Engineering Physics 1

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Module-05
Lecture-01
Kinetic Theory of Gases – Part 01

Welcome to the National Programme on technical enhanced learning lecture series, myself it is Dr. Binay Krishna Patra from the physics department, IIT, Roorkee. Today I will be giving a lecture on the topic Kinetic Theory of Gases. So, let me start it, let me start kinetic theory of gases. Basically the broad topic on which I will be giving this lecture series is thermal physics in thermal physics there are certain topics on which I will be giving. First I will be; today I will be giving lecture on the kinetic theory of gases.

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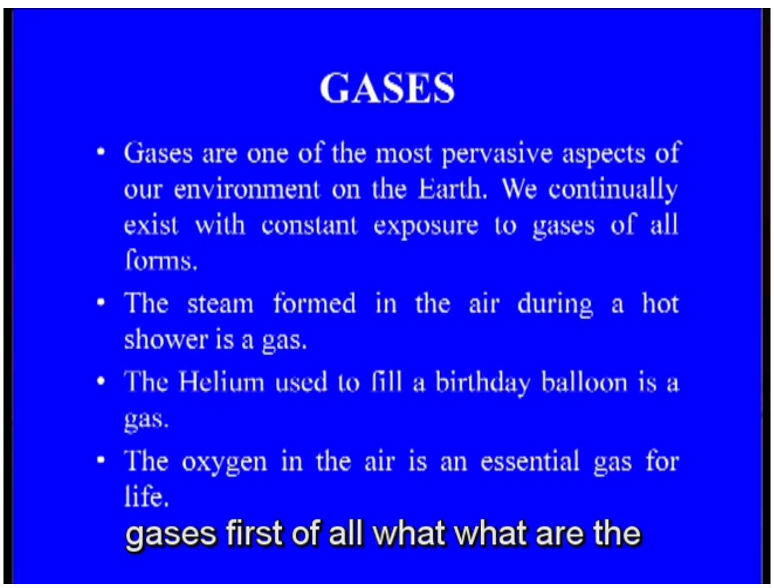

First of all what are the gases? Gases are one of the most pervasive aspects of our environment on the earth. We continually exist with constant exposure to gases of all forms. The steam formed in the air during a hot shower is a gas. The helium used to fill a birthday balloon is a gas. The oxygen in the air is an essential gas for life. There are important characteristics of the gases compared to solid or liquid.

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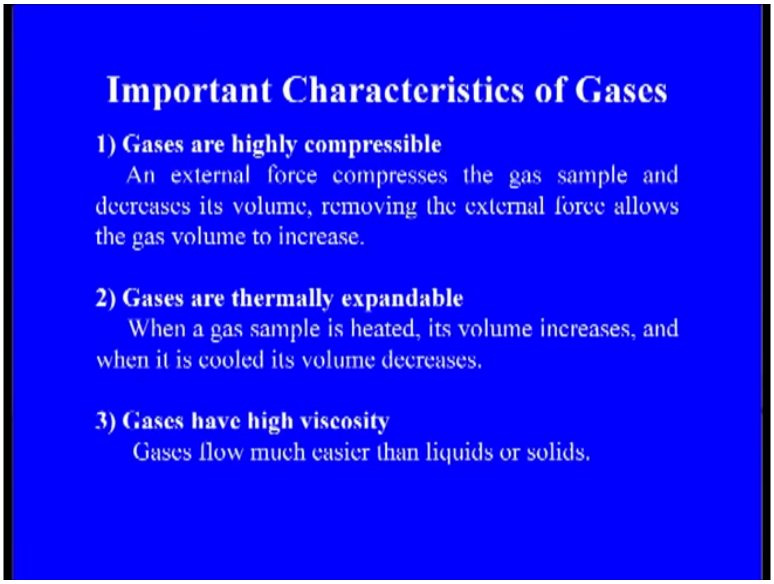

First of all I want to enumerate them. First gases are highly compressible in nature, any external force compress the gas sample and decreases its volume. If you remove the external force gas volume will increase. So, this is the most salient character of the gases compared to solid and liquid. Gases are thermally expandable when a gas sample is heated its volume increases and when it is cooled its volume decreases. Regarding the viscosity character, gases have high viscosity, gases flow much faster than liquids or solids.

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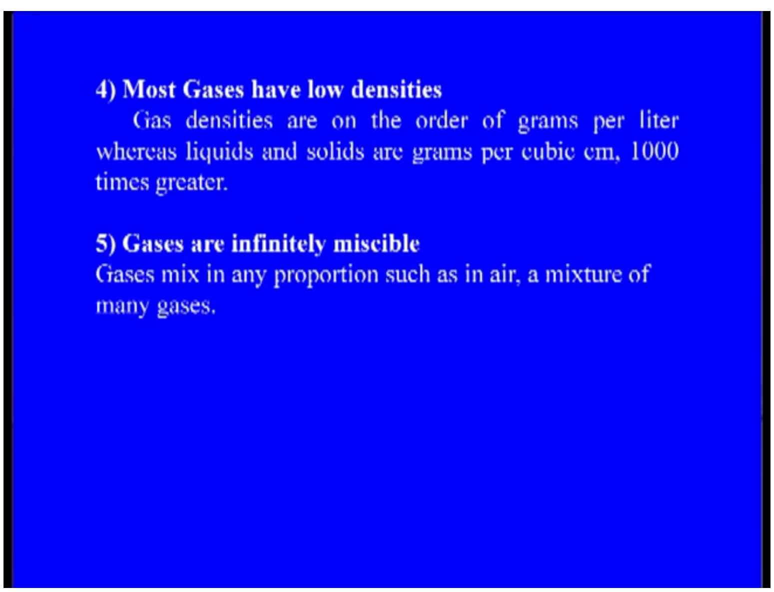

Most gases have low densities, gas densities are of the order of grams per liter whereas liquids and solids are grams per cubic centimeter almost thousand times greater. Gases are infinitely miscible that means gases mix in any proportion such as in air, mixture of many gases, nitrogen oxygen, carbon dioxide, carbon monoxide, nitrogen oxide, nitrogen dioxide etc. Now let me come, what is the idea? What is the motivation of kinetic theory of gases?

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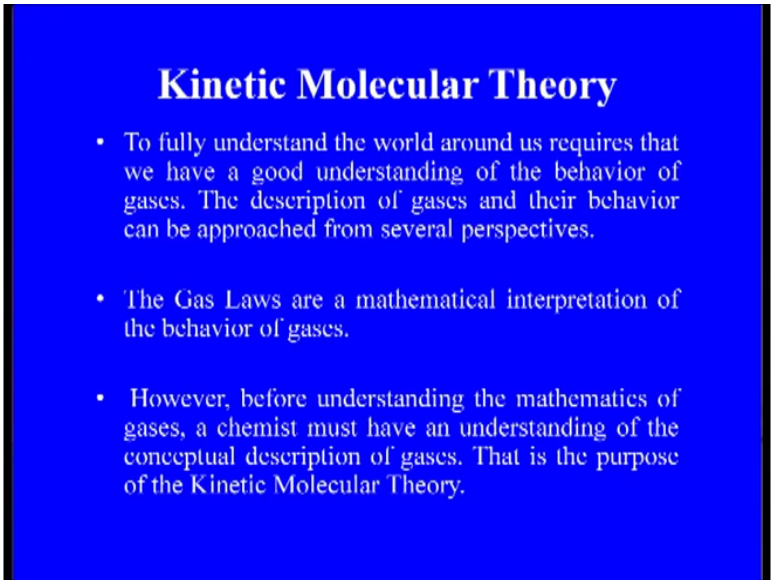

To fully understand the world around us records that we have a good understanding of the behavior of gases. The description of gases and their behavior can be approached from several perspectives. First the gas laws are mathematical interpretation of the behavior of gases however before understanding the mathematics of gases a chemist must have an understanding of the conceptual description of the gases that is the purpose of the kinetic molecular theory.

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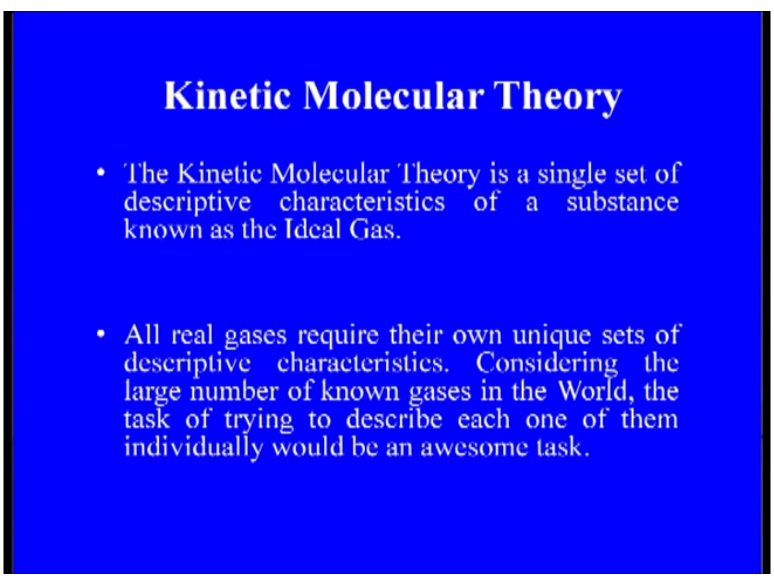

Now what are the kinetic molecular theories, in general? The kinetic molecular theory is a single set of descriptive characteristic of a substance known as ideal gas. We will explain what does it mean by ideal gas, latter? But all real gases required their own unique set of descriptive characteristics. Considering the large number of moon gases in the world. The task of trying to describe each one of them individually would be an ausum task.

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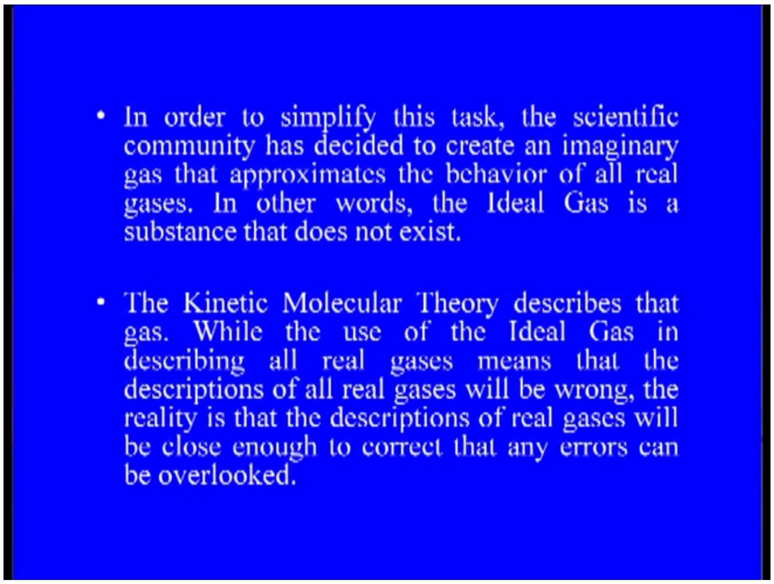

Then how to solve this problem? How to simplify this problem? In order to simplify this task the scientific community has decided to create an imaginary gas that approximates the behavior of all real gases. And in principle in the high temperature limit and low density limit real gas resemble like a ideal gas. But as such ideal gas does not exist in nature. In other words the ideal gas is a substance that does not exist.

The kinetic molecular theory describes that gas means that ideal gas while the use of ideal gas in describing all real gases means that the description of all real gases will be wrong. The reality is that the descriptions of all real gases will be close enough to correct that any errors can be overlooked. That means the algorithm of kinetic molecular theory is that initially you start with the concept of an ideal gas.

Then under some certain circumstances then you calculate the quantity and let me let check it how much errors you have come across. And then you try to build up your equations so that it can incorporate the real nature of the gases and again you calculate some quantity. Let check, let us tally with this experiment and it agrees well. Then you say that you are approaching towards the real description of the gases which is nothing but the real gases.

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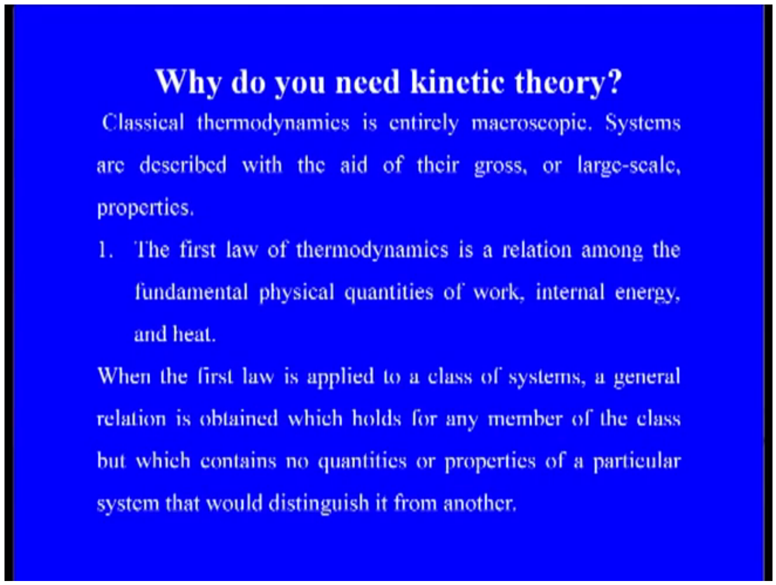

Why do we need kinetic theory because we have laws of thermodynamics in our hands since 500 years back and we know it explains beautifully different phenomena occurring in the nature. But suddenly why we abandoned that concept laws of thermodynamics. I will tell one by one why we did? Why do we need to have one done the laws of thermodynamics and look for the kinetic theory? Classical thermodynamics is entirely macroscopic systems.

Is entirely macroscopic, systems are described with the aid of their gross or large scale properties. The first law of thermodynamics is a relation among the fundamental physical quantities of work, internal energy and heat. That means when the first law is applied to a class of system a general relation is obtained which holds for any member of the class but which contains no quantities of properties of a particular system that would distinguish it from one another.

That means the first law of thermodynamic tells that if you will be give some amount supply some amount of it let us say dq it will be used in two ways. It will change the internal energy of the system by an amount du and rest of the amount will be used to do the external work that means in mathematical form dq = du + dw. But this is true for any gases there is no quantities which can distinguish the first law of thermodynamics from one gas to other.

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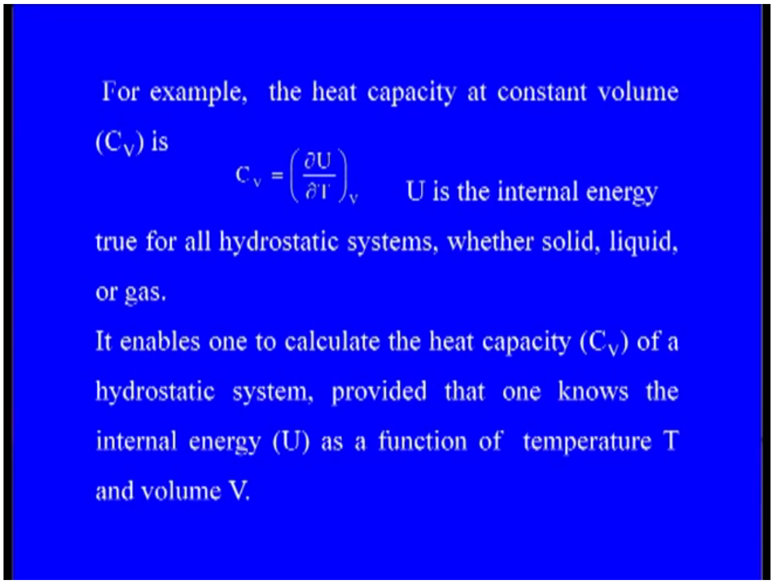

For example, let us calculate the heat capacity at constant volume Cv which is Cv equal to del U by del T at constant V who U is the internal energy. This expression is true for all hydrostatic systems whether solid, liquid or gas. But we know solid, liquid, gas they are very much different from one another but in this formalism of thermodynamics there is no way to distinguish Cv from liquid, gas and solid.

It enables one to calculate the heat capacity of a hydrostatic system provided that one knows the internal energy as a function of temperature and volume. However the other thing once you know Cv then you can calculate the heat capacity during an isochoric process.

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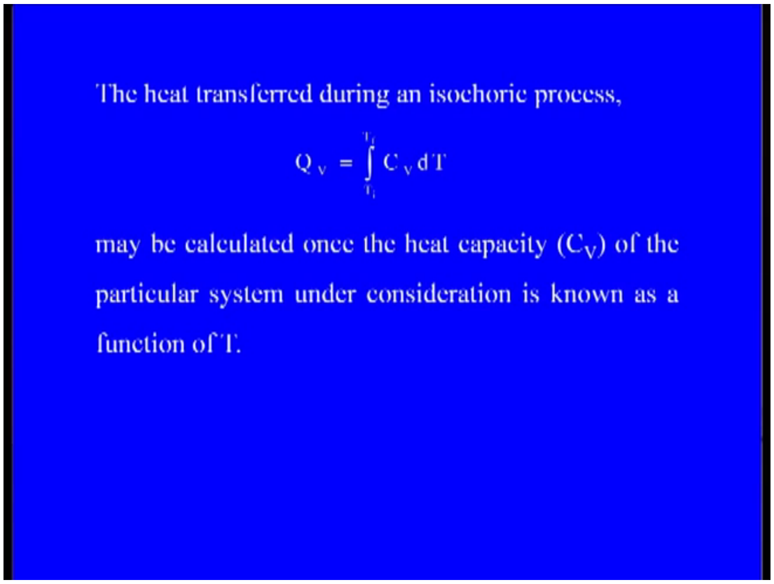

Defined by Qv equal to Ti to Tf for Ti is the initial temperature Tf is the final temperature integrated Cv dT. It can be calculated once the heat capacity of the particular system under consideration is known as a function of temperature T.

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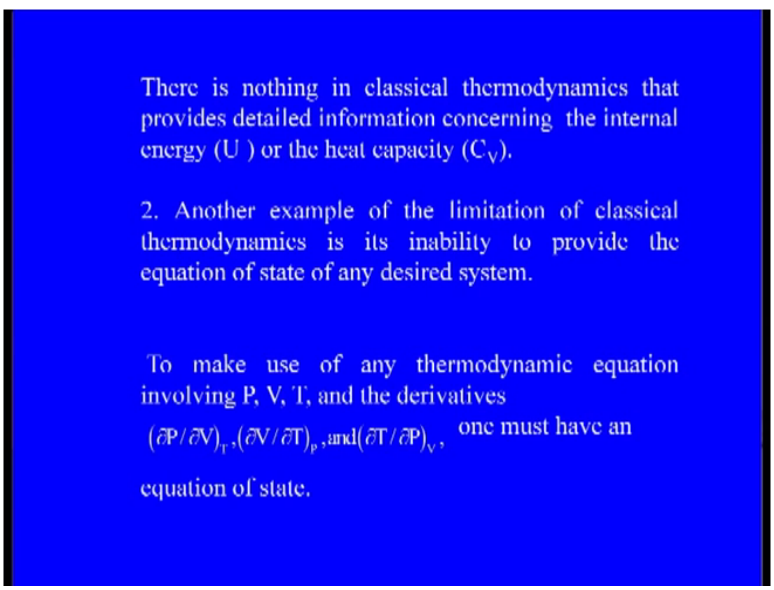

But there is nothing in classical thermodynamics that provides detailed information concerning the internal energy or the heat capacity. So, that forces to consider some theory some microscopic theory which is which will deal the system in terms of its fundamental constituents let us say atoms or molecules that means, we must resort to look for some microscopic theory instead of the macroscopic theory which is the thermodynamics.

Another example of the limitation of classical thermodynamics is its ability to provide the equation of state any desired system. I will tell you what does it mean by equation of state. To make use of any thermodynamic equation involving P, V, T or they are derivatives del P by del V at constant T or del V by del T at constant P or del T by del P at constant V etc. One must have some equation of state.

But unfortunately classical thermodynamics does not provide any equation of state that means it does not provide any relation any relation between the thermo dynamical quantities let us say pressure, volume or temperature. It does not have any predictive power to provide any relation among the thermo dynamical quantities.

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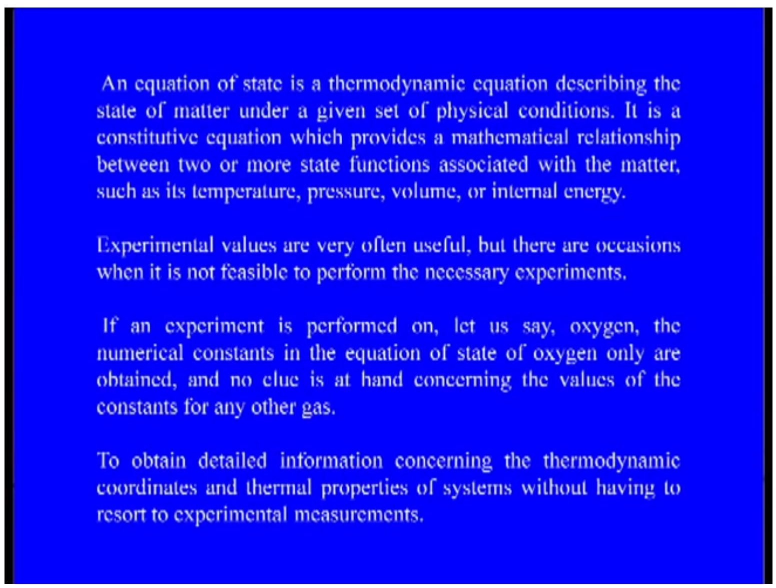

An equation of state is a thermodynamic equation describing the state of matter under a given set of physical conditions. Let us say what is the equation of state of water? What is the equation of state of steam? What is the equation of state of ice? Or other way around, suppose I have a water, suppose if I increase its pressure keeping volume and temperature constant, so what will happen.

So, the answer of this situation will be given by the equation of state. It is a constitutive equation which provides a mathematical relationship between two or more state functions associated with the matter. Such as its temperature, pressure, volume or internal energy or other some quantities gives potential enthalpy etcetera depending on the physical condition. Experimental values are very often useful but there are occasions where it is not feasible to perform the necessary experiment.

Suppose if an experiment is performed on let us say oxygen, the numerical constants in the equation of state of oxygen only are obtained and no clue is at hand concerning the values of constant for any other gas. Now let us say explain this thing. Suppose you want to perform some expose you want to calculate some constant of the gas at very low temperature.

Suppose let us say you want to perform a experiment for liquid nitrogen, liquid hydrogen which is not possible in the usual at usual circumstances. So then how to get it, so, that is the reason to obtain the detailed information concerning the thermodynamic coordinates and thermal properties of the system without having to resort to experimental measurements. We need some microscopic theory the to obtain the physical properties of the system under any conditions.

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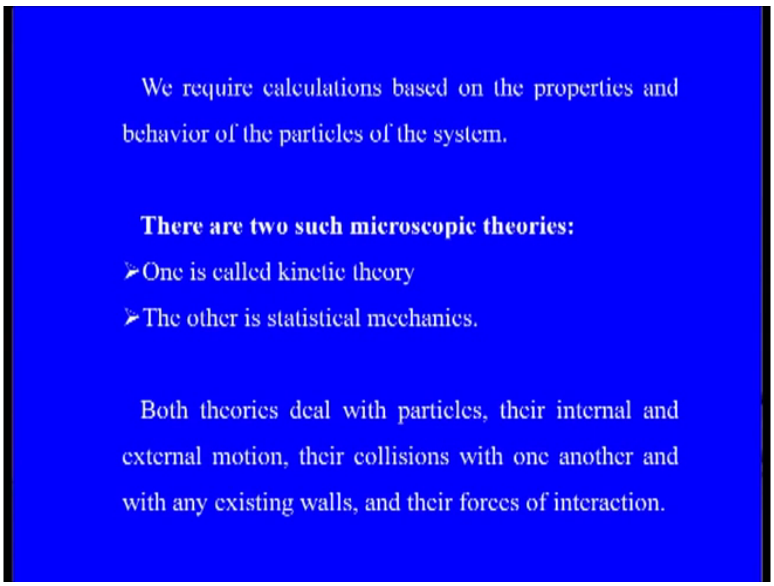

So, we require calculations based on the properties and behavior of the particles of the system. There are two such microscopic theory existed in literature, one is called the kinetic theory and the other is called the statistical mechanics. Both theories deal with particles they are internal and external motion. They are collisions with one another and with any existing wall and there are forces of interaction.

These two theories are microscopic theory their deals the con their deals with the constituent of the system microscopically whereas in classical thermodynamics system have been dealt in terms of their macroscopic properties pressure volume temperature but in the microscopic theory we will deal in terms of the interaction among the constituent how they interact with each other etcetera.

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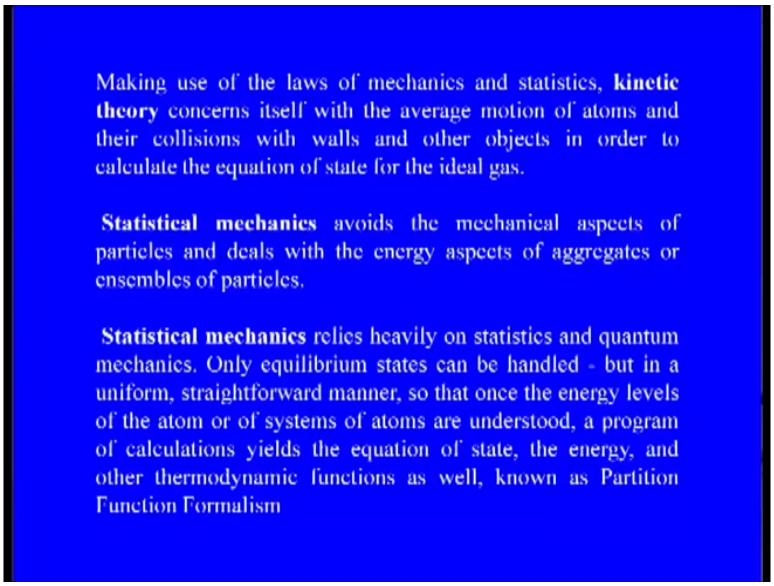

Making use of the laws of mechanics and statistics, kinetic theory concerned itself with the average motion of atoms and their collisions with the walls and other objects in order to calculate the equation of state for the ideal gas, whereas statistical mechanics avoids the mechanical aspects of the particles and deals with the energy aspects of aggregates or ensemble of the particles.

Actually statistical mechanics is based on the concept of and symbol theory. But right now I will not talk about the assemble theory. It is assemble of particles which can mimic a given system. There are three kinds of and symbol one is known as micro canonical ensemble, canonical ensemble and grand canonical ensemble. However these things will be dealt in the statistical mechanics.

But for the sake of this present lecture series I will confine myself only in the kinetic theory of gases. Statistical mechanics relies heavily on statistics and quantum mechanics only equilibrium states can be handled but in a uniform straightforward manner. So, that once the energy levels of the atoms or systems of atoms are understood a program of calculations yields the equation of state, the energy and other thermodynamic functions as well which is known as the partition function formalism.

Actually in statistical mechanics first of all you have to know what is the energy spectrum of the system. Basically you have to solve the Schrodinger equation to get the Eigen energy spectrum. Once you got the energy spectrum you calculate the partition function and once you got the partition function you can calculate all the quantities as you want. Suppose you want to calculate, you can calculate the pressure.

You can calculate the entropy; you can calculate other thermo dynamical quantity. Let us say internal energy gives potential enthalpy or any other quantities if you want, you can get it.

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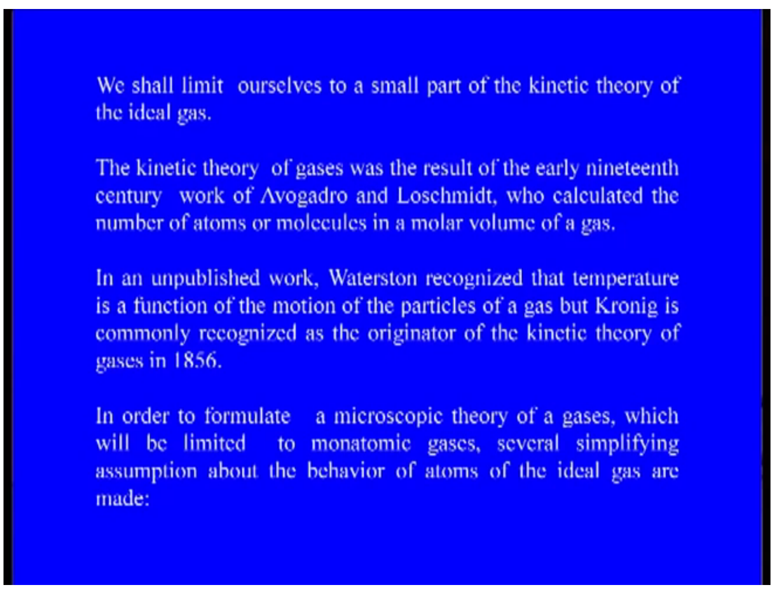

However we shall limit ourselves to a small part of the kinetic theory of the ideal gas. The kinetic theory of gases was the result of the early 19th century work of Avogadro's and law Smith, who calculated the number of atoms or molecules in a molar volume of a gas. In an unpublished work, Waterstone recognized that temperature is a function of the motion of the particles of a gas. But chronic is commonly recognized as the originator of the kinetic theory of gases in 1856.

Now let me start what are the basic assumptions is made for the kinetic theory of gases however here we will deal the kinetic theory of the ideal gases not only that we will deal a gases of monoatomic gases. So, first of all we will we will discuss in details what are the basic assumptions are made for the kinetic theory of gases. And then how using those basic assumptions, how to calculate the pressures and other quantities.

Let me start it, in order to formulate a microscopic theory of gases which will be limited to monoatomic gases. Several simplifying assumptions about the behavior of atoms of the ideal gases are made.

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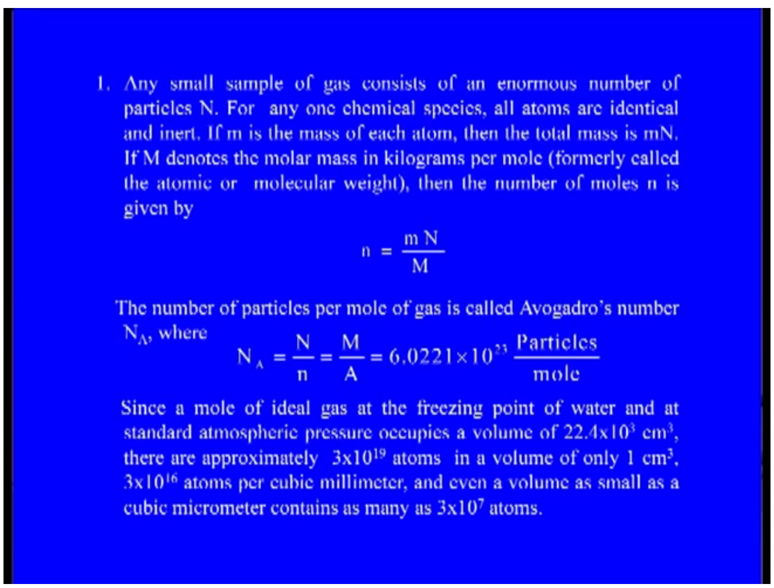

First any small sample of gas consists of an enormous number of particles for any one chemical species all atoms are identical and inert. If m is the mass of each atom then the total mass is m into Nand if M denotes the molecular mass in kilograms per mole formally called the atomic of molecular weight then the number of moles n is given by small m into capital N by Capital M. The number of particles per mole of gas is called the Avogadro number NA.

Which is defined as the total number of particles in divided by number of moles or in terms of molecular weight, molecular weight divided by A which is nothing but 6.022 into 10 to the power 23 number of particles per mole, since a mole of ideal gas at the freezing point of water and at standard atmospheric pressure occupies a volume 22.4 liter. So, there are approximately 3 into 10 to the power 19 atoms in a volume of one centimeter cube.

Whereas 3 into 10 to the power 16 atoms per cubic millimeter and even if volume as small as cubic micrometer contains as many as 3 into 10 to the power 7 atoms, so that means the assumptions that any small sample of gas consist of an enormous number of particles it is justified for the ideal gases.

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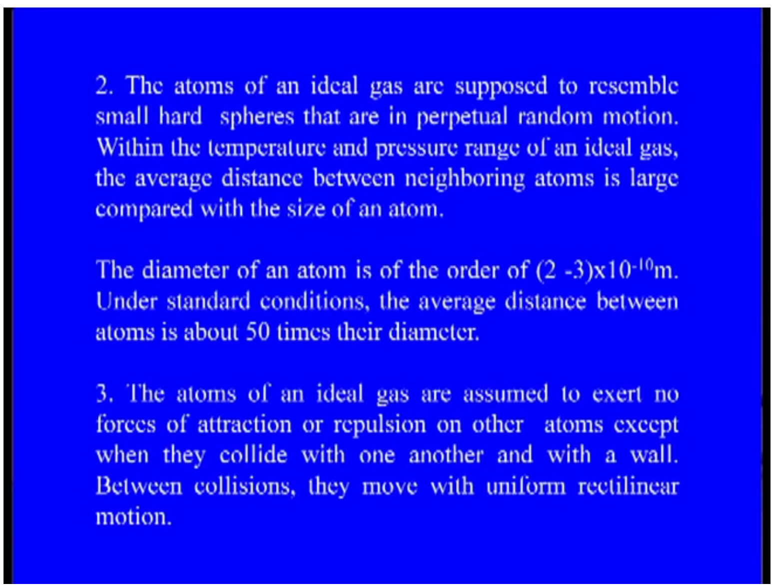

Next the atoms of an ideal gas are supposed to resemble small hard sphere that are in perpetual random motion. Within their temperature and pressure range of an ideal gas the average distance between neighboring atoms is large compared with the size of an atom. So, this assumption justifies that ideal gas means there is no interaction among the constituent of the gases. So, this is justifies since the average distance between the neighboring atoms is quite large compared to the size of the atom.

Let us take some calculate, let us do some calculation the diameter of an atom is of the order of 2 to 3 Armstrong. Under standard conditions the average distance between atom is about 50 times their diameter that means the interactions among the constituents are very small. So, they can be treated as a free streaming particle inside the container of the gas.

Third assumptions are the atoms of an ideal gas are assumed to exert no forces of attraction or repulsion on other atoms except when they collide with one other and with the wall. Between collisions they move with uniform rectilinear motion.

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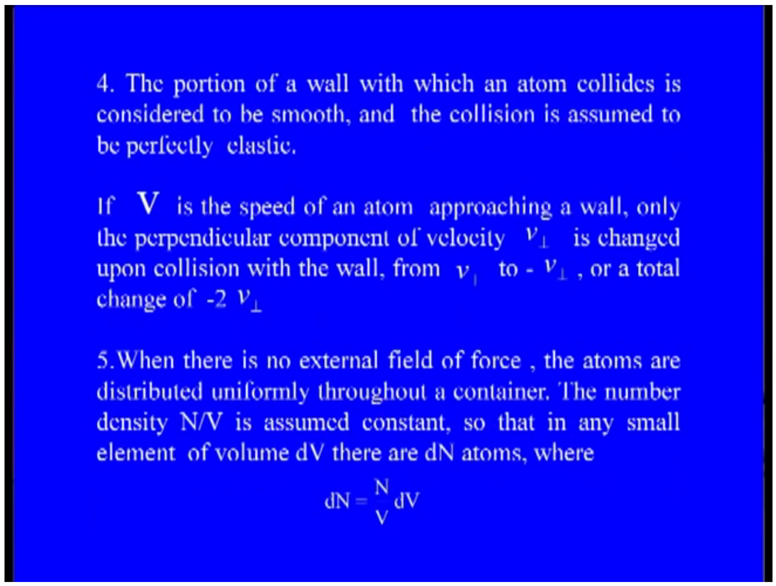

Fourth assumption is the portion of a wall with which an atom collides is considered to be smooth and the collision is assumed to be perfectly elastic okay. So, this is the one of the most important assumptions in the kinetic theory of gases that the collisions between the atoms and the walls of the container is perfectly elastic collisions. To make the elastic collision, so that is the reason the surface of the wall should be smooth enough. So, that collision will be perfectly elastic.

So, as we know if V is the speed of an atom approaching a wall only the perpendicular component of velocity V perpendicular is changed upon collisions with the wall. From V perpendicular to - V perpendicular just it changes its sign or a total change of -2V perpendicular. Fifth assumption when there is no external field of force the atoms are distributed uniformly throughout a container.

The number density N by V is assumed constant so that in any small element of volume dV there are d n number of atoms where dN is N by V into dV. Now let me start what is the concept of an infinitesimal volume element in the kinetic theory of gases. As you know in the thermodynamics the infinitesimal volume element is defined as the volume element which are too small compared which are small which are very small compared to the volume of the system.

So, same concept of an infinite sum volume element also holds good in the kinetic theory of gases. Let me justify that statement.

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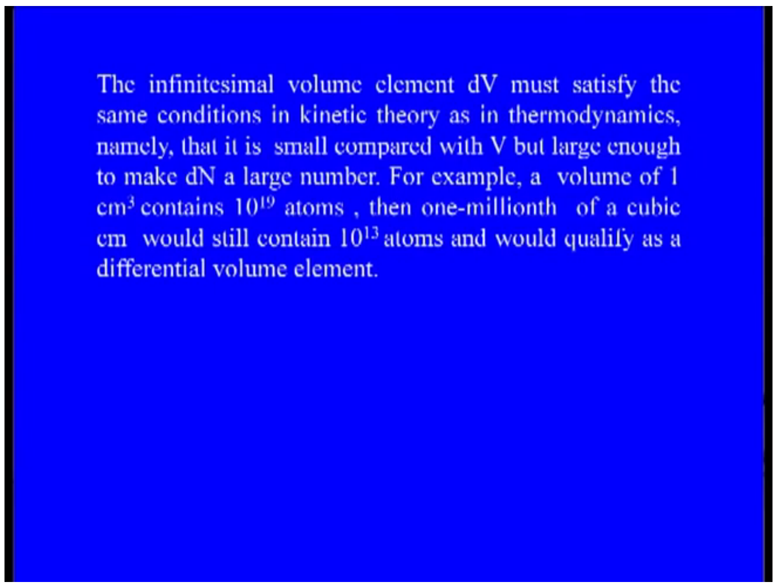

The infinitesimal volume element dV must satisfy the same conditions in the kinetic theory as in thermodynamics. Namely it is small compared with V but large enough to make dN a large number. For example a volume of one centimeter cube contains 10 to the power 19 atoms which is quite large. Then one millionth of a cubic centimeter would still contain three large atoms 10 to the power 13 atoms and would qualify as a differential volume element.

So, what is the idea of differential volume element in kinetic theory of gasses? These volume elements should be very small compared to the total volume of the system. But simultaneously it should contain a very large number of atoms so that it should satisfy the first assumptions in the kinetic theory. Let me show you that any small sample of gas consists of an enormous number of particles. So, it should satisfy the first assumptions of the kinetic theory.

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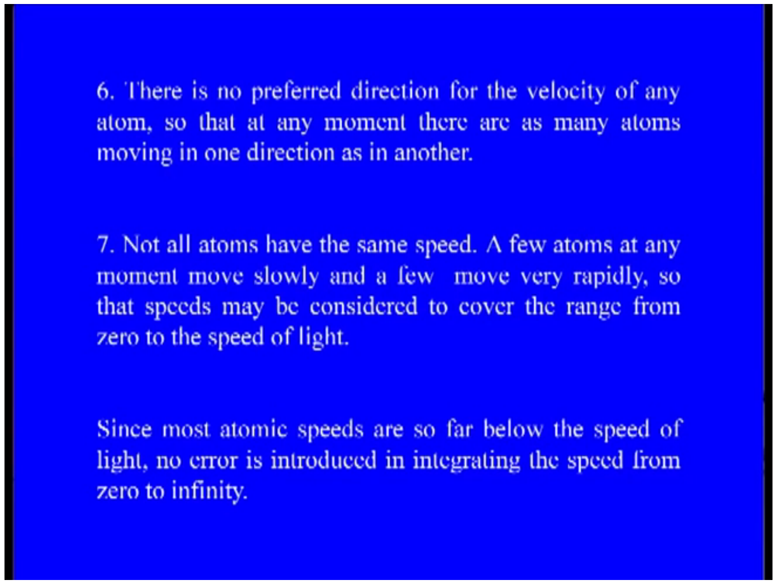

Assumption 6 there is no preferred direction of the atoms which are moving in a random motion that means I can find the equal number of atoms in any direction okay. So, there should not be any preferred direction for the velocity of any atom. So, that at any moment there are as many atoms moving in one direction as in another. This is the most crucial assumptions in the kinetic theory of gases.

Seventh so not all atoms have the same speed, a few atoms at any moment moves slowly and few move very rapidly. So, that speeds may be considered to cover the range from 0 to the speed of light. However no atoms can achieve the speed of light but for the sake of calculations we can take the velocity from 0 to infinity. However there will be no error introduced because there are no atoms which are velocity, whose velocity ranges from the velocity of light.

So, since most atomic speeds are so far below the speed of light no error is introduced in integrating the speed from 0 to infinity. Now let me summarize the assumptions which you have made and which you have discussed already in a very short form ok and which will be used in doing the calculation.

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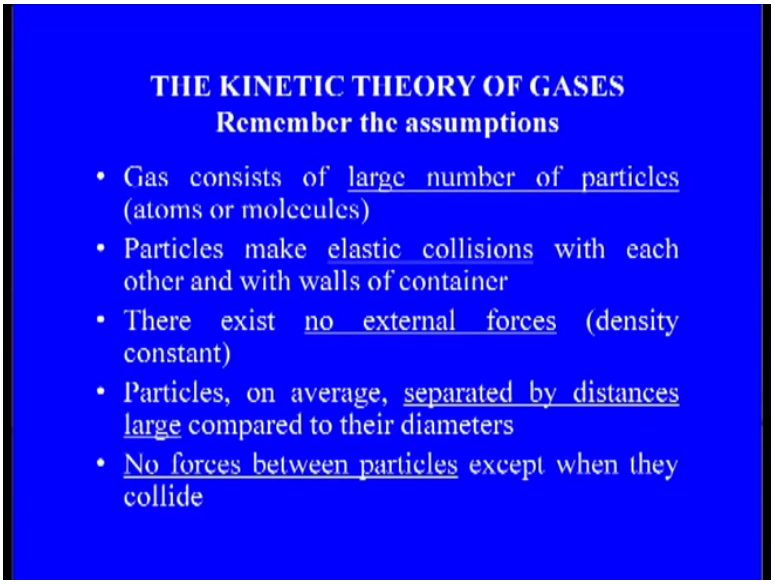

First assumptions we have made gas consist of large number of particles either it may be atoms or molecules. Particles make elastic collisions with each other and with walls of container. There exists no external forces that means where density in that case density will be constant. Particles on average separated by distances large compared to their diameters. No forces between particles except when they collide.

These are the main assumptions we have met. Now on the basis of that assumption we will try to calculate the pressure from the kinetic theory of gases.

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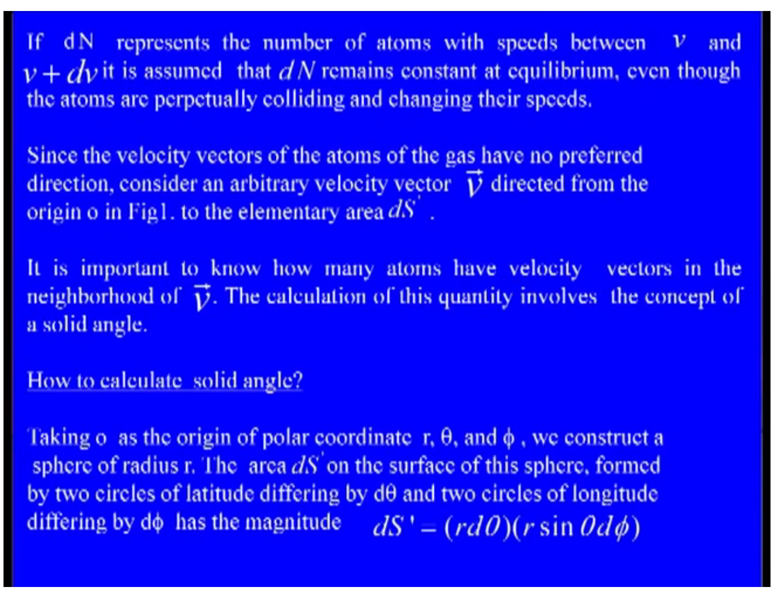

Suppose, if dN number of atoms having speed between v and v + dv it is assumed that dN remains constant at equilibrium even though the atoms are perpetually colliding and changing with their speed but dN remains constant at equilibrium. Since the velocity vectors of the atoms of the gas have no preferred directions as I have already mentioned in one of the assumptions that there are no directions are preferred.

So, consider an arbitrary velocity vector V directed from the origin as in figure to the elementary area dS prime.

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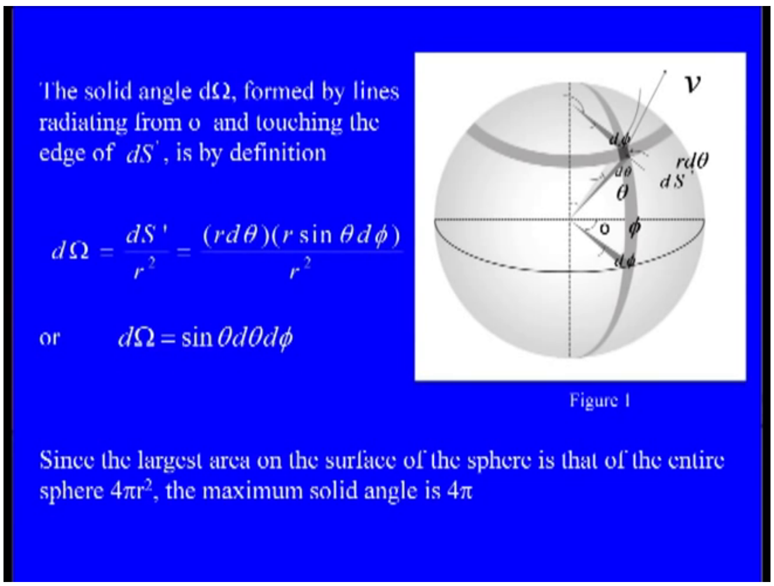

Let us show this figure, so this is the elementary area this is the elemental area dS as you can see in the figure. So, some velocity vector which is directed from the origin along the radial directions. So, the elementary area is normal to the r vector. So, in that case let us know how many atoms have velocity vectors in the neighbourhood of V. The calculation of this quantity involves the concept of a solid angle.

So, let me first calculate what is this solid angle? Okay. Taking o as the origin of the polar coordinate r, Theta, Phi, we construct a sphere of radius r the area dS prime on the surface of the sphere formed by two circles of latitude differing by d theta and two circles of longitude differing by d Phi has the magnitude dS prime is rd theta into r sine theta d Phi okay. So, this is the figure this is the dS infinitesimal area you can see in the figure.

So, then this followed angle d Omega formed by lines radiating from the origin and touching the edges of dS Prime is where definition is d Omega is dS prime by r square which is rd theta into r sine theta d Phi by r square which is nothing but the sine theta d theta d Phi, this is the solid angle. Now since the largest area on the surface of the sphere is that of the entire sphere 4Pi r square. The maximum solid angle is 4Pi.

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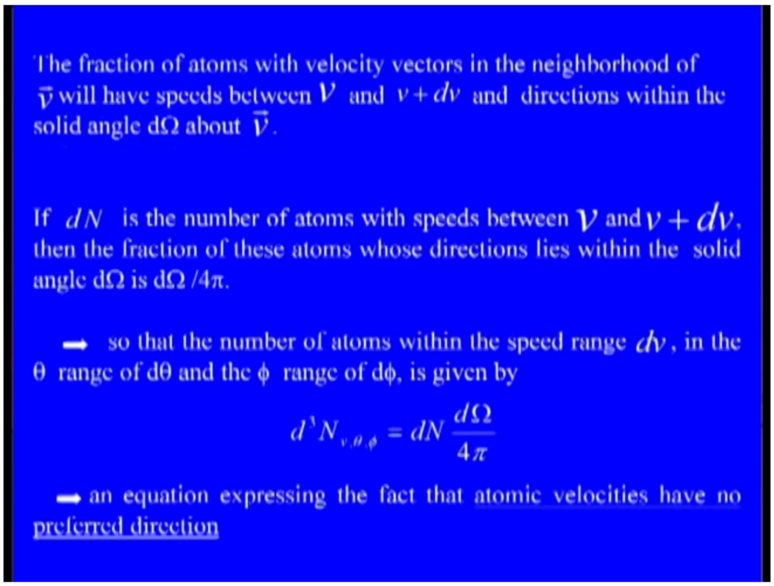

So, now we want to calculate what are the fraction of atoms with velocity vectors in the neighborhood of velocity V will have speeds between V and v + dv and directions within the solid angle d Omega around V. If dN is the number of atoms with speed between V and v + dv then the fraction of these atoms whose direction lies within this solid angle d Omega is d Omega by 4 Pi.

So, the number of atoms within the speed range dv means within the speed range between V and v + dv angle theta and theta + d theta and Phi and Phi + d Phi is given by dq N v theta Phi is dN into d Omega by 4 Pi. This equation expressed that atomic velocities has no preferred direction. So, that cause that is the reason you got the term d Omega by 4Pi which emphasizes the fact that atomic velocities has no preferred direction that means atoms will move randomly in all possible directions.

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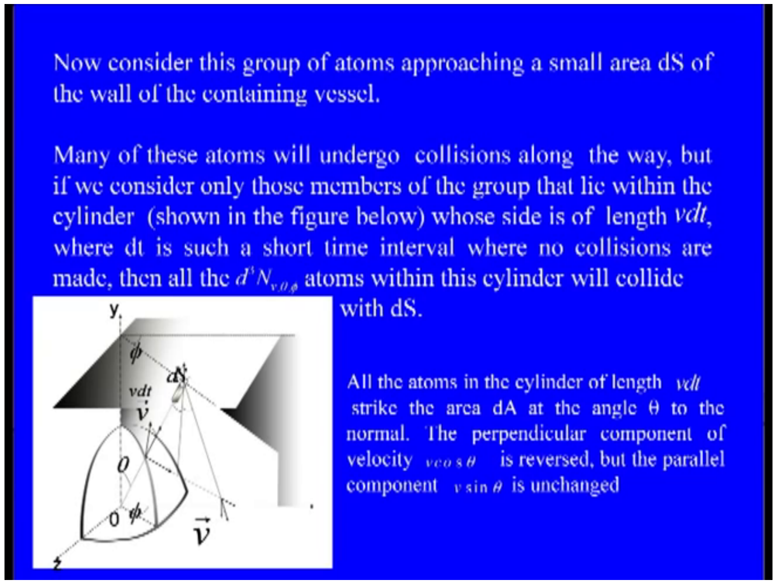

Second, now consider this group of atoms approaching a small area dS of the wall of the containing vessel. Many of these atoms will undergo collision along the way but if we consider only those members of the group that lie within the cylinder whose side is of length v dt where dt is very small time interval where no collisions are made in that case all dq Nv theta Phi atoms within this cylinder will collide, the will collide the atoms containing in the infinite small surface area dS okay as you can see from this figure.

All the atoms in the cylinder of length v dt strike the area dA at the angle theta to the normal. The perpendicular component of velocity is v cos theta which will be reversed because of elastic collision but the parallel component which is v sine theta which remains the same.

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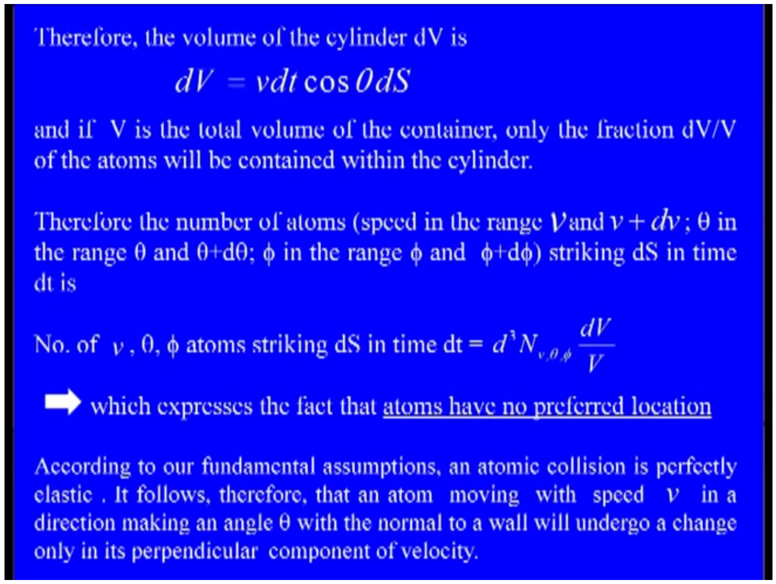

Now the volume of the cylinder is dV is v dt cos theta into dS and if V is the total volume of the container only the fraction dV by V of the atoms will be content within the cylinder. So, now finally we want to calculate what are the total number of atoms in the velocity range with the speed V and v + dv in the theta range theta and theta + d theta in the Phi Phi and Phi + d Phi okay.

So, therefore the number of atoms in the speed range V and v + dv in the theta range theta and theta + d Phi in the phi range Phi and Phi + d Phi striking dS in time dT is dq N v theta Phi dV by V. So, this equation emphasizes this fact that atoms has no preferred locations. So, atom can stay anywhere in the container, so that makes the quantity dV by V. According to our fundamental assumptions and atomic collision is perfectly elastic.

It follows therefore that an atom moving with speed V in a direction making an angle theta with the normal to a wall will undergo a change only in its perpendicular component of velocity. There will be no change in the horizontal component of velocity which will remain unaltered. So, finally we want to calculate what is the total change of momenta in the power collision? Okay. So, it consists of three terms which we have already derived.

One is based on the concept of there is no preferred direction, second one is based there is no preferred direction preferred location of the atoms, so using these two assumptions let me calculate what are the total change of momentum per collisions.

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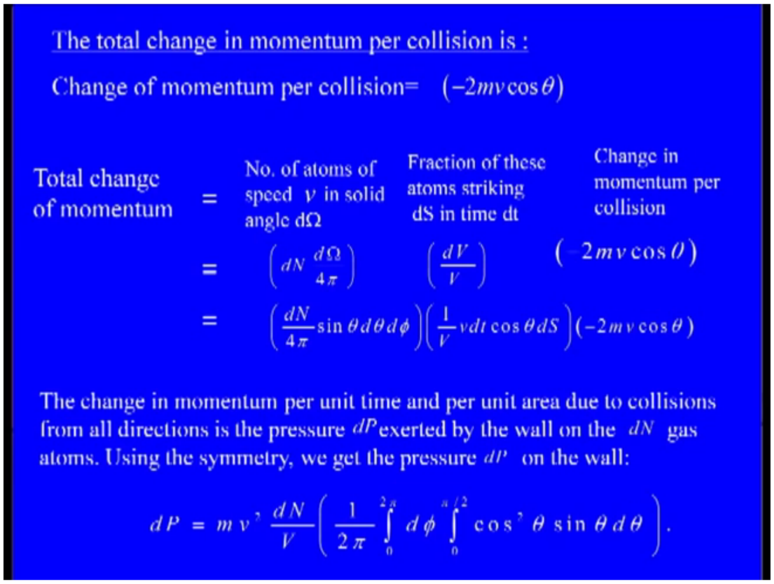

As we know change a moment of power collision is -2 mv cos theta where basically v cos theta is nothing but the perpendicular component of velocity. Let me show you in the figure, yes. In this figure you can see that v cos theta is the perpendicular component of velocity which can only be changed by the amount -2v perpendicular that is given 2mv cos theta okay. So, total change of momentum consists of three terms.

First term is number of atoms of speed v in the solid angle which is dN into d Omega by 4Pi fraction of these atoms striking dS in time dT which is dV upon V and change in moment of our collision which is -2 mv cos theta. So, we have got three terms and if you will product them together we got it dN by 4Pi sine theta d theta which is nothing but the d Omega and dV as we have already done dV is v dt cos theta dS.

So, 1 by V vdt cos theta into dS into -2mv cos theta so, finally we got the total change of momentum per collisions. The change in momentum per unit time and per unit area due to collisions from all directions is the pressure dP exerted by the wall on the dN gas atoms. So, using this symmetry argument we know since they are coming from all possible directions.

So, we can reverse the sign -2 mv cos theta is by 2 mv cos theta is dP = mv square dN by V, 1 by 2 PI, 0 to 2 Pi d Phi, 0 to Pi by 2 cos square theta sine theta d theta, 2 mv cos theta 2 in mv cos theta will cancel with the 4 Pi makes it 2 Pi. Now if I will do this angular integration I will get it, I will get a factor one third what does it physically mean physically it means that particles are coming from all possible directions.

So, this is an all possible directions are equally probable. So, that means you will get one third term by automatically that means this is the concept of isotropy city in the momentum space. When the average values of VX square will be same as average values of VY square as average values of VZ square then average values of V square is nothing but one third average values of either VX square or VY square or VZ square that is the physical meaning of one-third.

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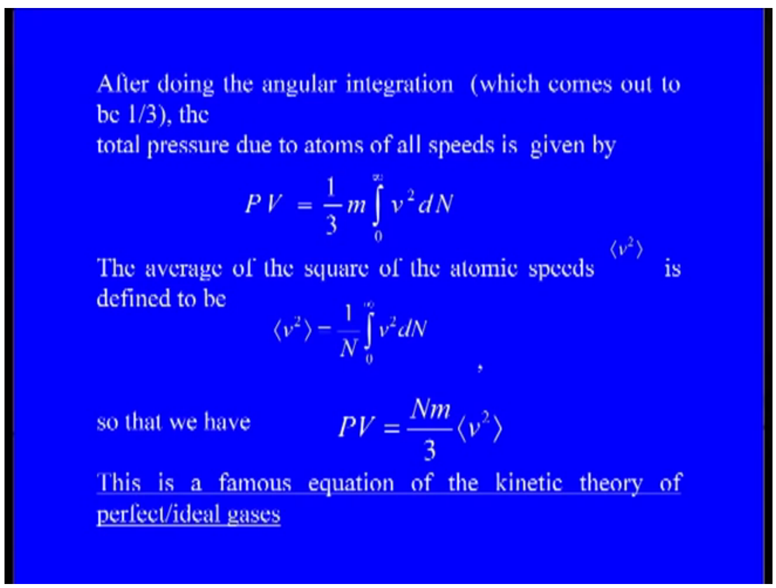

So, after doing the angular integration the total pressure d2 atoms of all speed is given by PV equal to one third m 0 to infinity V square into dN. As I have already told you that I will integrate velocity from 0 to infinity although no atoms have speed greater than the velocity of light but still I can write it 0 to infinity because I will not do any mistake in doing the integration because there are no atoms which have velocity of greater than the velocity of light.