Thermal Physics
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Lecture - 28
Other Equations of State

Hello and welcome back to another lecture on this NPTEL course on thermal physics. Now, in the yesterday's class or for last few classes, we are talking about Van der Waal's equations of state and in yesterday's lecture we have discussed about the weaknesses of Van der Waal's of equations of state.

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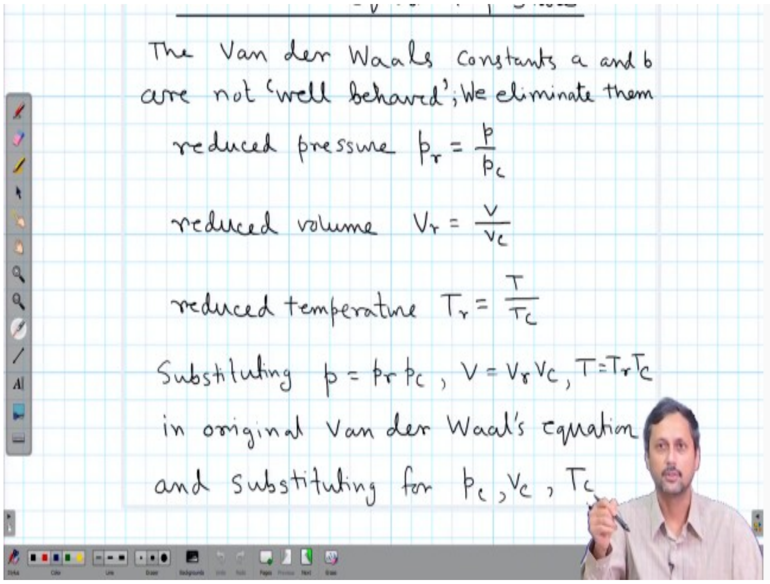

The Van der Waals constants a and b
are not 'well behaved'; We eliminate them
reduced pressure $p_r = \frac{p}{p_c}$
reduced volume $V_r = \frac{V}{V_c}$
reduced temperature $T_r = \frac{T}{T_c}$
Substituting $p = p_r p_c$, $V = V_r V_c$, $T = T_r T_c$
in original Van der Waal's equation
and substituting for p_c, V_c, T_c

So, in today's lecture, we will start from there where we have left in the last class. So, let us first talk about something called the reduced equation of state. Now, Van der Waal's constants a and b that are not well behaved, well behaved means a and b are not exactly constants, but the value as a function of temperature. And so, this is one of the primary weaknesses of the Van der Waal's equation.

So, in an attempt to eliminate a and b these constants from this Van der Waal's equation, we write the expression for reduced quantity like reduced pressure, reduced volume and reduced temperature by simply dividing it with the critical values. So, p r is equal to p / p c. Similarly, V r is equal to V / V c and T r is equal to T / T c. And of course, p r, V r and T r they are dimensionless numbers, because this is a division of 2 actually measured or 2 quantities of equal dimension.

So, now, if we substitute p is equal to so, if I just rearrange this equation, so, p will be equal to p r p c, V will be equal to V r times V c and T will be equal to T r times T c see, if we put this in place of p, V and T in the original Van der Waal's equation and then we substitute for p c, V c and T c in terms of the Van der Waal's constants a and b let us see what happens.

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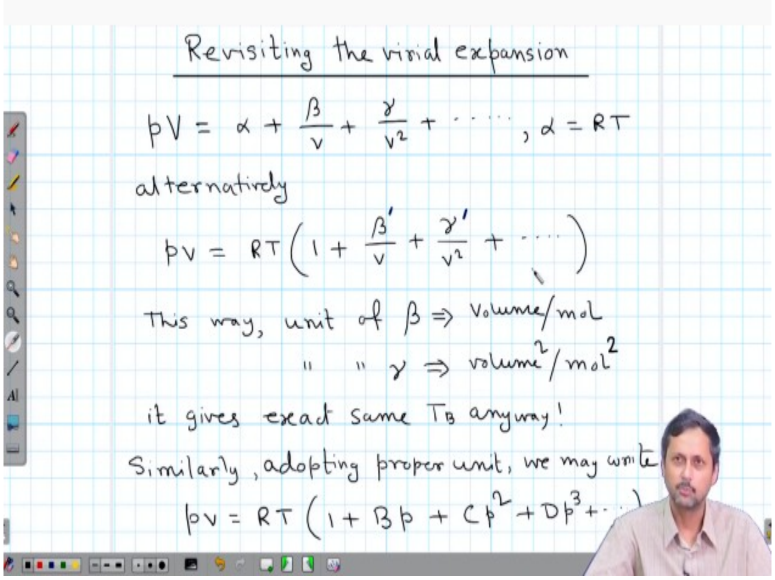

Revisiting the virial expansion

$$pV = \alpha + \frac{\beta}{V} + \frac{\gamma}{V^2} + \cdots, \quad \alpha = RT$$

alternatively

$$pV = RT\left(1 + \frac{\beta'}{V} + \frac{\gamma'}{V^2} + \cdots\right)$$

This way, unit of $\beta \Rightarrow$ Volume/mol

" " $\gamma \Rightarrow$ volume^2/mol^2

it gives exact same T_B anyway!

Similarly, adopting proper unit, we may write

$$pV = RT\left(1 + Bp + Cp^2 + Dp^3 + \cdots\right)$$

So, this substitution after substitution the equation becomes p r p c + a divided by V r square V c square time V r V c minus b is equal to R T r T c. And what we can do is we can substitute for p c, V c and T c in terms of a and b and I have not shown you the detail calculation this is something that is very simple little steps. So, if we do this substitution it will be simply p r times sorry it is 9a plus 9b p r plus 3 by V r square times V r minus one third is equal to there is once again a constant times T r.

So, this a by b and a by b cancels from both sides and we have this reduced equation of state which is p r plus 3 by V r square V r minus one third is 8 by 3 T r. Now in this equation, every quantity every function every parameter p r, V r and T r their dimensionless. So, there the reduced parameters now, there is a law of corresponding states that says if for any two substances out of this three reduced parameters T r, p r and V r. If two are equal for any substance, then the third one has to be equal. So, that means the equations of state in the reduced form will be identical.

So, but anyway this is just a more or less a mathematical manipulation and we do not gain much from the substitution, it is just for just because you need to know all this as you are dealing with Van der Waal's equation for such a long time I have mentioned this, we do not have any great advantage and this and the validity of this so called universal equation is, it is valid only to the extent of this original Van der Waal's equation is valid.

So, that means, it also is still carries although we have reduced the parameters a and b from this remove the parameter a and b completely from this equation of state, it also has certain weaknesses of the original Van der Waal's equation. So, let us talk about one more topic that we have already touched upon that is the virial expansion. Now in virial expansion we have of course, one pressure expansion and one volume expansion in terms of volume expansion the volume expansion it reads like PV is equal to alpha plus beta by V plus gamma by V square plus delta by V cube so on and so forth. And we know that alpha is equal to RT.

So, this is my alpha and this is equal to RT. Now, this is absolutely without I mean without any doubt, we can rely on this expansion but there is a problem, the problem being the coefficient beta and gamma, the dimensions we have in this particular form, we have an issue with the dimensions of quantity beta, gamma, delta. So, basically the virial coefficient, what is the problem? So, let us do one thing, let us simply take RT out from this equation.

Then actually we should have put a dot here, a dot here because this beta and this beta dash they are related by beta dash divided by RT is equal to beta similarly, gamma dash divided by RT is equal to gamma. But, the dimension we have advantage if we write in this particular manner, because in this particular way of writing the dimension of beta dash or gamma dash will be volume and volume square per mole, think of it left hand side PV has the dimension of energy that is Joule’s, alpha is equal to RT essentially.

So, that means, this is in the dimensions of Joule’s or it is Joule’s per mole per calorie sorry Joule’s per Kelvin per mole. So, for 1 mole of N, one mole of a real gas take n is equal to the number of moles is equal to 1 and RT is simply joules. So, this one, this quantity beta by V in this particular representation should also have the dimension of energy gamma by V square should also have the dimension of energy that means, the unit of beta in this particular representation will be volume times energy this one will be volume. I am just doing it for one mol.

So, otherwise there will be a volume per mole. So, let us say it is volume per mol, but it will be volume times energy per mol this will be volume square times energy per mol. So, similarly, the third one will be volume cube times energy divided by mole to the power 3 mol cube so on and so forth. So, by just by taking RT out from RT common from all this equation and replacing alpha with 1 we got we can reduce the dimension of this beta prime or gamma prime to beta we will have a dimension of mole sorry volume per mole this will have a dimension of volume per mole square so on and so forth.

Sorry this should be a mole square, so it will be volume per mole gamma will have volume per mole square. So, we stick to this representation because typically in engineering thermodynamics the virial coefficients are reported in terms of either by volume per mole or volume square but mole square units. So, unnecessarily if we just take RT out it becomes simple in a similar manner for the pressure expansion we can take PV is equal to RT times 1 plus B p plus C p square plus D p cube. So, once again the unit of energy will be dropped from the dimension of energy will be dropped from the unit of B C D this parameters. So, why we are doing this why all of a sudden I brought this up.

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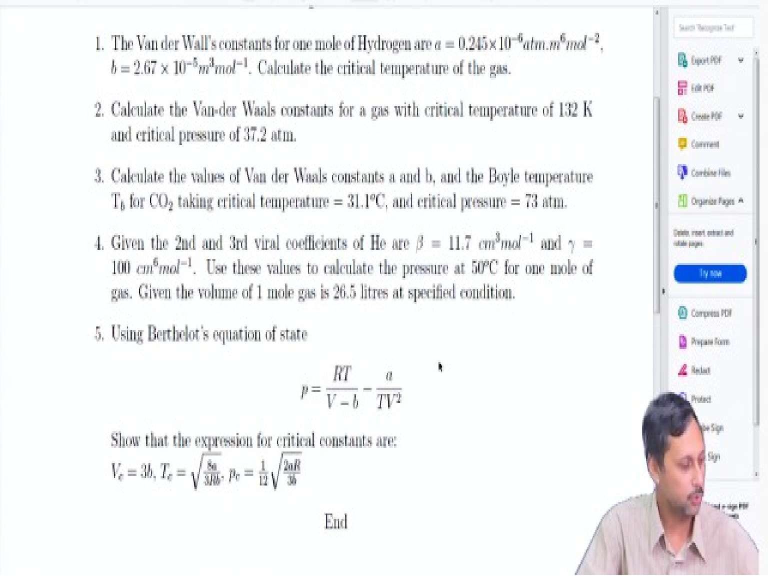

1. The Van der Wall's constants for one mole of Hydrogen are $a = 0.245 \times 10^{-6} atm.m^6 mol^{-2}$, $b = 2.67 \times 10^{-5} m^3 mol^{-1}$. Calculate the critical temperature of the gas.
2. Calculate the Van-der Waals constants for a gas with critical temperature of 132 K and critical pressure of 37.2 atm.
3. Calculate the values of Van der Waals constants a and b, and the Boyle temperature T_b for CO_2 taking critical temperature = 31.1°C, and critical pressure = 73 atm.
4. Given the 2nd and 3rd viral coefficients of He are $\beta = 11.7\ cm^3 mol^{-1}$ and $\gamma = 100\ cm^6 mol^{-1}$. Use these values to calculate the pressure at 50°C for one mole of gas. Given the volume of 1 mole gas is 26.5 litres at specified condition.
5. Using Berthelot's equation of state

$$p = \frac{RT}{V-b} - \frac{a}{TV^2}$$

Show that the expression for critical constants are:
$V_c = 3b, T_c = \sqrt{\frac{8a}{3Rb}}, p_c = \frac{1}{12}\sqrt{\frac{2aR}{3b}}$

End

Because I wanted to solve this particular problem number 4 here. So, what do we have given that the second and third sorry given the second and third virial coefficient of helium or beta is equal to 11.7 centimeter cubed mol inverse and gamma is equal to 100 centimeter to the power 6 mol to the power minus 1 and so, these are given the so, this is specified that 50 degrees centigrade by the way virial coefficients as we all know the change values. So, their values changes as the temperature changes.

So, these are specified for 50 degrees centigrade C. For one mole of gas. So, if one mole is given, so, we do not have to worry about that given the volume of one mole gas is 26.5 liters at specified condition. So, we have to calculate the pressure. So, what we have to do is we have to use this particular expression PV.

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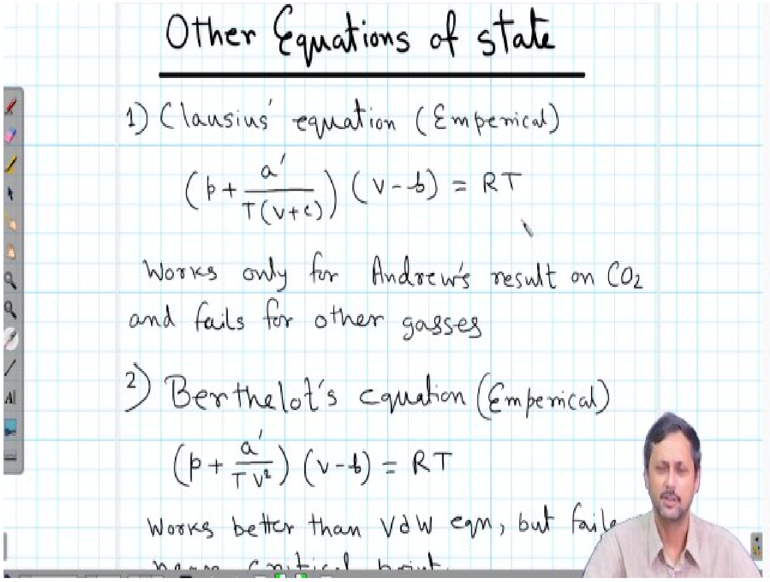

Other Equations of state

1) Clausius' equation (Emperical)

$$\left(p + \frac{a'}{T(v+c)}\right)(v-b) = RT$$

Works only for Andrew's result on CO_2
and fails for other gasses

2) Berthelot's equation (Emperical)

$$\left(p + \frac{a'}{Tv^2}\right)(v-b) = RT$$

Works better than VdW eqn, but faile
near critical point

So, let us start with this oh sorry, before going there we have I just missed, we have few more topics to cover okay. So, last thing in this chapter let me quickly do this and I will get back to this mistake. So, other equations of state. So, Clausius equation. So, let me quickly brief you about this Andrew's equation as we see is practical to use, it has simplicity you know, we can have physical explanation although it is an empirical equation.

We still have physical explanation for quantity V, sorry quantity a and b the parameters, but it is not very successful in explaining all the behaviors of real guesses. So, in an attempt to improve you know, the match with experimental data, so many other different equations of state has been proposed. So, in this next two pages, we will be reviewing some of this equations of state, some of these are empirical by nature and some of these are theoretical by nature the first one which is purely empirical by nature is proposed by Clausius.

So, what Clausius did is instead of p plus a by V square that is, in case of Van der Waal's gasses he just replaced this with a prime and took T down here and instead of V square he wrote a introduced a third parameter c and wrote V plus c and then V minus b the volume term has not changed is equal to RT, this is once again for one mole of gas otherwise, there should have been in New term like mole term here.

Now, this equation it works very well to explain the Andrew's results on carbon dioxide. So, that we have discussed in last I think, one of the last few lectures, those results are very well explained for this equation of state, but it is not that successful for other equations or other experimental data. So, of course, this could not gain the popularity like other theories by Clausius which are extremely popular in thermodynamics, this equation of state is but it needs a mention in the discussion.

Next, relatively more famous is Berthelot's equation of state which is p plus a by T V square and just the T is here. So, basically this T is there to take care of the temperature variation of this quantity a. So, it is similar very similar to the Van der Waal's equation of state except that there is an extra t term temperature term down here. So, this is once again empirical in nature and it works better than 100 Van der Waal's equation.

But, I mean for most of the ranges, it can work for a slightly higher I mean, it fits the experimental data for a higher range of pressure, but it fails very badly near the critical point. So, if you remember the critical point that is obtained by Van der Waal's equation is not in agreement with the experimental data. So, similarly, Waal's equation itself. So, we do not expect much from this equation, but it is in some sense it is better than the Van der Waal's equation of state.

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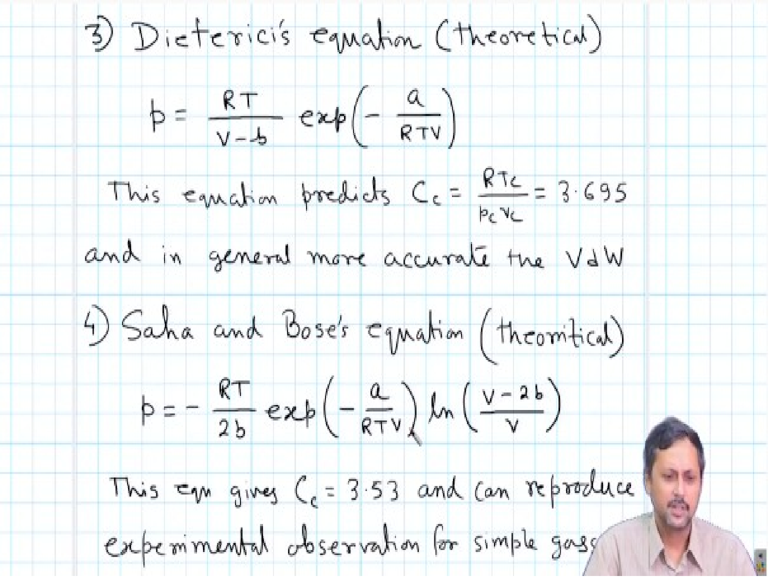

3) Dietericis equation (theoretical)

$$p = \frac{RT}{V-b}\,\exp\left(-\frac{a}{RTV}\right)$$

This equation predicts $C_c = \frac{RT_c}{p_c V_c} = 3.695$

and in general more accurate the VdW

4) Saha and Bose's equation (theomitical)

$$p = -\frac{RT}{2b}\,\exp\left(-\frac{a}{RTV}\right)\ln\left(\frac{V-2b}{V}\right)$$

This eqn gives $C_c = 3.53$ and can reproduce experimental observation for simple gas

Next comes the Dieterici's equation which is theoretical in nature. What do you mean by theoretical? That means, computed the density gradient as so, this was the primary picture that we have a box in which ideal gas molecules reside. So, towards the center of the one molecule at the center of the box, they experience one type of pressure because the net attractive or repulsive attractive forces are balanced out from all directions, whereas a gas molecule which is towards the edge of this container experiences a reduced pressure.

So, the reduced pressure expression was very crudely derived by in the Van der Waal's equation. So, there what Dieterici's did was he did a little more careful analysis of that and finally got to this equation which is p is equal to RT by v minus b exponential minus a by RTV. So, this is once again it has 2 constants a and b, but the form is slightly different. Now, this equation predicts the critical constant to be 3.695 which is once again in the range of measurement, the range of measurement is typically 3.1 to 4 in that range, maybe slightly higher than 4.

So, this is within the range of experimentally measured critical constant and in general more accurate in predicting the behavior of real guesses explaining the behavior of real guesses as compared to Van der Waal's equation. So, this is one equation of state that we have to keep in mind. And finally, the fourth one is by our very one professor Megnad Saha and professor S.N Bose. So, it is a theoretical equation which is derived by extensive use of statistical mechanics and the equation rates like p is equal to minus RT by 2b exponential minus a by RTV ln V minus 2b by V.

And we see that this is much more complicated as compared to the other equations of state that we have discussed. So, it has one exponential term, one logarithm victim but this equation works better and it predicts the C c of 3.53. And it can it is actually very successful in producing the experimentally observed isotherms or experimentally observed I mean behavior the measured behavior of simple gasses, but when it comes to complicated gasses.

Like for example a gas mixture or long little complicated bigger molecules which can be taken into gas form this equation balanced. Anyway so, with this background or with this, we stopped the theoretical discussion on this portion. So, we have two more problems to solve one problem we have already discussed which was I was about to start then have realized that I have to discuss this is this one. So, let us go back to this beta is equal to 11.7 centimeter cube mole inverse, gamma is equal to 100 centimeter to the power 6 mole sorry, it should be more to the power minus 2 there is a mistake which I will correct.

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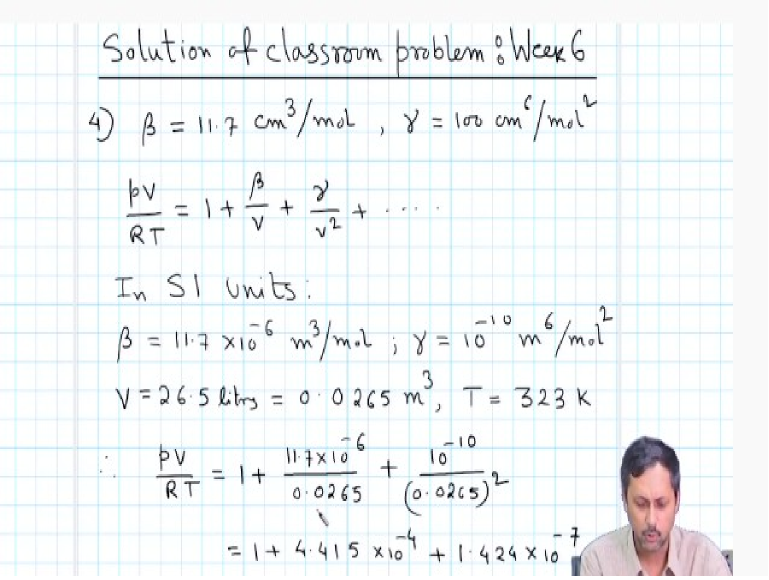

Solution of classroom problem : Week 6

4) $\beta = 11.7 \ cm^3/mol$, $\gamma = 100 \ cm^6/mol^2$

$$\frac{pV}{RT} = 1 + \frac{\beta}{V} + \frac{\gamma}{V^2} + \cdots$$

In SI units:

$\beta = 11.7 \times 10^{-6} \ m^3/mol$; $\gamma = 10^{-10} \ m^6/mol^2$

$V = 26.5$ litrs $= 0.0265 \ m^3$, $T = 323 \ K$

$$\therefore \frac{pV}{RT} = 1 + \frac{11.7 \times 10^{-6}}{0.0265} + \frac{10^{-10}}{(0.0265)^2}$$

$$= 1 + 4.415 \times 10^{-4} + 1.424 \times 10^{-7}$$

So, we have beta value and gamma value is given and of course, you see there is no energy units here. So, that immediately tells you that RT this particular form has been used that PV by RT is equal to 1 plus beta by V plus gamma by V square. So, RT has to be taken out of this equation. So, first thing is we have to convert it to SI units. Now, in SI units beta is equal to see the conversion from centimeter cube to meter cube into 10 to the power minus 6.

So, beta will be simply 11.7 into 10 to the power minus 6 meter cube per mole, gamma is a volume square. So, it will be a factor of 10 to the power minus 12 and there is already 100 here, so, it will be 10 to the power minus 10 meter to the power 6 moles square. Now the V is 26.5 liters at a temperature of 323 Kelvin, so, we can write V is equal to 0.0265 meter cube and T is this one. So, what we need to do is we need to compute the right hand side of this equation. So, PV by RT is equal to 1 plus 11.7 into 10 to the power minus 6 divided by 0.0 265 plus 10 to the power minus10 by 0.0265 whole square.

And then, if we compute this 2 terms, this one and this term we see the first term is 1, second term is 4.415 into 10 to the power minus 4 really small as compared to the first one and the third one is 1.424 into 10 to the power minus 7. So, you see these 2 hardly contributes to the numerical value.

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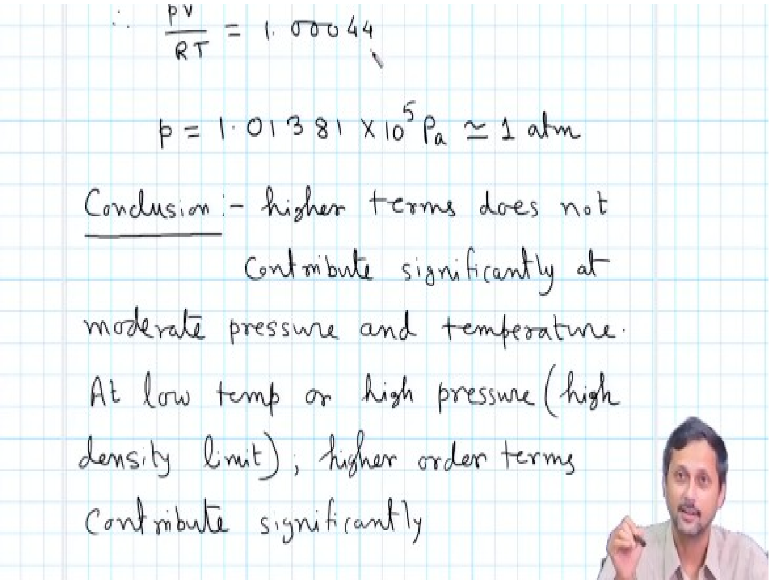

$$\therefore \frac{pv}{RT} = 1.00044$$

$$p = 1.01381 \times 10^5 \, Pa \simeq 1 \text{ atm}$$

Conclusion :- higher terms does not contribute significantly at moderate pressure and temperature.

At low temp or high pressure (high density limit); higher order terms contribute significantly

So, so, finally, we get pv by RT is equal to 1.00044 for an ideal gas it should be 1, so, the deviation is in the fourth decimal place and p is equal to 1.0. So, if I just you know do multiply it with R and T and divided by V in appropriate if we just compute the column and full column and execute the calculation we get p is equal to 1.01381 into 10 to the power 5 Pascal which is very close to 1 atmosphere. Now, let me ask you why this happens, why do we have hardly any effect of the second and third virial coefficient? The answer is line here see the value of pressure finally, is 1 atmosphere.

So, that is a very moderate pressure and low pressure I would say. So, typically for higher terms, it contributes significantly at moderate pressure, I mean slightly high pressure and temperature and basically low temperature at low temperature or high pressure, the higher order terms contribute significantly see what happens if you know have low temperature and high pressure situation the volume will be small, so, this volume is very, I mean I would say this is a large volume.

So, if the volume becomes even smaller, this term will contribute more and this term will contribute more and as we have to also keep in mind the virial coefficient itself the changes value with the temperature. So, this beta and gamma whatever we have described here this is only for the 50 degrees centigrade, but if we go lower in temperature the values are increasing, if we go higher in temperature the values are decreasing.

So, if you are given a table of the virial coefficients for a given gas, so, you can compute the pressure at different temperatures and you will see that at low temperature and in small volume when the gas is under already pressurized these terms will contribute the second and the third term will contribute significantly. So, this brings us to the last problem for this lecture and last problem on this topic of real gasses. So, in here the Berthelot's equation of state is given which is p is equal to RT by V minus b minus a by TV square. So, what we have to do is we have to compute the expression for V c, T c and p c let us do that it is.

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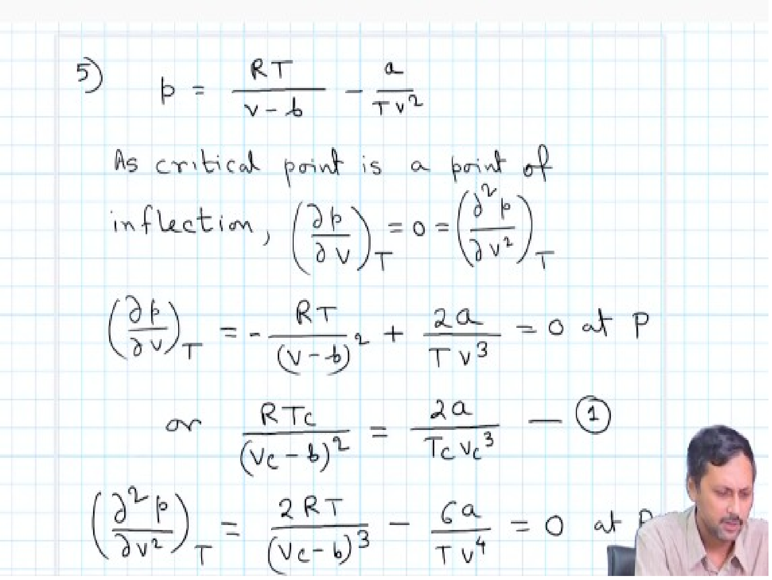

5) $p = \frac{RT}{V-b} - \frac{a}{TV^2}$

As critical point is a point of inflection, $\left(\frac{\partial p}{\partial V}\right)_T = 0 = \left(\frac{\partial^2 p}{\partial V^2}\right)_T$

$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{TV^3} = 0$ at P

or $\frac{RT_c}{(V_c-b)^2} = \frac{2a}{T_c V_c^3}$ — ①

$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V_c-b)^3} - \frac{6a}{TV^4} = 0$ at P

So, we start with this equation of state which is RT by V minus b minus a by TV square and will recall that at critical point is a because critical point is the point of inflection, we have del p del V at T is equal to 0 is equal to delta 2 p del V 2 at T. So, that means, on the critical isotherm at critical points, so, actually I should do sorry a small correction at T c it should be at T c. So, del p del V T c and delta 2 p del V 2 T c both are equal to 0.

So, on the critical isotherm at the critical point the both the first derivative of the pV plot and the second derivative. So, this we have discussed in details. So, all we have to do is we have to take this original equation and execute these 2 derivatives. So, we have del p del V T which is minus RT by V minus b square plus 2a by TV cube is equal to 0 at the critical point. So, substituting for T is equal to T c, V is equal to V c. And so, substituting a critical values, we get RT c V c minus b square is equal to 2a by T c V c cube this is equation 1, but the second derivative of this one, we see T is a constant.

So, it will be 2RT by V minus b whole cube and the second term is 6a, so there is a 3 here, so this 3 will multiply and will be minus 6a divided by TV to the power 4 is equal to 0 at p.

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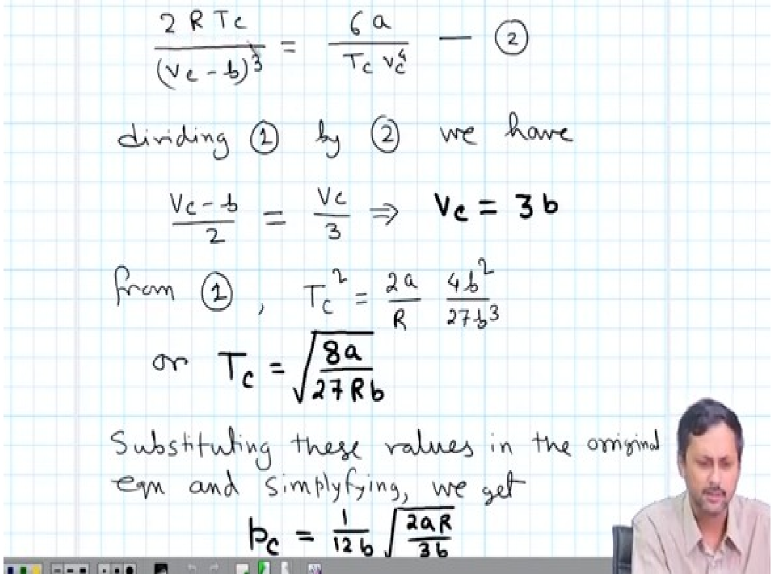

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{T_c V_c^4} \quad — ②$$

dividing ① by ② we have

$$\frac{V_c - b}{2} = \frac{V_c}{3} \Rightarrow V_c = 3b$$

from ①, $T_c^2 = \frac{2a}{R} \frac{4b^2}{27b^3}$

or $T_c = \sqrt{\frac{8a}{27Rb}}$

Substituting these values in the original eqn and simplyfying, we get

$$p_c = \frac{1}{12b}\sqrt{\frac{2aR}{3b}}$$

So, once again from this relation, we get an equation that 2RT c by V c minus b whole cube is equal to 6a by T c V c whole to the power 4. So, dividing 1 by 2 we have V c minus b. So, if I just divide this one, this quantity I am in this equation by this equation you see, there is a V c minus b whole square here and V c minus b whole cubed in the next equation, so, we have T c V c will cancel out. Similarly on the right hand side we have the c cubed here and this e to the power 4 here.

So, we have after division we have V c minus b by 2 is equal to V c by 3. So, the basically by dividing we eliminate T c from this equation and this will give you the V c is equal to 3b. once again this is exactly the same as the Van der Wall's gas which does not you know go very well with the experimentally measured value which is less than 3 anyway, so we go back to equation 1 or you can do it with equation 2 also, but equation 1 is simple.

So, put T c here. So, you see T c can be taken on this side we can write T c square is equal to 2a V minus b whole square divided by RV c cube. So, we substitute for V c is equal to 3b and this equation reduces to this form you see this b square here there is b cubed here. So, canceling we have only b left and we have T c is equal to root over of 8a by 27Rb. Now, once we have V c and T c all we have to do is we have to take this and substitute in the original equation which is this one.

So, then we will get p c is equal to see it will be RT c by V minus b. So, V is equal to 3b. So, it will be 2b divided minus a by 4V square T c. So, and then we have to substitute for T c, the simplification and after simplification we will get p c is equal to 1 by 12b root over 2aR by 3b. So, we have V c, T c and p c for this Berthelot's equation of state. Also, we can compute the critical constant C c I am just leaving it up to you and you can compute RT c by p c V c and see what number you get.

So, this is all for the real gasses, we have discussed all very many different aspects of real gases, we have discussed about Van der Waal's gas we have discussed about the strength and weakness of Van der Waal's equation. So, and also we have discussed about various experimental techniques, experimental results during this chapter. Now, and finally, we have discussed other equations of state other equations which are not very common to us.

So, we have found out that the Van der Waal's equation of state in general is not a very good tool to explain the experimental results. But nonetheless, we keep using it because it is extremely simple, simple in its form and it predicts the behavior of real gases better than the ideal gas equation. Of course, it is a correction over the original ideal gas equation, I request you to go through any of the standard textbooks which are listed in this chapter in this course and read the chapter related to real guesses of course.

You will have we could not cover every topic which is described in a book. This is true for any chapters we are doing. So, if you have any further question in the forum is there you can always ask, I will try to answer this question as much as I can. Our team is always active. So, we will try to answer your queries as much as we can and of course, you can ask questions to directly to me during the live session.

Now, in the remaining two lectures of this week, what we are going to do is we are going to talk about thermometry now, so for we have discussed about temperature we have you know we have discussed. So, whenever we have a discussion on thermodynamics or gas equation and anything, we talk about temperature. Now, so far we have no knowledge on how to measure the temperature and of course, you will tell me that of course, I know because you are all familiar with the concept of thermometer.

But the concept of thermometer is not so simple as it might look at the first class. So, there are certain things we have to keep in mind. And in the next remaining two lectures, we will be talking about the measurement of temperature, the absolute centigrade scale, the absolute scale. And of course, there are different ways different you know different thermometers that can measured the temperature.

So, we can have the historically speaking the first thermometer probably was the gas thermometer. Later on we have the mercury thermometer, but in modern day, we talk about sensors. So, electrically driven sensors, so, the one of this, such sensor is the platinum resister thermometer. So, we will talk about all of this in detail as much as we can, of course in the next two lectures, till then thank you.