Advanced Thermodynamics
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Lecture – 9
Molecular Theory of Corresponding States

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is Molecular Theory of Corresponding States. What is the principle of corresponding state is that defining a kind of potential function, which is suitable for all or which is applicable for all gases of a particular group or a particular class that is what means by principle of corresponding states. Then how to do this one? Those kind of things we are going to see in detail.

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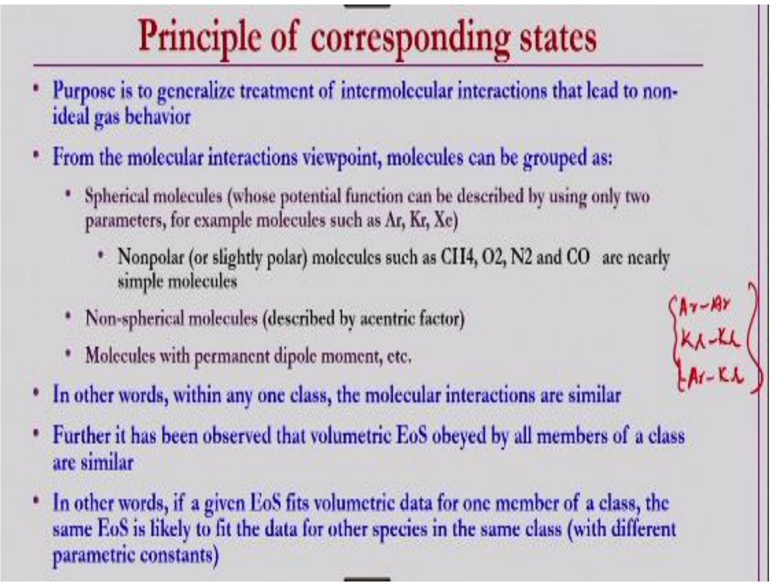

Principle of corresponding states

- Purpose is to generalize treatment of intermolecular interactions that lead to non-ideal gas behavior
- From the molecular interactions viewpoint, molecules can be grouped as:
  - Spherical molecules (whose potential function can be described by using only two parameters, for example molecules such as Ar, Kr, Xe)
    - Nonpolar (or slightly polar) molecules such as CH4, O2, N2 and CO are nearly simple molecules
  - Non-spherical molecules (described by acentric factor)
  - Molecules with permanent dipole moment, etc.
- In other words, within any one class, the molecular interactions are similar
- Further it has been observed that volumetric EoS obeyed by all members of a class are similar
- In other words, if a given EoS fits volumetric data for one member of a class, the same EoS is likely to fit the data for other species in the same class (with different parametric constants)

Ar-Ar
Kr-Kr
Ar-Kr

So, the principle of corresponding states purpose is to generalize treatment of intermolecular interaction that lead to non-ideal gas behavior. Let us say each non-ideal gas behavior whatever is there that is being represented by some kind of intermolecular potential that intermolecular potential may be including different types of forces, both repulsive and then attractive forces. So, can we have a kind of a generalization of this intermolecular potential for one particular group of non-ideal gases, which are having similar nature, right?

So, that is the purpose of this principle of corresponding states and then that is what we are going to do, okay? But before going into these principles of corresponding states, it is important to understand from molecular interactions viewpoint, how different are these intermolecular potentials, right? So, in order to understand those things, we must have a kind of classification of molecules from the molecular interactions viewpoint, so then we can have something like spherical molecules.

For a particular molecule if the intermolecular potential can be described by just 2 constants or 2 parameters, then we can say those molecules are more or less spherical molecules. For example, molecules such as Argon, Krypton, Xenon these are considered as spherical molecules because their intermolecular potential can be described by using only 2 parameters, okay? But there are a few molecules which are nearly spherical, they may not be completely spherical, they may be nearly spherical.

Something like you know some non-polar or slightly polar molecules such as methane, oxygen they are nearly simple molecules because they can be represented by these 2 parameter model, but there may be a kind of some deviation, discrepancies as well. Then we have non-spherical molecules which described by acentric factor, right? So, let us say if the intermolecular potential of a particular gas cannot be described by 2 parameter models in general, so then we can bring in another kind of parameter, third parameter that we can call it as a kind of acentric factor.

This acentric factor if it is 0, then we can call those molecules are a kind of spherical molecules or simple molecules or spherically symmetric molecules, okay? So, this principle of corresponding states is going to be different for simple spherical molecules and it is going to be different for non-spherical molecules, right? So, for both of them we are having different kind of approaches, those we are going to see anyway. Then also we can have molecules with permanent dipole moment, etc., okay?

So, now in other words, within one class, the molecular interactions are similar. Let us say if you take Argon, Krypton, Xenon these kind of molecules if you take, they are spherical molecules. So, whatever the interactions that they are there in Argon they may be quite similar with the interactions that are present in the Krypton molecules. So, how 2 Argon molecules are interacting maybe more or less similar to how 2 Krypton molecules Kr-Kr interactions are there, so that is possible, right?

That is what mean by classifying these molecules from the molecular interaction point of view. If the molecules are spherical, let us say Argon, so then whatever Ar-Ar interactions like interactions are there, so they may be similar to Krypton-Krypton that is Kr-Kr interactions. So, in such case, it is also possible that Ar and Kr interactions may also be similar. So, then we can group them together, we can put them in some one together group kind of thing, right? So, that is within one class like this class the molecular interactions are similar.

If you have a different types of non-spherical molecules, right? And then that non-sphericity is close to each other, then those molecules can also be kept as a kind of one particular group, okay? So, further it has been observed that volumetric equation of state obeyed by all members of a class are similar. So, if the intermolecular potentials are quite similar to each other, then it is possible that their equations of state also quite similar to each other, probably there may be slight difference in this constant.

Whatever the constant A and B constant that are present in equations of state that is possible, but they would be similar if their molecules are of similar nature. So, if the molecules of similar nature, so then molecular interactions would also be in similar nature. So, then their intermolecular potential functions would also be of similar nature, then obviously their equations of states are also going to be of a similar nature.

In other words, if a given equation of state fits volumetric data for one member of a class, the same equation of state is likely to fit the data for other species in the same class, probably with different parametric constants. Let us say Argon it is there, you fit the volumetric data PVT information of this Argon information or a wide range of PVT conditions, then you have the data and then you try to correlate that experimental data. Let us assume that for that Argon gas you are able to fit well one particular equation of state, let us call that equation of state x.

So, then it is also possible that the same equation of state x is going to be suitable for Krypton and Xenon as well because these molecules are similar and their interactions are also similar to Argon, so that is what it is possible, but only thing that in that equation of state x whatever it is suitable for these molecules, the constants may be slightly different from other, okay?

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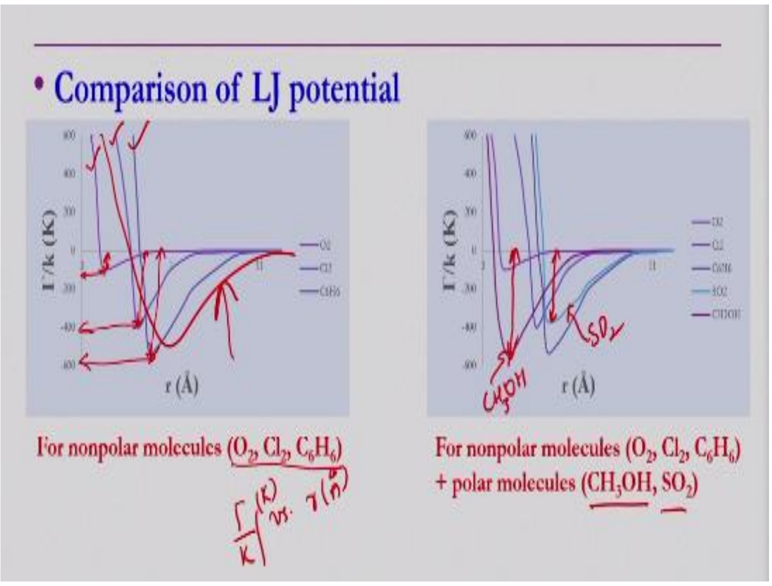

- Comparison of LJ potential

For nonpolar molecules (O_2, Cl_2, C_6H_6)

$\frac{\Gamma}{k}(K)$ vs. $r(\mathring{A})$

For nonpolar molecules (O_2, Cl_2, C_6H_6)
+ polar molecules (CH_3OH, SO_2)

How can we put like pictorially this similarity? So let us say you take Lennard-Jones potential of a few gases of few component and then compare it. So we will take a few nonpolar molecules like O_2, Cl_2, C_6H_6. If you observe, their intermolecular potential divided way this k, Boltzmann constant versus r the intermolecular separation distance. Then what will happen? This $\frac{\Gamma}{k}$ is going to have a kind of temperature unit and then r is let us take in Å.

Then if you take that experimental data, their PVT experimental data and then if you measure their intermolecular potential with respect to different separation distance and then plot them in this form $\frac{\Gamma}{k}$ versus r, then you can see for oxygen we have this plot, okay? For chlorine we have this plot, and then for the benzene C_6H_6, we are having this plot. So, you can see they are quite similar to each other, the only difference that you see here this, whatever the maximum attraction force are - ε, whatever the minimum potential function is there that is different.

Here it is something around 100 and the ratio $\frac{\Gamma}{k}$ ratio is for this case O_2 case is roughly 100, for the other case for Cl_2, it is roughly 450 to 500 and then for the case of C_6H_6, it is roughly 600 and their r minimum distance also different. So, here in this case it is small in the case of oxygen, chlorine it is moderate, and then for benzene it is still larger compare to chlorine and oxygen. What does it mean?

The C_6H_6 is having attractive forces for a longer range compared to the Cl_2 and O_2 that is what we can say by this, right? But they are quite similar only difference is this, the parameters are different, okay? So, we can have a kind of generalized one, something having generalized one like this and then this may be having some kind of parameters which are functions of reduced temperature, reduced pressure, reduced molar volume, etc. that is what we are going to develop now.

Not only for non-polar molecules if you take few polar molecules also in addition to these things like if you take a methanol and SO_2 sulfur dioxide, then you can see this methanol is this one and then this blue one is SO_2 in addition to the other three, that is O_2, Cl_2, C_6H_6, even they are also having similar nature, quite similar nature. Only thing that you know according to intermolecular potential function, these minimum energies whatever are there, they are different compared to the other and then r minimum distances are different.

So, having seen their qualitatively graphically quite similar, they are looking quite similar, so can we have a kind of generalized graph which is having similar nature which is like this but having some kind of adjustable parameters and those adjustable parameters are constant for any fluid, but one can obtain those constant A and B with certain kind of modifications that is what the purpose of this principle of corresponding states that is what we are going to do now, okay?

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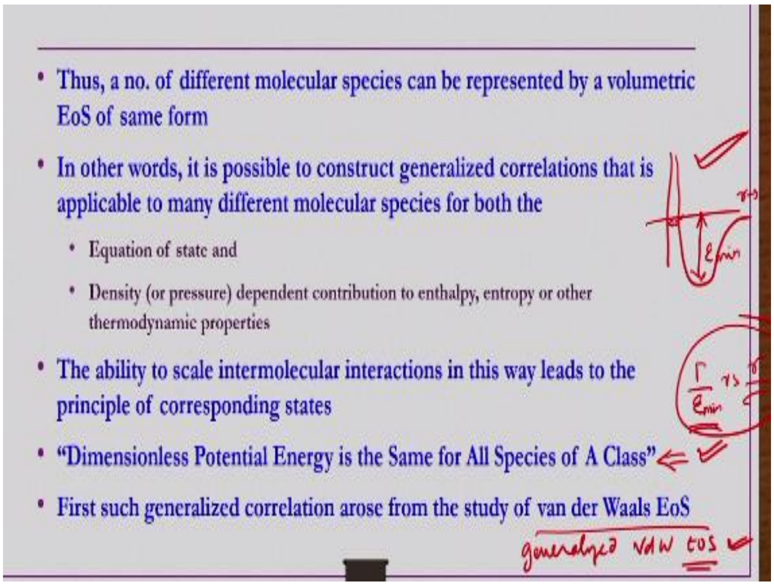

- Thus, a no. of different molecular species can be represented by a volumetric EoS of same form
- In other words, it is possible to construct generalized correlations that is applicable to many different molecular species for both the
  - Equation of state and
  - Density (or pressure) dependent contribution to enthalpy, entropy or other thermodynamic properties
- The ability to scale intermolecular interactions in this way leads to the principle of corresponding states
- "Dimensionless Potential Energy is the Same for All Species of A Class"
- First such generalized correlation arose from the study of van der Waals EoS

generalized VdW EoS

So, thus a number of different molecular species can be represented by a volumetric equation of state of same form as we have seen. In other words, it is possible to construct the generalized correlations that is applicable to many different molecular species for both the equation of state and then density or pressure dependent contribution to enthalpy, entropy or thermodynamic properties. Then the ability to scale intermolecular interactions in this way leads to the principle of corresponding states according to which what we can find out?

We can find out dimensionless potential energy is the same for all species of a class, okay? So that is what we are going to derive. So, because we have seen this Γ by some function, let us say if I take another energy function okay rather than Boltzmann constant, then Γ by this intermolecular potential energy and this is let say ε minimum, whatever the minimum potential energy that you get at the bottom, let us say this is nothing but ε minimum.

So, if this intermolecular potential if you non-dimensionalize with this ε minimum and then whatever this radial distance r is there that if you non-dimensionalize with respect to σ, σ is let us say σ is nothing but this distance where intermolecular potential is becoming 0, after overcoming the repulsive forces and then before starting the attractive forces, this particular point when it is Γ is becoming 0, okay? So, any component you take and their intermolecular potential versus r you plot them.

Then you find out whatever ε minimum and then that σ, then you re-plot them by non-dimensionalizing this $\frac{\Gamma}{\epsilon_{min}}$ and then separation distance r by sigma, then you are going to get the same function for all the components which are obeying this particular equation of state, okay? That is what we call it as a kind of universal function because now it is valid for all of them. Then first such generalized correlation arose from the study of Van der Waal’s equation of state.

So what we do? We take the same Van der Waal’s equation of state and then try to develop what is the generalized Van der Waal’s equations of state, okay? So, since we are trying to start with this one only because this is the first work where principles of corresponding states have been developed, but it is not only specifically valid to the Van der Waal’s equation of state, but it is valid for any equation of state.

However, any equation of state with only 2 constants it is easy to get, but if you have more than 2 parameters as constant, then there is a kind of correction is required in terms of acentric factor, those things we will see in the later course, but let us start with Van der Waal’s equation of state.

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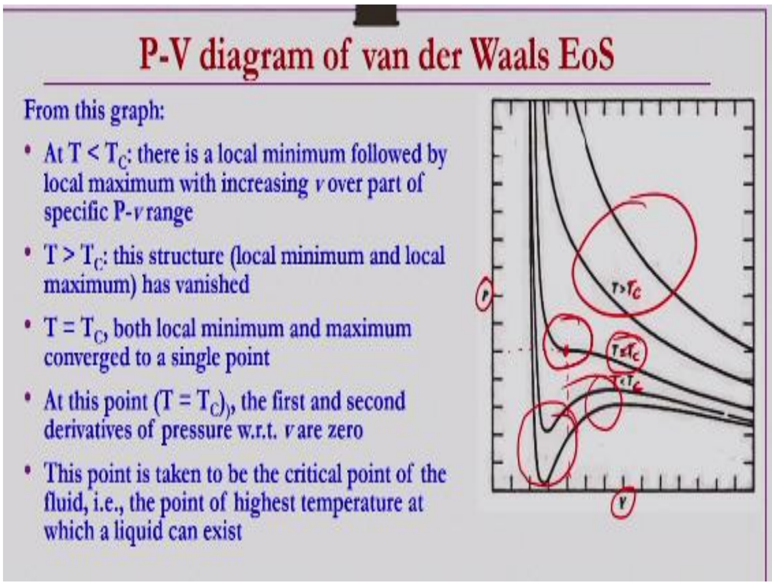

P-V diagram of van der Waals EoS

From this graph:

- At $T < T_C$: there is a local minimum followed by local maximum with increasing v over part of specific P-v range
- $T > T_C$: this structure (local minimum and local maximum) has vanished
- $T = T_C$, both local minimum and maximum converged to a single point
- At this point ($T = T_C$), the first and second derivatives of pressure w.r.t. v are zero
- This point is taken to be the critical point of the fluid, i.e., the point of highest temperature at which a liquid can exist

So, let us say P-V diagram of Van der Waal's equation if you plot, let us say if you draw P versus volume curve for any component that is obeying Van der Waal's equation at different temperature, then you can have curves like this. If the temperature is less than the critical temperature of that particular species, then what we are going to have? We are going to have the curve like this where we can have a kind of a local minimum followed by a local maximum, right?

The P versus V diagram if you plot for any Van der Waal's gas at different temperatures, then we can get this such kind of curve and if the temperature is less than the critical temperature of that particular gas, then we can have this PV curve like this where we can have a local minimum followed by a local maximum, but at the temperature T > the critical temperature T_c, then if you plot this P versus V diagram, then we can have curves like this, where you do not have any local minimum or local maximum kind of things, smoothly it is falling down.

The pressure is mostly decreasing as volume is increasing, right? So, then what is about the case where the temperature is equals to critical temperature right? If you have a kind of condition where operating temperature is equals to the critical temperature and then you measure pressure versus volume information and then that if you plot, you will have a curve like this, right? Where the local minimum and local maximum are merging to the same point and then corresponding temperature is known as the critical temperature.

Then corresponding volume is known as the critical volume and then corresponding pressure is known as the critical pressure. That point is known as the critical point or it is the point where the liquid can exist after that particular temperature liquid cannot exist, okay? So, from this graph, what we have seen? At $T < T_c$ that is critical temperature, there is a local minimum followed by a local maximum with increasing V over a part of specific PV range.

Then at $T > T_c$, the structure of whatever the local minimum followed by local maximum is not going to be occurring, it is going to be vanished, but at $T = T_c$, both local minimum and local maximum converge to a single point and this point that is at $T = T_c$ that is known as the critical point. The first and second derivatives of pressure with respect to v are 0. Obviously, for any curve if you wanted to find out the maximum point, then what you do? You take the first derivative, right?

Similarly, if you wanted to find out the minimum of any given curve, then what you have to do, you have to take the second derivative to be equals to 0. So, at this critical point, both the first derivative and second derivatives are going to be a 0 because both of them are merging to the same point. This point is taken to be the critical point of the fluid that is the point of highest temperature at which a liquid can exist. So, now, we make use of this information that is at particular temperature which is equal to the critical temperature.

The P versus V diagram in this curve, we are going to have one single point where both local minimum and local maximum are merging to the same point, that point we are calling as a kind of critical point. So, at this critical point since minimum and maximum are merging to the same points, the first derivative as well as the second derivative of P with respect to V has to be 0 at $T = T_c$ or at the critical point.

So, that information we make use and then try to develop the kind of information and then do some mathematical simplification to find out the generalized Van der Waal's equation of state which is applicable for all gases which are obeying Van der Waal's equations of state.

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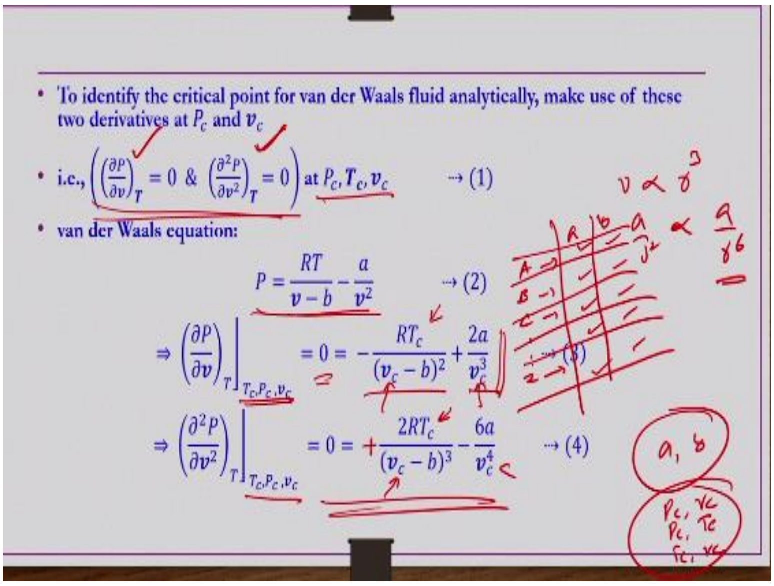

- To identify the critical point for van der Waals fluid analytically, make use of these two derivatives at P_c and v_c
- i.e., $\left(\left(\frac{\partial P}{\partial v}\right)_T = 0 \ \& \ \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0\right)$ at P_c, T_c, v_c ⇢ (1)
- van der Waals equation:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \dashrightarrow (2)$$

$$\Rightarrow \left(\frac{\partial P}{\partial v}\right)_T\Bigg|_{T_c,P_c,v_c} = 0 = -\frac{RT_c}{(v_c-b)^2} + \frac{2a}{v_c^3} \quad \dashrightarrow (3)$$

$$\Rightarrow \left(\frac{\partial^2 P}{\partial v^2}\right)_T\Bigg|_{T_c,P_c,v_c} = 0 = +\frac{2RT_c}{(v_c-b)^3} - \frac{6a}{v_c^4} \quad \dashrightarrow (4)$$

So, to identify the critical point for Van der Waal’s fluid analytically make use of these 2 derivatives at P_c and v_c that is $\left(\frac{\partial P}{\partial v}\right)_T = 0$ and $\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$ and then substitute in place of P, v, T. Simply substitute Pc, v_c and T_c, suffix c stands for critical point. Now, Van der Waal’s equation we will take. Van der Waal’s equation is nothing but P = $\frac{RT}{v-b} - \frac{a}{v^2}$.

Here you can see this$\frac{a}{v^2}$, v is actually you know is having r^3 form, right? Because v is volume, so then r is the distance, so r^3 terms kind of terms would be there. So, then $\frac{a}{v^2}$ in the sense something related to$\frac{a}{r^6}$. So, we have seen the attractive forces are inversely proportional to sixth power of separation distance. So, that means, in the second term in the RHS of this equation indicates the attractive forces, whereas the first time in the right hand side indicates something related to the repulsive forces.

This b is nothing but it is similar to like size of the molecules or it is related to the size of the molecule, okay? Now, for this equation what are we going to do? We are going to develop what is the generalized equation. Now, let us say if you take gas A, gas B, gas C and so and so up to gas Z like that. All of them are obeying Van der Waal’s equations of state, this equation of state. So, then for all of them a and b would be there, different values would be there like this.

So, for each gas, you know what is this small a, small b that you have different values experimentally, okay? But this is going to be valid, the nature of the curve is same, but only thing that is constants that are present in the curve are different. So, can we have a kind of one single curve where all these equations can collapse to the same equation of state under certain conditions that is what we are going to do. So, now that we can obtain when you apply these 2 conditions.

At this condition that is the local minimum, local maximum are there, so this $\left(\frac{\partial P}{\partial v}\right)_T$ = 0 will provide us the local maximum point and then $\left(\frac{\partial^2 P}{\partial v^2}\right)_T$ = 0 this will provide the point at which the local minimum is existing, okay? So, in fact they are existing at the same point if the condition is the critical condition or the temperature is equal to the critical temperature. Then, let us do this $\left(\frac{\partial P}{\partial v}\right)_T$ and then equate to the 0 and then substitute in place of P, v, T, simply substitute Pc, v_c, T_c because it is true only at the critical point, okay?

So, the differentiation of this equation we have to do. So, left hand side $\left(\frac{\partial P}{\partial v}\right)_T$ is there, right hand side $\frac{-RT_c}{(v_c-b)^2}$ we get $+\frac{2a}{{v_c}^3}$ we should get. But now here this T, v, etc. has to be replaced by T_c, v_c and then $\left(\frac{\partial P}{\partial v}\right)_T$ = 0. Similarly, $\left(\frac{\partial^2 P}{\partial v^2}\right)_T$ you do it and then whatever the expression that is coming replace P, v, T by simply P_c, v_c, T_c and then equate this $\left(\frac{\partial^2 P}{\partial v^2}\right)_T$ = 0.

So, that is now this equation whatever is there if once again if you differentiate, you will get $\left(\frac{\partial^2 P}{\partial v^2}\right)_T$. Once again if you differentiate this equation by v, then you will get this equation. When you differentiate this equation once again with respect to v, then you will get $+\frac{2RT_c}{(v_c-b)^3}-\frac{6a}{{v_c}^4}$ because now T and v are replaced by T_c, v_c. So, now what we are having? We are having 2 equations and then 2 unknowns.

So, let us find out this unknown a and b and then substitute them here because only this a and b are different from one gas to the other gas that is obeying Van der Waal's equation of state. So, you find out this a and b as function of P_c, v_c or P_c, T_c or T_c, v_c in any 2 independent variable form you find out and then substitute here, you will get the one same equation that is the generalized Van der Waal's equation of state, okay?

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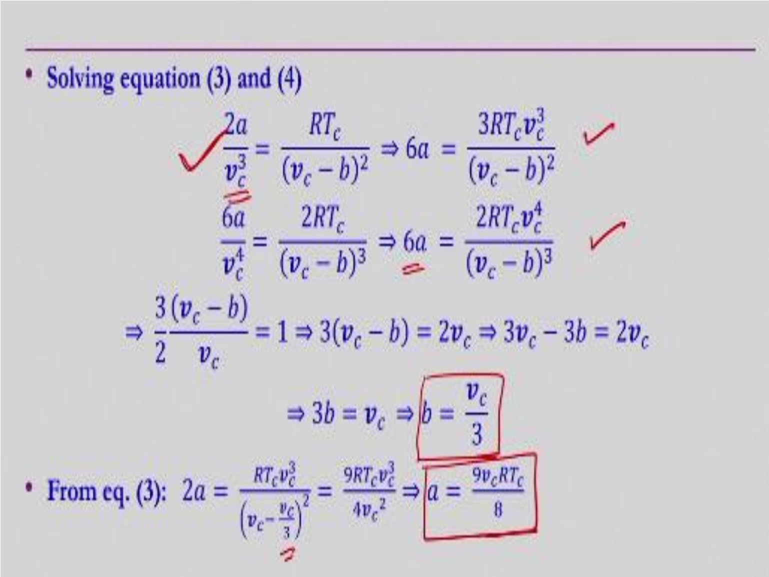

- Solving equation (3) and (4)

$$\frac{2a}{v_c^3} = \frac{RT_c}{(v_c-b)^2} \Rightarrow 6a = \frac{3RT_cv_c^3}{(v_c-b)^2}$$

$$\frac{6a}{v_c^4} = \frac{2RT_c}{(v_c-b)^3} \Rightarrow 6a = \frac{2RT_cv_c^4}{(v_c-b)^3}$$

$$\Rightarrow \frac{3}{2}\frac{(v_c-b)}{v_c} = 1 \Rightarrow 3(v_c-b) = 2v_c \Rightarrow 3v_c - 3b = 2v_c$$

$$\Rightarrow 3b = v_c \Rightarrow \boxed{b = \frac{v_c}{3}}$$

- From eq. (3): $2a = \frac{RT_cv_c^3}{\left(v_c-\frac{v_c}{3}\right)^2} = \frac{9RT_cv_c^3}{4v_c^2} \Rightarrow \boxed{a = \frac{9v_cRT_c}{8}}$

That if you do, so by solving equation 3 and 4, so let us say equation 3 is nothing but $\frac{2a}{v_c^3} = \frac{RT_c}{(v_c-b)^2}$. Now, this equation you multiply by 3 either side and then take whatever the v_c^3 in the denominator in the left hand side to the right hand side. So, then you have this equation. Then equation number 4, we are having this equation $\frac{6a}{v_c^4} = \frac{2RT_c}{(v_c-b)^3}$. Now 6a you keep one side and all other terms you take to the other side.

So, now these 2 equations if you divide one by other, the left hand side you will have 1 and then remaining terms you will be getting $\frac{3(v_c-b)}{2v_c}$ = 1. So, from here when you simplify this equation, what you get? You will get b = $\frac{v_c}{3}$. Now, you substitute this particular b in the equation number 3 that is $\frac{2a}{v_c^3} = \frac{RT_c}{(v_c-b)^2}$. So, in place of b, you substitute $\frac{v_c}{3}$ and then simplify, then you will get a = $\frac{9v_cRT_c}{8}$.

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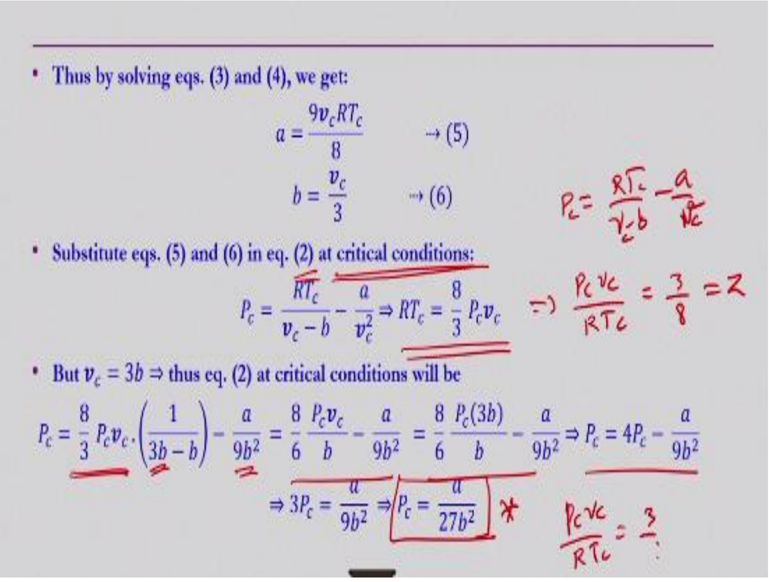

- Thus by solving eqs. (3) and (4), we get:

$$a = \frac{9v_c RT_c}{8} \rightarrow (5)$$

$$b = \frac{v_c}{3} \rightarrow (6)$$

$$P_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2}$$

- Substitute eqs. (5) and (6) in eq. (2) at critical conditions:

$$P_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2} \Rightarrow RT_c = \frac{8}{3} P_c v_c \Rightarrow \frac{P_c v_c}{RT_c} = \frac{3}{8} = Z$$

- But $v_c = 3b \Rightarrow$ thus eq. (2) at critical conditions will be

$$P_c = \frac{8}{3} P_c v_c \cdot \left(\frac{1}{3b - b}\right) - \frac{a}{9b^2} = \frac{8}{6}\frac{P_c v_c}{b} - \frac{a}{9b^2} = \frac{8}{6}\frac{P_c(3b)}{b} - \frac{a}{9b^2} \Rightarrow P_c = 4P_c - \frac{a}{9b^2}$$

$$\Rightarrow 3P_c = \frac{a}{9b^2} \Rightarrow \boxed{P_c = \frac{a}{27b^2}} * \quad \frac{P_c v_c}{RT_c} = \frac{3}{}$$

So, that is by solving equations 3 and 4, we get a is equals to this one, b is equals to this one. So, now substitute equations 5 and 6 that is constant a and b in equation 2 but at critical conditions. What is equation number 2 two? It is nothing but P = $\frac{RT}{v-b} - \frac{a}{v^2}$, but at critical condition. So now equation number 2 at critical conditions should by $P_c = \frac{RT_c}{v_c-b} - \frac{a}{v_c^2}$. So in that equation, you substitute a and b, when you simplify it you will get $RT_c = \frac{8}{3} P_c v_c$ or $\frac{P_c v_c}{RT_c} = \frac{3}{8}$ is nothing but compressibility factor at critical conditions, okay?

So, why I am doing this simplification? Because if I wanted to represent this a and b in terms of P_c or you know P_c and T_c or other P_c and v_c kind of terms, then it is required. This information is required because now these a and b are in terms of v_c and T_c are as independent variables, right? So, now you take a v_c = 3b and this equation at critical conditions, right? Then you have so $P_c = RT_c$, in place of RT_c you can write it $\frac{8}{3} P_c v_c$ and 1 by in place of v_c you take 3b, b is as it is $-a$ by, v_c is nothing but 3b, so $9b^2$.

Then you further simplify this equation so that you will get $P_c = \frac{a}{27b^2}$. So now you can make use of this condition as well as $\frac{P_c v_c}{RT_c} = \frac{3}{8}$.

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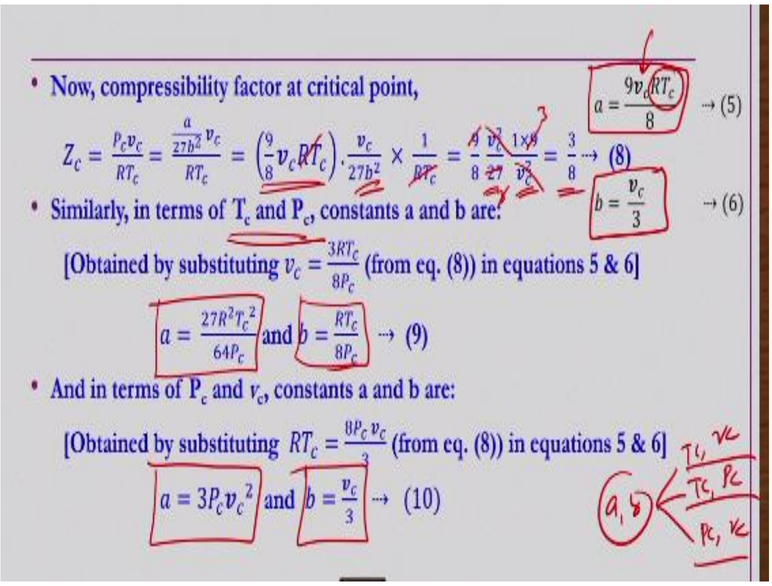

- Now, compressibility factor at critical point,

$$Z_c = \frac{P_c v_c}{RT_c} = \frac{\frac{a}{27b^2} v_c}{RT_c} = \left(\frac{9}{8} v_c \cancel{RT_c}\right) \cdot \frac{v_c}{27b^2} \times \frac{1}{\cancel{RT_c}} = \frac{\cancel{9}}{8} \frac{\cancel{v_c^2}}{\cancel{27}} \frac{1 \times \cancel{9}}{\cancel{v_c^2}} = \frac{3}{8} \dashrightarrow (8)$$

$$\boxed{a = \frac{9 v_c RT_c}{8}} \rightarrow (5)$$

$$\boxed{b = \frac{v_c}{3}} \rightarrow (6)$$

- Similarly, in terms of T_c and P_c, constants a and b are:

[Obtained by substituting $v_c = \frac{3RT_c}{8P_c}$ (from eq. (8)) in equations 5 & 6]

$$\boxed{a = \frac{27R^2T_c^2}{64P_c}} \text{ and } \boxed{b = \frac{RT_c}{8P_c}} \dashrightarrow (9)$$

- And in terms of P_c and v_c, constants a and b are:

[Obtained by substituting $RT_c = \frac{8P_c v_c}{3}$ (from eq. (8)) in equations 5 & 6]

$$\boxed{a = 3P_c v_c^2} \text{ and } \boxed{b = \frac{v_c}{3}} \dashrightarrow (10)$$

Now compressibility factor at critical point we will see that is $Z_c = \frac{P_c v_c}{RT_c}$ though we have already got it. So, Pc is now simply a by 27 b square, $v_c = V_c RT_c$. So this you rearrange in place of a, equation number 5 we have already got a is equals to $\frac{9}{8}$ v_c RT_c and then b and then this b^2 let us keep it as it is for the time being, right? So then, what we have, this v_c^2, this v_c^2, and then $\frac{9}{8}$, this RT_c this RT_c is cancelled out and then divided by 27, then $b = v_c$. So, what we write v_c^2.

So, now this v_c^2, v_c^2 is also cancelled out, so that we have 9 times one, 9 times 3, 3 times 1, 3 times 3, so $\frac{3}{8}$ the same thing we are getting in the previous equation. So, now, what we do? We convert this a and b constant in terms of temperature and pressure at critical conditions, that how you do? You simply write in this equation a and b, we have this equation already derived. In this equation in place of v_c you write $\frac{3RT_c}{8P_c}$. Similarly, here in this equation b that also we have got, here also in place of v_c you write $\frac{3RT_c}{8P_c}$.

Then you will get $a = \frac{27R^2T_c^2}{64P_c}$, whereas $b = \frac{RT_c}{8P_c}$, this is what you get. Now, here in this case a and b are represented in terms of T_c and P_c and then similarly in terms of P_c and v_c constants a and b can also be obtained, but what you have to do? In this equation in place of RT_c what you write, you simply write $\frac{8P_c v_c}{3}$, then we have $a = 3\ P_c\ v_c^2$ and then $b = \frac{v_c}{3}$ as it is. So, now this a and b constant here are in terms of P_c and v.

So, the same a and b constraints are written in 3 different forms. First one is like T_c, v_c terms, second one T_c, P_c terms, third one P_c, v_c terms. So, now we have 3 sets of a and b constants, in any one set then you substitute them in equation number 2 and simplify, then you will get generalized Van der Waal's equation of state, indeed that is what we are aimed to finding out a and b constants and then substituting them in an equation number 2.

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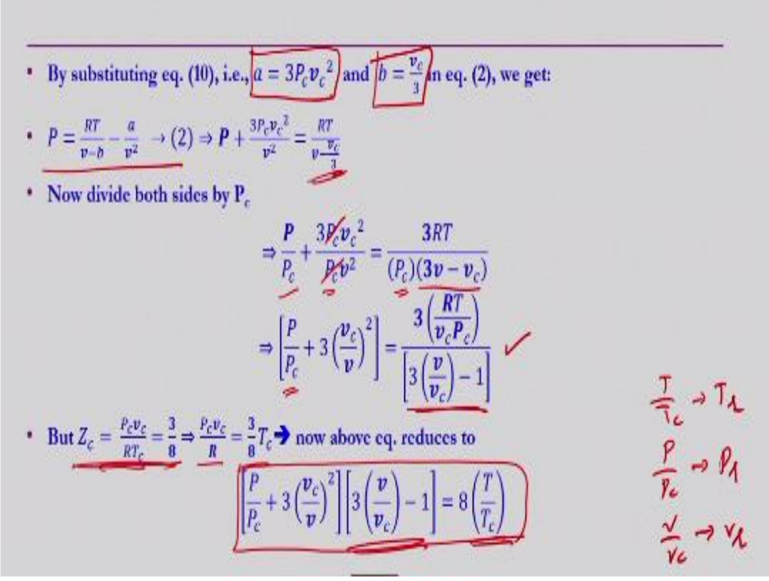

- By substituting eq. (10), i.e., $\boxed{a = 3P_c v_c^2}$ and $\boxed{b = \frac{v_c}{3}}$ in eq. (2), we get:
- $P = \frac{RT}{v-b} - \frac{a}{v^2} \rightarrow (2) \Rightarrow P + \frac{3P_c v_c^2}{v^2} = \frac{RT}{v - \frac{v_c}{3}}$
- Now divide both sides by P_c

$$\Rightarrow \frac{P}{P_c} + \frac{3\cancel{P_c}v_c^2}{\cancel{P_c}v^2} = \frac{3RT}{(P_c)(3v - v_c)}$$

$$\Rightarrow \left[\frac{P}{P_c} + 3\left(\frac{v_c}{v}\right)^2\right] = \frac{3\left(\frac{RT}{v_c P_c}\right)}{\left[3\left(\frac{v}{v_c}\right) - 1\right]} \checkmark$$

- But $Z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8} \Rightarrow \frac{P_c v_c}{R} = \frac{3}{8}T_c$ ➔ now above eq. reduces to

$$\boxed{\left[\frac{P}{P_c} + 3\left(\frac{v_c}{v}\right)^2\right]\left[3\left(\frac{v}{v_c}\right) - 1\right] = 8\left(\frac{T}{T_c}\right)}$$

$\frac{T}{T_c} \rightarrow T_r$

$\frac{P}{P_c} \rightarrow P_r$

$\frac{v}{v_c} \rightarrow v_r$

So, now what we do? We take this equation number 10 that is a is equals to 3 P_c v_c^2 and b = $\frac{v_c}{3}$ and substitute them in equation number 2. We can substitute any other equations also, okay? Any other form of a and b also to get those genaralized equation, but I am taking this one because of the simplicity. So, now, this is the equation number 2. P = $\frac{RT}{v-b} - \frac{a}{v^2}$. So, P whatever this $\frac{a}{v^2}$ is there, I am taking to the left hand side and then in place of a I have written $\frac{3P_c v_c^2}{v^2}$ and then right hand side our $\frac{RT}{v-b}$ as it is, in place of b, I have been written $\frac{v_c}{3}$.

Now both sides divide by P_c. So, I have $\frac{P}{P_c} + \frac{3P_c v_c^2}{P_c v^2} = \frac{3RT}{P_c}$ and then this term I have done the LCM. So then we have this term v - $\frac{v_c}{3}$ I can write $\frac{(3v - vc)}{3}$. So, the 3 I have taken to the numerator, so $\frac{3RT}{P_c(3v - vc)}$. So, now this P_C this P_C you can cancel it, okay? And then from this term next step what do you do? You take v_c common. So, when you take the v_c common, this term you can write $3\left(\frac{v}{v_c}\right)$ - 1 and then this v_c is multiplied by Pc.

So then that I can write $\frac{3RT}{P_c v_c}$ in the right hand side term, the left hand side term is as it is $\frac{P}{P_c} + 3\left(\frac{v}{v_c}\right)^2$, right? So, now what we can do here? This equation this part $\frac{3RT}{P_c v_c}$ is there, so $\frac{R}{P_c v_c}$, we can, what is the value in terms of T$_c$ that I can find out from this Z$_c$ information. Z$_c$ = $\frac{3}{8}$ =$\frac{P_c v_c}{RT_c}$. From here, I can get $\frac{P_c v_c}{R}$ = $\frac{3T_c}{8}$. Now in place of this $\frac{R}{P_c v_c}$ if I substitute $\frac{8}{3T_c}$, then I can get this expression $\frac{8T}{T_c}$. I can have and then this part I am taking to the left hand side here.

The remaining term in the left hand side is as it is, okay. So what we have after substituting this a and b in this equation, we are having this expression like$\left[\frac{P}{P_c} + 3\left(\frac{v}{v_c}\right)^2\right]$ $\left[3\left(\frac{v}{v_c}\right) - 1\right]$= $\frac{8T}{T_c}$ and we know this $\frac{T}{T_c}$is nothing but reduced temperature and $\frac{P}{P_c}$ is nothing but reduced pressure and then $\frac{v}{v_c}$ is nothing but reduced volume.

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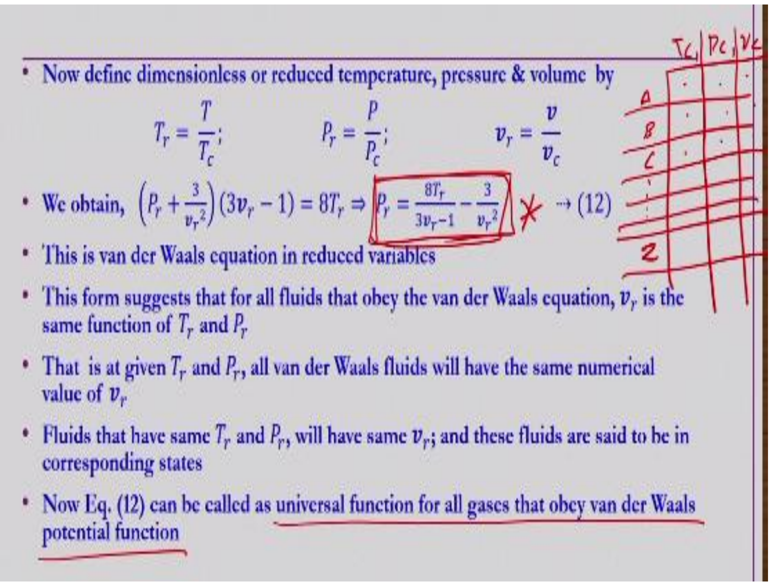

- Now define dimensionless or reduced temperature, pressure & volume by

$$T_r = \frac{T}{T_c}; \qquad P_r = \frac{P}{P_c}; \qquad v_r = \frac{v}{v_c}$$

- We obtain, $\left(P_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r \Rightarrow \boxed{P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}}$ → (12)
- This is van der Waals equation in reduced variables
- This form suggests that for all fluids that obey the van der Waals equation, v_r is the same function of T_r and P_r
- That is at given T_r and P_r, all van der Waals fluids will have the same numerical value of v_r
- Fluids that have same T_r and P_r, will have same v_r; and these fluids are said to be in corresponding states
- Now Eq. (12) can be called as universal function for all gases that obey van der Waals potential function

So, that we defined and then substitute in this equation, then we get $\left[P_r + \frac{3}{v_r^2}\right]$ $[3v_r - 1]$= $8T$$_r$. The same thing I can write P$_r$ = $\frac{8T_r}{3v_r - 1}$ - $\frac{3}{v_r^2}$. This is the generalized Van der Waal's equation of state that we wanted to develop. Now, this is universal function. So, how it is going to be separate for each gas? Let us say if you wanted to obtain this a and b constant separately for each quantity. So, you can use any of these constant that we developed in the equation number 5, 6, and 9, 10.

Then you can get those constant, individual constant for individual gases, okay? So, this is Van der Waal's equations in reduced variable or generalized the Van der Waal's equation of state that we call. This form suggests that for all fluids that obey the Van der Waal's equation V_r is same function of T_r and P_r, right? That is at given T_r and P_r, all the Van der Waal's fluids will have the same numerical value of v_r, okay? Fluids that have same T_r and P_r will have same v_r and these fluids are said to be in corresponding states, okay?

So, now let us say this A, B, C and so on so Z number of gases are obeying Van der Waal's equation of state, okay? So, now, these gases each one of them are having different T_c, P_c, v_c values obviously, right? So, for gas A whatever T_c, P_c, v_c are there, they are different from whatever the T_c, P_c, v_c. So, that way, so if they are different, so obviously their constants are also going to be different.

So but this information is clubbed such a way that now by using principle of corresponding states if you write the same information rather than an individual temperature, pressure, individual volume kind of thing, you write them as a kind of reduced temperature, reduced pressure, reduced volume. So, then that equation of state is going to have this one same equation for all gases which are obeying Van der Waal's equation of state that is what it mean by principle of corresponding states.

So, that here, this equation 12 can be called as a universal function for all gases that obey Van der Waal's potential, okay?

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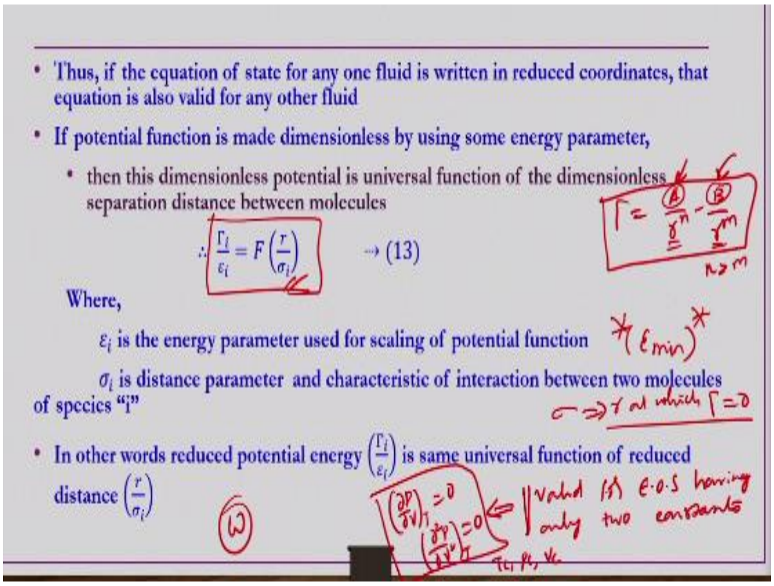

- Thus, if the equation of state for any one fluid is written in reduced coordinates, that equation is also valid for any other fluid
- If potential function is made dimensionless by using some energy parameter,
  - then this dimensionless potential is universal function of the dimensionless separation distance between molecules

$$\therefore \boxed{\frac{\Gamma_i}{\varepsilon_i} = F\left(\frac{r}{\sigma_i}\right)} \rightarrow (13)$$

$$\boxed{\Gamma = \frac{\textcircled{A}}{r^n} - \frac{\textcircled{B}}{r^m}}$$

$n > m$

Where,

ε_i is the energy parameter used for scaling of potential function *(ε_{min})*

σ_i is distance parameter and characteristic of interaction between two molecules of species "i"

$\sigma \Rightarrow r$ at which $\Gamma = 0$

- In other words reduced potential energy $\left(\frac{\Gamma_i}{\varepsilon_i}\right)$ is same universal function of reduced distance $\left(\frac{r}{\sigma_i}\right)$

ⓦ

$\left(\frac{\partial P}{\partial V}\right)_T = 0$

$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$ ⇐ Valid for E.O.S having only two constants

T_c, P_c, V_c

Thus if the equation of state for any one fluid is written in reduced coordinates that equation is also valid for any other fluid. So, that is if potential function is made dimensionless by using some energy parameters, then this dimensionless potential is universal function of the dimensionless separation distance between the molecules. That is as I mentioned, if the intermolecular potential if you non-dimensionalize using minimum potential energy ε minimum, okay?

Then it is going to be one single universal function of dimensionless separation distance $\frac{r}{\sigma_i}$ for any gas that you take, okay, for any gas of one particular class. There are several classes of gases. Class in the sense let us say for example all the gases obeying Redlich-Kwong equation can put them as in one class like that for simplicity, okay? So, why only it is function of reduced this separation distance or dimensionless separation distance, why not any other parameter?

Because this potential energy functions we have seen, they are a form A by r power n - B by r power n. This A and B are positive constant and n is greater than m, this is what we have seen, generalized one, though it looks like a Mie's potential but it is more generalized one right, more generalized one for any gas which is having 2 constants, okay? So, now here we can see these a and b are constants, only other independent variables is the separation distance, okay?

In some case it is inversely proportional to r, in some case it is inversely proportional to r^2. In some case it is inversely proportional to r^6. In some case it is inversely proportional to r^8. I am not specifying whether it is electrostatic force or whether it is permanent dipole or whether it is induction forces or it is a quadrupole-quadrupole interaction I am not mentioning. Whatever the kind of force it is there, it is inversely proportional to r power something like n or m something.

That is the reason we are having only one dimensionless separation distance as a kind of independent variable if you are going to write this potential function as a kind of universal function, okay? So where ε_i is the energy parameter used for scaling of potential function in general whatever ε minimum or minimum potential energy is there that is in general used for scaling and then σ is the distance parameter and characteristics of interaction between 2 molecules of species.

Then in general for σ_i, people, that is nothing but take the r at which this Γ is becoming 0 that is taken as σ, characteristic distance or collision diameter, sometimes as hard sphere diameter depending on the model, different names it is given, so but mostly that collision diameter or whatever the σ at which intermolecular potential becomes 0 after overcoming the repulsive forces and before developing the attractive forces, at that point where this Γ becomes 0 that separation distance is known as σ.

In some models it is called as a collision diameter, some model it is called as hard sphere diameter, etc., like that. So, in other words, reduced potential energy $\left(\frac{\Gamma_i}{\sigma_i}\right)$ is same universal function of reduced distance$\left(\frac{r}{\sigma_i}\right)$. So, this is how we can develop a kind of reduced or generalized equation of state for a class of gases which are obeying same equation of state, okay? Then finally most importantly it is valid for equations of state whose incremental potential are having only 2 constants.

Why because we have only 2 conditions, one is the $\left(\frac{\partial P}{\partial v}\right)_T$ = 0 and $\left(\frac{\partial^2 P}{\partial v^2}\right)_T$ = 0 and substitute at T_c, P_c, v_c that is at critical conditions. So, you take an equation of state and then do, $\left(\frac{\partial P}{\partial v}\right)_T$, equate it to 0. Similarly, you do, $\left(\frac{\partial^2 P}{\partial v^2}\right)_T$, equate to 0, and then these 2 equations if is you substitute T_c, P_c, v_c, so we get only 2 equations. So if these 2 equations have only 2 constants, maximum 2 constant, then only we can find out.

If any equation of state that is having more than 2 constants, then obviously it is not possible because there will be 3 constant and we will be having only 2 equations to find out that is not possible, okay? But anyway there are some kind of corrections or adjustments are available that we are going to see anyway, but in general such kind of intermolecular potentials where we have more than 2 constants or in general non-spherical molecules, for those non-spherical molecules we can have a kind of additional factor ω which is also known as the acentric factor. If it is 0, then we can say those molecules are spherical molecules, okay?

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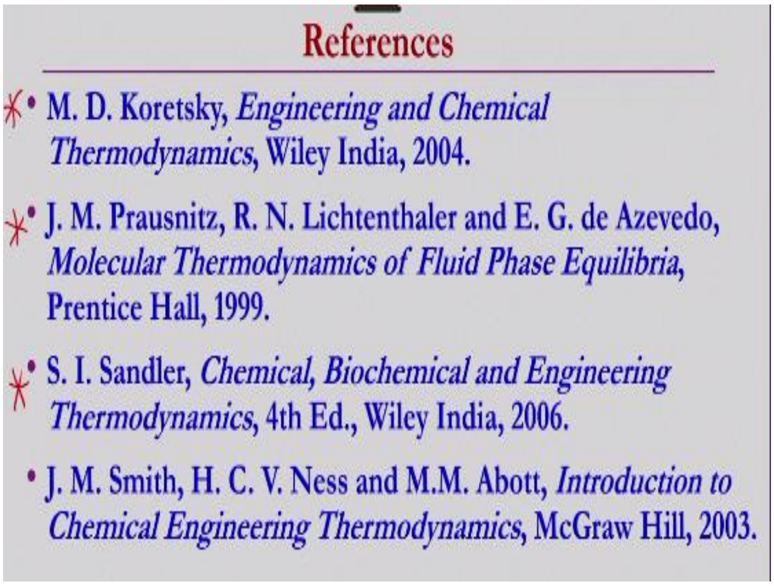

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References for this lecture. Engineering and Chemical Thermodynamics by Koretsky. Molecular Thermodynamics of Fluid Phase Equilibria process by Prausnitz et al. Chemical, Biochemical and Engineering Thermodynamics by Sandler and an introduction to Chemical Engineering Thermodynamics by Smith et al. So, the lecture notes prepared for this lecture are primarily taken from these 2 books, some information is also available in this book Koretsky as well.

Thank you.