Engineering Physics 1
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Module-05
Lecture-06
Vanderwaal's's equation of states Part 01

Now I will be speaking on Vanderwaal'ss equation of state, actually this is the equation of state for the real gas. So, in my talk first of all I will talk on the introduction of the equation of state. What does it mean by equation of state? Why is it so important and then I will talk about the equation of state for the perfect or the ideal gases from? There we will come to know what is its limitation? And how to incorporate the basic interaction of the real gases?

And one of the plausible candidate of the equation of state for the really gas is the Vanderwaal's equation of state. Then we will talk about the Vanderwaal's equation of state how he has modified the equation of state for the ideal gas. Which kind of limitation he has improved and how to take into account those real description of the real gases. Then I will talk how to get a heuristic derivation of the Vanderwaal's equation of state.

And then I will talk about how to derive Vanderwaal's equation of state from more microscopic theory using the virial expansion or virial theorem. And then I will talk about how to; what is the use of Vanderwaal's equation of state. How to verify it experimentally and what is their drawback etcetera. So, let me start it what does it mean by equation of state. So, now I will talk about what does it mean by equation of state.

So, let me start it imagine for the sake of simplicity a constant mass of gas that is a closed system in a vessel. So, equipped that the pressure volume. And temperature may be easily measured, if we fix the volume at some arbitrary value and cause the temperature to assume and arbiterally chosen value. Then we shall not be able to vary the pressure at all. Once V and T are chosen by us the value of P at equilibrium is determined by nature.

Similarly if I chose some other variables, suppose pressure and temperature are chosen arbitrarily then the value of V at equilibrium is fixed that is of the 3 thermodynamic coordinates pressure volume and temperature. Only two are independent variable that means one I fix P and the how temperature varies. Once I will if I will fix V and T how pressure varies or other way if I fix P and T how volume varies okay.

This implies that there exists an equation of equilibrium which connects the thermodynamic coordinates and which rob's one of them of its independence. Such an equation called an equation of state which is a mathematical function relating the appropriate thermodynamic coordinates of a system in equilibrium. Here I want to emphasize something equation of state always deals the relation between the thermodynamic coordinate so in the system is at equilibrium.

If the system is not at equilibrium then you cannot talk about a relation or mathematical formulations between the thermodynamic coordinates. This is only true when the system is at thermodynamic equilibrium okay. So, now every thermodynamic system has its own equation of state. Although in some cases the relation may be so complicated that it cannot be expressed in terms of simple mathematical function.

But always every system has its own equation of state. For a closed system the equation of state relates the temperature to other to other thermodynamic variables. So, an equation of state expresses the individual peculiarities of one system as compared with other another system. And must therefore be determined either by prevent or by molecular theory. A general theory like thermodynamics based on general laws of nature is incapable of generating an equation of state of any system.

In fact an equation of state it should be derived from a more microscopic point of view which can mimic the experimental observation which you know since 100 years just like Charles law, Boyle's law, Grahams Dalton's partial pressure law, Gallen’s diffusion law these kinds of; these are also equation of states and which you know since 100 and 100 years. This is the experimental fact this is the observation. So, equation of state is a relation mathematical relation between the thermo dynamical coordinate.

Which is derived from some molecular theory which will explain this kind of physical observations, so, an equation of state therefore is not a theoretical deduction from thermodynamics. But is usually an experimental addition to thermodynamics. It expresses the result of experiments in which the thermodynamic coordinates of a system were measured as accurately as possible within a limited range of values.

So, finally equation of state is therefore only as accurate as experiment that lead to its formulation and holds only within the range of values measured. As soon as this range is exceeded a different form of equation of state may be valid. And equation of state is a very vital mathematical relation between the thermodynamic coordinates. Sometimes actual equation of state is nothing but the free energy of the system.

Suppose if you want to study the phase transition suppose let us take ice to water, water to steam or other way around. If you want to study this kind of phase transition which regime of P,V,T these kind of edges exist in nature. So, for that you need have the equation of state for water, equation of state for ice, equation of state for steam. Once you know the equation of state for individual phases around which you are looking for the phase transition.

You need to have a good knowledge about the equation of state. So, now let me start the equation of state of any general gas. Sorry; here I want to I want to say something equation of state can be for any solid, liquid. But in this talk I will be talking the equation of state of a gas. In fact equation of state for solid and liquid is comparatively complicated than equation of state of a rarefied gas.

Reason is that interaction in solid or liquid is much more stronger than the interaction among the constituent in the gas. So, in that sense derivation of equation of state in solid or liquid is more complicated and then the equation of State for a rarefied gas. Obviously equation of state for a gas at very dense gas again it will be complicated. But in our day to day life or for chemists they are looking for the equation of state for gases at low pressure or at high temperature.

In that cases equation of state is not so complicated. So, let me start it how the concept of equation of state arises from this beautiful observation which I am going to tell now ok.

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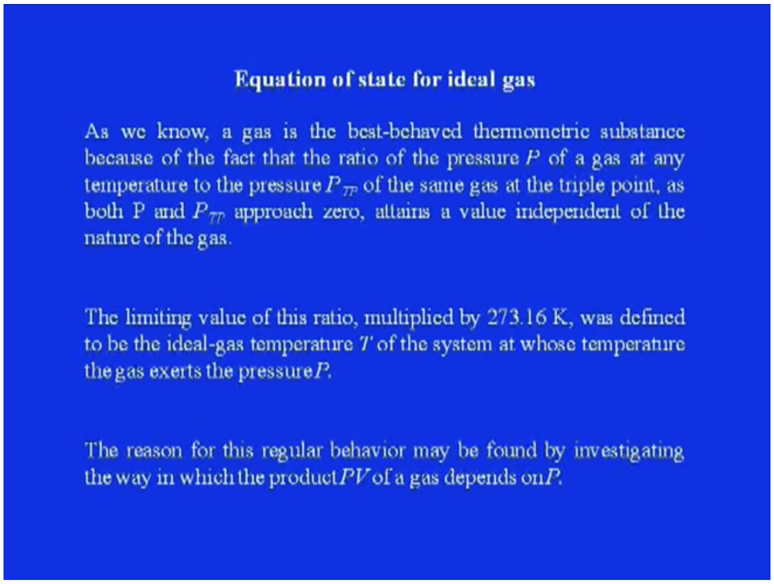

Equation of state for ideal gas

As we know, a gas is the best-behaved thermometric substance because of the fact that the ratio of the pressure P of a gas at any temperature to the pressure P_{TP} of the same gas at the triple point, as both P and P_{TP} approach zero, attains a value independent of the nature of the gas.

The limiting value of this ratio, multiplied by 273.16 K, was defined to be the ideal-gas temperature T of the system at whose temperature the gas exerts the pressure P.

The reason for this regular behavior may be found by investigating the way in which the product PV of a gas depends on P.

As you know a gas is the best behaved thermometric substance because of the fact that the ratio of the pressure of a gas at any temperature pressure of a gas at any temperature to the pressure of the same gas at the triple point. This ratio attains a value independent of the nature of the gas because as both P and PTP, PTP means presser at the triple point approach 0. So, this ratio attains a value independent of the nature of the gas.

This is the remarkable observation in the gas, so these limiting value of this ratio multiplied by 273.16 Kelvin was defined to be the ideal gas temperature T of the system at whose temperature the gas exerts the pressure P. So, this is the concept of ideal gas temperature by this observation and this ratio behaves universally to all gases. The reason for this regular behavior may be found by investigating the way in which the product PV of a gas depends on the pressure P okay.

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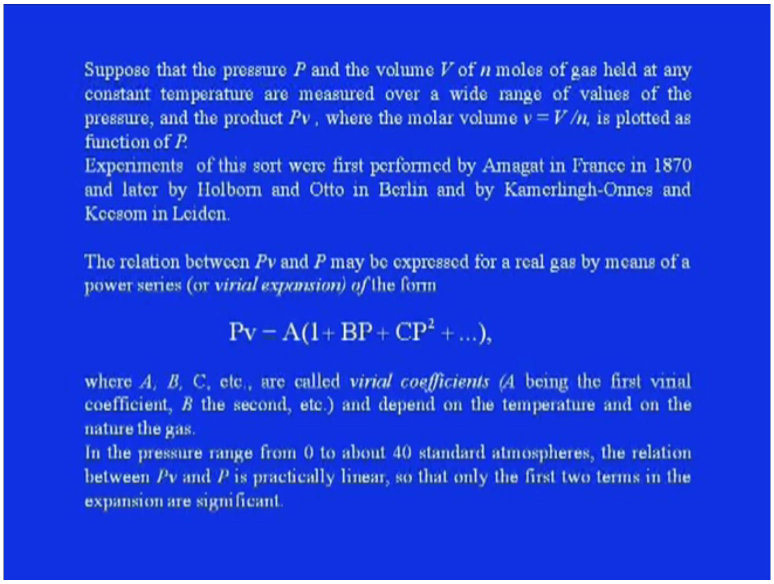

Suppose that the pressure P and the volume V of n moles of gas held at any constant temperature are measured over a wide range of values of the pressure, and the product Pv, where the molar volume $v = V/n$, is plotted as function of P.
Experiments of this sort were first performed by Amagat in France in 1870 and later by Holborn and Otto in Berlin and by Kamerlingh-Onnes and Keesom in Leiden.

The relation between Pv and P may be expressed for a real gas by means of a power series (or *virial expansion) of* the form

$$\mathrm{Pv} = \mathrm{A}(1 + \mathrm{BP} + \mathrm{CP}^2 + \ldots),$$

where A, B, C, etc., are called *virial coefficients* (A being the first virial coefficient, B the second, etc.) and depend on the temperature and on the nature the gas.
In the pressure range from 0 to about 40 standard atmospheres, the relation between Pv and P is practically linear, so that only the first two terms in the expansion are significant.

Suppose that the pressure P and the volume V of n moles of a gas held at some constant temperature are measured over a wide range of values of the pressure. And the product PV where the molar volume small v is capital V by n where capital V is the total volume of the system n is the number of moles. Is plotted as a function of P so experiments of this sort were first performed by a Amagat in France in 1870 and later by Holborn and Otto in Berlin.

And by Kamerlingh Onnes and by Keesam Leaden the relations between Pv and P may be expressed for a real gas by means of a power series or technically it is known as the virial expansion which is of the form PV = A times 1 + BP + CP square + dot, dot. So, where A, B, C etcetera are called the virial coefficient A being the first virial coefficient, B the second etcetera that depend on who is depend on the temperature and on the nature of the gases.

So, these virial coefficients who is depends upon the temperature as well as on the nature of the gases. What we will come to know that A will not depend on the nature of the gas which will depend only on the temperature whereas B, C etc they will depend on the nature of the gas they are value changes from one guess to other gas it means that virial second order or third order or higher order virial coefficient takes into account the molecular interaction among the constituent.

Since from molecular interaction changes from one description of gas to the other description of gas, so, A, B, C, D etcetera these virial coefficient changes from one guess to other gas okay. But we will find just now that A will depend only on the temperature of the system that I will show you. In the pressure range from 0 to about 40 standard atmospheric pressure the relations between PV and P is practically linear. So, that only the first two term in the expansion are significant other terms are not so significant.

So, I can neglect those higher order terms okay. In general the greater the pressure range the larger the number of terms in the virial expansion. Usually just you will see if the pressure range under which you have performed the performing the experiment if the pressure range are very small means 0 to about 20 or 30 standard atmospheric pressure. Then the first or second term in the virial coefficient is sufficient to explain the experimentally observed value.

But if you go for the higher precedence then higher and higher order terms in the virial coefficients are needed to explain the experimental values okay.

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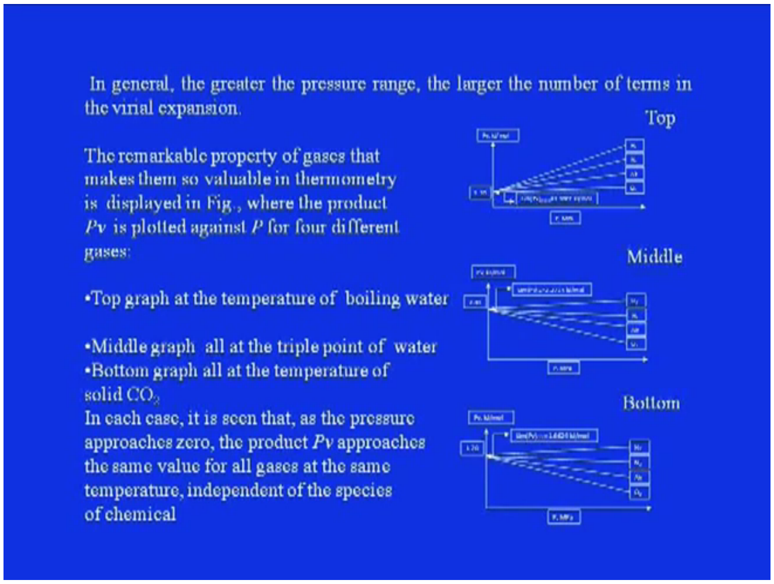

In general, the greater the pressure range, the larger the number of terms in the virial expansion.

The remarkable property of gases that makes them so valuable in thermometry is displayed in Fig., where the product *Pv* is plotted against *P* for four different gases:

- Top graph at the temperature of boiling water
- Middle graph all at the triple point of water
- Bottom graph all at the temperature of solid CO_2

In each case, it is seen that, as the pressure approaches zero, the product *Pv* approaches the same value for all gases at the same temperature, independent of the species of chemical

The remarkable property of the gas that makes them so valuable in the thermometry is displaced in the figure okay which is given in the side. Where the product PV is plotted against P for different gases hydrogen, nitrogen, air and oxygen and they are they have this thing has been plotted for three different temperatures. First one at the top of this figure it is plotted at the temperature of boiling point PV versus P.

Second middle of this figure is plotted PV versus P at the triple point of the water. Third one lower graph of this figure is plotted PV versus P at the temperature of solid carbon dioxide. We have seen a remarkable observation in all three figures top, middle and bottom. What we have seen that as the pressure approaches 0 the product PV approaches the same value for all gases at the same temperature independent of the species of the chemical and depends only on the temperature of the gas.

So, this is an remarkable observation let me tell you again if you plot PV versus P for any kind of gases then you will see as pressure approaches 0 or PV a then PV approaches the same value no matter whether it is for the hydrogen gas or nitrogen gas or air or oxygen it approaches a common value for any gas.

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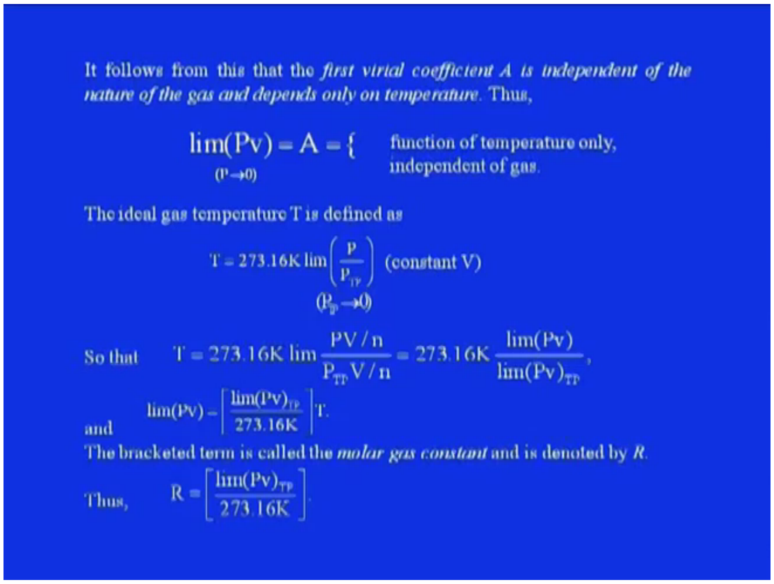

It follows from this that the *first virial coefficient A is independent of the nature of the gas and depends only on temperature*. Thus,

$$\lim_{(P\to 0)}(Pv) = A = \{ \text{ function of temperature only, independent of gas.}$$

The ideal gas temperature T is defined as

$$T = 273.16\text{K} \lim_{(P_{TP}\to 0)}\left(\frac{P}{P_{TP}}\right) \text{ (constant V)}$$

So that $T = 273.16\text{K} \lim \dfrac{PV/n}{P_{TP}V/n} = 273.16\text{K} \dfrac{\lim(Pv)}{\lim(Pv)_{TP}}$,

and $\lim(Pv) = \left[\dfrac{\lim(Pv)_{TP}}{273.16\text{K}}\right]T.$

The bracketed term is called the *molar gas constant* and is denoted by *R*.

Thus, $R = \left[\dfrac{\lim(Pv)_{TP}}{273.16\text{K}}\right].$

So, this observation from this crucial observation it reflects that that the first virial coefficient A is independent of the nature of the gas and depends only on the temperature of the gas. The limiting case means P tends to 0, PV we will take only the first term A which is a function of temperature only independent of the gas. This ideal gas temperature T is defined as T is 273.16 degree Kelvin limit PTP tends to 0 P by PTP.

While volume is held constant in that case temperature is defined as 273. 17 16 degree Kelvin times limiting PV by n by PTP V by n, if you write in other way the in terms of molar volume they need to look like 273.16 degree Kelvin times limiting times the ratio of limiting value of PV a limiting value of PV at the triple point. So, from this equation you can always write down that limiting value of PV at any temperature is nothing but limiting value of PV at the triple point by 273.16 degree Kelvin times temperature.

So, that means and the bracketed term which is which looks like a constant term. So, the bracketed term is called the molar gas constant and is denoted by R. So, if you if you will substitute R as the ratio of limiting term of PV at the triple point divided by 273.16 degree Kelvin then we will end up the beautiful equation which you know since 100 and 100 years PV =RT.

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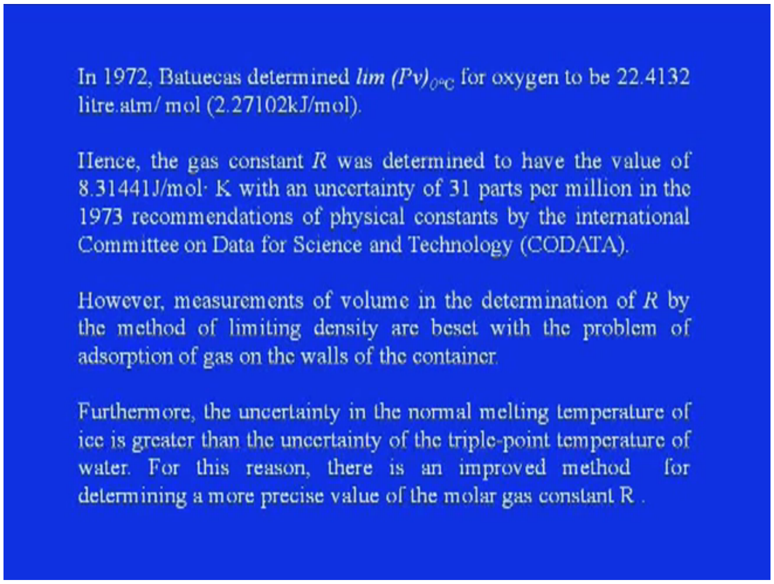

In 1972, Batuecas determined *lim* $(Pv)_{0°C}$ for oxygen to be 22.4132 litre.atm/ mol (2.27102kJ/mol).

Hence, the gas constant R was determined to have the value of 8.31441J/mol· K with an uncertainty of 31 parts per million in the 1973 recommendations of physical constants by the international Committee on Data for Science and Technology (CODATA).

However, measurements of volume in the determination of R by the method of limiting density are beset with the problem of adsorption of gas on the walls of the container.

Furthermore, the uncertainty in the normal melting temperature of ice is greater than the uncertainty of the triple-point temperature of water. For this reason, there is an improved method for determining a more precise value of the molar gas constant R .

In 1972 Batuecas was determined limiting PV at 0 degree centigrade for oxygen to be around 22.4132 liter atom per mole or 2.27102 kilo Joule per mole. Hence the gas constant R was determined to have the value of 8.31441 Joule per mole degree Kelvin with an uncertainty of 31 parts per million, in the 1973 recommendation of physical constant by the International Committee on Data for Science and Technology.

However measurements of volume in the determination of R by the method of limiting density are beset with the problem of adsorption of gas on the walls of the container. So, that restricts the that introduces the error in measuring the value in measuring and that volume of 1 mole means 1 mole gas will occupy a volume 22 liter. So, to measure this volume the air the source of error is to how to measure the volume.

In some cases because of the adoption of the gas you cannot measure exact value of this volume that introduces some error. So, that is the reason people have made different kinds of experiment to get more and more accurate measurement of this volume. Furthermore the uncertainty in the normal melting point of ice is greater than the uncertainty of the triple point of this water. For this reason there is an improved method for determining a more precise value of the molar gas constant R.

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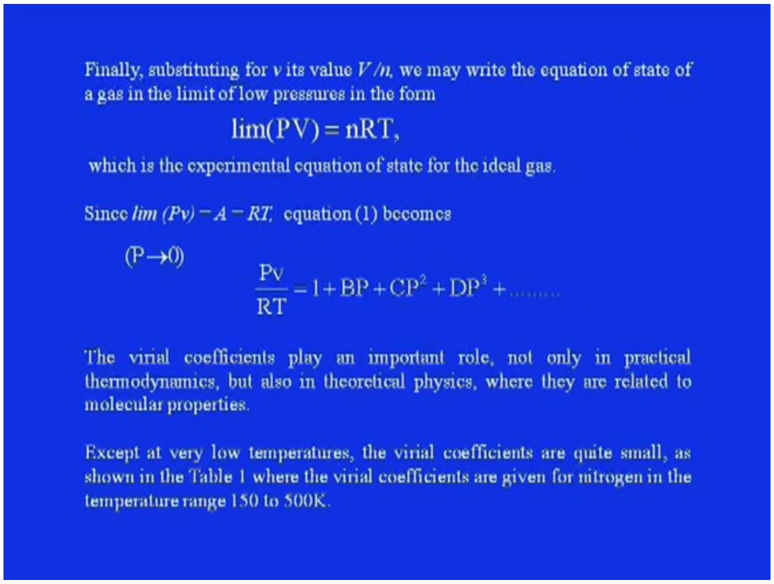

Finally, substituting for *v* its value *V*/*n*, we may write the equation of state of a gas in the limit of low pressures in the form

$$\lim(PV) = nRT,$$

which is the experimental equation of state for the ideal gas.

Since $\lim_{(P\to 0)} (Pv) - A - RT$, equation (1) becomes

$$\frac{Pv}{RT} = 1 + BP + CP^2 + DP^3 + \ldots\ldots$$

The virial coefficients play an important role, not only in practical thermodynamics, but also in theoretical physics, where they are related to molecular properties.

Except at very low temperatures, the virial coefficients are quite small, as shown in the Table 1 where the virial coefficients are given for nitrogen in the temperature range 150 to 500K.

So, finally substituting ah for the molar volume a small v which is nothing but the capital V by n capital V is the volume of the gas and n is the number of moles. If you will substitute it then I will get it this condition that the equation of state of a gas in the limit of low pressures in the form is PV = nRT which is the experimental equation of state for the ideal gas. So, limiting since the limit P tends to 0, Pv = A which is nothing but the RT.

So, equation 1 looks like PV by RT = 1 + BP + CP square + DP cube and some other terms. The virial coefficient B, C and D etcetera play an important role not only in practical thermodynamics but also in theoretical physics where they are related to the molecular properties of the system. As I have already told you in the low pressure limit only PV = RT that means you can neglect the values of the virial coefficient that will show you that the virial coefficient at the very low pressure limit are very small so you can neglect them.

But as far as you are interested in a comparatively larger precedence in there, B, C, D etcetera plays an important role. And the idea of theoretical physics particularly statistical mechanics which plays an important role to calculate values of B, C, D from the basic fundamental interaction among the constituents. So, however I am not going to describe how to calculate B, C, D from the statistical mechanics approach.

But I will talk about simply from the general physics point of view how to calculate the second order virial coefficient from the simple classical mechanics approach which is just close to the virial theorem ok. Except at low temperature, so finally to conclude this observation except at very low temperatures the virial coefficient are quite small as shown in the table one where the virial coefficient are given for nitrogen in the temperature range 150 to 500 Kelvin.

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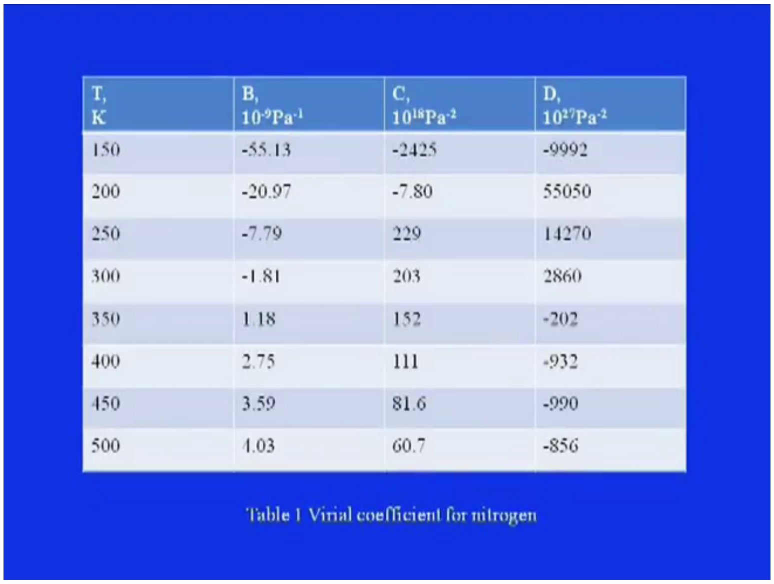

T, K	B, $10^{-9} Pa^{-1}$	C, $10^{18} Pa^{-2}$	D, $10^{27} Pa^{-2}$
150	-55.13	-2425	-9992
200	-20.97	-7.80	55050
250	-7.79	229	14270
300	-1.81	203	2860
350	1.18	152	-202
400	2.75	111	-932
450	3.59	81.6	-990
500	4.03	60.7	-856

Table 1 Virial coefficient for nitrogen

So, this is the table through which you will come to know that at very large temperature the virial coefficient makes are very small. So, or at low pressure which are varial coefficient are small that tells that the ideal gas equation of state which is good well and enough in the low pressure and high temperature limit. But as you will go away from the low temperature low pressure limit then you need to introduce some higher order virial expansion okay.

So, now let me start how to get the equation of state for the real gases or imperfect gases okay. First of all this is the most complicated thing in the theoretical physics but in this lecture I am not going to talk about the real equation of state or equation of state for the real or imperfect gases. What I am going to tell you that how to I am going to a heuristic derivation of some equation of state which almost takes into account the description of the real gases in a very schematic way.

However nowadays there are lots of theoretical derivation which tells you how to get this derivation which is already done long time back by Vanderwaal's okay. So, now people are able to derive this Vanderwaal's equation of state from the more fundamental theory which is known as the statistical mechanics okay. so, let me start how Vanderwaal's himself derived this equation of state which is claim to claim to mimic for the real gases.

The Vanderwaal's equation of state is an equation of state for a fluid composed of particles that have a nonzero size. And pair wise attractive interparticle forces. Exactly ideal gas equation of state assumes two things let me tell you although I have already talked about in my earlier lectures many times. When I talked about the kinetic theory of gases that time I have already or Maxwell distribution of speed that time I repeatedly told ideal gas ideal gas means there are two assumptions they have already taken.

First the atoms or molecules behave as a point like objects and second thing there are no interactions among the constituent of the gas. Now somebody could ask that how you can talk about the ideal gas equation of state PV = nRT where T is defined as the equilibrium temperature. If there is no interaction among the constituent how do you get the equilibrium temperature. I have already told it but not in lengthy the way.

But let me repeat it again in ideal gas concept the concept of equilibrium temperature has come through the coalitions of atoms with the container of the wall that brings the system to an equilibrium. And then the concept of equilibrium temperature is being justified but now how to get the equation of state for the real gas. Now let me start is it true that atoms are molecules they are point like objects? No it is not true.

So, first thing you have to improve these two concepts first there they are finite size although they are very small compared to the size of this volume size of this system. But still they are not a point like objects that gives raise a concept of excluded volume approximation. I am going to tell you in a couple of minutes. Second point as we have assumed that in ideal gas equation of state people have they are moving like a free particle.

They are and there are no interaction potential present among the constituent of the systems. So, is it any possible to take an attractive interaction between the constituent of the system. So, so idea of Vanderwaal's equation of state is of twofold. First they are not point size particles so you cannot put as many particles as we want in a given system which gives you gives raise the concept of excluded volume approximation.

Second point that there are some interactions present in among the constituent of the gas may be between their terms or between the molecules. So, he has attacked these two points and he has derived he has incorporated these two points who is lands up the concept of Vanderwaal's equation of state.

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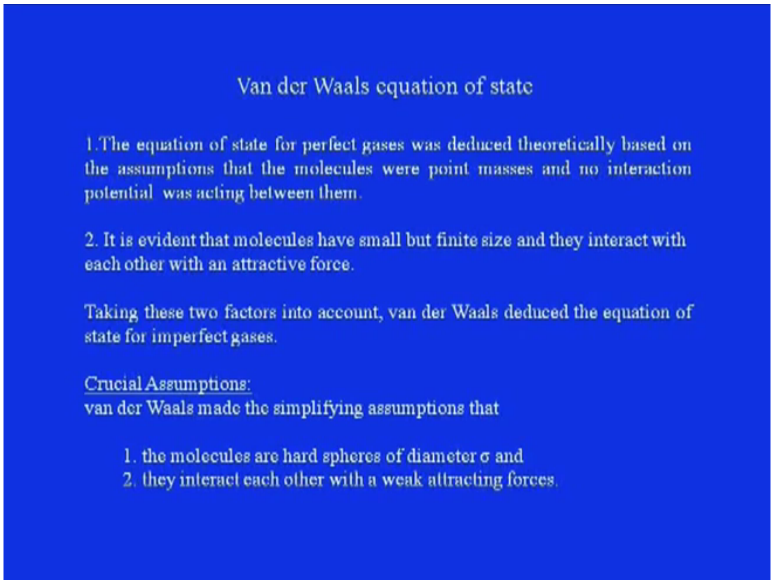

Van der Waals equation of state

1.The equation of state for perfect gases was deduced theoretically based on the assumptions that the molecules were point masses and no interaction potential was acting between them.

2. It is evident that molecules have small but finite size and they interact with each other with an attractive force.

Taking these two factors into account, van der Waals deduced the equation of state for imperfect gases.

Crucial Assumptions:
van der Waals made the simplifying assumptions that

1. the molecules are hard spheres of diameter σ and
2. they interact each other with a weak attracting forces.

So, now let me start the equation of state for perfect gases was deduced theoretically based on the assumptions that the molecules were point masses and no interaction potential was acting between them. It is evident that molecules have small but finite size and they interact with each other with an attractive force. So, taking these two factors into account Vanderwaal's in 1873 deduced the equation of state for the imperfect gases or for the real gases.

What are the crucial assumptions he took, Vanderwaal's was made the simplifying assumptions first the molecules are hard sphere of some diameter Sigma it is not a point like particle. They interact each other with weak attracting forces. So, these are the two simplifying assumptions which are which are the which are the deviating part from compared to the ideal gas equation of state where molecules have been treated as a point like objects.

And there are no interactions present among constitute. So, if you take into account these two assumptions made by Vanderwaal's how to change the equation of state, how to change the ideal equation of state okay. So, first I am going to incorporate the finite size effect which is known as the excluded volume approximation, effect of force of repulsion between molecules which is known as the excluded volume approximation.

However nowadays there are some field theoretic methods have come up in the literature which where people have constructed the partition function in the statistical mechanics formalism right from the beginning for the finite size particle okay. But however we are not following that thing we are following in a very trivial in a very schematic way. How the finite size affect, how the finite size effect of the molecules, how it is going to affect the ideal equation of state.

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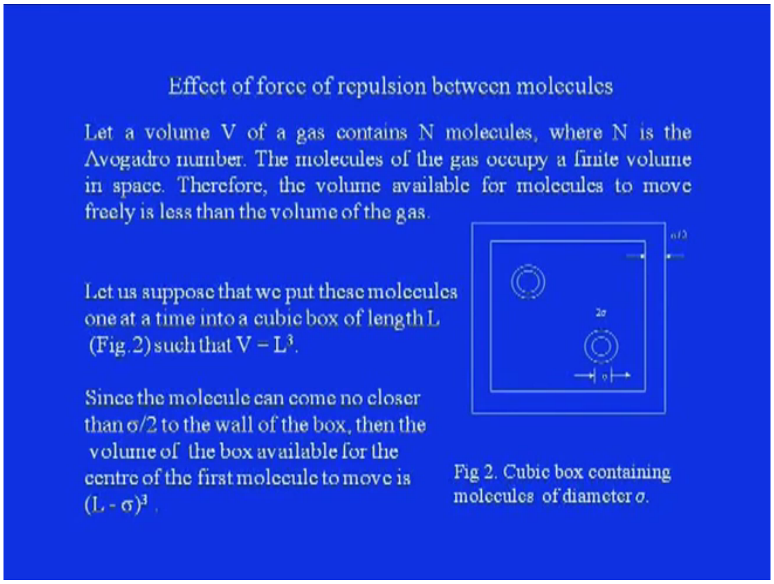

Effect of force of repulsion between molecules

Let a volume V of a gas contains N molecules, where N is the Avogadro number. The molecules of the gas occupy a finite volume in space. Therefore, the volume available for molecules to move freely is less than the volume of the gas.

Let us suppose that we put these molecules one at a time into a cubic box of length L (Fig.2) such that $V = L^3$.

Since the molecule can come no closer than $\sigma/2$ to the wall of the box, then the volume of the box available for the centre of the first molecule to move is $(L - \sigma)^3$.

Fig 2. Cubic box containing molecules of diameter σ.

Let us take a volume V of a gas contains N molecules where N is the Avogadro number the volumes of the gas occupy a finite volume the molecules of the gas occupy a finite volume in space. Therefore the volume are available for molecules to move freely is less than the volume of the gas. This is the excluded volume approach sensor that means total volumes are not available for the molecules which constitute a system.

This is the basic idea so, now let me start it first of all let me put one molecule in a system how much volume he can have him then I put second molecule how much volume is left for the second molecule. Then put the third fourth and ultimately if I want to put a Avogadro number of molecules, how much volume is left okay. So, let us suppose that we put this molecule one at a time into a cubic box of length L such that V = L cube.

Since the molecule can come no closer than Sigma by 2, Sigma is the diameter of the molecule to the wall of the box then the volume of the box available for the center of the first molecule to move is only L - Sigma whole cube okay.

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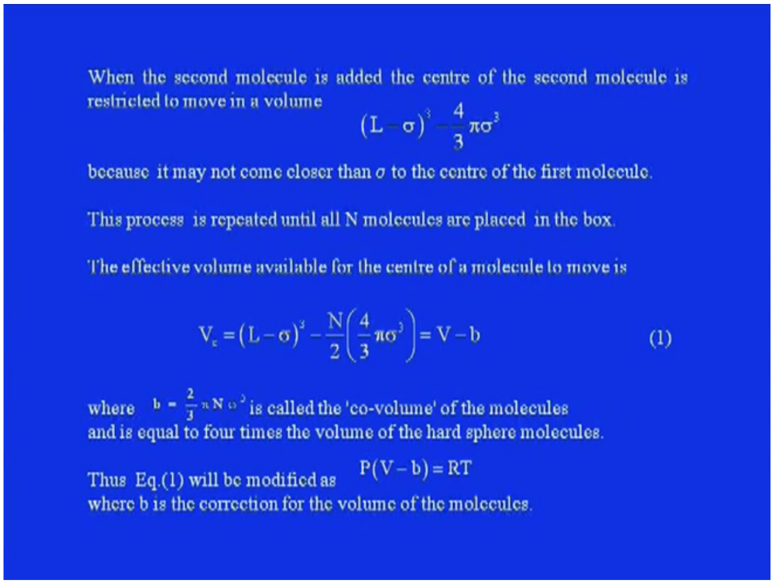

When the second molecule is added the centre of the second molecule is restricted to move in a volume

$$(L-\sigma)^3-\frac{4}{3}\pi\sigma^3$$

because it may not come closer than σ to the centre of the first molecule.

This process is repeated until all N molecules are placed in the box.

The effective volume available for the centre of a molecule to move is

$$V_c=(L-\sigma)^3-\frac{N}{2}\left(\frac{4}{3}\pi\sigma^3\right)=V-b \qquad (1)$$

where $b=\frac{2}{3}\pi N\sigma^3$ is called the 'co-volume' of the molecules and is equal to four times the volume of the hard sphere molecules.

Thus Eq.(1) will be modified as $P(V-b)=RT$ where b is the correction for the volume of the molecules.

When the second molecule is added the center of the second molecule is restricted to move in a volume L - Sigma whole cube - 4 by 3 Sigma cube that means as you are inserting more and more molecules to the system. So, the volume in which its motion is restricted is decreasing that is known as the excluded volume because it may not come closer than Sigma to the center of the first molecule.

So, that is that is in the volume available for the second molecule is less than the volume expected in the ideal gas approximation. So, this process is repeated until all N molecules are placed in the box. So, the effective volume available for the center of a molecule two move the effective is = L - Sigma whole cube into N by 2 into 4 by 3 Pi Sigma cube which is nothing but the V - B where I have neglected some terms which take which tells that Sigma volume of a single molecule is much, much lesser than the volume of the total system.

So, where B = 2 by 3 Pi N Sigma cube is called the co volume of the molecules and is = the 4 times the volume of the hard sphere molecules. So, then equation 1 will be modified as P into V - B = RT. So, that means the ideal gas equation of state will be modified from PV = RT to P into V - b = RT where b is the correction for the volume of the molecules which is known as the excluded volume.

So, now let me take into account the second part of this of this crucial assumption square which Vanderwaal's took second part of the assumptions is that there are still weak interaction present among the constituent of the system. There are weak interactions between either atoms or molecules basically now we know this is nothing but the Lennard-Jones potential okay. But anyway I am not going to tell all these things right now.

What is the idea of the second part effect of force of attraction between the molecules? Idea the way Vanderwaal's two is very simple okay let me talk you first then I will show you from my transparency. First is suppose you take a molecule in the bulk of the system you see there are all kinds of forces acting on the molecule from all sides. If you calculate the net force on the molecule which is in the bulk of the system net force will be the resultant force will be zero.

Now suppose you take a molecule in the only surface of the system then you see that it has large number of neighbors from the side of the bulk but there are small number of neighbors from the surface. Because that means it does not have sufficient amount of neighbor. So, that tells that the resultant force of a molecule which is on the surface is not 0 and the net force is directed inwards.

So, that causes that the resultant force is not 0, when a molecule is sitting on the surface of the container okay that is the idea okay. Now let me show you how to incorporate this idea in a mathematical form.

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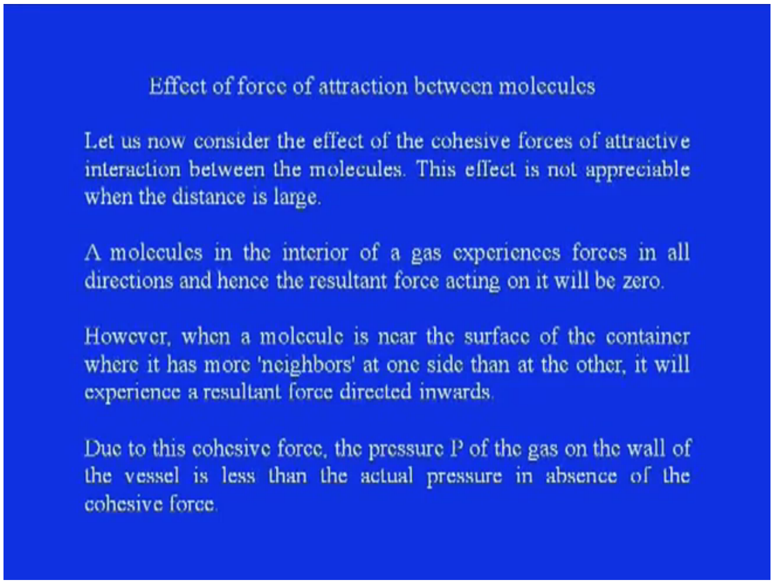

Effect of force of attraction between molecules

Let us now consider the effect of the cohesive forces of attractive interaction between the molecules. This effect is not appreciable when the distance is large.

A molecules in the interior of a gas experiences forces in all directions and hence the resultant force acting on it will be zero.

However, when a molecule is near the surface of the container where it has more 'neighbors' at one side than at the other, it will experience a resultant force directed inwards.

Due to this cohesive force, the pressure P of the gas on the wall of the vessel is less than the actual pressure in absence of the cohesive force.

So, let us now consider the effect of the cohesive force size of attractive interactions between the molecules this effect is not appreciable when the distance is large. A molecule in the interior or bulk of a gas experiences forces in all directions and hence the resultant force acting on it will be the 0, as I have already told you, however when a molecule is near the surface of the container where it has more neighbors at one side than at the other.

As a result it will experience a resultant force directed inwards that is the catchy point of this derivation. Due to these cohesive force the pressure P of the gas on the wall of the vessel is less than the actual pressure in absence of the cohesive force okay. So, now let me say if delta P be the cohesive pressure acting per unit area of the surface then stead of equation 1. We get the following equation for the pressure.

That means or pressure will be less than the ideal gas pressure that means P = RT by V - b - del P or P + delta P = RT by V – b. So, the pressure acting on the layer near the walls from the side of the molecules of the gas is equal to the force acting on the wall by the molecules on a unit surface of the layer. So, these forces proportional to the density n of the molecules on the other hand the number of molecules in the layer itself near the wall is also proportional to n.

So, hence delta P is a proportional to n into n that means n square. So, delta P is proportional to n square where n is the density of the gas which is nothing but the total number of molecules by total volume of the system capital N upon V. So, therefore delta P is proportional to 1 by V square or property constant is there which is nothing but the a by V square. If you will substitute the value of delta P in the equation number 2, so then you will get some equation of the state for the real gas.

Where a is a constant who is depends on the nature of the force of attraction between the molecules. So, finally thus the external pressure on the gas is increased by a by V square. So, using the result of delta P which is a by V square. So, you can write down P + a by V square which is nothing but the RT by V - b or other way P + a by V square into V - b = RT this equation is the celebrated equation of state for the real gas which is nothing but the Vanderwaal's equation of state.

It takes into account both forces of attraction as repulsion between the molecules. So, this equation was first given by Vanderwaal's in 1873 in the following section we shall deduce this equation rigorously using the virial theorem. So, before proceeding to its rigorous derivation let me summarize this heuristic derivation of the Vanderwaal's equation of state which he himself had done it in long time back.

And he has got the Nobel Prize in 1910 for this famous work of this equation of state. So, that means P has been increased by by by the attractive interaction maybe which is weak among the molecules, whereas we have been reduced by taking into account the repulsive interaction between the molecules which have come in form of the excluded volume concept.