Advanced Thermodynamics
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Lecture – 12
Virial Coefficients from Potential Functions

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is virial coefficients from potential functions. We have already seen in previous lecture that virial equation of state is better compared to the some other equations of state because of 2 reasons, one is that the parameters or the constants that are associated with the virial equation, the second, third, and fourth virial coefficients and so on. Those virial coefficients are directly related to the intermolecular interactions.

That is one reason and then other reason is that because of this direct relation between intermolecular potentials and then virial coefficient, the required mixing rules for mixtures are not composition dependent or the mixing rules you do not need to worry for mixture of gases. If you are applying virial equation of state, then you do not need to worry about the mixing rules because of such reason that virial coefficients are directly related to the intermolecular interactions. For the mixture these virial coefficients are not dependent on the composition. These are the advantages.

Then we have already seen these equations, whatever the equations required for obtaining this virial coefficient from intermolecular potential that we have seen, they are derived from the statistical mechanics. So, from those equations, we understand that if we know the intermolecular potential, then we can directly calculate, what are the values for these virial coefficients? We have also seen that the virial coefficients are dependent only on temperature and then independent of pressure and density, etc.

So, that is another advantage. So, having these advantages, it is always better to see more details how we can explore this virial equation of state. So, that is the reason in today's lecture we are going to calculate or obtain virial coefficient, especially second virial coefficient from intermolecular potential and then we see a few example problems followed by third virial coefficients, etc.

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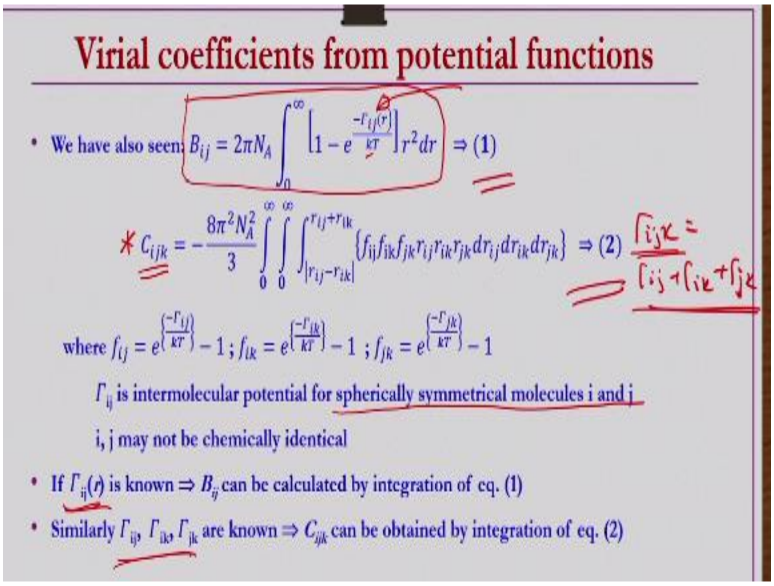

Virial coefficients from potential functions

- We have also seen: $B_{ij} = 2\pi N_A \int_0^\infty \left[1 - e^{\frac{-\Gamma_{ij}(r)}{kT}}\right] r^2 dr \Rightarrow (1)$

$$* \; C_{ijk} = -\frac{8\pi^2 N_A^2}{3} \int_0^\infty \int_0^\infty \int_{|r_{ij}-r_{ik}|}^{r_{ij}+r_{ik}} \{f_{ij} f_{ik} f_{jk} r_{ij} r_{ik} r_{jk} dr_{ij} dr_{ik} dr_{jk}\} \Rightarrow (2)$$

$\Gamma_{ijk} = \Gamma_{ij} + \Gamma_{ik} + \Gamma_{jk}$

where $f_{ij} = e^{\left\{\frac{-\Gamma_{ij}}{kT}\right\}} - 1$; $f_{ik} = e^{\left\{\frac{-\Gamma_{ik}}{kT}\right\}} - 1$; $f_{jk} = e^{\left\{\frac{-\Gamma_{jk}}{kT}\right\}} - 1$

Γ_{ij} is intermolecular potential for spherically symmetrical molecules i and j

i, j may not be chemically identical

- If $\Gamma_{ij}(r)$ is known $\Rightarrow B_{ij}$ can be calculated by integration of eq. (1)
- Similarly Γ_{ij}, Γ_{ik}, Γ_{jk} are known $\Rightarrow C_{ijk}$ can be obtained by integration of eq. (2)

So, we have already seen from the statistical mechanics the second virial coefficient can be related to the intermolecular potential that Γ_{ij} given by this equation that is $B_{ij} = 2\pi N_A \int_0^\infty \left[1 - e^{-\frac{\Gamma_{ij}(r)}{kT}}\right] r^2 dr$, this k is nothing but the Boltzmann constant. So, what B_{ij} indicates? It indicates whatever the non-ideality that is coming into the picture because of 2 molecules interaction. So, that information we can get from this B_{ij}.

So, now if you know this Γ_{ij} that is potential function, then you can find out this B_{ij} for any case, and then similarly, C_{ijk} that is the third virial coefficient or the coefficient that depicts the deviation from ideal behavior because of 3 molecular interactions that is i molecule, j molecule, and k molecules are interacting, right? However, in the C_{ijk}, whatever the interactions or whatever the potential function Γ_{ijk} is there that is kind of simplified as a kind of summation of $\Gamma_{ij} + \Gamma_{ik} + \Gamma_{jk}$.

That is 3 different combinations of two body interactions taken individually and then added together to get the three body in directions Γ_{ijk}. This is the assumption that is present in deriving this expression C_{ijk}. So, that is the reason this is again a kind of approximation and then it may not be very accurate as compared to the B_{ij} information. In these expressions $f_{ij} = e^{-\frac{\Gamma_{ij}}{kT}} - 1$ and then $f_{ik} = e^{-\frac{\Gamma_{ik}}{kT}} - 1$, $f_{jk} = e^{-\frac{\Gamma_{jk}}{kT}} - 1$, right?

Then we understand this Γ_{ij} is nothing but the intermolecular potential for spherically symmetrical molecules ij. These derivations have been done kind of the case or the limitation that they are applicable. They are derived based on the assumption that the molecules are spherically symmetrical molecules. However, it has been founded they are also valid for complex molecules as well.

Because these complex molecules for those complex molecules whatever Γ_{ij} is there that if you substitute here in place of Γ_{ij} in this expression, so then whatever the virial coefficients are found, they are also found to be reliable or matching better with the experimental results. So, for the complex molecules also if we use these expressions in order to get second and third virial coefficients and then compare with them the experimental results, it has been found that validity is good despite this derivations are derived only for spherically symmetrical molecules.

Then ij may not be chemically identical as well, okay? So, if Γ_{ij} is known, then B_{ij} can be found from equation 1 by simply integrating this equation. Similarly, if you know Γ_{ij}, Γ_{ik}, and Γ_{jk}, then C_{ijk} that is third virial coefficient can also be found by integrating this equation number 2, alright? So, now what we need? We need these functions Γ the intermolecular potential as function of radial distance that we need to have and then we understand there are so many intermolecular potentials are there.

So, we have taken a few intermolecular potential models in one of the previous lecture and then we will be taking some of them as a kind of example, and then using those intermolecular potential, we try to obtain the second virial coefficient.

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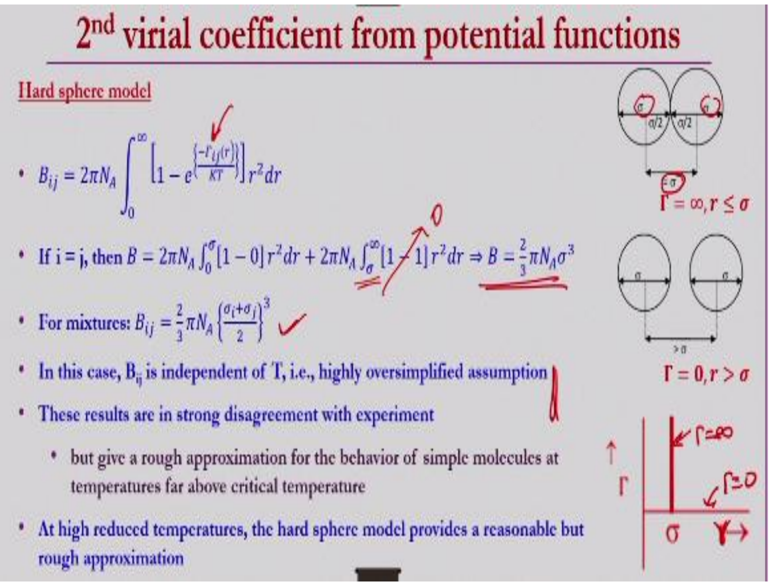

2^{nd} virial coefficient from potential functions

Hard sphere model

- $B_{ij} = 2\pi N_A \int_0^\infty \left[1 - e^{\left\{\frac{-\Gamma_{ij}(r)}{KT}\right\}}\right] r^2 dr$
- If i = j, then $B = 2\pi N_A \int_0^\sigma [1-0] r^2 dr + 2\pi N_A \int_\sigma^\infty [1-1] r^2 dr \Rightarrow B = \frac{2}{3}\pi N_A \sigma^3$
- For mixtures: $B_{ij} = \frac{2}{3}\pi N_A \left\{\frac{\sigma_i + \sigma_j}{2}\right\}^3$
- In this case, B_{ij} is independent of T, i.e., highly oversimplified assumption
- These results are in strong disagreement with experiment
  - but give a rough approximation for the behavior of simple molecules at temperatures far above critical temperature
- At high reduced temperatures, the hard sphere model provides a reasonable but rough approximation

So, hard sphere model we start with. Hard sphere model what it says? It talks about 2 spherical molecules which are very hard like billiard balls, right? So, they are not having any interpenetrating electron clouds etc., right? So, the size of this molecule is σ and then so what does it mean? Center to center distance between 2 molecules can be σ only, minimum σ, it cannot be less than σ because they are hard sphere kind of billiard balls kind of thing that is billiard balls moment they touch each other, they repel, they go away from each other, so that is the repulsion force is there.

So, when this intermolecular separation distance $r = \sigma$ that is collision diameter, then there is a repulsive force and then that repulsive forces are very high that is $\Gamma = \infty$, right? But moment these billiard balls they move away from each other, there is no interaction, how far, the distance may be very small, then also there is no interaction at all. There will not be any attraction force or repulsive force. So, the same is true in the hard sphere model.

So, moment this r is larger than the σ, then there is no interaction at all between these molecules, that means $\Gamma = 0$ if $r > \sigma$. So, this is about the hard sphere model, right? Mathematically, we can write $\Gamma = \infty$ for $r \leq \sigma$ and $\Gamma = 0$ for $r > \sigma$. That means, it takes account only repulsive forces and repulsive forces also a vertical line that is $\Gamma = \infty$, but it does not involve any kind of attractive forces.

So, if we assume that the intermolecular potential between 2 molecules is given by hard sphere model, so then what is the second virial coefficient? Okay, so, this Γ versus intermolecular separation distance r we can represent like this graphically like this, this is $\Gamma \rightarrow 0$ when $r = \sigma$, right? And then after here $\Gamma \rightarrow 0$ when $r > \sigma$, okay? So, there is no attraction that is there are no negative Γ values at all.

So, now here $B_{ij} = 2\pi N_A \int_0^\infty \left[1 - e^{-\frac{\Gamma_{ij}(\mathrm{r})}{kT}}\right] r^2 dr$. In this equation if you substitute Γ_{ij} for these 2 conditions 0 to σ and σ to ∞ and then simplify, then we get second viral coefficient for that particular system provided that intermolecular potential is having only repulsive forces as designated or described by hard sphere model. So, let us take i = j, that means both the molecules of the same system, then we can call B_{ij} as simply B, then $e^{-\infty} = 0$.

So, (1 – 0) r^2dr between r = σ and then e^0 = 1. So, 1 - 1 multiplied by r^2dr, this is for r = σ to ∞. So, when you do the integration and substitute the limits, so then what you can have? You can have simply $\frac{2\pi}{3}\ N_A\sigma^3$ because second term is anyway 0, only from the first term if you integrate you have $\frac{r^3}{3}$ under limits 0 to σ. So $\frac{2\pi}{3}\ N_A\sigma^3$you will get, right? For mixtures, if you have mixtures, then $B_{ij} = \frac{2\pi}{3}\ N_A$, the σ has to be the average of σ_i and σ_j, then you have this thing.

Now what you can understand from here clearly that this B or B_{ij} whatever, it is independent of temperature, there is no temperature term at all and it is approximation which is highly far away from the real situation, real conditions in general because the virial coefficients are strong functions of temperature though they are independent of pressure or density, right? So, this is a kind of highly oversimplified approximation, so then it may not be true for many cases, right? And obviously because of this assumption, experimental validity is very poor.

These results does not agree much with the experimental results obviously because of the limitations of the hard sphere model, but the second viral coefficient obtained by hard sphere model will not give a better approximation, but give me a rough approximation for the behavior of simple molecules, but a temperature far above the critical temperature and at high reduced temperature, the hard sphere model provides a reasonable but rough approximation again, okay?

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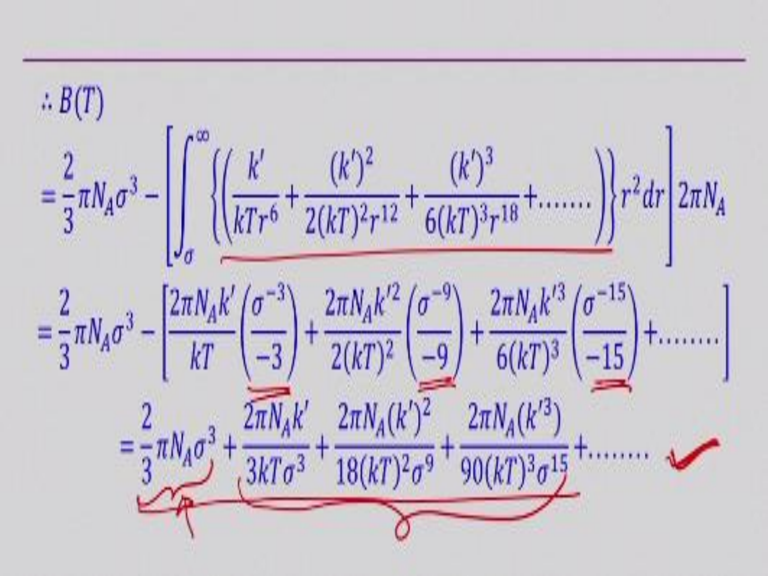

$$\therefore B(T)$$

$$= \frac{2}{3}\pi N_A\sigma^3 - \left[\int_\sigma^\infty \left\{\left(\frac{k'}{kTr^6} + \frac{(k')^2}{2(kT)^2r^{12}} + \frac{(k')^3}{6(kT)^3r^{18}} + \ldots\ldots\right)\right\} r^2dr\right] 2\pi N_A$$

$$= \frac{2}{3}\pi N_A\sigma^3 - \left[\frac{2\pi N_A k'}{kT}\left(\frac{\sigma^{-3}}{-3}\right) + \frac{2\pi N_A k'^2}{2(kT)^2}\left(\frac{\sigma^{-9}}{-9}\right) + \frac{2\pi N_A k'^3}{6(kT)^3}\left(\frac{\sigma^{-15}}{-15}\right) + \ldots\ldots\right]$$

$$= \frac{2}{3}\pi N_A\sigma^3 + \frac{2\pi N_A k'}{3kT\sigma^3} + \frac{2\pi N_A (k')^2}{18(kT)^2\sigma^9} + \frac{2\pi N_A (k'^3)}{90(kT)^3\sigma^{15}} + \ldots\ldots$$

So, next we take Sutherland potential. So, this potential is nothing but improvement over a hard sphere model. So, hard sphere model only repulsive forces are there, now Sutherland potential takes into the account in addition to this infinite repulsive forces there is also a kind of London's dispersion attractive forces or Van der Waal's attractive forces that is having this form $\frac{k'}{r^6}$, this form is there if you draw a potential between intermolecular potentials versus the separation distance r, right?

So, what is this? When $r \leq \sigma$, then the σ is the again collision diameter that is the center to center distance between 2 molecules and then the σ is known as the collision diameter, okay? So, that means the moment they touch each other, there is a kind of infinite repulsive force, but moment they slightly go away from each other, then there will be kind of attractive forces and then further if you go away, these attractive forces decreases.

Then there will be situation where attractive forces will become close to 0, that means indicating almost like no intermolecular potential and that is represented by this thing, this is also we have seen previously. So, mathematically if you write for $r \leq \sigma$, $\Gamma = \infty$, for $r > \sigma$, $\Gamma = -\frac{k'}{r^6}$. This is what we have, okay? So, this also we have seen. Now, if you make use this Γ expression and then obtain second virial coefficient, what you get that is what we are going to see now.

So it is a combined hard sphere model and London's theory of dispersion which includes attractive forces according to London's theory of dispersion. Then B_{ij} we are having this expression, right? Now, here this Γ_{ij} between r = 0 to σ it is ∞, between r = σ to ∞, this $\Gamma_{ij} = -\frac{k'}{r^6}$. So, that if you substitute for the case when you take i = j, then we have B, now it is obviously we can see it as a function of temperature which was not in the previous case of hard sphere model, right?

So, first case $\Gamma_{ij} = \infty$, second case $\Gamma_{ij} = -\frac{k'}{r^6}$. We substitute them here. Then, if you integrate first one is anyway this is 0. So, r^2dr, integration of r^2dr is nothing but $\frac{r^3}{3}$and then limits 0 to σ if you substitute $\frac{\sigma^3}{3}$ - 0, so that is first term is $\frac{2\pi}{3}$ $N_A\sigma^3$, N_A is the Avogadro's number, right? Now, the second term is 2 Π N_A $\int_0^\infty \left[1 - e^{\frac{k'}{kTr^6}}\right] r^2 dr$.

Now, if you have very high temperature or if you have the conditions such a way that this exponential of this term whatever is there if it is small, so then we have e^x form and then for small x e^x can be written as 1 + x + $\frac{x^2}{2!}$ and so on so we can write. So similarly, for small value of $\frac{k'}{kTr^6}$, then exponential of this term we can write 1 +$\frac{k'}{kTr^6}$ + $\frac{k'^2}{2(kT)^2 r^{12}}$ and so on so like this we can write.

So, this is the simplification we are doing, so that we can integrate this equation and then see the information, right? So, then we have B as function of temperature that is second virial coefficient as function of temperature this one, right? Integration of this one. So, now $\frac{r^2}{r^6}$ first term is nothing but r^{-4}. Integration of r^{-4} is $\frac{r^{-3}}{3}$, likewise all other terms also if you integrate and then substitute the limits $\frac{\sigma^{-3}}{-3}$ another case the ∞ power so that term will anyway be 0, okay? So that we are not considering.

So then another case is $\frac{\sigma^{-9}}{-9}$ you get. Another term you get $\frac{\sigma^{-15}}{-15}$ you will get, okay? So, that means B as a function of temperature you will get this expression, this series expression like that is $\frac{2}{3}\pi N_A \sigma^3$ + $\frac{2}{3}\pi N_A \frac{k'}{kT\sigma^3}$ and so on so. Now this part is nothing but, first part is nothing but when only repulsive forces are there.

So, that is according to hard sphere model, but when there is a kind of attractive forces because of London's dispersion attraction terms are there, so these additional terms are coming, okay? So, this is the modification over the hard sphere model by the Sutherland potential, okay?

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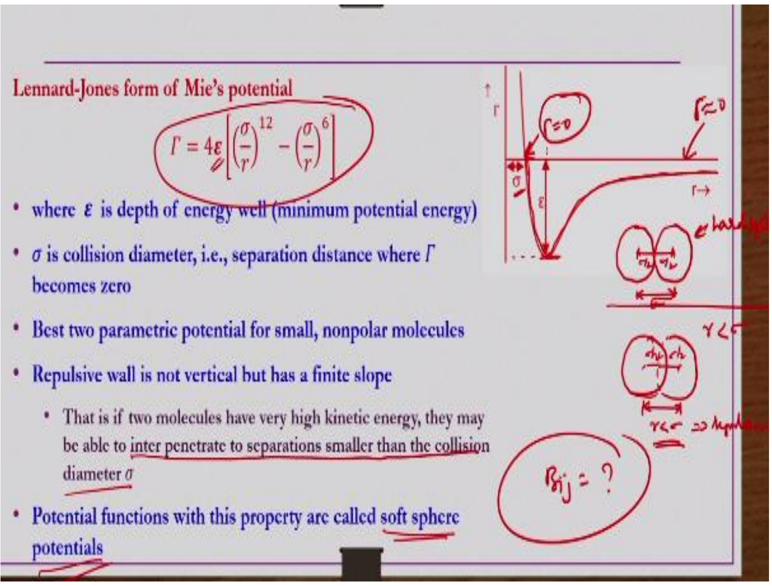

Lennard-Jones form of Mie's potential

$$\Gamma = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

- where ε is depth of energy well (minimum potential energy)
- σ is collision diameter, i.e., separation distance where Γ becomes zero
- Best two parametric potential for small, nonpolar molecules
- Repulsive wall is not vertical but has a finite slope
    - That is if two molecules have very high kinetic energy, they may be able to inter penetrate to separations smaller than the collision diameter σ
- Potential functions with this property are called soft sphere potentials

ε

So, now we take Lennard-Jones form of Mie's potential. So, we have seen this is having this form Γ = 4 ε$\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$. This is also we have seen. It is having similar to kind of this Sutherland potential, but here in this case what it is, it is not having a kind of vertical repulsive line, rather it is having some slope, that means repulsive forces are not infinite at for r = σ or r < σ rather it decreases with r value increasing from 0 to σ, right?

How it decreases, it represented by this one, right? Pictorially if you see, so now you can see this Γ, Γ is decreasing with increasing r between r = 0 to σ, earlier it was infinite, it was ∞ for all values of r between r = 0 to σ. Now, between r = 0 to σ, it decreases with certain slope and then after that other case in Sutherland potential for r ≥ σ, suddenly attraction force starts and then that gradually decreases with increasing the intermolecular separation distance.

But now, for r ≥ σ, the attraction force gradually increases that is going towards the other negative minimum value like this, this is ε minimum. So, that means, it is the position where the attraction force is maximum, right? So at r minimum, and after this point it starts decreasing as the separation distance increases, right? So, this is what Lennard-Jones form of Mie's potential. So, now here what does mean by when r ≤ σ?

This Γ is decreasing that means now they are not a kind of hard spheres, rather the molecules are having a kind of electron cloud such a way that there is a kind of interpenetration into each other. So, that is that molecules that r < σ is also possible. That means if you have let us say hard sphere like this, the minimum distance is possible between 2 molecules is only σ provided if this is $\frac{\sigma}{2}$ and this is also $\frac{\sigma}{2}$ because they are not interpenetrating, right?

So, that is in the case of hard sphere. This is in the case of hard sphere model right, but now for $r < \sigma$ also, this Γ is decreasing, that means here in the case what happens? So it is a kind of system like you know where some portion may be overlapping like this of the molecule, so the center to center distance between 2 molecules though their radius is $\frac{\sigma}{2}$for each case, these r_2 that is center to center distance between these two can be possible that $r < \sigma$ is also possible and for that $r < \sigma$, there is a kind of repulsion, right?

So, that means, when it is possible if they are hard spheres, they immediately repel. If they are not immediately repelling, they are interpenetrating into each other to certain distance. That means, the molecules are not kind of hard sphere, but they are kind of soft spherical core kind of thing, okay? So, that is what this equation says that is the modification over the Sutherland potential and then hard sphere model and this is one of the best model that is available, which is having 2 parameters.

There may be other models but they may be having more than 2 parameters. Now, here we have only two 2, okay? ε_0 ε minimum and then σ, these are the only 2 parameters they are present in this case, okay? So, where ε is nothing but depth of this energy well or the minimum potential energy or the maximum attractive force that is possible, okay? And then σ is the collision diameter that is the separation distance where Γ becomes 0.

Γ becomes 0 at this location that is after overcoming the repulsive force and then started developing this attractive force, but it is not somewhere very far, here also Γ is approximately 0, but this is not the case, right, far away. So, this collision diameter is taken at this point at this point or at this distance where the molecules are overcoming the repulsive forces and then before starting the attractive force that point, that junction that Γ becomes 0 that is the collision diameter, okay? These are the 2 parameters.

So, obviously this is best 2 parametric potential for small non-polar molecules. Repulsive wall is not vertical but has a finite slope. That is if 2 molecules have very high kinetic energy, then they may be able to interpenetrate to separations smaller than the collision diameter σ as well.

That is the reason this model is also known as the soft sphere potential, right? Now, if you make use this expression and then try to find out B_{ij} and then see the difference compared to the other models, so you can realize which the better model is by comparing with the experimental results, okay?

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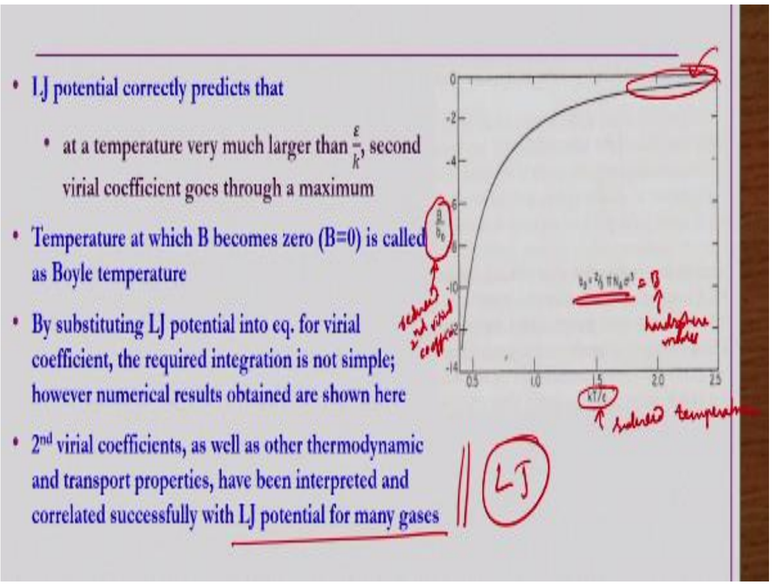

- LJ potential correctly predicts that
  - at a temperature very much larger than $\frac{\varepsilon}{k}$, second virial coefficient goes through a maximum
- Temperature at which B becomes zero (B=0) is called as Boyle temperature
- By substituting LJ potential into eq. for virial coefficient, the required integration is not simple; however numerical results obtained are shown here
- 2nd virial coefficients, as well as other thermodynamic and transport properties, have been interpreted and correlated successfully with LJ potential for many gases

This model predicts the second virial coefficient much better because at high temperature or a temperature very much larger than $\frac{\varepsilon}{k}$, ε is the minimum potential energy and then k is nothing but the Boltzmann energy. The ratio of these two is a kind of temperature units. So, at a temperature very much larger than the $\frac{\varepsilon}{k}$value, second virial coefficient must go through a kind of maximum and that behavior this model predicts. This model, LJ model predicts that behavior as well.

Then temperature at which this second virial coefficient becomes 0 is called the Boyle temperature. By substituting this LJ model in the B_{ij} expression, integration is not a simple and straightforward as in the case of previous things. So, that is the reason what we have, we have a kind of a numerical solution and then that numerical solution we have plotted $\frac{B}{b_o}$ versus $\frac{kT}{\varepsilon}$. This $\frac{B}{b_o}$ is nothing but reduced or dimensionless second virial coefficient, right, where b_o is nothing but $\frac{2}{3}\pi N_A \sigma^3$ that is the B value as per the hard sphere model.

This $\frac{kT}{\varepsilon}$is nothing but the reduced temperature that is $\frac{\varepsilon}{k}$is having temperature unit, so T by some temperature unit should be there. So, that is the reason this $\frac{kT}{\varepsilon}$ is known as the reduced temperature, right? So, now you can see at larger values of $\frac{\varepsilon}{k}$or the temperature very much larger than $\frac{\varepsilon}{k}$, what we have? We should have a kind of this virial coefficient should go through the maximum and that we can see here in this range, okay?

So, second viral coefficient as well as other thermodynamic and transport properties have been interpreted and correlated successfully with the LJ potential for many gases, that is the reason it has been found this LJ model is a better one compared to the any other intermolecular potential which are having 2 parameters, right? So, like this we can take n number of models and then associated second virial coefficient we can obtain, if possible by hand calculation, if not possible by the numerical solutions we can do and then we can make comparisons, okay? But we cannot keep taking n number of models, it is not possible.

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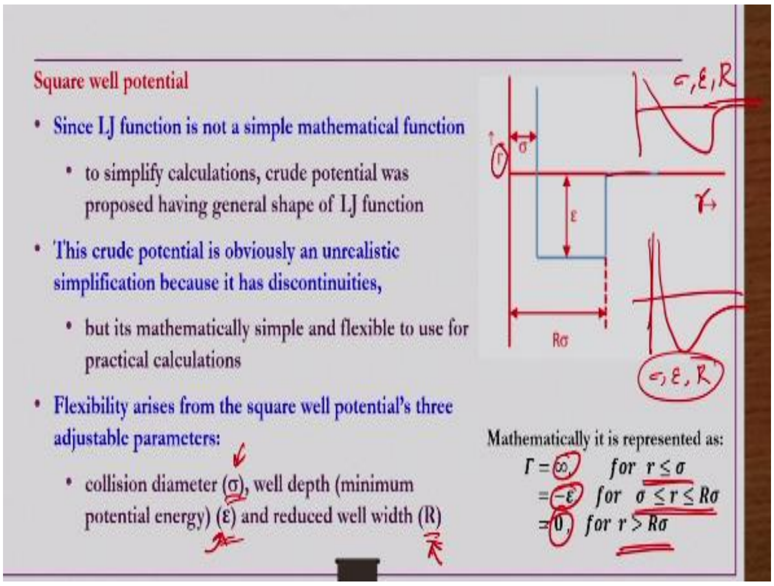

Square well potential

- Since LJ function is not a simple mathematical function
  - to simplify calculations, crude potential was proposed having general shape of LJ function
- This crude potential is obviously an unrealistic simplification because it has discontinuities,
  - but its mathematically simple and flexible to use for practical calculations
- Flexibility arises from the square well potential's three adjustable parameters:
  - collision diameter (σ), well depth (minimum potential energy) (ε) and reduced well width (R)

Mathematically it is represented as:

$$\begin{aligned} \Gamma &= \infty, \quad for\ r \le \sigma \\ &= -\varepsilon \quad for\ \sigma \le r \le R\sigma \\ &= 0, \quad for\ r > R\sigma \end{aligned}$$

So, now what we do? The next one is this square well potential. What we have seen mathematically LJ potential is not simple to do the integration, we have just now seen. So, in order to overcome such kind of limitation what have been done, square well potential have been developed, so which gives a kind of similar shape as LJ potential for the case of Γ versus r separation distance, right? But it is having mathematical simplicity, form is same but it is having mathematical simplicity that is possible by the square well potential, right?

Then pictorially we can have this square well potential like this. So, pictorially this intermolecular potential Γ versus separation distance r if you plot, square well potential will have this kind of form like this. So, for $r < \sigma$, there is an infinite repulsion, for $r = \sigma$ to $r = R\sigma$ distance, this distance there is a constant attractive force right, and then when $r > R\sigma$, this is traction force suddenly drops to the 0 and there will not be any kind of intermolecular potential.

So, now you can see like LJ model what we have, we have this kind of potential. Now, it is mathematically simplified, so that one can do a kind of a mathematical integration easily that is the only purpose, though it is a kind of unrealistic simplification because it has several discontinuities like this. So, it is not possible to have them, they argued that these are going to be much reliable, but obviously it is mathematically simple and flexible to use for practical calculations, right?

It is known as the square well potential because there is a kind of a well kind of shape which is having a square shape like this, okay? That is the reason it is known as the square well potential. Now, mathematically, this for $r \leq \sigma$ that is for collision diameter or < that one, there is an infinite repulsive force and then $r > R\sigma$ that is there is no intermolecular potential, then $\Gamma = 0$, but between $r = \sigma$ to $r = R\sigma$, there is a constant attractive force of well potential ε, okay?

So, $\Gamma = -\varepsilon$ for this case. So, flexibility of this model is only because of 3 important adjustable parameters as per requirement. Let us say your intermolecular potential is like this, accordingly you can have a kind of what could be the σ, what could be the ε, and then what could be the R value so that this model can be much better way represented by this square well potential. Let us say if you have a model like this, right? Then again here in this case σ, ε, R are going to be different.

So, according to the real situations one can have a kind of adjustable parameter. So, then these can be adjusted and then a kind of simplified square well potential can be developed, okay? So, where we can adjust the σ, ε, and then R as per the problem that we are considering or as per the system that we have taken.

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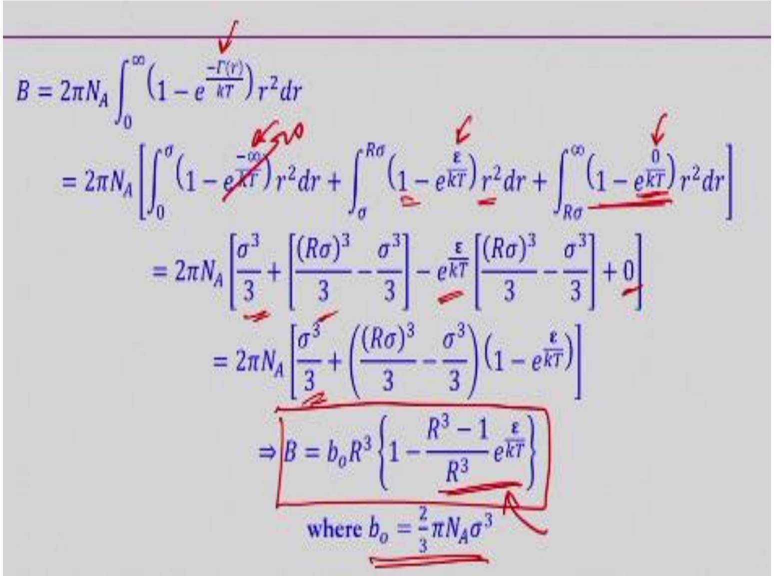

$$B = 2\pi N_A \int_0^{\infty} \left(1 - e^{\frac{-\Gamma(r)}{kT}}\right) r^2 dr$$

$$= 2\pi N_A \left[\int_0^{\sigma} \left(1 - \cancel{e^{\frac{-\infty}{kT}}}\right) r^2 dr + \int_{\sigma}^{R\sigma} \left(1 - e^{\frac{\varepsilon}{kT}}\right) r^2 dr + \int_{R\sigma}^{\infty} \left(1 - e^{\frac{0}{kT}}\right) r^2 dr \right]$$

$$= 2\pi N_A \left[\frac{\sigma^3}{3} + \left[\frac{(R\sigma)^3}{3} - \frac{\sigma^3}{3} \right] - e^{\frac{\varepsilon}{kT}} \left[\frac{(R\sigma)^3}{3} - \frac{\sigma^3}{3} \right] + 0 \right]$$

$$= 2\pi N_A \left[\frac{\sigma^3}{3} + \left(\frac{(R\sigma)^3}{3} - \frac{\sigma^3}{3} \right) \left(1 - e^{\frac{\varepsilon}{kT}}\right) \right]$$

$$\Rightarrow \boxed{B = b_0 R^3 \left\{ 1 - \frac{R^3 - 1}{R^3} e^{\frac{\varepsilon}{kT}} \right\}}$$

$$\text{where } b_o = \frac{2}{3} \pi N_A \sigma^3$$

Now, mathematically if you apply this square well potential in second virial coefficient expression and do the integration, you can get the values like this. So, first case between r = 0 to σ, Γ = ∞; between r = σ to R σ, Γ = - ε; between R = R σ to R = ∞, Γ = 0 that we have substituted in place of Γ as a function of r. Now, this is 0 and then this is 1.

So, altogether this integration does not have any this thing. So, then first term we have this σ $\frac{r^3}{3}$, so, $\frac{\sigma^3}{3}$. Second term, we have integral $r^2 dr$, so $\frac{r^3}{3}$, so $\frac{(R\sigma)^3}{3}$ - $\frac{\sigma^3}{3}$and then next is - $e^{\frac{\varepsilon}{kT}}$ as a constant and then $r^2 dr$ integration is $\frac{r^3}{3}$. So, $\frac{(R\sigma)^3}{3}$ - $\frac{\sigma^3}{3}$ and then this one is exponential of 0 is 1 and then here in the third term this exponential of 0 is 1, so altogether this 1 - 1, 0, so then 0 we are having here.

So, now, what do you do? You can simplify this term like this 2 ∏ N$_A$ you can take common and this $\frac{\sigma^3}{3}$, this $\frac{\sigma^3}{3}$ can be cancelled out and then further if you simplify this equation you can have B = b$_o$ $R^3 \left\{1 - \frac{R^3-1}{R^3} e^{\frac{\varepsilon}{kT}}\right\}$ where b$_o$ is nothing but second virial coefficient according to the hard sphere model that is $\frac{2}{3}\pi N_A \sigma^3$ which encounters only repulsive term, right?

So, because of the attractive terms whatever the additional term is there, the second part is coming into the picture. So, like that for any model for any intermolecular potential one can do such kind of simplification and find second virial coefficient and when can cross check with the experimental results how good, they are matching with experimental results and then whichever is matching better with the experimental region that model can be taken as a kind of a better intermolecular potential for a given system.

Then we cannot have a kind of generalized conclusion which intermolecular potential is going to be more reliable unless if you see the details of the system of consideration.

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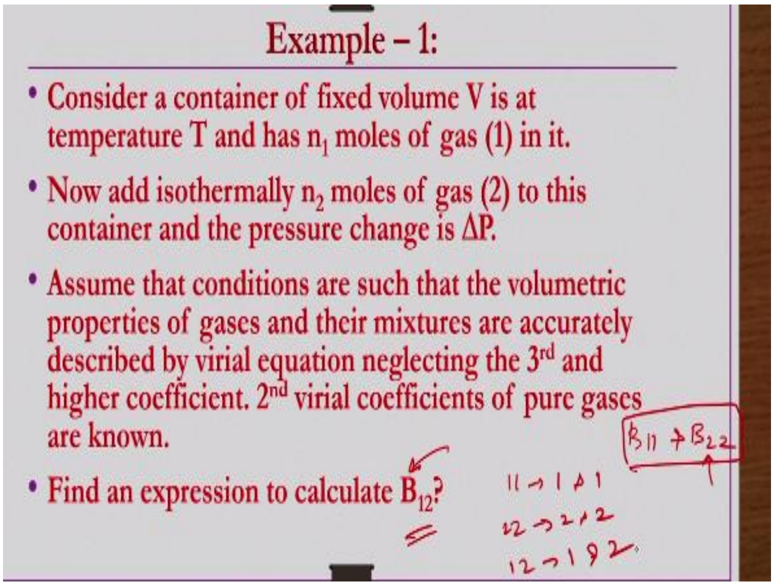

Example – 1:

- Consider a container of fixed volume V is at temperature T and has n_1 moles of gas (1) in it.
- Now add isothermally n_2 moles of gas (2) to this container and the pressure change is ΔP.
- Assume that conditions are such that the volumetric properties of gases and their mixtures are accurately described by virial equation neglecting the 3rd and higher coefficient. 2nd virial coefficients of pure gases are known.
- Find an expression to calculate B_{12}?

$\boxed{B_{11} + B_{22}}$

11 → 1 & 1

22 → 2 & 2

12 → 1 & 2

So, now we see a few example problems, okay? Now consider a container of a fixed volume V is at a temperature T and has n_1 moles of gas in it. Now, add isothermally n_2 moles of gas 2 to this container and the pressure change is ΔP. Initially in a container you have taken n_1 moles of gas 1 at temperature T. So that pressure is nothing but let say some initial pressure. Then what you have done, isothermally you added, maintaining the constant temperature you added n_2 moles of another gas 2.

So, initially it was a pure gas, next you have added something, so now it is a mixture, but the temperature and volume are maintained constant because of that one pressure is going to change and then whatever the change in pressure is ΔP. Assume that the conditions are such that the volumetric properties of gases and their mixtures are accurately described by virial equation neglecting the third and higher coefficient and second virial coefficients of pure gases are known.

Pure gases that means B_{11} and B_{22} are known, right? 11 for in the sense like you know for gas 1 whatever the pure gas 1 is there for that condition second viral coefficient is known, 22 means that is the only pure gas 2 is there. So, then whatever the second virial coefficient is there that is nothing but B_{22}. These things are known. Then find an expression to calculate the cross virial coefficient B_{12}, 11 is interaction between 2 molecules of gas 1, 22 is two molecular interaction between 2 molecules of gas 2, 12 is nothing but two molecular interactions between 1 molecule of gas 1 and another molecule of gas 2. So, this cross virial coefficient we have to find out.

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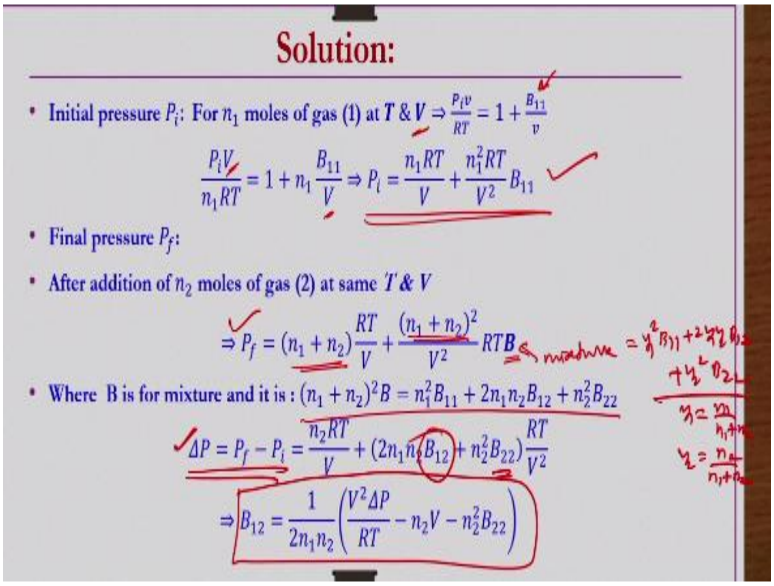

Solution:

- Initial pressure P_i: For n_1 moles of gas (1) at T & $V \Rightarrow \frac{P_i v}{RT} = 1 + \frac{B_{11}}{v}$

$$\frac{P_i V}{n_1 RT} = 1 + n_1 \frac{B_{11}}{V} \Rightarrow P_i = \frac{n_1 RT}{V} + \frac{n_1^2 RT}{V^2} B_{11}$$

- Final pressure P_f:
- After addition of n_2 moles of gas (2) at same T & V

$$\Rightarrow P_f = (n_1 + n_2)\frac{RT}{V} + \frac{(n_1+n_2)^2}{V^2} RT\mathbf{B}$$

mixture $= y_1^2 B_{11} + 2 y_1 y_2 B$ $+ y_2^2 B_{22}$

- Where B is for mixture and it is : $(n_1 + n_2)^2 B = n_1^2 B_{11} + 2 n_1 n_2 B_{12} + n_2^2 B_{22}$

$y_1 = \frac{n_1}{n_1 + n}$

$y_2 = \frac{n_2}{n_1 + n}$

$$\Delta P = P_f - P_i = \frac{n_2 RT}{V} + (2 n_1 n_2 B_{12} + n_2^2 B_{22})\frac{RT}{V^2}$$

$$\Rightarrow \boxed{B_{12} = \frac{1}{2 n_1 n_2}\left(\frac{V^2 \Delta P}{RT} - n_2 V - n_2^2 B_{22}\right)}$$

So, initial pressure let us take P_i, so for n1 moles of gas 1 at T and V that is constant temperature and volume, then the virial equation of state is nothing but $\frac{P_i v}{RT} = 1 + \frac{B_{11}}{v}$, B_{11} we are writing because it is pure gas initially. So, now molar volume I convert into the total volume because the volume of the system is constant, right? So, then I can get $\frac{P_i V}{n_1 RT} = 1 + \frac{n_1 B_{11}}{V}$. Now here it is V that is total volume, right? So, then if you rearrange this equation P_i is nothing but $\frac{n_1 RT}{V} + \frac{{n_1}^2 RT}{V^2} B_{11}$.

Now, isothermally you are adding n_2 moles of gas 2 to this container maintaining the same temperature and volume. So, if you maintain the same temperature and volume, obviously when you add the additional thing, the pressure is going to change that final pressure let us say P_f, right? Then the same equation initially it was like this and now P_f because moles are $n_1 + n_2$ because n_2 moles are added now. So, that is the only change you are going to get here and then this B is going to for mixture because n_2 moles of gas 2 is now added here.

So, that B for the mixture we already know it as a kind of B mixture is nothing but $y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}$, this is what we know for the B mixture, okay? Now, this y_1 if you write

$\frac{n_1}{n_1+n_2}$ and then y_2 you write $\frac{n_2}{n_1+n_2}$, then we can have $(n_1 n_2)^2$ B = $n_1^2 B_{11} + 2 n_1 n_2 B_{12} + n_2^2 B_{22}$. This now, what you do? The change in pressure is given as ΔP, so $P_f - P_i$ is nothing but ΔP. So, that means from this expression if you subtract this expression, then you will get $\frac{n_2 RT}{V} + 2 n_1 n_2 B_{12} + n_2^2 B_{22} \frac{RT}{V^2}$.

So, ΔP is given or known that is mentioned, right? In the right hand side everything is known are in the maintained constant temperature, volume are maintained constant, n_1 n_2 are known and then B_{11}, B_{22} are known. So only unknown in this equation is B_{12}. So, B_{12} you can find out as $B_{12} = \frac{1}{2n_1n_2}\left(\frac{V^2 \Delta P}{RT} - n_2 V - n_2^2 B_{22}\right)$. So, in the right hand side everything is known, then B_{12} one can calculate using this expression, right?

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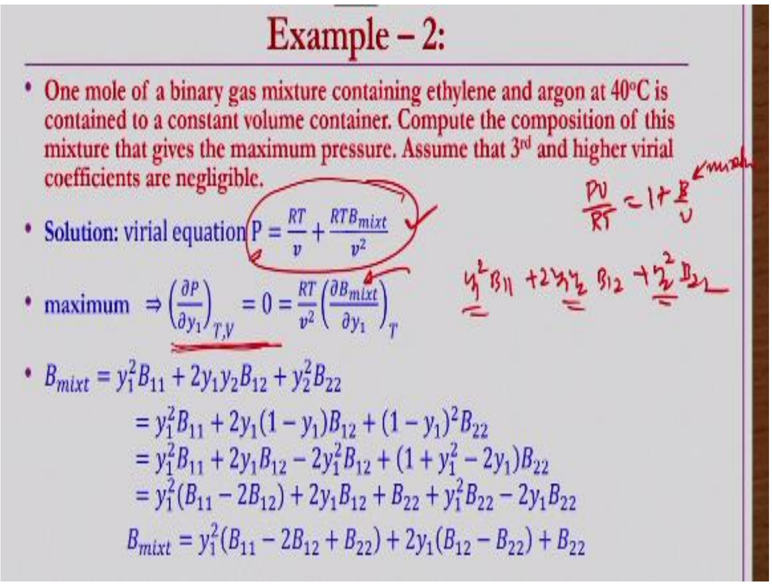

Example – 2:

- One mole of a binary gas mixture containing ethylene and argon at 40°C is contained to a constant volume container. Compute the composition of this mixture that gives the maximum pressure. Assume that 3rd and higher virial coefficients are negligible.
- Solution: virial equation $P = \frac{RT}{v} + \frac{RTB_{mixt}}{v^2}$
- maximum $\Rightarrow \left(\frac{\partial P}{\partial y_1}\right)_{T,V} = 0 = \frac{RT}{v^2}\left(\frac{\partial B_{mixt}}{\partial y_1}\right)_T$
- $B_{mixt} = y_1^2 B_{11} + 2y_1y_2B_{12} + y_2^2 B_{22}$

$$= y_1^2 B_{11} + 2y_1(1-y_1)B_{12} + (1-y_1)^2 B_{22}$$
$$= y_1^2 B_{11} + 2y_1 B_{12} - 2y_1^2 B_{12} + (1 + y_1^2 - 2y_1)B_{22}$$
$$= y_1^2(B_{11} - 2B_{12}) + 2y_1 B_{12} + B_{22} + y_1^2 B_{22} - 2y_1 B_{22}$$
$$B_{mixt} = y_1^2(B_{11} - 2B_{12} + B_{22}) + 2y_1(B_{12} - B_{22}) + B_{22}$$

$\frac{Pv}{RT} = 1 + \frac{B}{v} \leftarrow$ mixt

$y_1^2 B_{11} + 2y_1y_2 B_{12} + y_2^2 B_{22}$

So, now we take another example. One mole of a binary gas mixture containing ethylene and argon at 40 degrees centigrade is contained to a constant volume container. Compute the composition of this mixture that gives the maximum pressure. Assume that third and higher virial coefficients are negligible, right? Virial equation of state P = $\frac{RT}{v} + \frac{RTB_{mixt}}{v^2}$, this is what we know or we have $\frac{Pv}{RT} = 1 + \frac{B}{v}$. So, this one if you rearrange P = $\frac{RT}{v} + \frac{RTB}{v^2}$, this is what you get, now this B is for the mixture.

Then you have this expression. We are writing in this form because we wanted to have the composition which provides the maximum pressure. So, B mixture we know it, we will do it. So, now the composition at which the pressure becomes 0 if you wanted to find out you how to differentiate this above equation with respect to the composition and then equate it to the 0 at constant temperature and volume, then you get it.

So, we know this B mixture is a function of composition, it is independent of composition, but for the mixture because they are based on composition, you can find out. This we know, we know it as $y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}$. So, this y, y, etc., are known, so that means $\frac{RT}{v^2}\left(\frac{\partial B_{mixt}}{\partial y_1}\right)$ if you do and then equate to the 0, then you will get the condition or the composition at which the pressure is maximum, right? So, what we have to do?

This B mixture this expression we have to convert in terms of y_1 by taking $y_2 = 1 - y_1$ and then simplifying it. When you do it, you get this one.

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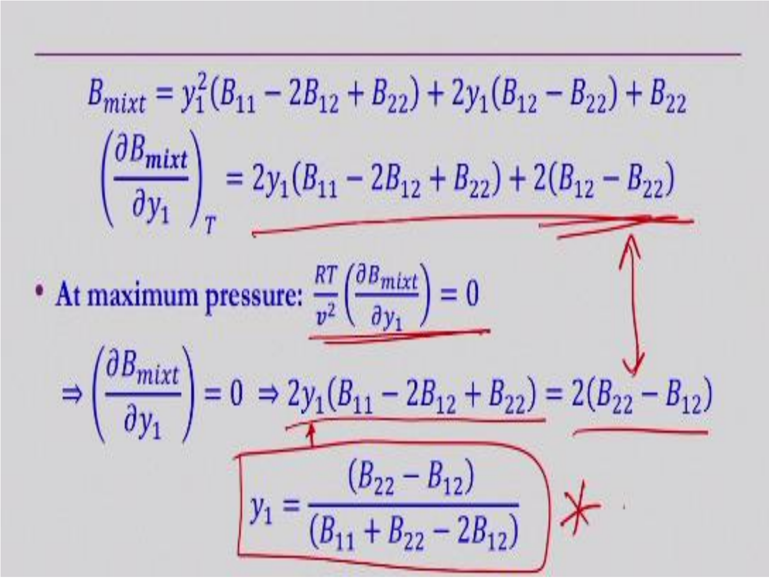

$$B_{mixt} = y_1^2(B_{11} - 2B_{12} + B_{22}) + 2y_1(B_{12} - B_{22}) + B_{22}$$

$$\left(\frac{\partial B_{mixt}}{\partial y_1}\right)_T = 2y_1(B_{11} - 2B_{12} + B_{22}) + 2(B_{12} - B_{22})$$

- At maximum pressure: $\frac{RT}{v^2}\left(\frac{\partial B_{mixt}}{\partial y_1}\right) = 0$

$$\Rightarrow \left(\frac{\partial B_{mixt}}{\partial y_1}\right) = 0 \Rightarrow 2y_1(B_{11} - 2B_{12} + B_{22}) = 2(B_{22} - B_{12})$$

$$\boxed{y_1 = \frac{(B_{22} - B_{12})}{(B_{11} + B_{22} - 2B_{12})}} \ *$$

So, B mixture is nothing but y_1^2 $(B_{11} - 2 B_{12} + B_{22}) + 2 y_1 (B_{12} – B_{22}) + B_{22}$. This expression now if you partially differentiate with respect to y_1 and maintaining the temperature constant T, then you will get $2 y_1 (B_{11} - 2 B_{12} + B_{22}) + 2 (B_{12} - B_{22})$, right? Now, if you equate this one to 0 because for the compression at where the pressure is maximum, this term is also 0, $\frac{RT}{v^2}\left(\frac{\partial B_{mixt}}{\partial y_1}\right)$ is also 0 zero, right? That we have just seen in the previous slide.

So, now that means this if you equate to the 0, then you will have $y_1 B_{11} - 2 B_{12} + B_{22} = 2 B_{22} - B_{12}$ just reverse way we have written this down, I mean like this - I have taken inside the parenthesis, so that I can write $2 (B_{22} - B_{12})$. Now, we wanted to find out what is y_1 from here,

$y_1 = \frac{(B_{22}-B_{12})}{(B_{11}+B_{22}-2B_{12})}$. That means, if you know the second virial coefficients of pure components as well as the cross virial coefficient if you know, then you can find out the composition at which the pressure is maximum by using this expression.

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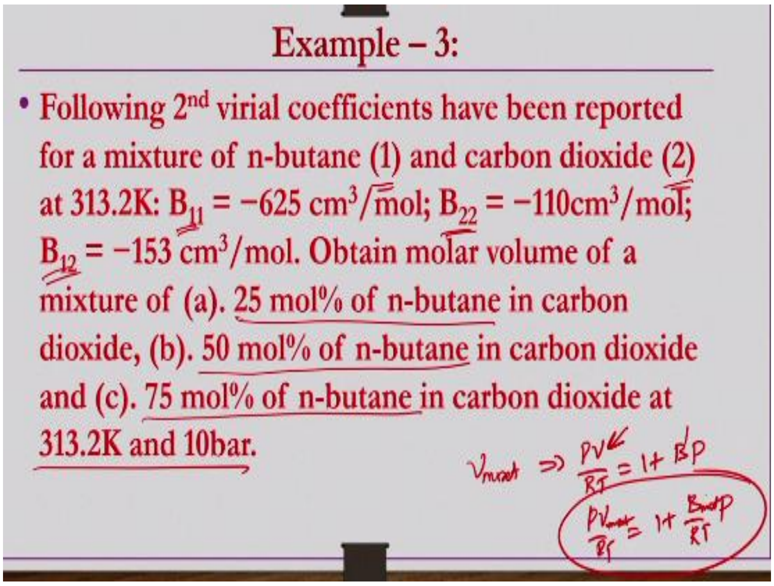

Example – 3:

- Following 2nd virial coefficients have been reported for a mixture of n-butane (1) and carbon dioxide (2) at 313.2K: B_{11} = −625 cm³/mol; B_{22} = −110cm³/mol; B_{12} = −153 cm³/mol. Obtain molar volume of a mixture of (a). 25 mol% of n-butane in carbon dioxide, (b). 50 mol% of n-butane in carbon dioxide and (c). 75 mol% of n-butane in carbon dioxide at 313.2K and 10bar.

$V_{mixt} \Rightarrow \frac{PV}{RT} = 1 + B'P$

$\frac{PV_{mixt}}{RT} = 1 + \frac{B_{mixt}P}{RT}$

Now, we take another example. Following second virial coefficients have been reported for a mixture of n-butane, n-butane is designated as 1 and carbon dioxide designated as 2 at 313.2 Kelvin and their second virial coefficient as well as the cross second virial coefficients are given. Obtain the molar volume of a mixture for three cases, one is the 25 mole percent of butane in the mixture and then 50 mole percent of n-butane and then 75 mole percent of n-butane in the mixture at 313.2 Kelvin and 100 bars, right?

So, we need to find out v mixture actually. So, this we can do from this P v by RT = 1 + B′ P, this one you can use or any other equations you can use. B′ we cannot use because B′ information’s are not given. So, this you can write $\frac{P}{RT}$ = 1 + B′ is nothing but $\frac{B}{RT}$ and then P, this expression you can calculate. So, this is for the mixture, so basically this B should also be for the mixture. So, that means first we have to find out B mixture, okay? For all the three cases and then using this expression you can find out v mixture.

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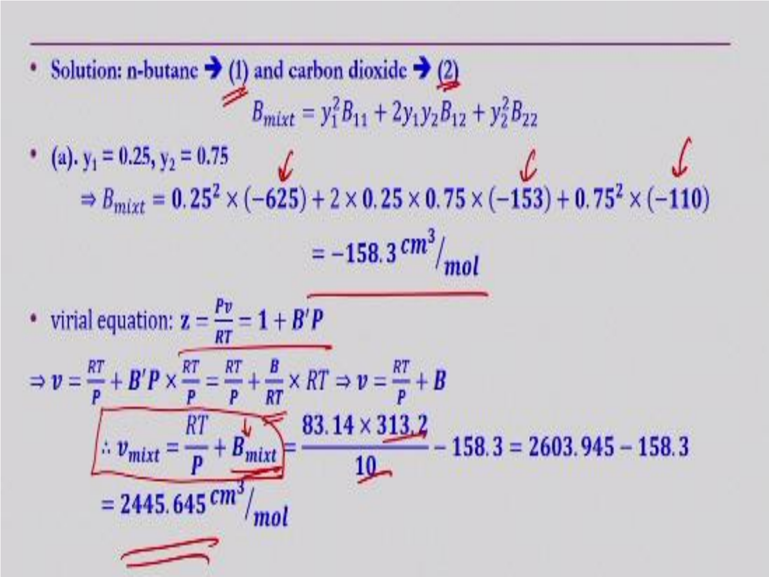

- Solution: n-butane → (1) and carbon dioxide → (2)

$$B_{mixt} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$$

- (a). $y_1 = 0.25, y_2 = 0.75$

$$\Rightarrow B_{mixt} = 0.25^2 \times (-625) + 2 \times 0.25 \times 0.75 \times (-153) + 0.75^2 \times (-110)$$

$$= -158.3\, {cm^3}/{mol}$$

- virial equation: $z = \frac{Pv}{RT} = 1 + B'P$

$$\Rightarrow v = \frac{RT}{P} + B'P \times \frac{RT}{P} = \frac{RT}{P} + \frac{B}{RT} \times RT \Rightarrow v = \frac{RT}{P} + B$$

$$\boxed{\therefore v_{mixt} = \frac{RT}{P} + B_{mixt}} = \frac{83.14 \times 313.2}{10} - 158.3 = 2603.945 - 158.3$$

$$= 2445.645\, {cm^3}/{mol}$$

So, B mixture is nothing but $y_1^2 B_{11}$ + 2 y_1 y_2 B_{12} + $y_2^2 B_{22}$ and then 1 is standing for the n-butane, 2 is standing for the carbon dioxide. So, for the first case y_1 is 0.25 and then y_2 = 0.75. Then when you substitute these values in B mixtures, you will get b mixture = - 158.3 centimeter cube per mole because B_{11}, B_{12}, B_{22} are given. Then molar volume of the mixture we have to find out, so we have z = $\frac{Pv}{RT}$= 1 + B ′ P. So, then we have v = $\frac{RT}{P}$+ B′P $\frac{RT}{P}$.

Now, B ′ we can write $\frac{B}{RT}$, then we can write this equation v = $\frac{RT}{P}$ + B mixture, okay? Now, this is for the mixture and this is also for the mixture. So, that means we can have v mixture = $\frac{RT}{P}$+ B mixture. So, B mixture you have already found just now that is - 158.3 centimeter cube per mole and then this T and P are given. So, then you have B mixture is 2445.645 centimeter cube per mole.

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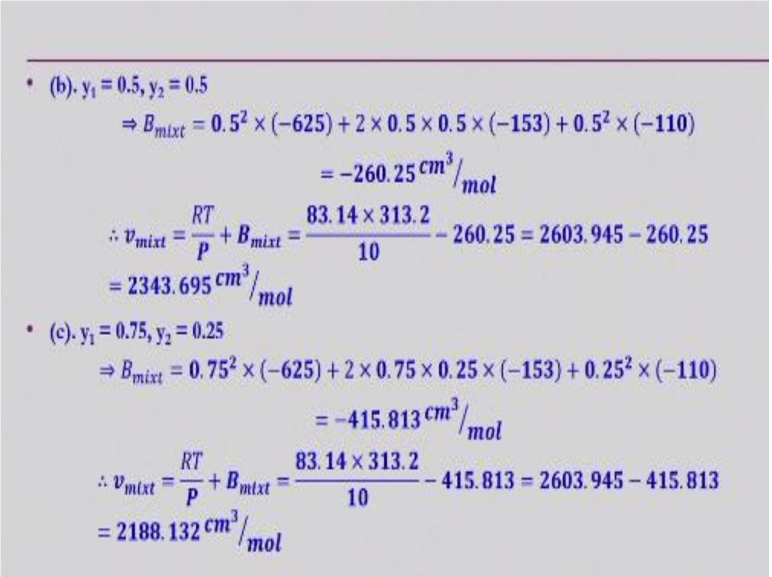

- (b). $y_1 = 0.5, y_2 = 0.5$

$$\Rightarrow B_{mixt} = 0.5^2 \times (-625) + 2 \times 0.5 \times 0.5 \times (-153) + 0.5^2 \times (-110)$$

$$= -260.25\, {cm^3}/{mol}$$

$$\therefore v_{mixt} = \frac{RT}{P} + B_{mixt} = \frac{83.14 \times 313.2}{10} - 260.25 = 2603.945 - 260.25$$

$$= 2343.695\, {cm^3}/{mol}$$

- (c). $y_1 = 0.75, y_2 = 0.25$

$$\Rightarrow B_{mixt} = 0.75^2 \times (-625) + 2 \times 0.75 \times 0.25 \times (-153) + 0.25^2 \times (-110)$$

$$= -415.813\, {cm^3}/{mol}$$

$$\therefore v_{mixt} = \frac{RT}{P} + B_{mixt} = \frac{83.14 \times 313.2}{10} - 415.813 = 2603.945 - 415.813$$

$$= 2188.132\, {cm^3}/{mol}$$

Similarly, second case when y_1, y_2 both are equals to 50 percentage, then B mixture you can find it out as - 260.25 centimeter cube per mole. Then v mixture is nothing but $\frac{RT}{P}$ + B mixture. So, then when you substitute this B mixture and temperature and pressure here, then you will get v mixture as 2343.695 centimeter cube per mole and then similarly third case $y_1 = 0.75$ and y_2 is 0.25, then again you can find out these numbers B mixture as a kind of - 415.813 centimeter cube per mole.

This if you substitute in this $v_{mixture} = \frac{RT}{P}$+ B mixture expression along with the temperature and pressure and then simplify, v mixture you can find it as 2188.132 centimeter cube per mole. What we can understand if you maintain the same temperature and pressure in the system and then keep changing the mole fraction of the system or the binary mixture, then what you can see if you are gradually increasing the mole fraction of n-butane, the molar volume of the mixture is gradually decreasing.

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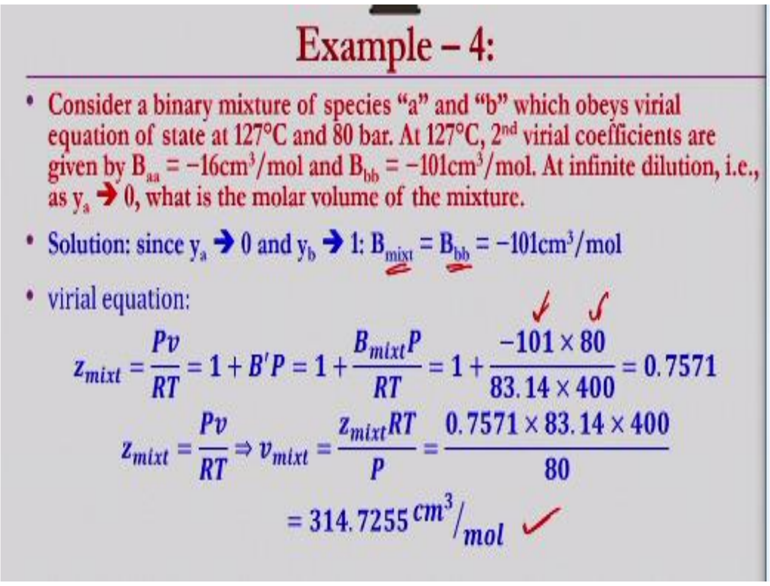

Example – 4:

- Consider a binary mixture of species "a" and "b" which obeys virial equation of state at 127°C and 80 bar. At 127°C, 2nd virial coefficients are given by $B_{aa} = -16 cm^3/mol$ and $B_{bb} = -101 cm^3/mol$. At infinite dilution, i.e., as $y_a \to 0$, what is the molar volume of the mixture.
- Solution: since $y_a \to 0$ and $y_b \to 1$: $B_{mixt} = B_{bb} = -101 cm^3/mol$
- virial equation:

$$z_{mixt} = \frac{Pv}{RT} = 1 + B'P = 1 + \frac{B_{mixt}P}{RT} = 1 + \frac{-101 \times 80}{83.14 \times 400} = 0.7571$$

$$z_{mixt} = \frac{Pv}{RT} \Rightarrow v_{mixt} = \frac{z_{mixt}RT}{P} = \frac{0.7571 \times 83.14 \times 400}{80}$$

$$= 314.7255 \, {cm^3}/{mol}$$

Now, another example consider a binary mixture of species a and species b, which obeys virial equation of state at 127 degrees centigrade and 80 bar, and at this temperature second virial coefficients of a and b are given as B_{aa}, B_{bb} and at infinite dilution that is when y_a tends to 0, what is the molar volume of the mixture? That is the question. Now, since it is infinite dilution, that means y_a tends to 0 that means whatever the mixture is there that is almost like a kind of pure B.

So obviously for B mixture, you can take as a kind of B_{bb}, B suffix bb are the second virial coefficient of b species whatever is there that you can take it as a kind of a second virial coefficient of the mixture because it is an infinite dilution, okay? Then virial equation of state we know that z mixture = $\frac{Pv}{RT}$= 1 + B ′ P = 1 + $B_{mixture}$ $\frac{P}{RT}$. B mixture is now - 101, P is 80 bar, temperature is 127 degrees centigrade so that is 400 Kelvin. So, then z mixture is coming out to be 0.7571, but z mixture is nothing but $\frac{Pv}{RT}$, that means v mixture is nothing but z mixture $\frac{RT}{P}$.

So, when you substitute this z mixture, temperature, and pressure here and then simplify, you will get v mixture as 314.7255 centimeter cube per mole So, this is how we can play around the finding of the second virial coefficient, the problems associated with the virial equation of state, how to find out the pressure, composition, mixture, molar volume of the mixture, etc., those kind of things we can find out as per these example problems.

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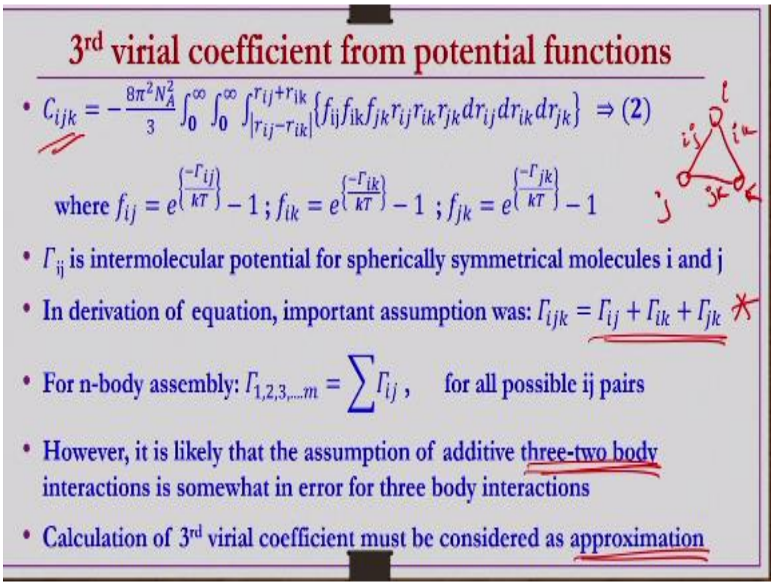

3rd virial coefficient from potential functions

- $C_{ijk} = -\frac{8\pi^2 N_A^2}{3}\int_0^\infty \int_0^\infty \int_{|r_{ij}-r_{ik}|}^{r_{ij}+r_{ik}} \{f_{ij} f_{ik} f_{jk} r_{ij} r_{ik} r_{jk} dr_{ij} dr_{ik} dr_{jk}\} \Rightarrow (2)$

  where $f_{ij} = e^{\left\{\frac{-\Gamma_{ij}}{kT}\right\}} - 1$; $f_{ik} = e^{\left\{\frac{-\Gamma_{ik}}{kT}\right\}} - 1$; $f_{jk} = e^{\left\{\frac{-\Gamma_{jk}}{kT}\right\}} - 1$
- Γ_{ij} is intermolecular potential for spherically symmetrical molecules i and j
- In derivation of equation, important assumption was: $\Gamma_{ijk} = \Gamma_{ij} + \Gamma_{ik} + \Gamma_{jk}$ *
- For n-body assembly: $\Gamma_{1,2,3,\ldots m} = \sum \Gamma_{ij}$, for all possible ij pairs
- However, it is likely that the assumption of additive three-two body interactions is somewhat in error for three body interactions
- Calculation of 3rd virial coefficient must be considered as approximation

So, now what we do? About the third virial coefficient from potential functions, C_{ijk} expression we have already seen, here f_{ij}, f_{ik}, and then f_{jk} are given by these expressions, right? As I mentioned already, this third virial coefficient expression whatever derived based on the statistical mechanics, it has been found whatever the interaction between the 3 molecules let us say you have one i molecule, one j molecule, one k molecule, so the 3 molecules are interacting.

So, three body interaction are taken consideration as a kind of summation of 3 two body interaction that is ij interaction, ik interaction, and jk interactions individually as a kind of 3 two body interactions and then adding them together whatever summation is there that is the Γ_{ijk} that is the assumption in deriving this third virial coefficient from statistical mechanics. Because of this assumption, whatever the C_{ijk} or the third virial coefficients are there, they are the kind of approximations.

So, if you have n body system, so then for those n body systems, all possible Γ_{ij} pairs are there. So, there all possible ij pairs are there, for all of them you have to find out what is the two body interactions and then add them together, then you can get for n body assembly what is that Γ 1, 2, 3 and so on so, right? So, it is unlikely that the assumption of additive three body interactions is somewhat in error for three body interactions, right? Because you are doing what, 3 two body interactions you are taking and then adding them together to say that it is a three body interaction.

It is an approximation. So, it may be erroneous many times. So, obviously the third virial coefficients that we get using this expression or integrating this expression are obviously a kind of approximation. So, they will obviously be less accurate compared to the second virial coefficient that we have derived simply by using a few potential models few minutes before.

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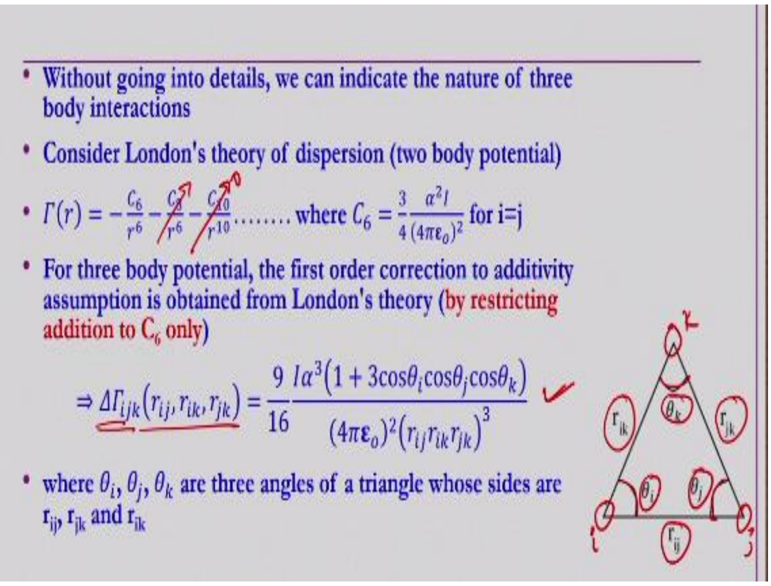

- Without going into details, we can indicate the nature of three body interactions
- Consider London's theory of dispersion (two body potential)
- $\Gamma(r) = -\frac{C_6}{r^6} - \cancel{\frac{C_8}{r^6}} - \cancel{\frac{C_{10}}{r^{10}}}$ .... where $C_6 = \frac{3}{4}\frac{\alpha^2 I}{(4\pi\varepsilon_0)^2}$ for i=j
- For three body potential, the first order correction to additivity assumption is obtained from London's theory (by restricting addition to C_6 only)

$$\Rightarrow \underline{\Delta\Gamma_{ijk}(r_{ij}, r_{ik}, r_{jk})} = \frac{9}{16}\frac{I\alpha^3(1 + 3\cos\theta_i\cos\theta_j\cos\theta_k)}{(4\pi\varepsilon_0)^2(r_{ij}r_{ik}r_{jk})^3} \checkmark$$

- where θ_i, θ_j, θ_k are three angles of a triangle whose sides are r_{ij}, r_{jk} and r_{ik}

So, let us say, we do not go into the all the details, but let us say we take few cases, let us say you have i molecule, you have a j molecule, you have a k molecule. So then, the intermolecular separation distance between i molecule and k molecule is r_{ik}. Similarly, r_{jk} is the intermolecular separation the distance between 1 j and 1 k molecule and then r_{ij} is nothing but the intermolecular separation distance between 1 i and 1 j molecule.

The angle between these two if you take theta$_i$ and then between these two if you take θ_j, if between these two if you take θ_k, then by using London's theory of dispersion and then taking only first term but by not taking the higher ordered terms, okay? We can find out this $\Delta\Gamma_{ijk}$ as function of r_{ij}, r_{ik}, r_{jk} can be found it as like this, okay? And then we are taking only that first term in the London's theory of dispersion, we are not taking all the details.

So, this will provide you Γ_{ijk} information and then this information you can make use in order to get the third virial coefficient, okay? This is how one can find out the second and third virial coefficients using the intermolecular potential and then by applying the principles of this second video coefficients from intermolecular potentials, we can solve any kind of problems to get the required information such as cross virial coefficients, maximum pressures, etc all those thing as we have seen in few example problems.

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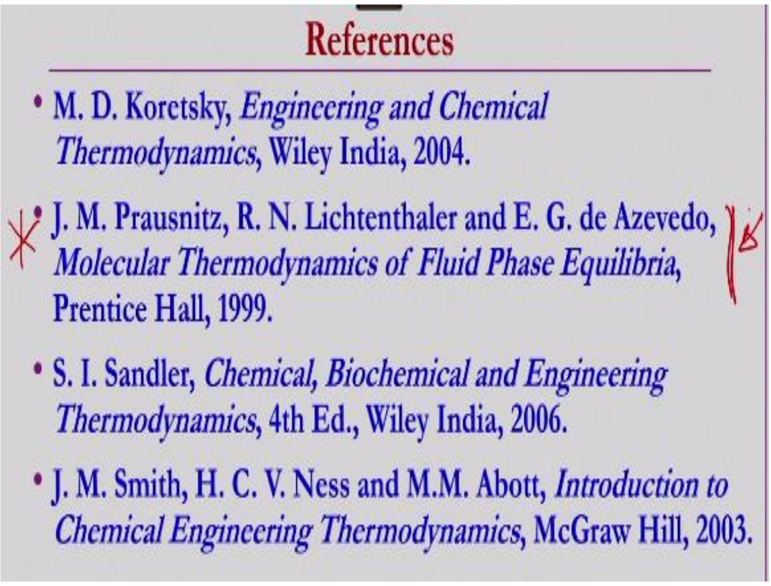

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So, the references for this lecture are Engineering and Chemical Thermodynamics by Koretsky, Molecular Thermodynamics of Fluid Phase Equilibria by Prausnitz et al, Chemical Biochemical and Engineering Thermodynamics by Sandler and then Introduction to Chemical Engineering by Smith et al. The details most of the lectures even the example problems are also taken from this reference book. In fact, some of the exam problems discussed here are the kind of exercise problems in this book.

Thank you.