

Molecules in Motion
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Lecture – 02
Kinetic theory of gases (Contd.)

Today we are going to continue with what we had done in the last class, then we are going to continue with the Kinetic theory of gases. Probably we will be doing this for a few more classes. But what we had had done in the last class was we had tried to derive a pressure expression for pressure in terms of the conditions where we had taken that the molecules were colliding with a particular surface of the container.

We had the total volume of the container v and then a the total number of molecules which were colliding on the surface and at a given time was found out and from that we got a expression for pressure.

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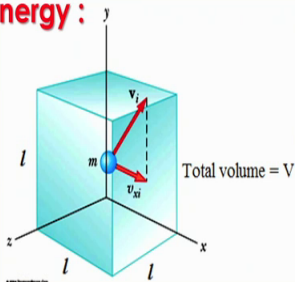
Pressure and the Molecular Kinetic Energy :

Velocity of a gas molecule is represented by a **vector**, so, it has a **magnitude** and a **direction**.

The component velocities, v_x , v_y , and v_z , of a molecule in velocity space have signs, but we are often more interested in the magnitude of the velocity vector than its direction.

The **magnitude of the velocity vector** is referred to as the **speed** of the particle.

The **speed** can be calculated from the components of the velocity vector by using the Pythagorean theorem


$$c = |v| = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

v. mean square

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(Refer Slide Time: 01:10)

Pressure and Kinetic Theory:

$$p = \frac{nM \langle v_x^2 \rangle}{V}$$

- Since the velocities of the molecules in the ideal gas are **completely random**, there is **no preference to any one direction**. Hence,

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \quad \text{or} \quad \langle c^2 \rangle = \langle v^2 \rangle = 3 \langle v_x^2 \rangle \quad \text{or} \quad \langle v_x^2 \rangle = \frac{\langle v^2 \rangle}{3} = \frac{\langle c^2 \rangle}{3}$$

$$P = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m \langle c^2 \rangle \right) \Rightarrow P = \frac{1}{3} \left(\frac{Nm}{V} \langle c^2 \rangle \right)$$

$$PV = \frac{1}{3} Nm \langle c^2 \rangle$$

$$n = \frac{m}{M} = \frac{N}{N_A}$$

$$N = \left(\frac{m}{M} \right) N_A$$

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Now, what we are going to look if you remember the expression for pressure was given something like this in the last class where, this was the volume of the total container this was the pressure of the gas which was generated when the molecules or particles of the gas were striking the wall of area a, within a distance of the distance was taken to be $v \times$ into delta t.

Within, this was considered to be the length of within which all of the particles which were striking on the surface of the wall. Area a, were found out and from this amount of whatever the rate of momentum which was transferred divided by the total area of the container on the wall was found out and from that expression because force by area is the pressure and the force was found by found out from the rate of change of momentum.

The rate of change of momentum, total rate of change of momentum was found out we take considering number of total number of collisions which were occurring that into that change in momentum for one collision. From so, from this expression what we had got? We had got the velocity with what we had taken as the velocity of the particles that were moving in the x direction and why we are say taking and y what velocity what is the term which we are going to call this? We are going to call this as the root mean square velocity.

The particles which means contained in the unit volume or the total volume of a gas is equally probable to be colliding in all the three surfaces; that means, they are moving in

x, y and z direction with equal probability. So, if we look into that we again visit what we were taking in the previous class, we had a unit volume, total volume of this container which was which was cubic was taken to be v with each of the lengths of the volume being l . So, the velocity of the gas molecules was represented as is represented itself velocity is a vector.

So, the x, y, z components of the velocity exist. So, we have to not only take consideration about the magnitude, but we also need to take account of the direction because vector means will have the x m the magnitude as well as the direction associated with the vector velocity component, but more often we have will be more interested in the magnitude of the velocity vector instead of also instead of the direction.

The magnitude of this velocity vector is a scalar term which we call as the speed. So, velocity is a vector term which has magnitude and direction associated with it we are looking into the velocities of the molecules which are moving in a system or of volume or a cube of side length l , total volume big equal to l cube equal to v . So, contained all the molecules contained in this we are talking about them exerting pressure on the wall through collision and we are looking in the vector in velocity space where the velocity of the of the molecules or the particles are resolved into x and y and z direction.

We were interpreting the entire derivation only considering the that the particles were moving in a one particular direction that is x direction parallel to the x direction and writing the surface which was on the right hand side. So, now if we are looking into the speed what we are looking into we are looking into the speed of the molecules what we write here this as the speed can be calculated speed; we are talking about only the magnitude part of the vector, velocity vector, the speed can be calculated from the Pythagoras theorem using the Pythagoras theorem you can find out what the speed will be.

Because you have the x, y and z component of speed a velocity only it considering the magnitude of it we can calculate using the Pythagoras theorem the velocity being the under root of the velocity component in the x square of the velocity in the x component plus the square of the velocity in the y component plus this square of the velocity under of the z component.

So, the c which we are looking into which we are calling as speed is also known as the root mean square velocity or root mean square speed.

(Refer Slide Time: 06:38)

Pressure and the Molecular Kinetic Energy:

The relationship between the pressure and the molecular kinetic energy of the gas particles comes from momentum and Newton's Laws

- Assuming the gas particles undergo **perfectly elastic collisions** of the with the walls of the container

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So, what is what is actually happening? What is actually happening? What we are seeing the velocity component which we are looking into? We are looking into this component of the velocity it is the particles are moving hitting striking the wall and this is the wall with the area a and there it is reverted back or moving back in the opposite direction. What we are looking into? We are looking; that means, what is possible that the number of particles which are striking the wall we are having a velocity plus v_x has there is likely that the same number of molecules will be there when the velocity minus v_x .

So, the for you need to realize this before we go into what is the root mean square velocity? We are going to be interpreting the pressure and the kinetic energy of the molecules based on certain assumptions like what we have done in the previous class that the molecules which are striking are undergoing perfect collision or a elastic collision where the total kinetic energy of the molecules is conserved.

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The diagram is divided into two horizontal sections. The top section is titled "Elastic Collision". On the left, a blue sphere of mass m moves to the right with velocity v_1 . In the middle, a red starburst indicates the collision point. On the right, a green sphere of mass m moves to the right with velocity v_2 . Below this, it says "Before elastic collision" and "After elastic collision". The bottom section is titled "Inelastic Collision". On the left, a blue sphere of mass m moves to the left with velocity v_3 . In the middle, a red starburst indicates the collision point. On the right, a green sphere of mass m moves to the right with velocity v_4 . Below this, it says "Before inelastic collision" and "After inelastic collision". To the right of the diagrams, text states: "Elastic Collision: Total Kinetic Energy and Momentum of the particles remains same before and after the collision (Conservation of Kinetic Energy and Conservation of Momentum, mv).". Below the diagrams, text states: "Inelastic Collision: ONLY Conservation of Momentum, mv ". At the bottom of the slide, there are logos for IIT KHARAGPUR and NPTEL ONLINE CERTIFICATION COURSES, and a video inset of a woman, Amita (Pathak) Mahanty, from the Department of Chemistry.

What do you mean by that if you look into a picture of what is what usually happens when you have an elastic collision or a perfect collision? What you have is, you have a particle which is moving with a certain set of velocity, it strikes another particle which is in the same volume element and after striking this molecule will be moving with another velocity maybe if the same velocity or may different velocity moving in the same direction.

So, the total kinetic energy and the in a elastic collision the total kinetic energy and that momentum of the particle remains the same, but when we have an inelastic collision then we do not have conservation of total kinetic energy, but there is a conservation of momentum. Suppose, you have an explosion and in an explosion then the number of particles moving away from as splinters; this splinters will have this have the condition where we have the momentum of the particles of each of the particle which is coming out in the explosion will be same, but the total kinetic energy may not be the same. For example, when we look into a m elastic collision it is colliding and it is reverting back in the same direction. The total kinetic energy is not transferred or is not held constant.

When we are talking about a particular molecule that the kinetic energy of after collision may not be exactly the same which I have through it may not be exactly what it was before; that means, we do not have exactly for each particle the conservation of energy is not held. But overall in the set of particles in a volume the total energy of the kinetic

energy of the system is conserved when they undergo elastic collision. So, this is to be understood very clearly.

Now, what we are looking at we are going to interpret the pressure and kinetic energy in terms of the colliding particles. So, if we are doing that let us come to the previous slide where we were talking about it. So, the slide which we had last ended in the last class was where we had given the expression of pressure, where this v was the total volume of the cubical which we were considering in which the gas was enclosed this was the number of moles of the gas and this was the molar mass of the gas which we had used.

If you remember the expression that what we derived in the last class this was the last expression we say we had stopped in our lecture. What is this? This is the velocity which we are writing as v_x , this is the x component of the velocity the resultant velocity which is along the parallel to the x axis.

So, now what we are saying, since the molecules are incomplete random motion there is no preferred direction that the molecules will go in x or in y the molecules will have a tendency to have either going in the x direction or in the z direction or in the y direction the m . They have equal chance there is no preferred any set of direction, if they have equal chance of a particle moving with a velocity x , along the x axis the same is a particle moving with the velocity y in the y direction and the velocity z along the z direction.

That means the probability of having any of these velocities by a particle is should be equal. They are equal equally probable to have either this or this or this. So, to find out what will be the velocity what we can take; that means, the and the velocity which we can have is either 3 times this or 3 times x or 3 times y . So, if we want to find out what is the velocity in the x direction, what we can say? This is what we call as the may be in standard absolute velocity or the root mean square velocity which should be equal to $1/3$ of the root mean square velocity.

So, the velocity component in along the x component will be nothing, but the root mean square velocity divided by 3, because they are all are equally probable. So, if I have that then I substitute that in the expression I have for this for the v_x component, v_x is what? We can write the velocity square this is the rms velocity or the root mean square velocity

divided by 3. So, this comes from this expression when all of the velocities are equally probable.

So, the root mean square velocity will be either the 3 times of any velocity in any one set of direction. So, the velocity at one set of direction will be given by nothing, but by the root mean square velocity by 3. So, here we are going to substitute this into this expression what we get is going to be something looks something like this, right have a look at this, what we are substituting? We are substituting n equal to number of mass of the molecule divided by the molar mass or it can be represented by the total number of molecules divided by the Avogadro number.

So, if I represent that by in the total number by the N by that total number of molecules divided by the Avogadro number, substitute in this, what do I get? I get and the total number of molecules is nothing, but the mass of the molecule divided by molar mass into the Avogadro number. So, if I substitute this here I get the expression can you just have a look, do it yourself and only then you get to write what you are seeing here.

So, what you are having here? This is the total number of molecules, this is the mass of the molecules and this is the total volume and this is the rms speed or rms velocity which is nothing, but the under root of velocity square in all the 3 square of the all the three components. Like we have written here this is the one which we are looking into sorry these things happen.

So, this is the velocity we are looking into this the root mean square velocity which we are representing is under root of the mean velocity the root mean square that means, you are taking the under root of the mean square of the velocity. This is the mean velocity of squaring above and you are taking the under root is how you define the root mean square velocity.

So, the it is the square of the mean velocity is along the x axis, y axis and x z axis and summing up them taking under root gives you the rms or c value or the rms p . So, if we have come to that we have now justified why we are having the 1 by 3 component. So, 1 by 3 component is now introduced in the pressure. So, the if we now represent this we take the volume to this side. Then what you have? We have an expression which is quite similar to the inert gas law, where we have PV equal to nRT and here we have PV equal

to 1 by 3 this is N is the total number of molecules, this is the mass of the gas and this is the rms speed.

So, we have derived the expression which in terms of the speed of the molecules the rms speed of the molecules. So, that we can find out interpret in terms of the speed of the molecules in the pressure in terms of the speed of the molecules.

(Refer Slide Time: 17:05)

Pressure and the Molecular Kinetic Energy:

- The relationship is
$$P = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m \langle c^2 \rangle \right)$$
 where, M (molar mass) = $m \times N_A$.
Handwritten note: $\frac{2}{3} N m \langle c^2 \rangle = P$
- This equation also relates the macroscopic quantity of pressure with a microscopic quantity of the average value of the square of the molecular speed.
Handwritten note: $P \propto \frac{1}{3} \rho \langle c^2 \rangle$
- This tells us that pressure is proportional to the number of molecules per unit volume (N/V) and to the average translational kinetic energy of the molecules
- This tells us that the pressure of the gas can be increased by increasing the number of particles per unit volume
- This tells us that the pressure can also be increased by increasing the speed (kinetic energy) of the molecules

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So, next we move on to the relationship which we have just now obtained that. This can be rewritten you can manipulate. See what I have done, I have done I have got the same expression as the one which was there previously m into V 1 by 3, it is it was 1 by 3. What was it? $N m$ root mean square velocity this was given to be the pressure.

What I have done I have and that was divided by V was the expression of pressure which we had now what we had we had taken now we manipulate we multiply 2 in the numerator and also multiplied to 2 in the denominator. If I multiply 2 in the denominator and rearrange the terms then what I can take I can take this separated out, this can be separated out.

And this another portion can be separated out what we are looking into here is we are trying to relate the macroscopic value of pressure which we are using in the ideal gas laws or the which has the expression which you use in the gas law equations.

So, this is that pressure which we are talking about in the macroscopic term and what we are trying to relate? We are trying to relate the macroscopic quantity of pressure with terms of the microscopic quantity in terms of the average or the square of the velocities of the molecular velocities of the particle and the proportion we have also found out the pressure is proportional to the number of molecules per unit volume.

So, what we are seeing pressure is proportional to the number of particles in the unit volume. We are also seeing that pressure is proportional to the root mean square speed, and this equation also tells us that pressure as the pressure of the gas can be increased by increasing the number of particles in the volume unit volume; that means, if I increase the number of particles in a unit volume the pressure should increase similarly, it also tells pressure can also be increased by increasing the speed.

So, interpretation of pressure from the kinetic molecular theory is what we have just now concluded is we have derived initially the expression of pressure based on the collision theory and from that collision of the molecules with the walls of the container from that what we have interpreted is the pressure term. And from this pressure term we have seen in a volume in the total volume V if the N is the total number of particles; how it is going to be dependent on number of number concentration of the particles or the concentration of the particles are number of particles in the unit volume and how it is also going to be proportional to the number of to the rms speed of the particle.

So, if you increase the speed the pressure is going to increase if you increase the number of molecules the pressure is going to increase. So, these are going to give rise to this part is also if you are looking into this part this is going to be something in terms of the kinetic energy. So, we can also that the pressure is proportional to the number of particles and to the average translational kinetic energy because we are taking on the movement of the molecules in either x or y or the z direction.

So, what we have found out? It is proportional to the translational kinetic energy it is proportional to the total number of molecules present per unit volume of the container and it is proportional to the speed. So, the pressure can also be increased by increasing the speed, we can increase it by increasing the number of particles. So, this being what we have derived.


(Refer Slide Time: 21:31)

Pressure and the Molecular Kinetic Energy:


- We can take **the pressure** as it relates to the kinetic energy and compare it to the pressure from the **equation of state for an ideal gas**

$$P = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m \langle c^2 \rangle \right) = \frac{N}{V} k_B T$$

- Therefore, **the temperature** is a direct measure of **the average molecular kinetic energy**




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Now, we can go into the expression what we can in terms of the energy. What we have taken? We have taken the pressure.

(Refer Slide Time: 21:42)

Translational Kinetic Energy of Molecules:

From **Kinetic Theory Model**, we have:

$$P = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m \langle c^2 \rangle \right)$$
$$\Rightarrow PV = \frac{2}{3} N \left(\frac{1}{2} m \langle c^2 \rangle \right)$$

From **Ideal gas law**, we know:

$$PV = nRT$$
$$\Rightarrow PV = \left(\frac{N}{N_A} \right) RT \quad \text{since, } \left(n = \frac{N}{N_A} \right)$$

Again, k_B (Boltzman constant) = $\left(\frac{R}{N_A} \right)$


Equating the two **PV** expression we get,

$$\therefore PV = k_B T$$


Where,

$$Nk_B T = \frac{2}{3} N \left(\frac{1}{2} m \langle c^2 \rangle \right) \Rightarrow \frac{1}{2} m \langle c^2 \rangle = \frac{3}{2} k_B T$$

$\langle c^2 \rangle = \langle v^2 \rangle \equiv$ Root mean square velocity




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We have found out what the pressure is and from the pressure expression we have we know that this is the pressure which we have derived from the kinetic model and if I take V to the other side I can rewrite as 2 by 3 n into half mc square this is the root mean square velocity.

Similarly, I have another a thing which is which can be obtained which from the ideal gas law. From ideal gas law, which we know this PV equal to nRT now, I substitute N with N by number of molecules by the Avogadro number because n is this is what the number of moles can be represented. So, PV equal to N by the Avogadro number into the R into T and if I we know another relationship which is a Boltzmann constant, according to Boltzmann constant the gas constant by the Avogadro number is equal to the Boltzmann constant. So, I can rewrite the whole thing in terms of the Boltzmann constant PV equal to kT .

And, this k , usually we do not say k_B , but we say it is kT when we say, but it is actually to represent that it is a Boltzmann constant that I have written the subscript B . So, what we have? We have two expressions of PV , just have a look this is what we have just now derived from kinetic model and this is what we have from the ideal gas law.

Now, equate these two. If I equate these two, what do I get? If you equate these two, this is what we have for from PV if I ideal gas law and this is what you have for the inert gas from kinetic model. Now, if you can look into this very closely this c is the root mean square velocity this is nothing, but the root mean square velocity which is represented in when I say it is in the in terms of v_x , or v_y , v_z .

So, this is the root mean square velocity which we have. So, what we have equated? We have equated this to this. What we have gained from here from this is half mc^2 square equal to $\frac{3}{2} kT$. This is something very familiar to what we know about the kinetic energy of a particle when we talk about the kinetic energy equal partition law let us go to that and let me see it show you that.

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Translational Kinetic Energy of Molecules:

Thus, we have: $\Rightarrow \frac{1}{2}m\langle c^2 \rangle = \frac{3}{2}k_B T$


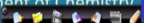
Again, $\frac{1}{2}m\langle c^2 \rangle =$ Average Translational Kinetic Energy (K_{tr})

$$\therefore K_{tr} = \frac{3}{2}k_B T = \frac{3}{2}\left(\frac{R}{N_A}\right)T$$

T : absolute temperature
 k_B : Boltzmann constant
 R : molar gas constant
 N_A : Avogadro constant



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So, we have this expression. From this expression what we have the this is half mc^2 is nothing, but the kinetic energy. So, the average the kinetic is translation kinetic energy can be represented by this. This is the representation of the average kinetic energy, translational kinetic energy and that is equal to $\frac{3}{2}kT$.

So, if I rewrite that I can rewrite the translation kinetic energy this equal to nothing, but $\frac{3}{2}kT$ and that is kT is what k is R by the Avogadro number. So, I can rewrite this as the kT as R by the Avogadro number.


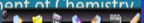
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Translational Kinetic Energy of Molecules:

- For N molecules of an ideal gas in the cubical container, the **total average (mean) translational kinetic energy**, E is given by

$$E = NK_{tr}$$
$$E = N\left(\frac{3}{2}kT\right) \quad E = \frac{3}{2}NkT \quad \text{or} \quad E = \frac{3}{2}nRT$$


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So, this is what we are going to get. So, what we are having for N number of ideal particles in a cubicle container, the total average kinetic translational kinetic energy can be given by the total number of molecules into the total and the kinetic energy per unit molecule. So, this is the total kinetic energy which we get for N number of molecules of ideal gas in a cubic container with the total average kinetic energy being represented by K. So, this is what we get.

(Refer Slide Time: 26:22)

Translational Kinetic Energy of Molecules:
Principle of Equipartition of Energy

- States : "the mean (average) kinetic energy of every degrees of freedom of a molecule is $\frac{1}{2}kT$."

Therefore, $\langle K \rangle = \frac{f}{2}kT$ → Mean (average) kinetic energy per molecule

Or, $\langle K \rangle = \frac{f}{2}RT$ → Mean (average) kinetic energy per mole

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So, if we talk about in terms of the principles of partition of energy the mean average kinetic energy of every degree of freedom of molecule is represented by half kT. So, depending on what is the degree of freedom you have degree of freedom into half kT the mean kinetic energy per molecule.

So, if we want to find out the mean kinetic energy per mole, we will write this will be nothing, but k is what R by the Avogadro number. So, if I have so, this is what we have got. So, this is what we are establishing is the I was trying to write down what the kB was the k and this is the kB or the Boltzmann constant. Boltzmann constant is nothing, but R by Avagadro number.

So, what we have got is, what is depending on the degree of freedom depending on the type of molecules we are dealing we can find out the mean or the average kinetic energy per degree of freedom of the molecule which is equal to half. We have to multiply by the

total number of molecules total degrees of freedom which we have and hence we can get the total kinetic a translational kinetic energy.

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Ideal Gas Laws: Pressure and the Molecular Kinetic Energy

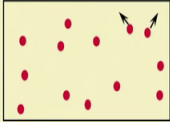
Boyle's Law: $P \propto \frac{1}{V}$

Avogadro's Law: $V \propto n$

Gay-Lussac's Law: $P \propto T$

Dalton's Law of Partial Pressures: $P_{\text{total}} = \frac{RT}{V} \sum n$


Charles Law: $V \propto T$




Boyle's Law: $P \propto \frac{1}{V}$


Dalton's Law of Partial Pressures:

$$P_{\text{total}} = \frac{RT}{V} \sum n$$


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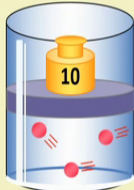
Now, we have obtained these information of pressure and kinetic energy. Now, I would like you like you to interpret how if I increase the pressure the and the temp if the temperature is held constant if I increase the pressure what happens with the volume. It is decreasing according to Boyle's law.

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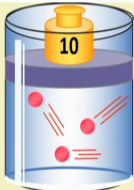
Pressure and the Molecular Kinetic Energy

Charles Law: $V \propto T$

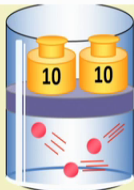
Gay-Lussac's Law: $P \propto T$



(a)
original temperature
original pressure
original volume



(b)
increased temperature
increased volume
original pressure





(c)
increased temperature
increased pressure
original volume

Boyle's Law: $P \propto \frac{1}{V}$

Dalton's Law of Partial Pressures:


$$P_{\text{total}} = \frac{RT}{V} \sum n$$


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Dorin, Demmin, Gabel, *Chemistry The Study of Matter*, 3rd E

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And, if I have this expression represented like this if I if this is the initial condition you have number of molecules the pressure temperature volume is held at constant. Now, if we are increase the temperature if I keep the pressure constant, if I pressure is held constant the total weight on the suppose it is on the constant, what happens if I increase the temperature? What I have if I increase the temperature what happens the kinetic energy of the molecules will increase, they will be going moving around with a much higher speed. So, what will happen to maintain the pressure constant what will happen if the gas has to increase in volume or expand.

Similarly, if I have the original volume constant and I have the pressure if I increase the pressure, what will happen? Since, the volume is now reduced and the number of particles which are held in that particular is constant and it is continuously colliding and moving around in the random speed, what will happen, with confinement of the volume.

If you are increasing the number of particles or increasing the pressure by say a temperature is constant you are putting more weight the pressure the volume, is if the pressure is increased and the volume held if the volume has to be held constant. What has to occur is increase in temperature because the number of collisions will be increasing. So, if your number of collisions are increasing then will give rise to the rise in the temperature.

I would like you to do this interpretation of the various laws in terms of the kinetic theory and judge yourself. So, this is what we are going to be looking into. So, I this I leave to you to interpret the various gas laws in terms of the ideas or properties which we have just now established; in terms of the kinetic energy of the molecule, in terms of the speed of the molecules, in a in terms of the total number of molecules in a particular volume, ok.

Thank you.