Thermodynamics of Fluid Phase Equilibria
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Lecture - 43
Fugacity of liquid mixture – 2

Welcome back in this lecture; we will continue the discussion which we were you know working on particularly on the different reference state depending on the concentration of solute if it is not valid within the temperature range of the system.

In other word what we discussed was that you need to have a different reference state; if the solute for example, in liquid phase do not exist at the temperature of the solution because of the fact that solutes are critical temperature is all that you know is less than the temperature of this solution.

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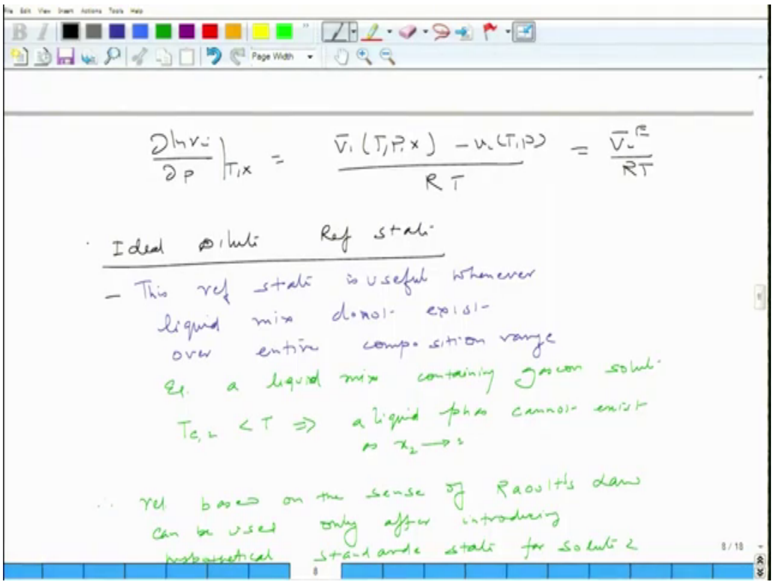

$$\left.\frac{\partial \ln \gamma_i}{\partial P}\right|_{T,x} = \frac{\bar{V}_i(T,P,x) - v_i(T,P)}{RT} = \frac{\bar{V}_i^E}{RT}$$

Ideal solution Ref state

- This ref state is useful whenever liquid mix do not exist over entire composition range

eg. a liquid mix containing gaseous solute

$T_{c,2} < T \Rightarrow$ a liquid phase cannot exist as $x_2 \to 1$

∴ ref based on the sense of Raoult's law can be used only after introducing hypothetical standard state for solute 2

So, this is what we were discussing last right; we are looking at the conditions that for solute let us say which is 2 if the liquid phase do not exist for the solute as solute concentration approaches towards 1, then you cannot make use of Raoult's law concept that would be a fictitious state because the solute at that temperature of the solution for composition closer to 1 would not be in a liquid phase.

And thus if you assume a pure state as a reference then that would be a fictitious state and in that case it is better to make use of Henry's laws concept.

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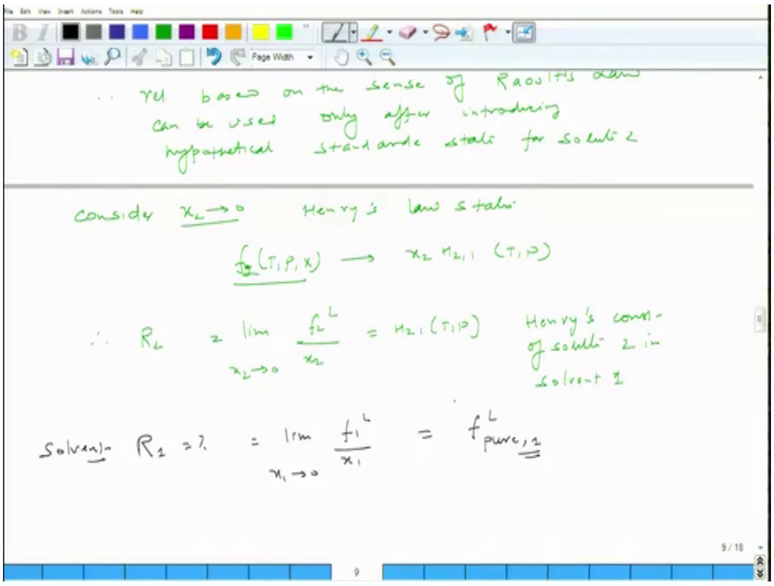

∴ ref based on the sense of Raoult's law can be used only after introducing hypothetical standard state for solute 2

consider $\underline{x_2 \to 0}$ Henry's law state

$$\underline{f_2(T,P,x)} \longrightarrow x_2 H_{2,1}(T,P)$$

$$\therefore R_2 = \lim_{x_2 \to 0} \frac{f_2^L}{x_2} = H_{2,1}(T,P)$$

Henry's const of solute 2 in solvent 1

$$\underline{\text{Solvent}} \quad R_1 = ? = \lim_{x_1 \to 0} \frac{f_1^L}{x_1} = f^L_{\text{pure},\underline{\underline{1}}}$$

So, this is what we say that you know Henry law for the case of composition which approaches towards 0; that means, extremely dilute solution you can consider the fugacity of the solute as proportional to the composition; that means, fugacity of solute is nothing, but equal to composition or the mole fraction of 2 multiplied by H to 1, which is nothing, but Henry's constant or solute 2 in solvent 1 ok.

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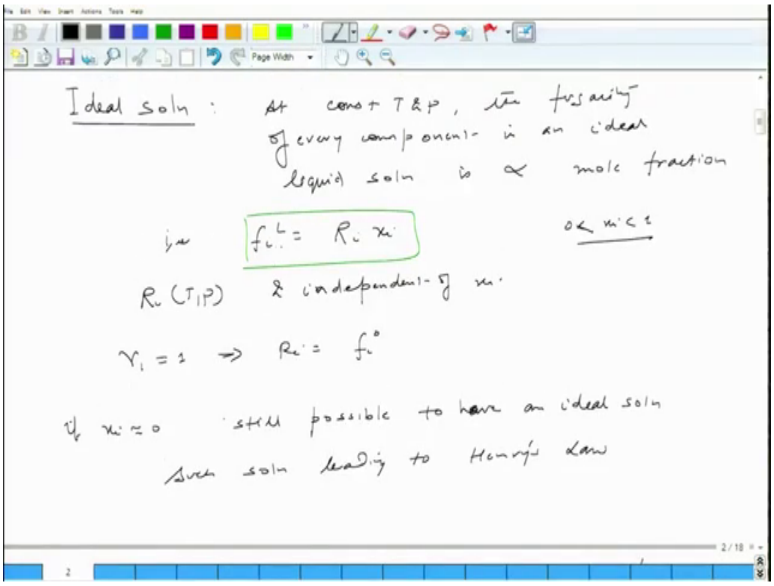

Ideal soln : At const T & P, the fugacity of every component in an ideal liquid soln is ∝ mole fraction

i.e. $\boxed{f_i^L = R_i x_i}$ $\underline{0 < x_i < 1}$

$R_i(T,P)$ & independent of x_i

$\gamma_i = 1 \Rightarrow R_i = f_i^{\circ}$

if $x_i \approx 0$ still possible to have an ideal soln

Such soln leading to Henry's Law

And then based on the concept of initial definition of your f which is this; which is nothing, but R i; x i for the case of the ideal solution where we assumed we have considered that f is proportional to x for all the case of ideal solution. Then R in the case of the Henry's law would be different from that of the Raoult's law and R in this case would be simply H 2 1 ok.

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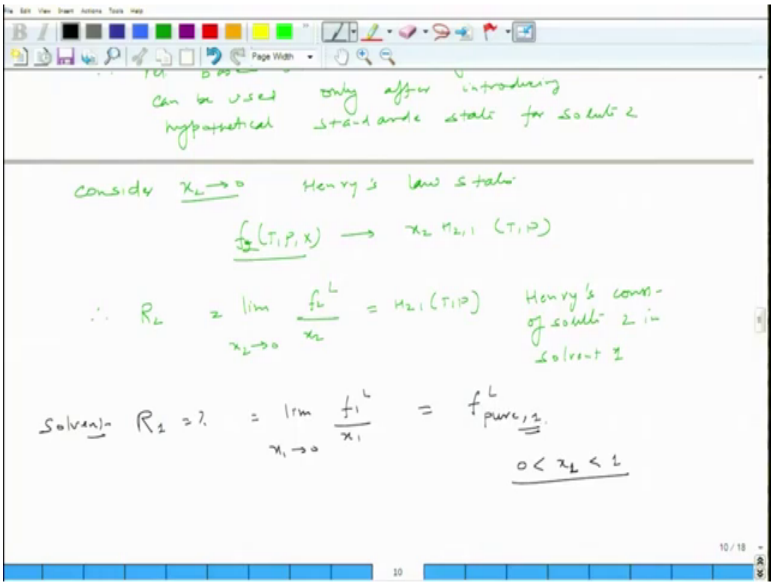

can be used only after introducing hypothetical standarde state for solute 2

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$$\underline{\text{Solvent}} - R_1 = ? = \lim_{x_1 \to 0} \frac{f_1^L}{x_1} = f^L_{pure,\underline{1}}$$

$$\underline{0 < x_1 < 1}$$

So, this is the definition, but; so, this was the case where the solute apparently does not remain in a liquid phase for the temperature of the solution because of the condition which you have already mentioned. But solvent would remain as it is in the liquid phase within the condition of the or within the temperature which we talked about.

So, in that cases; that means, the solution conditions or the solvent at this condition would remain in the liquid phase for this one from 0 to 1; in that case we will be looking at we will be considering the pure state of this solvent also as a reference state so; that means, we can make use of Raoult's law concept in this case and that is why R 1 would be simply f L pure 1 ok. So, now, I would like to connect this concept to the activity coefficient.

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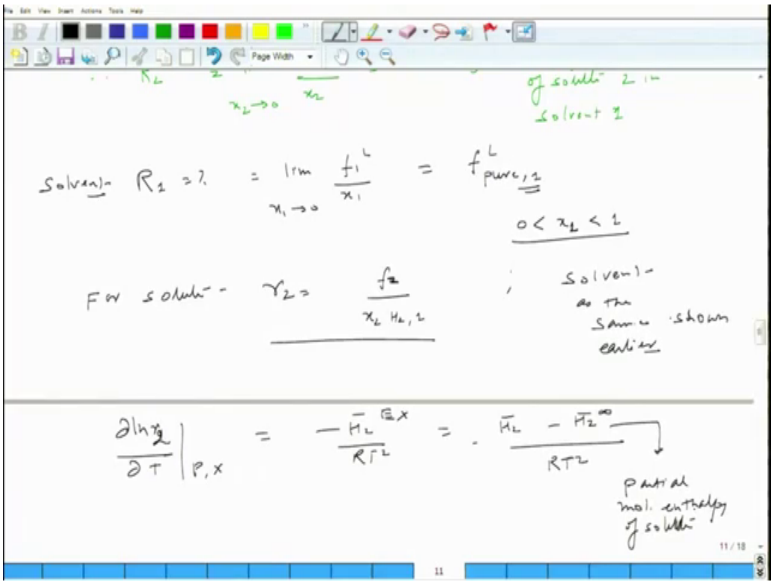

$x_2 \to 0$ x_2

of solute 2 in solvent 1

Solvent $R_1 = ? = \lim_{x_1 \to 0} \frac{f_1^L}{x_1} = f^L_{pure,1}$

$0 < x_2 < 1$

For solute $\gamma_2 = \frac{f_2}{x_2 H_{2,1}}$; solvent as the same shown earlier

$$\left.\frac{\partial \ln \gamma_2}{\partial T}\right|_{P,x} = -\frac{\bar{H}_2^{Ex}}{RT^2} = -\frac{\bar{H}_2 - \bar{H}_2^{\infty}}{RT^2}$$

partial mol. enthalpy of solute

So, for solute activity would be f 2 x 2 H 2 1 f 2 divided by the corresponding f for the pure limiting case; ideal solution. So, that will be your x 2 H 2 1; what would be for the case of solvent? Solvent would be the same as we talked about earlier. So, solvent will remain the same shown earlier, where it will be simply f 2 divided by f 1 in those cases solvent is 1 f L divided by x 1 f 1 pure ok.

Now, let us the pay attention to this part. So, if you take the derivative of this then we know this is defined by ok; now since here we will be considering the reference of the solution ideal solution for the case of gamma 2 would not be the case as we have to consider for the Raoult’s law concept; so, this will be your H 2 bar minus H 2 bar infinity ok.

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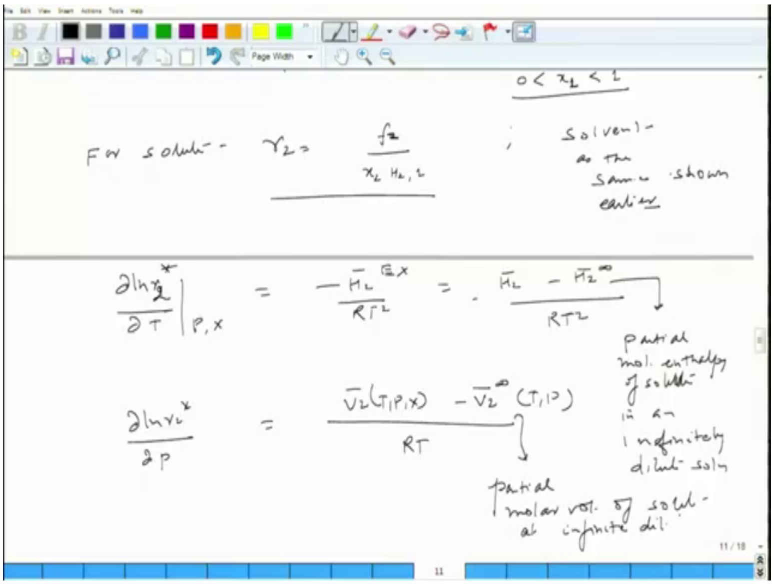

$0 < x_2 < 1$

For solute $\gamma_2 = \dfrac{f_2}{x_2 H_{2,1}}$; solvent as the same shown earlier

$$\left.\frac{\partial \ln \gamma_2^*}{\partial T}\right|_{P,x} = -\frac{\bar{H}_2^{Ex}}{RT^2} = -\frac{\bar{H}_2 - \bar{H}_2^{\infty}}{RT^2}$$

partial mol. enthalpy of solute in an infinitely dilute soln

$$\frac{\partial \ln \gamma_2^*}{\partial P} = \frac{\bar{V}_2(T,P,x) - \bar{V}_2^{\infty}(T,P)}{RT}$$

partial molar vol. of solute at infinite dil.

Now, considering that we are looking at the reference as a partial molar enthalpy of solute in an infinitely dilute solution. So in order to distinguish this from the earlier definition of the Raoult's law concert, where we consider simply the pure solution where it was simply H 0; so, in order to distinguish from that definition we are going to put this as star which indicates that this is with reference to the dilute solution compared to the pure solvent or pure fluid.

So, for the case of the pure fluid as a reference; we will making use of the earlier definition that would be from the Raoult's law constants of application. Whereas, if you consider dilute solution that this would be Henry's law you know based on Henry's law concept, but then we will be trying to distinguish this with a star in order to differentiate come with other definition.

Now, similarly I can make use of the corresponding definition for excess volume where this will be del ln gamma 2 star divided by del P or del by del P; that means, you are taking the partial derivatives; derivative of del log gamma 2 with respect to P, star indicates that we are going to take the reference of dilute solution T P R T, where this is the partial molar volume of solute at infinite dilution ok.

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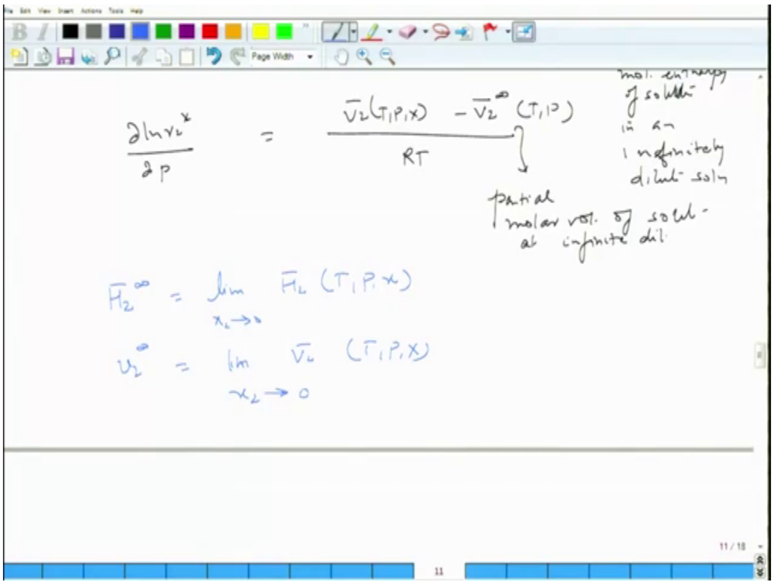

$$\frac{\partial \ln \gamma_2^*}{\partial P} = \frac{\bar{V}_2(T,P,x) - \bar{V}_2^\infty(T,P)}{RT}$$

mol. enthalpy of solute in an infinitely dilute soln

partial molar vol. of solute at infinite dil

$$\bar{H}_2^\infty = \lim_{x_2 \to 0} \bar{H}_2(T,P,x)$$

$$V_2^\infty = \lim_{x_2 \to 0} \bar{V}_2(T,P,x)$$

So, note that this H 2 infinity is nothing, but limit x 2 goes to 0; H 2 bar T P x and similarly v 2 infinity is limit V 2 bar T P x ok. So, this is the case for the solute which is in extremely usually dilute conditions, but the more important thing is that at the temperature the pure saw solute in liquid phase is non-existent.

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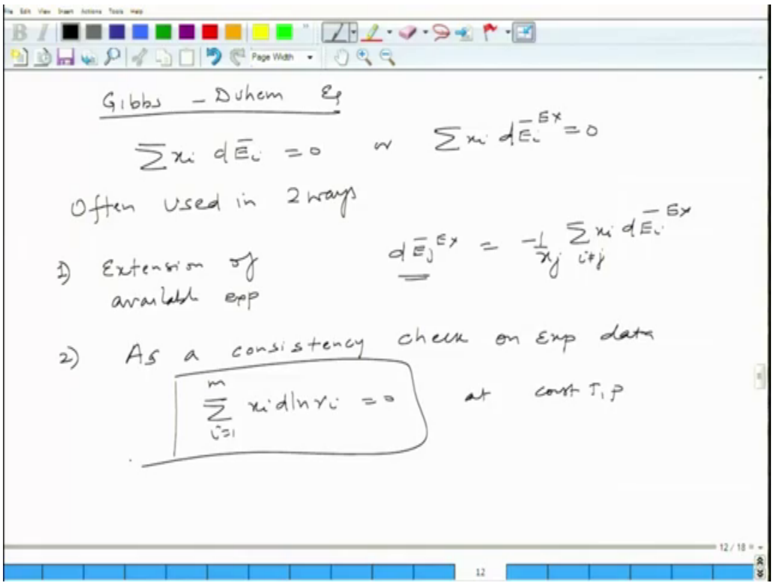

Gibbs – Duhem Eq

$$\sum x_i \, d\bar{E}_i = 0 \quad \text{or} \quad \sum x_i \, d\bar{E}_i^{Ex} = 0$$

Often used in 2 ways

1) Extension of available exp

$$d\bar{E}_j^{Ex} = -\frac{1}{x_j} \sum_{i \neq j} x_i \, d\bar{E}_i^{Ex}$$

2) As a consistency check on exp data

$$\boxed{\sum_{i=1}^{m} x_i \, d\ln \gamma_i = 0} \quad \text{at const } T, P$$

We should remember is about Gibbs Duhem equation which tells us that summation x i d E i is 0 and this we can write also in excess property d i E i E x is equal to 0 ok.

Now, we often use in two ways; so, often we use this expression in two ways. First is we can use extension of available data of available experimental data ok; such that we can connect you using this we can evaluate the other expressions where a is i is not equal to j, but most commonly we use this expression to check the experimental data in other word we check the consistency check as or this particular expression use is used as a consistency check on experimental data ok.

So, if you use replace E by g then this would be xi d g i re x here this one and we can rewrite this expression as x i d l n gamma i i is equal to 1 to m equal to 0 at constant T and P. So, this is most commonly used expression to check whether data are in fact, consistent. So, we will be trying to do some extra examples in the next lecture ok.

So, now let me again come back go back to the to the activity coefficients which we have evaluated depending on two conditions. One the solute was considered with reference to the Henry's law sense and solvent in the sense of Raoult's law. So, let us look at how do you try to correlate this understand this a bit more in detail.

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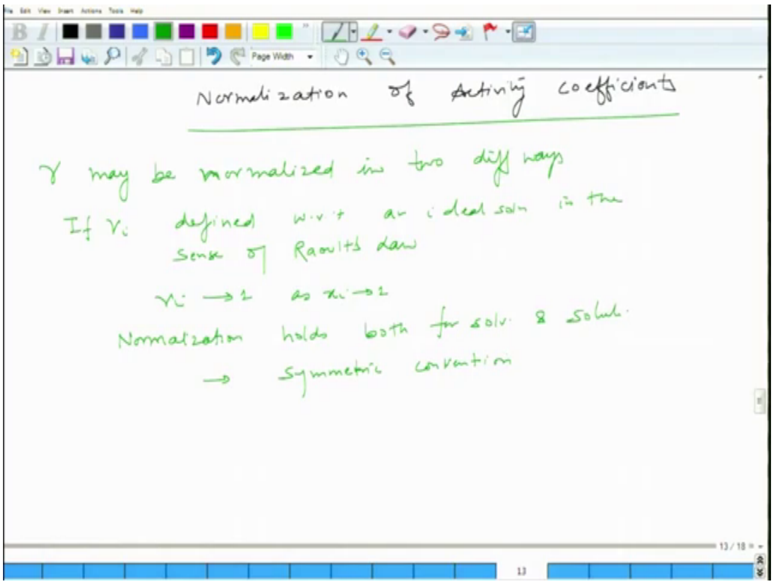

Normalization of Activity coefficients

γ may be normalized in two diff ways

If γ_i defined w.r.t an ideal soln in the sense of Raoult's law

$\gamma_i \to 1$ as $x_i \to 1$

Normalization holds both for solv. & solut.

$\to$ Symmetric convention

So, we call this as normalization of activity coefficient ok. Now considering this we are using gamma which is activity it can be normalized in two different ways ok. So, if gamma i are defined; so, with respect to an ideal solution in the sense of Raoult's law. In other word gamma i goes to 1 as x i equal to 1.

So, if you are using this then both solvent and solute or we because this will hold for both solvent and solute; then normalization in such case holds both for solvent and solute. And this would be something we will call it as symmetric convention, the problem comes in when you have a symmetric convention.

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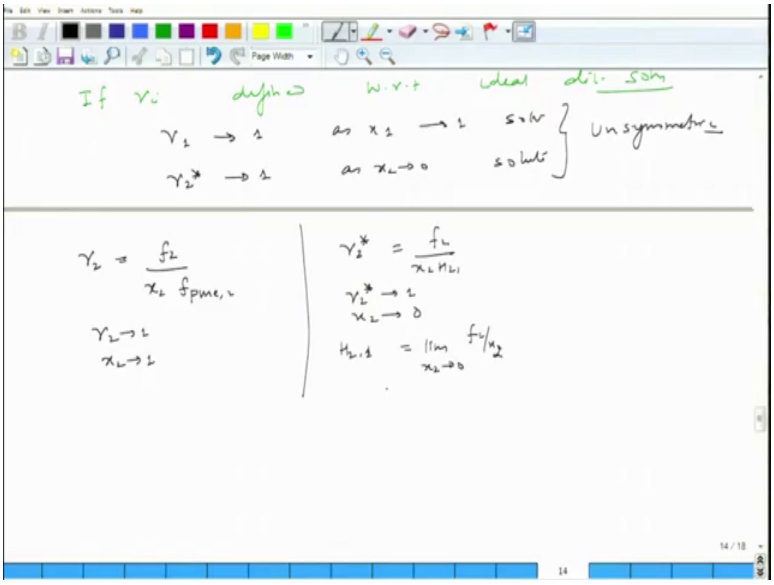

If γ_i defined w.r.t ideal dil. soln

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

$\gamma_2^* \to 1$ as $x_2 \to 0$ solute

Unsymmetric

$$\gamma_2 = \frac{f_2}{x_2 f_{pure,2}}$$

$\gamma_2 \to 1$

$x_2 \to 1$

$$\gamma_2^* = \frac{f_2}{x_2 H_{2,1}}$$

$\gamma_2^* \to 1$

$x_2 \to 0$

$$H_{2,1} = \lim_{x_2 \to 0} f_2/x_2$$

In other word that if gamma i is defined with respect to ideal dilute solution. Now in that case we already have discussed that gamma 1 which is a solvent goes to one as x 1 goes to 1 and gamma 2 star goes to 1 as x 2 goes to 0 ok. So, this is your solvent and this is your solute; so, this is this expert or this particular case would be unsymmetric ok.

So, remember that you know star is to indicate that this is with reference to the dilute solution for the case of solute ok. Let us first connect this thing to activity coefficient gamma 2; if you had used the Raoult's law concept then this would have been simply like this ok, where gamma 2 goes to 1 as x 2 goes to 1; so, this is the basically Raoult's law a concept.

On the other hand, for the ideal dilute solution is a reference if this would be f 2 x 2 H 2 1; that means, gamma 2 star goes to 1 as x 2 goes to 0 in other word gamma 2 1 is limit x 2 goes to 0 f 2 by x 2. So, this is based on the; so, Henry's law; that means, this is for the symmetric convention, this is un-symmetric or asymmetric convention. So, I can actually draw down this function; so, let me try to draw ok.

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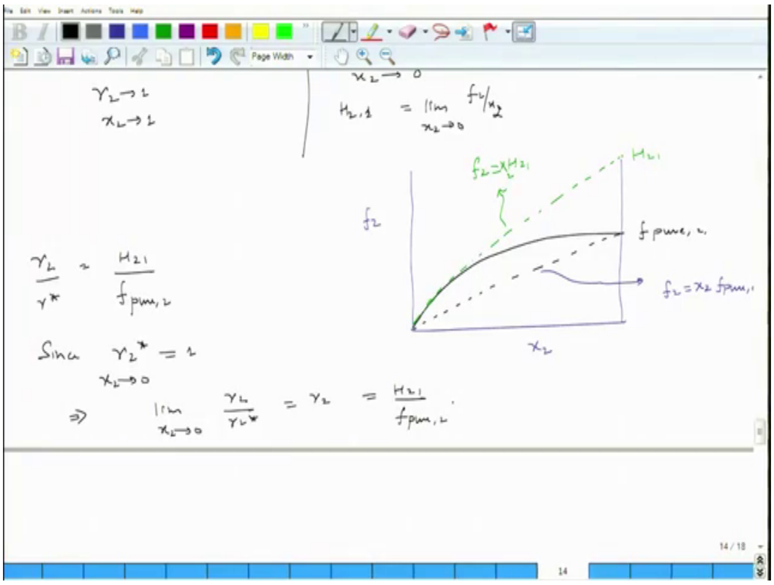

$\gamma_2 \to 1$
$x_2 \to 1$

$x_2 \to 0$

$H_{2,1} = \lim_{x_2 \to 0} f_2/x_2$

$$\frac{\gamma_2}{\gamma^*} = \frac{H_{21}}{f_{pure,2}}$$

$$\text{Since } \gamma_2^* = 1 \quad x_2 \to 0$$

$$\Rightarrow \lim_{x_2 \to 0} \frac{\gamma_2}{\gamma_2^*} = \gamma_2 = \frac{H_{21}}{f_{pure,2}}.$$

So, this is f 2 as a function of x 2 alright. So, let us say this is your this is the data we have this would be f pure 2. So, if you had to use the ideal mixture there is Raoult’s law constant then this is going to be this. So, this one is f 2 as x 2 f u 2.

On the other hand, if you use the ideal dilute mixture then this will be your H 2 1 and this expression is f 2; H 2 1 x 2. So, this is the how it looks like when you use different conventions here. So, how do you correlate gamma 2 with respect to gamma 2 star or vice versa; so, let us try to now connect these two.

So, let us try to first take the you know we divide it this expression gamma 2 which we have written here it is true. So, this would going to be H 2 1 divided by f of pure 2. Now since gamma 2 goes to goes to 1 for the case of x 2 approaches to 0; in that case your limit gamma 2 by gamma 2 star; x 2 up to 0 is nothing, but gamma 2 and this going to be H 2 1 divided by f of pure 2 ok.

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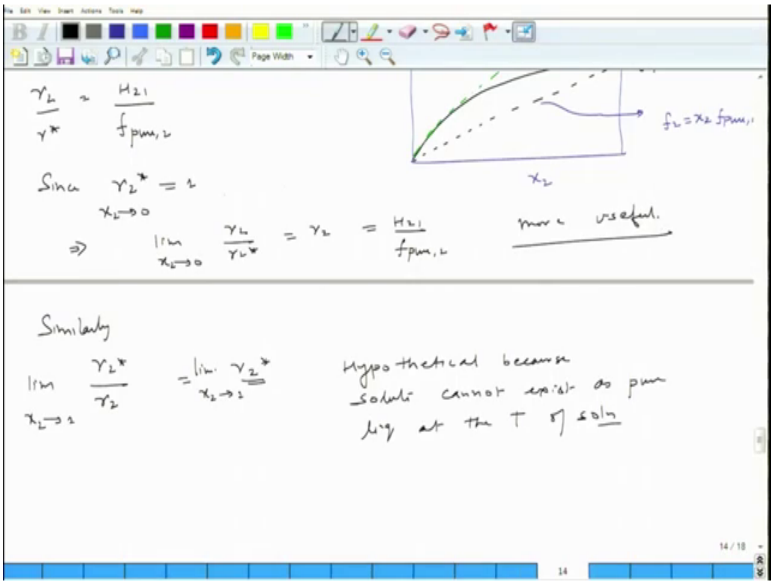

$$\frac{\gamma_2}{\gamma^*} = \frac{H_{21}}{f_{pure,2}}$$

Since $\lim_{x_2 \to 0} \gamma_2^* = 1$

$$\Rightarrow \lim_{x_2 \to 0} \frac{\gamma_2}{\gamma_2^*} = \gamma_2 = \frac{H_{21}}{f_{pure,2}}$$ more useful.

Similarly

$$\lim_{x_2 \to 1} \frac{\gamma_2^*}{\gamma_2} = \lim_{x_2 \to 1} \underline{\underline{\gamma_2^*}}$$

Hypothetical because solute cannot exist as pure liq at the T of soln

So, similarly what we can do is also the other way around where that we have gamma 2 star divided by gamma 2. And we consider limit of x 2 goes to 1 in that cases gamma 2 star limit x 2 goes to 1; now in this case this is kind of a hypothetical because solute cannot exist right as pure liquid at the temperature of the solution ok.

So, this is more actually useful the purpose of this exercise was to compare these two expression and to appreciate the reason for why we had to take different reference state. And you can connect this, you can normalize it with respect to each other if you want, but of course, for the case of this when x 2 approaches one; this would become a hypothetical state ok.

Now, let me move forward and now focus on activity coefficient calculations from excess property of binary mixtures.

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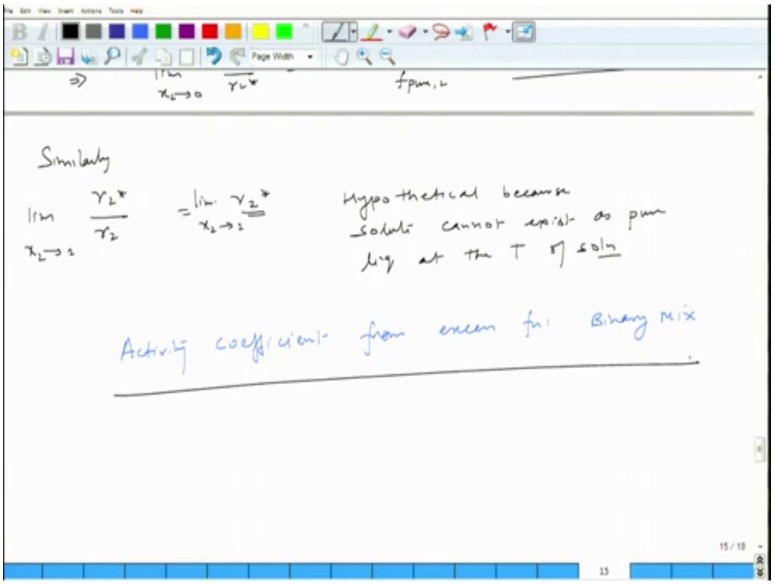

Similarly

$$\lim_{x_2 \to 1} \frac{\gamma_2^*}{\gamma_2} = \lim_{x_2 \to 1} \underline{\underline{\gamma_2^*}}$$

Hypothetical because solute cannot exist as pure liq at the T of soln

Activity coefficient from excess fn: Binary mix

So, let us now focus on activity coefficient from excess function and here we will be looking at only binary mixtures ok.

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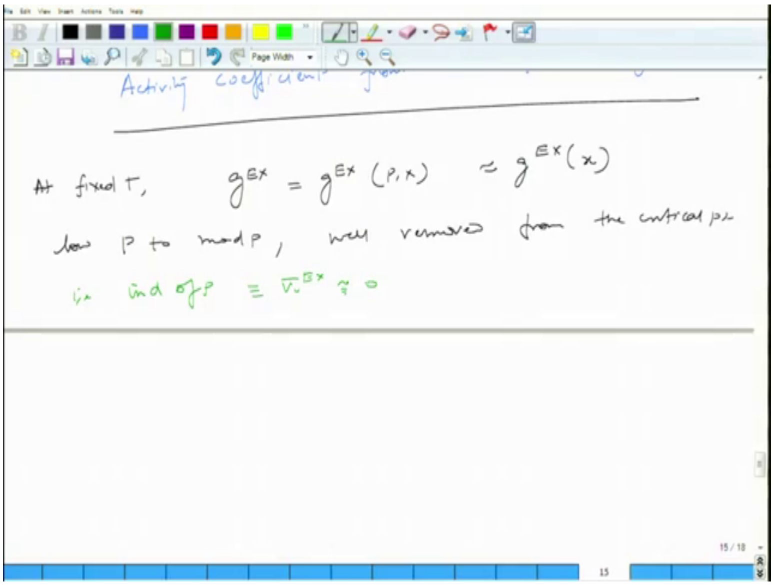

Activity coefficient

At fixed T, $g^{Ex} = g^{Ex}(P, x) \approx g^{Ex}(x)$

low P to mod P, well removed from the critical pt

i.e. ind of P $\equiv \bar{V}_i^{Ex} \approx 0$

So, let us consider for constant temperature or fixed T; we will be looking at E E x or we will be looking at g Ex as gx function of P and X pressure and composition. Now considering low pressure to moderate pressure and well removed from the critical point ok, we can approximate this as simply gx as a function of composition.

So, what we are saying is that that this condition; this will be independent of pressure which essentially means V i E x is approximately 0 now we will be considering a binary liquid mixture.

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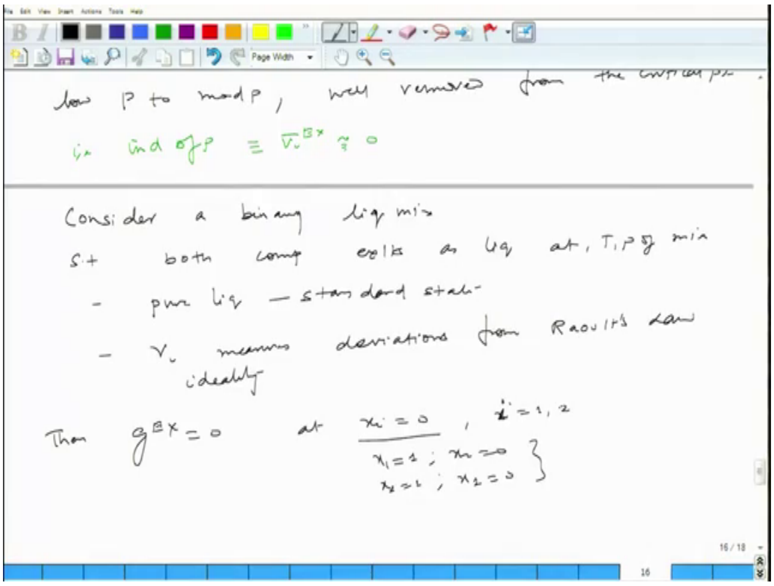

low P to mod P, well removed from the critical pt.

i.e. ind of P $\equiv \bar{V}_i^{Ex} \approx 0$

Consider a binary liq mix

s.t both comp exits as liq at, T, P of mix

- pure liq — standard state
- γ_i measures deviations from Raoult's law ideality

Then $g^{Ex} = 0$ at $x_i = 0$, $i = 1, 2$

$\left.\begin{matrix} x_1 = 1 ; x_2 = 0 \\ x_2 = 1 ; x_1 = 0 \end{matrix}\right\}$

So, consider a binary liquid mixture such that both the components exist as they could face at T and P of mixture. So, they can exist; that means, essentially we can consider pure liquid as a standard state ok.

So, in that case we can make use of gamma in the sense of Raoult's law and; that means, gamma measures deviation from the Raoult's law identity from the Raoult's law identity ok. Now, given this the g E is a function of x and both the components in the liquid can exist as a pure phase, which essentially means there is a limiting conditions or boundary conditions for such a function.

So, g Ex should be 0 at x i is equal to 0 the then where x is where i is 1 and 2 which essentially means when x 1 goes to 1; g Ex must be 0 because you have approached a pure liquid. Similarly when x 2 is equal to 0 or when x 2 is basically approaches towards 1 then also you have a pure liquid phase ok.

So, you can write in terms of when x 1 equal to 1; this means x 2 is equal to 0 and when x 2 is equal to 1 which essentially means x 1 equal to 0 ok. So, in such a case your g Ex must be equal to 0. So, that is what we wrote in a much simpler form that x i equal to 0 where i is 1 and 2. So, what is the simplest model we satisfy such a condition?

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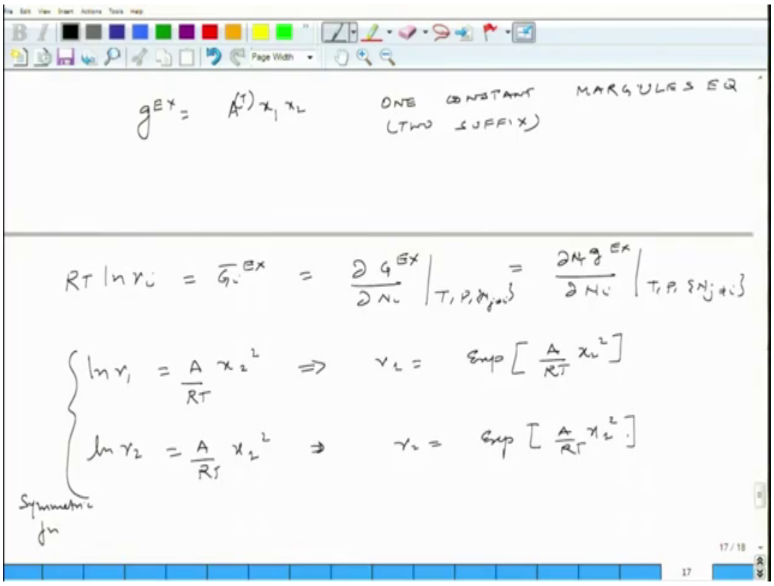

$g^{EX} = A^{(1)} x_1 x_2$ ONE CONSTANT (TWO SUFFIX) MARGULES EQ

$$RT \ln \gamma_i = \bar{G}_i^{EX} = \left.\frac{\partial G^{EX}}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \left.\frac{\partial N g^{EX}}{\partial N_i}\right|_{T,P,\{N_{j\neq i}\}}$$

$$\left\{\begin{array}{l} \ln \gamma_1 = \frac{A}{RT} x_2^2 \Rightarrow \gamma_1 = \exp\left[\frac{A}{RT} x_2^2\right] \\ \ln \gamma_2 = \frac{A}{RT} x_2^2 \Rightarrow \gamma_2 = \exp\left[\frac{A}{RT} x_2^2\right] \end{array}\right.$$

Symmetric fn

So, simplest model is g E x is a some constant multiplied by x 1 and x 2 ok. So, this is a simple model, which satisfy this condition and this is called one constant Margules equation ok. So, one constant or two suffix ok; so, in this what is a is some constant which is a basically a function of temperature and it has a unit of energy.

Now, what I can do is; I can little bit try to make use of the other definitions and connect this expression to the activity coefficient. So, we know that R T ln gamma i is G i x right which is nothing, but del g x divided by del N i at constant T P and all other and j is constant right.

Now, I can write this expression also in terms of molar excess Gibbs energy g Ex and multiply the total number of moles alright. Now, from here what we can do is we can show without going to more details that using these expressions and plugging this value I should be able to come up with this final expressions A by R T and here is going to be x 2 square and this is ln gamma 2 A by R T x 1 square ok.

So, you just have to plug in this expression here and essentially you can do the differentiation and you should be able to get it. Now do note that this is nothing, but symmetric function from here I can get gamma 1 which is exponential A by R T x 2 square and this is your gamma 2 which is exponential A by R T x 1 square ok.

Now, this kind of model is very simple model, but it is a very good representation of simple system such as for example, argon and oxygen or similar size similar kind of molecular structures.

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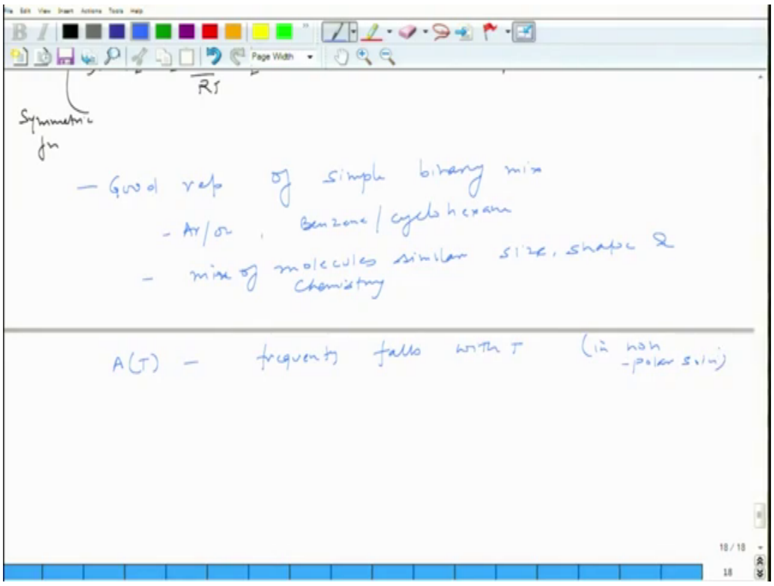

RT

Symmetric fn

— Good rep of simple binary mix

- Ar/O_2 , Benzene / cyclohexane

- mix of molecules similar size, shape & chemistry

A(T) — frequently falls with T (in non-polar soln)

So, this is a good representation for simple binary mixture ok; such as argon oxygen, benzene cyclohexane. They are similar size, similar shape, similar chemistry ok; so, mixture of molecules of similar size, shape and chemistry for such a system one constant Margules equation turns out to be pretty good ok.

Now, what about A in this equation? A is a function of temperature and it frequently falls with temperature. So, if you increase the temperature A decreases in non-polar solution; so, now let me just try to draw this function.

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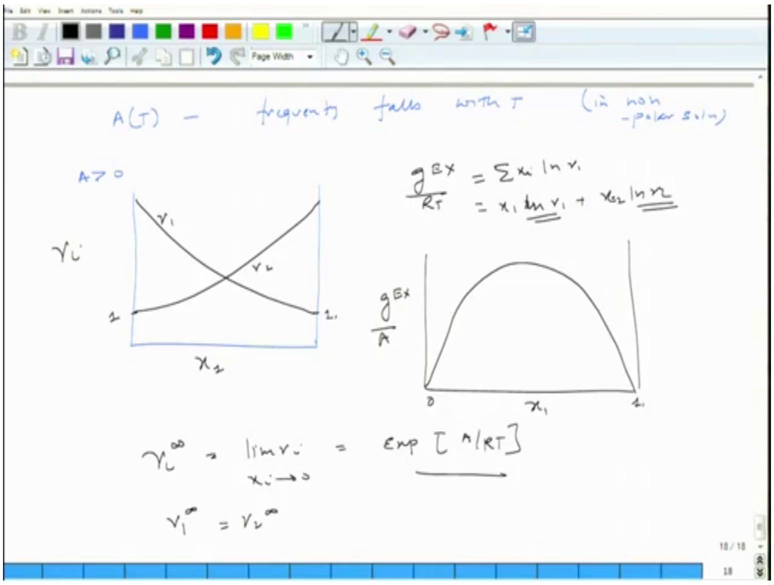

A(T) – frequently falls with T (in non-polar soln)

$$\frac{g^{Ex}}{RT} = \sum x_i \ln \gamma_i = x_1 \underline{\underline{\ln \gamma_1}} + x_2 \ln \underline{\underline{\gamma_2}}$$

$$\gamma_i^{\infty} = \lim_{x_i \to 0} \gamma_i = \underline{\exp[A/RT]}$$

$$\gamma_1^{\infty} = \gamma_2^{\infty}$$

Let us assume that A is greater than 0 and this is your gamma i as a function of x 1. So, since there is a limiting case; so, the gamma 2 will be like this, gamma 1 will be like this because it is symmetric this would be 1, this would be 1 for gamma 1 and this will be gamma 2.

Now, you can also write this g Ex by R T which will be if you look at the expression this will be your summation x i l n gamma i; this is going to be x 1 l n gamma 1 plus x 2 l n gamma 2. And you can draw that also after replacing this because this is nothing, but A by R T x 2 square and this is your A by R T x 1 square ok. So, thus you can come up with an expression where you can plot such a value here. And this would turn out to be something like this from 0 to 1; so, this is for very simple case alright.

Now, there is another thing which you can come up with this one constant Margules equation; gamma R infinity which is a limit gamma i; x i goes to 0 it would be same for both the solvent and solute ok. So, in other word gamma 1 infinity is gamma 2 infinity. So, note that here the value of a can be greater than 0 or less than 0, but here for this representation we have considered a greater than 0 ok.

Now, in practice such mixtures what we have looked into very rare; the majority of the mixtures and solutions are very complex. And in that case we must consider different kind of models which are more in number of parameters; which captures a different kind of interactions such as hydrogen bond and dissimilarity in the shape and size and so, forth.

So, I will be looking into that; I will be discussing such a those kind of equations, those kind of models in the next lecture along with some examples.

So, that will be this will be the end of the lectures. So, I will see you next week.