Thermodynamics of Fluid Phase Equilibria
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Lecture – 49
Theories of Solution – II

Welcome back. In this lecture I will be discussing Scatchard Hildebrand theory which has basically a theory which awards usage of the van der Waal equation and taking out the key issues with the Van Laar theory, ok.

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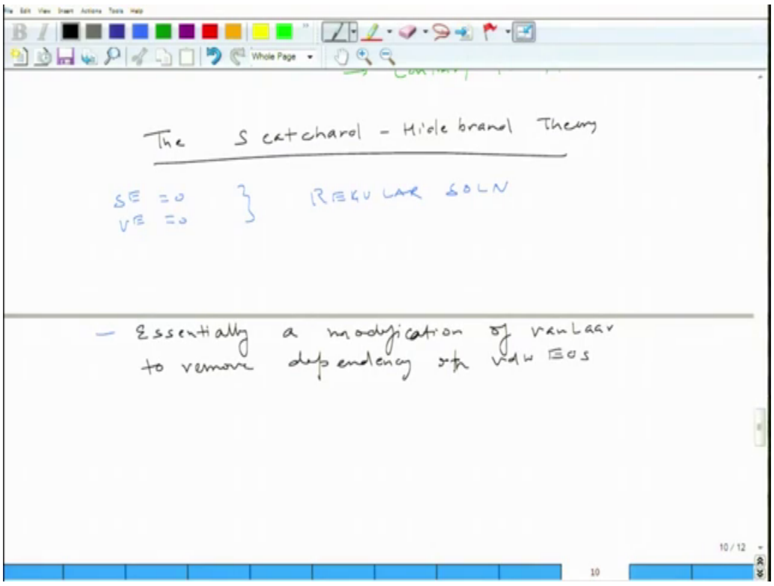

The Scatchard - Hildebrand Theory

$S^E = 0$
$V^E = 0$ } REGULAR SOLN

— Essentially a modification of van Laar to remove dependency of vdW EoS

If you recall Van Laar assumed the following for the theory ok; Now, Hildebrand defined such kind of systems as a regular solution ok. So, regular association assumption would be where you can consider S x and v x to be 0 ok.

So, what did Scatchard Hildebrand did? Basically or what basic contribution of Scatchard Hildebrand is basically to modify the van der Waal. To remove the dependency of a van der Waal equation of state, so the theory is nothing but essentially modification Van Laar theory to remove dependency on van der Waal equation of state ok. So, in order to do that what Scatchard Hildebrand did is a defined cohesive energy density ok.

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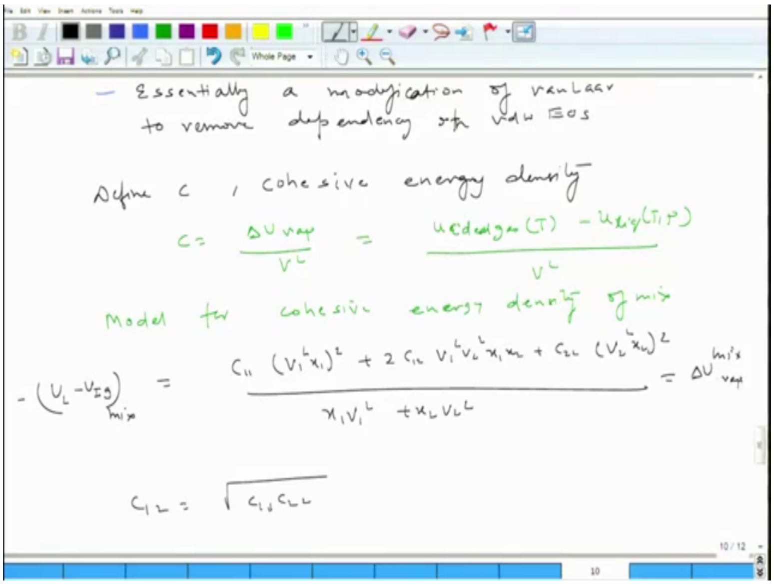

- Essentially a modification of van Laar to remove dependency on vdW EOS

Define C, cohesive energy density

$$C = \frac{\Delta U_{vap}}{V^L} = \frac{U_{ideal\,gas}(T) - U_{liq}(T,P)}{V^L}$$

Model for cohesive energy density of mix

$$-\left(U_L - U_{IG}\right)_{mix} = \frac{C_{11}\left(V_1^L x_1\right)^2 + 2C_{12}V_1^L V_2^L x_1 x_2 + C_{22}\left(V_2^L x_2\right)^2}{x_1 V_1^L + x_2 V_2^L} = \Delta U_{vap}^{mix}$$

$$C_{12} = \sqrt{C_{11} C_{22}}$$

So, they defined term C which is cohesive energy density C is equal to delta u vapour by v L. So, this is the formalism of the cohesive density where this is a molar volume and delta u wave vapour or vhip is nothing but the difference in the ideal gas at T minus the energy or internal energy of the liquid T P ok. So, this is the difference were. So, essentially the internal energy of the liquid with reference to the internal energy of the ideal gas at that temperature that is a cohesive energy ok.

And now, in order to come up with the mixing model where the major problem with the van der Waal equation of state was, so they in this theory the model for cohesive energy density of mixture is considered as C 11 v 1 L x 1 square plus 2 C 12 v 1 L v 2 L this is like molar volume of the liquid, x 1 x 2 plus C 22 v 2 L x 2 square x 1 v 1 L plus x 2 v 2 L, and C 12 is is basically C 11, and C 22 is. And this particular term is nothing, but your cohesive energy density of measure which is defined in terms following. So, this is like liquid minus u ideal gas mixture minus this, this is nothing but also would be your delta you mix of this vapour ok. So, this is the model considered by this Scatchard Hildebrand theory.

Now, this can be further simplified by considering the following that now, one of the important thing, in this case is we have considered v x to be 0 and s s x is of course, a 0 remember that.

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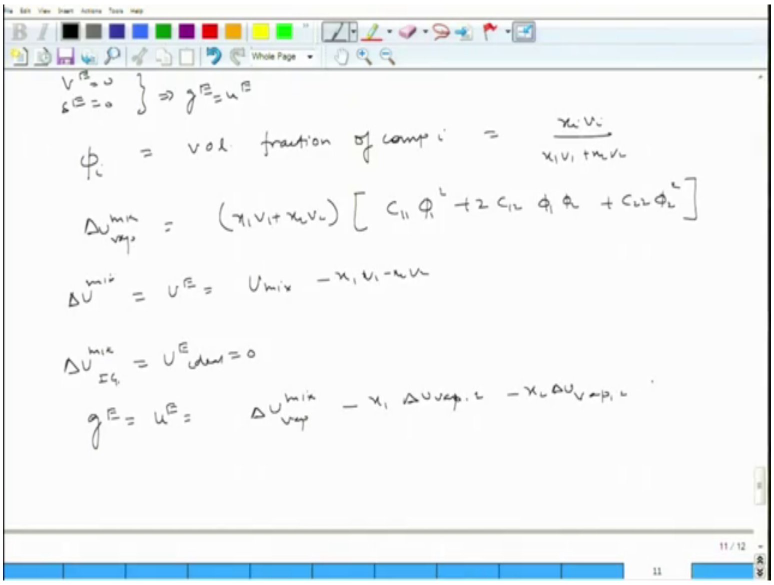

$$\left.\begin{matrix} v^E = 0 \\ s^E = 0 \end{matrix}\right\} \Rightarrow g^E = u^E$$

ϕ_i = vol fraction of comp i = $\dfrac{x_i v_i}{x_1 v_1 + x_2 v_2}$

$$\Delta u^{mix}_{vap} = (x_1 v_1 + x_2 v_2)\left[C_{11}\phi_1^2 + 2C_{12}\phi_1\phi_2 + C_{22}\phi_2^2\right]$$

$$\Delta U^{mix} = U^E = U_{mix} - x_1 U_1 - x_2 U_2$$

$$\Delta U^{mix}_{IG} = U^E_{ideal} = 0$$

$$g^E = u^E = \Delta U^{mix}_{vap} - x_1 \Delta U_{vap,1} - x_2 \Delta U_{vap,2}$$

Now, in order to simplify we defined term called volume fraction of component i is going to be x i v i divided by x 1 v 1 plus x 2 v 2. Now, with this your delta u mix is x 1 v 1 plus x 2 v 2 C 11 phi 1 square plus 2 C 12 phi 1 phi 2 plus C 22 phi 2 square ok. So, this is the expression we have it.

Now, since v x and s x is equal to 0 this also means that g is nothing, but u E and delta u mix is u excess is nothing but u mix for total minus x 1 u 1 minus x 2 u 2. So, this is something which we can also make use of the difference with respect to ideal gas knowing that delta u mix is nothing but u excess for ideal this is going to be 0. So, if you do that g E is u E and this is something which for ideal gas this is the vapour minus x 1 delta u vapour 1 minus x 2 delta u vapour 2 ok.

Now, this may look very complicated but it actually straightforward if you put down all this understanding of this individual variable.

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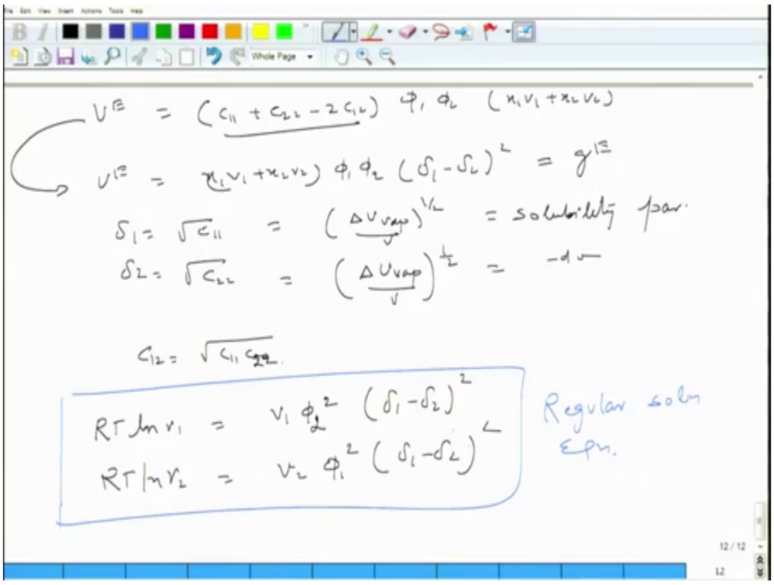

$$U^E = (C_{11} + C_{22} - 2C_{12})\, \phi_1 \phi_2 \, (x_1 v_1 + x_2 v_2)$$

$$U^E = x_1 v_1 + x_2 v_2)\, \phi_1 \phi_2 \, (\delta_1 - \delta_2)^2 = g^E$$

$$\delta_1 = \sqrt{C_{11}} = \left(\frac{\Delta U_{vap}}{V}\right)^{1/2} = \text{solubility par.}$$

$$\delta_2 = \sqrt{C_{22}} = \left(\frac{\Delta U_{vap}}{V}\right)^{\frac{1}{2}} = \text{-d-}$$

$$C_{12} = \sqrt{C_{11} C_{22}}$$

$$\boxed{\begin{aligned} RT \ln \gamma_1 &= v_1 \phi_2^2 (\delta_1 - \delta_2)^2 \\ RT \ln \gamma_2 &= v_2 \phi_1^2 (\delta_1 - \delta_2)^2 \end{aligned}}$$

Regular soln Eqn.

Now, I am going to write this now, u E because this is available and this also we can directly write the for example, this one would be your C 11 v L this is by definition and this will be your C 22 v L and this of course, we know from earlier. So, this further can be simplified phi 1 phi 2 x 1 v 1 plus x 2 v 2 ok, right.

And now, what I can do is I also can write this as x 1 v 1 plus x 2 v 2 and this phi 1 phi 2 and this can be written as delta 1 minus delta 2 square. And what is delta? Here this is the solubility parameter. So, delta 1 is nothing but C 11 is a square root of the cohesive energy density is the solubility parameter ok, and similarly delta 2 is C 22, again the solubility parameter ok. Now, this if you put it here you should be considering that that C 12 is nothing but C 11 C 22 ok.

So, that way you can list to expressions are synonymous ok. Now, this solubility parameter is something which you can extract from the experiment and that is why this becomes a very very useful theory in order to connect the experiments. So, we may be doing some example in the later stage ok.

Now, given that you have an expression of u E in terms of this and this is nothing, but g of E ok, well again remember that this is a mole fraction molar volume molar volume multiplied by x 2 volume fraction of component 1 volume fraction of component 2 multiplied by that difference in the solubility square of that and this is nothing but g of E. Now, you can connect this thing to your activity coefficient of which I am not going to derive I will just write it here and this is the very famous expression which is basically regular solution equation given by Scatchard and Hildebrand ok.

Now, so, you can rearrange this expression. So, please understand that basic assumption in the Van Laar equation and as well as the Scatchard Hildebrand is that your s E and v excess drop entropy and basically the volume is 0 so that means, they considering is regular solution. The difference in the Van Laar is it uses the van der Waal equation to get the mixing parameter whereas, here it is it relies on the cohesive energy density.

So, in other word the expression here I should be able to also connect to the Van Laar form, so, let me just try to do that. If I do make use of the Van Laar form then the A dash is going to be v 1 by RT and B dash is going to be v 2 by RT.

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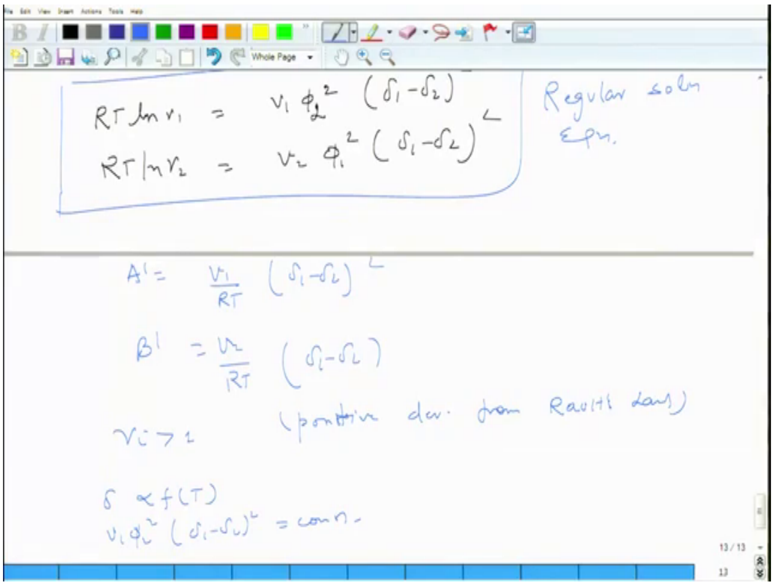

$$RT \ln \gamma_1 = v_1 \phi_2^2 (\delta_1 - \delta_2)^2$$
$$RT \ln \gamma_2 = v_2 \phi_1^2 (\delta_1 - \delta_2)^2$$

Regular soln Eqn.

$$A' = \frac{v_1}{RT} (\delta_1 - \delta_2)^2$$

$$B' = \frac{v_2}{RT} (\delta_1 - \delta_2)$$

$\gamma_i > 1$ (positive dev. from Rault's law)

$\delta \propto f(T)$

$v_1 \phi_2^2 (\delta_1 - \delta_2)^2 = \text{const.}$

So, here again you can clearly see all this are positive indicates that a log of gamma 1 is greater than equal to 0 or gamma is basically greater than 1, which means basically it is a positive deviation from the Rault's law ok.

Now, the other important thing is that the solubility is basically a function of temperature, but if you multiply with v by phi square and this is more or less constant as becomes independent of temperature, this is based on the experimental observations ok.

So, with this I will stop here ok. And in the next lecture I will start polymer solution followed by set of examples which would illustrate the concept which is shown here, and that would be the end of this course ok.

So, I will see you in the next lecture.