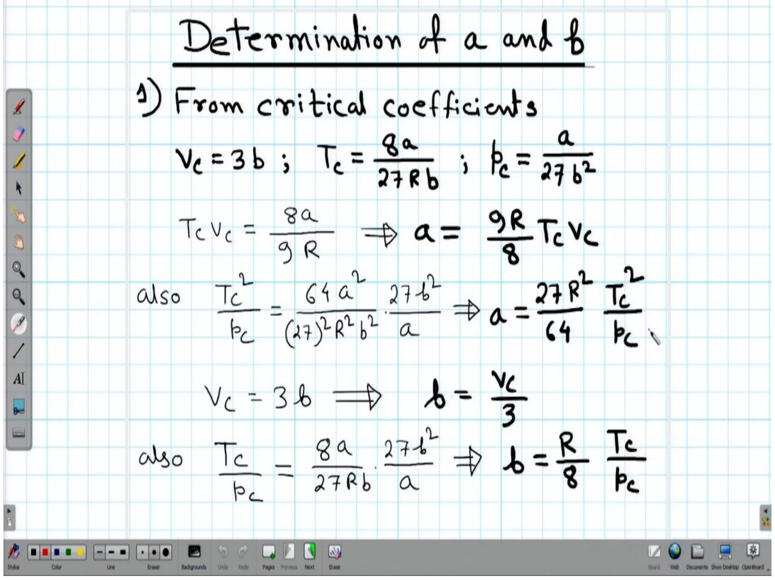
Thermal Physics
Prof. Debamalya Banerjee
Department of Physics
Indian Institute of Technology – Kharagpur

Lecture – 27
Determination of Van der Waal's Constants and Boyle Temperature

Hello and welcome back to another lecture of this NPTEL course on thermal physics. Now in the last class we were discussing Van der Waal's gases and we have discussed the critical parameters of course critical parameter is property of any real gas. And we have found out an expression for critical parameter, critical temperature, critical pressure and critical volume in terms of the Van der Waal's constants a and b.

And what we have found is that critical parameter is the critical coefficient C is underestimated when we are using a Van der Waal's gas equation of state. So, but still although Van der Waal's equation has certain drawbacks we will still keep using it and in today's lecture will start about the determination of the values of the Van der Waal's constants a and b.

(Refer Slide Time: 01:24)



Determination of a and b

1) From critical coefficients

$V_c = 3b$; $T_c = \frac{8a}{27Rb}$; $p_c = \frac{a}{27b^2}$

$T_c V_c = \frac{8a}{9R} \Rightarrow a = \frac{9R}{8} T_c V_c$

also $\frac{T_c^2}{p_c} = \frac{64a^2}{(27)^2 R^2 b^2} \cdot \frac{27b^2}{a} \Rightarrow a = \frac{27R^2}{64} \frac{T_c^2}{p_c}$

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

also $\frac{T_c}{p_c} = \frac{8a}{27Rb} \cdot \frac{27b^2}{a} \Rightarrow b = \frac{R}{8} \frac{T_c}{p_c}$

So, let us start with this. So, in order to determine a and b there are a few different ways and here in this lecture we will be discussing only two of those. The first one is the values of a and b can be determined directly from the critical coefficients. Now the expression of critical coefficients is something that we have derived in the last class or V c we know that V c = 3b, T c = 8a / 27Rb and p c = a / 27b square.

Now a combination of this any two of those can potentially give you a or b. So, for example if we look at this term T c times V c here you see T c has one over b term a by b term and V c is essentially equal to 3b. So, if I multiply T c with V c so this b and this b cancels out leaving only a behind and this is exactly what happens and the product T c V c = 8a / 9R. So that gives you a = 9R / 8 T c times V c.

Similarly but let us assume that only 2 of the critical coefficients have been specified and V c is not one of them. So, we have V c and T c, so in that case we look we examine this relation once again you see we have a by b here and we have a by b square here. So, if I take square of T c which will be of the order a square times I mean which will have a square by the square terms and but divided with a by b square.

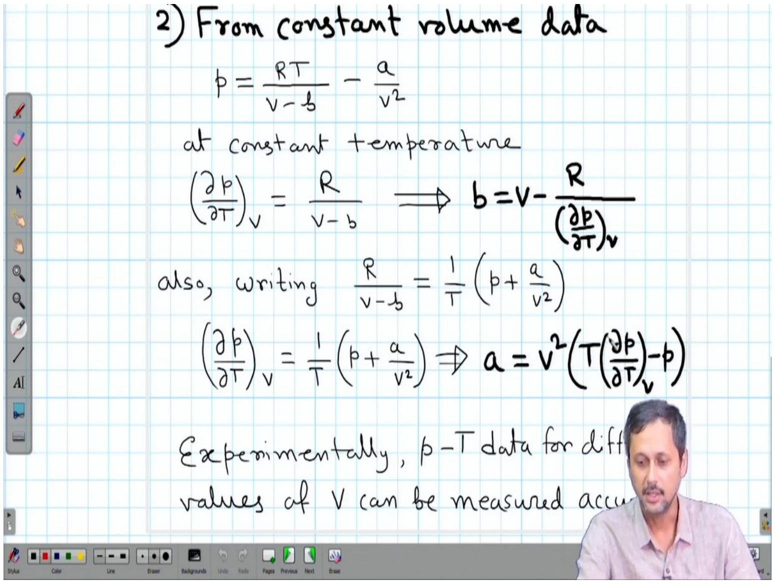
So that means this square and this square will cancel out, a square and a will cancel out leaving only one a behind and this is exactly what is done here T c square / p c this is 64 a square divided by some factors times b square and this is 1 over p c is equal to 27b square / a b square b square cancels a a square cancels leaving only one a behind and this keeps you a is equal to 27R square / 64 times T c square by p c.

So, this is a constant essentially similarly this one is also a constant essentially and we have T c square by p c. So, these are how a can be determined using the critical coefficients. The next one the next approach is you know we can in order to determine b what we can do is we can simply take V c is equal to 3b which gives you b is equal to V c / 3. So, we do not need anything else only if we know V c we automatically know b.

But then once again it might so happen that in a situation we have only T c and p c data available to us in that case we can also use this combination. So, look at this once again so T c has a by b, p c has a by b square. So, if I take the T c by p c which will be a by b times b square by a, so a, a cancels out and b and b square leaving they were between them there is only one b left. So, exactly this has happening here.

So, you see this, a and a cancels out here and there is only b, one b remaining equating I mean just changing sides we get b is equal to R divided by 8 times T c by p c. So, these are four expressions two for a and two for b and by this expression we can get the Van der Waal's coefficient from the critical parameter data. Now once again as we have already seen that these expressions are not very accurate but this is the best expression we can get using this Van der Waal's equation. So, we have to live with it, now the better and more reliable way of doing this is from the constant volume data.

(Refer Slide Time: 05:47)



2) From constant volume data

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

at constant temperature

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b} \Longrightarrow b = V - \frac{R}{\left(\frac{\partial p}{\partial T}\right)_V}$$

also, writing $\frac{R}{V-b} = \frac{1}{T}\left(p + \frac{a}{V^2}\right)$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{T}\left(p + \frac{a}{V^2}\right) \Rightarrow a = V^2\left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right)$$

Experimentally, $p-T$ data for diff

values of V can be measured accu

So, keeping the volume constant if we can measure the pressure versus temperature or rather the variation of pressure as a function of temperature for any gas that it will give us a very straightforward way of measuring a and b. So, let us explore it in slightly more detail we have p is equal to RT by V minus b divided by a by V square. So, this expression is something that we all know is the slightly you know what you call the rearrange version of the Van der Waal's equation.

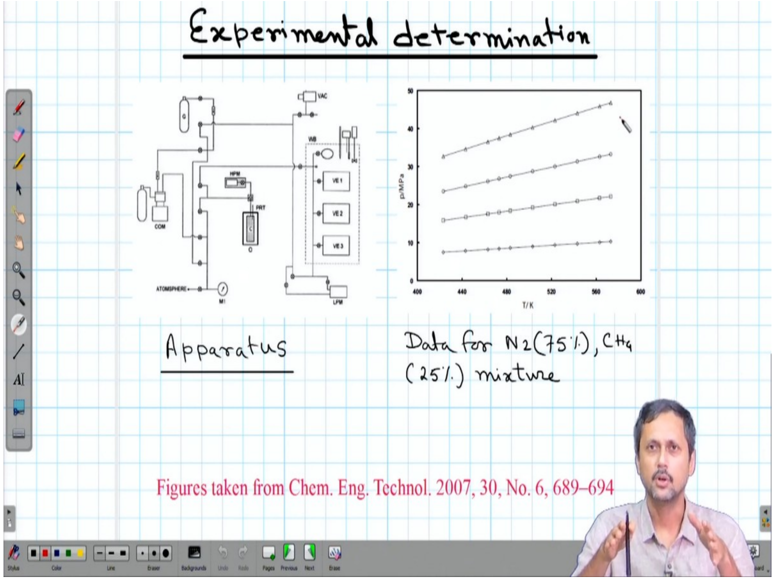
Now if we take a partial derivative with respect to T keeping V constant which essentially is equivalent of saying if we maintain the same volume of the gas we just change its temperature.

So, then what happens is del p by del T at V constant. So, the second term is treated as a constant and it becomes 0 the derivative of this becomes 0 the first term V is the constants so RT by V minus b provides R divided by V minus b.

And after rearranging this term we get b is equal to V minus R divided by del p del T V also if we write instead of R by see in this equation if I just once again rearrange this slightly so we have p plus a by V square is equal to RT divided by V minus b taking T into this left hand side we have 1 over T p plus a by b square is equal to 1 over T p plus a by V square is equal to R by V minus b. So, in this right hand side we can simply substitute this R by V minus b by 1 by T times p plus a by V square.

And then we have this equation del p del T V equal to this on rearrangement it gives you a is equal to V square times T del p del T V minus p, so all we have to do we can use this expression, so the expression of a and b both are available, once we know the variation of pressure as a function of temperature in constant volume, so experimentally this data can be measured very accurately with great precision and for a wide range of the temperature at pressure

(Refer Slide Time: 08:46)



Experimental determination

Apparatus

Data for N_2(75%), CH_4 (25%) mixture

Figures taken from Chem. Eng. Technol. 2007, 30, No. 6, 689–694

So, I mean there are many such measurements are available in literature, I have just chosen one so that you can get an idea. So, the apparatus they are using so you know in olden days people used to use gas manometer, the mercury you know the height of mercury column to measure pressure you know measurement of temperature is something that we are going to discuss anyway very soon.

So, but in nowadays everything is electronically controlled and here in this apparatus by the way this is taken from this particular paper chemical engineering technologies 2007 volume 30 number 6 page number, issue number 6 and page number 689. So, this is how we cite research article if you just use this volume number issue number and year actually you do not even need the issue number the volume and page number is sufficient to find the relevant publication in this particular journal.

Of course it might not be free of cost it might not be available to you freely but at least you can look at the abstract and look at some of the figures that is possible. Anyway so in this particular publication so this is where this is the chamber where the gas is inside this chamber c and the pressure is monitored using this pressure gauge, temperature is controlled by this arrangement and this entire thing is connected to computer.

So, everything is interfaced and computer controlled in their particular setup this is a pretty modern 2007. But let me tell you I mean this is nothing new this type of measurement is people are doing for last you know 150 years also. Only thing is the instrument used to be very primitive in nature. Now it is ultra modern set of instruments. So, the data which is provided is a mixture of nitrogen and methane nitrogen 75% and within 25% gas mixture not a pure gas.

But just to give you a better representation there were other datasets available to but they were not so easily represented, you see it is simply represented as a temperature versus pressure data. And you can have a very good view of the value of pressure which is given in mega Pascal's, what is the mega Pascal? 10 atmospheric pressure is approximately 1 mega Pascal. So, you see this range of variation is over a wide I mean it is a pretty wide range of radiation.

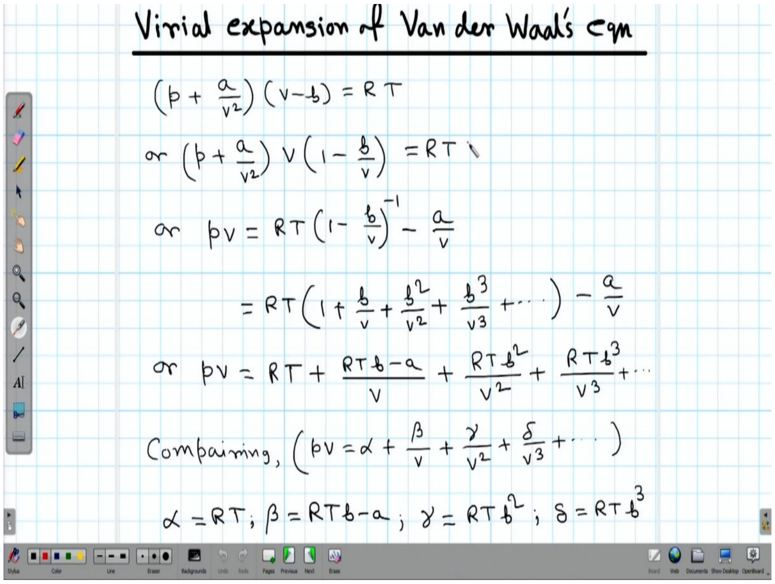
And so the temperature is also varied between roughly 420 Kelvin to you know 680 Kelvin or so now this different curves are for different constant volume, the volume of this is adjustable the volume of this cell is adjustable. So, we can you know keep us 1 volume which is fixed for that particular set of data. And we can take the pressure versus temperature curve then we set another volume and take another pressure versus temperature curve, another volume gives you this and another volume of the cell gives you this.

So, there are many other references also if you simply you know and these lines are called an isocode like constant temperature lines are called isotherm. Similarly constant volume lines are called isocode and constant pressure lines are called isobar. So, we will revisit this terms over and over again when we will be talking about discussing classical thermodynamics. So, now let us get back to this expression, see in order to get b what do we need we need V the volume at which this measurement has been done and the slope of this curve and that is it.

So, which is given that this curve we have almost like a straight line at least for this present experiment. So, for a given volume the slope of the curve is a constant. So, we have a value of b and that is it but for a look at the expression carefully here do you what do we have we have b square we have T and we have p so that means once again if given that the slope of one curve is constant or for a given value of V we have one particular value of a but it might so happen that the second curve gives you slightly different value.

And the third curve gives you slightly different value same goes for V as well because V is constant only on one curve. So, we have to use basically values of a and b is computed over a range of volume V and then the average value is reported. So, whatever it is this is a pretty accurate method and people have been using this for quite some time you know these techniques are essentially centuries old only things that instrumentation has become more.

(Refer Slide Time: 14:05)



Virial expansion of Van der Waal's eqn

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

or $\left(p + \frac{a}{v^2}\right) v \left(1 - \frac{b}{v}\right) = RT$

or $pv = RT\left(1 - \frac{b}{v}\right)^{-1} - \frac{a}{v}$

$$= RT\left(1 + \frac{b}{v} + \frac{b^2}{v^2} + \frac{b^3}{v^3} + \cdots\right) - \frac{a}{v}$$

or $pv = RT + \frac{RTb - a}{v} + \frac{RTb^2}{v^2} + \frac{RTb^3}{v^3} + \cdots$

Compairing, $\left(pv = \alpha + \frac{\beta}{v} + \frac{\gamma}{v^2} + \frac{\delta}{v^3} + \cdots\right)$

$\alpha = RT; \beta = RTb - a; \gamma = RTb^2; \delta = RTb^3$

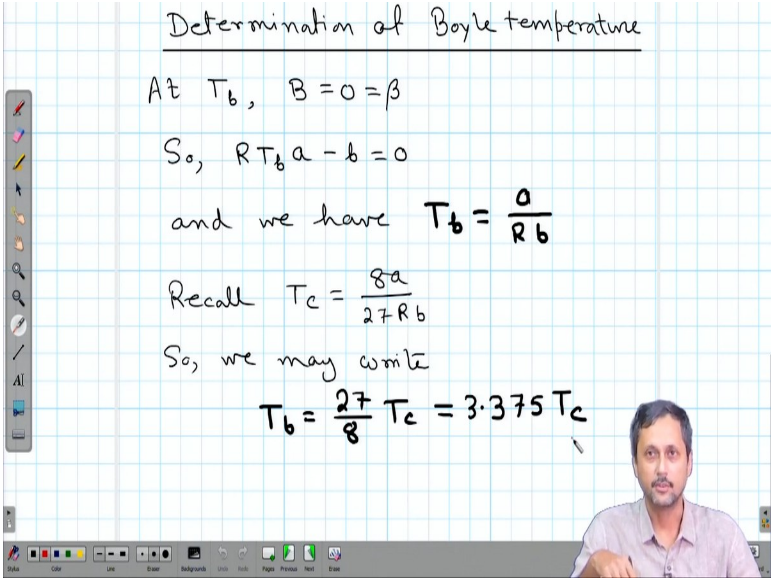
So, now let us go to another topic which is called the Virial expansion of Van der Waal's equation, what is Virial expansion we have discussed this already that if we have an expression of this form where pV is equal to alpha plus beta by V plus gamma by V square plus delta by V cube this is one example of a virial expansion. Similarly we can have pV is equal to a plus b p plus c p square plus d p cube that is also another form.

Now it so happens that for Van der Waal's gas we have this particular form easily available. So, you know we take the Van der Waal's equation we write pV = RT into 1 minus b by V whole to the power minus 1 minus a by V. So, this is just by simple manipulation of this simple mathematical manipulation of this equation. Now once we do that and we note that this is like a series so it is 1 by 1 minus x so basically 1 minus x whole to the power minus 1 and that series gives 1 plus x plus x square plus x cube up to infinity.

So, similarly this one will give you 1 plus b by V plus b square by V square plus b cube by V cube all the way up to infinity and there is a minus a by V which is present here. So, after rearranging we have pV = RT + RT b - a divided by V plus RT b square divided by V square plus RT b cubed divided by V cube so on and so forth. So, by comparing with this standard form of virial expansion in volume so, virial expansion can be in pressure and volume.

So, we are just comparing it with this one we see alpha is equal to RT as expected, beta is equal to RT b minus a, gamma is equal to RT b square, delta is equal to RT b cube and so forth. Now why do we want to do this because we are looking for the expression of Boyle temperature. Now what is Boyle temperature? Boyle temperature is the temperature at which the gas behaves like an ideal gas because the second virial coefficient is 0. And the third and fourth virial coefficient is not supposedly intervene much into this in the properties of the gas. So, at the boil temperature beta or b if we look at the pressure expansion there is a 0. So, we have RT b minus a is equal to 0.

(Refer Slide Time: 16:59)



Determination of Boyle temperature

At T_b, $B = 0 = \beta$

So, $RT_b a - b = 0$

and we have $T_b = \frac{a}{Rb}$

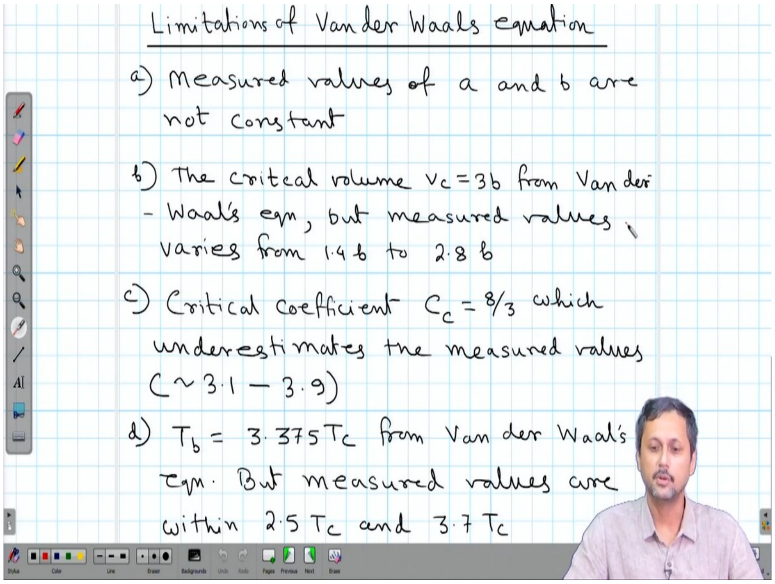
Recall $T_c = \frac{8a}{27Rb}$

So, we may write

$$T_b = \frac{27}{8} T_c = 3.375 T_c$$

Which gives you T b at the Boyle temperature T b which gives you T b = a / Rb. So, once again we recall the T c = 8a / 27Rb for a Van der Waal's gas. So, we may write T b is equal to 27 by 8 you see it is so it is a by Rb so if i just multiply it with 8 by 27 and divided by 27 by 8 or 8 by 27 same thing. So, we get T b is equal to 27 by 8 T c which is 3.375 T c. So, we get an expression for Boyle temperature as well in terms of the Van der Waal's constants.

(Refer Slide Time: 17:58)



Limitations of Van der Waals equation

a) Measured values of a and b are not constant

b) The critcal volume $V_c = 3b$ from Van der - Waal's eqn, but measured values varies from 1.4 b to 2.8 b

c) Critical coefficient $C_c = 8/3$ which underestimates the measured values $(\sim 3.1 - 3.9)$

d) $T_b = 3.375 T_c$ from Van der Waal's eqn. But measured values are within $2.5 T_c$ and $3.7 T_c$

Now let us close this discussion by discussing the limitations of this control situation. So, the main and you know the primary reason why Van der Waal's equation is not accurate because according to Van der Waal's equation a and b which is a is a measure of an intermolecular attraction and b is a measure of the co-volume basically that is occupied volume by the solid volume of the gas molecule these are supposedly constant.

But it turns out that they are not actually constant. So, they vary with temperature and there are so what I mean to say is if I go back to this curve you know experimentally if I measured the value on this point we get 1 and 1 number for a and b and if I measure at a higher temperature and pressure. So, if I go back see the expression of a we have T and p present. So, basically it is not only the slope but also you have to select a point experimental point.

And you know for example this point and the slope of this line. So, depending on the choice of your experimental point and also not for all gases the T versus p behaves in a linear manner. So, there are you know a slope change present so without doubt the values of a and b they keep changing with temperature. So that is where the main failure of Van der Waal's equations of state comes that it cannot predict the variation of a and b.

Now the critical volume is from the Van der Waal's equation of state V c is equal to 3b but the measured values they always live between 1.4 b to 2.8 b. So, it is possible to measure the co-volume in a so basically it is correlated with the net volume of solids assuming that the gas molecules a solid sphere it is correlated with the net volume of those gas molecules and it is experimentally found to be 1 between 1.4 and 2.8 b.

Also we have already discussed about this critical coefficient C c which is 8 by 3 according to Van der Waal's equation of state whereas the measured values the live between 3.1 and 3.9. And finally just before this slide we have derived an expression for Boyle temperature which is 3.375 T c which is a fixed number I mean ideally if the gas is the Van der Waal's gas then we have 3.375 T c.

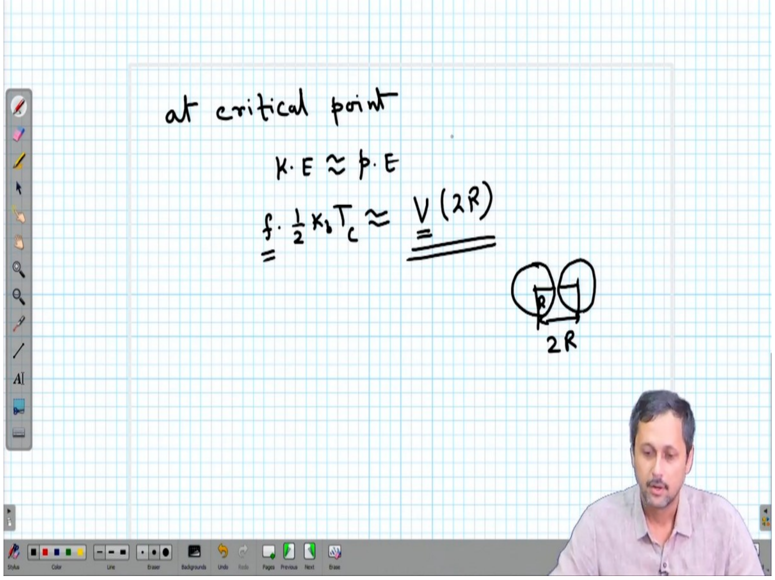
And it turns out that the measured values of Boyle temperature see Boyle temperature is something that is you know it is a an observed quantity, it is an observed phenomena that there is a particular temperature at which p V versus p becomes almost a flat straight line. So that is the Boyle temperature and of course critical temperature T c is also measured measurable quantity. So, the measurements suggest that the relation between T b and T c is that T b is equal to 2.5 T c and 23.7 T c and Van der Waal's equation predicts 3.375 T c.

Now there are explanations why the values of a and b are change. So, basically what happens is that very high temperature if as the temperature goes the values of a and b the decrease this is because first of all we assume that the molecules are Hartsfield. So, they collide but there is no deformation in shape but when the temperature is high the kinetic energy is high and so the 2 spheres the collide and the kind of you know contract and then you know goes away from each other and you know go back to their original shape.

So that was there is a shape change at higher temperatures. So that is why the value of the co-volume decreases from 3b. Similarly for a which is a measure of intermolecular interaction at high temperature the value of course decreases because as the thermal energy for the molecules or so called kinetic energy becomes dominant the potential energy becomes less and less effective and the value of a decreases. Actually this gives us another interesting definition of the critical point critical temperature what happens in a critical temperature?

Around critical temperature it is you know it is just about the temperature for which it can condensate. So, around this critical point we have a situation where the kinetic energy of the gas which is basically the available thermal energy balances the intermolecular attraction exactly. So, at critical point so let me try to give you an explanation of critical point in a physical point of view.

(Refer Slide Time: 23:13)



at critical point

$$K.E \approx p.E$$

$$\underline{f} \cdot \frac{1}{2} K_b T_c \approx \underline{\underline{V(2R)}}$$

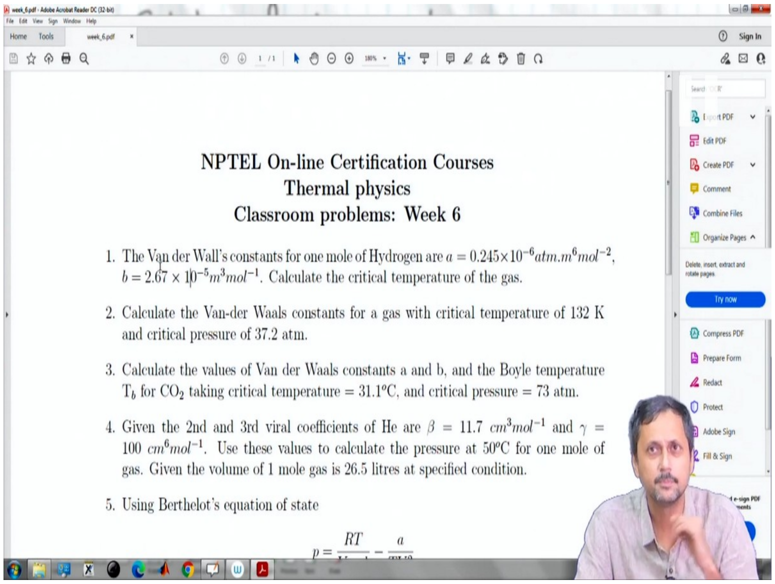
Kinetic energy is almost approximately equal to potential energy, now what is the value of kinetic energy if we have a system with f degrees of freedom? So, it is f into half K b T and what is the value of potential energy? Potential energy will be the measure of potential energies a by V square is the correction to the pressure. So, it would be I do not remember it exactly, so we just simply write the V of r so this is the intermolecular attraction.

So, let us call it this is a measure of the potential which is the R being the separation between two molecules. Now as the molecule is short in the attractive forces or short range we can consider this R which is basically the center to center distance and this force will be effective only when there is a collision. So, if this is R, this is my radius R and this is my radius R so when the intermolecular separation is approximately 2R only then this you know the potential energy V will come into action.

So, instead of writing R which is a generic term for distance we will write this is equal 2R. So, this is an equation which is when you can assume that at critical point when the gas just begins to condense it this equation holds. So, if we know the degrees of freedom, so there is a way of measuring approximating the value of this potential at around critical point. Now assuming that this; value of the nature of the potential does not change with temperature.

So, in case if we know this critical point T c we can have an idea of this strength of this interaction from this relation. But once again it is a very approximate relation do not take it too much I mean do not take it too seriously I would say but we have an approximate idea of what is happening inside. So, with this let us go to these problems a question answer.

(Refer Slide Time: 26:15)

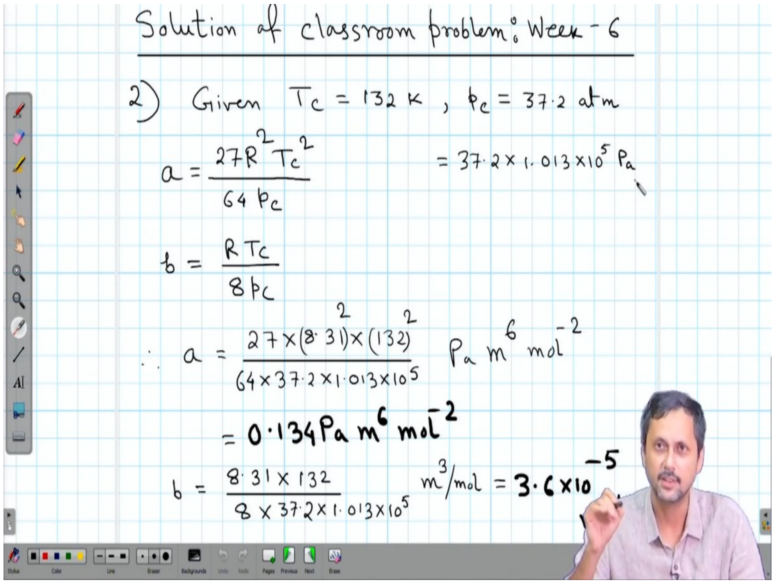


NPTEL On-line Certification Courses
Thermal physics
Classroom problems: Week 6

1. The Van der Wall's constants for one mole of Hydrogen are $a = 0.245\times10^{-6} atm.m^6 mol^{-2}$, $b = 2.67 \times 10^{-5} m^3 mol^{-1}$. 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

So, this is a problem set for this week we have already solved the first problem. Now calculate the Van der Waal's constant for a gas with critical temperature of 132 Kelvin and critical pressure of 37.2 atmosphere this is the second problem. So, here is the critical temperature is given and critical pressure is given not the critical volume. So, what we have to do go we back to this one. We have to use the second expression here this one because V c is not given the T c is given, p c is given and V c is not given. So, this is our expression that a is equal to 27R square by 64 times T c square by p c and b is equal to R by 8 T c by p c.

(Refer Slide Time: 27:18)



Solution of classroom problem: Week - 6

2) Given $T_c = 132\ K$, $p_c = 37.2\ atm$

$= 37.2 \times 1.013 \times 10^5\ Pa$

$$a = \frac{27R^2 T_c^2}{64\, p_c}$$

$$b = \frac{R T_c}{8 p_c}$$

$$\therefore\ a = \frac{27 \times (8.31)^2 \times (132)^2}{64 \times 37.2 \times 1.013 \times 10^5}\ Pa\ m^6\ mol^{-2}$$

$$= \mathbf{0.134\ Pa\ m^6\ mol^{-2}}$$

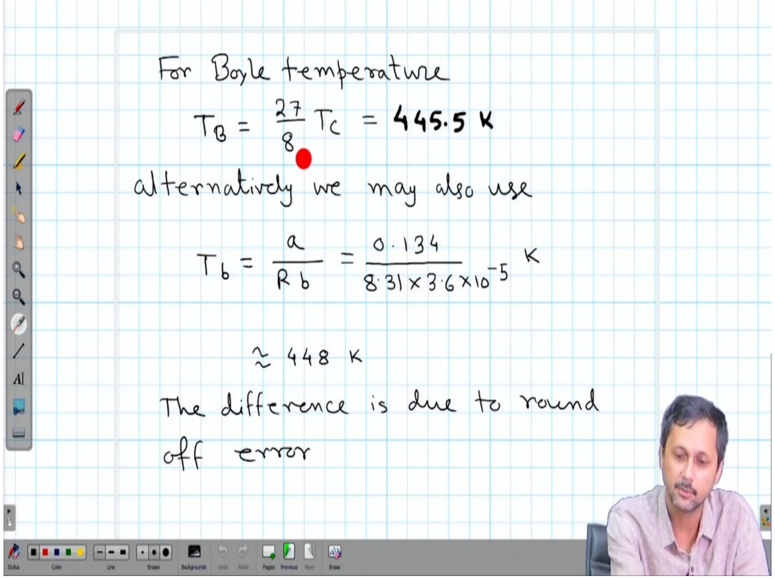
$$b = \frac{8.31 \times 132}{8 \times 37.2 \times 1.013 \times 10^5}\ m^3/mol = \mathbf{3.6 \times 10^{-5}}$$

So, we do exactly that and after and there is one small correction, so T c is given in Kelvin fine p c is given an atmosphere which is 37.2 atmosphere. So, we have to multiply this with 1.013 into 10 to the power 5 to convert it to pa at the Pascal unit which is the SI unit for pressure. So, a is equal to this, b is equal to this, so we just compute a by putting 27R square by 64 is a constant for T c we have to put 32 square T c square and for p c we have to put this number.

And we get a is equal to 0.134 Pascal meter to the power 6 mol to the power minus 2 which is a proper unit for a and for b we once again we have to use this relation p c is not given R is equal to T c by 8 p c and after substituting for T c and p c with improper units we get b is equal to 3.6 into 10 to the power minus 5 meter cube per mol there are actually two parts. So, there is a second problem where the once again the T c is given critical temperature is given and critical pressure is given and we have to calculate a and b and also we have to calculate the Boyle temperature.

Now in this problem what we did here actually because these problems are very similar to each other we just have to put you know once again we have to convert this critical pressure to a proper unit and critical temperature in this case it has to be converted to Kelvin. Other than that there is no difference between these two problems. What we did is just took this problem and computed the Boyle temperature instead of doing number 3 we just did number 2 with Boyle temperature.

(Refer Slide Time: 29:24)



For Boyle temperature

$$T_B = \frac{27}{8} T_c = \mathbf{445.5\ K}$$

alternatively we may also use

$$T_b = \frac{a}{Rb} = \frac{0.134}{8.31 \times 3.6 \times 10^{-5}} K$$

$$\simeq 448\ K$$

The difference is due to round off error

So, for Boyle temperature all we have to do is we have to either so we can do it both in two ways. We can either substitute for T b is equal to 27 by 8 T c which gives you 445.5. Kelvin or alternatively what we can do is we can directly write the expression for Boyle temperature in terms of Van der Waal's constant and we get a divided T b = a / Rb. So, we put the value of a, value of b and R of course and we get 448.

Now this is a slightly different number so 448 and 445.5 there is a gap of 2.5 Kelvin which is not significant but why that should come that is the question and let me tell you this comes primarily from the round off error see here T c is already given and this there is only one factor we have to multiply 27 by 8 is the one factor we have to multiply with T c and of course there is a rounding off here.

And in this case we have already computed I mean a and b they are given look at the values of a and b, the values of a and b this is already derived from this T c and p c and the values are in a truncated to second or third decimal place and value of these already very small. So, there is already a truncation error. So, once again if we are using those numbers those truncated numbers to back calculate the value of T b then we get difference which is absolutely.

Now although the difference is 2.5 Kelvin but in terms of percentage it will be less than 1% it will be like approximately 0.2% or something. So that is where we stopped for today's lecture. Now there are 2 more problems, in the problem set like so this and some more things has to be discussed. Of course we have not done the third problem because third problem and second problem is extremely similar. You can do it yourself I am just leaving it to you and you know other problems and related discussion, let us wait till next class. Thank you.