Thermal Physics
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Lecture - 26
Critical Parameters from Van der Waal's equation

Hello and welcome back to another week of this NPTEL course on thermal physics. So, we are essentially into week 6 now, we have completed week 5. And so far, we have discussed like in the last week we have been discussing the behaviour of real gases. Previous to that we have discussed in details about the kinetic theory and transport phenomena and other related topics. Now, this week we will also continue with real gases.

And in the second half of this week, we will we will be talking about thermometry which is related to the measurement of temperature. Because although we have used the word measurement of temperature many times during this last 5 weeks, we have not discussed anything on how to measure this temperature. So, of course, we are familiar with the mercury thermometer I think every household has at least one mercury thermometer.

But there are other ways other more accurate ways of measuring the temperature. And have also we have not discussed in details about the temperature scale, which once again is to some extent familiar to you, you will know about Centigrade scales, Fahrenheit scale. And some of you might also be familiar with the absolute scale of temperature. Anyways, we will revisit those things towards the end of this week. But for now, at least for first two lectures, we will be continuing with the behaviour of real gases.

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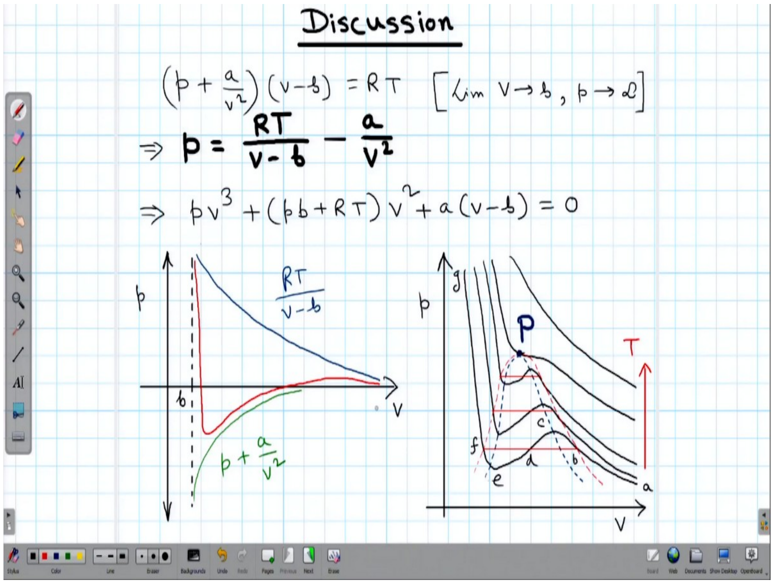

Discussion

$$\left(p+\frac{a}{v^2}\right)(v-b) = RT \quad \left[\lim V\to b,\ p\to \infty\right]$$

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

$$\Rightarrow pv^3 + (pb+RT)v^2 + a(v-b) = 0$$

So, let us talk about the Van der Waal's equation once again. So, this is one equation that will be coming back to us many at times during the course of this discussion. Now, the equation for one mole of Van der Waal's or one mole of gas is p plus a by V square times V minus b is equal to RT and as we will see that although this gas is not in this equation is not probably the best representation of this real gas, it has its drawbacks, but still because of its immense simplicity and ease of use, we keep using this Van der Waal's equation.

Now, the first thing I would like to do is I would like to rearrange this particular equation into this particular form which is p is equal to RT by V minus b minus a by V square. Now, if we examine this particular form of equation for a given temperature, let us assume that the temperature is fixed. So, that means this right hand side is a function of volume only and left hand side is pressure. So, essentially we are looking at one high pressure volume, isotherm of this equation of this system.

So, we immediately notice that the first term close as V tends to b, so, when V is equal to b this denominator of this term is equal to 0 and pressure becomes infinity and if we kind of think of I mean you know not think of let us say, if I just take these two terms individually and plot them in a pv diagram, then what I will get? See the first term varies as 1 over V minus b and for obvious reason, it cannot go I mean, this term is not defined below the equal to b. So, of course, and that makes more physical sense because b is the co-volume and the co-volume is some somewhat related to the actual molecular volume.

So, if we take all the molecules and calculate the volume of those molecules together, so the volume of the whole gas cannot be less than that particular volume and of course, we know that b is not exactly this total molecular volume but there is a factor of that, but assuming that this is somewhat strongly related to the actual volume. So, we cannot be defined beyond below the value of b. So, and of course, we see at V is equal to b there is a discontinuity.

So, this is the RT by V minus b term in blue here and it is defined only up to V is equal to b. Now, for the other term minus a by V square, this term is starting it has a negative terminal, it has a negative sign in the in front of it. So, it starts from the negative side and it falls faster sorry, it should be there is a mistake. So, this is simple a by V square not p plus a by V square. So, actually it is minus a by V square that makes more sense.

So, basically it becomes infinity at V is equal to 0. So, this term also diverges at low values of V and it falls of faster as compared to this one because this is proportional to V minus b whole to the power minus1 and this is proportional to V square. So, this will be falling off faster as compared to this one and the red line is the resultant curve which is given by this equation here which is a combination of these two terms.

So, what do we see? We see that at very low value this term dominates and intermediate term intermediate value this term dominates, intermediate value of V this term dominates and once again at very high value this term takes over because this term becomes minus a by V square is falls of faster as compared to this term and after a certain while this term has no significant contribution in the value of p and at very high V values, it will be only this right. So, this is a quantitative plot, but it gives you some useful information.

So, it actually tells you that when at very high volume and low pressure, this gas behaves more more or less like ideal gas and which is kind of expected because we know that Van der Waal's equation that we have already seen that at very low pressure the Van der Waals equation becomes equivalent to the ideal gas equation because of this ideal expansion. Now, next is we open this bracket, I mean we compute this multiplication and just write one single the equation in one single line.

And this is a pV cube plus pb plus RT V square times plus a into V minus b is equal to 0. So, this equation once again if I think of p I mean and think of it in a pV plane, this is a cubic equation in V. Now, in a cubic equation, it has to have three roots, cube cubic equation will have three roots and there are theorems in algebra which actually says that out of the three roots, either one is real and two is imaginary or all three are real.

So, these are the only two possibilities how we can have these three roots. Now, once again if I examine this equation here, so, three roots means, p will be equal to 0 for three values of V. So, this is one value here, the other value here and the third value is somewhere in the very high V value. So, it is essentially at V is equal to infinity. So, at V is equal to infinity both this term and this term goes to 0 and this term will also go to 0.

So, it is a cubic equation. So, roots are 1, 2 and 3, so, let us write it here. So, root 1, root 2 and root 3 will be somewhere far. Now if now, what we can do is we can shift this curve upwards or downwards by choosing suitable value of T. So, what will happen if I choose a higher value of T this curve will move upwards, this curve will more or less remain intact. So, the whole the red line will be shifting upwards right.

So, we will not have this 0 crossing exactly, but this the quantitative pictured that it will be it will have this quantitative shape this curve will remain intact. So, in the right hand side what do we have here, we go back to this Andrew's experiment on carbon dioxide. We here it is the reproduced assuming that carbon dioxide behaves like Van der Waal's gas, the right hand side curve has been plotted by choosing suitable values of the Van der Waals constant a and b and at suitable temperature.

So, I am not putting this temperature in here because we already have discussed you know, what you call the quantitative nature of this curve. So, we are not going back to that. So, what we are going to discuss essentially is this at low pressure or sorry low values of temperature we have an altogether you see this particular shape is maintained especially at low temperature. So, at low temperature we have quantitative shapes something like this and we know from experiment this inside this dotted red line in experiment we get a single spread curve.

So, that instead of this having this single straight line we have a down and an up portion in the inside this curve which is once again something that is considered as a drawback of Van der Waal's equation it cannot reproduce the experimental data exactly, but in general the quantitative shape is very well reproduced look at this at high temperature we have the vapour state, at low temperature and high volume low pressure we have the vapour phase at low volume high pressure we have the liquid phase this quantitatively is very well introduced to you.

And in between only when this condensation starts over instead of a straight line we have this wavy pattern like and of course, we have kind of 2 0 crossings one here and one here actually 3 so, 1, 2 and 3 now and then as the temperature increases, this condensation area becomes shorter and shorter and that is exactly how we observe it in the experiment, as the temperature goes to the critical point, the condensation portion the region of volume in the pV diagram over which the condensation takes place becomes shortened.

That is exactly what is happening and at one point the three roots, so basically this 3 the red line processing these three positions. So, this can be considered as three roots of this cubic equation, you see this three roots coincide kind of coincide to give you one intersection only. So, this is the critical point at which instead of an above critical point, instead of having three roots, we start having only one real root. So, this is where the critical point is kind of a turning point for this curve. So, the quantitative nature is very well reproduced right.

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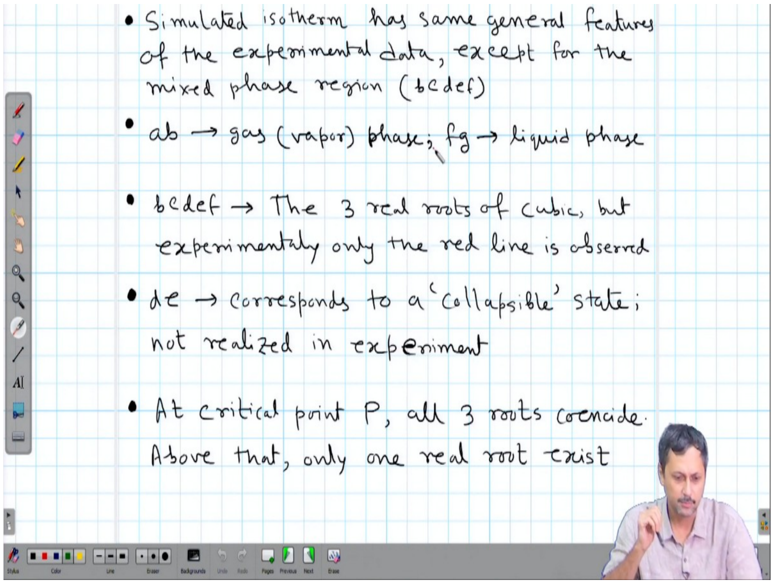

- Simulated isotherm has same general features of the experimental data, except for the mixed phase region (bcdef)
- ab → gas (vapor) phase; fg → liquid phase
- bcdef → The 3 real roots of cubic, but experimentally only the red line is observed
- de → corresponds to a 'collapsible' state; not realized in experiment
- At critical point P, all 3 roots coencide. Above that, only one real root exist

So, let us review some of these aspects quickly. So, simulated isotherms as we had already discussed has some general feature of the experimental data except for the mixed phase region which is given by this b, c, d, e, f plot. So, a b is when the gas is in the vapour phase, this d e is correspond to the sorry a b is in the gas in the vapour phase, f g is where the gas is in the liquid phase, this is something that we have already discussed this is the vapour phase and this is the liquid phase.

In the mixed phase the three real roots of cubing but experimentally only one red line is observed. This is once again we have discussed this is one drawback. Now, if we closely examine this part, see this part de over here when the pressure and volume increasing simultaneously. So, between d and e is as the volume decreases, the pressure also decreases. Now, this is extremely counterintuitive and cannot be realized in real systems because this corresponds to a collapsible state.

What do you mean by collapsible state that means, you know the system this actually remains the equilibrium you know the lines here in this plot that represent the equilibrium condition of a particular system. Now, in a system if the pressure decreases and the volume decreases simultaneously that means the pressure of the system is driven towards a collapse. So, that means in the limit of 0 volume there will be 0 pressure.

So, this collapsible state can never be realized in reality whereas, this one is actually called a superheated state. So, we are not going into the details of this. So, basically these are once again as I mentioned is the drawback of Van der Waal's equation, that it cannot exactly reproduce the experimental data. So, once again at critical point p all three roots coincide above that only one real root exists. So, above this critical point, whatever you do, you get only one real root and that is at p is equal to 0 at T is equal to infinity.

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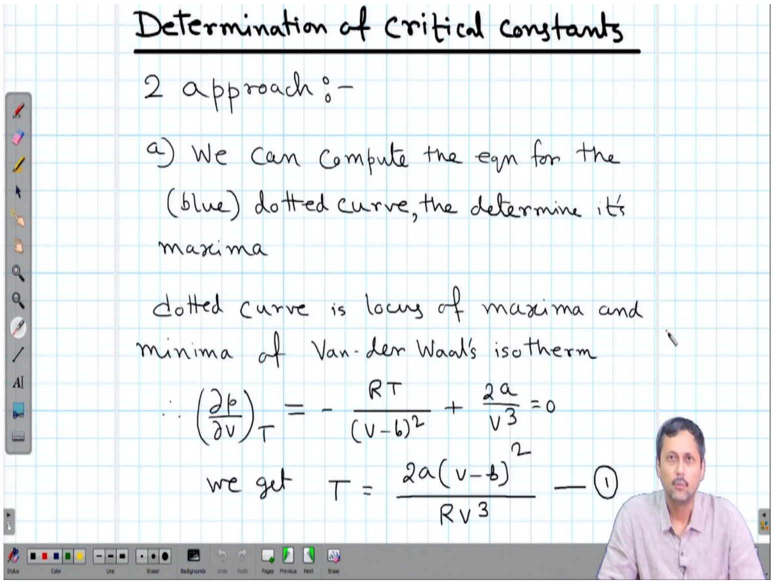

Determination of critical constants

2 approach :-

a) We can compute the eqn for the (blue) dotted curve, the determine it's maxima

dotted curve is locus of maxima and minima of Van-der Waal's isotherm

$$\therefore \left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0$$

we get $T = \frac{2a(v-b)^2}{Rv^3}$ — ①

Now, the next thing is, we want to determine the critical constants, we have found out critical point p experimentally and in this set of curves, we actually found it theoretically. Now, there are two possible approaches of determining the critical point starting from the Van der Waal's equation. So, that is a theoretical prediction and both approaches gives you exactly the same result because both approaches more or less they are the same only the thinking process is slightly different.

So, what we can do is we can you see it is not this red line is kind of arbitrary here because this is where, this is what we see experimentally the red dots, but what I have done here? I have taken the minimum the locus of the minimum. So, because, there are three roots the curve in between here goes once through a minimum and the time is goes through a maximum. So, what I have done here is I have just joined this minima and this maxima with a single blue line which also goes through p.

So, basically at p this blue curve and this experimentally observed red touch but forget about the red point line for now, let us talk about the blue line which does exist. If we examine the Van der Waal's equation, so, this is basically the locus of the minima and the maxima. So, what we can do is we can compute the equation of this blue line somehow and please understand that the topmost point of this blue line is the critical point p that is why I have also marked p here with blue just to make a one to one correspondence.

So, once we can somehow determine the equation of this blue line in terms of p and V, then take one derivative and set it to is equal to 0. And of course, we get condition for the point p, now that can be done assuming that I mean if we understand this blue line is nothing but the locus of the minima and the maxima. Now, for minima and maxima both the starting from Van der Waal's equation you know del p del V at constant and this is on an isotherm. So, each of these set of minima and maxima is on an isotherm.

So, del p del V at constant temperature T has to be equal to 0. So, we did exactly the same thing del p del V at constant temperature T is minus RT by V minus b square plus 2a by V cube which is equal to 0. So, by solving this we get T is equal to 2a times V minus b square by 3 RV cube. Now, all we have to do is we have to go back to the original Van der Waal's equation, which is p plus a by V square times V minus b is equal to RT that T has to be replaced by substituted by this value of T.

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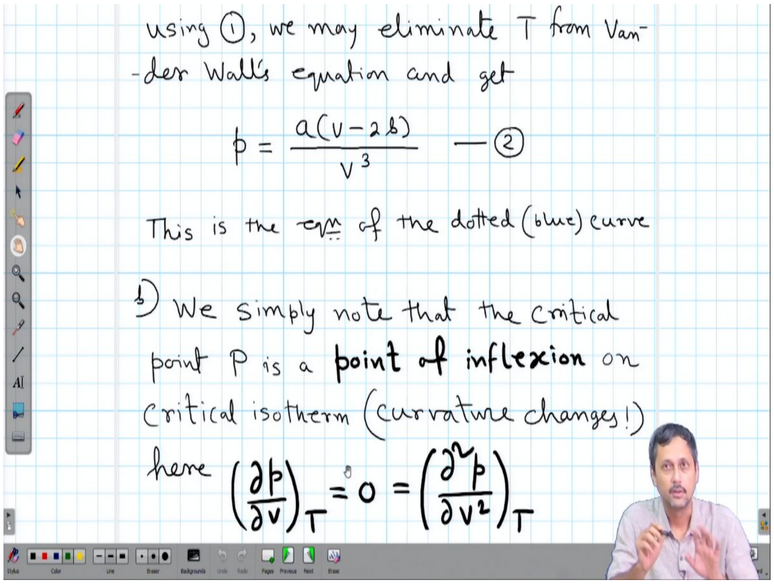

using ①, we may eliminate T from Van--der Wall's equation and get

$$p = \frac{a(V-2b)}{V^3} \quad — ②$$

This is the eqn of the dotted (blue) curve

b) We simply note that the critical point P is a **point of inflexion** on critical isotherm (curvature changes!)

here $\left(\frac{\partial p}{\partial V}\right)_T = 0 = \left(\frac{\partial^2 p}{\partial V^2}\right)_T$

And we get an equation which is p is equal to a times V minus 2b / V cube, we call this equation 2 and this equation is exactly the equation of this blue dotted line. So, this equation corresponds to this blue dotted line. Now, all we have to do is we have to take one more derivative of this equation, we have to come to another del p del V no T anywhere that we have to set that equal to 0 and we get a condition for critical point. This is something that is you know absolutely doable, but it is even simpler.

If we understand mathematically that this point p is the point of inflection in this pivot diagram, what do you mean by point of inflection? Point of inflection is where a curve changes its curvature. Now, look at this, this is concave and this is convex. So, p is the point in which it is a tangential point the tangent is actually along this x axis along the V axis. Not only that, it is where the curve changes from the concave this isotherm this particular isotherm the critical isotherm, so it changes from concave to convex.

So, this is why we call point p, mathematically we can call it this one the point of inflection. Now at a point of inflection, not only the first derivative but also the second derivative has to be equal to 0 once and we will see very and of course you see setting del p del V t is equal to 0, we got to this equation and taking one more derivative, when setting the second derivative also is equal to 0, it is essentially taking derivative of this curve and setting t is equal to 0. So, we are doing exactly the same thing, but in a slightly straightforward mathematical way. So, all we have to do is we have to take 2 derivatives of the original Van der Waal's equation and set them both equal to 0.

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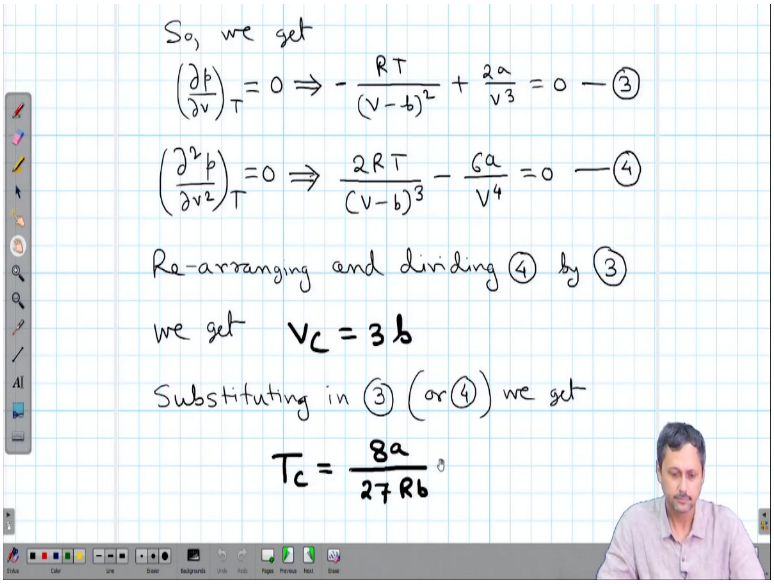

So, we get

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 \Rightarrow -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \quad — ③$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0 \Rightarrow \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0 \quad — ④$$

Re-arranging and dividing ④ by ③

we get $V_c = 3b$

Substituting in ③ (or ④) we get

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

We do that and we get equation number 3 and 4 the equation 3 is already familiar to you, we have done that in here already and then take a derivative of 3 and you get equation 4. So, all we have to do is and see both terms has a sign difference. So, the first term is RT by V minus b whole square is equal to 2a by V cube and the second term is 2RT by V minus b whole cube is equal to 6 a by V to the power 4. So, we have V cube here V to the power 4 here.

So, after rearranging if we just divide 4 by 3 in a, proper manner, so we essentially get V c is equal or maybe actually, it has to be division of 3 by 4, right. Because it is in the denominator does not matter, you understand you can do it yourself. So, we get V c is equal to 3 b that means, the critical volume is 3 times the co volume. Next is we have to substitute this equation in any of these 3 and 4, 3 or 4 and we get T c see once we do that, these equations are free of p.

So, it is only V and T. So, once we put for substitute for V is equal to V c, all we have to do all we have to do is we have to substitute for V is equal to V c and we get T c = 8a / 27 Rb. Next we go back to the original Van der Waal's equation and substitute see here.

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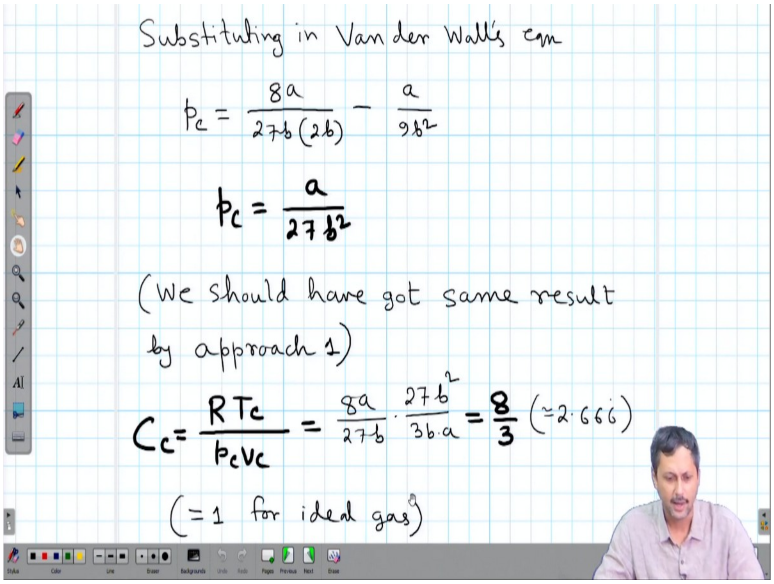

Substituting in Van der Wall's eqn

$$p_c = \frac{8a}{27b(2b)} - \frac{a}{9b^2}$$

$$p_c = \frac{a}{27b^2}$$

(We should have got same result by approach 1)

$$C_c = \frac{RT_c}{p_cV_c} = \frac{8a}{27b}\cdot\frac{27b^2}{3b\cdot a} = \frac{8}{3} \quad (\simeq 2.666)$$

(= 1 for ideal gas)

So, p is = RT / V - b - a / V square. So, we have to substitute for T c RT c R R cancels out 8a / 27 Rb so R that R cancelled out times 2b because V c is equal to 3b so V c minus b is equal to 2b and this one a by b square will be a by 9b square and simplifying we get p c is equal to a by 27b square. So, absolutely, if we have followed approach one that is if we have taken another derivative of this curve which is mathematically exactly the same treatment, what we are doing we would have got same result.

Next is we compute the critical coefficient which is quantity RT c divided by p c V c. If we substitute T c is equal to this one, what is 8a by 27 Rb. So, RT c will be 8a by 27b. And 1 by p c V c is 27b square by 3ab, and we get every Van der Waal's constant cancels out and we get a quantity 8 by 3 which is 2.666 is a constant. And if you recall, if we just take the ideal gas equation RT c by p c V c will be equal to one. So, in terms of this coefficient, there is a huge deviation from the real ideal gas approximation.

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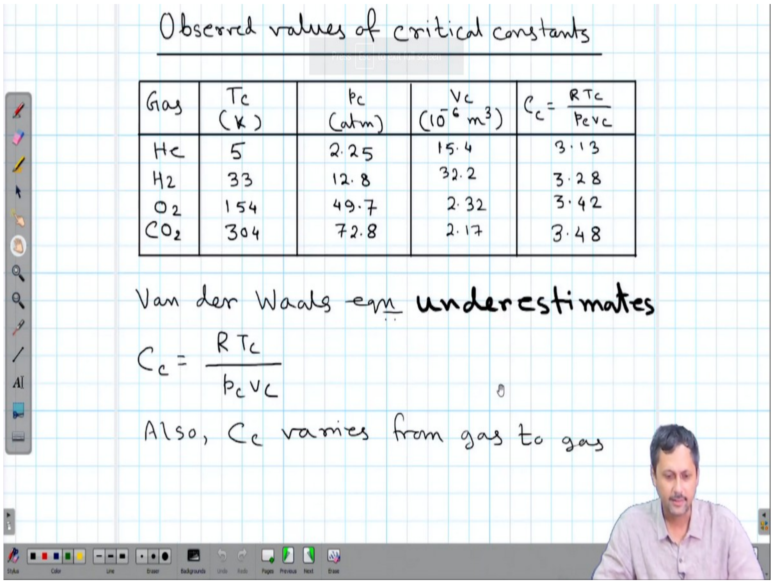

Observed values of critical constants

Gas	T_c (K)	p_c (atm)	V_c (10^{-6} m^3)	$C_c = \frac{RT_c}{p_c V_c}$
He	5	2.25	15.4	3.13
H_2	33	12.8	32.2	3.28
O_2	154	49.7	2.32	3.42
CO_2	304	72.8	2.17	3.48

Van der Waals eqn **underestimates**

$$C_c = \frac{RT_c}{p_c V_c}$$

Also, C_c varies from gas to gas

Now in the next we look at some of the experimentally measured value of this critical parameters and corresponding critical coefficient RT c by p c V c. So, for helium, we get T c is is equal to 5 Kelvin p c is is equal to 2.25 atmosphere and V c well it has given as 10 to the power minus 6 meter cube which is actually litres or with C c, so it is 15.4 C c. Similarly, for hydrogen, it is 33, 12.8 and 32 so on and so forth. And we see that the ratio C c is 3.13, 3.28, 3.42 to 3.48, which is way over what is estimated from the Van der Waal's equation.

Now from Van der Waals equation it was estimated to be 8.3 which is 2.67 roughly and for all real gasses. We see that the measured value of this coefficient is between 3.1 and 3.5. So, this is more or less the range where all the measured experimentally measured values stay. So that means Vander Waal's equation, underestimates the value. Also according to Van der Waal's equation C c should be a constant, but here we see that C c the coefficient here varies from gas to gas. So, with this knowledge, what do we do?

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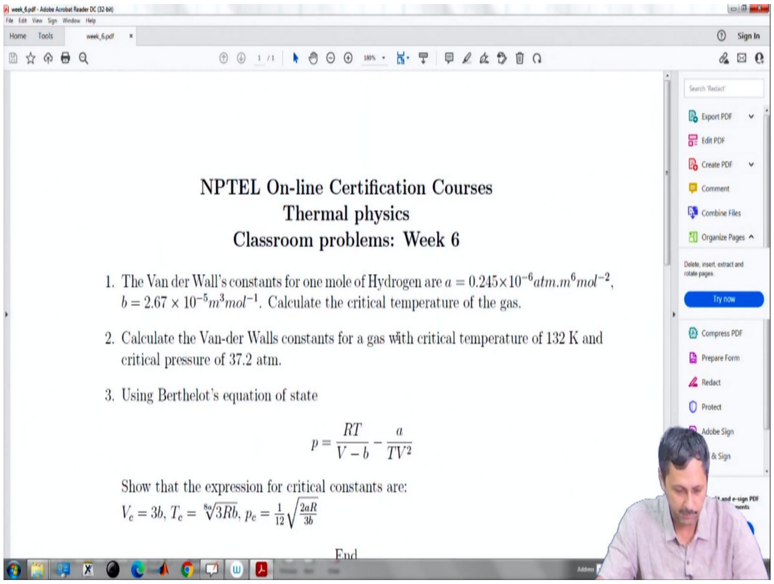

NPTEL On-line Certification Courses
Thermal physics
Classroom problems: Week 6

1. The Van der Wall's constants for one mole of Hydrogen are $a = 0.245 \times 10^{-6} atm.m^6 mol^{-2}$, $b = 2.67 \times 10^{-5} m^3 mol^{-1}$. Calculate the critical temperature of the gas.
2. Calculate the Van-der Walls constants for a gas with critical temperature of 132 K and critical pressure of 37.2 atm.
3. Using Berthelot's equation of state

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

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

End

So, now, what do we do we go back to the classroom problem set here for week 6 and perform one problem to end this class now. So, the Van der Waals constant for one mole of hydrogen are given as a is equal to 0.245 into 10 to the power minus 6 atmospheres m to the power 6 mole to the power minus 2 b is equal to 2.67 into 10 to power minus 5 meters per mole, we have to calculate the critical temperature of the gas.

So, this is a very straightforward problem, because if we go back to this expression for critical temperature, we see this is given by 8a by 27Rb all we have to do is we have to put these numbers here, but there is a small catch. To see the constant a is given in atmosphere per m to the power 6 per mole to be power minus 2 and b is given as meter cube per mole. So, b is already in SI units, whereas a is not in SI units.

So, our first job would be to bring a into SI units. Now, the only unit that is not in SI's atmosphere, and I think in the last class of last week, we have discussed about what we can do is we can in some problems, we can take a suitable value of R, you know in a different unit and substitute for that, but here there is no option because it has to be it is a ratio of a by b, and it has to be you know, equal in both a and b has to be in SI unit. So, this problem is essentially an unit conversion problem which I would request you to pay attention because this unit conversion is something that we have to you might have to do many times.

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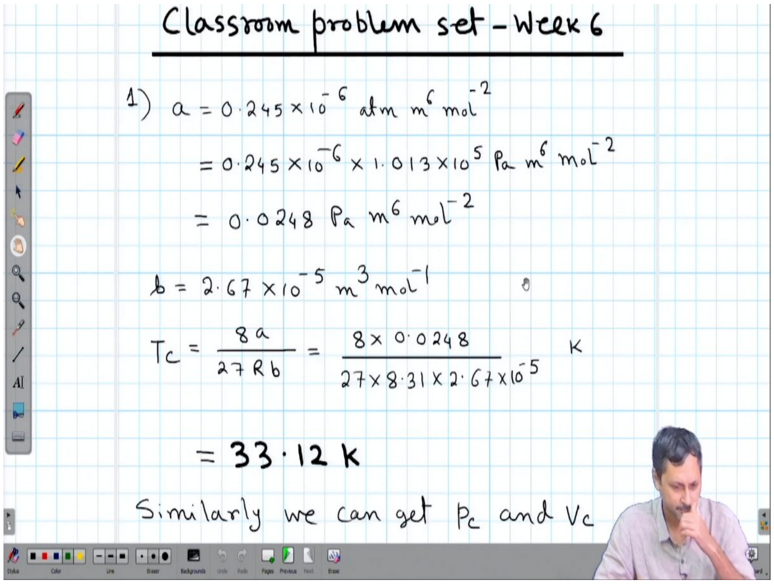

Classroom problem set - Week 6

1) $a = 0.245 \times 10^{-6}$ atm m^6 mol^{-2}

$= 0.245 \times 10^{-6} \times 1.013 \times 10^{5}$ Pa m^6 mol^{-2}

$= 0.0248$ Pa m^6 mol^{-2}

$b = 2.67 \times 10^{-5}$ m^3 mol^{-1}

$$T_c = \frac{8a}{27Rb} = \frac{8 \times 0.0248}{27 \times 8.31 \times 2.67 \times 10^{-5}} \text{ K}$$

$= \mathbf{33.12\ K}$

Similarly we can get P_c and V_c

See a is equal to 0.245 into 10 to the power minus 6 atmosphere meter cube mole to the power minus 2. So, from atmosphere to Pascal, the conversion is 1.013 into 10 to the power 5, so one atmosphere is 1.013 into 10 to the power 5 Pascal, all you have to do is you have to multiply this quantity with this one and if we do that there is a minus 6 here there is a 10 power minus 6 here, 10 to the power 5 here all to, after completing the multiplication, we get 0.0248 Pascal meter to the power 6, mole to the power minus 2.

And b is equal to 2.67 into10 the power minus 5 meter cube mole inverse substituting 8a by 27 Rb in Kelvin, we get 33.12 Kelvin. So, this is a one relation that we have and of course, we see I mean just by comparing with the previous table that gas most likely is hydrogen. Most likely, but of course, we have to verify with other constants and also 3 we have to verify with other constant and there will be a mismatch as well because this 3 combines to give 3.28. But whatever we calculate from this from our calculation, assuming Van der Waals gas will give you 2.66.

So, it is hard to say but we can assume that this is somewhat close to hydrogen and see in a similar manner we can also compute the other constant like p c and V c. V c though is very simple because once we have b we just have to multiply it with by 3 and we get V c and for p c also we just have to use another relation. So that is where we stopped in today's lecture. Now, for the next lecture tomorrow what we are going to do is we are talking we will be talking about measurement of the Van der Waal's constants a and b.

Some limitations, some more limitations in detail discussion about the limitations of Van der Waal's gas and then we will look into other available equations of state and if their prediction of critical parameters are slightly better than the Vander Waal's equations of state. So, this is all for today's lecture. See you again tomorrow. Bye.