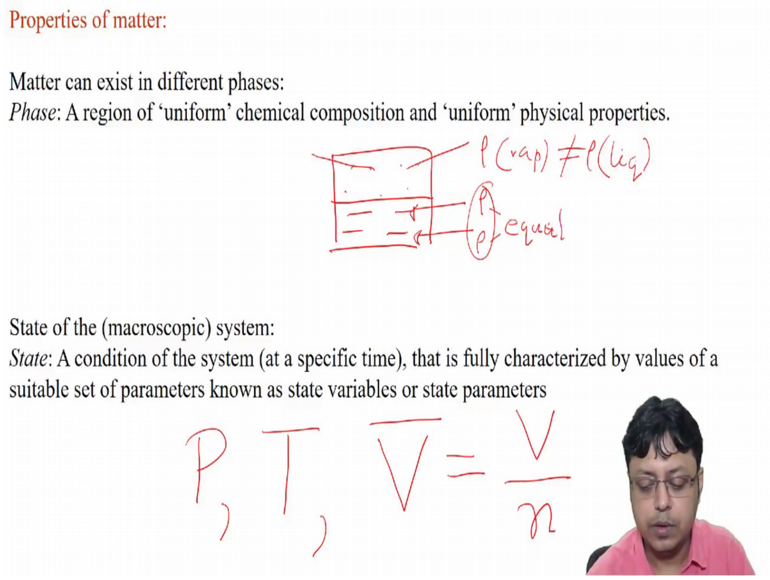
Introduction to Chemical Thermodynamics and Kinetics
Prof. Arijit Kumar De
Department of Chemistry
Indian Institute of Science Education and Research, Mohali

Lecture – 02
Properties of Gases

Hello everyone. Welcome to the course on Introduction to Chemical Thermodynamics and Kinetics. We will first begin with the properties of matter.

(Refer Slide Time: 00:23)



Properties of matter:

Matter can exist in different phases:
Phase: A region of 'uniform' chemical composition and 'uniform' physical properties.

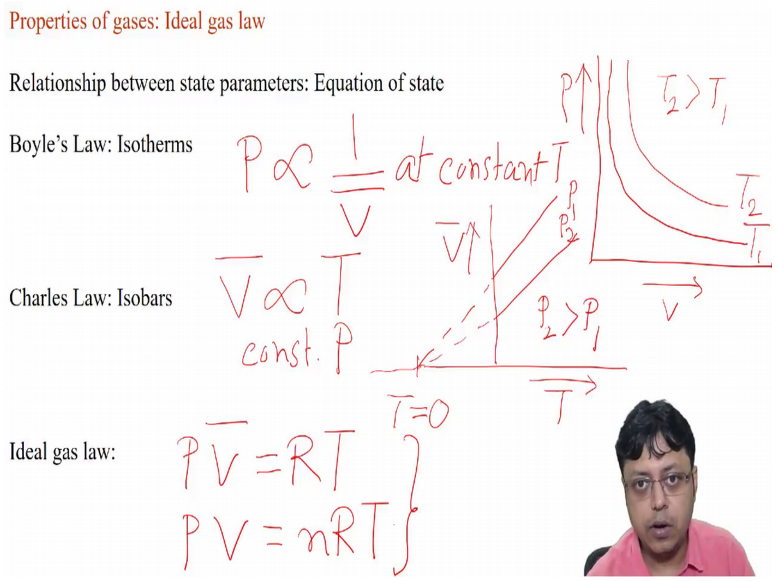
State of the (macroscopic) system:
State: A condition of the system (at a specific time), that is fully characterized by values of a suitable set of parameters known as state variables or state parameters

Now, you know matter can exist in different phases for example, the phases are solid phase liquid phase and gas phase or vapour phase. Now what is the definition of a phase a region of uniform chemical composition and uniform physical properties by that what we mean is consider a liquid in a sealed container.

Now, the liquid is in equilibrium with it is vapour now if you ask what is the density at 2 different points inside the liquid these 2 densities must be equal. So, that is the meaning of uniformity similarly the densities at any 2 point in the vapour phase will also be equal. However, the densities in the liquid and the densities in the vapour phase will not be equal, which means the liquid phase and the vapour phase are 2 different phases. Now the next thing is what descries the state of any macroscopic system by state we mean a condition of the system at a specific time of course, we are talking about time independent properties that is fully characterised by values of a suitable set of parameters and these parameters are called state parameters or state variables.

Now, the common state parameters are pressure which we denote as P temperature which we denote as T usually by temperature we mean the absolute temperature and the volume which we denote by V instead of volume we frequently use molar volume, which is volume of one mole and we will denote it by a bar. So, V bar is nothing, but the following per unit mole where n is the number of moles.

(Refer Slide Time: 02:51)



Properties of gases: Ideal gas law

Relationship between state parameters: Equation of state

Boyle's Law: Isotherms $P \propto \frac{1}{V}$ at constant T

Charles Law: Isobars $\bar{V} \propto T$ const. P

Ideal gas law: $P\bar{V} = RT$

$PV = nRT$

Now, let us first start a discussion on the gaseous phase or the vapour phase. Now you know that there is a celebrated gas law which is known as ideal gas law. Of course, by ideal we mean it is a idealised concept and no gas or no real gas strictly follow ideal gas law.

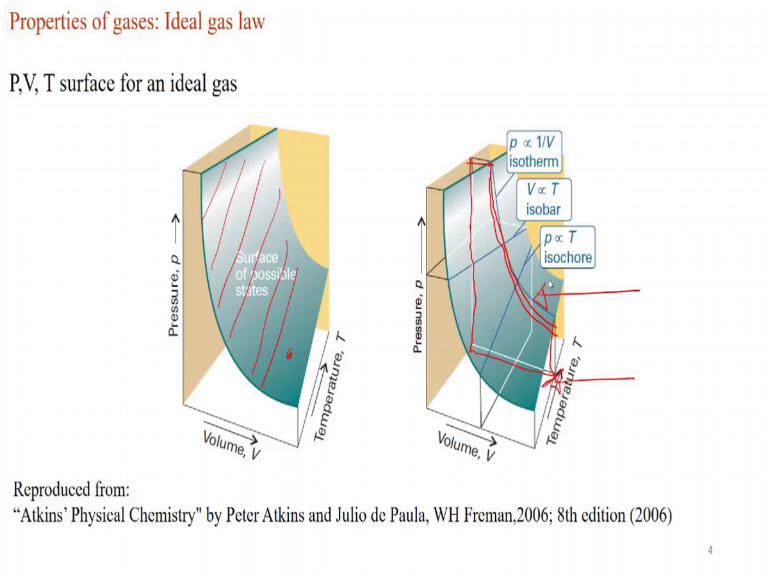
Now, why you need a gas law or something like a equation of the state in order to understand the relationship between different state parameters we need this equation of state that will completely characterise the properties of the state, you have learnt Boyles law which states the pressure is inversely proportional to the volume at nay constant temperature. So, we can write pressure is inversely proportional to volume at constant T if we plot it the pressure versus volume curve looks like a rectangular hyperbola, which we call as a isotherm because it is taken at a constant temperature now we can have several isotherms at different temperatures.

For example here I am drawing 2 different isotherms at 2 different temperatures T 1 and T 2 where T 2 is a higher temperature than T 1. Similarly you can ask what are the relation between the other 2 state parameters volume and temperature and that is given by Charles law which also you studied, according to the Charles law the molar volume is proportional to the absolute temperature. If we plot it we will get a linear curve like this we can extrapolate the curve to get a concept of absolute 0 of temperature, now this law is valid for a constant pressure. So, similarly just like Boyles law we can draw at varying temperature we can also plot the Charles law at varying pressure.

So, here I have plotted the Charles law at 2 different pressure P 2 and P 1 where P 2 is greater than P 1 combining the Boyles law and Charles law is the ideal gas law which is where R is the molar gas constant in this case we have also used the concept provided by amagat we could also write the equation in the other form which is P v is equal to n R T. So, this is ideal gas law this is nothing, but an equation of a state for ideal gases.

Now, what about real gases how do they behave before we discuss the real gas let us ask a question here when I plotted the boyles law or the charles law we showed that for boyles law the isotherms for 2 different temperatures. Similarly for Charles law we plotted isobars for 2 different pressures, but can we plot the equation of statue which is P v equal to R T be varying pressure temperature and volume simultaneously.

(Refer Slide Time: 07:07)



Properties of gases: Ideal gas law

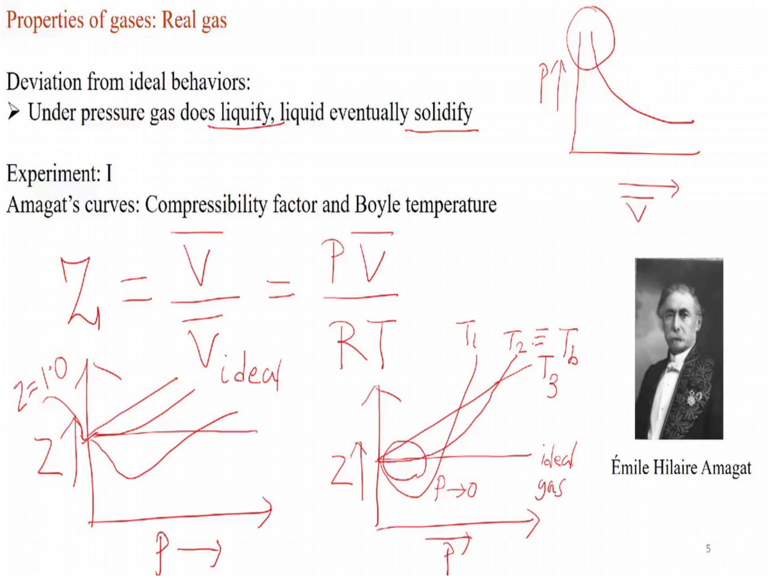
P,V, T surface for an ideal gas

Reproduced from:
“Atkins’ Physical Chemistry" by Peter Atkins and Julio de Paula, WH Freman,2006; 8th edition (2006)

What is shown here is an surface for an ideal gas which is known as pressure volume temperature surface. Now any point on this surface represents or satisfies the equation of state which is the gas law if a point lies outside the surface that point does not represent a state of an system which obeys ideal law. Now the interesting this is that if you have this surface you can readily deduce the Boyles law or Charles law for example, Boyle's law is variation of pressure versus following at cost and temperature.

So, if you fix a particular temperature as shown in this figure and take a slice along this temperature you will see an isotherm that represents the Boyle's law or isotherm at that temperature. Similarly you can also recover the following versus T which is the Charles law the isobar Charles law or the iso core how pressure varies with temperature from this 3 dimensional curve which is a surface in this case.

(Refer Slide Time: 08:37)



Properties of gases: Real gas

Deviation from ideal behaviors:

- ➢ Under pressure gas does liquify, liquid eventually solidify

Experiment: I

Amagat's curves: Compressibility factor and Boyle temperature

$$Z = \frac{\overline{V}}{\overline{V}_{ideal}} = \frac{P\overline{V}}{RT}$$

Émile Hilaire Amagat

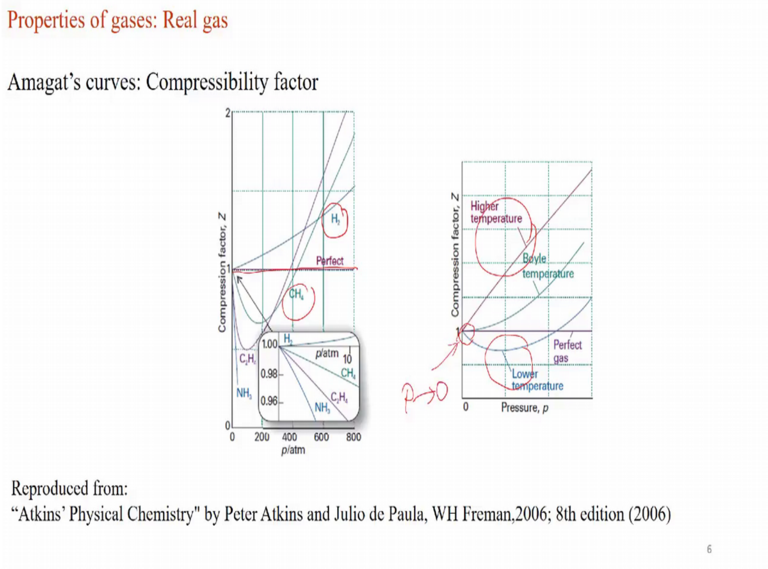
Now, let us discuss how real gases behave as you know that ideal gas equation was a hypothesized version meaning no real gas will show ideal behaviour except for certain conditions that we are going to discuss.

Now, the question is what are the deviations that we observe experimentally when our real gas is pressurised any gas under sufficient pressure forms liquid and eventually the liquid form solid; however, the ideal gas law does not predict it if you remember your pressure volume isotherm. It always predicts that even at very very high pressure region there is no change from gas to liquid or there is no phase transition, but phase transition happens in reality, we will first discuss few experimental facts that showed the deviation from this ideal behaviour one of the first experiments were carried out by amagat who gave the concept of compressibility factor the compressibility factor, which we denote as capital Z is defined as the ratio of the volume of the gas a real gas to the volume of the ideal gas.

Now using the ideal gas equation this relationship becomes amagat studied various cases and he plotted the compressibility factor Z as a function of pressure and the plots look like this for an ideal gas of course, the compressibility factor will be 1, for many gases amagats found that they behave very differently like some gas the slope of the curve is always positive for some gas thus there is a deep initial followed by a rise. If you plot the compressibility factor for the same gas at different temperatures we get a very interesting behaviour here I have drawn the compressibility factor at 3 different temperatures T 1 T 2 and T 3 where T 3 is a higher temperature than T 2 and T 1.

Now, you see that there is a region where the curve more or less follows the ideal gas curve also note that this region is only when the pressure is almost 0 the temperature at which this behaviour is observed is known as Boyle temperature which we denote as T suffix B. So, in this case according to this drawing T 2 is the Boyle temperature.

(Refer Slide Time: 12:37)


Properties of gases: Real gas

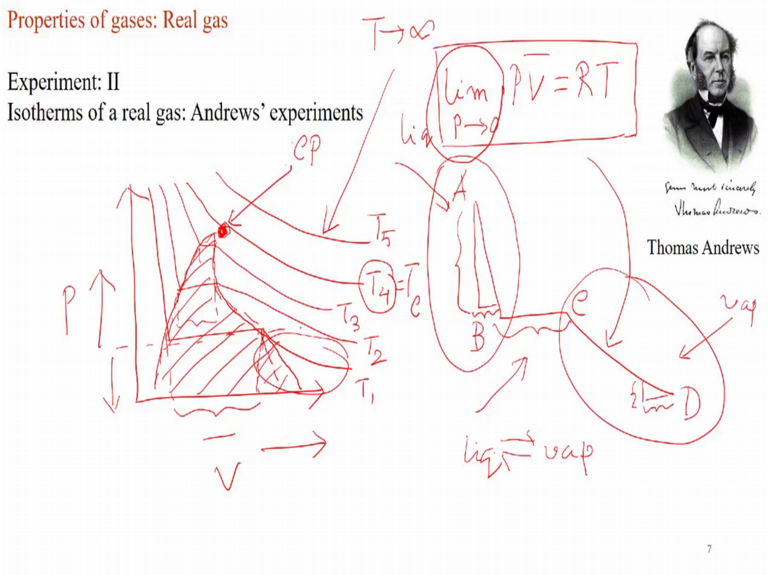
Amagat's curves: Compressibility factor

Reproduced from:
“Atkins’ Physical Chemistry" by Peter Atkins and Julio de Paula, WH Freman,2006; 8th edition (2006)

Here, I show few real experimental curves for compressibility factor as a function of pressure. Now you see here on the left hand side the plot shows the compressibility factor or the variation of compressibility factor as a function of pressure for different gases, you see for hydrogen the slope is always positive these were taken all data were taken at 0 degree centigrade or to 73.1 5 Kelvin; however, for methane there is a deep followed by a rise and the horizontal straight line shown here denotes that for a ideal gas or a perfect gas the right hand figure shows.

The same compressibility factor as a how it varies as a function of pressure for a particular gas in this case this is carbon dioxide and as you see that high temperature the slope is positive and low temperature there is a initial negative slope followed by positive slope and right at the boyle temperature the curve merges with the perfect gas or the ideal gas curve, but only in the region of very low pressure. Now we will discuss another experiment where the pressure volume isotherms were recorded.

(Refer Slide Time: 14:10)



Properties of gases: Real gas

Experiment: II

Isotherms of a real gas: Andrews' experiments

Thomas Andrews

This was done by Thomas Andrews where he carried out a set of experiments with different gases and found the isotherms for different gases.

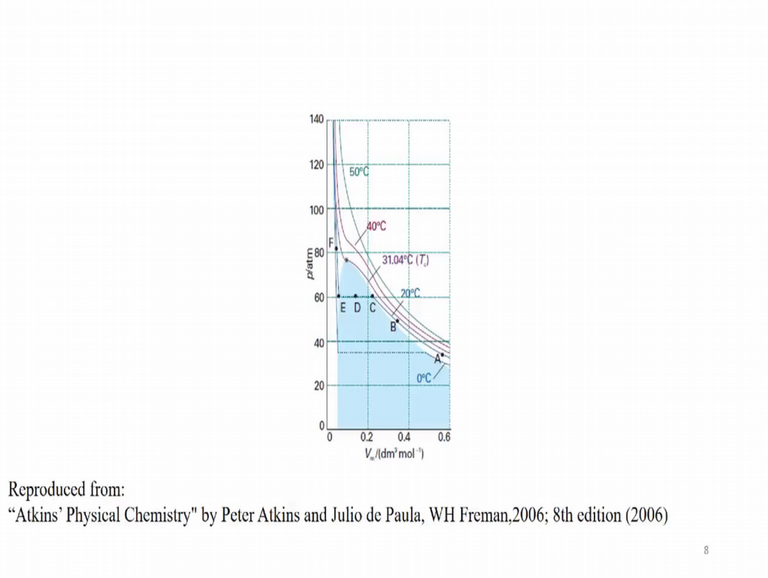
Let us schematically draw how the Andrews curves look like as before it as isotherm. So, it is a pressure volume curve, but the nature of the curve is very very different from what we see in the ideal gas behaviour. Now here I plot the pressure volume curve at different temperatures I chose 5 different temperatures and as before T 5 is the highest temperature and T 1 is the lowest temperature. Now let us first talk about the isotherm activa now look at the shape of this curve, let us also level the points or level the entire curve as A B C D let us first look at the region which is the C D region this region occurs at a low pressure where the following is very high here the gas behaves ideal.

So, we can the equation of state as P V equal to R T, but only for this region now note that if we want to change the volume by a certain amount we have to apply a little pressure in this case. However, this is totally opposite for the case in the A B region which represents the liquid state here, if we want to change the volume by the same amount we have to insert huge pressure. The reason being liquids are more or less compressible than gases the region in between which is the B C region represents a equilibrium between the liquid with it is vapour.

So, this A B region represents the liquid and this c d region represents the vapour or gas. So, following his discussion it is now clear that ideal gas law will be ovate only when the pressure is very low. So, we can write or we can modify the notation for the ideal gas equation that it will be valid only in the limit of very low pressure. Now let us focus on this B C region where the liquid is in equilibrium with it is vapour, now note that as we increase the temperature the region of volume or which the liquid vapour equilibrium occurs that decreases. And finally, it reduces to a particular point. So, if we draw a line which connects these regions will get a region where the liquid is always in equilibrium with it is vapour; however, this region straights as we increase the temperature. Now above this temperature which is differ in this case the substance or the material always behaves as gas.

So, this point in the isotherm is called as a critical point and the corresponding temperature at which the critical point occurs is known as critical temperature. So, the ideal behaviour S also observed above the critical temperature where the substance the is present always in the gaseous straw. Therefore, we can say that the ideal gas behaviour is obeyed for any gas as long as either the pressure is low or the temperature is very high which is above the critical temperature.

(Refer Slide Time: 19:05)

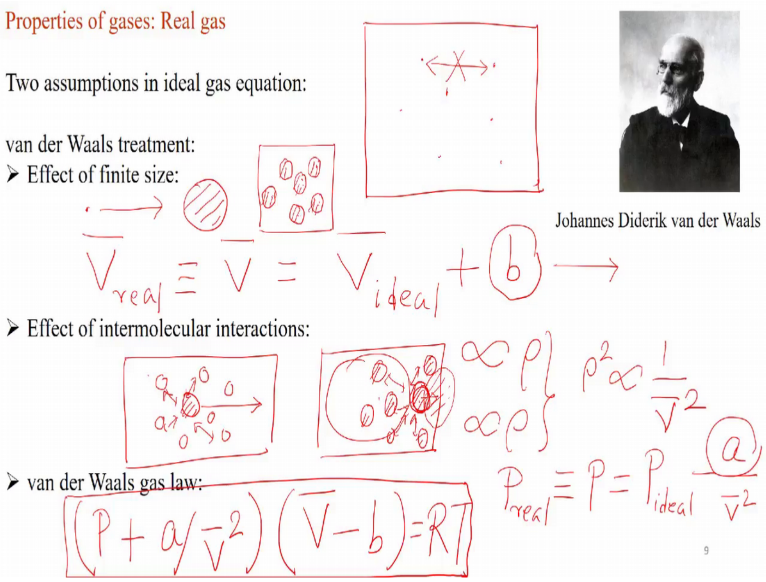


Reproduced from:
"Atkins' Physical Chemistry" by Peter Atkins and Julio de Paula, WH Freman,2006; 8th edition (2006)

Here I show some real experimental data for the liquefaction of the gas carbon dioxide as you see the location of the critical point is here and the corresponding critical temperature is 31. o 4 degree centigrade the shaded region which is coloured in blue here denotes that in this region of the isotherm the liquid is in equilibrium with it is vapour

So, far what we have discussed is that we said that for real gases a departure or a deviation from the ideal behaviour is observed and that was experimentally verified by amagat by measurement of the compressibility factor and also by Andrews by measuring the real gas isotherms. Now in order to explain the deviation or departure we need to device a model a model for a gas which can satisfactorily explain the non ideal life behaviour of real gases.

(Refer Slide Time: 20:18)



Properties of gases: Real gas

Two assumptions in ideal gas equation:

van der Waals treatment:

- Effect of finite size:

$$\bar{V}_{real} = \bar{V} = \bar{V}_{ideal} + \boxed{b}$$

- Effect of intermolecular interactions:

$\propto \rho$

$\propto \rho$

$\rho^2 \propto \frac{1}{\bar{V}^2}$

$$P_{real} = P = P_{ideal} - \frac{\boxed{a}}{\bar{V}^2}$$

- van der Waals gas law:

$$\boxed{\left(P + a/\bar{V}^2\right)\left(\bar{V} - b\right) = RT}$$

Johannes Diderik van der Waals

The first such model was put forward by van der walls who actually wept 2 crucial assumptions which we made in the ideal gas equation when it was formulated from the kinetic theory of gases.

These 2 assumptions are for example, consider a container the ideal gas law will be ovate if the sizes of the molecule are vanishingly small or the molecules are point like objects. So, there is no finite size for the molecules.

Secondly, any inter molecular innervations between molecules were ignored now van der walls made a correction to both these assumptions. Let us see what is the treatment that van der walls made, the first thing van der walls did is to consider the finite size of molecules from point like objects to something like a hard sphere, now imagine a situation we have container if the molecules were all point like objects the volume of the gas will be equal to the volume of the container itself.

However, if each molecule is supposed to have a finite size, then the situation will be very very different now for one mole of gas the number of molecules are fixed which is Amagats number of molecules and so the volume or the total volume of amagats number of molecules will also be constant for a particular gas. So, van der walls said that the actual volume or the real molar volume which is denote simply as V bar will be more than the ideal gas volume by an amount which is constant in this case, because we are considering only 1 mole of gas and this constant he denoted as b of course, this constant will be different for different gases.

For example methane will have some value of b which is different from the b for carbon dioxide for n mole of gas the volume will be simply or the increase in the volume will be simply n multiplied by b. So, this was the effect of the finite size; now the second thing which van der walls took into account in inter molecular interactions, now let us discuss how that affects the total pressure of gas as before consider the container and consider a particular molecule at the centre of this container.

Now this molecule is surrounded by many other molecules and all of them are attracting this molecule; however, for a system at thermal equilibrium this distribution of molecules inside the container is isotropic. So, this molecule will fill equal attraction in all direction. So, there will be no net attraction in any particular or any favoured direction. So, if this molecule moves there will be no change in it is velocity in a particular direction and it will more or less obey the ideal gas behaviour; however, the pressure of a gas is exerted when it is strikes the wall of the container now let us consider when this molecule starts moving and tries to hit the wall of the container.

Now, when this molecule hits the wall at that instant it also attracted by the molecules which are near the surface and also by the molecules which are in bulk or inside the container. Now since the number of molecules near the surface are less than the number of molecules, which are in the bulk there will be a difference in attraction the attraction will be ore from the molecules in the bulk because they are just large in number. So, the speed of this molecule will be slowed down and as a result the molecule will strike with a less force on the wall or the pressure will be reduced now we can mathematically formulate it in order to understand that let us consider on what factors this pressure will depend on.

Now, the definition of pressure is force per unit area which means it will depend on how many molecules are hitting this surface of unit area per unit time, now this number if of course, proportional to the density of the molecules or how many moles of the molecules are present per unit follow. Secondly, these molecules are also attracted by the molecules which are present in bulk. So, it will also be proportional how many molecules are present in the bulk that number is also proportional to the density of the gas.

So, together the pressure or the reduction in the pressure will be proportional to the square of density and since density is inversely proportional to molar volume it will eventually be inversely proportional to Inverse Square of molar volume. So, as before we can write a correction for the pressure the real pressure which will just simply denote as P will be less than the ideal pressure by an amount which is proportional to one over molar volume square and this proportionality constant we call as a and as before a will be different for different gases.

Now, f we combine these pressure expression and the volume expression for real gases and put it in the ideal gas equation which is P ideal into V ideal is equal to R T and if you replace it by the real volume and the real pressure we get the van der walls gas equation which is. So, this is the famous van der walls equation n the molar volume form if we have or if we confront the molar volume into the actual volume the equation will be just P plus n square a by V square into v minus n b is equal to n R T we can use either of this equation, but we will mostly use this equation in the molar volume form.