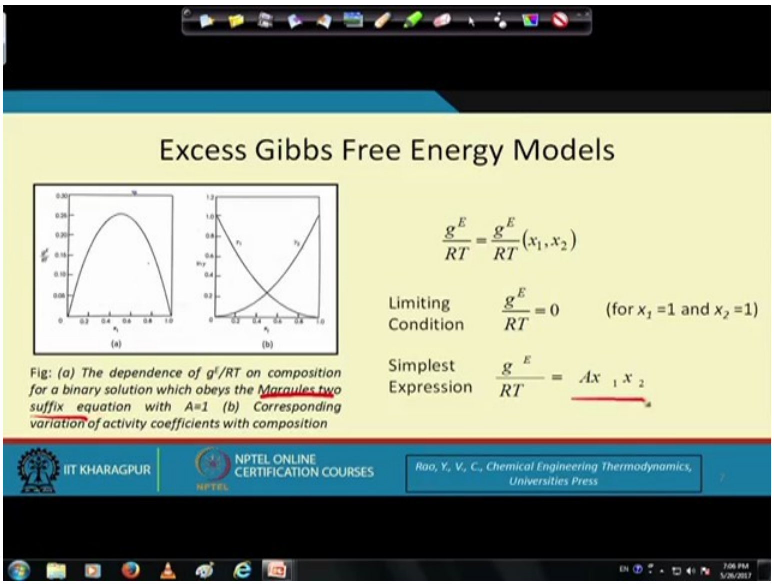
$$\frac{g^E}{RT} = A(x_1 x_2) \Rightarrow$$ 2 ~~Mar~~ suffix Margules eqn

↳ parameter

$$\boxed{\begin{array}{l}\ln\gamma_1 = A x_2^2 \\ \ln\gamma_2 = A x_1^2\end{array}}$$

And from here if we find out the expressions for ln gamma 1 and ln gamma 2 which as I have told you we can find it out from this particular expression we will find that in this case ln gamma 1 equals to A X2 square ln gamma 2 equals to A X1 square.

(Refer Slide Time: 32:57)



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 $\frac{g^E}{RT} = Ax_1 x_2$

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | *Rao, Y. V. C., Chemical Engineering Thermodynamics, Universities Press*

e

So this is the simplest equation and for this particular equation we will find that while for A equals to 1 while g by RT is symmetric about X1 equals to 0.5 you will find that the activity coefficient curves they are mirror images when ln gamma is plotted against X1 and this particular parameter A this can be 0 when it reduces to an ideal solution this can be greater than 0 or this can be positive which signifies g by RT is positive or a positive deviation from Raoult's law.

This can be negative which signifies a negative deviation from Raoult's law and this equation which is known as the 2 suffix Margules equation as has been mentioned here this particular equation we find this is quite accurate or it is adequate to represent the behaviour of liquid solutions when the components are of similar shape, the similar size and similar nature.

And for such cases it is good but for most of the situations we will find that the case is slightly more complex and we need to modify the simplest expression which we have shown in order to predict the behaviour of slightly more complex liquid solutions. We are going to deal with it in the next class.