Thermodynamics of Fluid Phase Equilibria
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Lecture – 48
Theories of Solution – I

Welcome back in this lecture I will be discussing theories of solution. So, ok, so what is the aim of solution theory?

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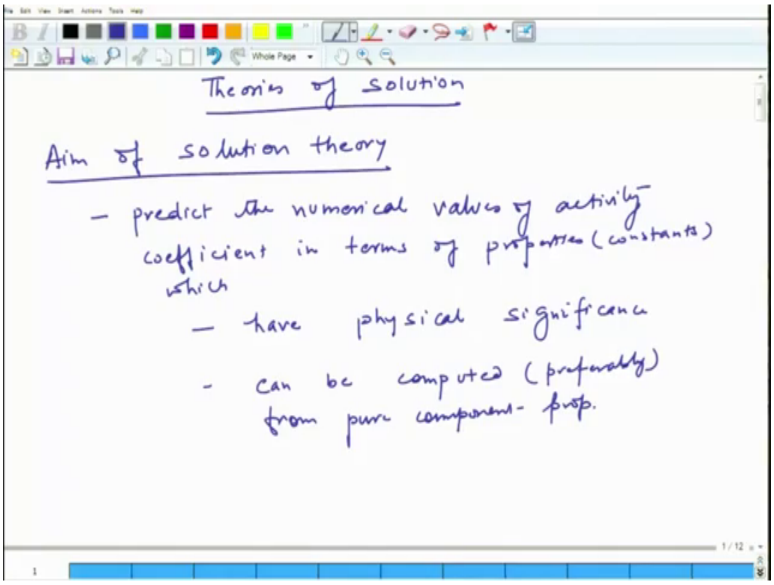

Theories of Solution

Aim of solution theory

- predict the numerical values of activity coefficient in terms of properties (constants) which
  - have physical significance
  - can be computed (preferably) from pure component prop.

So, basically if you already seen some of those theories such as Margules equation that is one such solution theory similarly we will discuss a little bit more about others, but there is a fundamental way it has been derived. And all of them have this similar aim the aim is basically to predict the numerical values of activity coefficient in terms of properties or some kind of constants which must have some physical significance of physical property associated with it ok.

So, the properties which are related to activity coefficient I should have some physical significance and should be rather preferably be computed preferably from pure component properties ok. So, this is basically the major aim of solution theory. Of course, there are various different theories which we will see all exist in today's set of solution theories.

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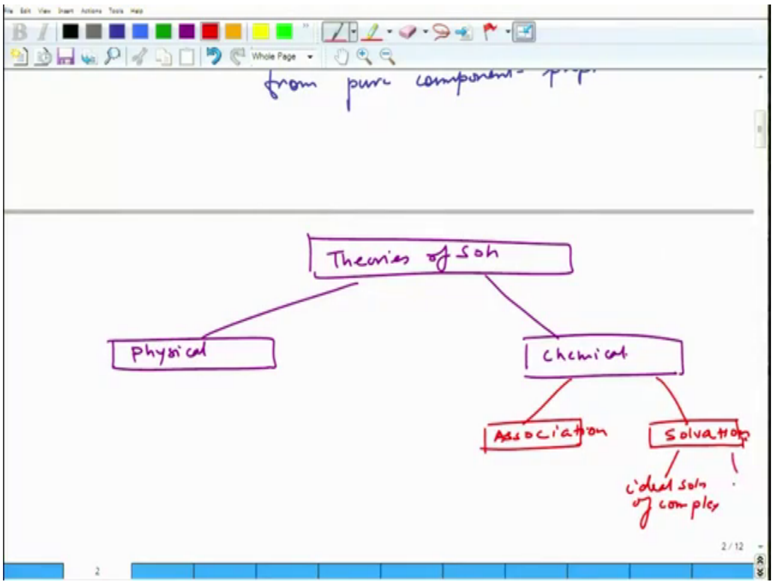

Now, you can segregate these kind of theories in two form, one which has a basis of physical interactions ok. So, I can differentiate the theories based on the concept of physical interaction, other is based on chemical in nature chemical interactions such as like bonding and salvation.

So, within this type of theories you have other kind of sub topics such as association which are theories which are based on associating nature of the fluid salvation. So, within salvation you can have ideal solution of complexes.

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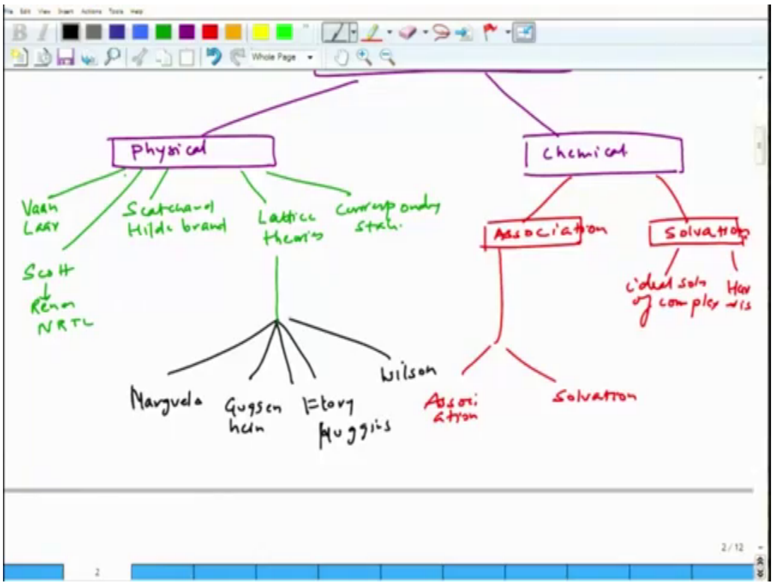

And this is another one is Henry's theory ok. And in case of association you have basically divided into two part one is basically association another again you can have salvation kind of concept in that. We are not going to discuss chemical type of theories ok, its altogether exhaustive analysis and I would like to avoid that we can just focus on the theories which have physical type and Margules was one of the example which we have looked into earlier.

So, here you can have many different theories Van Laar, Scatchard Hilderbrand and there is a large set of theories which are based on lattice theories and you have corresponding state ok. And then you have this another one which is a Scott and Renon NRTL, non random is one of the example NRTL. And lattice theory has many different possibilities or the different theories which has come up with. So, Margules is one and this Guggenhein then this Flory Huggin's and this Wilson ok.

Now, as you can see that it is exhaustive in terms of the number of theories and of course, I cannot cover everything within this theory as a solution, but what we can do is we can illustrate one or two theories to get an idea how it has been derived. And so one of the two popular theories which we are going to look at is Van Laar and particularly Scatchard Hildebrand and later on I am going to discuss the polymer solution there I will look into the Flory Huggin's theories ok.

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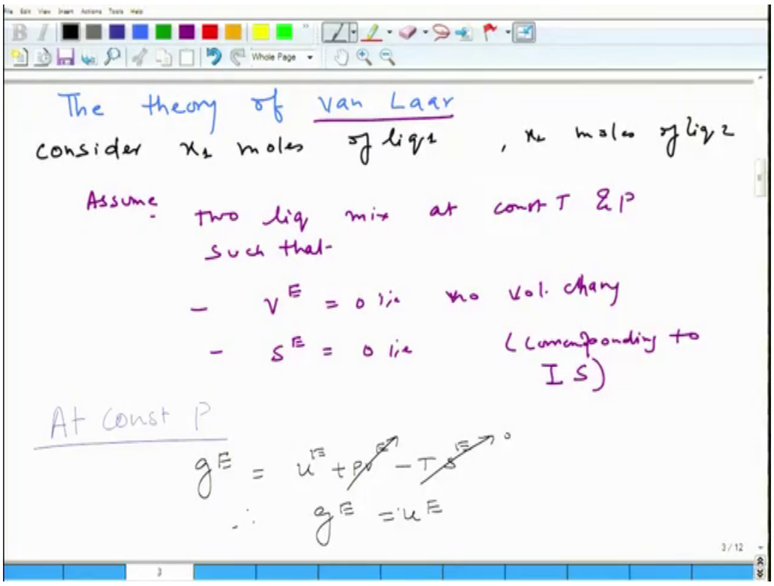

The theory of Van Laar

consider x_1 moles of liq 1 , x_2 moles of liq 2

Assume: two liq mix at const T & P such that

- $v^E = 0$ i.e no vol. chang
- $s^E = 0$ i.e (corresponding to I S)

At const P

$$g^E = u^E + \cancel{pv^E}^{\,0} - T\cancel{s^E}^{\,0}$$

$$\therefore \; g^E = u^E$$

So, let me start with the Van Laar theory ok. So, consider let us say x 1 moles ok, mole fraction of liquid 1 and x 2 of liquid 2 ok. And what we are assuming in this case as far as Van Laar is concerned is the two liquid which has liquid 1 and liquid 2 mixes at constant temperature and pressure such that such that excess volume 0 that is there is no change or there is no volume change and S E excess entropy is 0 that is entropy of mixing is 0 which corresponds to ideal solution ok. So, in such case at constant P we can consider g of E as u plus P v minus T S, since its x s E I am going to put here.

Now, with this assumption this is going to be 0, this is going to be 0. So, therefore, g E is equal to u E n and u E in this case would be nothing, but delta u change in u, when two liquids are mixed at temperature and pressure.

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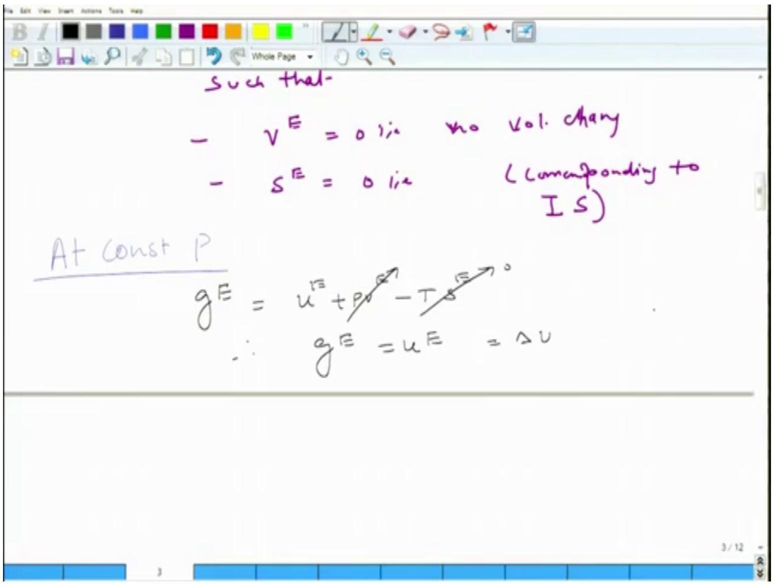

such that

- $v^E = 0$ i.e. no vol. chang
- $s^E = 0$ i.e. (corresponding to I S)

At const P

$$g^E = u^E + P\cancel{v^E}^{\,0} - T\cancel{s^E}^{\,0}$$

$$\therefore g^E = u^E = \Delta U$$

So, let us first consider how this mixing would be thermodynamically path can be considered for this particular mixing of two liquids ok.

So, we will be looking at 3 different stages where we can bring the liquid from almost ideal gas, mix the ideal gas and then later on compress it to the liquid. So, that will become the liquid mixture. So, let me just schematically represent that in order to explain it.

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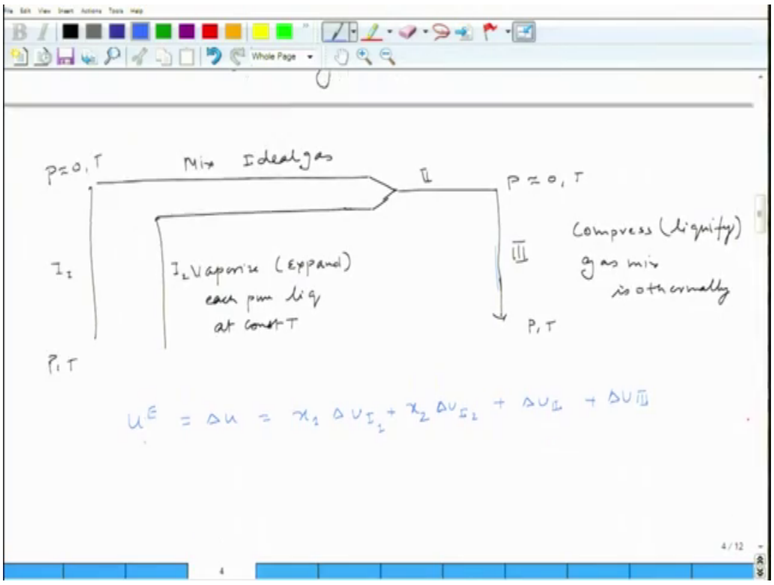

$$u^E = \Delta u = x_1 \Delta u_{I_1} + x_2 \Delta u_{I_2} + \Delta u_{II} + \Delta u_{III}$$

So, you have two liquids ok. So, let us say this is at P and T both at P and T all right, and you take this liquid 1 to extremely small pressure keeping the temperature constant making it to be ideal gas and then you mix this pour this liquid 1 and 2 which are now, ideal gas at low very pressure goes to almost 0; that means, you are vaporizing each pure liquid at constant temperature or expand, and I am going to represent this as I one first one first path 2, and here we are going to mix it somewhere here. So, this is mixing occur. So, mix ideal gas ok.

So, this is mixing is this is again at 0 to keep it temperature T and then from here we are going to compress it. So, you compress or liquefy this gas mixture at constant temperature; that means, isothermally and this I am going to define as third path to get the liquid mixture at P and T. Now, in this process what is the change in the what is the basically g axis or u axis or delta u.

So, u x s or delta u is going to be the mixing of here in this path that is from P T to P equal to 0 T, ok. So, I am going to add this and since it has x 1 moles fractional in general we can wait this changes in the energy. So, this is x 1 times delta u 1 2 that is that means, this one ok, plus x 2 delta u of this path plus delta u for this mixing of the ideal gas plus delta u of this path ok. So, you have this component which you need to evaluate in order to get u axis ok.

So, what I am going to do now, next is let us consider step one ok. So, step one was to vaporize isothermally.

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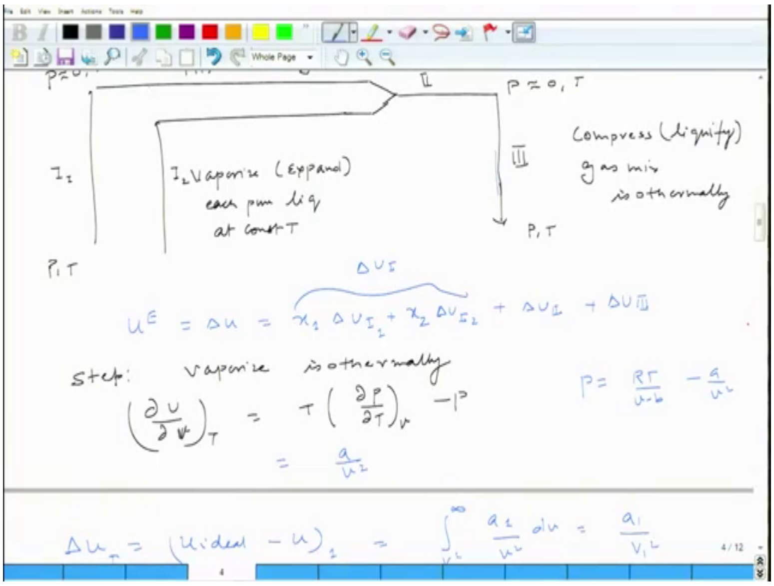

$$u^E = \Delta u = \overbrace{x_1 \Delta u_{I_1} + x_2 \Delta u_{I_2}}^{\Delta u_I} + \Delta u_{II} + \Delta u_{III}$$

step: vaporize isothermally

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P \qquad P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$= \frac{a}{v^2}$$

$$\Delta u_{I} = (u_{ideal} - u)_1 = \int_{v_L}^{\infty} \frac{a_1}{v^2}\, dv = \frac{a_1}{V_1^L}$$

So, let us consider the basic relations of the partial derivative of internal energy with respect to the volume at constant temperature, is nothing but this. So, this you can show you have done this kind of exercises earlier in the course. So, we use this because at the end what we are doing is we are changing the volume because we are expanding. So, we need the change in the internal energy with respect to the change in the volume and that is related to the partial derivative of the pressure and temperature. Now, at this point you need some kind of equation of state and this is where when the unfortunately took the van der Waal equation of state ok.

So, if you consider a van der Waal equation of state; and if you are wondering why he had to take the van der Waal equation of state because van der was a collaborative van der Waal. So, if you use this equation of state then this particular expression will turn out to be a by v square, ok. Now, you can integrate this delta u, u ideal minus u of the first liquid is going to be v L 1 infinity a 1 indicate that its basically liquid 1 and this is going to be a, this is going to be a by v 1 ok.

So, this is the expression of delta u. So, this will be your delta v u. Now, similarly you can get for delta u I 2 that will be your a 2 v 2 L ok.

Now, you need this term which will be your delta u 1 that is combining this both vaporization or the liquid. Now, I can combine this.

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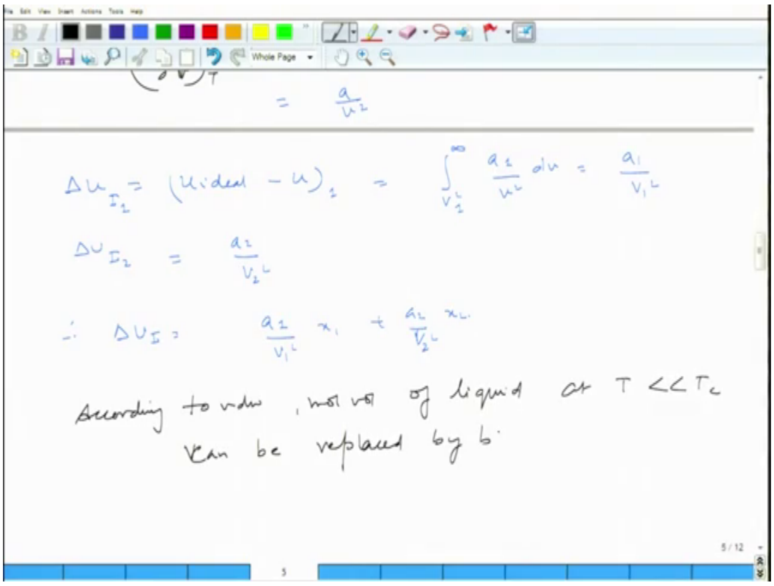

$= \frac{a}{v^2}$

$\Delta u_{I_2} = (u_{ideal} - u)_2 = \int_{V_2^L}^{\infty} \frac{a_2}{v^2}\, dv = \frac{a_1}{V_1^L}$

$\Delta U_{I_2} = \frac{a_2}{V_2^L}$

$\therefore \Delta U_I = \frac{a_1}{V_1^L} x_1 + \frac{a_2}{V_2^L} x_2$

According to vdw, mol vol of liquid at $T << T_c$ can be replaced by b

Therefore delta u 1 is a 1 v 1 L x 1 plus a 2 v 2 L and x 2. Now, according to the van der Waal theory molar volume of liquid below T such that you know at T such that, so that T is much much less than T c then the molar volume at T can be replaced by b ok.

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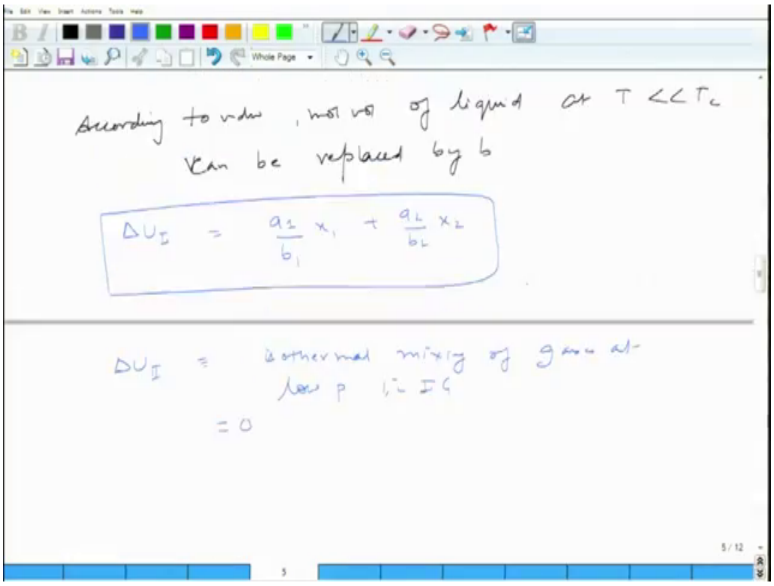

According to vdw, mol vol of liquid at $T << T_c$ can be replaced by b

$$\boxed{\Delta U_I = \frac{a_1}{b_1} x_1 + \frac{a_2}{b_2} x_2}$$

ΔU_{II} = isothermal mixing of gases at low p i.e IG

$= 0$

So, considering that I can now, write this expression ok. So, this is for delta u 1 what about delta u 2 which is basically corresponding to the isothermal mixing of gases at low pressure that is basically nothing, but ideal gas. So, ideal gas mixing at a constant temperature the changes in the internal energy should be nothing but 0, ok.

So now, what remains is basically the third part which is this. So, here we are going to compress it from low pressure to the pressure of the system and in the similar way as we have done we will be using this ok, but instead of v 1 infinite we want to infinity will be infinity to b and a will be now a mix and v mix. So, let me just write down here.

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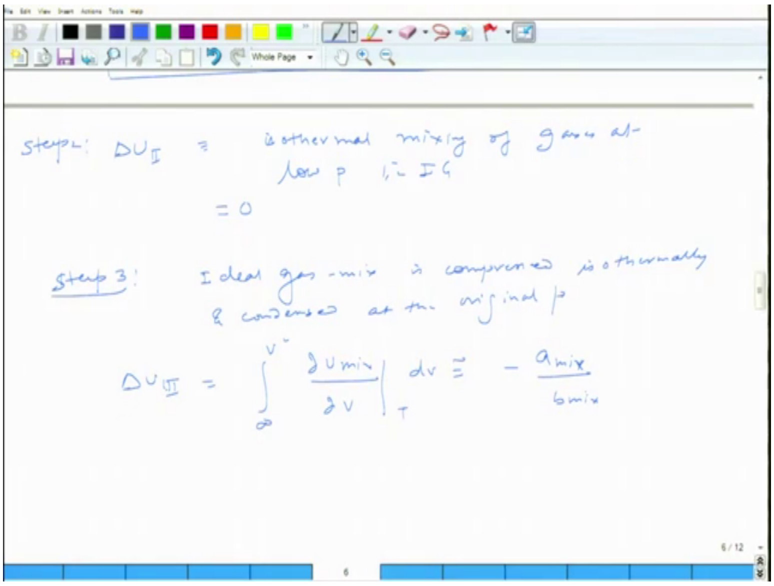
step 2: ΔU_{II} = isothermal mixing of gases at low p i.e. IG

= 0

step 3: Ideal gas-mix is compressed isothermally & condensed at the original p

$$\Delta U_{III} = \int_{\infty}^{V^L} \left.\frac{\partial U_{mix}}{\partial V}\right|_T dV \cong -\frac{a_{mix}}{b_{mix}}$$

So, third step 3 is basically ideal gas this is step 2 ideal gas mixture is compressed isothermally and condensed at the original pressure ok. So, delta u 3 is infinity to v L does you mix divided by del v at T d v and this is nothing minus a of mix divided by b of mix ok. We may not know at this point that the effective a and b of the mixture. So, this is what is going to be delta u mix ok.

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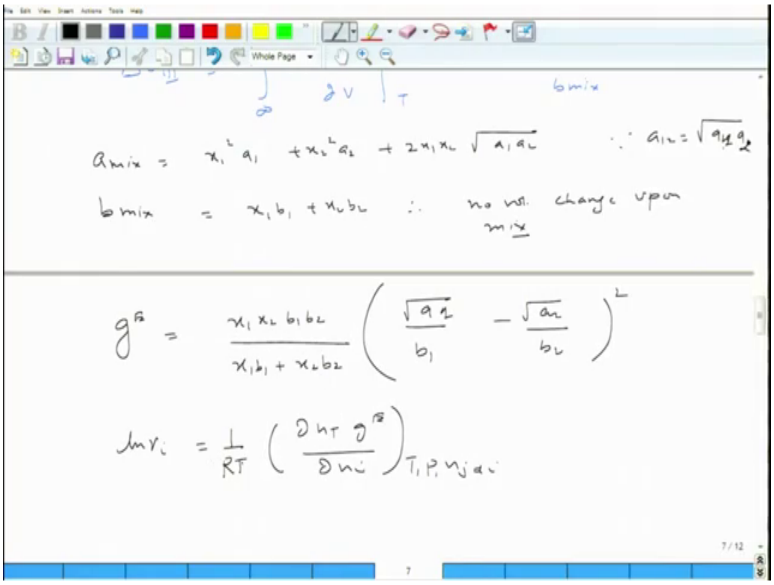

$$a_{mix} = x_1^2 a_1 + x_2^2 a_2 + 2 x_1 x_2 \sqrt{a_1 a_2} \quad \because a_{12} = \sqrt{a_1 a_2}$$

$$b_{mix} = x_1 b_1 + x_2 b_2 \quad \therefore \text{ no vol. change upon mix}$$

$$g^E = \frac{x_1 x_2 b_1 b_2}{x_1 b_1 + x_2 b_2} \left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2$$

$$\ln \gamma_i = \frac{1}{RT} \left(\frac{\partial n_T g^E}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

Now, van der Waal of course, has worked on this and is defined this a mix in terms of the pure component. So, this is x 1 square a 1 plus x 2 square a 2 plus 2 x 1 x 2 a 1 a 2 ok. So, this is, so this was nothing, but a 12 and so a 12 is considered to be the geometric mean of a 11 and a 12. So, that is a 1 multiplied by a 2 ok, so that means, here all the interaction between the 1 and 2 is important.

Now, on the other hand b mix is simply considered as a weighted average of the sizes x 1 x 2 b 2; that means, there is no volume change upon mixing therefore, no volume change upon mixing ok. Now, with this information you can plug all this back in this expression and since u access is nothing, but g access I can rearrange this data and obtain g E in terms of x 1 x 2, b 1 b 2, x 1 b 1 plus x 2 b 2 ok. So, this is a divided by b 1 minus a 2 divided by b 2 squared ok.

So, this is the expression which comes out after coming with this simplifications of the expression by plugging in all these different parts which we have calculated back in u access ok, and then using the fact that the g access is nothing but you have access. Now, given that you have obtained x is the value of g access, now you can connect this to the activity coefficient ok. So, that is that you may like directly use this expression here ok. So, this is the total number of moles multiplied by g E here.

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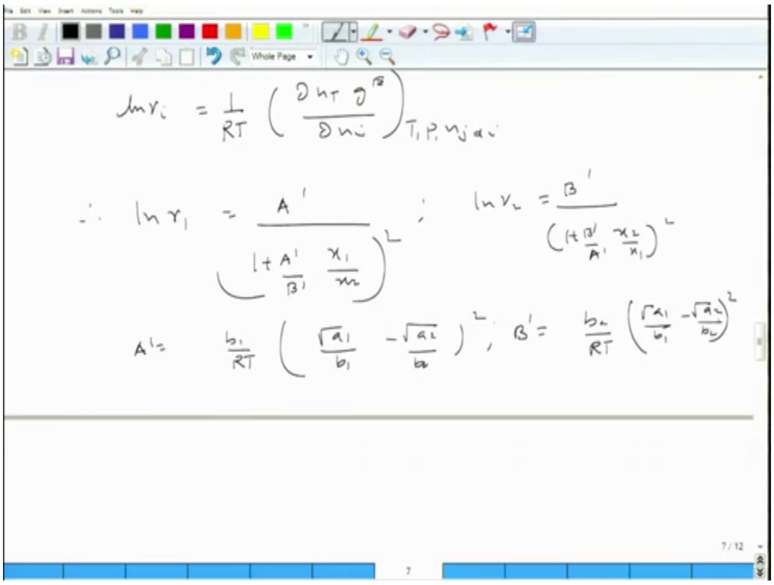

$$\ln \gamma_i = \frac{1}{RT}\left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$\therefore \ln \gamma_1 = \frac{A'}{\left(1+\frac{A'}{B'}\frac{x_1}{x_2}\right)^2} ; \quad \ln \gamma_2 = \frac{B'}{\left(1+\frac{B'}{A'}\frac{x_2}{x_1}\right)^2}$$

$$A' = \frac{b_1}{RT}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2 ; \quad B' = \frac{b_2}{RT}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2$$

So, with this you should be able to obtain for the binary mixture the expression which we have written without going through the detail derivation earlier in the lecture, this is nothing but the two parameter model ok. So, this is for the log gamma 1 and this is log gamma 2.

And what is A and B? So, A dash is given by b 1 by RT square where is B dash is b 2 by RT again the terms are same as in the case of a 1 ok. So, this is a positive value b is a positive they does A dash and B dash and this they are positive ok, but this is important that this is proportional to 1 by T ok, for both the cases.

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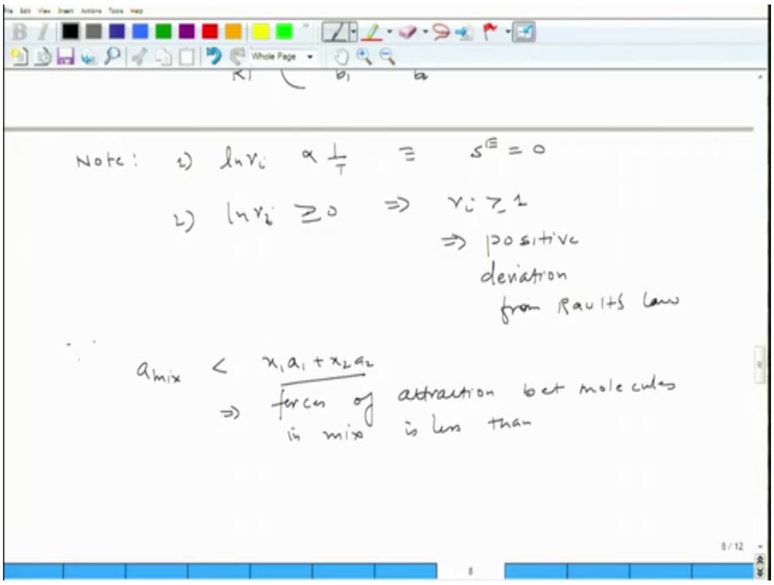

Note: 1) $\ln \gamma_i \propto \frac{1}{T} \equiv S^E = 0$

2) $\ln \gamma_i \geq 0 \Rightarrow \gamma_i \geq 1$

$\Rightarrow$ positive deviation from Raults law

$a_{mix} < \underline{x_1 a_1 + x_2 a_2}$

$\Rightarrow$ forces of attraction bet molecules in mix is less than

Considering this you can summarize or you note the following points that log of gamma i is proportional to 1 by T and as we have discussed in the last lecture that this is essentially indicative of that s x is 0. The second point is that both the cases log i is greater than equal to 0 which essentially means that gamma i is greater than equal to 0 one ok.

So, log gamma i is greater than equal to 0 is directly from here that this a positive value and that is why it has greater than equal to 0 which indicates this and this is nothing but implies when gamma is greater than one it is a positive deviation from the Raults law ok. So, this is this imply, this is a positive deviation from Rault' law ok.

So, you should also note here that a mix which we have considered here ok, a mix here. This a mix the expression that you have used is less than x 1 a 1 plus x 2 a 2 ok. So, and remember this what is a? a is basically nothing, but is a proportional to the forces between the molecules.

So, it tells you this expression tells you that the forces of attraction between molecules in mixture is less than they would have been if they were added in additive on molecule or molar basis is less than the you know if they were added in a in a molar basis ok.

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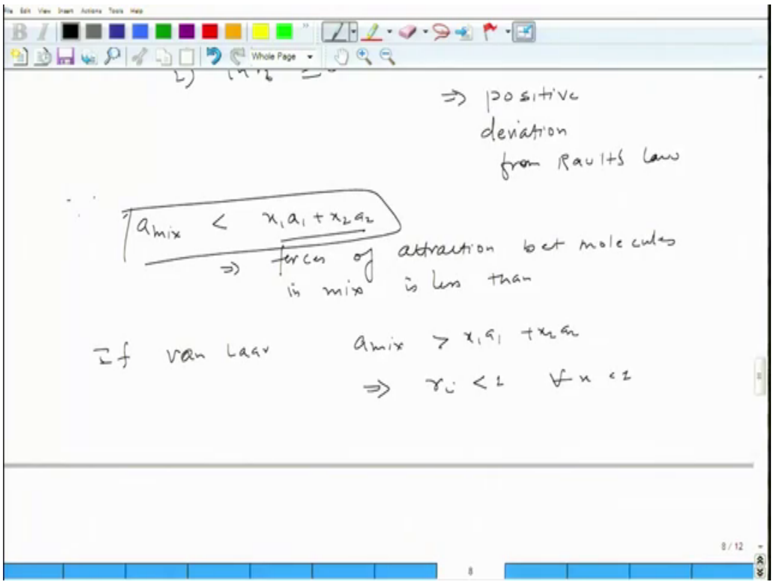

$\Rightarrow$ positive deviation from Raults law

$$\boxed{a_{mix} < x_1 a_1 + x_2 a_2}$$

$\Rightarrow$ forces of attraction bet molecules in mix is less than

If van Laar $a_{mix} > x_1 a_1 + x_2 a_2$

$\Rightarrow \gamma_i < 1 \quad \forall x < 1$

So, assume that if Van Laar had taken the following this would imply that in such case you would have got this for all values of x, ok. So, which would have been this a negative deviation. But since they took on this essentially this model this assumption that is why you are getting the positive deviations and for gamma equal to one you know that would be your ideal solution.

So, the difference is mainly you know the assumption is mainly because of this assumption of a mix and for that you getting a specific kind of behaviour using this kind of theory ok.

Now, there is certain salient features of Van Laar theory. This is something which is important to note.

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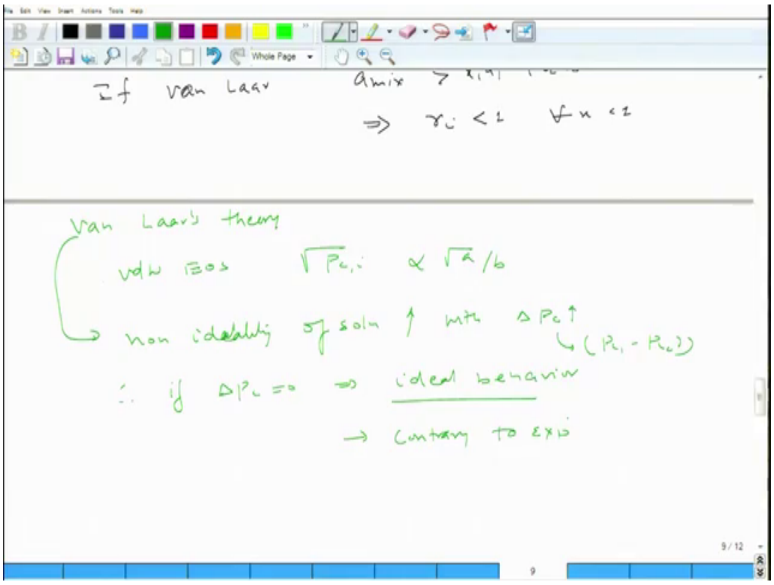

If van Laar a_{mix} >

⇒ $\gamma_i < 1$ ∀ $x < 1$

Van Laar's theory

vdW EOS $\sqrt{P_{c,i}} \propto \sqrt{a}/b$

non ideality of soln ↑ with ΔPc ↑

$(P_{c_1} - P_{c_2})$

∴ if $\Delta P_c = 0$ ⇒ ideal behavior

→ contrary to exp

So, Van Laar theory basically relates non ideality to a critical pressure of the pure component ok. So, according to van der Waal equation of state P c of i is proportional to the root of a by b. So, Van Laar theory say is that the non ideality of solution increases with the difference between the pure components P c increases ok. So, therefore, if delta P c is 0 which means we would expect to be ideal behaviour ok, but this is contrary to experimental observation ok.

And thus you can clearly see there is a flaw in the one van der Waal or there is there is a flaw in Van Laar's theory. So, one of the basic reasons for this is the usage of Van Laar equation a van der Waal equation of state ok. So, that was a major problem and many theories came out later which tried to remove this kind of obstruction.

So, one of the other one of the common theory which has done that is basically Scatchard Hildebrand theory and that is something which I am going to discuss in the next lecture. So, that will be it for this.

See you in the next lecture.