Advanced Thermodynamics
Prof. Dr. Nanda kishore
Department of Chemical Engineering
Indian Institute of Technology – Guwahati, India

Lecture-20
Models for Excess Gibbs Energy

Welcome to the MOOCs course advanced thermodynamics the title of this lecture is models for excess Gibbs energy. We start with Wohl's expansion for excess Gibbs energy which is a kind of a generalized one. Because generalized one in the sense by applying some kind of constraints or restrictions, you know we can reduce to some other model for excess Gibbs energy from this Wohl's expansion.

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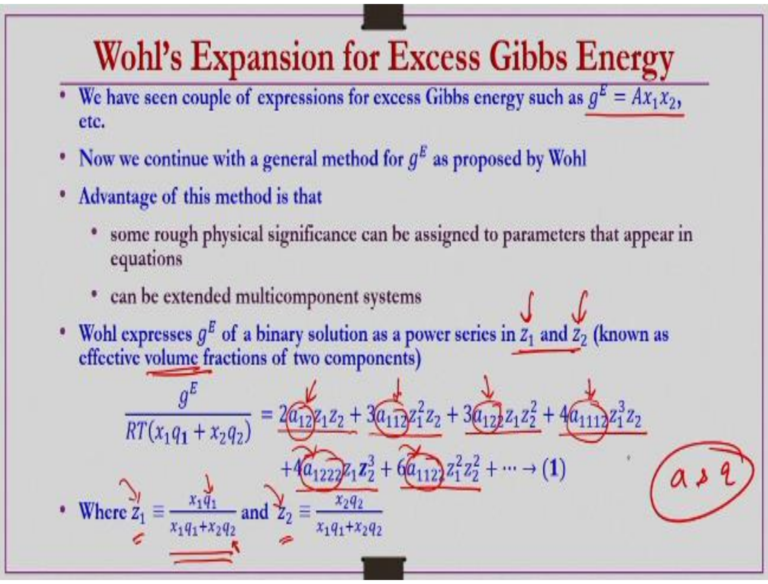

Wohl's Expansion for Excess Gibbs Energy

- We have seen couple of expressions for excess Gibbs energy such as $g^E = Ax_1x_2$, etc.
- Now we continue with a general method for g^E as proposed by Wohl
- Advantage of this method is that
    - some rough physical significance can be assigned to parameters that appear in equations
    - can be extended multicomponent systems
- Wohl expresses g^E of a binary solution as a power series in z_1 and z_2 (known as effective volume fractions of two components)

$$\frac{g^E}{RT(x_1q_1 + x_2q_2)} = 2a_{12}z_1z_2 + 3a_{112}z_1^2z_2 + 3a_{122}z_1z_2^2 + 4a_{1112}z_1^3z_2 + 4a_{1222}z_1z_2^3 + 6a_{1122}z_1^2z_2^2 + \cdots \rightarrow (1)$$

- Where $z_1 \equiv \frac{x_1q_1}{x_1q_1+x_2q_2}$ and $z_2 \equiv \frac{x_2q_2}{x_1q_1+x_2q_2}$

a & q

We have already seen a few simple expressions for excess Gibbs energy like a two suffix margules equation that is $g^E = A\, x_1\, x_2$ something like that then also we have seen expansion or extension of this equation like $x_1\, x_2\{A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \cdots\}$. So, like this. So, if we include the only first term in the parenthesis then it is a 2 suffix margules equation if we include the second term also.

Then it reduces to the rate known as a kind of a three suffix margules equation if you include the next term also then it is known as the 4 suffix margules equation like the simple models we have seen and then their corresponding activity coefficients also we have seen for a binary mixture.

So, now what we do, we have a kind of generalized 1, you know, we continue with the general method for the g^E. It has 2 advantages, first of all the; you know, whatever the parameters that are present in this Wohl's expansion. They will be assigned with some kind of physical significance that is one important advantage and another advantage is that, it can also be extended to multi component mixtures. So, these are the 2 important advantages of this method. So, let us say what is this g^E. Wohl's expresses g^E of a binary solution as a power series of z_1 z_2, z_1 and z_2 are known as the effective volume fractions of 2 components component 1 and component 2. This is effective volume fraction of component 1 this is an effective volume fraction of component 2.

So, it is a kind of power series of z_1 and z_2 what kind of power series it is? In this power series only these terms are there or any other terms are there that is what we see. So, if you write this Wohl's expansion for a binary solution, then we have $\frac{g^E}{RT(x_1q_1+x_2q_2)}$ = 2 a_{12} z_1 z_2 + 3 a_{112} z_1^2 z_2 + 3 a_{122} z_1 z_2^2 + 4 a_{1112} z_1^3 z_2 + 4 a_{1222} z_1 z_2^3 + 6 a_{1122} z_1^2 z_2^2 and so on so.

Where this z_1, which is nothing but the effective volume fraction of component 1 $z_1 \equiv \frac{x_1q_1}{x_1q_1+x_2q_2}$. z_2, similarly, $z_2 \equiv \frac{x_2q_2}{x_1q_1+x_2q_2}$whereas this x_1 and x_2 are nothing but the mole fraction of those components 1 and 2 in the mixture. So, now, when we call z_1 z_2 are kind of effective volume fractions of 2 components and then x_1 x_2 are nothing but the mole fraction of those component 1 and 2.

Then obviously, this ratio $\frac{x_1q_1}{x_1q_1+x_2q_2}$ is nothing but effective volume fraction of 2 components and then this q_1 and q_2 are having, I know some relation with the size of the molecule or volume of the molecule because we are calling it is a kind of effective volume fraction of component as z_1 or z_2 respectively for component 1 and 2. So, that is one and then what else we see in this equation other than z_i or z_1 z_2 etc. We also have some constant a_{12}, a_{112}, a_{122} and so on like this a constant.

So, that means, in addition to this z_1 that is an effective volume fraction, we are also having some kind of other multiplication factors on the constant for each term. So, what are they indicate that is the other thing. And then what is this q? q is indicating the size of the molecules and z is indicating the effective volume fraction of the molecules of the component that we are taking. So, now, we see in this equation we have a and then q constants. a and q are the constants that we see in this Wohl's expansion.

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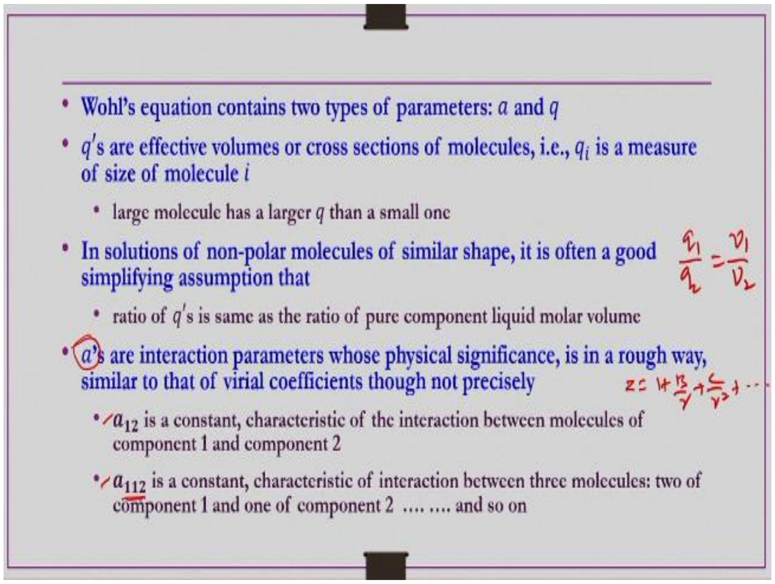

- Wohl's equation contains two types of parameters: a and q
- q's are effective volumes or cross sections of molecules, i.e., q_i is a measure of size of molecule i
  - large molecule has a larger q than a small one
- In solutions of non-polar molecules of similar shape, it is often a good simplifying assumption that
  - ratio of q's is same as the ratio of pure component liquid molar volume
- a's are interaction parameters whose physical significance, is in a rough way, similar to that of virial coefficients though not precisely
  - a_{12} is a constant, characteristic of the interaction between molecules of component 1 and component 2
  - a_{112} is a constant, characteristic of interaction between three molecules: two of component 1 and one of component 2 …. …. and so on

$\frac{q_1}{q_2} = \frac{v_1}{v_2}$

$z = 1 + \frac{B}{v} + \frac{C}{v^2} + \cdots$

q's are effective volumes or cross sections of molecules that is q_i is a measure of the size of the molecules that means, bigger molecule is obviously going to have a kind of larger q value and then in solutions of non polar molecules of similar shape it is often a good simplifying assumption to take that $\frac{q_1}{q_2} = \frac{v_1}{v_2}$ that is the ratio of this q_1, q_2 may be taken as a kind of a ratio between molar volume of component 1 and 2.

And then this is having a significance are kind of related to the interaction. So, a's are interaction parameters whose physical significance in a rough way analogous to so called the virial coefficients. Let us say in the virial equation of state if you remember that $= 1 + \frac{B}{v} + \frac{C}{v^2}$ and so on. So, this B second virial coefficient, C is third virial coefficient and B and C, respectively indicate the interaction between 2 molecule or combination of molecules and combination of 3 molecules at a time respectively.

Or B indicates the deviation from ideal behavior because of the interaction between 2 molecules and then C indicates the deviation from ideal behavior, because of the interaction between3 molecules. Similarly, this a it does not say directly what is how it is related to the non-ideality and all that. But obviously, if you have a different interactions or dissimilar interactions there is going to be non identity of this solution.

So, those interactions between the molecules is represented by “a” that means a_{12} is nothing but the interaction between 2 molecules of component 1 and component 2. One molecule of component 1 and another molecule of component 2 like that it indicates a_{12} it is a constant, and then it is a characteristics of the interaction between 2 molecules, one molecule of component 1 and another molecule of component 2.

Similarly, a_{112} is also a constant and it is a characteristic of interaction between 3 molecules, 2 molecules of component 1 and 1 molecule of component 2. So, this is a_{112} these are the, you know the suffix whatever they indicate the, you know molecule of which component. 211’s are they that means 2 molecules of component 1 and then 2 is only 1’s that means one molecule of component 2 like that, all other a's are having you know, some kind of physical significance related to the interaction amongst the molecules.

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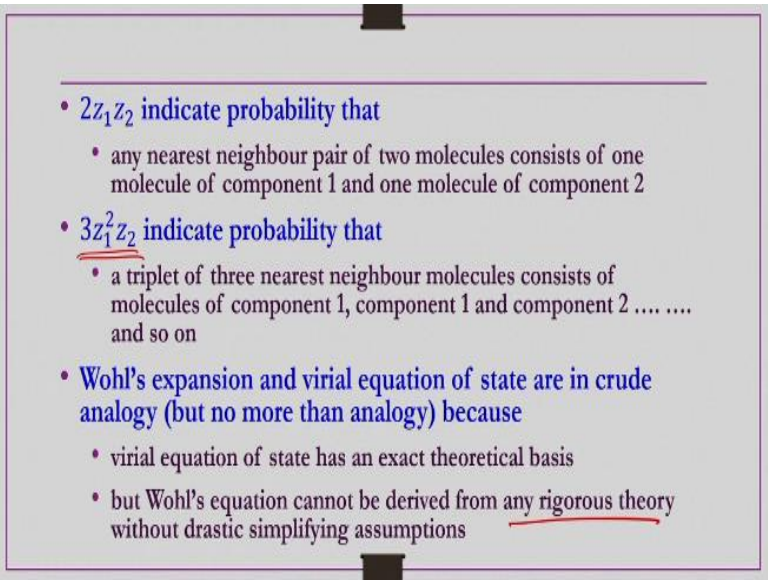

- $2z_1z_2$ indicate probability that
  - any nearest neighbour pair of two molecules consists of one molecule of component 1 and one molecule of component 2
- $3z_1^2z_2$ indicate probability that
  - a triplet of three nearest neighbour molecules consists of molecules of component 1, component 1 and component 2 …. …. and so on
- Wohl’s expansion and virial equation of state are in crude analogy (but no more than analogy) because
  - virial equation of state has an exact theoretical basis
  - but Wohl’s equation cannot be derived from any rigorous theory without drastic simplifying assumptions

So, then, what this factors 2 z_1 z_2 indicate? In the equation we have 2 z_1 z_2 a_{12} like that we have these terms on it and then similarly, 3 z_1^2 z_2 a_{112} like those constants that is whatever the z_1 z_2 are the powers of z_1 z_2 other there multiplied by some kind of constants. So, any 2 z_1 z_2 indicate probability that any nearest neighbor pair of 2 molecules consists of one molecule of component 1 and then one molecule of component 2.

Similarly, 3 z_1^2 z_2 indicate the probability any triplet of 3 nearest neighbor molecules consisting of 2 molecules of component 1 and then one molecule of component 2 that is what and so on. So, Wohl's expansion and variable equation of state are in crude analogy only, only analogy because virial equation of state has an exact theoretical basis for its derivation, whereas, the Wohl's equation cannot be derived from any rigorous theory without making any drastic simplifying assumptions.

And then if you make drastic simplifying assumptions, you may not be able to mathematically represent the true picture of the problem. So, it is a just an analogy between 2.

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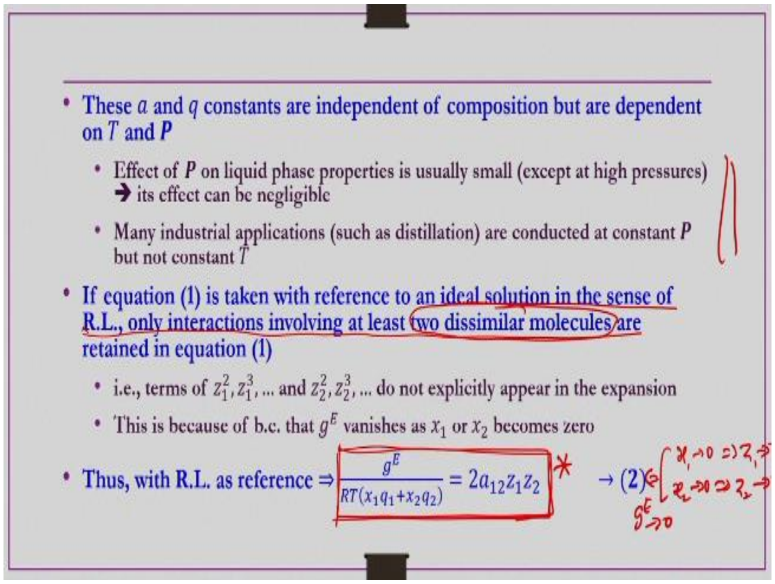

- These a and q constants are independent of composition but are dependent on T and P
  - Effect of P on liquid phase properties is usually small (except at high pressures) ➔ its effect can be negligible
  - Many industrial applications (such as distillation) are conducted at constant P but not constant T
- If equation (1) is taken with reference to an ideal solution in the sense of R.L., only interactions involving at least two dissimilar molecules are retained in equation (1)
  - i.e., terms of $z_1^2, z_1^3, \ldots$ and $z_2^2, z_2^3, \ldots$ do not explicitly appear in the expansion
  - This is because of b.c. that g^E vanishes as x_1 or x_2 becomes zero
- Thus, with R.L. as reference ⇒ $\boxed{\frac{g^E}{RT(x_1q_1+x_2q_2)} = 2a_{12}z_1z_2}$ * → (2)

$x_1 \to 0 \Rightarrow z_1 \to$

$x_2 \to 0 \Rightarrow z_2 \to$

$g^E \to 0$

And these constants a and q are independent of combination but they are dependent on the temperature and pressure. However, we know that the effect of P is very small in the case of liquid solutions unless the pressure is very high. So, considering that fact maybe effect of P can be neglected but effect of temperature cannot be neglected it is very much essential but many industrial applications such as distillation are conducted at constant P but not at constant T. So, this has these have to be obtained for a different temperature conditions etc. as per the applications.

So, let us say if equation 1 is taken with reference to an ideal solution in the sense of Raoult's law, only interactions involving at least 2 dissimilar molecules that is we are taking 2 molecules only and they have to be dissimilar. So, that means, we cannot take 2 molecules of same component like 11 you cannot take 22 you cannot take because they are similar, they have to be dissimilar.

So, 12 type of interactions we are taking dissimilar unlike interactions. So, those molecules we are taking and then we take a reference ideal solution in the sense of Raoult's law. Raoult's law what does it mean? Raoult's law says like you know it is ideality of the solution is applicable for the entire range of mole fraction from $x_i = 0$ to 1. So, under such conditions you know, whatever the ideal behavior is there, that is, you know, represented by $f_i = \Re_i\ x_i$, $\Re_i$ is nothing but f_i^0 or f_i^0 is $\Re_i$ many times is nothing but the P_i^{sat} if the pressure is low pressure.

That is when you are taking only dissimilar interactions, if you are taking only dissimilar interactions. So, whatever the $z_1^2\ z_2^2\ z_1^3\ \ z_2^3$ etc. These terms will not be there because these terms are because of the you know whatever the constants that multiplication factors are there they're indicating interaction because of similar molecules as we just have seen 2 z_1^2 indicates the probability of 2 nearest molecules being from a component 11.

So, if interaction whatever is there that is the similar interaction between 2 molecules of same component. So, that is the reason this $z_1^2\ z_2^2\ z_1^3$ is nothing but the interaction between a triplet of molecules and then all 3 molecules of same component. So, then that means again though it is a 111 interaction, it is still similar interaction, it is not dissimilar interaction. So, this term will also be not there. So, in the Wohl's expansion if you exclude all these $z_1^2\ z_2^2$ and $z_1^3\ z_2^3$ terms etc.

Then what you have, you will be getting this equation $\frac{g^E}{RT(x_1q_1+x_2q_2)} = 2\ a_{12}\ z_1\ z_2$. Because this g^E has to vanish it $x_1 \rightarrow 0$ and $x_2 \rightarrow 0$ as well because if $x_1 \rightarrow 0$ then $z_1 \rightarrow 0$. So, g^E would be $\rightarrow 0$ then $x_2 \rightarrow 0$ then also $z_2 \rightarrow 0$. So, then again in the either of these conditions $g^E \rightarrow 0$ according to this equation. So, this equation is Raoult's law as a kind of reference. So, now, this is the equation that we are going to consider and then we are going to find out it is activity coefficient. So, this is one simplification.

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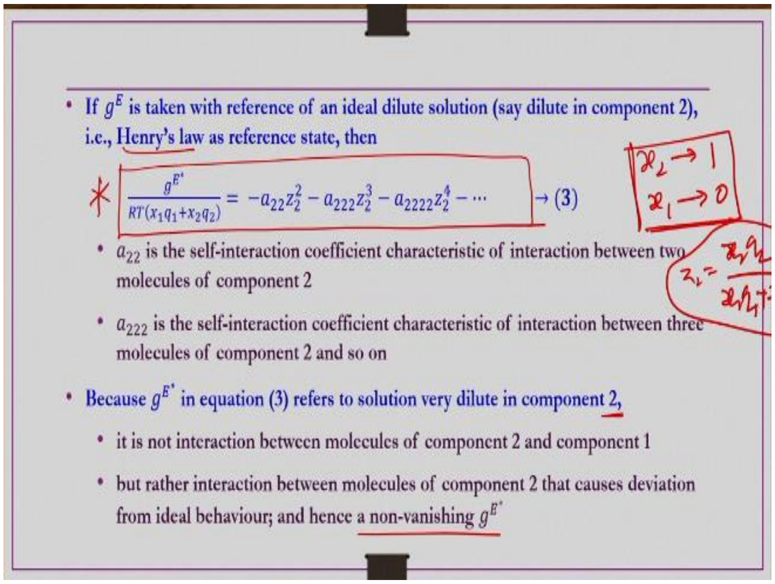

- If g^E is taken with reference of an ideal dilute solution (say dilute in component 2), i.e., Henry's law as reference state, then

$$* \boxed{\frac{g^{E^*}}{RT(x_1q_1+x_2q_2)} = -a_{22}z_2^2 - a_{222}z_2^3 - a_{2222}z_2^4 - \cdots} \rightarrow (3)$$

$$\boxed{\begin{matrix} x_2 \rightarrow 1 \\ x_1 \rightarrow 0 \end{matrix}}$$

$$z_2 = \frac{x_2q_2}{x_1q_1+}$$

  - a_{22} is the self-interaction coefficient characteristic of interaction between two molecules of component 2
  - a_{222} is the self-interaction coefficient characteristic of interaction between three molecules of component 2 and so on
- Because g^{E^*} in equation (3) refers to solution very dilute in component 2,
  - it is not interaction between molecules of component 2 and component 1
  - but rather interaction between molecules of component 2 that causes deviation from ideal behaviour; and hence a non-vanishing g^{E^*}

So, if g^E is taken with reference of an ideal dilute solution, say diluting component to that is Henry's law as a reference state getting back to the reference states, like you know, for liquid cases liquid solutions or f_i^0 = $f_{\text{pure } i}$ for the case of a reference state. You take Levy's random state, where this $x_i \rightarrow 1$ if you take Henry's law as a kind of reference then this $f_i^0 \rightarrow H_i$ in the component 1 or whatever in this case, this $x_i \rightarrow 0$ that means x_i component is very, very small.

So, whatever let us say x_i component is a dissolved in j solvent. So, then j is dominating most of the solution is containing j component i component is very, very small. So, that is what under such condition f_i^0 and is taken H_{ij}. So, x_i is tending to 0 that means, here whatever the interactions are there, you know those interactions are similar interactions of you know, same component j is going to be dominating here or if you take for a binary system. So, f_1^0 because component 1 with respect to 1 we are doing.

So, this should be H_{12} for a binary system and this H_{12} are dominating are having dominating interactions between 2 2 molecules. This is the dominating one, it is less dominated between the 1 2 molecules that means, they are this when you do when you take these Henry's law as a kind of a reference, you are going to have the terms because of z_2^2, z_2^3etc. these kind of terms you are going to have whatever the terms related to z_{12}, z_{112}, these are going to be very small they are not going to be present in large quantities.

Large quantities in the sense, dominating. So, these are going to be more dominated z_2^2, z_2^3 etc. are going to be more dominated than these z_{12} z_{112} terms etc. So, under such limiting conditions or when you take Henry's law as a kind of reference state then whatever the interaction between component 2 similar interaction between component 2 are going to be dominating because that component is present in large quantity, whereas, the component 1 is present in small quantity.

Because it is Henry's law valid for dilute solutions, dilute in component 2 that is what we have taken. So, all 12 112 122 kind of interactions are going to be weaker compared to 22 or 222 you know quadrate 2 kind of interaction So, that is the reason this $\frac{g^{E^*}}{RT(x_1q_1+x_2q_2)}$ we are going to have $-$ a_{22} z_2^2 $-$ a_{222} z_2^3 $-$ a_{2222} z_2^4 $- \cdots$. So, a_{22} is the self-interaction coefficient characteristic of interaction between 2 molecules of component 2.

And then a_{222} is the self interaction coefficient characteristics of interaction between 3 molecules of component 2 and so on. So, and then g^{E^*} in equation 3 refers to solution very dilute in component 2, right? So, that means, it is not interaction between molecules of component 2 and component 1 because component is very small quantity present but rather interaction between molecules of component 2 that causes deviation from ideal behavior. Hence, a non-vanishing g^{E^*} is present.

So, whatever the interaction between molecules of 2 is ideal so, that is going to cause a kind of some kind of non-reality in the sense of Henry's law. So, that is the reason this equation whatever this g^{E^*} equation $\frac{g^{E^*}}{RT(x_1q_1+x_2q_2)}$, whatever is the case, you know, you are not going to have a kind of g^{E^*} tending to 0 for any combination of this z_2 because z_2 is very close to 1 and then z_1, because x_2 is very close to 1 and the x_1 is very close to 0. So this is not going to be vanishing under whatever the circumstances.

Because now, this z_2 is nothing but what $z_2 = \frac{x_2q_2}{x_1q_1+x_2q_2}$. So, if $x_2 \rightarrow 1$, this is not going to be 0 and then this overall this equation is not going to be 0 anyway. So, now let us illustrate the generality of equation 1 by considering a few models of g^E.

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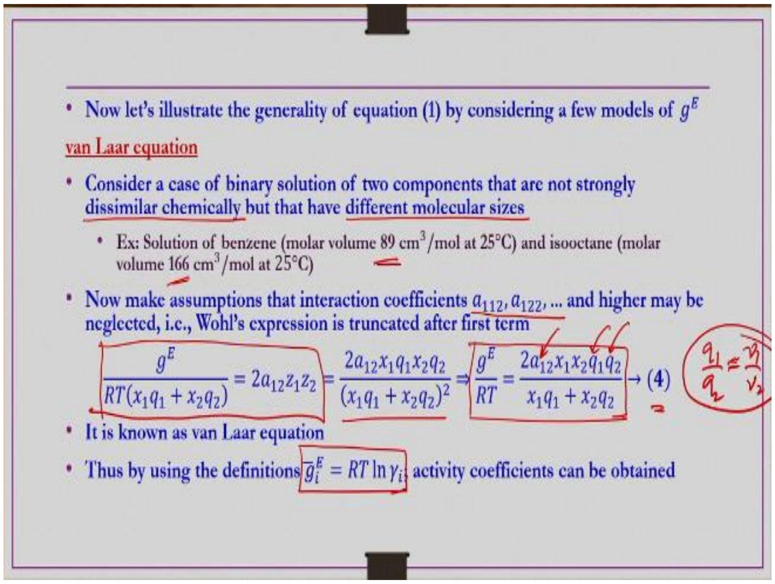

- Now let's illustrate the generality of equation (1) by considering a few models of g^E

van Laar equation

- Consider a case of binary solution of two components that are not strongly dissimilar chemically but that have different molecular sizes
    - Ex: Solution of benzene (molar volume 89 cm^3/mol at 25°C) and isooctane (molar volume 166 cm^3/mol at 25°C)
- Now make assumptions that interaction coefficients $a_{112}, a_{122}, \ldots$ and higher may be neglected, i.e., Wohl's expression is truncated after first term

$$\boxed{\frac{g^E}{RT(x_1q_1 + x_2q_2)} = 2a_{12}z_1z_2} = \frac{2a_{12}x_1q_1x_2q_2}{(x_1q_1 + x_2q_2)^2} \Rightarrow \boxed{\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1 + x_2q_2}} \rightarrow (4) \qquad \frac{q_1}{q_2} = \frac{v_1}{v_2}$$

- It is known as van Laar equation
- Thus by using the definitions $\boxed{\bar{g}_i^E = RT \ln \gamma_i}$ activity coefficients can be obtained

So what we do we start with a simplest one van Laar equation and write van Laar equation that we take consider the case of binary solution of 2 components that are not strongly dissimilar chemically, but how the different molecular size. So, let us say you how to take a molecule 2 molecules, which are chemically not very dissimilar but their size wise if you this if you see this size then they are going to be very dissimilar by size in a sense let us say if you take the molar volume of these components 2 components.

If they are very different from each other then you can say that by size they are dissimilar. So, for example, you take the solution of benzene and iso-octane. So, they are chemically not very dissimilar, first of all, but the molar volume is if you see benzene 89 cc per mol and iso-octane 166 cc per mol. So, they are very different molar volume which they are very different though chemically they are not very different.

So, if you take such kind of solution and then make assumption that interaction coefficient higher interaction coefficients rather that is 3 molecular interaction 4 molecular interactions, you are not considering you are considering only to molecular interaction that is considering only first term in the Wohl's expansion and after that whatever the remaining terms are there, you are discarded. You are not taking that a_{112} a_{122} those kinds of terms are higher terms, you are not considering you are considering only 2 molecular interactions.

And then that are also dissimilar interactions. So, then you will have if you retain only the first term in the RHS of Whol's expansion, then you will get this equation $\frac{g^E}{RT(x_1q_1+x_2q_2)}$ = 2 a_{12} z_1 z_2, now z_1 z_2 if you substitute $\frac{x_1q_1}{x_1q_1+x_2q_2}$ and $\frac{x_2q_2}{x_1q_1+x_2q_2}$ respectively, then you have this one this term and then the square of x_1 q_1 + x_2 q_2 in the RHS is canceled out with the 1 x_1 q_1 + x_2 q_2.

So, then you have $\frac{g^E}{RT}$= $\frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2}$ this is known as the van Laar's equation. So, here what you have q_1 q_2 are the 2 constants and then a_{12} is another constant, it looks like a three parameter model. But however, you know the activity coefficient that we are going to get that is going to have only 2 parameters because it is not the individual queues that are important in such kind of applications.

It is the ratio is important and then for simpler molecules we have seen $\frac{q_1}{q_2}$ = $\frac{v_1}{v_2}$ roughly, it is a kind of approximation and then true also for simple molecules. So, by considering this one you can say that is the kind of one constant. So, this equation number 4 is known as the van Laar equation. Now, for this equation we applied the definition $\bar{g}_i^E$= RT ln γ_i and then try to find out γ_i, i = 1 and 2, because we are doing all this for binary solution.

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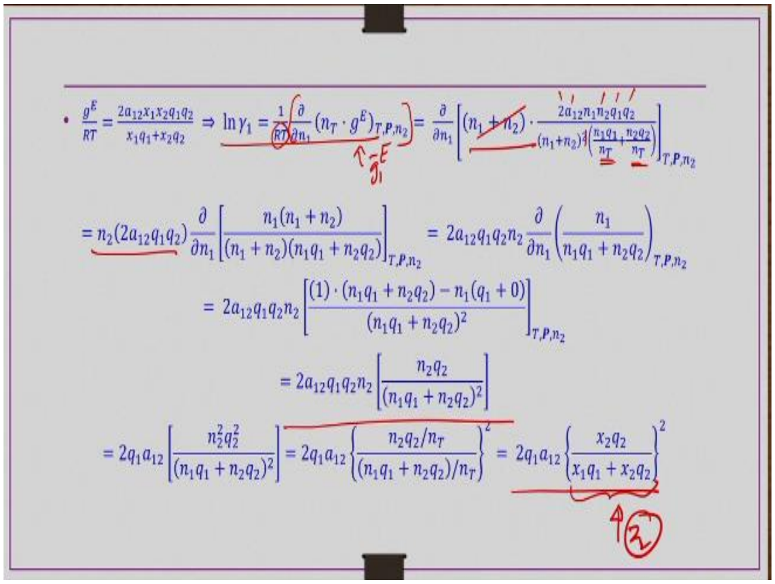

- $\frac{g^E}{RT}=\frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2} \Rightarrow \underline{\ln\gamma_1 = \frac{1}{RT}\frac{\partial}{\partial n_1}(n_T\cdot g^E)_{T,P,n_2}} = \frac{\partial}{\partial n_1}\left[(n_1+\cancel{n_2})\cdot\frac{2a_{12}n_1n_2q_1q_2}{(n_1+n_2)\cancel{^2}\left(\frac{n_1q_1}{n_T}+\frac{n_2q_2}{n_T}\right)}\right]_{T,P,n_2}$

$\uparrow \bar{g}_1^E$

$$= \underline{n_2(2a_{12}q_1q_2)}\frac{\partial}{\partial n_1}\left[\frac{n_1(n_1+n_2)}{(n_1+n_2)(n_1q_1+n_2q_2)}\right]_{T,P,n_2} = 2a_{12}q_1q_2n_2\frac{\partial}{\partial n_1}\left(\frac{n_1}{n_1q_1+n_2q_2}\right)_{T,P,n_2}$$

$$= 2a_{12}q_1q_2n_2\left[\frac{(1)\cdot(n_1q_1+n_2q_2)-n_1(q_1+0)}{(n_1q_1+n_2q_2)^2}\right]_{T,P,n_2}$$

$$= 2a_{12}q_1q_2n_2\left[\frac{n_2q_2}{(n_1q_1+n_2q_2)^2}\right]$$

$$= 2q_1a_{12}\left[\frac{n_2^2q_2^2}{(n_1q_1+n_2q_2)^2}\right] = 2q_1a_{12}\left\{\frac{n_2q_2/n_T}{(n_1q_1+n_2q_2)/n_T}\right\}^2 = 2q_1a_{12}\underbrace{\left\{\frac{x_2q_2}{x_1q_1+x_2q_2}\right\}^2}_{\uparrow ②}$$

So, that ln γ1 you do that should be $\frac{1}{RT}\left[\frac{\partial}{\partial n_1}(n_T.g^E)\right]_{T,P,n_2}$. $\bar{g}_1{}^E = \left[\frac{\partial}{\partial n_1}(n_T.g^E)\right]_{T,P,n_2}$, this part is nothing but $\bar{g}_1{}^E$, now n_T you write $n_1 + n_2$ and then $\frac{g^E}{RT}$ is nothing but whatever $\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2}$. So, x_1 you write $\frac{n_1}{n_T}$. Similarly, x_2 also you write $\frac{n_2}{n_T}$ like that, you simplify this one. So, then you have this expression.

Here in this expression what we have this q_1 q_2 and then n_2 a_{122} or constant that you take common and then remaining terms you keep here and then simplify. So, the $(n_1 + n_2)^2$ and this $n_1 + n_2$ is gone so, then you have remaining n_1 ($n_1 + n_2$) because here also you have our n_T. So, that is $n_1 + n_2$. So, that simplification if you do simply and then differentiate then you will be getting this equation.

So this equation if you convert in terms of x_1 x_2 by dividing both numerator and denominator by n_T, then you will have 2 q_1 $a_{12}\left\{\frac{x_2q_2}{x_1q_1+x_2q_2}\right\}^2$. So, now, we know this $\frac{x_2q_2}{x_1q_1+x_2q_2}$ is nothing but z_2. So, if you write z_2 in place of this 1 you will get 2 q_1 a_{12} z_2^2.

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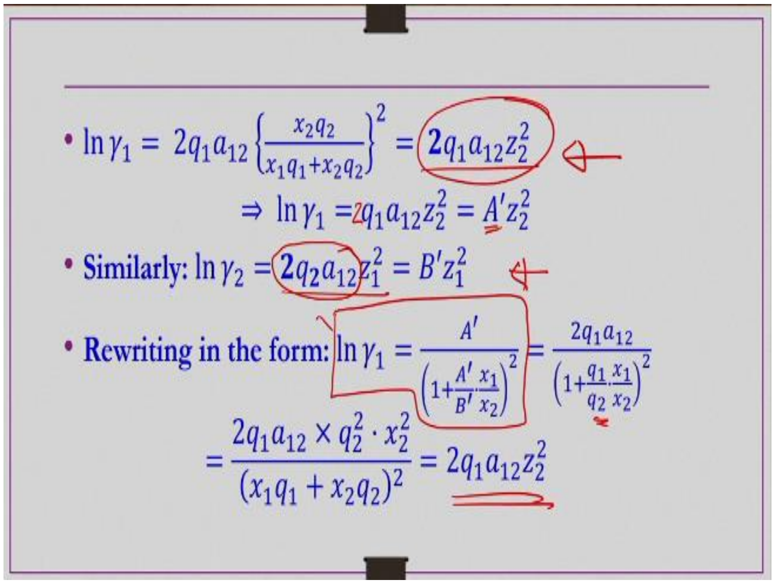

- $\ln\gamma_1 = 2q_1a_{12}\left\{\frac{x_2q_2}{x_1q_1+x_2q_2}\right\}^2 = \mathbf{2q_1a_{12}z_2^2}$

  $\Rightarrow \ln\gamma_1 = 2q_1a_{12}z_2^2 = A'z_2^2$

- **Similarly:** $\ln\gamma_2 = \mathbf{2q_2a_{12}}z_1^2 = B'z_1^2$

- **Rewriting in the form:** $\ln\gamma_1 = \frac{A'}{\left(1+\frac{A'}{B'}\cdot\frac{x_1}{x_2}\right)^2} = \frac{2q_1a_{12}}{\left(1+\frac{q_1}{q_2}\cdot\frac{x_1}{x_2}\right)^2}$

  $= \frac{2q_1a_{12} \times q_2^2 \cdot x_2^2}{(x_1q_1+x_2q_2)^2} = 2q_1a_{12}z_2^2$

So, let us say whatever this 2 q_1 a_{12}, if you write it as A' then you will have A' z_2^2 is nothing but ln γ1 I am just representing our combining these constant as 1 constant A'. Similarly, if you do ln γ2 and then simplify and then try to obtain the expression you will get ln γ_2 = 2 q_2 a_{12} $z_1^2$and that whatever these 2 q_2 a_{12} if you write as B' it is nothing but B'z_1^2.

So, if you rewrite whatever this ln γ_1 and then ln γ_2 equations respectively in this particular form, in terms of is A' and B' then you have ln γ_1 = $\frac{\mathrm{A}'}{\left(1+\frac{\mathrm{A}'}{\mathrm{B}'}\cdot\frac{x_1}{x_2}\right)^2}$. So, this A' whatever I have taken B' whatever I have taken that is 2 q_1 a_{12} and 2 q_2 a_{12} respective to those things I substituted here and then cross check that we are getting back to the same expression this. So, this form in the books in generally you find ln γ_1 as in this particular form.

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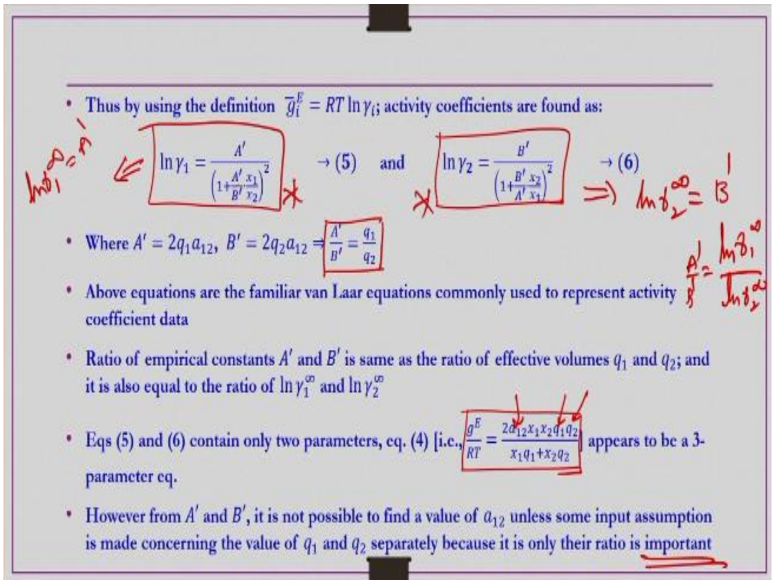

- Thus by using the definition $\bar{g}_i^E = RT \ln \gamma_i$; activity coefficients are found as:

$$\ln\gamma_1^\infty = A' \Leftarrow \boxed{\ln \gamma_1 = \frac{A'}{\left(1+\frac{A'}{B'}\frac{x_1}{x_2}\right)^2}} \rightarrow (5) \quad \text{and} \quad \boxed{\ln \gamma_2 = \frac{B'}{\left(1+\frac{B'}{A'}\frac{x_2}{x_1}\right)^2}} \rightarrow (6) \Rightarrow \ln\gamma_2^\infty = B'$$

- Where $A' = 2q_1a_{12}$, $B' = 2q_2a_{12} \Rightarrow \boxed{\frac{A'}{B'} = \frac{q_1}{q_2}}$

$$\frac{A'}{B'} = \frac{\ln\gamma_1^\infty}{\ln\gamma_2^\infty}$$

- Above equations are the familiar van Laar equations commonly used to represent activity coefficient data
- Ratio of empirical constants A' and B' is same as the ratio of effective volumes q_1 and q_2; and it is also equal to the ratio of $\ln \gamma_1^\infty$ and $\ln \gamma_2^\infty$
- Eqs (5) and (6) contain only two parameters, eq. (4) [i.e.,$\boxed{\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2}}$ appears to be a 3-parameter eq.
- However from A' and B', it is not possible to find a value of a_{12} unless some input assumption is made concerning the value of q_1 and q_2 separately because it is only their ratio is important

Similarly, ln γ_2 you will find in this particular form in textbooks. So, these are ln γ_1 and ln γ_2. So, here A' = 2 q_1 a_{12} and B' = 2 q_2 a_{12} or $\frac{\mathrm{A}'}{\mathrm{B}'} = \frac{q_1}{q_2}$. So, the above equations are the familiar van Laar equations commonly used to represent activity coefficient data and they are very famous because of their simplicity and then validated to a large range of simpler molecules.

And then ratio of these components $\frac{\mathrm{A}'}{\mathrm{B}'}$ are the same as ratio of the effective volumes $\frac{q_1}{q_2}$respectively. Also from this equation, if you try to get ln γ_1^∞ that means the component 1 is very small, ∞ly diluted in component 2, then ln γ_1^∞ is nothing but A' because x_1 → 0 or x_1 close to 0, so, whatever the denominator term is there $(1+0)^2$ so, 1 is there.

Similarly, here also if you take ln γ_2^∞ that means, component 2 is ∞ly diluting component 1 that is component 2 is very, very small quantity compared to the component 1 so, x_2 is very small so, then this our x_2 is close to 0 so, then whatever the in the denominator you will be getting 1 + a very small number close to 0 whole square so that you will get B'. So, this $\frac{A'}{B'}$ is not only $\frac{q_1}{q_2}$ but also it = $\frac{ln\gamma_1^\infty}{\ln \gamma_2^\infty}$.

Now, as I mentioned these equations ln γ_1 and ln γ_2 these expressions we got from this expression $\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2}$ and then here you see q_1 q_2 and then a_{123} parameters are there whereas, their activity coefficient it is having only 2 parameters. So, however from A' and B' it is not possible to find out a value of a_{12} unless some input assumption is made concerning the value of q_1 and q_2 separately because it is only the ratio is important in applications rather than their individual size.

Because we see that A' and B' is there here. So, that means that q_1 q_2 you need. You do not need q_1 individually q_2 individually.

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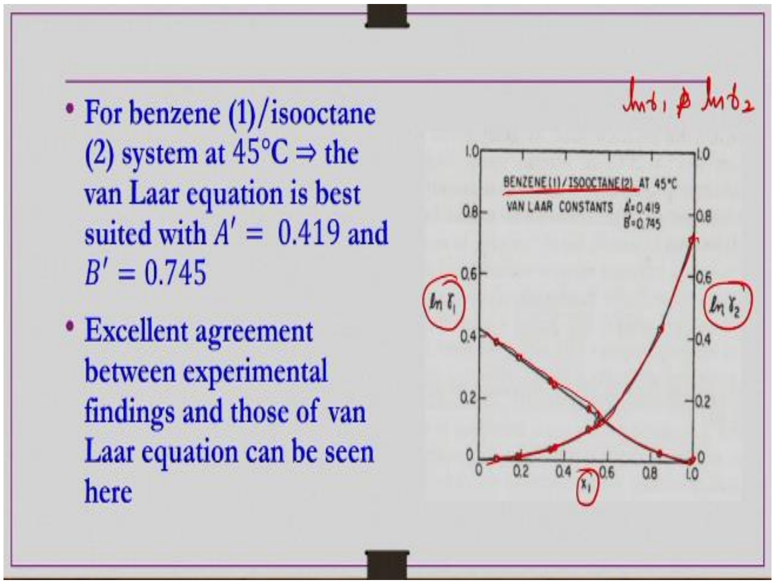

- For benzene (1)/isooctane (2) system at 45°C ⇒ the van Laar equation is best suited with $A' = 0.419$ and $B' = 0.745$
- Excellent agreement between experimental findings and those of van Laar equation can be seen here

So, now, we take an example this is benzene and iso-octane we have taken as a kind of assumption to describe this van Laar equation. So, whatever the activity coefficients that we get for benzene and then iso-octane respectively, that you plot with respect to or against the mole fraction of benzene. So, then you can see they are you know their experimental points are given by these circles here like this.

And then this curve fitting if you do using the ln γ_1 and then ln γ_2 expression that we just derived you can see they are matching very good their excellent match you can see between experimental and then theoretical result that we just derived suggested good validity of this van Laar equation especially for chemically. Similar, but dissimilar size molecules are simple molecules having dissimilarity of smaller range.

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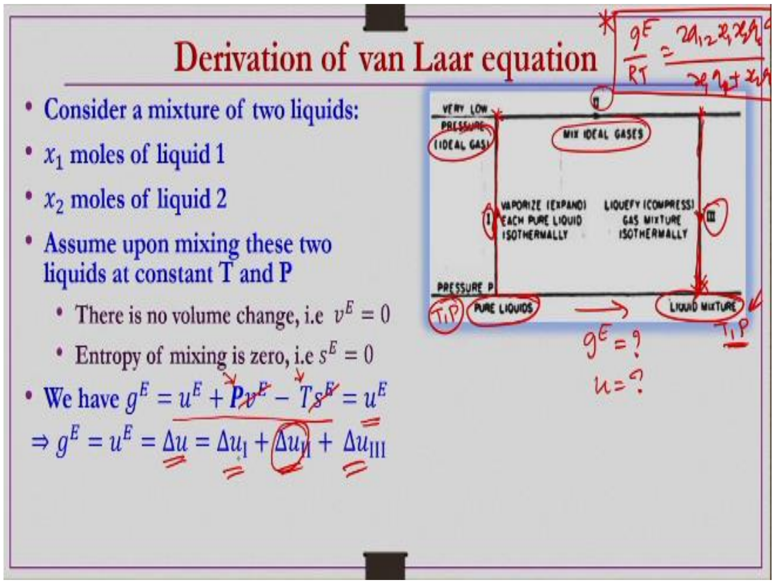

Derivation of van Laar equation

- Consider a mixture of two liquids:
- x_1 moles of liquid 1
- x_2 moles of liquid 2
- Assume upon mixing these two liquids at constant T and P
  - There is no volume change, i.e $v^E = 0$
  - Entropy of mixing is zero, i.e $s^E = 0$
- We have $g^E = u^E + P\cancel{v^E} - T\cancel{s^E} = u^E$

$\Rightarrow g^E = u^E = \Delta u = \Delta u_I + \Delta u_{II} + \Delta u_{III}$

So, we have seen that van Laar equation are we reduced from the Wohl's expansion by doing some assumption that is not taking the higher molecular interactions taking only 2 molecular interaction that also 2 molecular dissimilar interaction we have consider and then we obtain the activity coefficient and all that but whatever the $\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2}$ is there, can we derive it by some means? That is what we try to do now.

It is quite simple. So, what we do, we take pure liquids at certain temperature and pressure at and then we want to make a kind of liquid solutions or liquid mixture at the same temperature and pressure. So, now what we rather mixing thermodynamically we define a path rather directly mixing it. So what we do, we maintain the temperature constant and then vaporize it or expand it by decreasing the pressure. So, that this liquid solutions will vaporize and then that is that we call it as you know, step 1.

And then we decrease the pressure to very low pressure so that they can be comfortably you know, get into the vapor phase, or gather vapor phase and then the pressure is also, so that for the vapor phase we can apply ideal gas. So, then what we do we mix them ideally because once here at this after completion of step 1 and the 2 pure liquids individually we are not mixed up until now in the step 1 they are pure individual liquids are vaporized at constant temperature by reducing the pressure to very low pressure.

So, now, the vapors are in an ideal gas state. So, now, we are mixing ideally so, here that makes ideal gases the step 2. Now, what we have here we have a kind of mixture of ideal gases, which is at the temperature of the liquid mixing temperature but the pressure is very low pressure, very low pressure. And now what we do keeping the temperature constant again the same temperature constant we are liquefying this ideal gas mixture by increasing the pressure or by the compression.

So, that you know we are increasing the pressure to the initial temperature and pressure or initial pressure at which we wanted to make the mixture. So, then we have a kind of liquid mixture. So, this step we are calling step 3. So, now, for this process thermodynamic process we have to find out what is g^E and this g^E is it same this one or not that is what we are going to check. Actually we are going to derive this one. So, for this process we make a couple of assumptions.

The first assumption is that you know volume of mixing is 0 and then entropy of mixing is also 0 that is v^E and s^E both of them are 0 those are the kind of important assumption we are making. And then this vaporize the conditions whatever they pure components are there pure components are you know described by Van der Waal's equation of state these are the 2 important assumptions that we are making.

So, we do for a binary mixture for simplicity having x_1 moles of liquid 1 and then x_2 moles of liquid 2 and then upon mixing these 2 liquids at constant temperature and pressure there is no volume change and then there is no entropy change or entropy of mixing is also 0. So, we have to find out $g^E = u^E + Pv^E - Ts^E$ this pressure and temperature are constant we are mixing at the constant temperature and pressure but upon mixing this v^E and then s^E are 0 so, that g^E whatever is there that is nothing but u^E.

So, now that means whatever $g^E = u^E = \Delta u$ should be taken our estimated for this thermodynamic process and then get this information since u^E is a state function, so, whether you directly whatever the u that is required from this pure liquids T-P before mixing to after mixing this liquid to get the liquid solutions, whatever the u^E there that should be same whether you directly get this u for this step or you follow this step 1, step 2, step 3 and then add them together to get this point because this u^E state function.

So, now, individual processes, what is Δu, we have to find out or individual steps 3 steps, we have to find out and then we have to add them together and then whatever the u^E that you are going to get that is nothing but Δu and that is nothing but g^E and then that will be having this equation and then we know for the ideal gases Δu is 0. So, that step any way you can strike off.

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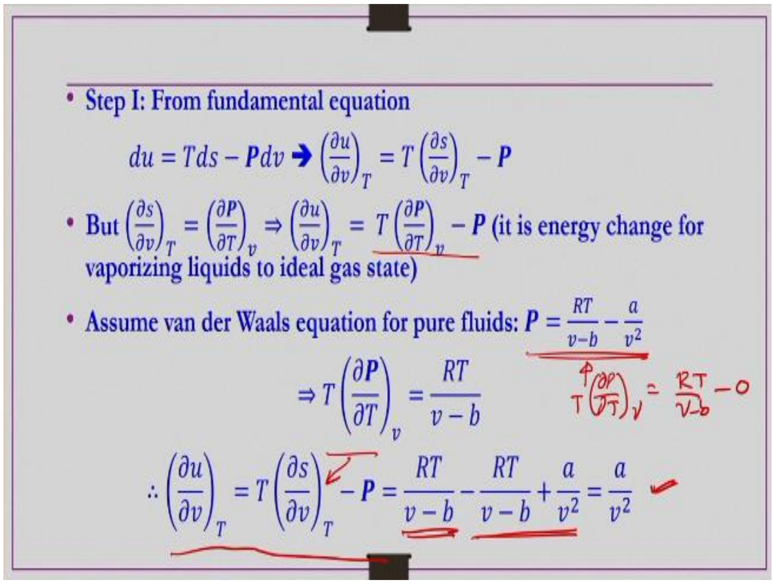

- Step I: From fundamental equation

$$du = Tds - Pdv \rightarrow \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P$$

- But $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = \underline{T\left(\frac{\partial P}{\partial T}\right)_v} - P$ (it is energy change for vaporizing liquids to ideal gas state)
- Assume van der Waals equation for pure fluids: $\underline{P = \frac{RT}{v-b} - \frac{a}{v^2}}$

$$\Rightarrow T\left(\frac{\partial P}{\partial T}\right)_v = \frac{RT}{v-b} \qquad T\left(\frac{\partial P}{\partial T}\right)_v = \frac{RT}{v-b} - 0$$

$$\therefore \underline{\left(\frac{\partial u}{\partial v}\right)_T} = T\left(\frac{\partial s}{\partial v}\right)_T - P = \underline{\frac{RT}{v-b}} - \underline{\frac{RT}{v-b} + \frac{a}{v^2}} = \frac{a}{v^2} \checkmark$$

So, step 1 fundamental equation that you have du = Tds − Pdv. So, $\left(\frac{\partial u}{\partial v}\right)_T$ because that we are doing at a constant temperature. So, it is nothing but T $\left(\frac{\partial s}{\partial v}\right)_T - P$. But, from Maxwell's equation we know $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$. So, that means, $\left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v - P$ and it is the energy change for vaporizing liquids to ideal gas state.

Whatever this $\left(\frac{\partial u}{\partial v}\right)_T$, you get that is nothing but the energy requirement for you know energy change for vaporizing the liquids to ideal gases. By keeping the temperature constant but decreasing the pressure from P pressure to very low pressure. Now, we are assuming Van der Waal's equation of state for pure liquids. So, for Van der Waal's equation of state, what is the T $\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b} - 0$. Now, if you multiply this one by T we will get $\frac{RT}{v-b}$.

But $\left(\frac{\partial u}{\partial v}\right)_T$ = T $\left(\frac{\partial s}{\partial v}\right)_T - P$ and $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$. So, that is nothing but this term so, that is $\frac{RT}{v-b}$ and then $-P$ is nothing but $-\frac{RT}{v-b} + \frac{a}{v^2} = \frac{a}{v^2}$. So, this is step 1 we are not mixing individually we are doing so, this generalized one we have done and then we have to do it for component 1 and component 2.

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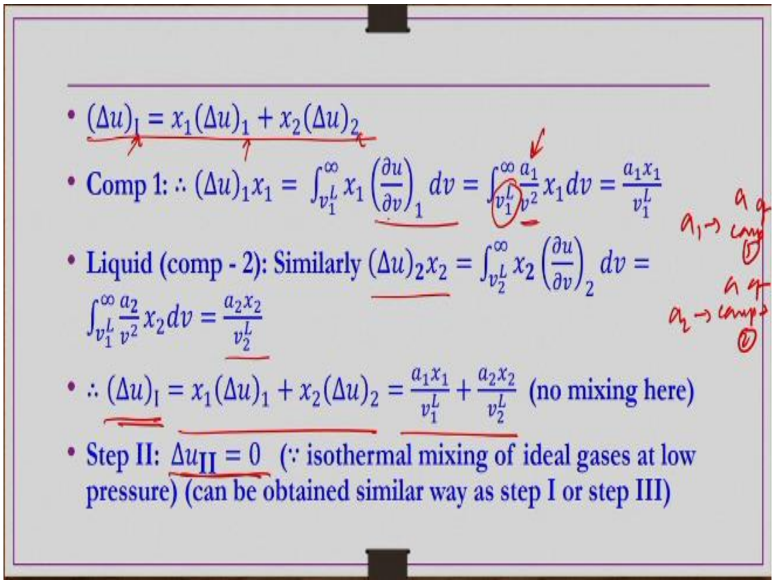

- $(\Delta u)_I = x_1(\Delta u)_1 + x_2(\Delta u)_2$
- Comp 1: $\therefore (\Delta u)_1 x_1 = \int_{v_1^L}^{\infty} x_1 \left(\frac{\partial u}{\partial v}\right)_1 dv = \int_{v_1^L}^{\infty} \frac{a_1}{v^2} x_1 dv = \frac{a_1 x_1}{v_1^L}$
- Liquid (comp - 2): Similarly $(\Delta u)_2 x_2 = \int_{v_2^L}^{\infty} x_2 \left(\frac{\partial u}{\partial v}\right)_2 dv = \int_{v_1^L}^{\infty} \frac{a_2}{v^2} x_2 dv = \frac{a_2 x_2}{v_2^L}$
- $\therefore (\Delta u)_I = x_1(\Delta u)_1 + x_2(\Delta u)_2 = \frac{a_1 x_1}{v_1^L} + \frac{a_2 x_2}{v_2^L}$ (no mixing here)
- Step II: $\Delta u_{II} = 0$ ($\because$ isothermal mixing of ideal gases at low pressure) (can be obtained similar way as step I or step III)

$a_1 \to$ a of comp ①

$a_2 \to$ a of comp ②

So, Δu step 1 should be x_1 $(\Delta u)_1$ + x_2 $(\Delta u)_2$ this 1 and 2 stands for the component 12 and then this capital I stands for the step 1. So, for the component 1 x_1 $(\Delta u)_1$if you do x_1 $(\Delta u)_1$ if you write $\left(\frac{\partial u}{\partial v}\right)_1$dv then you can have x_1 and then $\frac{\partial u}{\partial v}$ just now we derived it $\frac{a}{v^2}$ and then since it is component

1 a should be for the component 1 that is a_1, a_1 Van der Waal's constant for the pure component 1, $\frac{a_1}{v^2}$ x_1 dv and then when you integrate you will be having $-\frac{a_1}{v_1}$ x_1.

And then when you substitute this limits v_1 lowest possible v_1 is nothing but the molar volume of the pure component 1. So, that is v_1^L it should be the lower limit and upper limit is ∞. So, $\frac{a_1 x_1}{v_1^L}$ we are having. Similarly, for component 2, if you do x_2 $(\Delta u)_2$, if you do x_2 del u_2, you will get $\frac{a_2 x_2}{v_2^L}$ and then here a_2 is component 2 for a of component 2 and then a_1 is nothing but a of component 1. So, that is the Van der Waal's constant a for pure component 1 is a_1 and then Van der Waal's constant a for pure component 2 is a_2.

So, for the entire process it should be x_1 $(\Delta u)_1$ + x_2 $(\Delta u)_2$for the step 1 entire step 1 for both the components we are doing individually now. These individual components are having different mole fraction. So, for the total Δu it should these 2 quantities should be added. So, that is a_1 x_1 + a_2 x_2 when you add these 2 components you will get $\frac{a_1 x_1}{v_1^L} + \frac{a_2 x_2}{v_2^L}$ and for step 2 it is ideal gases we are mixing. So, for ideal gases Δu any way 0. So, that we know or otherwise in the similar way as we have done step 2 you do then also you will get this $(\Delta u)_2$for step 2 as 0.

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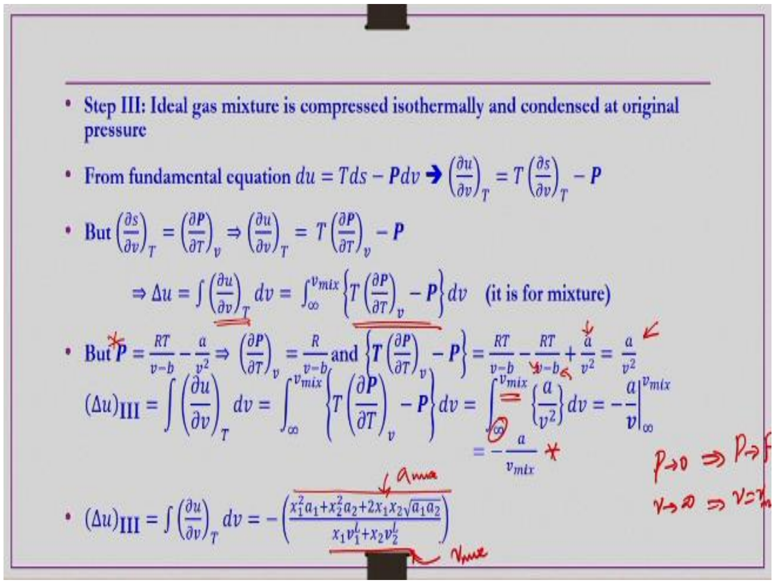

- Step III: Ideal gas mixture is compressed isothermally and condensed at original pressure
- From fundamental equation $du = Tds - Pdv \rightarrow \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P$
- But $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$

$$\Rightarrow \Delta u = \int \underline{\left(\frac{\partial u}{\partial v}\right)_T} dv = \int_{\infty}^{v_{mix}} \underline{\left\{T\left(\frac{\partial P}{\partial T}\right)_v - P\right\}} dv \quad \text{(it is for mixture)}$$

- But $\overset{*}{P} = \frac{RT}{v-b} - \frac{a}{v^2} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}$ and $\left\{T\left(\frac{\partial P}{\partial T}\right)_v - P\right\} = \frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2} = \frac{a}{v^2}$

$$(\Delta u)_{III} = \int \left(\frac{\partial u}{\partial v}\right)_T dv = \int_{\infty}^{v_{mix}} \left\{T\left(\frac{\partial P}{\partial T}\right)_v - P\right\} dv = \int_{\infty}^{v_{mix}} \left\{\frac{a}{v^2}\right\} dv = -\frac{a}{v}\Bigg|_{\infty}^{v_{mix}}$$

$$= -\frac{a}{v_{mix}} \, *$$

$P \to 0 \Rightarrow P \to$

$v \to \infty \Rightarrow v =$

- $(\Delta u)_{III} = \int \left(\frac{\partial u}{\partial v}\right)_T dv = -\left(\frac{\overset{a_{mix}}{\overline{x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2\sqrt{a_1 a_2}}}}{\underset{v_{mix}}{\underline{x_1 v_1^L + x_2 v_2^L}}}\right)$

Or the next step, step 3, we are doing that way also if you follow for step 2 you will get $(\Delta u)_2$and 0. So, ideal gas mixture is compressed isothermally and condensed that original initial pressures of you know mixture that is required that is step 3. So now, again here also fundamental equation du = Tds − Pdv. So, = $\left(\frac{\partial u}{\partial v}\right)_T$ = T $\left(\frac{\partial s}{\partial v}\right)_T$ − P, but $\left(\frac{\partial s}{\partial v}\right)_T$ = $\left(\frac{\partial P}{\partial T}\right)_v$.

So, then $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$. So, now, this $\left(\frac{\partial u}{\partial v}\right)_T$ it has to be for the mixture actually. So, that is this 1. So, for the mixture also we assume Van der Waal's equation of state. So, for this equation in $\left(\frac{\partial P}{\partial T}\right)_v$ is nothing but $\frac{R}{v-b}$ and obviously T $\left(\frac{\partial P}{\partial T}\right)_v$ v − b is going to be $\frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2}$. So, you will get $\frac{a}{v^2}$.

And now here this a, b and then v are for the mixtures, because now, we are doing it for the mixture together as a combined mixture of component 1 and 2 having mole fractions x_1 and x_2. So, now when you substitute $\int \frac{a}{v^2}$ dv now the limits you can see here the pressure we are actually going from the low pressure to the high pressure, P → 0 was initial step of this step 3 or the lower limit of step 3 P → 0.

And then P → some original pressure P is the, you know upper limit of this step 3. So, correspondingly if P → 0 then v → ∞ and then at pressure P = P whatever v is there that is nothing but v_{mix}. So, that is the reason here limits are in other way ∞ to v_{mix}. So, here we have $-\frac{a}{v_{mix}}$ and then a we know it has nothing but $a_1 x_1^2 + 2 x_1 x_2 \sqrt{a_1 a_2} + a_2 x_2^2$ this is what we know and then v_{mix} also we can write it as $x_1 v_1^L + x_2 v_2^L$.

So, this is x_1 this is $a_1 x_1^2 + 2 x_1 x_2 \sqrt{a_1 a_2} + a_2 x_2^2$ is nothing but a_{mixt} or a and this is nothing but v_{mixt} that is $x_1 v_1^L + x_2 v_2^L$.

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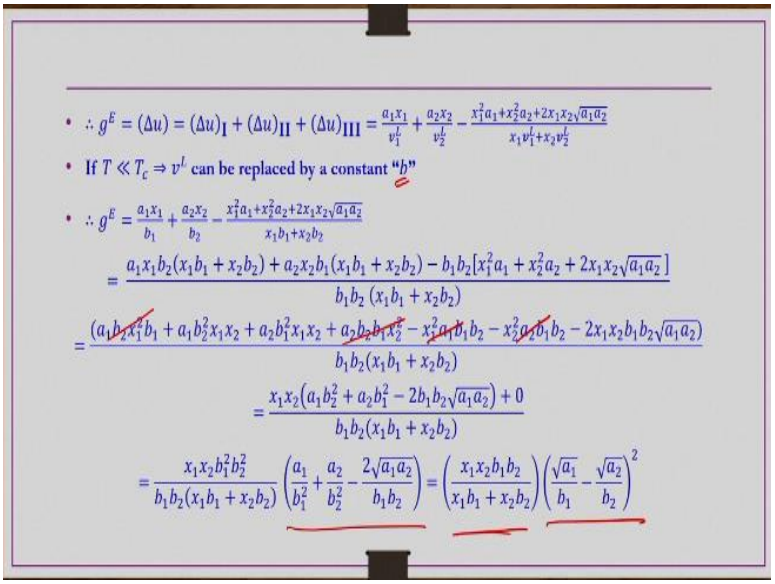

- $\therefore g^E = (\Delta u) = (\Delta u)_{\mathrm{I}} + (\Delta u)_{\mathrm{II}} + (\Delta u)_{\mathrm{III}} = \frac{a_1 x_1}{v_1^L} + \frac{a_2 x_2}{v_2^L} - \frac{x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 \sqrt{a_1 a_2}}{x_1 v_1^L + x_2 v_2^L}$
- If $T \ll T_c \Rightarrow v^L$ can be replaced by a constant "b"
- $\therefore g^E = \frac{a_1 x_1}{b_1} + \frac{a_2 x_2}{b_2} - \frac{x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 \sqrt{a_1 a_2}}{x_1 b_1 + x_2 b_2}$

$$= \frac{a_1 x_1 b_2 (x_1 b_1 + x_2 b_2) + a_2 x_2 b_1 (x_1 b_1 + x_2 b_2) - b_1 b_2 [x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 \sqrt{a_1 a_2}\,]}{b_1 b_2\,(x_1 b_1 + x_2 b_2)}$$

$$= \frac{(a_1 \cancel{b_2 x_1^2} b_1 + a_1 b_2^2 x_1 x_2 + a_2 b_1^2 x_1 x_2 + \cancel{a_2 b_2 b_1 x_2^2} - x_1^2 \cancel{a_1 b_1} b_2 - x_2^2 \cancel{a_2 b_1} b_2 - 2x_1 x_2 b_1 b_2 \sqrt{a_1 a_2})}{b_1 b_2 (x_1 b_1 + x_2 b_2)}$$

$$= \frac{x_1 x_2 \left(a_1 b_2^2 + a_2 b_1^2 - 2b_1 b_2 \sqrt{a_1 a_2}\right) + 0}{b_1 b_2 (x_1 b_1 + x_2 b_2)}$$

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

So, now, for all the 3 steps we got the Δ u if you add them together and then simplify you will get the g^E because g^E = Δu. Δu = summation of 3 steps, Δu of 3 steps, so then we have this thing. Now, if the temperature is very much smaller than the critical temperature, then whatever the v^L or molar volume is that can be replaced by the constant b of the Van der Waal's equation b whatever they want while constant b that we can use here because this b is a kind of representative of the size of the molecule.

So, that if you do, then we get $g^E = \frac{a_1 x_1}{b_1} + \frac{a_2 x_2}{b_2} - \frac{a_1\, x_1^2 + 2\, x_1\, x_2\, \sqrt{a_1 a_2} + a_2\, x_2^2}{x_1 b_1 + x_2 b_2}$. Now you do the LCM and then simplify. So, then what you have this one some of the terms are quite similar this x_1^2 a_1 b_1 b_2 and this $x_1^2 a_1$ b_1 b_2 cancelled out similarly this $x_2^2 a_2$ b_1 b_2, this x_2^2 a_2 b_1 b_2 are canceled out because they are having the + − sign respectively.

So, the remaining terms you take x_1 x_2 common, in the next step what you do, you take b_1^2 b_2^2 also common from the numerator. So, we have $\frac{x_1 x_2 b_1^2\, b_2^2}{b_1 b_2 (x_1 b_1 + x_2 b_2)} \left(\frac{a_1}{b_1^2} + \frac{a_2}{b_2^2} - \frac{2\sqrt{a_1 a_2}}{b_1 b_2}\right)$ that we can write $\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2$ and then this term is as it is.

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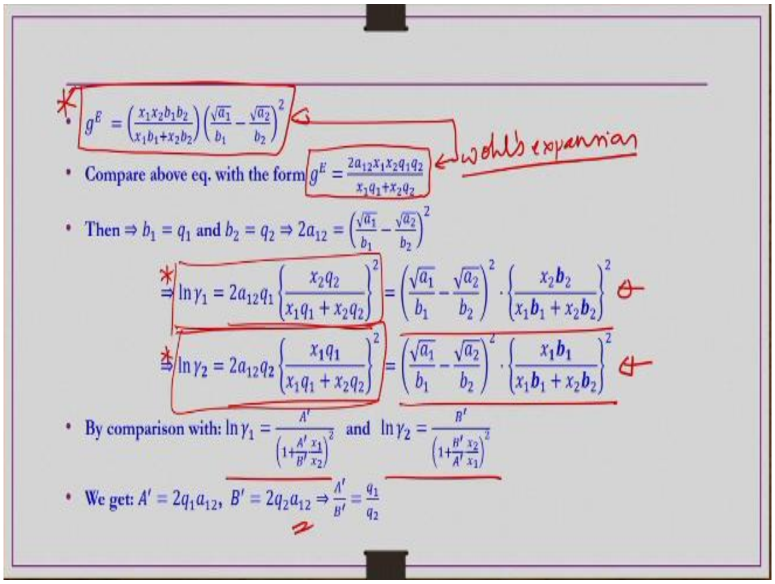

- $g^E = \left(\frac{x_1x_2b_1b_2}{x_1b_1+x_2b_2}\right)\left(\frac{\sqrt{a_1}}{b_1}-\frac{\sqrt{a_2}}{b_2}\right)^2$
- Compare above eq. with the form $g^E = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1+x_2q_2}$ ← wohl's expansion
- Then ⇒ $b_1 = q_1$ and $b_2 = q_2 \Rightarrow 2a_{12} = \left(\frac{\sqrt{a_1}}{b_1}-\frac{\sqrt{a_2}}{b_2}\right)^2$

$$\Rightarrow \ln\gamma_1 = 2a_{12}q_1\left\{\frac{x_2q_2}{x_1q_1+x_2q_2}\right\}^2 = \left(\frac{\sqrt{a_1}}{b_1}-\frac{\sqrt{a_2}}{b_2}\right)^2\cdot\left\{\frac{x_2\mathbf{b}_2}{x_1\mathbf{b}_1+x_2\mathbf{b}_2}\right\}^2$$

$$\Rightarrow \ln\gamma_2 = 2a_{12}q_2\left\{\frac{x_1q_1}{x_1q_1+x_2q_2}\right\}^2 = \left(\frac{\sqrt{a_1}}{b_1}-\frac{\sqrt{a_2}}{b_2}\right)^2\cdot\left\{\frac{x_1\mathbf{b}_1}{x_1\mathbf{b}_1+x_2\mathbf{b}_2}\right\}^2$$

- By comparison with: $\ln\gamma_1 = \frac{A'}{\left(1+\frac{A'}{B'}\frac{x_1}{x_2}\right)^2}$ and $\ln\gamma_2 = \frac{B'}{\left(1+\frac{B'}{A'}\frac{x_2}{x_1}\right)^2}$
- We get: $A' = 2q_1a_{12}$, $B' = 2q_2a_{12} \Rightarrow \frac{A'}{B'} = \frac{q_1}{q_2}$

So, $g^E = \frac{x_1x_2b_1b_2}{x_1b_1+x_2b_2}\left(\frac{\sqrt{a_1}}{b_1}-\frac{\sqrt{a_2}}{b_2}\right)^2$ this if you compare with this equation this is we got by reducing the Wohl's expansion that is taking dissimilar interaction between only 2 molecules and then neglecting the higher order terms then we got this equation. So, they are same equation only thing that is constants are different slightly.

So, now, here b_1 is nothing but q_1 when you compare these 2 equations and then b_2 is nothing but q_2 because obviously, these q's and b's are representative of the size of the molecules and then these 2 $a_{12} = \left(\frac{\sqrt{a_1}}{b_1}-\frac{\sqrt{a_2}}{b_2}\right)^2$. So, then now it should get the ln γ_1 expression for this expression for this form of equation you will get this one that is $\left(\frac{\sqrt{a_1}}{b_1}-\frac{\sqrt{a_2}}{b_2}\right)^2 . \left\{\frac{x_2b_2}{x_1b_1+x_2b_2}\right\}^2$.

And then ln γ_2 you will get $\left(\frac{\sqrt{a_1}}{b_1}-\frac{\sqrt{a_2}}{b_2}\right)^2 . \left\{\frac{x_1b_1}{x_1b_1+x_2b_2}\right\}^2$ and then they are you know, equal into whatever the quantities expression that we got by using this expansion whatever this form. So, both the way I have written, so this for comparison purpose it will be easier. So, the boxed one we got by Wohl's expansion or reduced also expansion and written van Laar equation.

And then this right hand side second terms you know they are obtained by partially differentiating this g^E with respect to n_1 and n_2 respectively and then Simplifying to get this ln γ_1 and ln γ_2 respectively. So, now, that is by comparison if you write the same equation in this form also you can write, when you write it, you get $A' = 2 q_1 a_{12}$ $B' = 2 q_2 a_{12}$ and $\frac{A'}{B'} = \frac{q_1}{q_2}$ and then $2 a_{12}$ is nothing but $\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2$. This is what we get.

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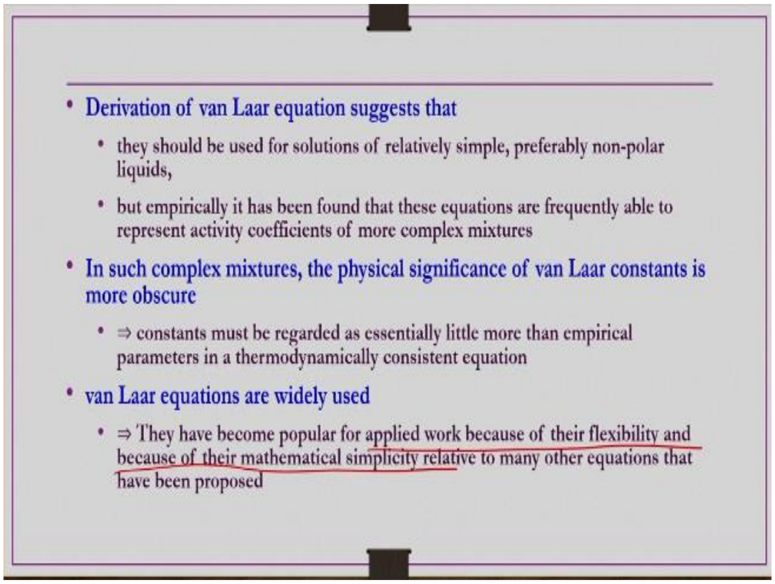

- Derivation of van Laar equation suggests that
  - they should be used for solutions of relatively simple, preferably non-polar liquids,
  - but empirically it has been found that these equations are frequently able to represent activity coefficients of more complex mixtures
- In such complex mixtures, the physical significance of van Laar constants is more obscure
  - ⇒ constants must be regarded as essentially little more than empirical parameters in a thermodynamically consistent equation
- van Laar equations are widely used
  - ⇒ They have become popular for applied work because of their flexibility and because of their mathematical simplicity relative to many other equations that have been proposed

Now, we discuss what are that we understand from this derivation, we realize that they should be used for solutions of relatively simple preferably non-polar liquids because we are taking only 2 molecular interactions we are not taking any higher end interactions etc. into the consideration. But empirically it has been found that these equations are frequently able to represent activity coefficients of more complex mixtures as well may not be excellent agreement but satisfactory agreement with the experimental results may also be obtained.

If this; van Laar equation if you are applying to complex mixtures as well. In such complex mixtures, the physical significance of van Laar constants is a bit more obscure. This constant must be regarded as essentially little more than empirical parameters in a thermodynamically consistent equation. These equations are very widely used van Laar equation because they have become popular for applied work because of their flexibility and because of their mathematical simplicity as I mentioned, related to the other models.

We will be discussing more models of g^E in subsequent class, we can see there are more much more complex even if you take that 3 suffix and 4 suffix margules equation that we have already discussed in one of the previous lecture, they are much more complex. So, this equation van Laar equation is as simple as 2 suffix margules equation but it has a kind of better applicability compared to the two suffix margules equation because of flexibility and mathematical simplicity.

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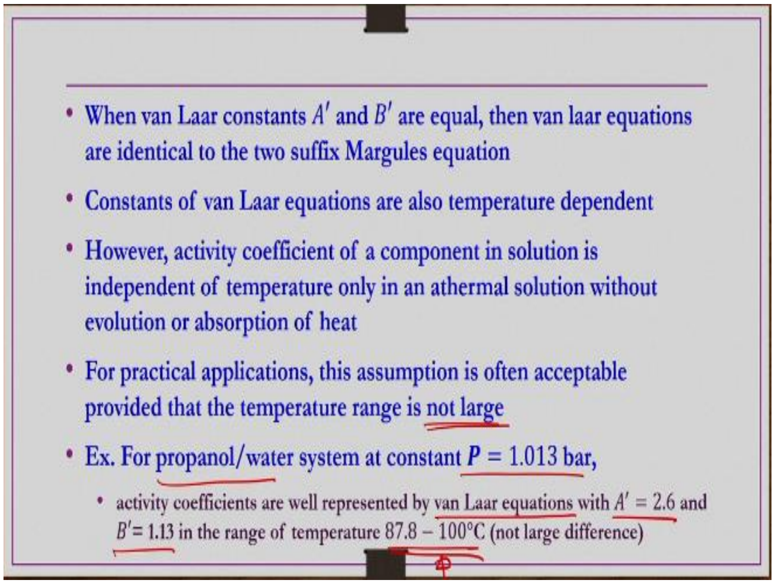

- When van Laar constants A' and B' are equal, then van laar equations are identical to the two suffix Margules equation
- Constants of van Laar equations are also temperature dependent
- However, activity coefficient of a component in solution is independent of temperature only in an athermal solution without evolution or absorption of heat
- For practical applications, this assumption is often acceptable provided that the temperature range is not large
- Ex. For propanol/water system at constant P = 1.013 bar,
  - activity coefficients are well represented by van Laar equations with $A' = 2.6$ and $B' = 1.13$ in the range of temperature 87.8 – 100°C (not large difference)

So, when van Laar constant A' and B' are equal. So, then this van Laar equation is nothing but it reduces to the two suffix margules equation. Constants of van Laar equations are also temperature dependent but activity coefficient of component in solution is independent of temperature only in an athermal solution without evaluation or absorption of heat. But for practical applications, this assumption is often acceptable provided that the temperature ranges not very large.

For example, if you take propanol water system it pressure of 1.013 bar, then activity coefficients of this system are well represented by van Laar equation with A' = 2.6 and B' = 1.13 in the range of temperature 87.8 to 100 degrees centigrade that is not a very large temperature difference. So, under this range of temperature we can say this A' B' are constants or independent of the temperature.

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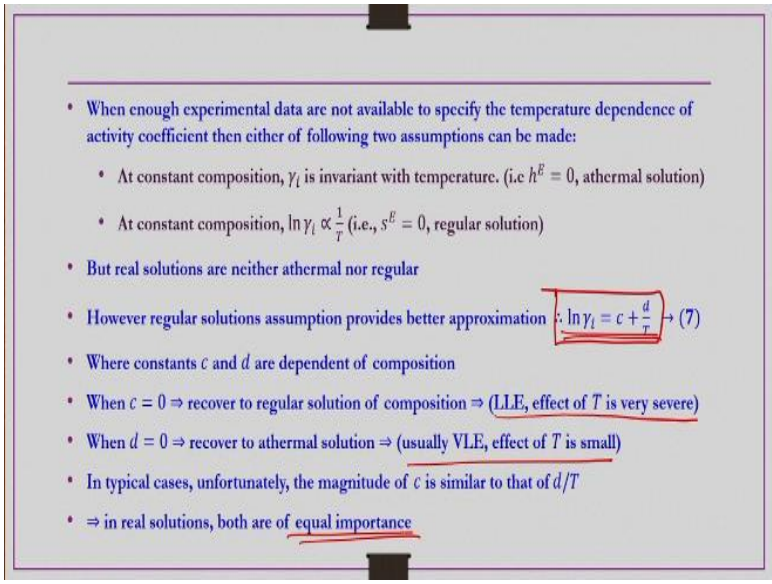

- When enough experimental data are not available to specify the temperature dependence of activity coefficient then either of following two assumptions can be made:
    - At constant composition, γ_i is invariant with temperature. (i.e $h^E = 0$, athermal solution)
    - At constant composition, $\ln\gamma_i \propto \frac{1}{T}$ (i.e., $s^E = 0$, regular solution)
- But real solutions are neither athermal nor regular
- However regular solutions assumption provides better approximation $\therefore \boxed{\ln\gamma_i = c + \frac{d}{T}} \rightarrow (7)$
- Where constants c and d are dependent of composition
- When $c = 0 \Rightarrow$ recover to regular solution of composition $\Rightarrow$ (LLE, effect of T is very severe)
- When $d = 0 \Rightarrow$ recover to athermal solution $\Rightarrow$ (usually VLE, effect of T is small)
- In typical cases, unfortunately, the magnitude of c is similar to that of d/T
- $\Rightarrow$ in real solutions, both are of equal importance

When enough experimental data are not available to specify the temperature dependence of activity coefficient then neither of the following 2 assumptions can be made. One is it constant composition γ_i is invariant with the temperature or independent of the temperature that is the case where $h^E = 0$ are known as the athermal solution are other ways we can say this ln γ_i is inversely proportional to temperature that is the case where $s^E = 0$ are known as the regular solution. But real solutions are neither athermal nor regular.

However, regular solutions assumption provides a better approximation because $\ln\gamma_i = c + \frac{d}{T}$, when you take this constant c and d are dependent of the composition but if you take $c \rightarrow 0$ then it is the case of regular solution, where ln γ_i is inversely proportional to temperature and then it is the case much applicable in LLE's where the effect of T is very severe. But when you take T = 0 then usually that is really the effect of T is small at constant temperature they have been done you know that is usually VLE case where effect of T is small.

So, under such condition, this the solution recovered to the case of athermal solution. In typical cases, unfortunately, the magnitude of c is similar to that of magnitude of $\frac{d}{T}$. So, in practical applications in real solutions both are of equal importance.

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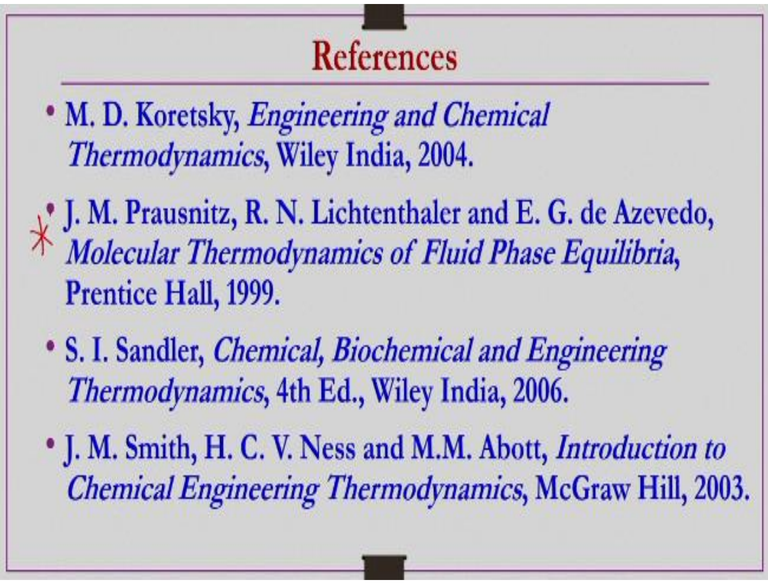

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The references for this lecture are provided here. And then most of the notes are prepared from this reference book, Praus Lichter. Thank you.