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Chemical Engineering Thermodynamics

By

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Lecture 14

Van Laar model

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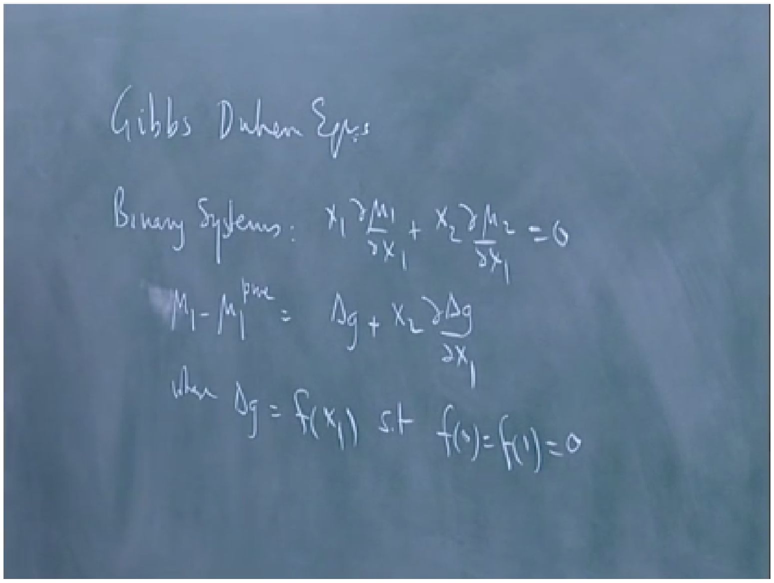

Gibbs Duhem Eqns

Binary Systems: $x_1 \frac{\partial \mu_1}{\partial x_1} + x_2 \frac{\partial \mu_2}{\partial x_1} = 0$

$\mu_1 - \mu_1^{pure} = \Delta g + x_2 \frac{\partial \Delta g}{\partial x_1}$

when $\Delta g = f(x_1)$ s.t $f(0) = f(1) = 0$

I am going to continue talking about the Gibbs Duhem equation, I think for quite some time. I am going to talk about, we have two equations I had $\mu 1 - \mu 1^{pure}$. So binary systems actually the equation itself, I do not know if I wrote it in the final form, yeah I wrote this. We wrote this to get solutions in this form where Δg is any function of composition such that of course f(0)=f(1)=0. Because when x1 is 0 or x1 is 1 you got the pure state, you do not have a mixing process at all. So this is automatically conditioned here.

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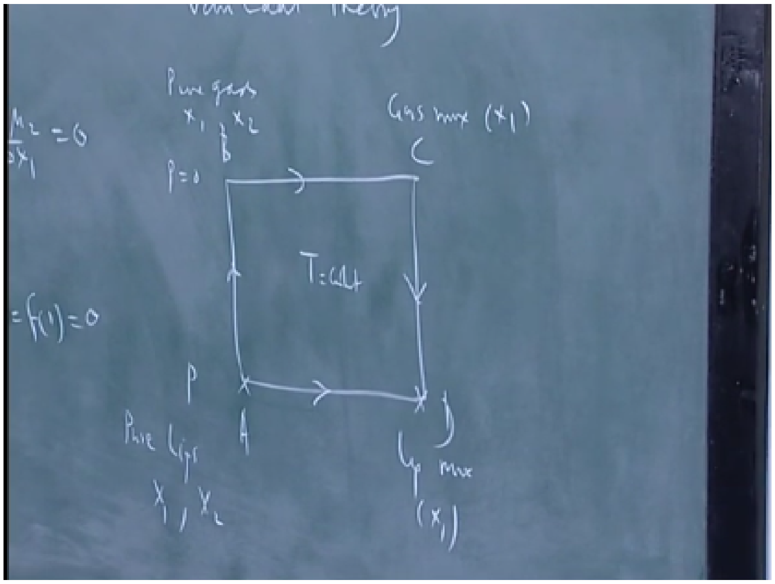

Now we are discussing the Van Laar equations or the Van Laar theory, what Van Laar said he started with this, this is what I want, but this is what I can do. Luckily thermodynamics tells me if I go around this way, I get the same answer if I do this, if I do it from A to B. So this is pressure P, this is pretty equal to 0, P = constant. This is pure liquids x1, x2 this is mixture liquid mixture of composition x1. This is gas mixture of composition x1, this is pure gases. We made some assumptions, we talked about excess properties.

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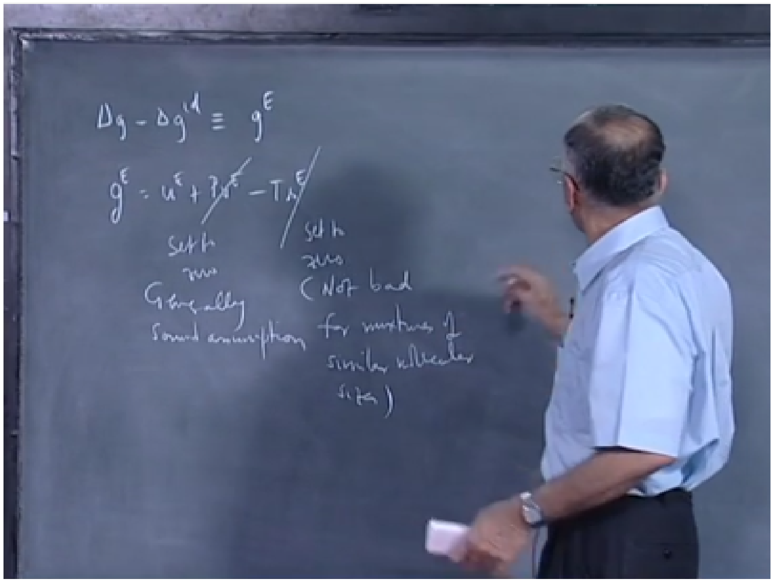

So you have $\Delta g - \Delta g^{ideal}$ = it is defined as g excess. We said U excess is or the other way wrong. Now this is said to 0, this is an assumption, I told you it is not a bad assumption in the case of molecules of similar size, this is also said to 0, this is generally a good assumption. When we say sound assumption, I mean you can verify using experimental data that the volume changes on mixing are generally very small. There is no ideal change in volume, there is no actual change in volume either.

So $\Delta v - \Delta v^{ideal}$ is actually 0, both are 0. So this is generally a very good assumption except in their cases, in fact you will be hard to define counter examples, there it is significant, there are some cases. This said to 0, I will say it is not on the same classes, that is the thing not bad for just of similar molecular sizes. When I say similar you can go up to five times roughly it does not matter.

One molecule can be five times as big as the other, and still you would not have significant s Δs, other than the ideal entropy change in mixing. So having said that he simply wanted to find u.

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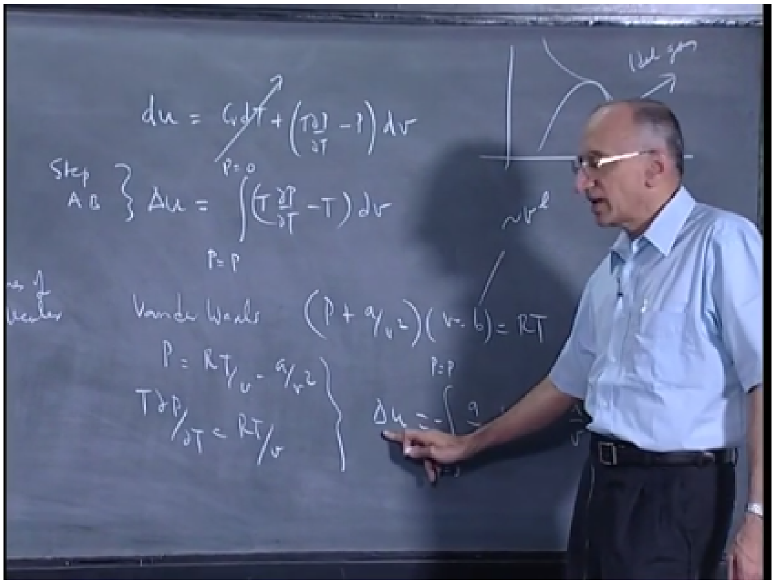

So we started with this equation du, where du = CvdT + he was calculating change in u at constant temperature in all the processes. so to calculate Δu from one point to the other, he said Δu simply integral of (T ∂P/ ∂T – T) dv from P = P to P = 0, this is Δu for AB. Now this is where we g o stepped in Van der Waals, he said all fluids obey the Van der Waals equation. Van der Waals equation is $(P + a/v^2)$ (v-b) = RT.

Because the physical arguments of Van der Waals was very simple, simply said there is a volume occupied by molecules V, Pv = RT was already known, he said the actual volume is the volume minus the volume occupied by the molecules which is B. and Van der Waals already predicted that B would be of the order of the specific volume of the liquid. Because after condensation it says that is the space occupied by the molecules.

The balance space is available as for a ideal gas, the ideal gas conserve point particles plus free space. This is not point particle, so he said this is, he expected this to be of the order of V liquid. And generally densities have liquids are constant, so when we said V liquid he took it at the triple point, but he could have taken it almost in condition. The argument here, whereas the pressure is change of moment to exchange of momentum with the wall.

So rate of change of momentum, so when a molecule colloids and comes back you take the change in momentum divided by the time between collisions. And then you will get an estimate of the momentum exchange, you can get the pressure, this is an ideal gas. In actual gas he said that the forces are primarily attractive, the number of molecules striking the one is proportional to the density which is proportional to the 1/v specific volume.

The number of molecules pulling these molecules away from the wall and therefore reducing the momentum is also proportional to the number density which is also proportional to 1/v. so effectively he said the effect of attractive forces between molecules is proportional to $1/v^2$ depending on the molecule you have different A values, different strengths. So he argued that a/v^2 is the reduction and pressure caused by attractive forces.

So if he had treated the system as an ideal gas, the ideal gas would have actually exerted a pressure equal to $(P + a/v^2)$ that is, this would have been absent in the ideal gas. So this is effectively the ideal pressure, this is effectively the ideal volume and PV=RT. So Van der Waal said you have to use this equation and this equation, because the attractive forces will predict for you condensation.

And actually do that, you can predict, you go on compressing the gas below its critical temperature it will condense at some point. At some point thermodynamics will tell you what the chemical potential vapor is, chemical potential liquid is, and you can calculate this. In fact one assignment that we used to prepare the Van der Waals chart, the HP chart for a Van der Waals swift.

If you do that once then you know practically how the others are obtaining. But let us look at this, because if I do not have these attractive forces, you cannot reduce condensation. So you would not get, when I do the chart here, you will get only this region for an ideal gas, there will be n o condensation at all, if you want condensation you have to introduce attractive forces. This v-b will still would not give you condensation, in fact $P(v-b) = RT$ is sometimes called a hard swift model.

But let me get back here, I have got the Van der Waals equation has to be used, so if I calculate P, so you get $P = RT/v - a/v^2$, so $T\, \partial P/ \partial T = RT/v$ which assumes that A is an absolute constant, it is not a function of temperature. Improvements and the Van der Waals fluid actually show that A is dependent on temperature, and therefore you have to use, it is rewritten in terms of another constant times the function of temperature.

It is the Redlick equation, there is some slight changes where there is very successful equation state called the Redlick-Kwong equations state, not Redlick state. But when I went as graduate student to US, that time Berkeley had Redlick teaching the course, teaching thermodynamics. Apparently it started in Redlick-Kwong equation state and ended with the Redlick-Kwong equation state.

He said that there is no other fluid, so everything was done for the Redlick-Kwong equation state. So you get this, so this difference is actually a/v^2 $T\partial P/\partial T - P$ is actually $+a/v^2$, so you get this implies, then Δu for a Van der Waals fluid is actually a/v^2 dv, so it will give $-a/v$, if I switch the saying a/v at $P = 0$, v is ∞, so we will simply a/v. I am writing this from $P = 0$ to P, P with the minus sign.

And $P = P$ the volume is V, that is given by this equation, you have to solve the cubic and find the correct route, but a/b. So a has the interpretation of essentially the latent heat evaporation Δu is actually the internal energy change when this pure substance goes from liquid to vapor. So this is actually the, it is the enthalpy of vaporization is the latent heat, but enthalpy internal energy change approximately equal $P\Delta v$ is negligibly small.

So this has an estimate of the latent heat, so A can be calculated as density times the latent heat, whereas V is V liquid, because you are talking of at pressure P, we started with b liquid. And B liquid according to Van der Waals is B is the parameter B in this equations. So approximately equal to a/b.

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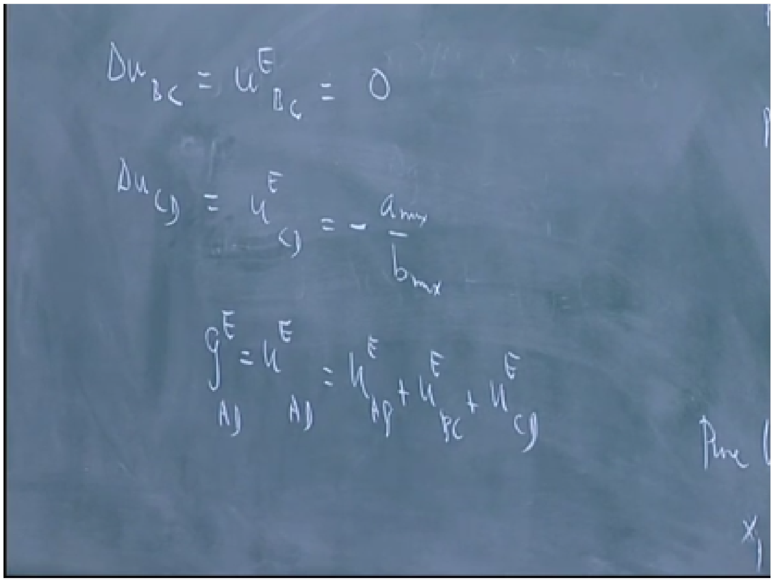

$$\Delta u_{BC} = u^E_{BC} = 0$$

$$\Delta u_{CD} = u^E_{CD} = -\frac{a_{mix}}{b_{mix}}$$

$$g^E_{AD} = u^E_{AD} = u^E_{AB} + u^E_{BC} + u^E_{CD}$$

So he has got Δu AB = u excess AB, because Δu, this was an ideal gas, Δu changes 0, because u is the function only of B, so doing the whole process at constant temperature. So Δu AB is the same as U excess, because Δu AB – Δu^{ideal} would have been this, Δu^{ideal} is 0. In fact for the whole process Δu^{ideal} is 0. So this is equal to this and it is equal to A/B, it is actually it is not A/B exactly, X1 moles of 1 which you are evaporating separately.

Per mole it is a11/b that equation is written per mole, so this is Δu it is the specific internal not the change per mole, for the pure substance I have to write X1 and X1 moles of 1, b1 is the parameter for pure 1, a11 is the parameter, because it represents interaction between two molecules you have to write two subscription plus of course X2 moles times a22/b. Then ΔuBC = U excess BC which h is mixing of ideal gases.

There is no change in energy when you mix ideal gases to form a mixture, there is no interaction might to begin this, so there is a change in interaction. Then ΔuCD = U excess CD, instead of this you are now doing condensation, so you will get a minus sign right, the integral will go from P = 0 to P = P so you will get a minus sign, you get – a mix/ b mix. So I have G excess for the process is equal to U excess for the process. This is AB, this is equal to U excess for AB + U excess for BC + U excess for CD

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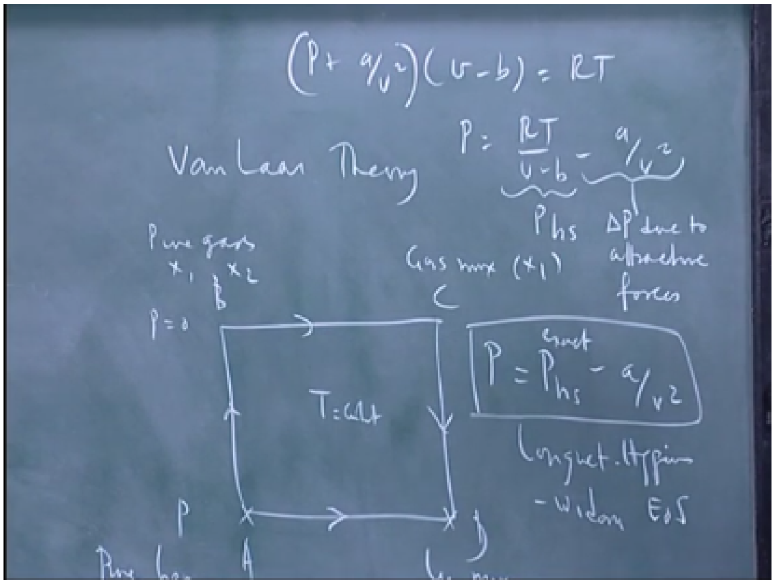

So you G excess is equal to x1 a11/b1 + x2 a22/b2 – amix/bmix, the conception of this equation are basically valid, but this particular final result is restricted to the Van der Waals swift. So if you have a more complicated equation of state, you can use that into the same calculations. Not many people have done that, you can do that and get other expressions to be excess.

Because it represents attractive forces and Van der Waals recognize that if you mix there will be an a12, a11 is between 1 and 1, a22 is characteristic of the pure fluid 2, it represents interaction between two molecules. A12 is if you have one molecule and 12 molecule the interaction between then, because all these will be multiplied by avogadro number, because you are talking of per mole whereas your interactions are actually between molecules.

No you can put RT/v-b if I made that change, even if you put v-b, as long as b is constant you differentiate with respect to b it will disappear. If I wrote v it is a mistake it is v-b. in fact incidentally when I am on this topic let me say this, so you get this, this is P = RT/v-b – a/v^2, so this is what we call P hard sphere, and then this is P or ΔP due to attractive forces, that is what Van der Waals argued.

Much later now we have an exact molecular theory of hard sphere fluids, you have a different expression for P hard sphere which is different from the Van der Waals expression, and you can actually derive an exact theory for hard sphere fluids, and you can verify this, because now you can do computer experiments, you can do multi carlo calculations. I will just describe that briefly, because a very interesting set of calculations.

P hard sphere now we have an exact expression, so you can rewrite this equation as P hard sphere exact plus the same thing, -a/v^2, this equation has been, this is also called longuet hygins widom equation state after three people who wrote it down. They borrowed the P hard sphere exact from molecular theory. It is being fairly successful theory, that is Van der Waals and had many limitations, qualitatively it is always right, but in terms of agreement with experiment has a large number of limitations.

The Longuet Hygins Widom equation will state this much better way, that means Van der Waals is able to essentially quantify the effect of attractive forces quite right. The mistake he made was in the hard sphere estimate, you cannot call it is a mistake. In 1870 that was well ahead of mistakes.

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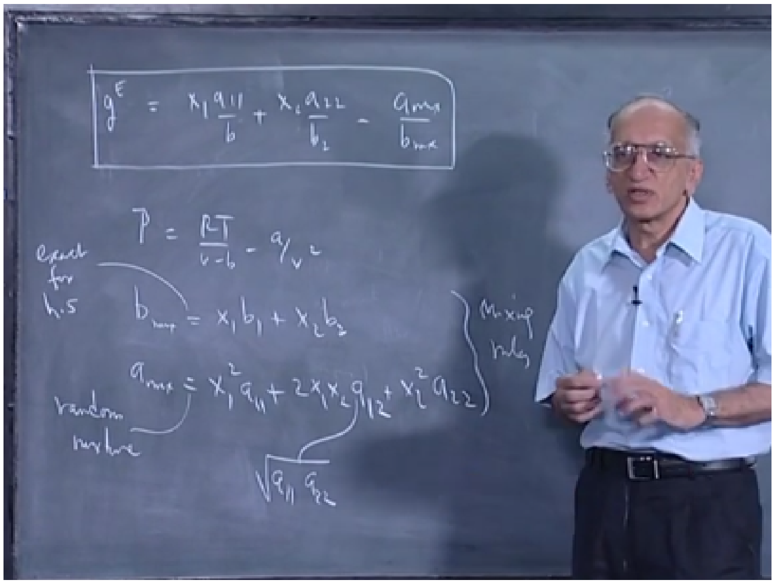

So let me get back here, so what this tells you is, that if you have an equation of state you will anyway have to have parameters set of functions of composition. Because when you write Van der Waals equations you write $P = RT/v\text{-}b - a/v^2$ it is written for a homogenous fluid. So A and B have to be functions of composition. So what the Van der Waal suggested law, at least at that time it was law hard spheres. HS is hard spheres.

If you take A mix the probability of mixture, probability of finding a one-one pair is proportional to $x1^2$, so you get $x1^2$ a11, probability of finding a one-two pair and two-one pair which are both characterized by an interaction one-two, is 2x1 x2 + $x2^2$ a22, so he has assumed that the mixture was a random mixture. Even to dead molecular models only ask what is the departure from randomness.

So you can get mixing that are slightly different from this, much longer although I call this a theory, basically you have one degree of freedom, that is going to be always guessing at one point. What he does is, he uses a equation of state and finally gets it in terms of these, and you have to put in expressions for these. These are called mixing rules till date they are all empirical in classical thermodynamics.

You simply put in a mixing rule and derive results compared with the experiment t if it agrees and accept mixing rule. So hundreds of mixing rules is a whole paper on mixing rules in 1960s, I do not think a review has been written off for that, because there are not many new mixing rules. When you should realize that these coefficients of these, coefficients are such that $x1^2$ + 2x1 + $2x2^2$ is 1 it is always to all these equations will be of that form.

Then there is one more a12, see I can get a11 and a22 b1 and b2 by fitting data for pure substances, whereas I take this equation of state. So pure 1, a red P is equal to $RT/v\text{-}b1 - a11/v^2$. Then I collect lot of experimental data on PVT and fit the data take off. So I will get the best values of b1 and a11, one simple way of getting b1 is simply to take the density at the triple point.

The triple point is invariant, so you can go to the triple point measure the density of the liquid and you will get the value of b, that is one way of doing, then you can fit a/v^2 by taking the data. That is one parameter fit to V, so you get these, so I can get a11 and a22 from the experiment. A12 is hypothetical fluid in which all the interactions are of the form 12, that you cannot get.

Because in any mixture you will have 11 interactions, 22 interactions and 12 interactions, I cannot isolate 1 to alone. So this is invariably produced from experimental data on mixtures knowing the pure parameters to different substance parameters. The other way is to suggest what a12 would be, which has to be a mean between 11 and 22, we are not very imaginative, we only know the arithmetic mean and the geometric mean. So we use one of them actually Van der Waal suggested the geometric mean.

So I will write this as K times view of what has happened afterwards. This K12 is approximately 1, but if you put 0.98 and if you put 1 you will get huge difference in calculated the one and put it. So subsequently browse nets and co-workers have actually determined K12 for a very large number of mixtures. In some limiting cases, where the forces, the dispersion forces are the dominant, there are many intermolecular forces.

And even now our knowledge of intermolecular forces is not complete, but for flow of dispersion forces you can show that this kind of result is exact, so it is exact in a certain limit, but as far as Van der Waals has concerned this combining rule was completely empirical, this is called combining rule. So one way of getting excess free energy is through the equation of state of process, this whole thing is called equation of state approach, because you have a fluid described by an equation of state.

Equation of state should describe both the gaseous state and the liquid state, ideally that is true we still do not have a single equation of state that are correctly described about the liquid and the vapor. But qualitatively the Van der Waals fluid has many, many equations of state would predict approximate the correct qualitative shape, it is still difficult to get exact definition, but every equation of state has parameters that are empirical which are composition dependent according to what are called the mixing rules.

These can be derived from theory to some extent in special cases, in other cases you have to approximate them. Right now we do not have, we have deriving this one here. When we have limiting cases where we can derive this from theory, but in all other cases we do not the rules, so what we do is the usually the geometric approximation is used with a constant and front empirical constant you fit that with the data.

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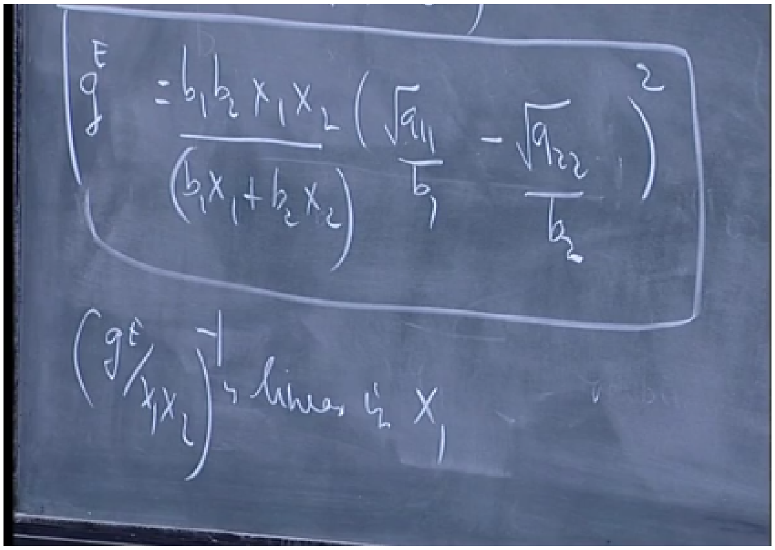

$$g^E = \frac{b_1 b_2 x_1 x_2}{(b_1 x_1 + b_2 x_2)} \left(\frac{\sqrt{a_{11}}}{b_1} - \frac{\sqrt{a_{22}}}{b_2} \right)^2$$

$\left(g^E / x_1 x_2 \right)^{-1}$ is linear in x_1

But if I write this as a11, a22, then amix is clearly equal to x1, if I put that m there it is clearly $(x1 \sqrt{a11} + x2 \sqrt{a22})^2$. So I can now write what g excess is, from the x1 a11/b1 – amix okay, I will just expand this. 1/(b1x2+b2x2)b1b2, this one would become this b1 so you should write b2, we see if I can get that g okay. This is b 2 (b1x1+b2x2) a11x1 that is one term + b1 (b1x1 + b2x2)a22x2 – b 1b2 $(x1^2$ a11).

So we can see the cancellations now it is $b1b2x1^2a11$ this term will cancel with this term. And similarly this term b1b2x2 this second term will cancel with this term. What I have left is g excess is equal to, there is an x1 x2 here, x1 x2 here, x1 x2 everywhere, so I pull out the x1 x2. In $(a11\ b2^2 + a22\ b1^2 – 2b1b2^2 \sqrt{a11\ a22})$ this is what $x1\ x2(\sqrt{a11}\ b2 - \sqrt{a22}\ b1)^2$ what I am going to do is multiply this by b1 b2 and divide by b1 b2, so I already have a b1 b2 here, so it has become $b1^2\ b2^2$ if I take it in here it will become b1 b2 inside the square sign. So it will become

$(a11/b1 - a22/b2)^2$ then of course I have the thing b1 x1 + b2 x2. This is the expression that Van der Waal finally got.

See √a11/b1 - √a22/b2 is a constant, so what he is saying is g excess is equal to x1 x2/b1 x1 + b2 x2 or if you would take g excess by x1x2 and take its reciprocal it is a linear in x1. So if you plot, if you actually measure Δg and get g excess you have to subtract of Z that is the ideal and plot it against x1 if you get a straight line, then you know the Van der Waal equation will fit this data very well.

It was very important when I was a student the straight line business, now it is not and we choose the computer and seem the damping on the head it will tell you it is a good to fit or not. It will tell you what the standard deviations. Now we are used to do with visual if you go on plotting this data and show that is a straight-line. It is still the graphically it is a good to see, there are some significant things that Van der Waals had and which is why Van Laar also find out, Van Laar pointed out and became.

Therefore, he accepted it very widely, I do not have you done the principle of corresponding states, have you shown these constant done that a bit. So you can show that the constant A is proportional to PC Vc^2 B is proportional to BC.

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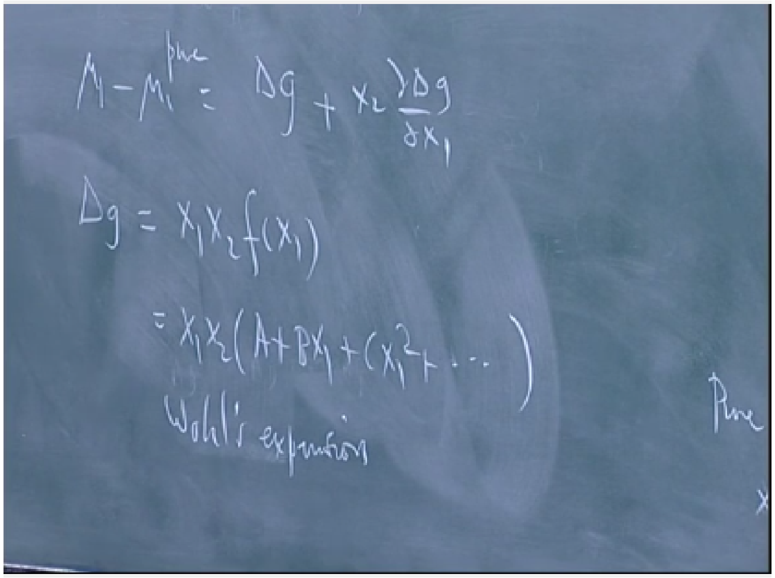

$$\mu_1 - \mu_1^{pure} = \Delta g + x_2 \frac{\partial \Delta g}{\partial x_1}$$

$$\Delta g = x_1 x_2 f(x_1)$$

$$= x_1 x_2 (A + Bx_1 + Cx_1^2 + \dots)$$

Wohl's expansion

So this quantity a/b √a/b is proportional to PC for Van der Waals fluid is proportional to PC. So Van Laar said in the critical pressures are the same, the fluids will makes ideally, because excess free energy will be 0. See if a/b for 1 is equal to √a/b for 1 is equal to √a/b for 2. This will be 2 if critical pressures are equal. So he said all fluids is approximately same, critical pressure will makes ideally.

In the limited data they had at that time showed that does not fact to, so it failed at that time is a very successful theory of liquids. So this is the final result in Van Laar theory, but nowadays we handle this much more easily. We do not do, we do not go through the equations of state, we do not go through mixing rules and combining rules.

The equation of state approach still remains the same, this is the method, everywhere you can change things, you can change the equation of state from Van der Waals to any other compliable equations state you like, you can take a more modern and substitute in there. You can change your mixing rules, mixing rules simply have to show that in the limits they have to go to the pure component properties, but B can be written as any combination that goes to b1 in the limit as x1 goes to 1 and b2 as x1 goes to 0.

Similarly, for A, and then you have resume a combining rule for a12, if you do all that you will get a theory of mixtures, and that people have done this repeatedly through, it is simply the ones that survey where the ones that are who agree with the experimental data for a large number of systems. For each system you cannot have a model. The easier way of doing the same thing is you recognize again µ1 – µ1 pure is simply Δg + x2 partial of Δg with respect to x1.

So all I need is an expression for Δg, what Waal said was, what can Δg be in a binary system it has been x1 x2 times some function of x1, and many function of x1 according to why has that can be approximated they are polynomial. So he said just use a polynomial for example, you write this as x1 x2 ($a + bx1 + cx1^2 + \ldots$). If you want very accurate data you have to see $x1^n$ x1 and you go on increasing and you want an accuracy.

You have to arrive at the, and is seen at the right time. And people already know the result, but have not stated it, then quickly stated, then your name is in the books everywhere. Waal did not do anything, you people had already being using the polynomial approximation. Simply wrote a paper what I do not remember them, it is not an important paper. But somehow he managed to get credit for it.

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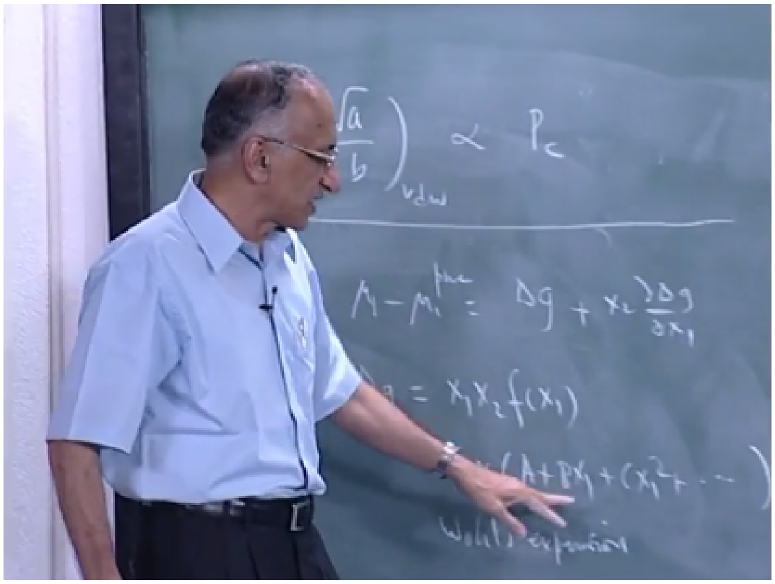

So everybody uses Waals expansion, and when too many terms are required, some why sort of had the idea that instead of doing this you make x1 x2 by and see this is Δg/x1 x2 = f(x1), so if you write this as some other polynomial of x1, this is equal to A'+B'x1, in case this request too many terms, the reciprocal hopefully will require fewer terms. Now this equation here having A not equal to all the other A not equal to 0.

We take this is 1 and their names because of people who derived various expressions earlier A0 = 0 that means all others are 0, it is called Porters equations, you get the same equation with A' is not equal to 0. A' will be 1/a, when if A and B are not equal to 0 you will get what is called margules it is called the two-suffix equation, because margules wrote it as a12, he wrote these with subscripts a1 a2 and so on.

So it is called two-suffix equation all had these are two-suffix estimate, and does not matter it is in two are missing, then you can similarly have ABC AB CD etc.. So you get various all these are called margules equation, so that he wrote them down. When A' and B' are not equal to 0 that Van Laars equation, the structure is the same, because if you look at Van Laars equation x1 x2 by this is b1 x1 + b2 x2.

So in this case they are called Van Laar's equations now compared with van Laar x1 x2 by this you will call this parameter α, just call it α write α12. So you will get A'+B'x1 = a1x1 + b2x2 / b1b2 α12. So this is b1 – b2 (x1) + b2. So your A' is simply b2/b1 or 1/b1α12 and B' is the coefficient of x1. Exact according to Van Laar b1 b2 are actually volumes according to Van der Waals right.

So they are known from pure component properties, so this b1 b2 all these are known only constant that is unknown is α12. Whereas in practice people treat A' B' as independent parameters. And only if you treat it as independent parameters you get a good fit to the data. If you try to use the original Van Laar equation with values of b1 b2 from experimental data you do not get a good fit, this equation fit it all mixture data.

Even now for alcohol water mixtures is probably one of the best correlating equations. This works very well and Porters equations very well for like suppose if you have A=0, this one works very well for simple mixtures where molecules are very similar. And then the second this one works a little better if molecular separations are the larger number of study is earlier were funded by petroleum industry.

So they are ones who had these various hydrocarbons coming out of the distillation column. They were similar, but they varied in molecular weight from very low to very high, they could do all the wave from methane, molecular weight and what about 15, 16, all the way down to which could be C56 of a way, a very huge molecular weight ranges. And if you have these mixtures, you could describe them by various margules equations to ABC are not equal to 0 have been used quite weight.

So this is really is the sum of the way you do is, you simply show that you can get from Δg and arbitrary model for Δg you can get all the μ1s. Once you show that all you have to do is guess Δg, there is no restriction on Δg in thermodynamics except that reasonable restrictions like it has to go to 0, and you go to the pure state, it has to be a smooth function, you do not go on produce that functions and say Δg jumps here, jumps there, it does not do that experiment.

So you have to can have a smooth of experiment. And the easiest way to get us more functions you get a polynomial or its reciprocals, so you do it actually.

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