Thermal Physics
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Lecture-24
Topic-Behaviour of Real Gases

Hello and welcome back to another lecture on this NPTEL course of thermal physics. So, as promised in today's lecture we are going to start with real gases. So, for remaining of this week 5 these 2 lectures we will be discussing real gases, their deviation from the ideal gas law, their different properties and we will be solving some problems of course. Now of course, what are, we all know what real gases.

Real gases are the gases we talk about all the time, hydrogen, nitrogen, oxygen, helium and of course air is a gas mixture as we all know, it is a mixture of nitrogen, oxygen, carbon dioxide, argon and many other even some water vapour is also present there. Now the ideal gas equation as we all know it is for an ideal gas, now in real world nothing is ideal. So, there must be some deviation from this ideal gas equation which is also observed experimentally.

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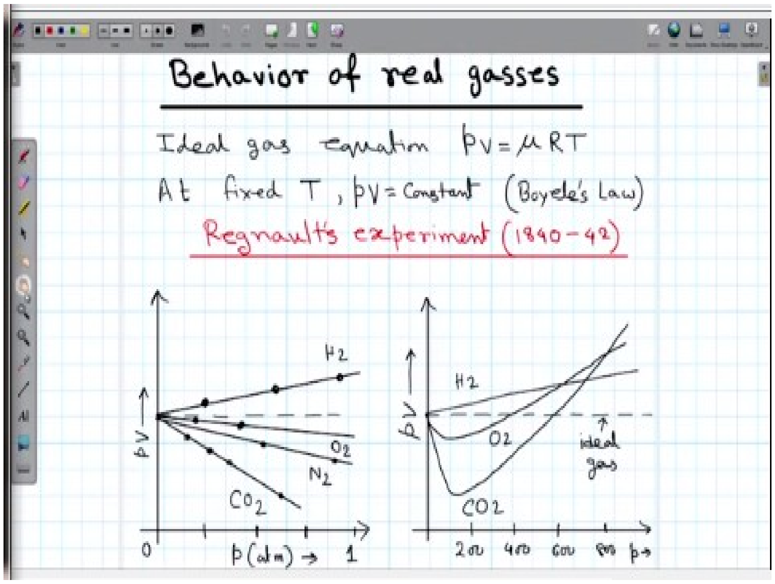

Behavior of real gasses

Ideal gas equation $pV = \mu RT$

At fixed T, pV = Constant (Boyele's Law)

Regnault's experiment (1840-42)

So, let us start with this some of these experimental results and then we will be slowly going into the ways of tackling these deviations. So, the first experiment, first meaningful experiment that shows that ideal gas equation which is pv is equal to mu RT, mu being the number of moles in this case. Now at fixed temperature pv is equal to constant, the right hand side is only a function of temperature here as you can see. And we know that the Boyle's law which is actually once again it is a phenomenological law or empirical law which was deduced from the experimental measurement itself. But the experiment was at low pressure and at relatively high temperature.

Now at Boyle found this law, the pv actually remains constant over a certain pressure range. Now the first experiment that actually shows conclusively that this ideal gas equation or Boyle's Law, which is pv is equal to constant is not valid for the entire pressure range is the Regnault's experiments, I do not know what is the actual pronunciation because these are French names and it is not so easy to pronounce, but it does not matter really.

So, what Regnault did was he measured the pv value as a function of pressure. Now pv we see that the ideal gas equation right hand side is only a function of temperature. So, if temperature remains constant, then pv should be as a function of pressure the product p and v should remain constant. So, we see that the dotted line here if I plot pv versus p the dotted line here or here is for ideal gas.

Now what happens? What he has found out is that not only none of these gases actually behave ideally if the pressure is slightly on the higher side. So, he applied in the first panel it is only up to maybe 1 atmosphere which is a moderate pressure, can we cannot call it a high pressure anyway. Because 1 atmosphere pressure is for the pressure we all live with all the time. So, even at this pressure when the applied pressure is up to within 1 atmosphere, the ideal gas behavior is not followed by any of the gases hydrogen, oxygen, nitrogen and carbon dioxide.

And all this although they, so in a sense the gases actually follow the Boyle's law because all of them at extrapolated to 0 pressure they more or less meet at the same point. So, we can assume that at really low pressure the Boyle's law is obeyed properly. But even at a moderate pressure of 1 atmosphere, we see that there are deviations from this ideal gas law. Now when he repeated his experiment or rather he extended his pressure range up to 800 atmosphere, which is very high pressure, I would say 800 times the pressure we experience on a daily basis.

Then he we actually saw that almost all the gases they go through a minima the pv the product pv, the first come down goes through a minima and then it goes up once again. For hydrogen is an exception but later on it was found out it is just that this turning point for hydrogen is at a very low pressure, so which was not detectable in the initial experiment. So, what he did? He could he could not take all the way down to very low pressure that time the equipment.

So, in this experiment was carried out around between 1840 and 1842 and it was first reported I think few years later. So, for hydrogen it was later found out hydrogen also follows the exact same behavior the quantitative behavior. That the product pv with as a function of pressure first goes down, then it goes up and continues. So, this actually tells you that for the general behavior is there is a minima in the pv versus p diagram.

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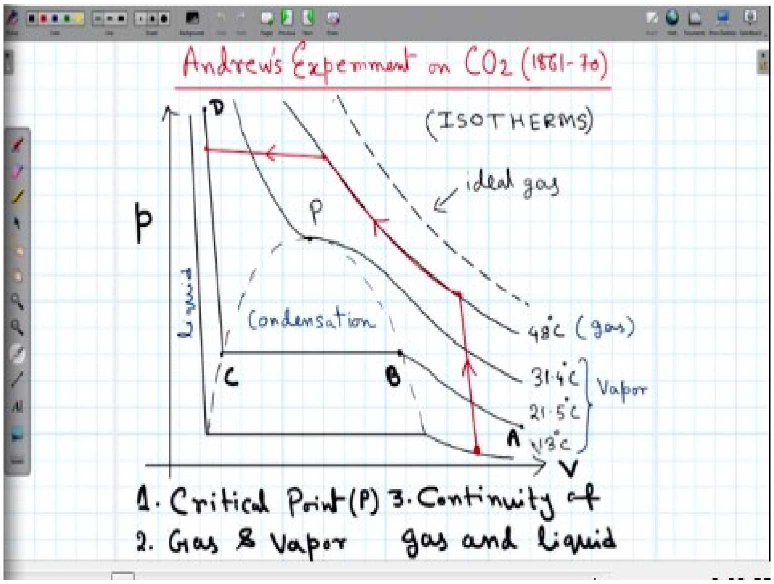

Now the next experiment few years after the initial experiment of Regnault's was the Andrew's experiment 1961 between 1861 and 1870 and it is carbon dioxide. Now if you look at it carefully, you see that carbon dioxide among the gases that has been chosen by the Regnault's experiment by Regnault's. Carbon dioxide shows the most dramatic decrease in the product pv and then it goes up. So, what Andrew did was, he actually he chose carbon dioxide and please remember that all these are on the measured at the same temperature. So, basically these were room temperature measurement.

Now what Andrew did is he varied the temperature and instead of plotting pv as a function of p, he plotted p versus v. Now the ideal gas equation is pv is equal to constant, so see the dotted line is kind of a hyperbolic line that should be the behavior of an ideal gas in the pv diagram. So, we are all familiar with this, it should be like this, okay, there are many lines here, so we have to be careful in understanding this.

So, first of all I would request you to ignore this red points and the joining lines, this is something that we will be discussing in the very last or rather in a later phase when I will be describing this experiment in more details. So, let me first start with the experiment, the experiment is the following. Andrew took, so I am not discussing the apparatus and how this experiment was performed.

So, the simply speaking the experiment was the pressure versus volume curve has been traced at different temperatures for carbon dioxide. Now if we come down, we see as the temperature decreases, the curve shifts downwards. So, if I focus on the topmost curve which is taken at 48 degrees Centigrades. We see that the behavior is to some extent matching with the ideal gas of course it is not exactly hyperbolic not exactly parallel to this dotted line but it is more or less.

So, at 48 degrees we can say that carbon dioxide is more or less behaving like an ideal gas in terms of this pv diagram. As the temperature decreases around 31.4 degrees centigrade, we observe that there is a kink, there is a flat part although very short but there is a flat part in this isotherm. So, these are called the isotherms, isotherms means therm means temperature and iso means constant.

So, these are lines that are recorded in constant temperature. So, 48 degree isotherm is this one, 31.4 degree isotherm is this one. Now as the temperature becomes lower and lower we see the general characteristics. So, we start from the low pressure and high volume side. So, then as the pressure increases, so you have to understand that the pressure always increases in an experiment.

So, as the pressure increases the volume starts to decrease and at some point, let us talk about this curve A, B, C, and D. And at some point below this 31.4 degrees centigrades, every curve has the same general characteristics that at some point it starts to condensate, condensate means it starts to liquefy. And this liquification goes over a certain period; it is not something that is happening instantly, the temperature remains constant but it goes over there is a drastic volume change.

So, specific volume of liquid is low specific volume of vapour phase is high, all this we will be discussing later on in more details when we will be discussing phase transition. But I think you all realize that if I take 1 grams of water, it takes only 1 centimeter cube volume. And once we vaporize the water at under atmospheric pressure, the vapour will take a lot larger volume, so that is something that we understand.

So, although when at point B when the condensation starts until the point C when the condensation ends, there is a drastic volume change but the pressure does not really change, why because the pressure remains constant at a value of the saturated vapour pressure. And at point C the liquification is complete, after that whatever may be the pressure change the volume change is really tiny infinitesimal and that is understood because liquid is very difficult to compress.

So, gas is much easier to compress that compress as compared to liquid. Liquid can be compressed but when we compare it with gas it is very less. So, basically the stiff part CD means pressured goes from here to here, but the volume is changed only a tiny bit. So, we have 3 distinct parts there A to B this is a gas phase, B to C this is a condensation phase which is actually a mixed phase.

So, it takes time or rather if you change the pressure even by a tiny bit, you go from here to here, you go from this gas phase 2 this liquid phase when this portion is reached, when point B is reached. So, over a certain range the volume changes for practically no change in pressure. And then all of a sudden the volume does not change at all whatever pressure you may apply. So, this is how this is isotherm looks like. And for any isotherm which is recorded below a temperature of 31.4 degrees centigrade, this is more or less the general scenario.

So, let us say look at the 13 degree isotherm which also looks very similar to this one. But of course the condensation starts at a slightly higher volume that means slightly lower pressure and condensation ends at a slightly lower pressure also. So, the volume change is rather big at lower temperature. So, you see this volume change here is this much whereas for the 21.5 degrees centigrade the volume change is this much during the condensation process? So, now if I can just draw this dotted line is the locus of these two turning points or rather the two parts of the straight line and we see as we go up in temperature in general the volume change during condensation is less.

And when we are at this 31.4 degrees centigrade, whatever we do the volume does not change. So, that means or rather I would say the condensation phase becomes a point here. So, in principle it condenses but only at a particular pressure which is given by this value here and the volume is also it becomes a point, so it is a particular pressure corresponds to a particular volume and corresponds to a particular temperature.

So, this is called the critical point, this point P is called the critical point. So, what we have learned from this, first of all there exist a critical point, so beyond which, so there is a critical point which is occurring at 31.4 degrees centigrade. Now if I take any other isotherm, I have just drawn the 48 degrees centigrade here but if I draw any other isotherm this flat part or this condensation will be totally absent there.

So, above the critical temperature there is absolutely no condensation and that is when we have the real gas phase. There is a distinction between a gas and a vapour, what is that? A vapour is a phase which can be liquified by just by applying pressure. Take any curve below this critical isotherm, actually this critical isotherm should not be called vapour, it is kind of a boundary gas but let us call it vapour for now.

So, if I start compressing this by applying pressure at some point it will condense it into liquid, but take any isotherm above the critical isotherm whatever pressure I apply it will not be liquified, the liquid phase will be totally absent. So, above critical point a substance is purely gas and below critical point it is called vapour which can be liquified by application of direct pressure, nothing else.

So, this is a very important result because you see these are early days of experimental liquification of gas and all. So, people try to liquefy the gases they succeeded in some cases, they did not succeed in other cases. Because the primary method was first cool the gas to a certain low temperature whichever is available, then apply pressure. Now certain gases like hydrogen could not be liquified at that time, why?

Because whatever the lowest temperature available at that time was available at that time to the experimental is was higher than the critical temperature of hydrogen. So, that means for hydrogen the curve it was always above the critical isotherm. So, that is why the liquification could not be achieved, so that is a very important result. So, this property was first clear from this sort of experiment.

And then we of course distinguish between gas and vapour and then also now look at this red point, this also talks about the continuity of gas and a liquid phase or the gaseous phase I should not call it gas actually but ideally it can be called vapour as well. But basically it is gaseous, let it be vapour, let it be gas, these are all gaseous phase. So, there is a continuity between the gas and the liquid phase, how?

Let us look at this one, of course if I go by this route you know in between there is a mixed face coming in this dotted area and you can say that okay, they are not exactly continuous but when there is a liquid exist, coexist with it is own vapour, there must be a meniscus in between. There must be a layer that separates these 2; there is an interface that is to say. But now look at this, what I can do is, I can take it to we can start from this red dot and then we can change the pressure and temperature such that we reach to this point.

So, it change the temperature to 48 degrees and of course we increase the pressure by some extent, so that we can reach from this point to this point, so pressure and temperature can be changed independently. Next is we start compressing this phase and we get to this particular point here. Now what do we do? Keeping the same everything, we just reduce the temperature, keeping the pressure the same; we just reduce the temperature, what will happen? We will immediately go to this point which is liquid. So, this part here is liquid, this part here is vapour and we can see that there is a continuous pathway from liquid to vapour.

See at this point also this is actually pure gas, yeah. So, from vapour we go to the gas phase which is once again vapour and gas you cannot otherwise unless and until you start compressing those, there is no way that you can distinguish whether it is gas or this is vapour, so both are gaseous. So, we go from one gaseous phase to the other gaseous phase, we compress it further, then we suddenly change the temperature and go to the liquid phase. So, these are the very important finding from this Andrew's experiment on carbon dioxide.

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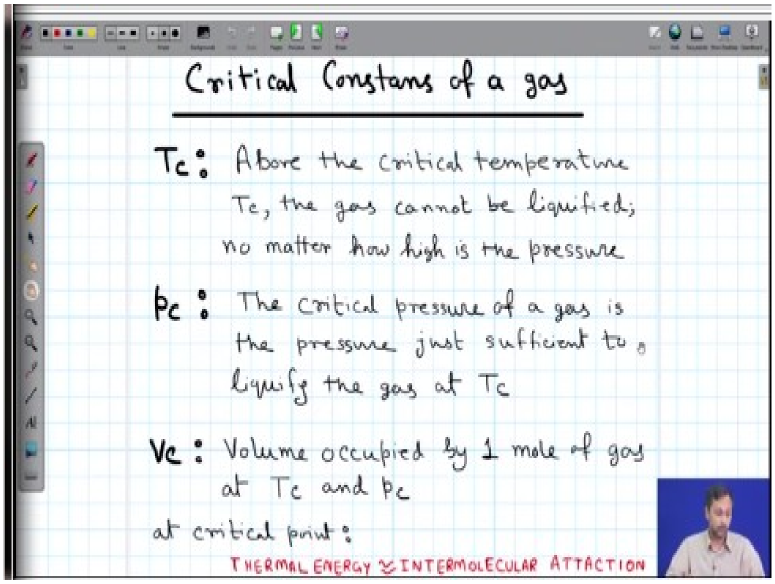

Critical Constans of a gas

Tc : Above the critical temperature Tc, the gas cannot be liquified; no matter how high is the pressure

pc : The critical pressure of a gas is the pressure just sufficient to liquify the gas at Tc

Vc : Volume occupied by 1 mole of gas at Tc and pc

at critical point :

THERMAL ENERGY ≃ INTERMOLECULAR ATTRACTION

Next is and of course we learn about these critical constants of a gas. So, what are the critical constants? Tc is the critical temperature above which a gas cannot be liquefied, no matter how high pressure do we apply; pc is the critical pressure of the gas at which it is that the pressure which is just sufficient to liquify the gas at critical temperature. So, essentially this point here corresponds to the critical pressure and temperature.

So, this is the critical point, critical temperature is here, the pressure corresponding to this point is called the critical pressure where the gas just liquifies. And then there comes the critical volume which is this point over here, which is the volume of 1 mole of gas or 1 mole of substance at critical temperature and critical pressure. Now what happens the physics of critical point is extremely important, which is beyond the scope of this lecture series.

But let me tell you very briefly that at critical point the available thermal energy which we know is purely kinetic in nature is kind of equal to the intermolecular attraction that acts between the molecules. Now you might say that, okay, in the ideal gas assumption, we never talk about intermolecular attraction and that is exactly where an ideal gas and a real gas differs. So, we will come to that in a moment.

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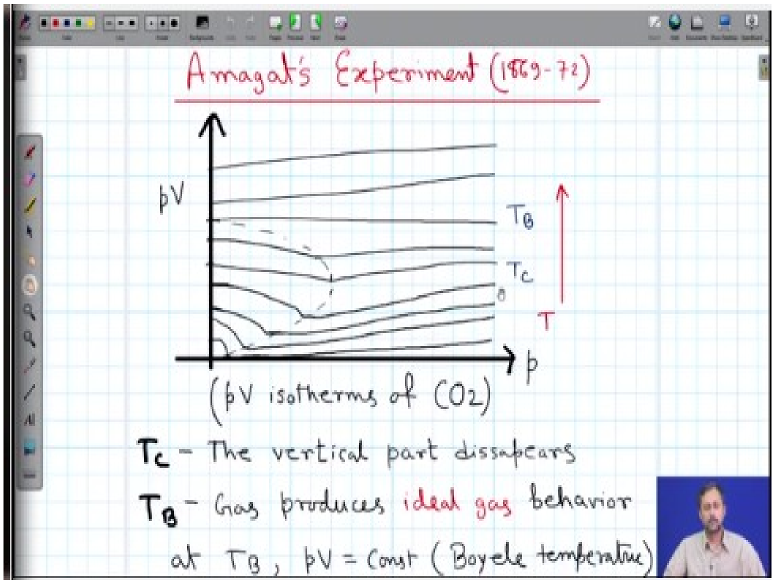

Amagat's Experiment (1869-72)

(pV isotherms of CO_2)

T_c - The vertical part dissapears

T_B - Gas produces ideal gas behavior

at T_B, $pV = Const$ (Boyele temperatue)

But before that, let me take you through another experiment once again on carbon dioxide. This is why this is called the Amagat's experiment which is performed between 1869 and 1872. Now in this set of experiment, this is by nature very similar to what Regnault's did. So, pv as a function of pressure but he chose only one gas. So, in this Amagat's experiment, this is only one gas but here it is actually a combination of both this experiment and Andrew's experiment.

So, here pv versus p is measured, when the temperature is varied continuously. Now, what do we see here? We see, so basically these are the curves. So, this is the first curve at low temperature then as the temperature increases we see that the nature of the curve changes and then at some point this dip actually kind of vanishes I should not call it dip. So, what we see here is actually a vertical portion, now this vertical portion corresponds to condensation which is equivalent to this change here, think of it.

In pv diagram also the change will look something similar something very sharp. So, exactly like this, so this is the liquification condensation part. Now this condensation part as the temperature increases the condensation this point shifts to the higher and higher pressure and if I trace the locus of this point at one point it will vanish. So, this is the critical point in which there is a decrease present see, let me go back to here.

You see that in carbon dioxide, there is a initial decrement and then it goes up, this decrement over here is related to this condensation as the pressure increases. So, if I go to low pressure below the critical temperature at some point this will happen and as the temperature increases, at critical point this vertical part will become a point and above critical part the general trend continues there is a minima but there is no vertical part which is present here or here or here or here.

Maybe the drawing is not very good but you can always look into any standard textbook where Amagat's experiment has been discussed, so you will understand it little better. And also the general trend is there is a drop and then it becomes flat. But there is a temperature which is called T B at which these minima actually vanishes. So, what we have traced here this dotted line is actually the locus of these minima. So, these minima at T B there is no minima. So, it becomes a flat line and above T B the slope changes it starts going slightly upward and it continues like that.

So, there are two main features, one is at T C the vertical part disappears, the vertical part which I once again point out this is the vertical part once again the drawing is not very good but there should be a vertical part. And at T B the gas produces ideal gas behavior; see at T equal to T B, the isotherm becomes flat, almost flat. So, this is how the ideal gas should behave because pv should remain constant, the product pv should remain constant. And this temperature where the Boyle's law is obeyed by a gas is called the Boyle's temperature; it is called the Boyle temperature actually.

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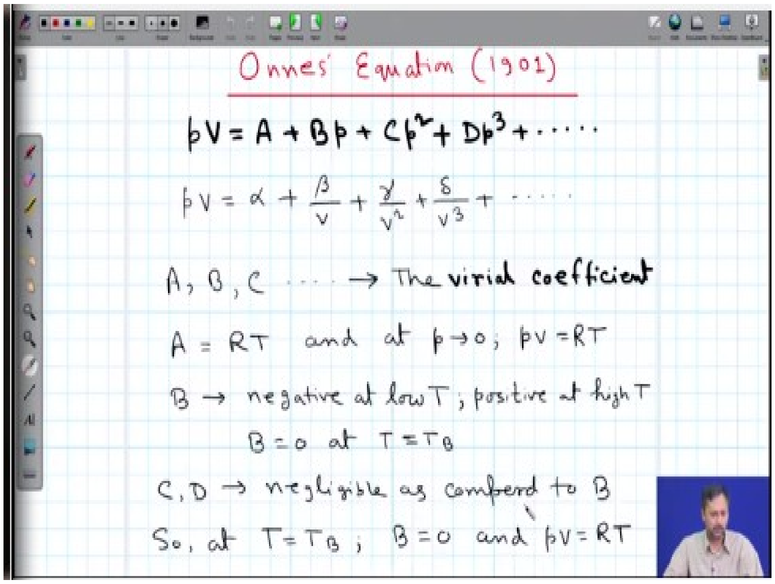

Onnes' Equation (1901)

$$pV = A + Bp + Cp^2 + Dp^3 + \cdots$$

$$pV = \alpha + \frac{\beta}{V} + \frac{\gamma}{V^2} + \frac{\delta}{V^3} + \cdots$$

A, B, C ... → The virial coefficient

$A = RT$ and at $p \to 0$; $pV = RT$

B → negative at low T; positive at high T

$B = 0$ at $T = T_B$

C, D → negligible as comperd to B

So, at $T = T_B$; $B = 0$ and $pV = RT$

Now with this knowledge after almost 30 years Onne came up with the empirical equation which could fit the experimental behavior that is observed. So, this is only one experiment that has been shown on carbon dioxide but there are several other such experiments on different types of gases where the pv isotherms for different pressure values has been recorded. Now after studying all this experimental result Onne came up with an equation of the form pv is equal to A plus B plus Bp plus Cp square plus Dp cubed and other higher order terms.

And this is once again; it is a purely empirical equation. He just found out that this type of equation basically it is a polynomial which can actually fit the experimentally observed behavior. Onne in his first original work published in 1901, has actually used 47 sub components. And later on it was found out that keeping first four component is good enough for almost all the gases up to a moderately high pressure and moderately low temperature.

If it goes to extreme high pressure or extreme low temperature the situation becomes very complicated. So, we are not going into those domains once again. And an alternative form of this equation is pv is equal to alpha plus beta by v plus gamma by v square plus delta by v cubed and so on and so forth. So, one equation is a polynomial of p, another equation is a polynomial of 1 by v, basically the same thing. Because p and v they are inversely correlated anyway.

Anyway, the first equation which is written in bold is more famous and more widely used. The coefficient A, B, C, they are called the virial coefficient. Now this term virial the word virial is actually borrowed from classical dynamics, which was first and the reason for this is there is something called virial for any classical system which can be used to calculate the theoretical values of A, B and C which is beyond the scope of this lecture. I will just use the name here and we will discuss some properties of this virial how to get to this virial coefficient but not in the details of derivation.

Now if we studied this equation, the Onnes' equation which is also called the virial equation of virial expansion. We see that for A has to be equal to RT because the ideal gas equation is pv is equal to RT. By the way this is for 1 mole of ideal gas, 1 mole of gas, so there is no nu or n term the number of moles term, so it is A is equal to RT. And as in the limit p goes to 0 all other terms actually vanish.

So, at very low pressure, all the gas behave like an ideal gas, there is a reason for it, there is actually physical reason why at very low pressure all the gas becomes ideal? We will come back to that this lecture only. And now look at the virial coefficient, the first coefficient A is equal to RT, the second virial coefficient is negative at low temperature and positive at high temperature.

And at T is equal to T B the Boyle temperature B is equal to 0. So, at Boyle temperature even if we are not going into the limit p goes to 0, the second virial coefficient is 0. The third and the fourth virial coefficient they are very less compared to AB is less and compared to B, C and D are already very less negligible. So, at Boyle temperature when D goes to 0 we can simply neglect these terms and we can say pv is equal to RT.

Now, so this is once again it is an empirical equation, empirical equation means the equation that is used in order to explain the experimentally observed behavior and at present there is no physics behind it when one is derived is there was not of course I should not say there is no physics or no science behind it. Of course there are some science that is how the virial coefficients were then the term virial coefficients were quite but anyway, so the understanding was not very clear.

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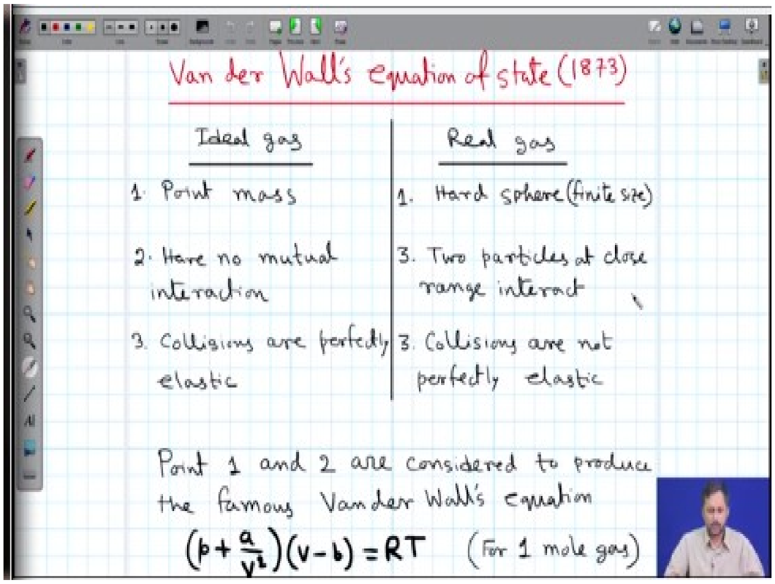

Van der Wall's equation of state (1873)

Ideal gas	Real gas
1. Point mass	1. Hard sphere (finite size)
2. Have no mutual interaction	3. Two particles at close range interact
3. Collisions are perfectly elastic	3. Collisions are not perfectly elastic

Point 1 and 2 are considered to produce the famous Van der Wall's equation

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT \quad \text{(For 1 mole gas)}$$

And actually before Onne came up with his equation, Van der Waal's equation of state which is very famous was first derived in the 1873. So, during the derivation of this equation, the basic difference between an ideal gas and a real gas has been considered. What are those three basic differences? One is the ideal gas are considered gas particles are considered pointless, whereas the real gas they are hard sphere of finite size.

Ideal gas no mutual interaction, that is very important because one of the assumption that there is only kinetic energy present, there is no potential energy term which is not right. In a real gas two particles at close range they always interact with each other. So, there are some sort of a potential energy that is acting only at short range and that is why a gas behaves like an ideal gas at very low pressure.

Low pressure means number density of molecule is small, so the intermolecular separation in general is very large. So, this short range interaction, close range interaction does not affect the properties of the gas assembly anymore. So, that is why at low pressure every gas behaves like real gas and that is exactly mentioned in this equation in the limit p tends to 0 pv is equal to RT. And the third point is collisions are perfectly elastic that is for an ideal gas one of the assumption but collisions are not perfectly elastic.

Now this point if you remember we had a discussion on why the major transport the calculated first principle transport properties are not exactly what we accept in the modern day. And one of the reasons was the inelasticity of this collision. So, this third is not considered while deriving the Van der Waal's equation. But part 1 and 2 that means the hard sphere, the finite size and finite interaction between gas particles was considered.

And finally the derivation of this famous equation which is p plus a by v square into v minus b is equal to RT for 1 mole of gas is meant. So, we will stop here today and in the next lecture we will be starting from here and we will tell you how these two terms came into picture, this what is the origin of the a by v square and minus b term in this equation and of course we will be discussing about other equations of states and later we will be solving some problems. So, until then good bye.