Advanced Thermodynamics
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Lecture – 11
Intermolecular Potential and EoS

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is intermolecular potential and equations of states. So, we will be discussing a few equations of state. In those equations of state, how the intermolecular potential is playing rule that is what we are going to see. Because for real gases, we know that the intermolecular potentials are important and then what are those intermolecular potentials we have already seen in a couple of previous lectures, right?

So, now we try to make use of those intermolecular potential in describing the equations of state or delineating the existing equations of state that is what we are going to see in this and in coming couple of lectures. There are hundreds of equations or states are available, even more, but we cannot go through in details of all of them. So, what will we be doing? We will be taking the basic, very first one Van der Waal's equation of state and then we take a few equation of state which are having similar form except the change in attractive force term. Those equations of state we will be discussing.

Then we will be discussing Virial equation of state. Virial equation of state is one such equation of state where the parameters are constants associated with that equation of state are directly related to intermolecular potentials. How are they related to intermolecular potentials and all those things we are going to see, okay?

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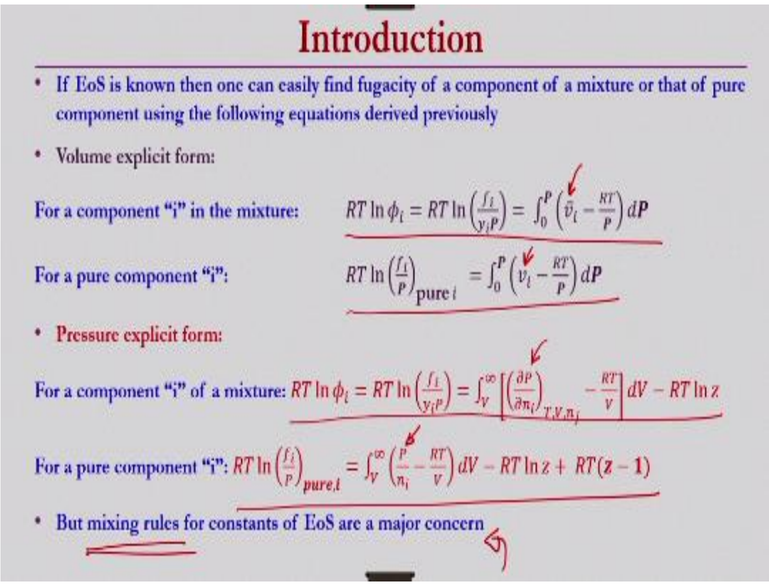

Introduction

- If EoS is known then one can easily find fugacity of a component of a mixture or that of pure component using the following equations derived previously
- Volume explicit form:

For a component "i" in the mixture: $RT\ln\phi_i = RT\ln\left(\frac{f_i}{y_iP}\right) = \int_0^P \left(\bar{v}_i - \frac{RT}{P}\right) dP$

For a pure component "i": $RT\ln\left(\frac{f_i}{P}\right)_{\text{pure } i} = \int_0^P \left(v_i - \frac{RT}{P}\right) dP$

- Pressure explicit form:

For a component "i" of a mixture: $RT\ln\phi_i = RT\ln\left(\frac{f_i}{y_iP}\right) = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - RT\ln z$

For a pure component "i": $RT\ln\left(\frac{f_i}{P}\right)_{pure,i} = \int_V^\infty \left(\frac{P}{n_i} - \frac{RT}{V}\right) dV - RT\ln z + RT(z-1)$

- But mixing rules for constants of EoS are a major concern

Now, why do we need information about the equations of state? Because if you know the equations of state, so whether the equation of state is given in a kind of pressure explicit form or volume explicit form, then whether it is for pure gas or for mixture of gases, then we can know the fugacity of a particular component of a mixture or the fugacity of a pure component provided in which form these equations of state. So, those corresponding equations, generalized equations for fugacity when the equation of state is available as pressure explicit form or volume explicit form, those things we have already derived.

So, but now, we need to have the information of equation of state, then only those equations are useful, right? So, now that is the important of equation of state. If you have the equation of state, then we can obtain those fugacity information either for a component, any component of the mixture or for a pure component, right? So, what those equations the fugacity equations that we have already derived that we just have a kind of recapitulation before going into the details of the rule of intramolecular potentials in equations of state which are valid for real gases.

If the equation of state is available in volume explicit form, then for the fugacity of component i in a mixture, then you can use this expression, right? This expression we have already derived here, only that from the equation of state whatever the information is there that information you write in volume explicit form, then you obtain this $\bar{v}_i$ that is $\left(\frac{\partial v}{\partial n_i}\right)_{T,P,n_j}$. If you have a pure component, then the fugacity of the pure component you can find out using this expression where you just need to have a kind of a molar volume of that particular component.

Because for pure component molar volume = the partial molar volume, partial molar volume and molar volume are equal to each other. If the equation of state is available in pressure explicit form, then if you wanted to find out the fugacity of component i of a mixture, then you can use this expression here whatever the equation of state available in pressure explicit form that you do $\frac{\partial P}{\partial n_i}$ and then substitute here and then do the simplification to get the required fugacity of component i in the mixture.

Then if you have a pure component, then you can use this equation, right? Here whatever the equation of state in pressure explicit form is there, so that P information you substitute here and then simplify the equation, but the mixtures in general the major concern is the mixing rules because all these equations of state are having some parameters or constants which are nothing but a kind of curve fitting parameters kind of things, right? So, those parameters are available only for pure components, they are not available for a mixture of gases.

So, that is the reason we have to use of mixing rules if you want to obtain those constant for mixtures and there is no guarantee about which mixing rule has to be used, there is no clear cut information that which mixing rule has to be used and all that and then sometimes mixing rules may not give a constant which relate or which provide a kind of physical significance about the mixture of those gases. So, that is another disadvantage, right?

So, however, we are going to see some of the equations of state where we can even need not to worry about such kind of mixing rules that is by using Virial equation of state, etc., those things we are going to see now.

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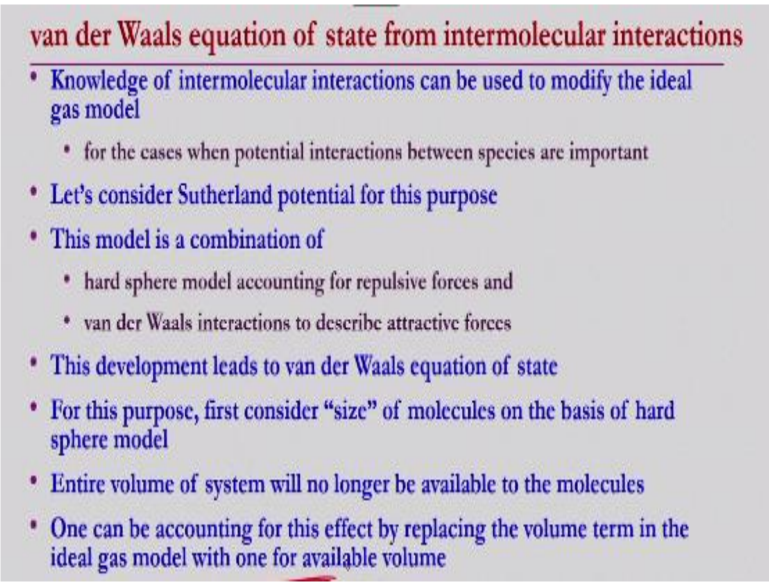

van der Waals equation of state from intermolecular interactions

- Knowledge of intermolecular interactions can be used to modify the ideal gas model
  - for the cases when potential interactions between species are important
- Let's consider Sutherland potential for this purpose
- This model is a combination of
  - hard sphere model accounting for repulsive forces and
  - van der Waals interactions to describe attractive forces
- This development leads to van der Waals equation of state
- For this purpose, first consider "size" of molecules on the basis of hard sphere model
- Entire volume of system will no longer be available to the molecules
- One can be accounting for this effect by replacing the volume term in the ideal gas model with one for available volume

So, coming to the equations of state, so we start with Van der Waal's equation of state which consider the intermolecular interactions, okay? So, we start with that one. So, this Van der Waal's equation of state how we can start you know describing it, probably we can see it as a kind of modification to the ideal gas behavior. Ideal gas behavior what we have, we have a container in that let us take, then if you take ideal gas in a container, so the entire volume is available for occupying.

Because we know the major assumption of ideal gas behavior is that molecules of the gas does not occupy any volume or they are infinitesimally small that their volume can be negligible. So, whatever the volume of container is there that entire thing is available in general, but in real gases, what happens you know you have the molecules of certain size, right? If you take 1 mole of gas and then fill it in a container, so that 1 mole of gas may be whatever the number of molecules are present in that 1 mole of gas, they will be occupying a certain volume.

So, the entire volume is not available for the occupying. So, whatever the unoccupied volume is there that may be used as a kind of correction for this volume. Then other thing about the ideal gas behavior is that these molecules, whichever infinitesimally small molecules are occupying negligible volume, these molecules they are not interacting with each other. Whatever the interaction is there that is only because of the collision with the walls and then coming hitting and those kinds of things are only possible.

Between the molecule, there are no kind of interactions, that is what ideal gas behavior says that is the another important assumption, but what we have you know in reality for real gases when the molecules come close to each other, if they come very much close to each other or touching to each other, there may be a kind of repulsion force and then as they move away after certain distance collision diameter that we call, then after that if you further increase the distance between the molecules, then there may be attraction force.

As we move further apart, you know gradually the attraction force increases to certain distance and after that if you further increase the distance between 2 molecules, the attraction force further decreases and then when these molecules are sufficiently away from each other, the interaction force almost become negligible. Those kinds of intermolecular interactions that we have seen.

So, now the second point is this interaction, how can we bring in that molecules are repelling each other when they are touching each other or if they are certain distance apart from each other, there is attraction force, how to bring in the concept of attraction force in this ideal gas behavior that is Pv = RT. Now, the ideal gas behavior whatever the Pv = RT is this, so this molar volume here we can make some adjustment for unoccupied volume or whatever the real volume that is available for occupying, right?

So, that will give take over the one assumption that the molecules are having negligible volume for the ideal gas, right? Negligible volume this assumption that can be overcome by replacing this v with certain kind of adjustment or correction factor. Then whatever the attractive forces or intermolecular potential attractive or repulsive whatever the forces are there, we have seen these forces majorly affected by the pressure. If you increase the pressure, what happens?

Molecules will come closer and closer to each other and then more interactions are possible, right? So, then these interactions whatever is there ideal gas, no interactions, this can be corrected if you make some kind of correction with this pressure, okay? So, this is the basis to develop or start with some kind of adjustment correction to overcome these assumptions that are existing in the ideal gas behavior. Two important assumptions in ideal gas behavior is that the molecules of gas occupy no volume or negligible volume, right?

So, that correction you can make in molar volume term of this Pv = RT and then in ideal gases there are no interactions, but interactions are stronger especially when pressure increases gradually. So, if you can make some correction in this pressure term to account for the interactions, then we can have some kind of a prior information or first order information or first order approximation about the real gas behavior. So, that is how these equations of state, Van der Waal's equation of state have been started developing, right?

So, those details we see now. So, knowledge of intermolecular interactions can be used to modify the ideal gas model. That is for the cases when the potential interactions between species are important for a given real gas, okay? So, whatever the intermolecular interactions between the species are there in the case of real gases, if you incorporate that information in ideal gas model Pv = RT, so then you can make adjustment of or incorporation of intermolecular interactions and then you can have a kind of model for real gases.

So for this purpose what we do? We will be considering Sutherland potential that we have already discussed. If you remember in one of the previous lectures, Sutherland potential we have seen, this Γ versus, capital Γ is intermolecular potential, is y axis and the x axis is the intermolecular separation distance. So this we know, it is a kind of having this kind of form, right? So where this is known as the σ collision diameter, right? So this is the diameter.

So, when the molecules are coming to the distance closer to this one or smaller, they will immediately be repelling with infinite repulsion forces, but moment this distance between the molecules start exceeding this collision diameter σ, then what happens, the attraction forces would be there and then this attraction forces gradually decreases with increasing the this intermolecular separation distance. So, this is what Sutherland potential, actually it is a combination of hard sphere model and then inclusion of the Van der Waal's attraction forces, okay?

So, the attraction force part or the intermolecular attraction whatever is there that is having this form and then that can be represented by some constant $-\frac{k}{r^6}$, this is what we have already seen. So, this model is a combination of hard sphere model accounting for repulsive forces that is moment they touch each other or the moment the distance between these 2 becomes equals to σ, σ is nothing but the size of the hard sphere that we have which is also known as the collision diameter in this case.

When they touch each other that is when they are at σ distance from each other, so immediately they repel and then repulsive force is very high and then Van der Waal interactions that describe the attractive forces as I mentioned just now. This development leads to the Van der Waal's equation of state. So, for this purpose, first consider size of molecules on the basis of hard sphere model and then entire volume of system will no longer be available to the molecules unlike in the case of ideal gas.

In the case of ideal gas, whatever the gas you keep on giving, so the entire volume of the container is available because these molecules of the gas whatever ideal gas is there they have a negligible or zero volume, okay? So but in the case of real gases that is not true, it is not possible to have an entire volume of the system for occupying, okay? So now one can be accounting for this effect by replacing the volume term in the ideal gas model with one for the available volume. So, that is what we first see and then we see the other part.

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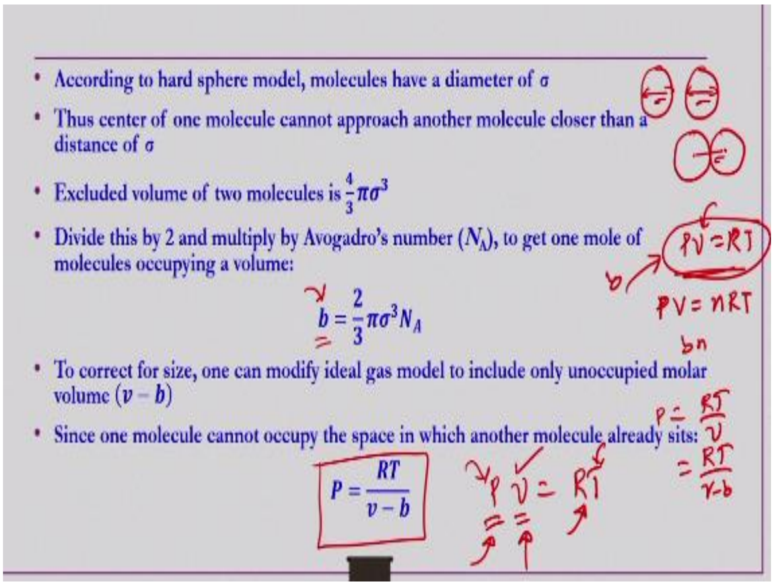

- According to hard sphere model, molecules have a diameter of σ
- Thus center of one molecule cannot approach another molecule closer than a distance of σ
- Excluded volume of two molecules is $\frac{4}{3}\pi\sigma^3$
- Divide this by 2 and multiply by Avogadro's number (N_A), to get one mole of molecules occupying a volume:

$$b = \frac{2}{3}\pi\sigma^3 N_A$$

- To correct for size, one can modify ideal gas model to include only unoccupied molar volume ($v - b$)
- Since one molecule cannot occupy the space in which another molecule already sits:

$$\boxed{P = \frac{RT}{v - b}}$$

According to hard sphere model, molecules have a diameter of σ that is you have 2 spheres like this, hard spheres, so each one having the diameter of σ like this. So, that means when they come close to each other or when they are touching each other, the center to center distance is again σ, right? All the molecules are of same size and shape. So, then this σ is also known as the collision diameter.

So, that is moment they touch each other, then immediately repel, that means the center of one molecule cannot approach another molecule closer than a distance of σ because of this reason because these molecules are considered as a kind of hard sphere, non-interpenetrating spherical molecules, that is hard spherical molecules. Now, excluded volume of 2 molecules is obviously $\frac{4}{3}\Pi\sigma^3$, right? So, this is the volume that is occupied by 2 molecules, right?

So, now you have to divide it by 2, then you will be getting the volume of 1 molecule that is occupying in the system, right? Then whatever that after dividing by 2, whatever the final number is that is $\frac{2}{3}\Pi\sigma^3$. If you multiply it by N_A that is Avogadro's number, then you will be getting the volume that 1 mole of molecules that are present in the gas occupying, okay? That much volume the molecules of one mole gas would be occupying and that is nothing but this $\frac{2}{3}\Pi\sigma^3$ N_A.

Now let us call it as b, b is nothing but the volume that 1 mole of molecule should be occupying, right? So that is b. So, Pv = RT expression that we have taken in terms of molar volume. So, that is the reason here b also we are taking in terms of moles, otherwise if you take a number of molecules kind of thing, then this b should be multiplied by the number of moles n. So, we are taking molar basis, so we are not having any b multiplied by n etc., those kinds of things are not there.

If you are taking ideal gas like PV = nRT form, then this b should be multiplied by n, but we are taking this form, P v (that is smaller volume) = RT, so here in this case if you use this form, so then that volume whatever that should be subtracted from the available volume is b, not the bn, okay? This is this small difference, okay? Now to correct for size, one can modify ideal gas model to include only unoccupied molar volume that is v - b, okay?

So, whatever now P = RT by v is there, now it should be P = $\frac{RT}{v-b}$ because now, we are making this correction for whatever unoccupied molar volume available for the ideal gas to occupy. So, then under such conditions since one molecule cannot occupy the space in which another molecule already sits, then we have P = $\frac{RT}{v-b}$. So, now, the 2 terms out of this Pv = RT, T is anyway constant for the constant temperature system we are doing, R is anyway constant, now out of this P and v we have to make an adjustment according to the case of the real gas.

For the real gas, the size of the molecules is not negligible. So, whatever the correction is there that we have already made in v. So, that is P * (v – b) = RT. Now, next what we do? Attractive forces, the intermolecular interactions are negligible in ideal gas, but in real gas they are existing. So, what are those interactions that we have to list out and then write in mathematical form and then make a correction to the pressure?

Because whatever these intermolecular interactions are there they are there because of the pressure okay or the pressure is the one that is most affecting the intermolecular potential that we already understood from previous lectures. Because as the pressure increases, molecules come closer and closer to each other and then intermolecular potential or intermolecular interactions will obviously increase with the increasing pressure that is the reason interaction terms whatever are there, they should be made a kind of correction to the pressure in this Pv = RT. So, one is done. So, now we will be doing the other one.

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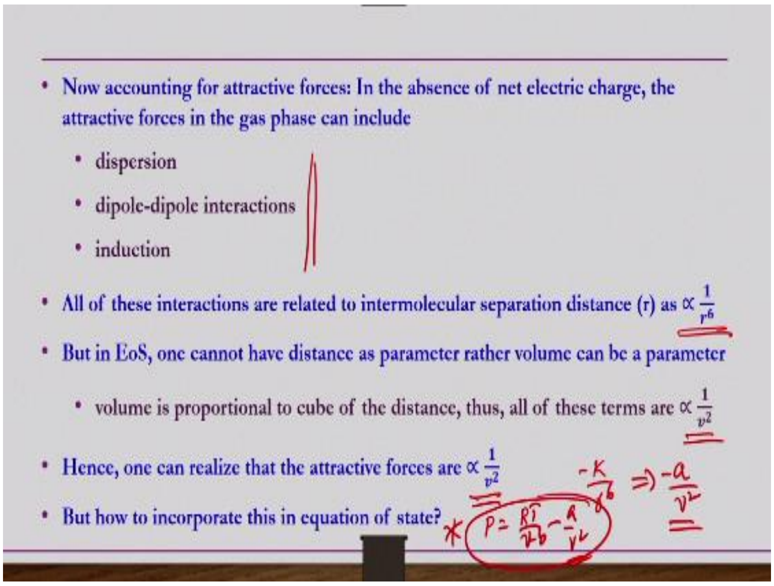

- Now accounting for attractive forces: In the absence of net electric charge, the attractive forces in the gas phase can include
  - dispersion
  - dipole-dipole interactions
  - induction
- All of these interactions are related to intermolecular separation distance (r) as $\propto \frac{1}{r^6}$
- But in EoS, one cannot have distance as parameter rather volume can be a parameter
  - volume is proportional to cube of the distance, thus, all of these terms are $\propto \frac{1}{v^2}$
- Hence, one can realize that the attractive forces are $\propto \frac{1}{v^2}$
- But how to incorporate this in equation of state?

$-\frac{K}{r^6} \Rightarrow -\frac{a}{v^2}$

$* \boxed{P = \frac{RT}{v-b} - \frac{a}{v^2}}$

Now accounting for attractive forces, in the absence of net electric charge, the attractive forces in the gas phase can include dispersion force, dipole-dipole interactions, induction force, etc. These things we have already seen. We have seen that these are the kind of attractive forces and we have already seen from the intermolecular potential lecture that all these interactions are related to the separation distance as inversely proportional to r^6.

That is whatever the intramolecular attraction forces because of the dispersion, dipole-dipole interactions and inductions are they that we have already seen they are inversely proportional to r^6, but in equations of state we cannot have a kind of separation distance as a kind of parameter, right? Because separation distance changes from molecule to molecule and system to system depending on the temperature, pressure, and all that. So, we cannot have that one as a kind of parameter, but what we can have we can have a kind of volume as a kind of parameter in the equation of state and then what we understand?

Volume is related to the distance as you know volume is proportional to distance power 3 or cube of the distance whatever is there. So, taking that consideration volume is proportional to the cube of the distance, then we can say that whatever the attractive forces are there, they are inversely proportional to the v^2, okay? So, hence one can realize that attractive forces are proportional to $\frac{1}{v^2}$ that means we can have some constant, right?

So, this is nothing but whatever $\frac{k}{r^6}$term is there in Van der Waal's attractive force or Sutherland potential that we are writing, some constant let us say $\frac{a}{v^2}$, this is what we are writing, okay? Now, these are attractive processes, so there are the - kind of things are there. So this is the force that has to be subtracted from the pressure that is there in the ideal gas, okay? So, that means whatever the ideal gas now after incorporating this size of the molecules, then we have this P = $\frac{RT}{v-b}$.

Now, there is attractive forces $\frac{a}{v^2}$, this $\frac{a}{v^2}$has to be subtracted from the pressure, so that this $-\frac{a}{v^2}$ is coming. So, this is nothing but Van der Waal's equations of state, so but how to incorporate this in equation of state?

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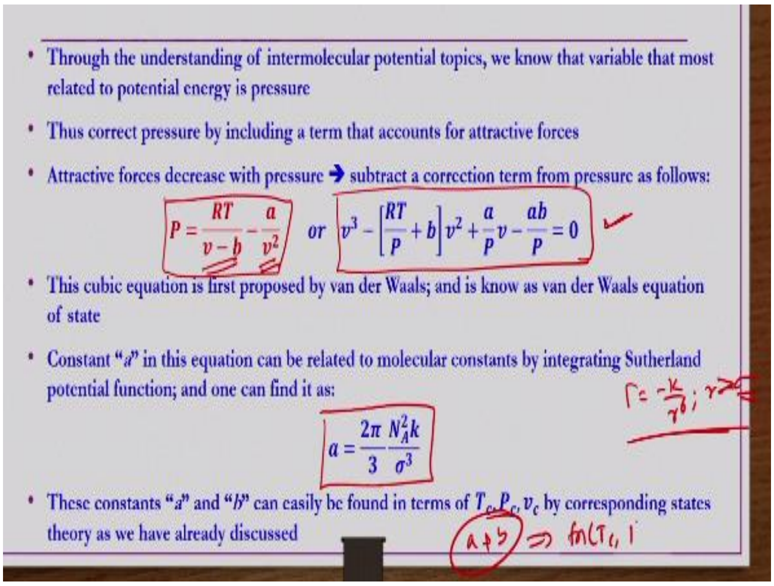

- Through the understanding of intermolecular potential topics, we know that variable that most related to potential energy is pressure
- Thus correct pressure by including a term that accounts for attractive forces
- Attractive forces decrease with pressure → subtract a correction term from pressure as follows:

$$\boxed{P = \frac{RT}{v-b} - \frac{a}{v^2}} \quad or \quad \boxed{v^3 - \left[\frac{RT}{P} + b\right]v^2 + \frac{a}{P}v - \frac{ab}{P} = 0} \checkmark$$

- This cubic equation is first proposed by van der Waals; and is know as van der Waals equation of state
- Constant "a" in this equation can be related to molecular constants by integrating Sutherland potential function; and one can find it as:

$\Gamma = -\frac{k}{r^6};\ r >$

$$\boxed{a = \frac{2\pi}{3}\frac{N_A^2 k}{\sigma^3}}$$

- These constants "a" and "b" can easily be found in terms of T_c, P_c, v_c by corresponding states theory as we have already discussed

$a+b \Rightarrow fn(T_c,$

So, that is through the understanding of intermolecular potential topics, we already realized that the variable that most related to the intermolecular potential is the pressure because as pressure increases, molecules come closer to each other, and then when they come closer to each other, then only the interactions would be significant, okay? So, that is the reason this thing, whatever this intermolecular potential or intermolecular attractive force is there that should be related to the pressure.

Thus correct pressure by including a term that account for the attractive forces and then attractive forces decrease with the pressure, why should we subtract this, whatever the attractive force is, $\frac{a}{v^2}$ or $\frac{k}{r^6}$? Why should we subtract them from the pressure? Because as the pressure increases these forces decreases, attractive forces decrease with the pressure, so that is the reason subtract a correction term for pressure as follows.

So, that is P $=\frac{RT}{v-b}$ is already there by incorporating the unoccupied volume or the only unoccupied molar volume in the ideal gas, and now we are subtracting the attractive forces from this pressure, right? After incorporating the repulsive forces or by incorporating the molar size of the molecules in the ideal gas behavior, then we have this P = $\frac{RT}{v-b}$, this $\frac{RT}{v-b}$is the pressure. Now, this pressure has to be subtracted with the correction that arising because of attractive forces that correction is nothing but proportional to $\frac{1}{v^2}$.

So, we are writing $\frac{a}{v^2}$, some constant a is coming here into the picture, okay? The same thing we can write in cubic form. If you expand this equation and then you write in cubic form, then we have $v^3 - \left[\frac{RT}{P} + b\right] v^2 + \frac{a}{P} v - \frac{ab}{P}$, this is cubic equation of state. This is called as a cubic equation of state because this is cubic in volume and this is known as Van der Waal’s equation of state. So, the constant a in this equation can be related to molecular constants by integrating Sutherland potential.

So, whatever the Sutherland potential that is there Γ = $-\frac{k}{r^6}$, for r > σ, σ is collision diameter. If you integrate this one at constant temperature, then you can find it out this one, you can obtain this constant as a $=\frac{2\pi}{3}\frac{N_A^2 k}{\sigma^3}$, k is nothing but Boltzmann constant, N_A is nothing but Avogadro's number. So, we are not going into those details anyway, right? So, further we also realized that this constant a and b can also be found by using critical temperature, critical pressure, or critical molar volume according to corresponding states theory, right?

Whatever the principle of corresponding state theory is there or whatever the principle of corresponding states that we have seen in previous lecture, right? So, then there we have seen the constant a and b of Van der Waal's equation of state found as a function of T_c, P_c, v_c, so, we can use them as well, okay? So, now we realize how these intermolecular potentials are coming into the picture in the equation of states of real gases. So, like that there are hundreds of equations of states are available, but we cannot go into details of all those equations.

So, we have started with this simple basic Van der Waal's equation of state because of one reason, it incorporates or describes the connection with intermolecular potential in much more simpler and straightforward manner as we have seen, right? Repulsive forces are connected straightforward and then attractive forces also straightforward and in simpler manner brought into the model.

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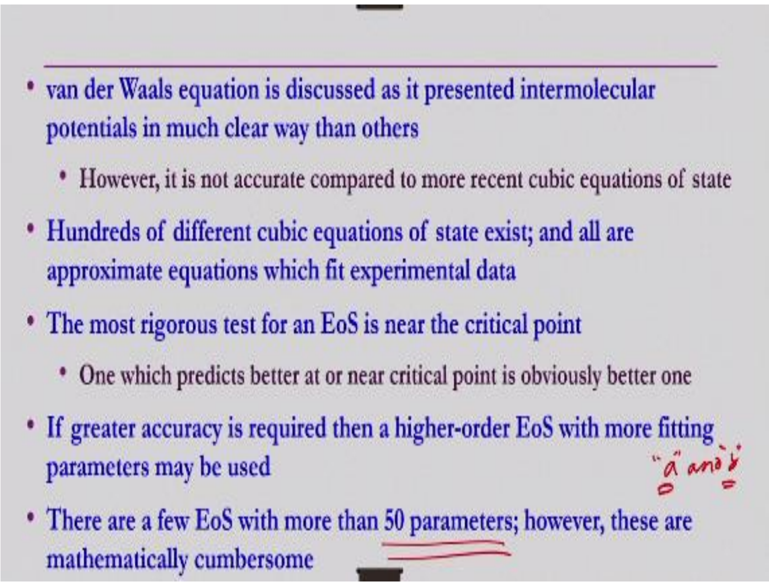

- van der Waals equation is discussed as it presented intermolecular potentials in much clear way than others
  - However, it is not accurate compared to more recent cubic equations of state
- Hundreds of different cubic equations of state exist; and all are approximate equations which fit experimental data
- The most rigorous test for an EoS is near the critical point
  - One which predicts better at or near critical point is obviously better one
- If greater accuracy is required then a higher-order EoS with more fitting parameters may be used

"a" and "b"

- There are a few EoS with more than 50 parameters; however, these are mathematically cumbersome

However, this Van der Waal's equation we have discussed only because the reason it presented intermolecular potential is in much clear way than the others, but it is not accurate compared to more recent cubic equations of state, but it is the simplest one to start with the models or start with the equations of state for real gases. Hundreds of different cubic equations of state exist and all are approximate equations which fit experimental data. The most rigorous test for an equation of state is near the critical point.

The reliability of a given equation of state depends on how accurate it is at critical point, right. If it is more accurate at critical point, then you can say that the equation of state is much more reliable than the others. One equation of state which predicts better at or near critical point is obviously the better one compared to the other ones which do not predict better at critical point. If greater accuracy is required, then a higher order equation of state with more fitting parameters may be used.

We have seen this Van der Waal's equation of state it is having only 2 fitting constants a and b, right? So, if you are expecting a kind of better equation of state or if you need a better equation of state obviously which is required at high pressures and then higher densities, etc., then under such condition higher-order equation of state with more fitting parameters are found to be reliable. There are a few equation of state with more than 50 parameters as well, but they become mathematically very cumbersome to use in the subsequent calculations to find out the thermodynamic properties.

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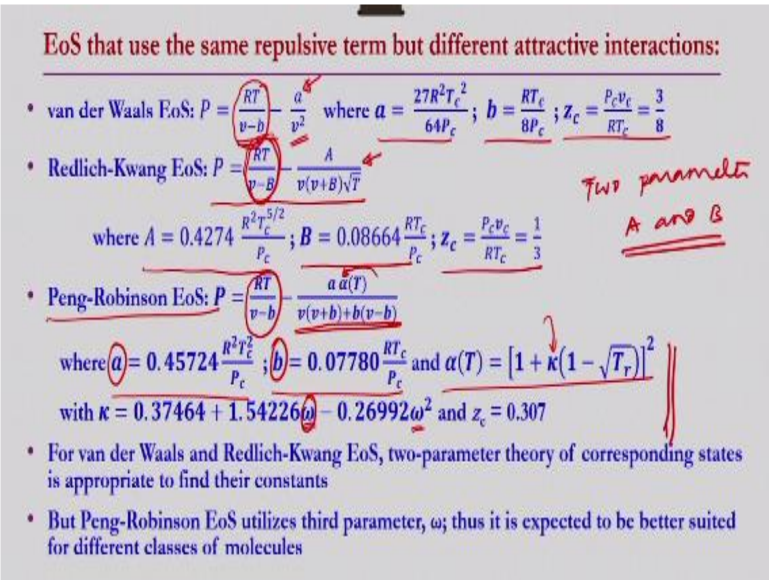

EoS that use the same repulsive term but different attractive interactions:

- van der Waals EoS: $P = \frac{RT}{v-b} - \frac{a}{v^2}$ where $a = \frac{27R^2T_c^2}{64P_c}$; $b = \frac{RT_c}{8P_c}$; $z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8}$
- Redlich-Kwang EoS: $P = \frac{RT}{v-B} - \frac{A}{v(v+B)\sqrt{T}}$

  where $A = 0.4274\frac{R^2T_c^{5/2}}{P_c}$; $B = 0.08664\frac{RT_c}{P_c}$; $z_c = \frac{P_c v_c}{RT_c} = \frac{1}{3}$
- Peng-Robinson EoS: $P = \frac{RT}{v-b} - \frac{a\,\alpha(T)}{v(v+b)+b(v-b)}$

  where $a = 0.45724\frac{R^2T_c^2}{P_c}$; $b = 0.07780\frac{RT_c}{P_c}$ and $\alpha(T) = \left[1+\kappa\left(1-\sqrt{T_r}\right)\right]^2$

  with $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$ and $z_c = 0.307$
- For van der Waals and Redlich-Kwang EoS, two-parameter theory of corresponding states is appropriate to find their constants
- But Peng-Robinson EoS utilizes third parameter, ω; thus it is expected to be better suited for different classes of molecules

Two parameters
A and B

So, now, we see equations of state that use the same repulsive term as Van der Waal's equation of state that we are seen, but different attractive force terms, right? Or different attractive interactions terms. So, the first one is the Van der Waal's equation of state that we have already seen. This constant as I mentioned from the corresponding states theory can be found as function of critical temperature, critical pressure, or critical molar volume and then compressibility at critical point is also we have seen in one of the previous lecture.

Like that, now you can see this is the, this part of the equation of state that is $\frac{\mathrm{RT}}{v-b}$ indicative of the repulsive forces, whereas $\frac{a}{v^2}$ is a kind of indicative of the attractive force. Now, we see a few equations of state which are having repulsive force terms same as $\frac{\mathrm{RT}}{v-b}$, but attractive force slightly different. So, that also we have seen previously in one of the lecture on corresponding state theory that is Redlich-Kwong equation of state. So, here we can see $\mathrm{P} = \frac{\mathrm{RT}}{v-b} - \frac{\mathrm{A}}{v(v+b)\sqrt{T}}$.

You can see the repulsive force term here exactly similar form as in the case of Van der Waal's equation of state, but here you can see the attractive forces are having different form, and then here again this constant we have already found through corresponding states theory that A is given this one, B is given this one, and then compressibility at critical point is $\frac{1}{3}$. This is also we have derived previously, right? So, this is also 2 parameter theory. This is also 2 parameter model, but much accurate compared to the Van der Waal's equations.

Much accuracy in the sense it is much better way reproduces or predicts the data at critical or near critical point compared to the Van der Waal's equations that is what it mean by it is much better than the other one. For a given system if you apply both Van der Waal's and Redlich-Kwong equation, so Redlich-Kwong equation is going to predicting the experimental data with much better accuracy at or near critical point compared to the Van der Waal's equation that is what it means by better one, okay?

How better way it predicts at critical point or near critical point is going to determine whether the given equation of state is reliable or not. If it is predicting the experimental results much better way at critical point or near critical point, then we can say that those equations of state are much more reliable compared to the other one. The other one is Peng-Robinson equation. Here also you can see the repulsive forces that is $\frac{\mathrm{RT}}{v-b}$ exactly same as Van der Waal's equation of state, but the attractive forces they are having quite different term that is $\frac{\mathrm{a}\,\alpha(\mathrm{T})}{v(v+b)+b(v-b)}$.

This is what we are having and then this α is function of temperature and then that α function is having third parameter as well. So, we can see we can obtain this a in terms of critical conditions like this and then b like this and then α T is nothing but this one, $\mathrm{T_r}$ is nothing but the reduced temperature that is $\frac{T}{T_c}$ and then this κ is nothing but it is a function of acentric factor.

Acentric factor we have seen omega, this omega is known as the acentric factor and then we have seen it gives a kind of prediction how non-spherical a molecule is.

Non-spherical in the sense, if the force field around the molecule is symmetric then we call that molecule as a kind of simple or spherical or spherically simple molecule or spherically symmetric molecule that is what we call. If the force field around the molecule is not symmetric, then we call them non-spherical or complex molecules. For that how much it is non-spherical that you can realize through this omega, this is also we have seen in one of the previous lecture, okay, acentric factor, right? So, now, we can see this Peng-Robinson equation of state is having 3 constants, one is the a, and another one is the b, another one is the omega.

So, obviously this is going to predict the experimental results much more accurately compared to the Redlich-Kwong or Van der Waal's equation, right? Because if you have more parameters, it is possible that it is going to predict the experimental data much more better way at critical or near critical point, okay? So, these are a few equations of state that we can discuss, but there are hundreds of equations of states are there, we cannot go into the details of all of those equations of state.

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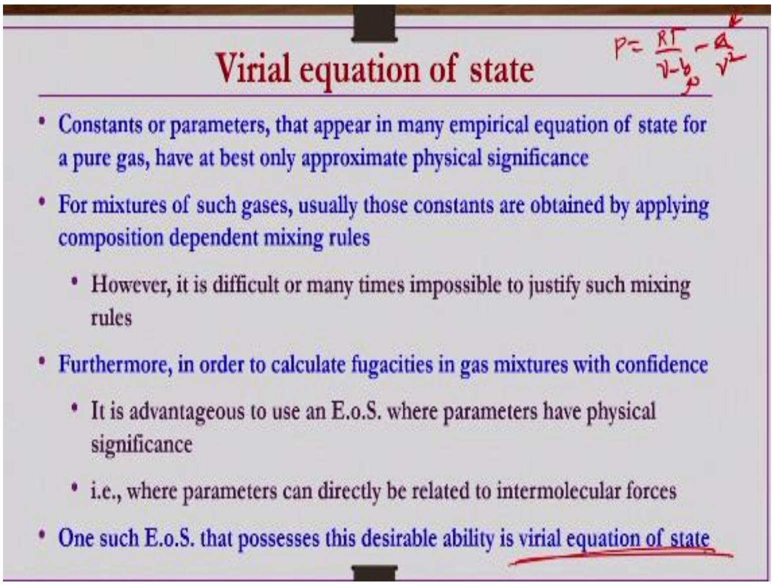

Virial equation of state

$P = \frac{RT}{v-b} - \frac{a}{v^2}$

- Constants or parameters, that appear in many empirical equation of state for a pure gas, have at best only approximate physical significance
- For mixtures of such gases, usually those constants are obtained by applying composition dependent mixing rules
  - However, it is difficult or many times impossible to justify such mixing rules
- Furthermore, in order to calculate fugacities in gas mixtures with confidence
  - It is advantageous to use an E.o.S. where parameters have physical significance
  - i.e., where parameters can directly be related to intermolecular forces
- One such E.o.S. that possesses this desirable ability is virial equation of state

Now, what we do? We take Virial equation of state, okay? As I mentioned, let us start with the same simple this $P = \frac{RT}{v-b} - \frac{a}{v^2}$, v is molar volume, P is the pressure, T is the temperature, b is the parameter relating to the size of the molecules of the gas system whatever we have taken, a represents some kind of proportionality constant of interaction forces or attractive intermolecular potentials, okay? So, this is what we have seen. Now, this a and b constant as I already mentioned can also be found through critical conditions that is P_c, T_c, etc.

Those things you can use and then find out, right? But this constant a and b are available for pure systems only, pure gasses only they are available, right? But if you have a mixtures or a mixture of gases, then these constants a and b are not available, right? And this a and b for mixtures one has to found from the mixing rules and then there are many mixing rules, which one to use for a given system is again a difficult task that is one thing.

So, there is no reliability of this a and b constant for the mixtures and then for even for the pure components also this a and b constants are hardly having any physical significance with the real system, okay? So, for here b may be relating to the size of the molecules, but not exactly the size of the molecules, related to the size of the molecules, okay? a is what? How it is related to the physical significance? Are they physically related to the system?

These are the kind of problems that are there for many equations of state, but this Virial equation of state is the one which takes into the consideration of the molecular interaction directly while taking this parameters are constants, right? So, that is indirectly whatever the constants or parameters that are present in the Virial equation of state, they are directly related to the intermolecular interactions or intermolecular potentials and whatever the mixtures, for the mixtures also they are directly related to the intermolecular potentials.

The constant or the parameters of Virial equations of state for mixtures also does not depend on the composition that is the advantage. So, both things have been taken care of by this Virial equation of state, but the major problem with this Virial equation of state it is valid, they gives a better approximation for the low to moderate pressure or densities only, it is not suitable for high density systems. So, those things we are going to see now.

So, constants or parameters that appear in many empirical equation of state for the pure gas have at best only approximate physical significance, approximate physical significance only not true physical significance. For mixtures of such gases, usually those constants are obtained by applying composition dependent mixing rules and it is difficult or many times impossible to justify such mixing rules, which means a mixing rule should be used as there exists many mixing rules, okay?

Further in order to calculate fugacity in gas mixtures with confidence, it is advantageous to have an equation of state where parameters have physical significance that is parameters can directly related to the intermolecular forces or intermolecular potential, okay? So, one such equation of state is nothing but Virial equation of state.

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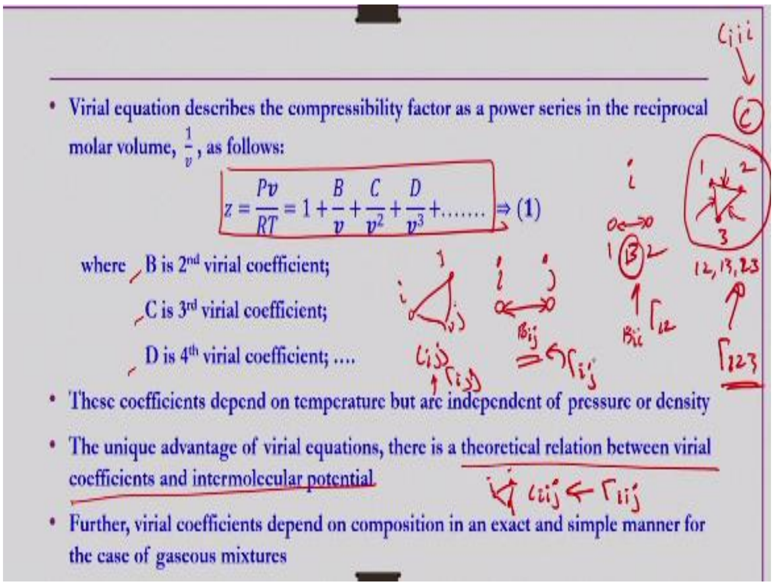

- Virial equation describes the compressibility factor as a power series in the reciprocal molar volume, $\frac{1}{v}$, as follows:

$$\boxed{z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \ldots\ldots} \Rightarrow (1)$$

where B is 2nd virial coefficient;

C is 3rd virial coefficient;

D is 4th virial coefficient; ….

- These coefficients depend on temperature but are independent of pressure or density
- The unique advantage of virial equations, there is a theoretical relation between virial coefficients and intermolecular potential
- Further, virial coefficients depend on composition in an exact and simple manner for the case of gaseous mixtures

So, Virial equation describes the compressibility factor as a power series in the reciprocal of molar volume that is $z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3}$ and so on so, series continues, where this coefficient B is known as the second Virial coefficient, coefficient C is known as the third Virial coefficient, and coefficient D is known as the fourth Virial coefficient and so on so. This coefficient B that is second Virial coefficient, it describes the deviation from ideal gas behavior because of the interaction between 2 molecules.

Whether it is a pure system or a kind of mixture because of the interaction between 2 molecules, whatever the intermolecular potential is there because of that one, there is a deviation from the ideal behavior. So, that deviation is counted by this second Virial coefficient. Likewise, there may be 3 molecules or interactions as well. Let us say if you have a pure system i, so, let us say molecule 1 and molecule 2, right? They may be interacting amongst themselves and there may be a kind of intermolecular interaction and that is causing a kind of deviation from ideal behavior bringing in the non-ideality, right?

For the same system or gases i, if you take 3 molecules 1, 2, 3, right? So, then this may be interacting like this 1, 2, 3 like this. This may be simplified as a 1 2, 1 3 and then 2 3 interactions that is interaction between these 2 molecules 1 2, 1 3 interaction between these 2 molecules 1 3 and interaction between 2 3. So, this interaction between these 3 molecules again can be simplified as a combination of interaction between 2 different molecules that is 1 2, 1 3, 2 3 and all that.

So, when the 3 molecules like this molecule 1, molecule 2, and molecule 3 are interacting and because of such interaction if there is a kind of deviation from the ideal behavior, so that deviation is brought into the system or model through this constant C, okay? B brings in the deviation from the ideal behavior due to the 2 molecule interactions, C brings in the deviation from the ideal behavior due to the 3 molecule interactions and so and so, analogously we can take the higher order coefficients, okay?

That is the reason this equation of state is found to be better compared to the other one because it directly incorporates the intermolecular interactions in the parameters that are existing in this model that is B, C, D, etc., right? These coefficients further most importantly depend only on temperature. We are going to see an expression, we are not going to derivations or all part of the physical chemistry, right? We will take the equations and discuss them, right?

So, we will be seeing soon these coefficients or functions of only temperature and most importantly they are independent of the pressure or density. Then further the unique advantage of Virial equation, there is a theoretical relation between Virial coefficient and intermolecular potential. So, when we are saying this, this B is because of the interaction between 2 molecules and the C is because of the interaction between the 3 molecules, so that means there is an intermolecular potential is there.

That means, these coefficients are directly related to let us say Γ_{12} here and then here in the case of C probably Γ_{123}, 3 molecular interactions. So, those things are directly related to the intermolecular potentials. So, those things are also we are going to see. This is another most important advantage of this Virial equation of state. Further, Virial coefficients depend on composition in an exact and simple manner in the case of gases mixture. Let us say we have gas i and j, right?

So, then 1 molecule of i and then 1 molecule of j are interacting, then there will be a kind of a second Virial coefficient, but that is known as B_{ij}, something like this. Here, we can say if it is i, this B is nothing but B_{ii} same interaction and this C we can call it as C_{ii} because same molecules. If you have different molecules, then like this it is possible, right? So, that means whatever the interactions, for the mixtures also these coefficients are directly related to the intermolecular potential in a similar way as they are valid for the pure gases.

The equations we are going to see now anyway, right? If you have you know same ij mixture, binary mixture but 2 molecules, 1 i molecule, 2 j molecules, then it is C_{ijj} or if you have a kind of 2 i molecules and 1 j molecule, then we can now C_{iij}. So like this, here also this is related to Γ_{iij}, we can find out what it is and substitute it in the equation to find this one and then here it is related to the Γ_{ijj} and then here it is related to the Γ_{ij}.

So, one can find out this intramolecular potential through the basic concept of intermolecular interaction that we have seen and then substitute here and then get this Virial coefficient. So, that means directly, even for the mixtures they are directly related to the intermolecular potential in much more similar way as they are related to the constants of pure system or the coefficients of pure system.

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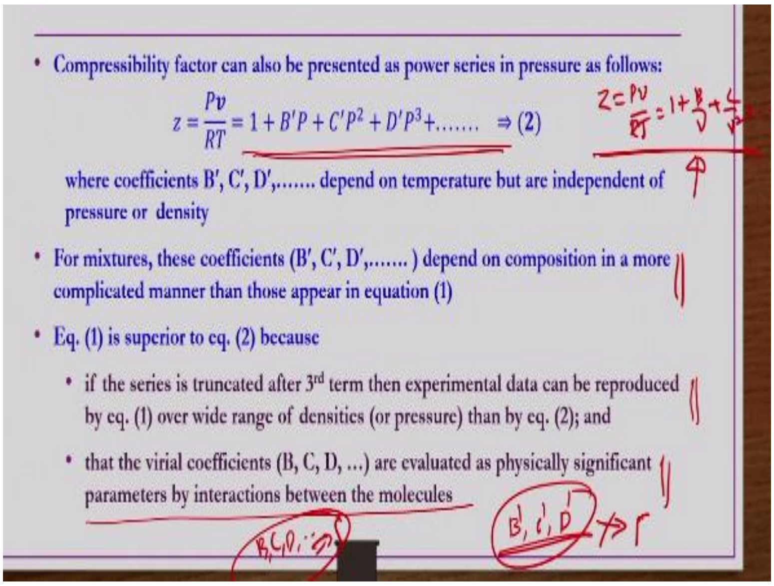

- Compressibility factor can also be presented as power series in pressure as follows:

$$z = \frac{Pv}{RT} = 1 + B'P + C'P^2 + D'P^3 + \ldots\ldots \Rightarrow (2)$$

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

where coefficients B′, C′, D′,……. depend on temperature but are independent of pressure or density
- For mixtures, these coefficients (B′, C′, D′,…….) depend on composition in a more complicated manner than those appear in equation (1)
- Eq. (1) is superior to eq. (2) because
  - if the series is truncated after 3rd term then experimental data can be reproduced by eq. (1) over wide range of densities (or pressure) than by eq. (2); and
  - that the virial coefficients (B, C, D, …) are evaluated as physically significant parameters by interactions between the molecules

B, C, D, …

$B', C', D' \nrightarrow \Gamma$

So, this Virial coefficient is also represented as a kind of compressibility as a function of a power series of pressure like $z = \frac{Pv}{RT} = 1 + B'P + C'P^2 + D'P^3$ and so on so and these coefficients B′, C′, D′ again they are dependent only on temperature but not dependent on the pressure or density that is one of the advantage, but however, this B′, C′, D′ for mixtures they depend on composition in a more complicated manner than those appear in equation 1.

Equation 1 is nothing but z = $\frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2}$ and then so and so, this is equation number 1. So, here in this case it is dependent on the composition in much simpler and straightforward manner, but here if you use this form of the equation, this B′, C′, D′ are dependent on the composition in more complicated manner compared to the case of equation 1. This is one of the disadvantage, not disadvantage or you wanted to make a decision which equation should you use, whether the equation 1 and equation 2.

One is the straightforward whether you want in a volume explicit form or pressure explicit form that should be the one basic criteria. If that is not very important, then you should see the other ones which way it is better or which way it is simpler for the mixture or which way it is directly related to the intermolecular potential for the mixtures also, those kind of things we hope to see. Further also, there are other advantages of equation 1 compared to the equation 2, remember both of them are same, right?

One is written in a power series of reciprocal of molar volume, another one is written in a power series of pressure, okay? However, if you write this in terms of power series of reciprocal of molar volume, it is advantageous compared to writing in power series of pressure because if the series you truncate after third term, then experimental data can be reproduced by equation number 1 over wide range of densities or pressure than equation number 2.

This is an experimental observation for many systems. Further, that Virial coefficients B, C, D are evaluated as physically significant parameters by interactions between the molecules, whereas B′, C′, D′ remember we are not calling them Virial coefficients right, we are calling the coefficient, they are temperature only and temperature but they are not directly related to this intermodal potential, whereas this B, C, D etc., they are directly related to the intermolecular potential Γ, okay?

This is another advantage why should you use this Virial equation of state in the form of equation number 1 that is z = $\frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3}$ and so on so.

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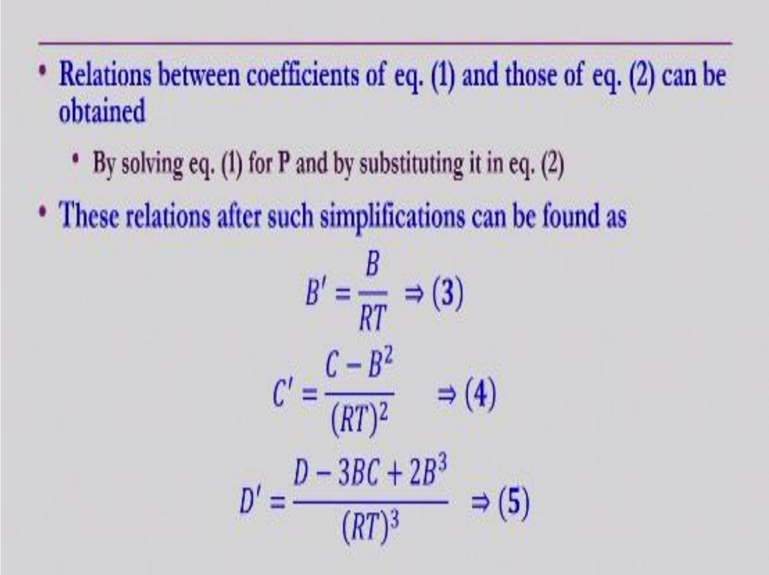

- Relations between coefficients of eq. (1) and those of eq. (2) can be obtained
    - By solving eq. (1) for P and by substituting it in eq. (2)
- These relations after such simplifications can be found as

$$B' = \frac{B}{RT} \Rightarrow (3)$$

$$C' = \frac{C - B^2}{(RT)^2} \Rightarrow (4)$$

$$D' = \frac{D - 3BC + 2B^3}{(RT)^3} \Rightarrow (5)$$

There is a relation between these coefficients of equation 1 and 2 obviously, right? So, equation number 1 you can solve for P by using z = $\frac{Pv}{RT}$ and then substituting that P in equation number 2 simply then you can get the relation between these coefficients that is B ′ = $\frac{B}{RT}$ and then C ′ =$\frac{C-B^2}{(RT)^2}$, D ′ = $\frac{D-3BC+2B^3}{(RT)^3}$.

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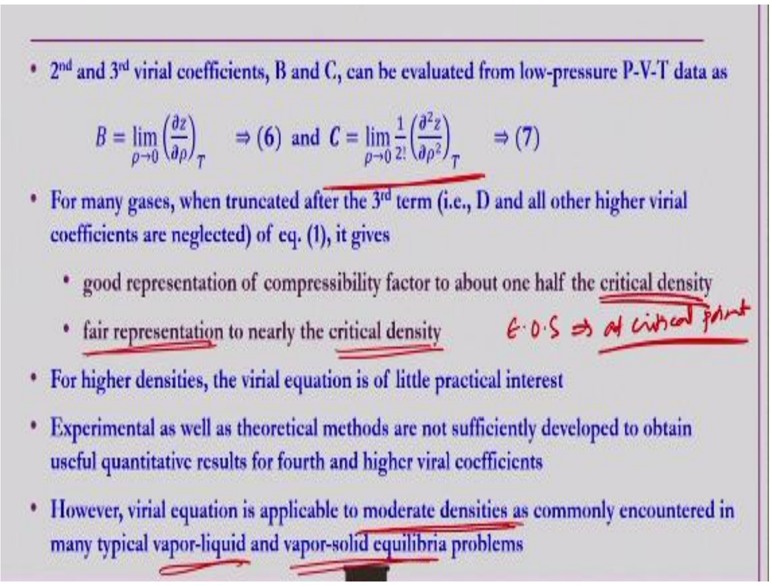

- 2nd and 3rd virial coefficients, B and C, can be evaluated from low-pressure P-V-T data as

$$B = \lim_{\rho \to 0} \left(\frac{\partial z}{\partial \rho}\right)_T \Rightarrow (6) \text{ and } C = \lim_{\rho \to 0} \frac{1}{2!} \left(\frac{\partial^2 z}{\partial \rho^2}\right)_T \Rightarrow (7)$$

- For many gases, when truncated after the 3rd term (i.e., D and all other higher virial coefficients are neglected) of eq. (1), it gives
    - good representation of compressibility factor to about one half the critical density
    - fair representation to nearly the critical density

E·O·S ⇒ at critical point

- For higher densities, the virial equation is of little practical interest
- Experimental as well as theoretical methods are not sufficiently developed to obtain useful quantitative results for fourth and higher viral coefficients
- However, virial equation is applicable to moderate densities as commonly encountered in many typical vapor-liquid and vapor-solid equilibria problems

Now, the second and third Virial coefficient that is B and C can be evaluated from low pressure volume data as you know B = $\lim_{\rho \to 0} \left(\frac{\partial z}{\partial \rho}\right)_T$ and C = $\lim_{\rho \to 0} \frac{1}{2!} \left(\frac{\partial^2 z}{\partial \rho^2}\right)_T$ because z = 1 + $\frac{B}{v}$ + $\frac{C}{v^2}$ and so on so. This we can write it as z = 1 + Bρ + C ρ^2 and so on so. Let us say if $\rho \to 0$, then higher terms can be neglected, then we can have, what we can do?

If you do $\left(\frac{\partial z}{\partial \rho}\right)_T$, we can get 0 + B when you take only this up to Bth term. So, that means, B = $\lim_{\rho \to 0}$ then $\left(\frac{\partial z}{\partial \rho}\right)_T$. Likewise, C also you can get it by $\lim_{\rho \to 0} \frac{1}{2!} \left(\frac{\partial^2 z}{\partial \rho^2}\right)_T$. This is how you can get them, right? For many gases when truncated after third term that is D term and higher Virial coefficient terms are neglected in equation number 1.

Then it gives good representation of compressibility factor to about one half the critical density that is the advantage and fair representation to nearly the critical density. As I mentioned, the equation of state whether it is reliable better one or not it depends on how it predicts the experimental data at critical point or near critical point and we can see at or near critical point, this Virial equation of state is giving fair representation of experimental data, these are experimental observation.

But one half of the critical density, it gives a very good representation of the compressibility factor and that are obtained from experimental data, okay? So, we can say that this particular equation of state, Virial equation of state is better when compared to the other one because it gives a fair representation of experimental compressibility factor even at critical densities, okay? For higher densities, the Virial equation is of little practical interest, because experimental as well as theoretical methods are not sufficiently developed to obtain useful quantitative results for fourth and higher Virial coefficients.

However, this Virial coefficient or Virial equation of state is applicable to moderate densities which are in general whatever the vapor-liquid or vapor-solid equilibrium problems that we have in real-life situations, this vapor phase usually it is at moderate densities. So, obviously this Virial equation can be made use of because Virial equation is applicable to moderate densities as commonly encountered in many typical vapor-liquid and/or vapor-solid equilibrium problems.

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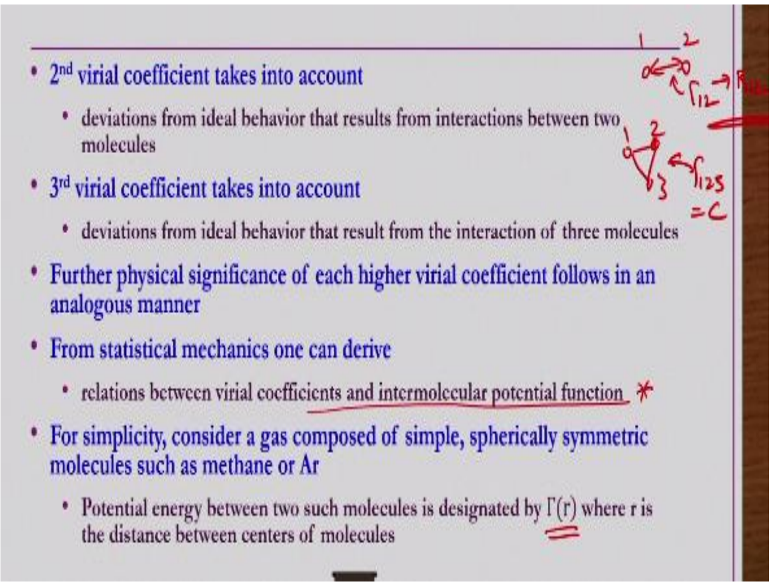

- 2^{nd} virial coefficient takes into account
  - deviations from ideal behavior that results from interactions between two molecules
- 3^{rd} virial coefficient takes into account
  - deviations from ideal behavior that result from the interaction of three molecules
- Further physical significance of each higher virial coefficient follows in an analogous manner
- From statistical mechanics one can derive
  - relations between virial coefficients and intermolecular potential function *
- For simplicity, consider a gas composed of simple, spherically symmetric molecules such as methane or Ar
  - Potential energy between two such molecules is designated by $\Gamma(r)$ where r is the distance between centers of molecules

Now, as I already mentioned, second Virial coefficient takes into account the deviation from ideal behavior that results from interaction between 2 molecules. If you have 2 molecules, molecule 1, 2, then if they are interacting whatever the interaction is there Γ_{12}, this is directly related to B_{12}, okay? If it is a same molecule, then we can have B_{11} like that or B_{22} like that. Third video coefficient takes into account deviation from ideal behavior that result from the interaction of 3 three molecules, let us say 1, 2, 3 molecules if you are having like this.

So, interaction between 3 molecules is causing some kind of non-ideality. So, whatever this Γ_{123} is there that can be related to this C that is third Virial coefficient directly. We are going to see those expressions, though we are not going to derive them. Similar way further physical significance of each higher Virial coefficient follows in an analogous manner. From statistical mechanics, one can derive relation between Virial coefficients and then intermolecular potential, right? We are going to use them, we are not going to derive them.

For simplicity, consider a gas composed of simples, spherically symmetric molecules such as methane or argon, then potential energy between 2 such molecules is designated as Γ (r), where r is the distance between the 2 molecules.

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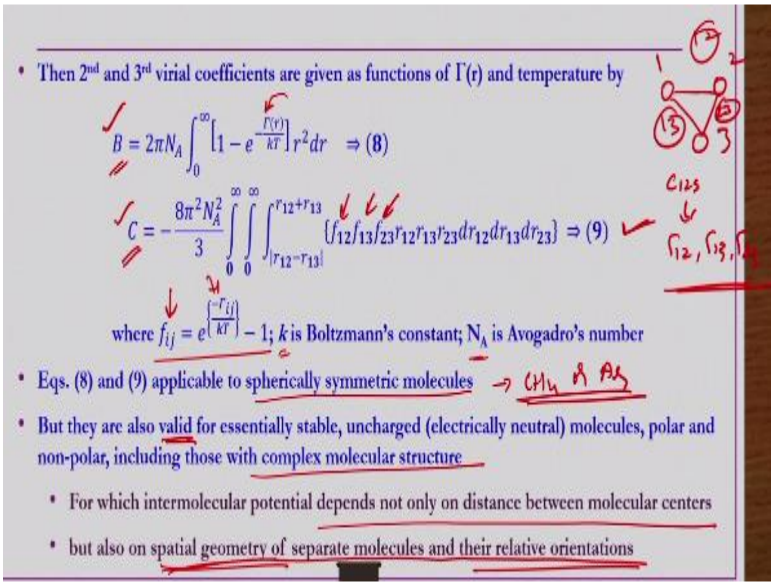

- Then 2nd and 3rd virial coefficients are given as functions of Γ(r) and temperature by

$$B = 2\pi N_A \int_0^\infty \left[1 - e^{-\frac{\Gamma(r)}{kT}}\right] r^2 dr \Rightarrow (8)$$

$$C = -\frac{8\pi^2 N_A^2}{3} \int_0^\infty \int_0^\infty \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} \{f_{12} f_{13} f_{23} r_{12} r_{13} r_{23} dr_{12} dr_{13} dr_{23}\} \Rightarrow (9)$$

where $f_{ij} = e^{\left\{\frac{-\Gamma_{ij}}{kT}\right\}} - 1$; k is Boltzmann's constant; N_A is Avogadro's number

- Eqs. (8) and (9) applicable to spherically symmetric molecules
- But they are also valid for essentially stable, uncharged (electrically neutral) molecules, polar and non-polar, including those with complex molecular structure
  - For which intermolecular potential depends not only on distance between molecular centers
  - but also on spatial geometry of separate molecules and their relative orientations

Then the second and third Virial coefficients are related to the intermolecular potential Γ (r) and temperature by these 2 equations B = $2\pi\ N_A\ \int_0^\infty \left[1 - e^{-\frac{\Gamma(r)}{kT}}\right] r^2 dr$. So, whatever the intermolecular potential that you have between 2 molecules that you know that if you substitute here, you can straight forward find out what is this B. So, now you can see this Virial coefficient is directly related to the intermolecular potential through statistical mechanics, right?

Similarly, third Virial efficiency C is given by this equation right where this f_{12}, f_{13}, etc., if you write generalized way f_{ij}, f_{ij} = $e^{-\frac{\Gamma_{ij}}{kT}} - 1$ where k is Boltzmann constant and N_A is the Avogadro's number. So, it is clear that this Virial coefficient or the parameters they are the constant that they are present in the Virial equation of state, they are directly related to these intermolecular potentials, right? So you can see. So, you find out this intermolecular potential accordingly for the 2 molecular interaction as well as 3 molecular interactions.

Then substitute in this equation and integrate them, then you can find out these constants, okay? So, these 3 molecules interactions also for the same component i molecule 1, 2, 3 are there. So, these 3 molecule interactions are directly not possible in general in reality, whatever the interactions are there, they are taken as a kind of combination of interaction between 1 2, interaction between 1 3 molecule and then interaction between 2 3 molecules. So, these binary interactions are again coming into the picture.

So, whatever these 3 molecule interaction is there, C_{123} it is again related to the Γ_{12}, Γ_{13}, and Γ_{23}, binary interactions anyway they are coming into the picture. So, this equation number 8 and 9 applicable to spherically symmetric molecules as mentioned, something like methane or argon something like that, right? The statistical mechanics point of view, they are developed for such simple molecules, but they are having these terms Γ intermolecular potential, right? But these intermolecular potentials if you have for complex molecules or polar molecules, etc., then also they can be used.

That is they are applicable for this B expression, C expression given by equation number 8 and 9, they are applicable spherically symmetrical molecule, but they are also valid for essentially stable uncharged neutral molecules, polar and non-polar molecules including those with complex molecular structure for which the intermolecular potential depends not only on distance between molecular centers or center between the molecules, but also on the spatial geometry of separate molecules and their relative orientations.

So, this information should also be included in this Γ. Once you incorporate this additional information about the molecules other than spherical molecules, then when you include those additional information for non-spherical molecules in Γ, so then these equations can also be valid for complex molecules, non-spherical molecules as well, though these are developed for a symmetrically spherical molecules.

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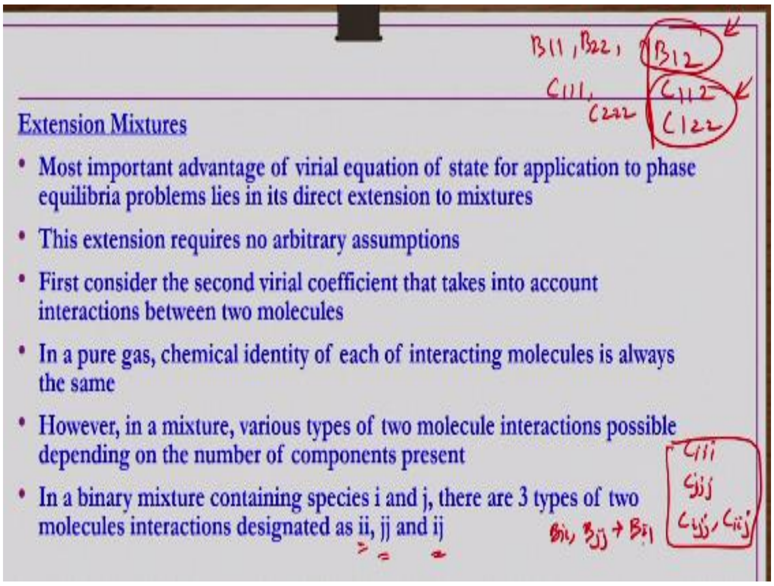

B_{11}, B_{22}, B_{12}

$C_{111}, C_{222}, C_{112}, C_{122}$

Extension Mixtures

- Most important advantage of virial equation of state for application to phase equilibria problems lies in its direct extension to mixtures
- This extension requires no arbitrary assumptions
- First consider the second virial coefficient that takes into account interactions between two molecules
- In a pure gas, chemical identity of each of interacting molecules is always the same
- However, in a mixture, various types of two molecule interactions possible depending on the number of components present
- In a binary mixture containing species i and j, there are 3 types of two molecules interactions designated as ii, jj and ij

$B_{ii}, B_{jj} + B_{ij}$

C_{iii}

C_{jjj}

C_{ijj}, C_{iij}

Now, coming to the extension to the mixture, most important advantage of Virial equation of state for application to phase equilibria problems lies in its direct extension to mixture because we have seen even this cross Virial coefficient whatever the B_{12}, C_{112}, C_{122} these are cross

Virial coefficient because they are of not of the same molecules, 1 from the molecule 1, 2 from the molecule 2, 1 from the gas 1, 2 from the gas 2 to let us say, gas 1 and gas 2 are mixed.

So, there is a binary mixture B_{11}, B_{22} are possible but there is also possible that this B_{12} as well, this B_{12} we call it as a kind of a cross Virial coefficient. Similarly if it is about 3 molecular interactions, not only this C_{111}, C_{222}, but also possible C_{112}, C_{122} these are cross Virial coefficients. Because of this reason, we can say that this is the advantage that they are directly extendable or applicable to the mixtures as well. These extensions require no arbitrary assumption, right?

So, if you are using some kind of mixing rules, then you have to make some kind of assumption, etc., but now here there are no such assumptions are involved because directly we are taking the interaction between different types of molecules in the case of mixture. First, consider the second Virial coefficient that takes into account the interaction between 2 molecules. In a pure gas, chemical identity of each of interacting molecules is always the same because it is a pure gas, all molecules are same molecule, so their interactions are going to be same.

However, in a mixture, various types of 2 molecule interactions are possible depending on the number of components present. Let us say if you have a binary mixture containing species i and j, there are 3 types of interactions are possible as ii, jj, ij interactions. I have taken here one two example kind of thing. If you do the same thing ij kind of thing, so then B_{ii}, B_{jj}, B_{ij} are possible. Similarly, 3 molecule interactions if you do, then C_{iii}, C_{jjj} are any way possible, in addition to them cross Virial coefficient C_{ijj} and then C_{iij} they are also possible for the 3 molecular interactions. If it is 2 molecular interactions, then B_{ii}, B_{jj} and B_{ij} are possible.

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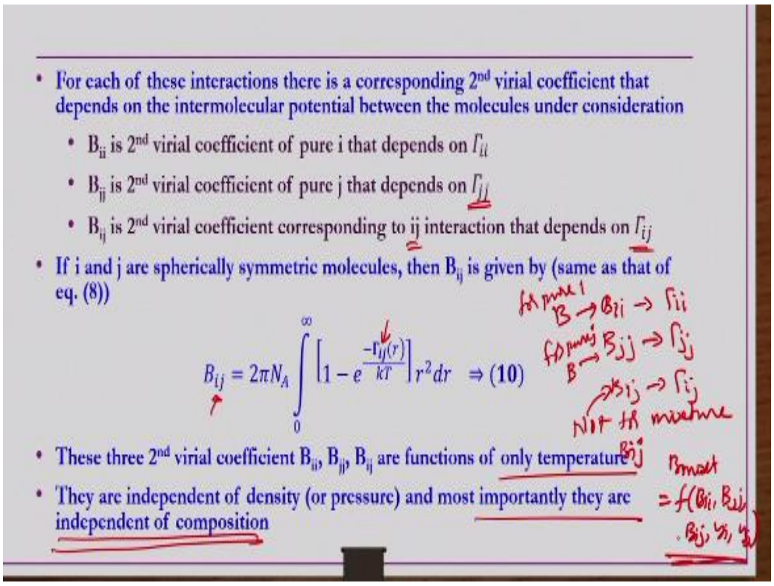

- For each of these interactions there is a corresponding 2nd virial coefficient that depends on the intermolecular potential between the molecules under consideration
  - B_{ii} is 2nd virial coefficient of pure i that depends on Γ_{ii}
  - B_{jj} is 2nd virial coefficient of pure j that depends on Γ_{jj}
  - B_{ij} is 2nd virial coefficient corresponding to ij interaction that depends on Γ_{ij}
- If i and j are spherically symmetric molecules, then B_{ij} is given by (same as that of eq. (8))

$$B_{ij} = 2\pi N_A \int_0^\infty \left[1 - e^{\frac{-\Gamma_{ij}(r)}{kT}}\right] r^2 dr \Rightarrow (10)$$

for pure i $B \rightarrow B_{ii} \rightarrow \Gamma_{ii}$

for pure j $B \rightarrow B_{jj} \rightarrow \Gamma_{jj}$

$B_{ij} \rightarrow \Gamma_{ij}$

Not for mixture

- These three 2nd virial coefficient B_{ii}, B_{jj}, B_{ij} are functions of only temperature
- They are independent of density (or pressure) and most importantly they are independent of composition

$B_{mixt} = f(B_{ii}, B_{jj}, B_{ij}, y_i, y_j)$

For each of these interaction, there is a corresponding second Virial coefficient that depends on the intermolecular potential between the molecules under consideration. B_{ii} is second Virial coefficient of pure i that depends on Γ_{ii} and B_{jj} is second Virial coefficient of pure j that depends on Γ_{jj} whereas B_{ij} is second Virial coefficient corresponding to ij interaction that depends on Γ_{ij}. This is also known as the cross Virial coefficient. If i and j are spherically symmetrical molecules, then B_{ij} is given by same as that of equation number 8.

Equation number 8 we have written exactly same without this ij subscript ij here and ij here, okay? If i = j, then it is B_{ii} or B_{jj}, if i is not equal to j, then B_{ij}, so corresponding. If you wanted to you get B_{ii}, then you have to get Γ_{ii} and then substitute here, if you wanted to get B_{jjj} you have to get Γ_{jj} and then substitute here, if you wanted to get B_{ij} then you have to find out Γ_{ij} and substitute here. Remember this B_{ii}, B_{jj} are nothing but B for pure i and then B_{jj} is nothing but B for pure j and this B_{ij} is nothing but it is B_{ij} but not for mixture, it is a cross Virial coefficient which is having B_{ij}, okay?

It is taking interactions for ij interactions, but if you wanted to know for the entire mixture, then we have to have a kind of different rules that we are going to see, and then all these 3 Virial coefficients whatever B_{ii}, B_{jj}, or B_{ij} are there, they are functions of temperature only and they are independent of pressure or density, right? And most importantly they are independent of composition. For what composition you need that is anyway composition will come into the picture, but composition is not making a role in kind of measurement of these parameters, okay?

So, B_{ij} is cross coefficient that is taking an interaction between 2 molecules of species i and then species j, okay? But for the B mixture, this B mixture if you wanted to find out, this is going to be a function of this B_{ii}, B_{jj}, and then B_{ij} + y_i y_j. How it is that we are going to see now.

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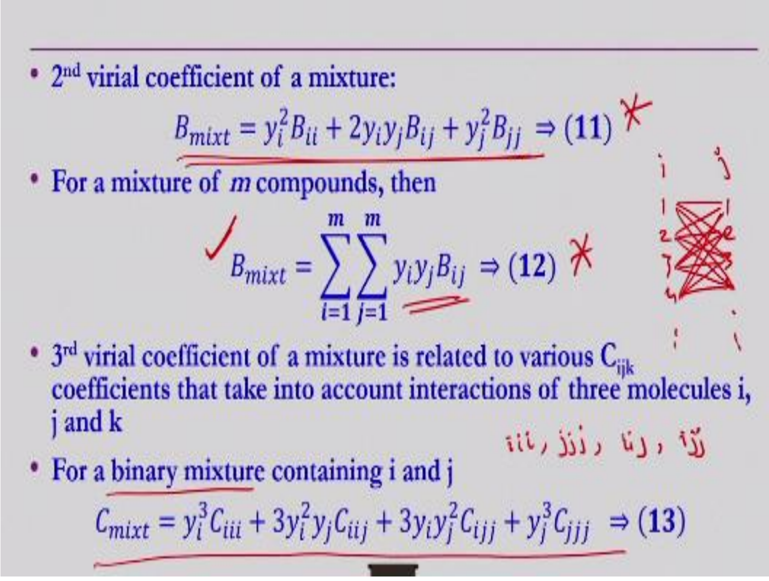

- 2^{nd} virial coefficient of a mixture:

$$B_{mixt} = y_i^2 B_{ii} + 2y_i y_j B_{ij} + y_j^2 B_{jj} \Rightarrow (11) \ast$$

- For a mixture of m compounds, then

$$✓ \; B_{mixt} = \sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j B_{ij} \Rightarrow (12) \ast$$

- 3^{rd} virial coefficient of a mixture is related to various C_{ijk} coefficients that take into account interactions of three molecules i, j and k

iii, jjj, iij, ijj

- For a binary mixture containing i and j

$$C_{mixt} = y_i^3 C_{iii} + 3y_i^2 y_j C_{iij} + 3y_i y_j^2 C_{ijj} + y_j^3 C_{jjj} \Rightarrow (13)$$

Second Virial coefficient of a mixture then you can write it if it is a binary mixture, then $B_{mix} = y_i^2 B_{ii} + 2y_i y_j B_{ij} + y_i^2 B_{jj}$. If you have m number of components, then $B_{mix} = \sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j B_{ij}$. Let us say ij if you take 1, 2, 3, 4 something like this, here also 1, 2, 3, 4 something like this with 1 whatever these interactions are there, all should be taken into the consideration, added together by this formula and then 2 of i then all these binary interactions whatever possible all should be taken into consideration.

Then, third molecule of i, whatever all these interactions are there all with 1, 2, 3, 4 and so on j should be taken into consideration. Like this with the fourth molecule of i, so, all these interactions with whatever this 1, 2, 3, 4 components of j series like this, they should be taken into the consideration. So, all that if you write in a kind of mix summation form, then we have this expression. If you only binary mixture, then we have this expression, okay? This is for the multi-component system, this is for the binary system.

Third Virial coefficient of a mixture is related to various C_{ijk} coefficient that take into account interactions of 3 molecules i, j, and k in a similar manner and then for the binary mixture containing i and j but 3 molecule interactions. Remember binary mixture, but 3 molecule interaction that is iii, jjj, iij, or ijj these kind of interactions, 3 molecule interactions but for the binary system. Then we can have C mixture is given by this expression.

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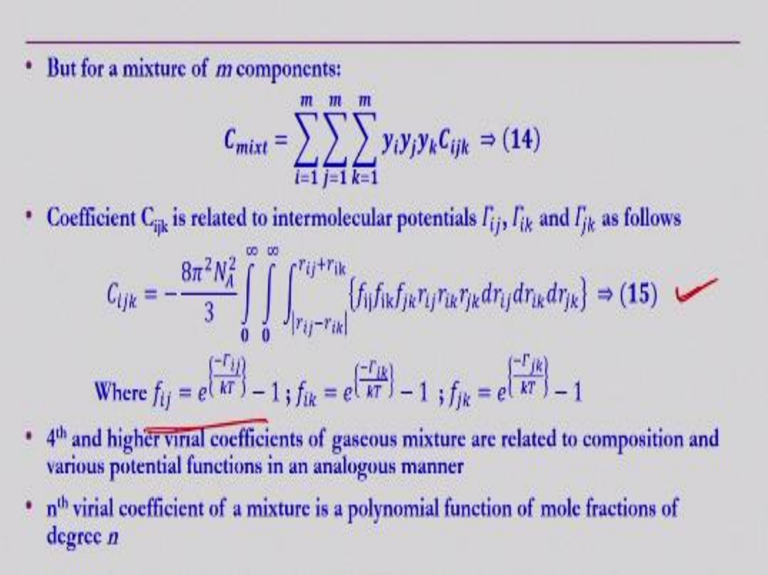

- But for a mixture of *m* components:

$$C_{mixt} = \sum_{i=1}^{m}\sum_{j=1}^{m}\sum_{k=1}^{m} y_i y_j y_k C_{ijk} \Rightarrow (14)$$

- Coefficient C_{ijk} is related to intermolecular potentials Γ_{ij}, Γ_{ik} and Γ_{jk} as follows

$$C_{ijk} = -\frac{8\pi^2 N_A^2}{3}\int_0^\infty\int_0^\infty\int_{|r_{ij}-r_{ik}|}^{r_{ij}+r_{ik}} \{f_{ij} f_{ik} f_{jk} r_{ij} r_{ik} r_{jk} dr_{ij} dr_{ik} dr_{jk}\} \Rightarrow (15)$$

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

- 4th and higher virial coefficients of gaseous mixture are related to composition and various potential functions in an analogous manner
- nth virial coefficient of a mixture is a polynomial function of mole fractions of degree *n*

Whereas, if you have m number of components, then $C_{mix} = \sum_{i=1}^{m}\sum_{j=1}^{m}\sum_{k=1}^{m}\sum_{j=1}^{m} y_i y_j y_k B_{ijk}$, this is for the multi-component system having m number of components. Coefficient C_{ijk} is related to the intermolecular potential Γ_{ij}, Γ_{ik}, and Γ_{jk} exactly the same way as we have seen previously that the C_{ijk} is given by this expression and then $f_{ij} = e^{-\frac{\Gamma_{ij}}{kT}} - 1$ whereas $f_{ik} = e^{-\frac{\Gamma_{ik}}{kT}} - 1$ and $f_{jk} = e^{-\frac{\Gamma_{ik}}{kT}} - 1$, k is nothing but Boltzmann constant.

This distance between 1i and 1j molecules is r_{ij}, r_{ik} is nothing but distance between 1i molecule and 1k molecule like this, okay? r_{jk} is nothing but distance between 1j molecule and 1k molecule like this. So, fourth and higher Virial coefficients of gaseous mixtures are related to composition and various potential functions in an analogous manner as we have done for the 2 and 3 molecular interactions just now, but they are not required. Three molecule interaction that equation we got a cubic equation for the binary system like that, n^{th} Virial coefficient of a mixture is a polynomial function of mole fraction of degree n.

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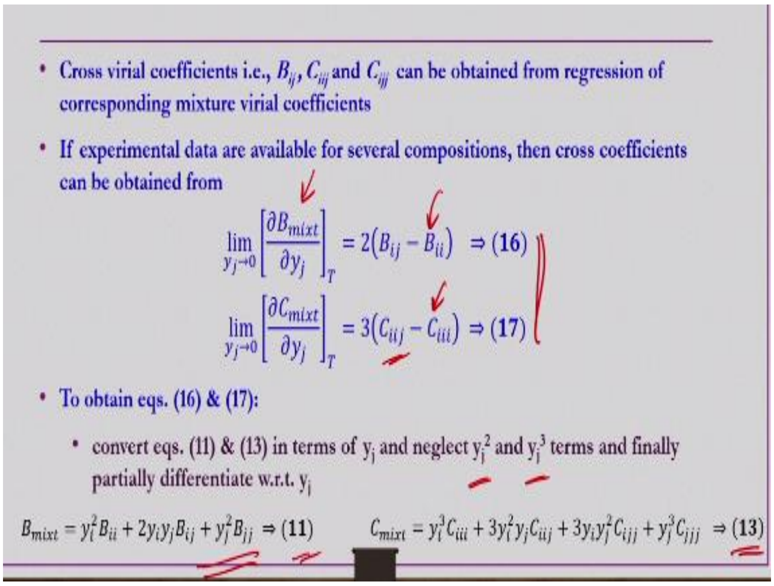

- Cross virial coefficients i.e., B_{ij}, C_{iij} and C_{ijj} can be obtained from regression of corresponding mixture virial coefficients
- If experimental data are available for several compositions, then cross coefficients can be obtained from

$$\lim_{y_j\to 0}\left[\frac{\partial B_{mixt}}{\partial y_j}\right]_T = 2\left(B_{ij} - B_{ii}\right) \Rightarrow (16)$$

$$\lim_{y_j\to 0}\left[\frac{\partial C_{mixt}}{\partial y_j}\right]_T = 3\left(C_{iij} - C_{iii}\right) \Rightarrow (17)$$

- To obtain eqs. (16) & (17):
  - convert eqs. (11) & (13) in terms of y_j and neglect y_j^2 and y_j^3 terms and finally partially differentiate w.r.t. y_j

$B_{mixt} = y_i^2 B_{ii} + 2y_i y_j B_{ij} + y_j^2 B_{jj} \Rightarrow (11)$ $C_{mixt} = y_i^3 C_{iii} + 3y_i^2 y_j C_{iij} + 3y_i y_j^2 C_{ijj} + y_j^3 C_{jjj} \Rightarrow (13)$

Then finally cross Virial coefficient that is B_{ij}, C_{iij}, and C_{ijj} can be obtained from regression of corresponding mixture and Virial coefficients. Let us say, if experimental data is available for several composition, then cross coefficients can be obtained from using this expression $\lim_{y_j\to 0}\left[\frac{\partial B_{mixt}}{\partial y_j}\right]_T$ = 2 (B_{ij} - B_{ii}), B_{ii} is known, so B_{ij} you can know if you know what is $\left[\frac{\partial B_{mixt}}{\partial y_j}\right]_T$. Similarly, $\lim_{y_j\to 0}\left[\frac{\partial C_{mixt}}{\partial y_j}\right]_T$ = 3(C_{iij} - C_{iii}), C_{iii} is known for the pure system.

So, then this cross Virial coefficient C_{iij} can be known. Similarly, C_{ijj} can also be known. How do you get these equations, it is simple and straightforward. Whatever this equation number 11 and 13 that is for the B mixture and then C mixture for a kind of binary system that we have written. So, in these equations what you do, you write in y_j terms by taking $y_i = 1 - y_j$ because it is a binary mixture. So, this equation would be in y_j forms.

Then what you do? You neglect y_j square and then y_j cube terms and then higher terms if at all existing, then you apply limit y_j tends to 0, then you can get this equation straightforward, okay? These are the few basics of Virial equation of state. We have seen Virial equation of state and then how this Virial coefficient or the parameters associated with the Virial equation of state are related to the intermolecular potentials, etc., we have seen.

Virial equation of state in 2 different forms we have seen and then we have seen the relation between those parameters that is B, B ′, C, C ′, D, D ′, etc., those things we have seen, right? We have also seen how to find out this Virial coefficient from the intermolecular potential or the expression that we have seen. In the next class, what we do? We take a few intermolecular potentials and for those intramolecular potentials, we are going to find out this Virial coefficients, B, C, etc.

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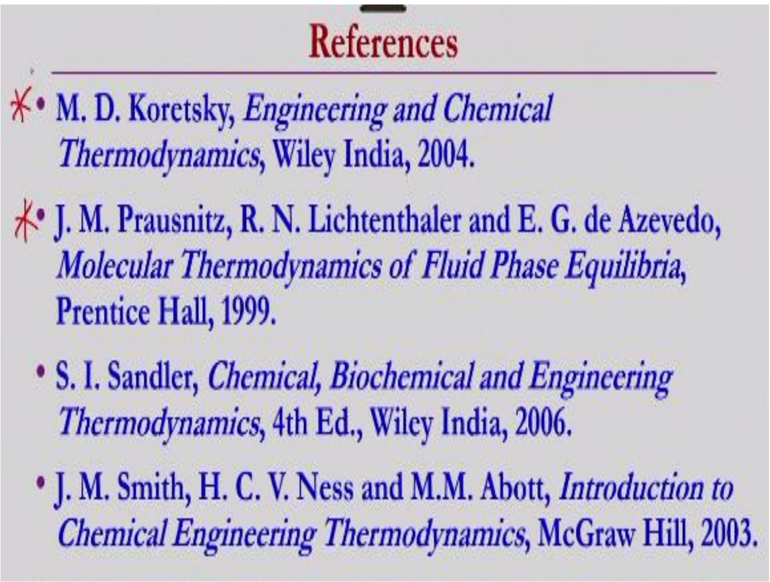

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The references for this lecture are given here. Most of the details presented in this lecture are taken from these 2 books, Prausnitz et al and Koretsky.

Thank you.