Advanced Thermodynamics
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Lecture – 10
Molecular Theory of Corresponding States - 2

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is Molecular Theory of Corresponding States part 2. Since it is a continuation of previous lecture, we will have a kind of recapitulation of what we have studied in previous lecture.

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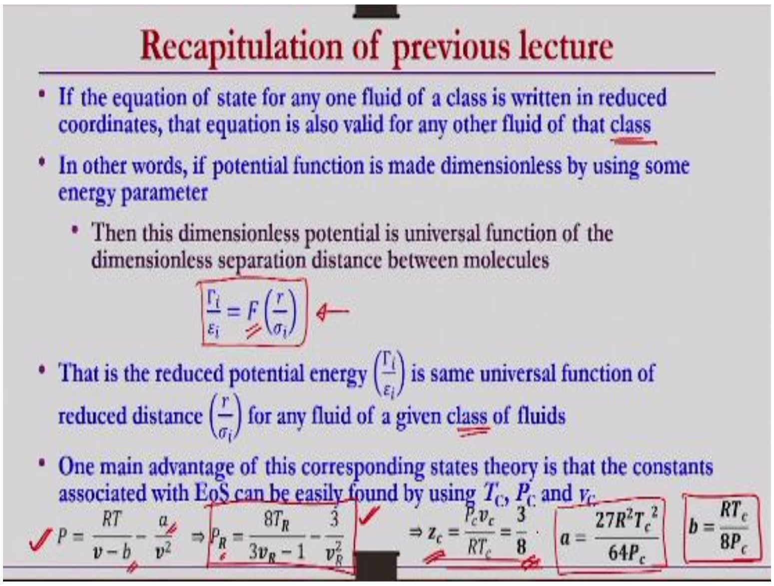

Recapitulation of previous lecture

- If the equation of state for any one fluid of a class is written in reduced coordinates, that equation is also valid for any other fluid of that class
- In other words, 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

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

- That is the reduced potential energy $\left(\frac{\Gamma_i}{\varepsilon_i}\right)$ is same universal function of reduced distance $\left(\frac{r}{\sigma_i}\right)$ for any fluid of a given class of fluids
- One main advantage of this corresponding states theory is that the constants associated with EoS can be easily found by using T_C, P_C and v_C

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \Rightarrow \boxed{P_R = \frac{8T_R}{3v_R - 1} - \frac{3}{v_R^2}} \Rightarrow z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8}. \quad \boxed{a = \frac{27R^2T_c^2}{64P_c}} \quad \boxed{b = \frac{RT_c}{8P_c}}$$

A kind of summary of the previous lecture is that if the equation of state for any one fluid of a class is written in reduced coordinates that equation is also valid for any other fluid of that class. So, let us say if you have a class of several fluids and all those fluids are obeying one particular equation of state for example, then if you write that equation of states in reduced coordinate for any one fluid that equation of state in reduced coordinates will also be applicable for all other fluids of that particular class.

In other words, if potential function is made dimensionless by using some kind of energy parameter, then this dimensionless potential is a universal function of the dimensionless separation distance between 2 molecules and then that is $\frac{\Gamma_i}{\varepsilon_i} = F\left(\frac{r}{\sigma_i}\right)$. Ei is some kind of energy parameter, usually it is minimum potential energy that is ε minimum is taken as ε_i.

Then σ_i is usually taken as a kind of collision diameter which is nothing but the distance between two particles at which the intermolecular potential becomes 0 after overcoming the repulsive forces and then before proceeding to the attractive forces, right? So, this if you write for one particular fluid, so, it is also valid for all other fluids of that particular class. That is the reduced potential energy is same universal function of reduced distance for any fluid of a given class of fluids, okay? This is what we have seen.

So, one main advantage of this corresponding states theory is that whatever the constant associated with the equation of state of particular class of fluids can be found by using the temperature, pressure and molar volume at critical conditions. And this particular theory, whatever we have seen it is valid only for the cases where there are only 2 constants. As previously discussed where there are only 2 constants, then it is possible that we can easily find out those constants.

If there are more constants, so there may be some kind of additional parameter maybe coming into picture. Those things we will be discussing at the end of this lecture. Then further what we have seen, we have taken van der Waals equation of state $P = \frac{RT}{v-b} - \frac{a}{v^2}$ and then we applied corresponding state theory, then what we got? We got the same Van der Waal's equation of state, we were able to write in reduced coordinates like you know $P_R = \frac{8T_R}{3v_R-1} - \frac{3}{v_R^2}$, where this suffix R stands for the reduced properties.

That is P_R is nothing but reduced pressure that is $\frac{P}{P_c}$ and T_R is nothing but reduced temperature that is $\frac{T}{T_c}$ and then v_R is nothing but reduced molar volume, which is nothing but $\frac{v}{v_c}$. Then further we found for this particular fluid, the compressibility factor at critical condition that is $z_c = \frac{Pv_c}{RT_c} = \frac{3}{8}$, that is 0.375 that is what we have found. Then, the constants a and b as we were citing these constants, we can find out in terms of critical temperature, critical pressure and then critical molar volume if at all required.

So, this is what we have found. This a and b can also be written in terms of T_c v_c and then P_c v_c other coordinates as well by applying this $z_c = \frac{Pv_c}{RT_c} = \frac{3}{8}$, those things we have seen and then one thing to observe that in this summary of previous lecture everywhere we are writing class of fluids, right? So far one particular class only it is valid that is what we are saying. So that means whatever this reduced equation of state is there, it is valid only for those fluids which obey Van der Waal's equation of state, right?

So, it is not true that it is valid for all the fluids universally. If some other fluids which are better represented by some other equation of states let us say Redlich-Kwong equation. So then the universal function for those fluids obeying Redlich-Kwong equation of state better is going to be different function. So, this function whatever the universal function is there that is going to be true only for a class of fluids, only for one particular class of fluids, only for specific class of fluids which are obeying one particular equation of state much better compared to the other ones.

So, like that one has to see and then these here we can see there are only 2 constants are there a and b. So, if there are 2 constants, then we can use these corresponding states theory more comfortably. Theory of corresponding states can be valid or more reliable if there are only 2 constants. What if there are more than 2 constants are there? So, then we have to think of a better theory of corresponding states, so that to have a kind of reliable information, okay, without losing the accuracy, right?

So, is it really true that it is for this universal function is valid only for one particular class of fluids, only one class fluids which are represented by one particular equation of state, okay? That also we can crosscheck, indeed it is true, but by how can we crosscheck? We can like previous lecture, we have taken one equation of state and then tried to found this same equation of state in reduced coordinates and then corresponding compressibility factor also we have found.

So, now we take another equation of state and then try to do the same thing and then find whether we are getting the same compressibility for those fluids, are that particular equation of state obeyed fluids, are they going to have a kind of same $\frac{3}{8}$, z_c or is it going to be different that we have to check. If it is going to be different, then that whatever the class of fluid that we are specifying that has to be specified clearly, okay?

So, this F is valid for only one particular class fluids and then for different class of fluids or for a different group of fluids, this function is going to be slightly different okay? That is what we are going to prove by taking Redlich-Kwong equation, okay?

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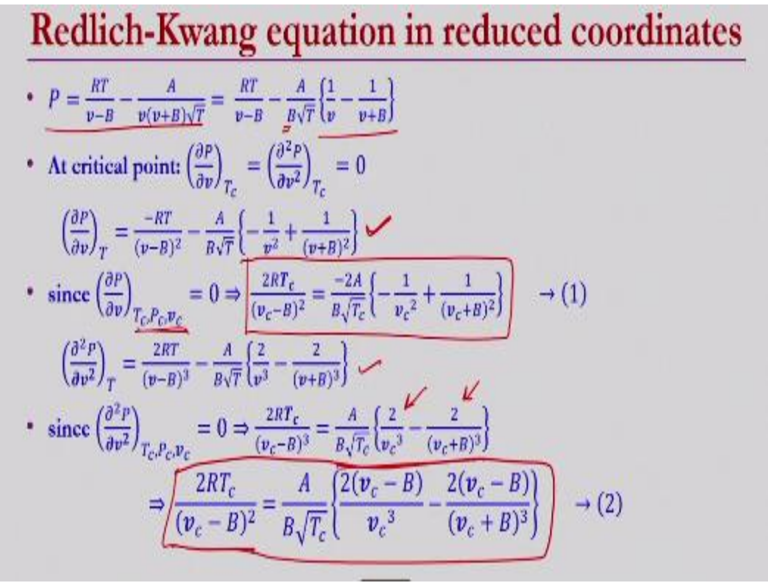

Redlich-Kwang equation in reduced coordinates

- $P = \frac{RT}{v-B} - \frac{A}{v(v+B)\sqrt{T}} = \frac{RT}{v-B} - \frac{A}{B\sqrt{T}}\left\{\frac{1}{v} - \frac{1}{v+B}\right\}$
- At critical point: $\left(\frac{\partial P}{\partial v}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0$

$$\left(\frac{\partial P}{\partial v}\right)_T = \frac{-RT}{(v-B)^2} - \frac{A}{B\sqrt{T}}\left\{-\frac{1}{v^2} + \frac{1}{(v+B)^2}\right\} ✓$$

- since $\left(\frac{\partial P}{\partial v}\right)_{T_c,P_c,v_c} = 0 \Rightarrow \boxed{\frac{2RT_c}{(v_c-B)^2} = \frac{-2A}{B\sqrt{T_c}}\left\{-\frac{1}{v_c^2} + \frac{1}{(v_c+B)^2}\right\}} \rightarrow (1)$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2RT}{(v-B)^3} - \frac{A}{B\sqrt{T}}\left\{\frac{2}{v^3} - \frac{2}{(v+B)^3}\right\} ✓$$

- since $\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c,P_c,v_c} = 0 \Rightarrow \frac{2RT_c}{(v_c-B)^3} = \frac{A}{B\sqrt{T_c}}\left\{\frac{2}{v_c^3} - \frac{2}{(v_c+B)^3}\right\}$

$$\Rightarrow \boxed{\frac{2RT_c}{(v_c-B)^2} = \frac{A}{B\sqrt{T_c}}\left\{\frac{2(v_c-B)}{v_c^3} - \frac{2(v_c-B)}{(v_c+B)^3}\right\}} \rightarrow (2)$$

So Redlich-Kwong equation in reduced coordinates that is what we are going to see and then we are going to find out what is z_c for this Redlich-Kwong equation. Is it different from the Van der Waal's equation of state or not under reduced coordinates that is what we are going to check now. So Redlich-Kwong equation is nothing but P = $\frac{RT}{v-b} - \frac{A}{v(v+B)\sqrt{T}}$. So, this I can write $\frac{1}{v(v+B)}$. I can write $\frac{1}{v} - \frac{1}{(v+B)}$ and then multiplied by $\frac{1}{B}$. So that I can write $\frac{A}{B\sqrt{T}}\left\{\frac{1}{v} - \frac{1}{(v+B)}\right\}$.

This is we are writing so that to make differentiation easier because we know at critical point $\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$. So, now let us do $\left(\frac{\partial P}{\partial v}\right)_T$. Then we have $\frac{-RT}{(v-B)^2} - \frac{A}{B\sqrt{T}}$ as it is and then here $\frac{-1}{v^2}$ and then here - of -$\left(+\frac{1}{(v+B)^2}\right)$. Now what I am doing, I am equating it to the 0. Then I can have $\frac{RT}{(v-B)^2} = \frac{A}{B\sqrt{T}}\left\{\frac{-1}{v^2} + \frac{1}{(v+B)^2}\right\}$, but this $\left(\frac{\partial P}{\partial v}\right)_{T_c,P_c,v_c} = 0$.

So, all these things has to be you know the P, T, V, etc., should be replaced by P_c, T_c, v_c respectively and then when we rearrange this equation by taking this $\frac{RT_c}{(v_c-B)^2}$ one side and by keeping all other terms other side and then further I multiplied by 2 either sides because it will be useful in the further simplifications, okay? So, next step $\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$.

So, this particular equation if you once again differentiate with respect to v, then you get $\frac{2RT}{(v-B)^3} = \frac{-A}{B\sqrt{T}}\left\{\frac{2}{v^3} - \frac{2}{(v+B)^3}\right\}$, right? So, now again we know at T_c, P_c, v_c this second derivative is as well 0. So, then when I equate it to the 0. I can write $\frac{2RT_c}{(v_c-B)^3}$ one side and remaining terms I take to the other side so that I can have $\frac{A}{B\sqrt{T_c}}\left\{\frac{2}{{v_c}^3} - \frac{2}{(v_c+B)^3}\right\}$. This is what we have.

Now, what I do? I take one of the $(v_c - B)$ from left hand side to the right hand side, so that in the left hand side I can have only $\frac{RT_c}{(v_c-B)^2}$ and then the right hand side these 2 terms would be multiplied by $(v_c - B)$, right? So, now this equation number 2 and then equation number 1 if you see, left hand side are equal, right? So, then what we can do?

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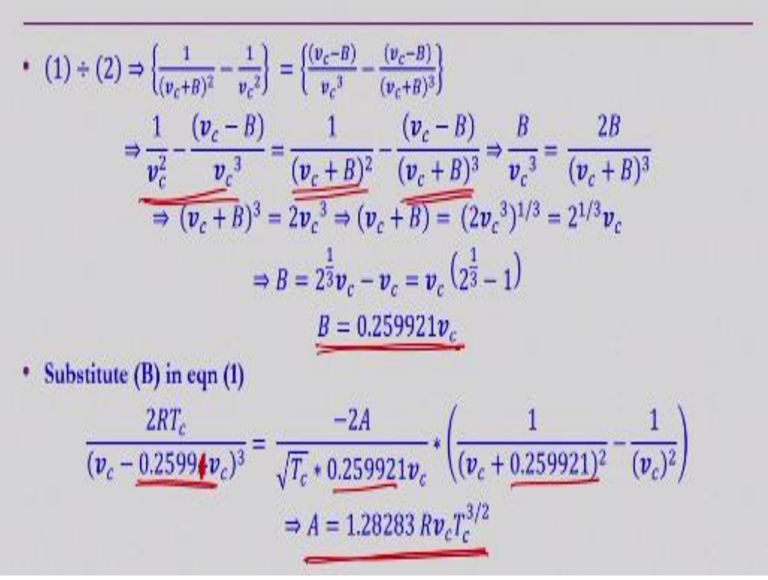

- $(1) \div (2) \Rightarrow \left\{\frac{1}{(v_c+B)^2} - \frac{1}{{v_c}^2}\right\} = \left\{\frac{(v_c-B)}{{v_c}^3} - \frac{(v_c-B)}{(v_c+B)^3}\right\}$

$$\Rightarrow \frac{1}{v_c^2} - \frac{(v_c-B)}{{v_c}^3} = \frac{1}{(v_c+B)^2} - \frac{(v_c-B)}{(v_c+B)^3} \Rightarrow \frac{B}{{v_c}^3} = \frac{2B}{(v_c+B)^3}$$

$$\Rightarrow (v_c+B)^3 = 2{v_c}^3 \Rightarrow (v_c+B) = (2{v_c}^3)^{1/3} = 2^{1/3}v_c$$

$$\Rightarrow B = 2^{\frac{1}{3}}v_c - v_c = v_c\left(2^{\frac{1}{3}} - 1\right)$$

$$B = 0.259921v_c$$

- Substitute (B) in eqn (1)

$$\frac{2RT_c}{(v_c - 0.259921v_c)^3} = \frac{-2A}{\sqrt{T_c} * 0.259921v_c} * \left(\frac{1}{(v_c + 0.259921)^2} - \frac{1}{(v_c)^2}\right)$$

$$\Rightarrow A = 1.28283\, Rv_cT_c^{3/2}$$

Right hand side we can equate or if you do equation 1 by 2, then you will get $\frac{1}{(v_c+B)^2} - \frac{1}{{v_c}^2} = \frac{(v_c-B)}{{v_c}^3} - \frac{(v_c-B)}{(v_c+B)^3}$, right? So, now this if you further do some simplification by taking all denominator terms, all the terms which are having in the denominator v_c terms or ${v_c}^2$, ${v_c}^3$ terms one side and then terms in the denominator having $(v_c + B)$terms, those if you write other side and then simplify, then you will get this $\frac{B}{{v_c}^3} = \frac{2B}{(v_c+B)^3}$.

From here, you can get this B = $v_c\left(2^{\frac{1}{3}} - 1\right)$, which is nothing but 0.259921 v_c. So this is your B, okay? Now, if you substitute this B in equation number 1, equation number 1 is nothing but $\frac{2RT_c}{(v_c-B)^3} = \frac{-2A}{B\sqrt{T_c}}\left\{\frac{1}{(v_c+B)^2} - \frac{1}{{v_c}^2}\right\}$ is that equation number 1. So, in that place wherever this B is there, we are writing 0.2521 v_c, then simplify this equation, so then you will get A = 1.28283 R v_c $T_c^{3/2}$. This is what we get, okay?

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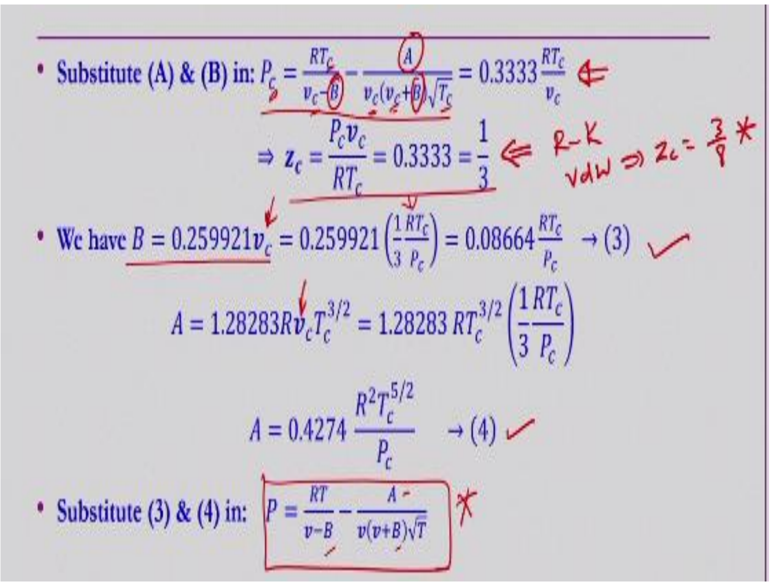

- Substitute (A) & (B) in: $P_c = \frac{RT_c}{v_c - B} - \frac{A}{v_c(v_c+B)\sqrt{T_c}} = 0.3333\frac{RT_c}{v_c}$ ⇐

$$\Rightarrow z_c = \frac{P_c v_c}{RT_c} = 0.3333 = \frac{1}{3}$$ ⇐ R-K

vdW ⇒ $z_c = \frac{3}{8}$ *

- We have $B = 0.259921 v_c = 0.259921\left(\frac{1}{3}\frac{RT_c}{P_c}\right) = 0.08664\frac{RT_c}{P_c} \rightarrow (3)$ ✓

$$A = 1.28283 R v_c T_c^{3/2} = 1.28283\, RT_c^{3/2}\left(\frac{1}{3}\frac{RT_c}{P_c}\right)$$

$$A = 0.4274\frac{R^2 T_c^{5/2}}{P_c} \rightarrow (4)$$ ✓

- Substitute (3) & (4) in: $\boxed{P = \frac{RT}{v-B} - \frac{A}{v(v+B)\sqrt{T}}}$ *

So, now what we can do? We can substitute this A and B in Redlich-Kwong equation but at the T_c, P_c, v_c. Then Redlich-Kwong equation is nothing but actually P = $\frac{RT}{v-B} - \frac{A}{v(v+B)\sqrt{T}}$. So, now at critical condition the same equation this temperature, pressure, volume, they should be replaced by the critical condition values. So, that is $P_c = \frac{RT_c}{v_c-B} - \frac{A}{v_c(v_c+B)\sqrt{T_c}}$. Now here we already calculated what is A and then what is B.

So, if you substitute these things, then further simplify, then you will get this equation is nothing but 0.3333 $\frac{RT_c}{v_c}$ or $\frac{1}{3}\frac{RT_c}{v_c}$, that is what you get. When you rearrange this equation $\frac{P_c v_c}{RT_c}$ is nothing but $\frac{1}{3}$. That is $z_c = \frac{1}{3}$ in the case of Redlich-Kwong equation, but in the case of Van der Waal's equation, the same z_c is nothing but $\frac{3}{8}$. So, now, this indicates whatever this universal function is there, it is valid only for a class of fluids which are obeying certain equation of state much appropriate way than the others, okay?

But it is not that whatever the universal function is there, it is universally for all fluids okay. Because now, clearly we see for the Redlich-Kwong equation this z_c is 0.333 whereas in the case of Van der Waal's equation it is point 0.375, quite different from each other. So, now we have this B = 0.259921 v_c. Now, this A and B, I am trying to convert in terms of T_c and P_c. So, in place of v_c, what I do? I take $\frac{1}{3}\frac{RT_c}{P_c}$ from this Z information. From this z information, I take this one so that I can get B = 0.08664 $\frac{RT_c}{P_c}$.

Then similarly in A also wherever this v_c is there if I substitute $\frac{1}{3}\frac{RT_c}{P_c}$, then I can get this final A is nothing but 0.4274 $\frac{R^2T_c^{5/2}}{P_c}$, this is what I get, right? So, now whatever this A and B that we obtained in terms of T_c and P_c, these 2 from equation number 3 and 4 that we substitute in Redlich-Kwong equation that is $P = \frac{RT}{v-B} - \frac{A}{v(v+B)\sqrt{T}}$.

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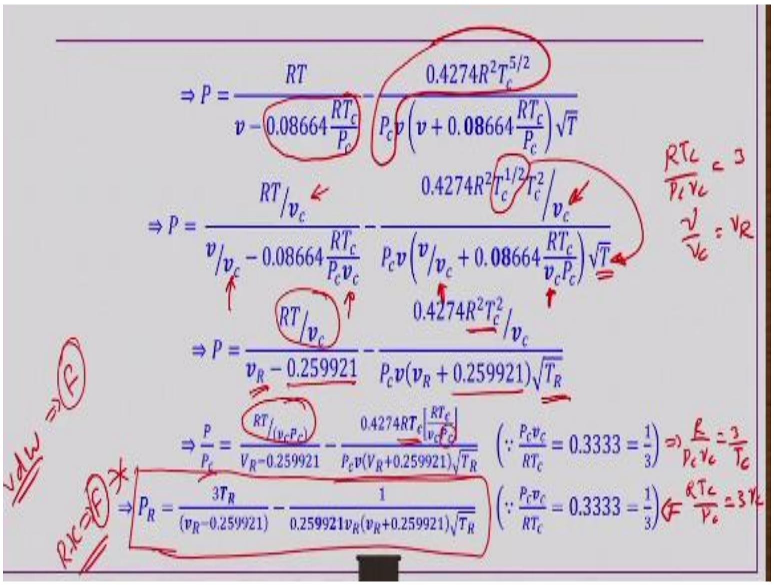

$$\Rightarrow P = \frac{RT}{v - 0.08664\frac{RT_c}{P_c}} - \frac{0.4274R^2T_c^{5/2}}{P_c v\left(v + 0.08664\frac{RT_c}{P_c}\right)\sqrt{T}}$$

$$\Rightarrow P = \frac{RT/v_c}{v/v_c - 0.08664\frac{RT_c}{P_c v_c}} - \frac{0.4274R^2T_c^{1/2}T_c^2/v_c}{P_c v\left(v/v_c + 0.08664\frac{RT_c}{v_c P_c}\right)\sqrt{T}}$$

$$\Rightarrow P = \frac{RT/v_c}{v_R - 0.259921} - \frac{0.4274R^2T_c^2/v_c}{P_c v(v_R + 0.259921)\sqrt{T_R}}$$

$$\Rightarrow \frac{P}{P_c} = \frac{RT/(v_cP_c)}{V_R - 0.259921} - \frac{0.4274RT_c\left[\frac{RT_c}{v_cP_c}\right]}{P_c v(V_R + 0.259921)\sqrt{T_R}} \quad \left(\because \frac{P_cv_c}{RT_c} = 0.3333 = \frac{1}{3}\right) \Rightarrow \frac{R}{P_cv_c} = \frac{3}{T_c}$$

$$\Rightarrow P_R = \frac{3T_R}{(v_R - 0.259921)} - \frac{1}{0.259921v_R(v_R + 0.259921)\sqrt{T_R}} \quad \left(\because \frac{P_cv_c}{RT_c} = 0.3333 = \frac{1}{3}\right) \Leftarrow \frac{RT_c}{v_c} = 3P_c$$

So, in place of A and in place of B, we substitute whatever that we got from equation number 3 and 4, then we get this is nothing but the B and this is nothing but A and this is nothing but B. So that is simply we substituted here A and B and then further we are trying to simplify, okay? So now here in this first term in the RHS, both numerator and denominator I am trying to divide by v_c, okay? So the same thing I am trying to do the second term also here.

So, here v_c, so the v_c, v_c is coming here okay, so that wherever I have $\frac{RT_c}{P_cv_c}$, I can substitute simply 3 or $\frac{P_cv_c}{RT_c}$. I can substitute simply $\frac{1}{3}$ and then wherever I have $\frac{v_c}{v_c}$, I can substitute v_R that is reduced molar volume. So then when I do this is v_R here and then 0.08664 multiplied by 3 is nothing but 0.259921 and then this is as it is and then here this $\frac{v}{v_c}$ is nothing but v_R and then this is nothing but this 0.08664 multiplied by 3 is nothing but 0.259921 and then this square root of whatever T is here. So $\sqrt{T_c}$ whatever here I am dividing with this one here. So, $\frac{\sqrt{T}}{\sqrt{T_c}}$ is nothing but $\sqrt{T_R}$. So here we are remaining only with the T_c^2, it was earlier $T_c^{5/2}$, okay? So now both sides what we do? We divide by P_c. So left hand side $\frac{P}{P_c}$ on here and then right hand side first term $\frac{RT}{v_c}$ I was having earlier, now it is $\frac{RT}{v_c P_c}$, here earlier it was having $\frac{R^2 T_c^2}{v_c}$. So now that I write $\frac{RT}{v_c}$ and then 1 P_c we are dividing now.

So $\frac{RT_c}{P_c v_c}$ one term and then remaining term RT_c is as it is and then rest all other terms are as it is without any change, okay? So, then this $\frac{P}{P_c}$ I can write it as P_R and then this here what we have I can write as $\frac{R}{P_c v_c}$is nothing but $\frac{3}{T_c}$, right? From here $\frac{R}{P_c v_c}$is nothing but $\frac{3}{T_c}$. I can write that is $\frac{RT_c}{P_c v_c}$ is nothing but 3. So, $\frac{R}{P_c v_c}$ if I write $\frac{3}{T_c}$3 by T_c, so $\frac{3}{T_c}$and then there is a T, so $\frac{T}{T_c}$ is nothing but T_R here, rest all other items are as it is and then here also $\frac{RT_c}{P_c}$ we are having.

So then wherever this $\frac{RT_c}{P_c}$ is there that I can write 3 v_c here in this equation R, so $\frac{RT_c}{P_c}$if I write 3 v_c, 3 $\frac{v_c}{v}$, so that that I can write $\frac{v_c}{v}$. So $\frac{v}{v_c}$ I can write here, so then that is coming as v_R and then whatever 3 multiplied by 0.4274 etc is there that we can write it as a kind of 0.259921, yeah this is what we get here now, okay? So, now finally when you do this simplification and rearrange this equation, Redlich-Kwong equation in reduced coordinates is given by this equation.

In the case of Van der Waal's equation, whatever that universal function F is there, so that is different compared to here RK whatever this universal function F it is here. So, we cannot say this F is universal for all the fluids, it is universal for only a class of fluids which are being described by a specific equation of state or specific potential intermolecular potential function, okay? So, this is how we can crosscheck.

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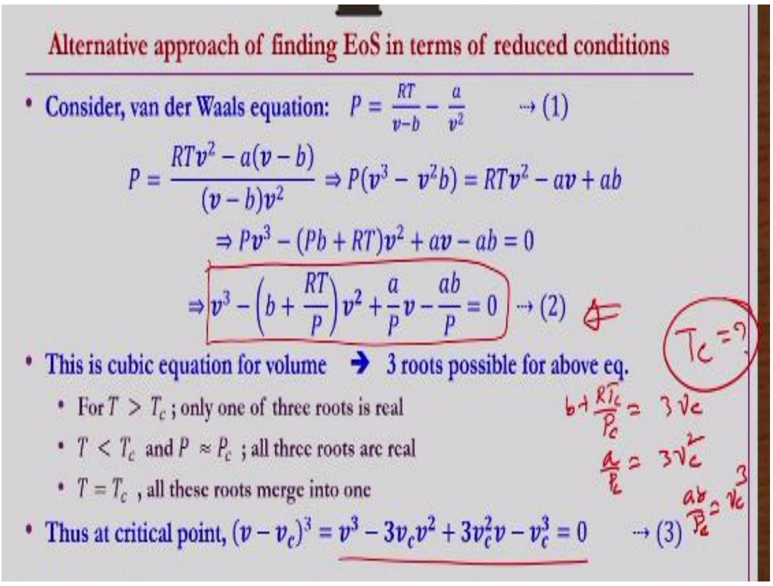

Alternative approach of finding EoS in terms of reduced conditions

- Consider, van der Waals equation: $P = \frac{RT}{v-b} - \frac{a}{v^2}$ ⇢ (1)

$$P = \frac{RTv^2 - a(v-b)}{(v-b)v^2} \Rightarrow P(v^3 - v^2 b) = RTv^2 - av + ab$$

$$\Rightarrow Pv^3 - (Pb + RT)v^2 + av - ab = 0$$

$$\Rightarrow \boxed{v^3 - \left(b + \frac{RT}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0} \dashrightarrow (2)$$

$\boxed{T_c = ?}$

- This is cubic equation for volume ➔ 3 roots possible for above eq.
  - For $T > T_c$; only one of three roots is real
  - $T < T_c$ and $P \approx P_c$; all three roots are real
  - $T = T_c$, all these roots merge into one
- Thus at critical point, $(v - v_c)^3 = \underline{v^3 - 3v_c v^2 + 3v_c^2 v - v_c^3 = 0}$ ⇢ (3)

$b + \frac{RT_c}{P_c} = 3v_c$

$\frac{a}{P_c} = 3v_c^2$

$\frac{ab}{P_c} = v_c^3$

So, but there is a kind of alternative approach of finding this equation of states in terms of reduced conditions or reduced coordinates that is what we are going to see now. So, what we have, we take the same Van der Waal's equation P = $\frac{RT}{v-b} - \frac{a}{v^2}$ as it is, right? But this equation we write in kind of a cubic equation form. So, then we can expand this equation, so that we have this P = $\frac{RTv^2 - a(v-b)}{(v-b)v^2}$. Further if you simplify, then you get P$(v^3 - v^2 b)$ = RT v^2- av + ab.

And this equation further you can write Pv^3- (Pb + RT) v^2+ a v - ab. Now divide by P this so that you have $v^3 - \left(b - \frac{RT}{P}\right) v^2 + \frac{a}{P}\ v - \ \frac{ab}{P}$ = 0. So now this is a cubic equation in terms of v, right? So 3 roots are possible for that above equations. So what could be the nature of these 3 roots that depends on what is the value of T_c, whether the temperature at which we are finding is < T_c or > T_c or = T_c, right?

For the case of temperature greater than critical temperature, only one of the 3 roots is real or remaining 2 roots are imaginary. If the T < T_c and then P ≈ Pc, all 3 roots are real, but when T = T_c all these roots merge into one that is only 1 real root will be there, right? So, that is we can right at this critical point, $(v - v_c)^3$ = 0 because if all 3 roots are merging to the same point, then at that point whatever the molar volume is there that should be the kind of the root. So, that is nothing but v_c.

So, v_c should be that one single root. So, we can write in terms of cubic equation form $(v - v_c)^3$ = 0 and then when you expand this equation then you have $v^3 - 3v_c v^2 + 3\,v_c^2\ v\ \ - v_c^2$.

Now, this is at critical conditions, but if this equation also if you take at critical conditions and then compare this equation number 2 and 3, then you will get b + $\frac{RT}{P}$ = 3 v_c, but this is now at critical conditions comparing the cube terms, square terms, and then power one term, constant terms like that.

Then a by P should be equal to 3 v_c^2 and then this P is it critical conditions. Then finally, $\frac{ab}{P}$ = $v_c^3$and then this P is nothing but P_c because the comparison we are doing at critical condition.

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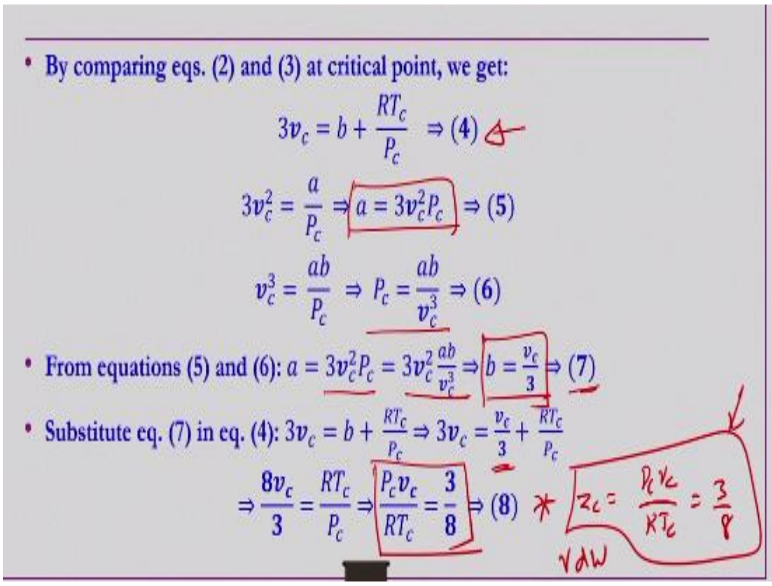

- By comparing eqs. (2) and (3) at critical point, we get:

$$3v_c = b + \frac{RT_c}{P_c} \Rightarrow (4)$$

$$3v_c^2 = \frac{a}{P_c} \Rightarrow \boxed{a = 3v_c^2 P_c} \Rightarrow (5)$$

$$v_c^3 = \frac{ab}{P_c} \Rightarrow \underline{P_c = \frac{ab}{v_c^3}} \Rightarrow (6)$$

- From equations (5) and (6): $a = \underline{3v_c^2 P_c} = \underline{3v_c^2 \frac{ab}{v_c^3}} \Rightarrow \boxed{b = \frac{v_c}{3}} \Rightarrow \underline{(7)}$
- Substitute eq. (7) in eq. (4): $3v_c = b + \frac{RT_c}{P_c} \Rightarrow 3v_c = \frac{v_c}{3} + \frac{RT_c}{P_c}$

$$\Rightarrow \frac{8v_c}{3} = \frac{RT_c}{P_c} \Rightarrow \boxed{\frac{P_c v_c}{RT_c} = \frac{3}{8}} \Rightarrow (8) \; * \; \boxed{z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8}}$$

VdW

So, when we do this thing then we have 3 v_c = b + $\frac{RT_c}{P_c}$ as I mentioned and then 3 v_c^2 = $\frac{a}{P_c}$that this is a is nothing but $v_c^2$$P_c$ and then from the third term v_c^3= $\frac{ab}{P_c}$ that means P_c = $\frac{ab}{v_c^3}$. So, now here what we do in this equation number 5 wherever a = 3 $v_c^2$$P_c$ is there, in place of P_c we are writing $\frac{ab}{v_c^3}$, so that b = $\frac{v_c}{3}$ we can get. So, a we are having and then b also we are having.

So now this equation number 7 and if you substitute here, then equation number 4 that is 3 v_c = b + $\frac{RT_c}{P_c}$ and then in place of b we are writing $\frac{v_c}{3}$ and then if you rearrange this, you will get 8 $\frac{v_c}{3}$= $\frac{RT_c}{P_c}$. That means $\frac{P_c v_c}{RT_c}$ = $\frac{3}{8}$. It is same as previous approach whatever we have obtained. In the previous obtained approach also z_c = $\frac{P_c v_c}{RT_c}$ = $\frac{3}{8}$ we got for the same Van der Waal's equation of state, okay? So this we got by applying $\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$. Then we got the same expression here. So, now what we do?

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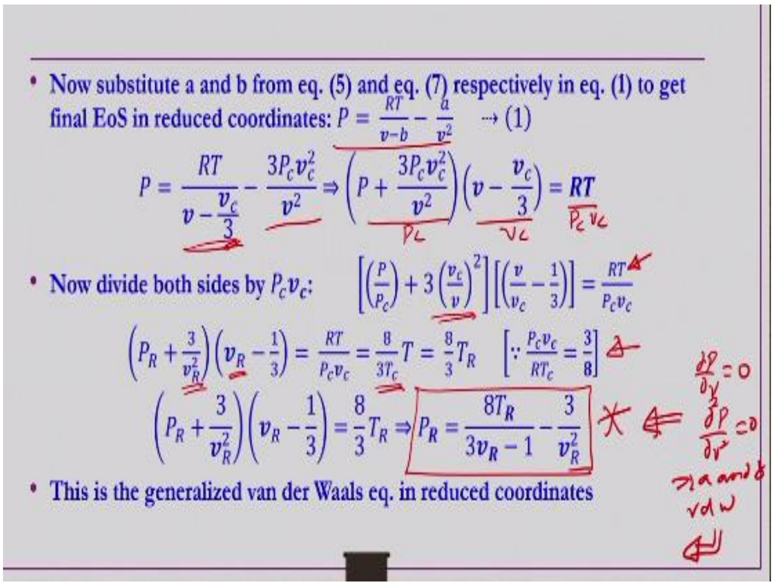

- Now substitute a and b from eq. (5) and eq. (7) respectively in eq. (1) to get final EoS in reduced coordinates: $P = \frac{RT}{v-b} - \frac{a}{v^2} \dashrightarrow (1)$

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

- Now divide both sides by $P_c v_c$: $\left[\left(\frac{P}{P_c}\right) + 3\left(\frac{v_c}{v}\right)^2\right]\left[\left(\frac{v}{v_c} - \frac{1}{3}\right)\right] = \frac{RT}{P_c v_c}$

$$\left(P_R + \frac{3}{v_R^2}\right)\left(v_R - \frac{1}{3}\right) = \frac{RT}{P_c v_c} = \frac{8}{3T_c}T = \frac{8}{3}T_R \quad \left[\because \frac{P_c v_c}{RT_c} = \frac{3}{8}\right]$$

$$\left(P_R + \frac{3}{v_R^2}\right)\left(v_R - \frac{1}{3}\right) = \frac{8}{3}T_R \Rightarrow \boxed{P_R = \frac{8T_R}{3v_R - 1} - \frac{3}{v_R^2}}$$

- This is the generalized van der Waals eq. in reduced coordinates

We can substitute whatever the a and b constants that obtained from equation 5 and 7 in this particular equation. So, when we substitute this one, a is nothing but 3 P_c v_c^2 and b is nothing but $\frac{v_c}{3}$ that we substituted and now what we have taken this 3 $\frac{P_c v_c^2}{v^2}$ I have taken to the left hand side and then whatever this $\frac{v - v_c}{3}$ that also have taken to the left hand side so that in this right hand side I have only RT. Now this equation both sides I am dividing by P_c v_c.

So, this P_c first term I am dividing by P_c, so $\frac{P}{P_c}$ + 3 $\frac{P_c v_c^2}{P_c v^2}$, P_c P_c got cancelled, so $3\left(\frac{v_c}{v}\right)^2$. And then here this second term I am dividing by v_c. So we $\frac{v}{v_c}$ - $\frac{1}{3}$, right hand side $\frac{RT}{P_c v_c}$ that we are having, right? So now, wherever this $\frac{P}{P_c}$ is there, we can write P_R and $\frac{v}{v_c}$ we can write v_R and then $\frac{T}{T_c}$ we can write T_R, but here what we have, this T, but we cannot write T_R here right now. So what we do for next step, you know in place of $\frac{R}{P_c v_c}$ I can write $\frac{8}{3}$ T_c.

So from this expression $z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8}$. So in place of $\frac{R}{P_c v_c}$ I can write $\frac{8}{3}$ T_c. So $\frac{8}{3}$ T_R I can write in the right hand side because $\frac{T}{T_c}$ is nothing but T_R. So now, this equation further I can write like this form wherever this $\frac{v}{v_c}$, v_R I am writing and then wherever $\frac{T}{T_c}$, T_R I am writing and wherever

$\frac{P}{P_c}$ I am writing P_R. So, this is what we get this equation. So, further if you rearrange this equation like in the given form P = $\frac{RT}{v-b}$ - $\frac{a}{v^2}$ form we are writing.

That is P_R = $\frac{8T_R}{3v_R-1}$ - $\frac{3}{v_R^2}$. So, we can see the same equation we are getting by this approach also. When we apply $\left(\frac{\partial P}{\partial v}\right)_T$ = 0 and d$\left(\frac{\partial^2 P}{\partial v^2}\right)_T$ = 0 and then found a and b and then we substituted in Van der Waal's equation of state. So then whatever that final Van der Waal's equation of state in reduced coordinate that we got that is same as this one.

So either of the approaches we can use to find out what are those constant associated with the equations of state and then once finding those constants in terms of critical temperature, critical pressure and critical molar volume and then substituting them in the equations of state, so then we can get those equation of states in reduced coordinates like this. However, this approach is valid only for the cases where the equations of states are having only 2 constants. So, this is generalized Van der Waal's equation in reduced coordinates.

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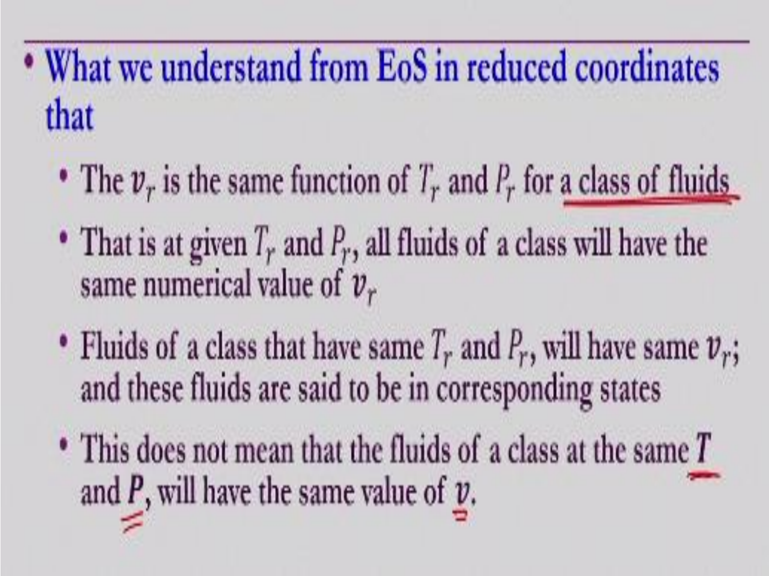

- What we understand from EoS in reduced coordinates that
  - The v_r is the same function of T_r and P_r for a class of fluids
  - That is at given T_r and P_r, all fluids of a class will have the same numerical value of v_r
  - Fluids of a class that have same T_r and P_r, will have same v_r; and these fluids are said to be in corresponding states
  - This does not mean that the fluids of a class at the same T and P, will have the same value of v.

So, what we understand from equation of state in reduced coordinates that we have taken for 2 cases that v_r is the same function of T_r and P_r for a class of fluids. In the sense those fluids obeying Van der Waal's equation of state. So, there will be only one particular v_r function would be there. The class of fluids which are obeying Redlich-Kwong equation, there would be different function, okay? That is at a given T_r and P_r all the fluids of a class will have the same numerical value of v_r.

Fluids of a class that have the same T_r and P_r will have the same v_r and these fluids are said to be in corresponding states. This does not mean that the fluids of a class at the same T and P will have the same v. So, it is not true for the operating temperature or pressure conditions, this applied only at the reduced to temperature and pressure conditions, okay? So, now what we do? We take a few example problems in order to understand how to make use of this corresponding states theory.

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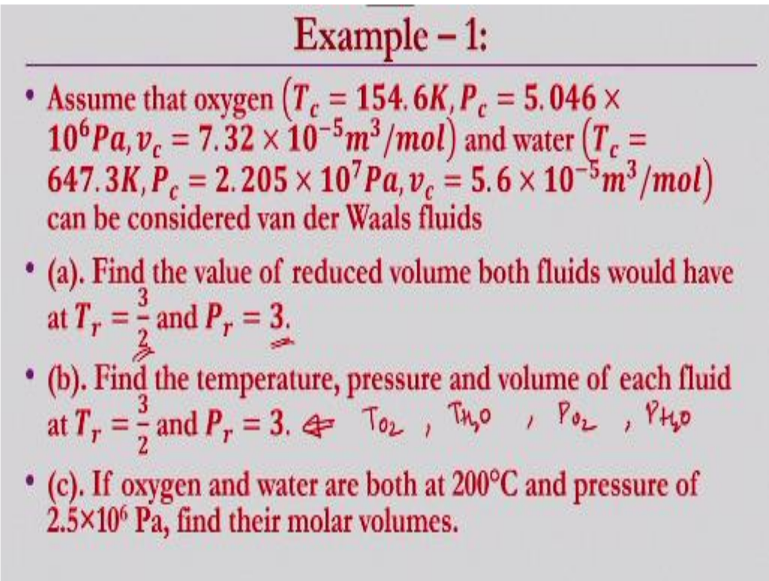

Example – 1:

- Assume that oxygen $(T_c = 154.6K, P_c = 5.046 \times 10^6 Pa, v_c = 7.32 \times 10^{-5} m^3/mol)$ and water $(T_c = 647.3K, P_c = 2.205 \times 10^7 Pa, v_c = 5.6 \times 10^{-5} m^3/mol)$ can be considered van der Waals fluids
- (a). Find the value of reduced volume both fluids would have at $T_r = \frac{3}{2}$ and $P_r = 3$.
- (b). Find the temperature, pressure and volume of each fluid at $T_r = \frac{3}{2}$ and $P_r = 3$. $\leftarrow$ T_{O_2} , T_{H_2O} , P_{O_2} , P_{H_2O}
- (c). If oxygen and water are both at 200°C and pressure of 2.5×10^6 Pa, find their molar volumes.

Example 1. Assume that oxygen of T_c = 154.6 K, P_c = 5.046 * 10^6Pascal and then v_c = 7.32 * 10^{-5} meter cube per mole and water with T_c = 647.3 K, P_c = 2.205 * 10^7Pascals and then v_c = 5.6 * 10^{-5}meter cube per mole can be considered as Van der Waal's fluids, okay? Oxygen and water that T_c, P_c, v_c informations are given and then it is mentioned that Van der Waal's equation can be valid for these fluids, oxygen and water. Find the value of reduced volume that is v_r for both would have at $T_r = \frac{3}{2}$ and P_r = 3.

What does it mean by? Because the T_c, P_c are different for both the fluids. If the T_r and P_r are same for the fluid that means the operating conditions like T and P are different for either of the cases, right? So, how different? It is different such a way that for one case certain temperature, another case or for one fluid certain temperature and another fluid certain other temperature would be there, but for both the case when we do $\frac{T}{T_c}$ that is you find out T_r, $T_r = \frac{T}{T_c}$.

Then you will get $\frac{3}{2}$ at such conditions, same about the pressure also, okay? So, if the reduced temperature and pressure are same for a given group of fluids, then reduced volume should also be same. So, we will be getting only one v_r value for both the fluids. Then second part is find the temperature, pressure, and volume of each fluid at $T_r = \frac{3}{2}$ and $P_r = 3$. That is indirectly it says that if you wanted to maintain certain T_r, P_r for body fluids, what should be the TO_2, what should be the TH_2O and then what should be PO_2 and then what should PH_2O for these 2 fluids.

Obviously, they are going to be different, those things we have to find out and then if oxygen and water are both at 200 degree centigrade and pressure of $2.5 * 10^6$ Pascal find their molar volumes? These are 3 questions.

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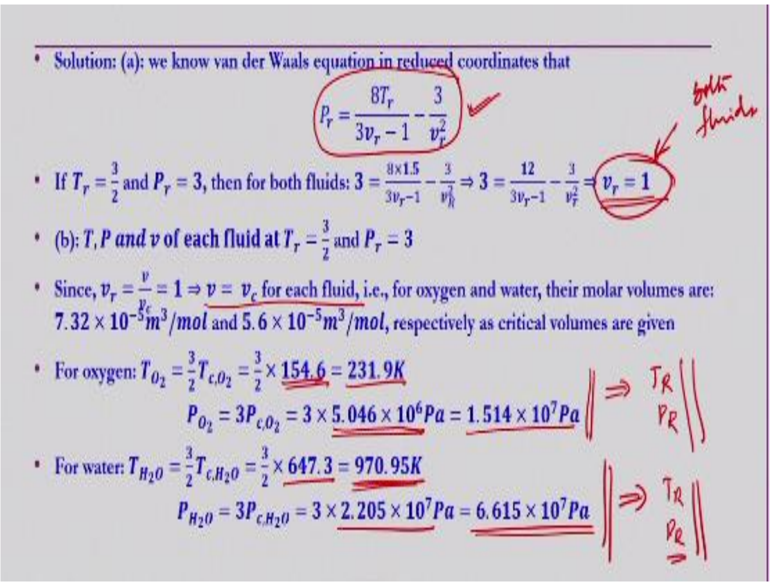

- Solution: (a): we know van der Waals equation in reduced coordinates that

$$\boxed{P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}} \checkmark$$

both fluids

- If $T_r = \frac{3}{2}$ and $P_r = 3$, then for both fluids: $3 = \frac{8\times1.5}{3v_r-1} - \frac{3}{v_R^2} \Rightarrow 3 = \frac{12}{3v_r-1} - \frac{3}{v_r^2} \Rightarrow \boxed{v_r = 1}$
- (b): T, P and v of each fluid at $T_r = \frac{3}{2}$ and $P_r = 3$
- Since, $v_r = \frac{v}{v_c} = 1 \Rightarrow \underline{v = v_c \text{ for each fluid}}$, i.e., for oxygen and water, their molar volumes are: $7.32 \times 10^{-5} m^3/mol$ and $5.6 \times 10^{-5} m^3/mol$, respectively as critical volumes are given
- For oxygen: $T_{O_2} = \frac{3}{2}T_{c,O_2} = \frac{3}{2} \times \underline{154.6} = \underline{231.9 K}$

$$P_{O_2} = 3P_{c,O_2} = 3 \times \underline{5.046 \times 10^6 Pa} = \underline{1.514 \times 10^7 Pa} \Rightarrow T_R, P_R$$

- For water: $T_{H_2O} = \frac{3}{2}T_{c,H_2O} = \frac{3}{2} \times \underline{647.3} = \underline{970.95 K}$

$$P_{H_2O} = 3P_{c,H_2O} = 3 \times \underline{2.205 \times 10^7 Pa} = \underline{6.615 \times 10^7 Pa} \Rightarrow T_R, P_R$$

So, we know Van der Waal's equation in reduced coordinates that $P_r = \frac{8T_r}{3v_r-1} - \frac{3}{v_r^2}$, right? Then if $T_r = \frac{3}{2}$, $P_r = 3$, then for both fluids we can find v_r by substituting simply T_r and P_r values in this expression. Substitute T_r and P_r in this expression and then simplify, so then you can find out v_r is nothing but 1. This is the first part and this $v_r = 1$ for both fluids, okay? Because this equation is valid for both the fluids. Now, second part is finding our T, P, and v for each fluid if the T_r is $\frac{3}{2}$ and P_r is 3.

So, let us start doing v_r. Since $v_r = 1$, v_r is nothing but $\frac{v}{v_c}$, right? So, that means, $v = v_c$ for each fluid because v_r is nothing but that is equal to 1 that we found in the first part of the problem.

If $v_r = 1$ that means $v = v_c$. That means, whatever the critical volumes are given for the oxygen and then water in the problem statement, they are going to be their molar volumes as well. They are going to be their molar volumes as well.

So that means the temperature, pressure conditions are such a way that the molar volume of these fluids are equals to the critical volume of these fluids, okay? And that is about v. Now T, for oxygen you know it is given that $T_r = \frac{3}{2}$. That means $\frac{T}{T_c} = \frac{3}{2}$. So $T = \frac{3}{2} T_c$. For the case of oxygen T_c is 154.6. So that means, T is going to be 154.6 multiplied by $\frac{3}{2}$that is 231.9 K, right? This is how we have to find out. Then PO_2 that is the pressure of oxygen, P_r is given as 3 that means $\frac{P}{P_c} = 3$.

That means $P = 3 P_c$. So, 3 multiplied by P_c for oxygen is given $5.046 * 10^6$. So, it is coming out to be $1.514 * 10^7$ Pascal, right? Similarly, we can do for the water. For the water, T_c is given a 647.3 and then if you multiply this one by 3.2, then you will get T of water that is 970.95 Kelvin, right? And then similarly P of water is going to be 3 into critical pressure of water. So, 3 and then critical pressure of water is given this one, so $6.615 * 10^7$ Pascal is going to be water.

So, what does it mean? When the temperature for oxygen is 232 Kelvin approximately and then pressure for oxygen is approximately $1.514 * 10^7$Pascal, then whatever the T_r and then P_r are there, okay? The same T_r, P_r we can get for the water when the temperature of water is 971 Kelvin approximately and then pressure $6.615 * 10^7$Pascal, then whatever the T_r and P_r, then they will be same thing. So, for reduced coordinate, in some books subscripts r people use, some books we use R, anything is fine actually.

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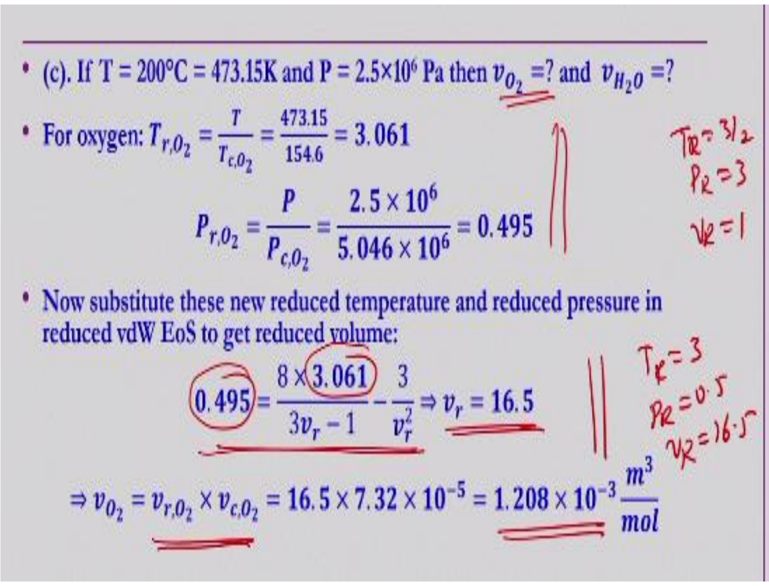

- (c). If T = 200°C = 473.15K and P = 2.5×10⁶ Pa then $\underline{v_{O_2}}$ =? and v_{H_2O} =?
- For oxygen: $T_{r,O_2} = \frac{T}{T_{c,O_2}} = \frac{473.15}{154.6} = 3.061$

$$P_{r,O_2} = \frac{P}{P_{c,O_2}} = \frac{2.5\times10^6}{5.046\times10^6} = 0.495$$

- Now substitute these new reduced temperature and reduced pressure in reduced vdW EoS to get reduced volume:

$$\underline{\boxed{0.495} = \frac{8\times \boxed{3.061}}{3v_r-1} - \frac{3}{v_r^2}} \Rightarrow \underline{v_r = 16.5}$$

$$\Rightarrow \underline{v_{O_2}} = v_{r,O_2}\times v_{c,O_2} = 16.5\times7.32\times10^{-5} = \underline{1.208\times10^{-3}}\,\frac{m^3}{mol}$$

$T_R = 3/2$
$P_R = 3$
$V_R = 1$

$T_R = 3$
$P_R = 0.5$
$V_R = 16.5$

If T = 200 degree centigrade and then P = 2.5 *10^6Pascal, then what is the molar volume of oxygen and water that is the third part of the question. So, here for oxygen T_r we have to find out, right? T_r is nothing but $\frac{T}{T_c}$. For oxygen if you do that is coming out to be 3.061 and then P_r O_2 also we have to find out, that is $\frac{P}{P_c}$for the O_2, then that comes out to be 0.495. So, once you know T_r, P_r, you can find out the v_r because if you wanted to find out v you have to know v_c.

You have to know v_r because v_c is only given, so v_r if you know, then from v_c v_r these 2 information, you can find out v molar volume, okay? So that is the reason we are doing this one because we know equation in terms of T_r, P_r, and v_r. So, now we substitute them in reduced coordinate equation of state. That is P = $\frac{8T_r}{3v_r-1}$ - $\frac{3}{v_r^2}$, this is what we are having. So here T_r is nothing but 3.061, P_r is nothing but 0.495. So, now what we found? We can find this v_r = 16.5.

In the previous case when $T_r = \frac{3}{2}$ and P_r = 3, then we found v_r = 1. Now in this case when T_r = 3 and then P_r = 0.5, then v_r we are getting approximately 16.5, okay? So, if v_r is known, so v_r multiplied by v_c if you do, you can get v. So, this is the molar volume of the oxygen. Similarly, we can do for the water also.

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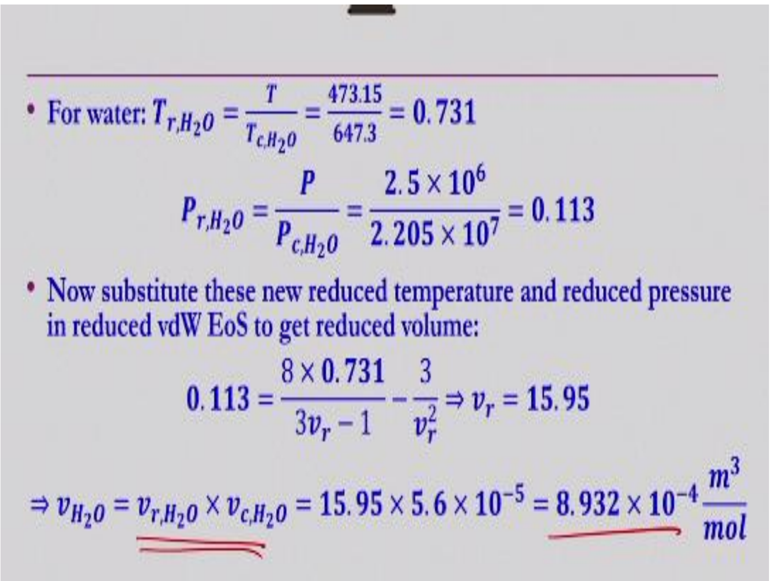

- For water: $T_{r,H_2O} = \frac{T}{T_{c,H_2O}} = \frac{473.15}{647.3} = 0.731$

$$P_{r,H_2O} = \frac{P}{P_{c,H_2O}} = \frac{2.5 \times 10^6}{2.205 \times 10^7} = 0.113$$

- Now substitute these new reduced temperature and reduced pressure in reduced vdW EoS to get reduced volume:

$$0.113 = \frac{8 \times 0.731}{3v_r - 1} - \frac{3}{v_r^2} \Rightarrow v_r = 15.95$$

$$\Rightarrow v_{H_2O} = v_{r,H_2O} \times v_{c,H_2O} = 15.95 \times 5.6 \times 10^{-5} = 8.932 \times 10^{-4} \frac{m^3}{mol}$$

So, for water T_r if you similarly find out it comes out to be 0.731 and then P_r it comes out to be 0.113 and the when you substitute this T_r, P_r in reduced Van der Waal's equation of state, then you get $v_r = 15.95$. So, v_r and v_c are known now for this temperature and pressure conditions, v_r is known, so v_c is given. So you can get v molar volume of water as simply by multiplying this v_r and v_c that is $8.932 * 10^{-4}$meter cube per mole. So, this is one of the advantages of having the equations of state in according to corresponding sates theory or in reduced coordinates.

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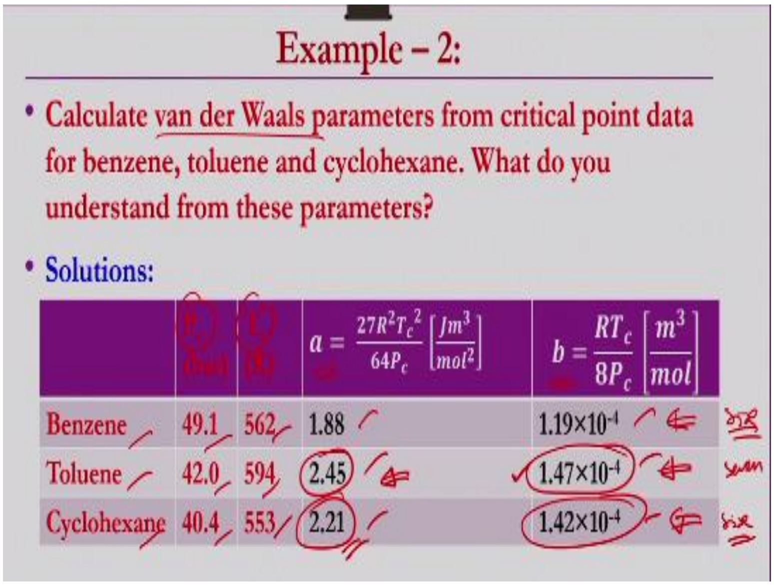

Example – 2:

- Calculate van der Waals parameters from critical point data for benzene, toluene and cyclohexane. What do you understand from these parameters?
- Solutions:

	P_c (bar)	T_c (K)	$a = \frac{27R^2T_c^2}{64P_c} \left[\frac{Jm^3}{mol^2}\right]$	$b = \frac{RT_c}{8P_c} \left[\frac{m^3}{mol}\right]$
Benzene	49.1	562	1.88	1.19×10^{-4}
Toluene	42.0	594	2.45	1.47×10^{-4}
Cyclohexane	40.4	553	2.21	1.42×10^{-4}

So, we take another example. Calculate Van der Waal's parameters from critical point data for benzene, toluene, and cyclohexane and what do you understand from these parameters? For benzene, toluene, cyclohexane P_c and T_c are given or they are available from standard books. Then this Van der Waal's constants a and b we have already derived as you know $a = \frac{27R^2T_c^2}{64P_c}$

and then b we have already found it as $\frac{RT_c}{8P_c}$. So, now when you substitute this T_c and P_c information here for each case, you can get a and b constants for 3 fluids.

What we can see here toluene is having the highest value of a as well as the highest value of the b, okay? So then, next one is that cyclohexane is having second highest value of a and then second highest value of b as well, then finally the benzene. Why it is happening? What does it mean? So actually toluene is having 7 C atoms, obviously it is going to be having the higher b value because b value is something related to the size of the molecule, whereas this benzene and cyclohexane they are having 6 carbon atoms here whereas the toluene is having 7.

So, because of that one it is going to be bigger one. If here both 6, here also both 6 because benzene and cyclohexane 6, 6 carbon atoms are there. So, then why these 2 values are different from each other. Benzene is having smaller b value compared to this thing cyclohexane because benzene is having a compact packed kind of resonance structure because of that one it is having smaller b value. Then coming to the attractive forces also, since the 7 carbon atoms are there, so then it is obviously possible that polarizability is going to be higher.

So, because of that one, the attractive dispersion forces are going to be strong in the case of toluene compared to the other 2 components. Then in the next case, cyclohexane is the second highest because in the case of cyclohexane, the electrons are much more free compared to the compact resonance structure of the benzene, because of that one also the cyclohexane is having larger a value compared to the benzene, okay?

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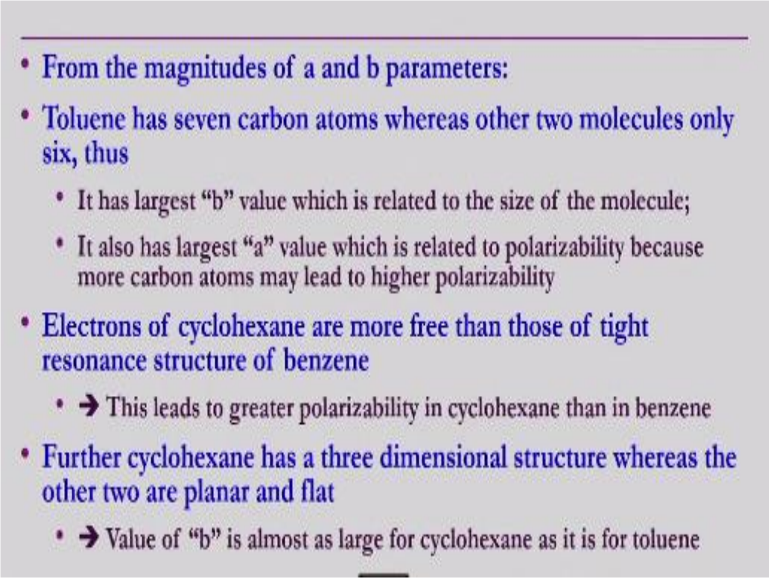

- From the magnitudes of a and b parameters:
- Toluene has seven carbon atoms whereas other two molecules only six, thus
  - It has largest "b" value which is related to the size of the molecule;
  - It also has largest "a" value which is related to polarizability because more carbon atoms may lead to higher polarizability
- Electrons of cyclohexane are more free than those of tight resonance structure of benzene
  - → This leads to greater polarizability in cyclohexane than in benzene
- Further cyclohexane has a three dimensional structure whereas the other two are planar and flat
  - → Value of "b" is almost as large for cyclohexane as it is for toluene

That is the information. The discussion is presented as a kind of notes here.

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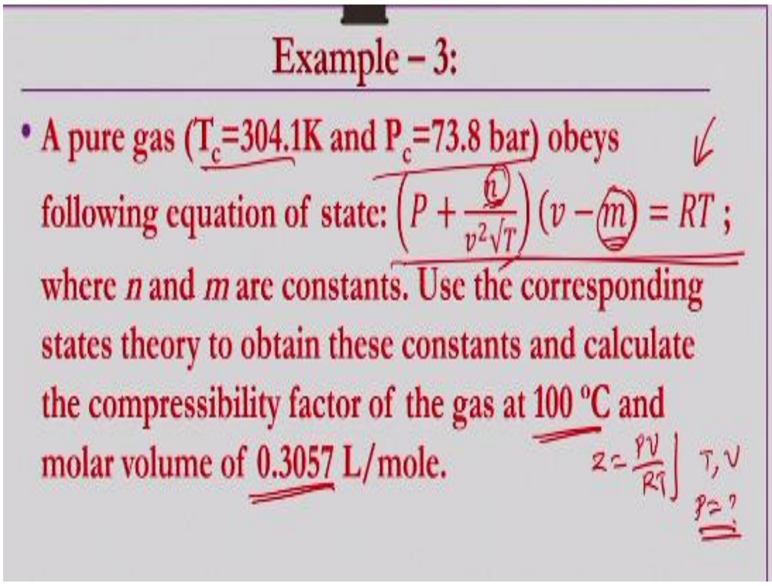

Example – 3:

- A pure gas (T_c=304.1K and P_c=73.8 bar) obeys following equation of state: $\left(P+\frac{\textcircled{n}}{v^2\sqrt{T}}\right)(v-\textcircled{m})=RT$; where *n* and *m* are constants. Use the corresponding states theory to obtain these constants and calculate the compressibility factor of the gas at 100 °C and molar volume of 0.3057 L/mole.

$z = \frac{Pv}{RT}\Big|_{T,v}$

$P = ?$

Now, we take another example. A pure gas is found to be obeying this equation of state, okay? And then for this equation of state T_c and then P_c are given. This constant n, m are given rather than writing a and b, it is written as n and m now, that is the only different. Now, here we have to find out what is z that is $\frac{Pv}{RT}$ at 100 degrees centigrade and then when v = 0.3057 liters per mole, right? So, simply you can actually 2 are given, temperature is given, v is given, so R is anyway constant.

If you can find out P, then you can substitute here z = $\frac{Pv}{RT}$ and then find it out and then that you can do by simply substituting T and v in this equation of state provided these 2 constants are known, provided these 2 constants n and m are known, but they are not known. However, T_c, P_c information is given for this equation of state and then we know that using the corresponding states theory, we can find out the constants associated with the equation of state, right, in terms of critical conditions like T_c, P_c, v_c.

So, we can apply the critical, we can apply the theory of corresponding states and then find out first this n, m values and then substitute them here and then find out the P and then simply find out what is compressibility factor.

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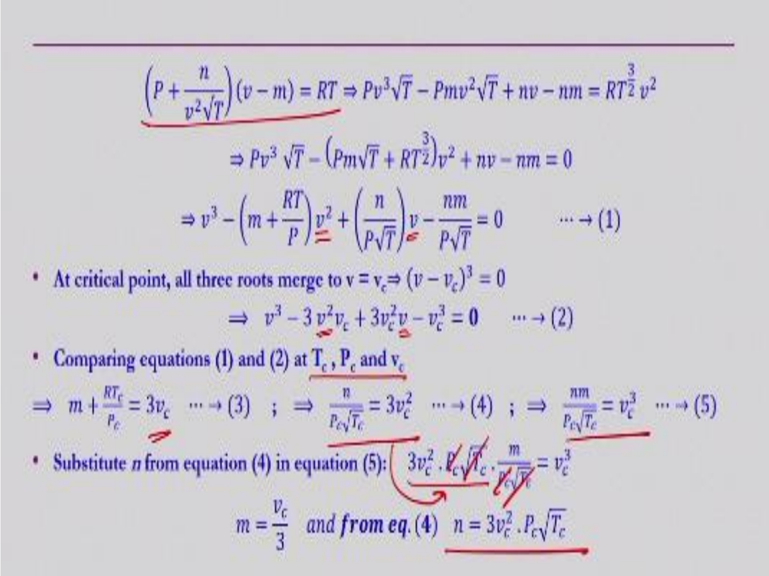

$$\underline{\left(P+\frac{n}{v^2\sqrt{T}}\right)(v-m)=RT} \Rightarrow Pv^3\sqrt{T}-Pmv^2\sqrt{T}+nv-nm=RT^{\frac{3}{2}}v^2$$

$$\Rightarrow Pv^3\sqrt{T}-\left(Pm\sqrt{T}+RT^{\frac{3}{2}}\right)v^2+nv-nm=0$$

$$\Rightarrow v^3-\left(m+\frac{RT}{P}\right)\underline{\underline{v^2}}+\left(\frac{n}{P\sqrt{T}}\right)v-\frac{nm}{P\sqrt{T}}=0 \qquad \cdots\to(1)$$

- At critical point, all three roots merge to v = $v_c \Rightarrow (v-v_c)^3=0$

$$\Rightarrow v^3-3v^2v_c+3v_c^2v-v_c^3=0 \qquad \cdots\to(2)$$

- Comparing equations (1) and (2) at $\underline{T_c, P_c \text{ and } v_c}$

$$\Rightarrow m+\frac{RT_c}{P_c}=3v_c \quad \cdots\to(3) \quad ; \Rightarrow \underline{\frac{n}{P_c\sqrt{T_c}}=3v_c^2} \quad \cdots\to(4) \quad ; \Rightarrow \underline{\frac{nm}{P_c\sqrt{T_c}}=v_c^3} \quad \cdots\to(5)$$

- Substitute n from equation (4) in equation (5): $3v_c^2\cdot\cancel{P_c\sqrt{T_c}}\cdot\frac{m}{\cancel{P_c\sqrt{T_c}}}=v_c^3$

$$m=\frac{v_c}{3} \quad \text{and from eq.}(4) \quad \underline{n=3v_c^2\cdot P_c\sqrt{T_c}}$$

So, first what we do? This equation of state whatever it is given, so that we expand and then write it in terms of cubic equation in terms of molar volume. So, then we have this equation and then we know at the critical point, v = v_c is the root, all 3 roots are merged to the same point one single point and at that point v = v_c. So, then we can write $(v-v_c)^3 = 0$ and then when you expand this one, you will get this equation. Now, if you compare this equation 1 and 2, but at T_c, P_c, v_c.

Then here if you see the multiplication factors of v square here, here, then we can have 3 v_c = m + $\frac{RT}{P}$, but this is a T_c, P_c, v_c. So, m + $\frac{RT_c}{P_c}$. So that is 3 v_c = m + $\frac{RT_c}{P_c}$. Similarly, when you compare the factors of v, then we can have $3v_c^2 = \frac{n}{P_c\sqrt{T_c}}$ and then similarly $v_c^3 = \frac{nm}{P_c\sqrt{T_c}}$. So from here, we get the n values straightforward that is n = 3 v_c^2 P_c $\sqrt{T_c}$, right? That if you substitute here in the equation number 5, equation number 5 is $\frac{nm}{P_c\sqrt{T_c}} = v_c^3$.

In place of n, we can write 3 v_c^2 P$_c$ $\sqrt{T_c}$ from equation number 4 and then $\frac{m}{P_c\sqrt{T_c}}$ = v_c^3. So, this P$_c$ $\sqrt{T_c}$ and P$_c$ $\sqrt{T_c}$ is cancelled out. So, then you get m = $\frac{v_c}{3}$and n = 3 v_c^2 P$_c$ $\sqrt{T_c}$ from equation number 4.

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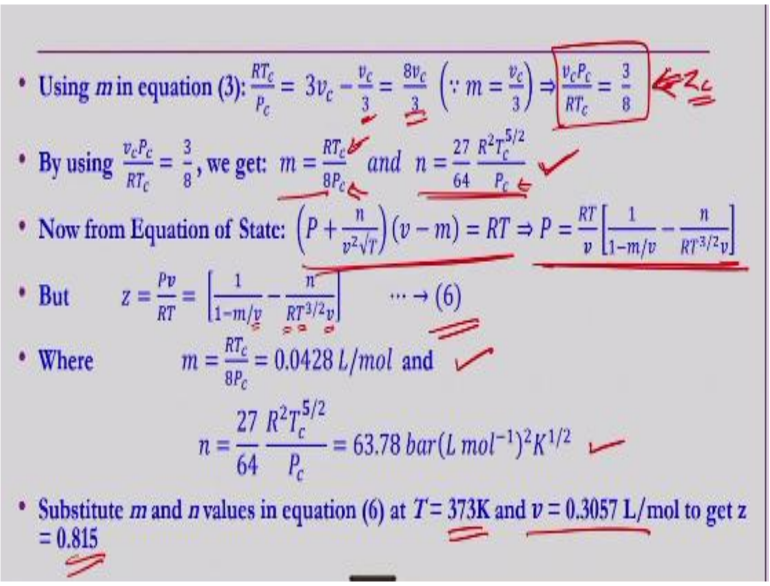

- Using m in equation (3): $\frac{RT_c}{P_c} = 3v_c - \frac{v_c}{3} = \frac{8v_c}{3}$ $\left(\because m = \frac{v_c}{3}\right) \Rightarrow \boxed{\frac{v_cP_c}{RT_c} = \frac{3}{8}}$ $\Leftarrow z_c$
- By using $\frac{v_cP_c}{RT_c} = \frac{3}{8}$, we get: $m = \frac{RT_c}{8P_c}$ and $n = \frac{27}{64}\frac{R^2T_c^{5/2}}{P_c}$
- Now from Equation of State: $\left(P + \frac{n}{v^2\sqrt{T}}\right)(v - m) = RT \Rightarrow P = \frac{RT}{v}\left[\frac{1}{1-m/v} - \frac{n}{RT^{3/2}v}\right]$
- But $z = \frac{Pv}{RT} = \left[\frac{1}{1-m/v} - \frac{n}{RT^{3/2}v}\right]$ $\cdots \rightarrow (6)$
- Where $m = \frac{RT_c}{8P_c} = 0.0428\ L/mol$ and

  $n = \frac{27}{64}\frac{R^2T_c^{5/2}}{P_c} = 63.78\ bar(L\ mol^{-1})^2K^{1/2}$
- Substitute m and n values in equation (6) at T = 373K and v = 0.3057 L/mol to get z = 0.815

So, now this m if you substitute in equation number 3, equation number 3 is nothing but m + $\frac{RT_c}{P_c}$ = 3 v$_c$, m is nothing but $\frac{v_c}{3}$. So, $\frac{RT_c}{P_c}$ = 3 v$_c$ - m, in place of m, $\frac{v_c}{3}$. So, that it is nothing $\frac{8v_c}{3}$. So, then if you rearrange this one you get $\frac{P_cv_c}{RT_c}$ = $\frac{3}{8}$. So, you have the information about z$_c$, but we do not want, the question is the compressibility at certain different temperature and then volume, it is not at the critical conditions, okay?

At critical conditions, we know anyway it is constant and then that constant is $\frac{3}{8}$ for equations which are in the similar form as van der Waals equation of state. So, now we use this $\frac{P_cv_c}{RT_c}$ = $\frac{3}{8}$ to get m and n values in terms of T$_c$ and P$_c$ because what is v$_c$ is not given, it is not given in the problem statement, problem statement P$_c$ and T$_c$ are given. So, this m and n values whatever the constant that you have found they have to be in terms of T$_c$ and P$_c$.

So, in place of wherever the v$_c$ is there, you can write in place of v$_c$, $\frac{3}{8}\frac{RT_c}{P_c}$, then you can get m and n values as given like this. Now, when you substitute this new m and n values in this equation of state here and then rearrange, so then you will have this equation. Rearranging way so that we can write $\frac{Pv}{RT}$ one side. So, then $\frac{Pv}{RT}$ that is nothing but z = $\frac{1}{1-\frac{m}{v}} - \frac{n}{RT^{1.5}v}$. So, now in this equation T is given, v is given, R is constant, right? So, only m and n and values are needed.

So, if you substitute T_c, P_c values here in this m and n expressions, then what you get? You get m = this value and then n = you will get this value. So, along with this T = 100 degrees centigrade that is 373 Kelvin and v = 0.3057 liter per mole in addition to this m and n value if you substitute in this equation number 6, then you will get z = $\frac{Pv}{RT}$ = 0.815. So, this is the other advantage of having corresponding state theory as well.

So, now, whatever the corresponding state theory we have seen that they are only valid for simple spherical molecules or the equations of state which are having only 2 constants. If there are more constants, so we have to make adjustment, more constants are possible if the molecules are not simple or spherical, okay?

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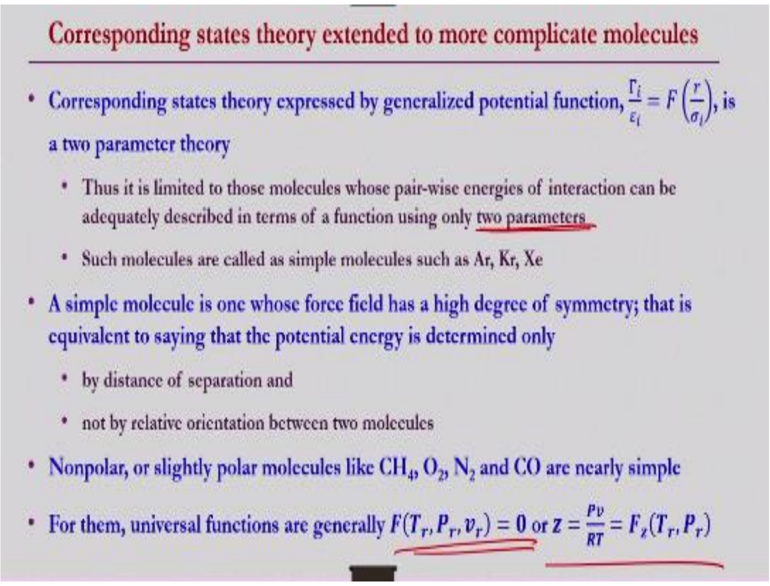

Corresponding states theory extended to more complicate molecules

- Corresponding states theory expressed by generalized potential function, $\frac{\Gamma_i}{\varepsilon_i} = F\left(\frac{r}{\sigma_i}\right)$, is a two parameter theory
  - Thus it is limited to those molecules whose pair-wise energies of interaction can be adequately described in terms of a function using only two parameters
  - Such molecules are called as simple molecules such as Ar, Kr, Xe
- A simple molecule is one whose force field has a high degree of symmetry; that is equivalent to saying that the potential energy is determined only
  - by distance of separation and
  - not by relative orientation between two molecules
- Nonpolar, or slightly polar molecules like CH_4, O_2, N_2 and CO are nearly simple
- For them, universal functions are generally $F(T_r, P_r, v_r) = 0$ or $z = \frac{Pv}{RT} = F_z(T_r, P_r)$

So, corresponding state theory extended to more complicated molecules. So, whatever the theory that is expressed by $\frac{\Gamma_i}{\varepsilon_i}$ = F$\left(\frac{r}{\sigma_i}\right)$ is a 2 parameter corresponding state theory. Thus, it is limited to those molecules whose pair-wise ways energies of interaction can be adequately described in terms of functions having only 2 parameters, Van der Waal's equation a and b, 2 constants, Redlich-Kwong equation A B or α or β sometimes, different books different constants are there, but only 2 constants.

So, for such kind of things only it is valid. If there are more constants, so then it is not valid, it is not possible to find out because we have 2 limitations that is $\left(\frac{\partial P}{\partial v}\right)_T = 0$, $\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$. So, when we apply these 2 conditions at critical conditions for a given equation of state, then we will get 2 equations. So, if you have 2 equations, at the max 2 constants you can find out, you cannot find out the third one.

So, that means, that is the reason this theory is valid for only such kind of equation of states where only 2 parameters or constants are there, okay? Such molecules are in general called as simple or spherical molecules, something like Argon, Krypton, Xenon these are a kind of simple molecules, spherical molecules. A simple molecule is one whose force field has a high degree of symmetry that is equivalent to saying that the potential energy is determined only by separation distance, but not by the orientation, etc., but not by the relative orientation between 2 molecules.

Relative orientations, etc., will come into the picture when the molecules are polar, etc., right? When the molecule is polar, so then induction forces would be there, permanent dipoles would be there, and then induction forces would also be there. So, then because of that one, a kind of orientation of the dipole moments, quadrupole moments, etc., might be there. So, obviously, if there are such kind of relative orientations while interacting for these molecules are existing, so then these 2 parameter corresponding states theory is not valid.

So, non-polar or slightly polar molecules like CH_4, O_2, N_2, and CO are nearly simple or nearly spherical. For them also, we can apply these constants, but there may be a small discrepancy, a small error kind of thing, but that is acceptable that depends on how much they are polar. If they are very slightly polar, then we can say they are very simple or nearly simple or nearly spherical. So, for them, this universal function would have this particular function form $F(T, P_r, v_r) = 0$ or z function of T_r and P_r only, okay?

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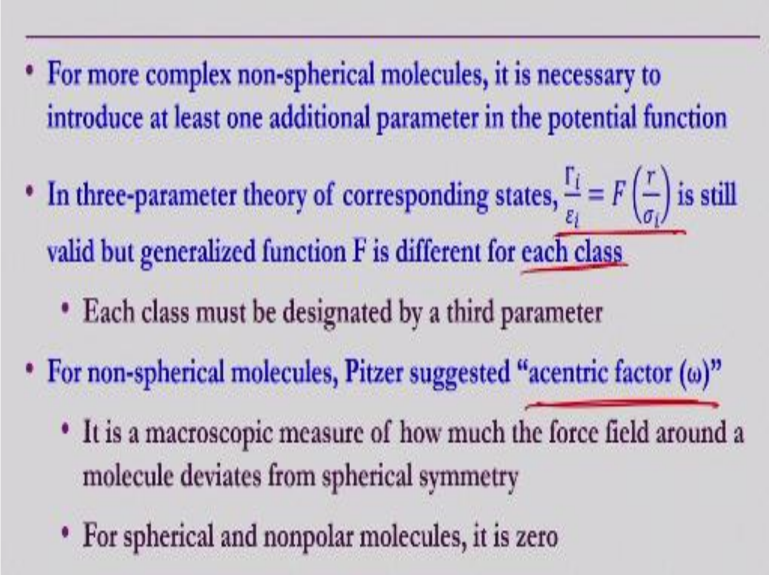

- For more complex non-spherical molecules, it is necessary to introduce at least one additional parameter in the potential function
- In three-parameter theory of corresponding states, $\frac{\Gamma_i}{\varepsilon_i} = F\left(\frac{r}{\sigma_i}\right)$ is still valid but generalized function F is different for each class
  - Each class must be designated by a third parameter
- For non-spherical molecules, Pitzer suggested "acentric factor (ω)"
  - It is a macroscopic measure of how much the force field around a molecule deviates from spherical symmetry
  - For spherical and nonpolar molecules, it is zero

For more complex non-spherical molecules, it is necessary to introduce at least one additional parameter in the potential function, okay? In 3-parameter theory of corresponding states, the equation, whatever the $\frac{\Gamma_i}{\varepsilon_i}$ = F$\left(\frac{r}{\sigma_i}\right)$ is still valid, but generalized function F is different for each class as I mentioned, for one class one particular F function would be there, for another class of fluids another function will be there. Each class must be designated by a third parameter and for non-spherical molecules Pitzer suggested acentric factor omega as the third parameter.

It is a macroscopic measure of how much of the force field around the molecule deviates from spherical symmetry that information this factor gives. And then actually there are many ways of bringing in different parameters, but this is found to be one of the best one, especially to have a kind of validity with the experimental results. So, for spherical and nonpolar molecules, obviously it should be 0 because in the case of spherical simple molecules, non-polar molecules, the force field is mostly spherically symmetric.

So, basically this ω has to be 0. So, actually how to find out this omega? So, that is the big question. So, for that also there is a kind of basis. What is that basis? Basis again two parameter corresponding states theory.

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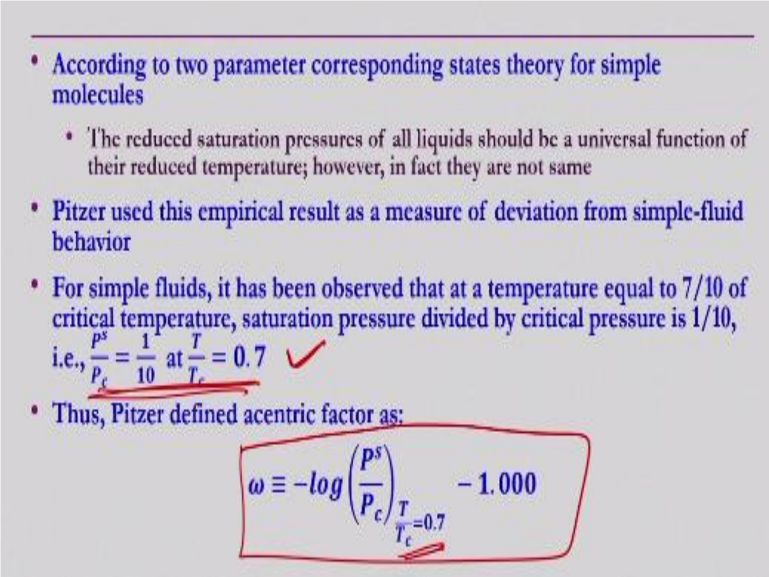

- According to two parameter corresponding states theory for simple molecules
  - The reduced saturation pressures of all liquids should be a universal function of their reduced temperature; however, in fact they are not same
- Pitzer used this empirical result as a measure of deviation from simple-fluid behavior
- For simple fluids, it has been observed that at a temperature equal to 7/10 of critical temperature, saturation pressure divided by critical pressure is 1/10, i.e., $\frac{P^s}{P_c} = \frac{1}{10}$ at $\frac{T}{T_c} = 0.7$ ✓
- Thus, Pitzer defined acentric factor as:

$$\boxed{\omega \equiv -\log\left(\frac{P^s}{P_c}\right)_{\frac{T}{T_c}=0.7} - 1.000}$$

According to 2 parameter corresponding states theory for simple molecules, the reduced saturation pressure that is $\frac{P^S}{P_c}$ of all liquid should be a universal function of the reduced temperature that $\frac{T}{T_c}$. However, that is not true, that is not obeyed for most of the cases. So, Pitzer and his crew have made use of this empirical result as a measure of deviation from simple fluid behavior. For simple fluids it has been observed that at temperature equal to $\frac{7}{10}$of critical temperature, then the saturation pressure divided by the critical pressure is $\frac{1}{10}$.

That is $\frac{P^S}{P_c} = \frac{1}{10}$ at $\frac{T}{T_c} = 0.7$ for all simple fluids, for all spherical molecules or the fluids which are having spherical molecules or the fluids which are simple as mentioned before. For those fluids, this condition has to be valid. Molecules are non-spherical, so then there would be a deviation. So, how much deviation that one can find out using this factor by taking this relation as a kind of basis. By taking this observation for simple fluids whatever the $\frac{P^S}{P_c} = 0.1$ at $\frac{T}{T_c} = 0.7$.

This observation that has been found for the simple molecules by taking that as a kind of basis, acentric factor has been defined like this. ω = - log $\left(\frac{P^S}{P_c}\right)_{\frac{T}{T_c} = 0.7} - 1$. So, this is when $\frac{T}{T_c} = 0.7$ for the simple molecules, then $\frac{P^S}{P_c}$ is nothing but 0.1. So, - log (0.1) is nothing but +1, so 1 - 1, 0. So, for simple fluids it is 0. So, obviously if it is not simple fluids, for non-spherical molecules or the fluid having non-spherical molecules when $\frac{T}{T_c}$ = 0.7, then what is corresponding $\frac{P^s}{P_c}$ one can find out.

If it is non-spherical molecule, then obviously it is not going to be 0.1. So, accordingly this omega would be found. It gives the measure of how much non-spherical is the molecule or how much the force field around the molecule is deviating from spherical symmetry that measure it will give, okay?

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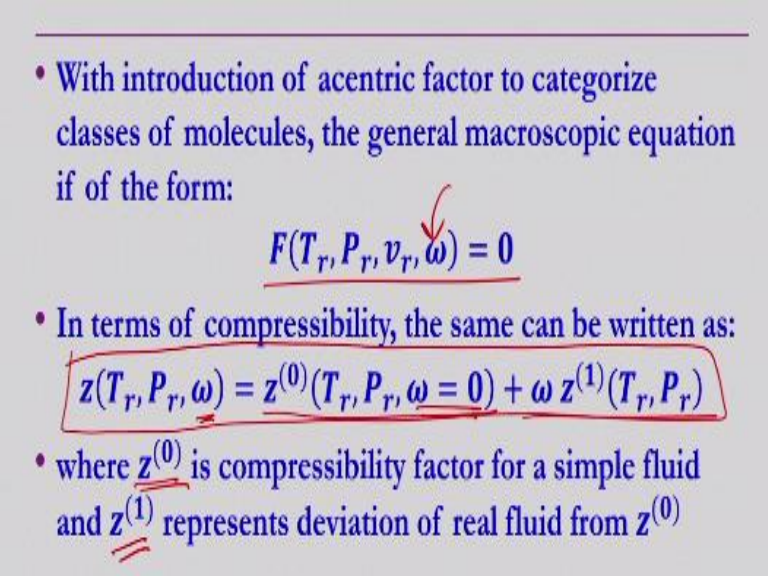

- With introduction of acentric factor to categorize classes of molecules, the general macroscopic equation if of the form:

$$F(T_r, P_r, v_r, \omega) = 0$$

- In terms of compressibility, the same can be written as:

$$\boxed{z(T_r, P_r, \omega) = z^{(0)}(T_r, P_r, \omega = 0) + \omega\, z^{(1)}(T_r, P_r)}$$

- where $z^{(0)}$ is compressibility factor for a simple fluid and $z^{(1)}$ represents deviation of real fluid from $z^{(0)}$

So, finally with the introduction of acentric factor to categorize classes of molecules, the general macroscopic equation is of the form. Now we have this omega as well or in terms of the compressibility factor, we have another parameter omega. So, that is $z\ (T_r, P_r, \omega) = z^{(0)}\ (T_r, P_r, \omega = 0) + \omega\ z^{(1)}\ (T_r, P_r)$. That means, for a simple spherical molecules whatever the compressible factor is there that is nothing but $z^{(0)}$.

So, it is going to be whatever, for this case omega is going to be 0 anyway and the fluids which is having deviation from spherical symmetry whose force field is having deviation from spherical symmetry, then this omega would be there, so obviously $z^{(1)}$ will be there. So, this is the generalized compressibility factor now we can have for any fluid.

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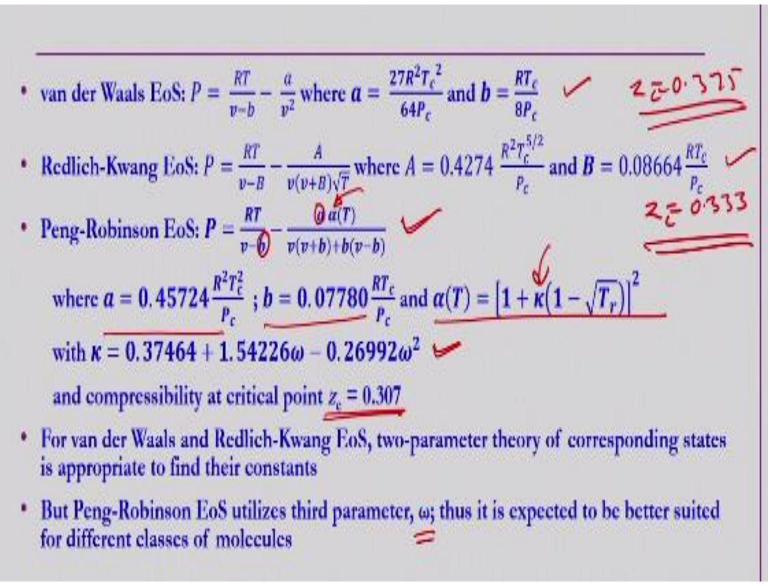

- van der Waals EoS: $P = \frac{RT}{v-b} - \frac{a}{v^2}$ where $a = \frac{27R^2T_c^{\,2}}{64P_c}$ and $b = \frac{RT_c}{8P_c}$ ✓ $z_c = 0.375$
- Redlich-Kwang EoS: $P = \frac{RT}{v-B} - \frac{A}{v(v+B)\sqrt{T}}$ where $A = 0.4274\frac{R^2T_c^{5/2}}{P_c}$ and $B = 0.08664\frac{RT_c}{P_c}$ ✓ $z_c = 0.333$
- 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 compressibility at critical point $z_c = 0.307$
- 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

So, in summary, Van der Waal's equation, we have this one and then these constants a and b we found. So, Redlich-Kwong equation, we have this equation and then constant A B we found like this, but if you have Peng-Robinson equation it is having this form. Here in addition to this a and then b constants, there is another parameter alpha which is function of T. So, for this case, a can be obtained like this, b can be obtained like this, but alpha is function of temperatures.

So, it is function of reduced temperature as given here and then this K is function of ω, okay? What is that function of ω is given here, right? So, this can be obtained anyway. So, now, for this case if you find the compressibility factor, it is going to be 0.307. For Van der Waal's equation, it is 0.375. For Redlich-Kwong equation, it is a 0.333 that is 1 by 3. In the case of Peng-Robinson equation it is 0.307. These are at critical conditions, okay? So, that means for each group of fluid, the z_c is going to be different.

If that is going to be different, that means, we cannot have a one single universal function for the all fluids, we can have one universal function for one group of fluids that is what it indicate by different z_c values. So, finally, Van der Waal's and Redlich-Kwong equations 2 parameter theory of corresponding states can be found appropriate to find this constant, but this Peng-Robinson equation it is having third parameter omega also. So, basically it is expected to be better suited for different classes of molecules.

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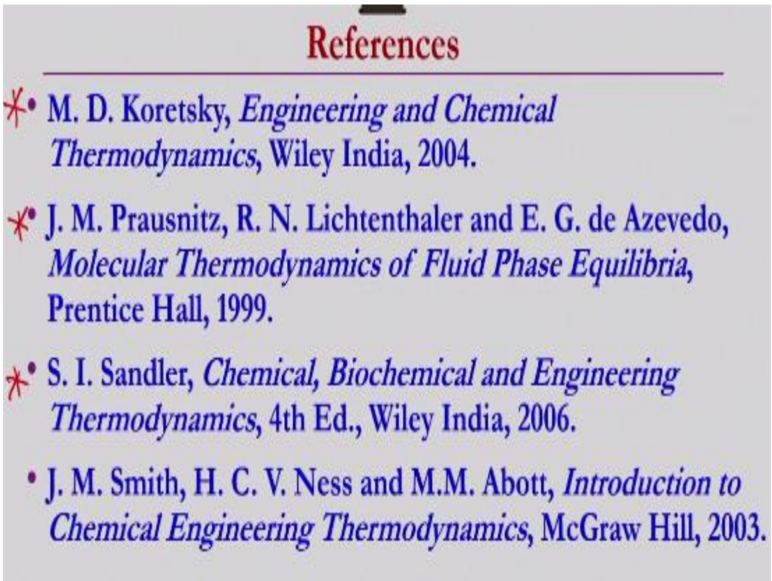

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References for this lecture are Engineering and Chemical Thermodynamics by Koretsky; and then Molecular Thermodynamics of Fluid Phase Equilibria by Prausnitz et al and then Chemical, Biochemical and Engineering Thermodynamics by Sandler and then Introduction to Chemical Engineering Thermodynamics by Smith et al. So, most of the lecture is prepared from these 2 books and other few details have also been taken from this Koretsky as well.

Thank you.