Thermodynamics of Fluid Phase Equilibria
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Lecture - 45
Models for Fugacity of Liquid Mixtures-2

Welcome back. So now, I am going to make use of Wohl's equation expression to get a Van Laar equation out of it, ok.

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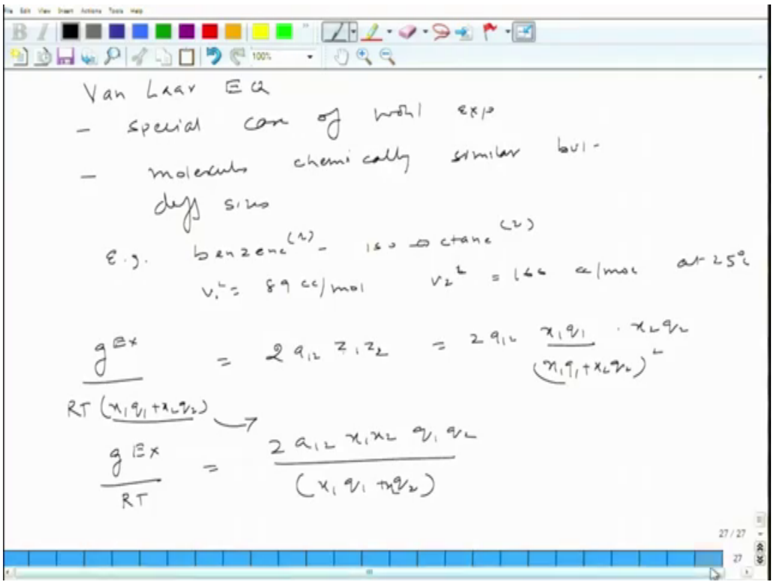

So, Van Laar is a special case of Wohl, so special case of Wohl it is used for mixtures having a molecules which are chemically similar, but different sizes. Some examples are benzene and iso-octane with the same example which we are we have been trying to use ok. So, if you look at let us say if it is 1 and if it is 2, it is molar volume is 89 cubic centimeter per mole whereas, here is 166 cubic centimeter per mole ok, at 25 degree Celsius, clearly suggesting that these are of different sizes.

Now, if you ignore a higher order term in Wohl expression if you consider just a first expression right and this expression if you consider you are going to get the Van Laar equation So, if you remember this z i is equal to x i q i divided by x 1 q 1 plus x 2 q 2. So, let me get there and write it here. So, what I am trying to say is the following g x by RT x 1 q 1 plus x 2 q 2 if I consider only the first term right. So, this is nothing, but Van Laar. Now, you can plug in z here. So, this can be written as two this one and this is x 1 q

1 divided by x 1 q 1 plus x 2 q 2 this is square and this would be multiplied by x 2 q 2 ok.

So now, you can simplify this expression you should be getting g x if I take this part the other side then I get RT and this is going to be 2 a 12 x 1 x 2 q 1 q 2 divided by x 1 q 1 plus x 2 q 2, ok. Now, remember that we are little bit comfortable with a’s and b’s because the reason is that that makes equation simpler and start from this one constant Margules equation.

So, we can actually write it in that form. If you do the calculations you know that from the fact that activity is related to partial Gibbs excess property and so that means, you should be able to get this expression similar to what how we got one constant Margules equation and obtain the activity coefficient ok.

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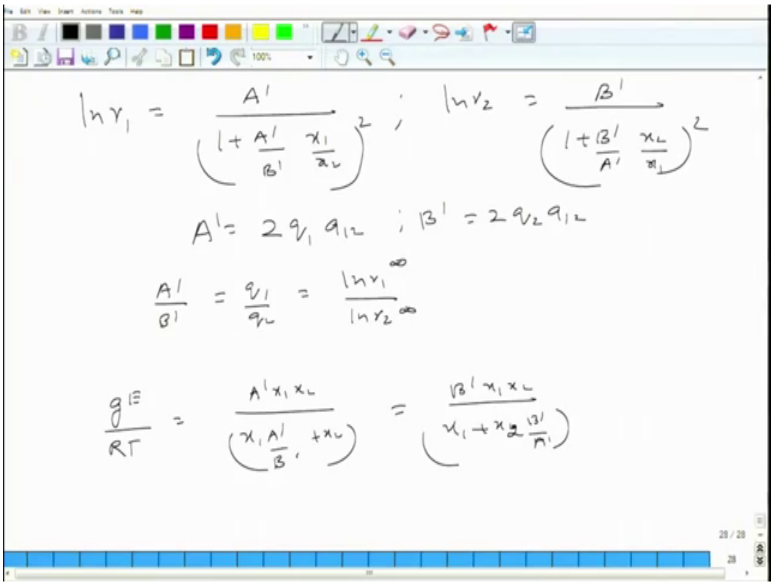

So, if you do that. So, I am not deriving it I get the following expression A bar 1 plus A B x 1 by x 2 1 and ln gamma 2 is B dash 1 plus B dash by A dash x dash 2 by x 1 2, where A dash is 2 q 1 a 12. Remember that A we referred earlier also as interaction parameter. So, indeed if you consider a 12 is a interaction energy and q. What was q?

Student: Effective volume.

So, it basically the q is basically the volume effective volume molecule. So, not the volume ratio as z is a volume ratio. So, A dash is 2 q 1 a 12, is B dash is 2 q 2 a 12. Now, we need to use some kind of exponent data to obtain a dash or b dash usually a dilute solution informations are available from the experimental data. So, if you use that information from the experimental data then A dash by B dash is nothing but q 1 by q 2 ok. And what is A dash? How do you get the A dash here?

So, if you consider let us say in dilute solution x 1 goes to 0 then this will be simply ln gamma one infinity is nothing, but A dash. Similarly ln gamma 2 infinity, where x 2 goes to 0 will be B dash. So, A dash where B dash ratio which is q 1 by q 2 is nothing but ln gamma 1 infinity by ln gamma 2 infinity. So, this is relation you can obtain from the experiment there is a relation between these constants ok, which is related to the infinite in a dilution activity coefficient ok.

So, often we use the relation in this form, or we use in this form this is nothing but a two constant or two parameter expression or two parameter theory where I say that ok. So, this is a Van Laar expression. You can easily make use of this for benzene iso-octane as well as n-propanol and water it works very well ok. So, it captures a complexity of that nature of dissimilar things. Remember that for n propanol water it is basically hydrogen bond is also playing a role

Now, this expression I can rewrite actually, let me just further. Now, though the derivation of Van Laar suggests that it is good for solution of relatively simple system non-polar, but it is also used outside this assumption. So, it is used for polar also that is what I said n-propanol and water system ok.

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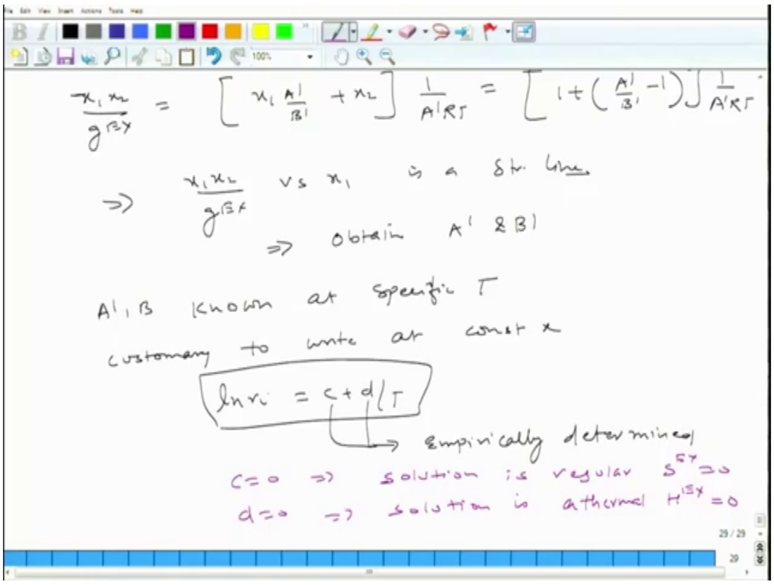

So, it is capable of reproducing data for complex mixtures. So, let me rewrite this expression rewrite this here in this form x 1 x 2, I now writing this one ok, x 1 x 2 divided by g E this can be written as x 1 A dash by B dash plus x 2, 1 by A dash RT or I can write this as 1 plus A dash by B dash minus 1 1 by A dash RT ok.

So, what this suggests that x 1 x 2 by g E or g E or g x is the same thing same nomenclature in this course versus x 1. This versus x 1 is a straight line, and this expression this if you have the data available we can this can be used to obtain a dash and b dash right this is what it tells you. If you have the data of this composition and g x is you can plug it and obtain the A dash and B dash out of it ok.

Now, usually a dash and b dash are insensitive to pressure, but not to temperature because it is it depends on the temperature but if it is insensitive to temperature then this will be a thermal solution ok. Now, practically A and B are often assumed to be independent temperature if the temperature range is not too great ok, this is a practical consideration.

Now, often you may have A and B known at specific temperature. So, and then you would like to find at different temperature ok. So, it is customary to write at constant x and then gamma i is c plus d T. So, you can you have the information you can get it at different temperature, but using this kind of customary expressions ok, where c and d are empirically determined.

So, usually when you see this kind of expression and if c is equal to 0 this also indicates the solution is regular. Now, this is something which I am going to spend last few lectures on it. Solution is regular which essentially means s excess entropy is 0 if d is equal to 0, that means, is independent of temperature then solution is a thermal which means H excess is ok. This is something which you can we can save by looking at it if you are aware of all the derivations, but I will just assert it now, and we will look at it in the later part of this course; that means, last few lectures ok.

So, now, that we have expressed very well the Van Laar equation the other set of equations are also available which can be derived from the again the Wohl's equation expressions.

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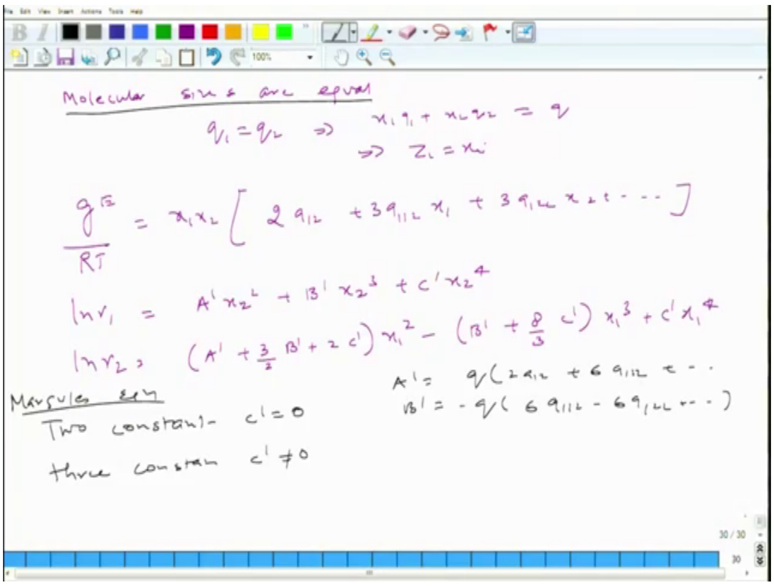

So, if you consider molecular sizes to be equal which means q 1 is equal to q 2 this essentially means that x 1 q 1 plus x 2 q 2 is nothing but q which essentially means that I is equal to x i, ok. If you go back go to the definition of the z, z i will be nothing, but x i ok. In that case I can consider the expression of the Wohl's expression in this form ok. So, this will continue. This should have been say x 1 x 2 here I think yeah. So, two times right fine, x 2 and then there this a high order terms of x 1 and x 2 all right.

You can come up with this expression particularly containing only till x 2 or 2 till 4th order of composition this. So, again I am skipping all the derivation and you do not need to remember you know the most important thing is that how it is derived or could be important as well as the philosophy of these expressions is actually I feel that more important rather than remembering this expressions ok.

So, this is the expression which comes out for ln for binary mixtures having the molecular sizes a constant from here we should be able to connect or get this something is you know this Margules equation of two constant and three constant for two constants c dash is equal to 0 ok, for three constants c is c is not equal to 0 ok. Where A's and B's are connected to nothing but for example, A dash is nothing, but q 2 a 12 plus 6 a 112 and so forth similarly B dash is q 6 a 112 minus 6 a 122 so forth So, once you derive you should be able to find all these things.

So, this Margules equations for two constant and three constants has a basis of molecular sizes to be equal and it is derived from the Wohl's equations ok. So, in practice you can see that you know this two constant and three constant Margules equation should not be used for the system having dissimilar sizes, but in practice they are also used ok.

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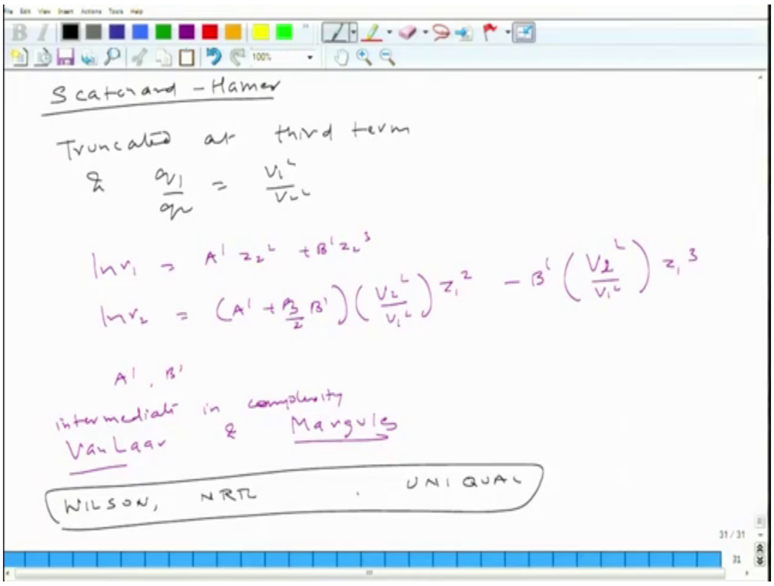

So, last equation or expression is due to Scatchard which I am going to talk and this and then I will stop and focus on some examples. So, this is a expression where the Wohl's expression is truncated at the third term, and we put the ratio of this size is as simply this as I said this one model remember that earlier I said that one model is this is nothing, but is Scatchard-Hamer equation. And here if you use this expression then the following expression of activity coefficient comes into. So, this is again I am writing this without deriving it where A dash and B dash are functions of you know there is a's and b's.

So, I will not write it in details because I do not expect you to remember this as well, but what is important is that Scatchard-Hamer captures the complexity in between Van Laar and Margules ok, so intermediate in complexity ok. So, we may use some of this expression to do some kind of examples as a different matter, but the idea is that this is another possibility if you have intermediate in complexity now. What is the intermediate in complexity, where of course, the size differences are there that is something which is part of this the complexity.

Now, in addition to this we can also discuss various different expressions which has some sound basis Wilson NRTL which is a non-random to liquid local composition and uni quac which is universal quasi chemical theory ok. So, this is something which I will not go into details, but the one can get an expression of the activity with respect to different variables ok.

So, at this point I will stop here, and I will start I will work on some examples in the next lecture ok. So, see you in the next lecture.