

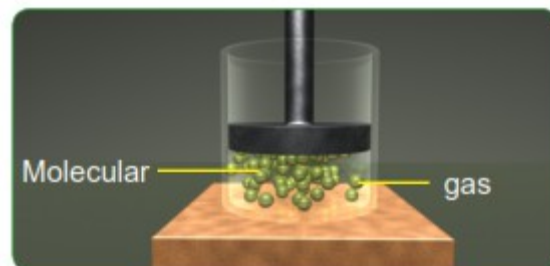
KINETIC THEORY OF GASES

INTRODUCTION:

Kinetic theory of gases relates the macroscopic properties of gases (like pressure, temperature, volume.... etc) to the microscopic properties of the gas molecules (like speed, momentum, kinetic energy of molecules....etc)

This theory attempts to study the behavior of an ideal gas.

Kinetic theory explains the behavior of gases based on the idea that the gas consists of rapidly moving atoms or molecules.

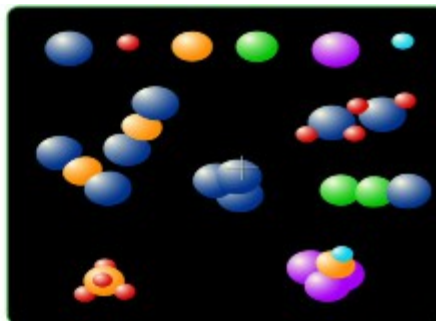
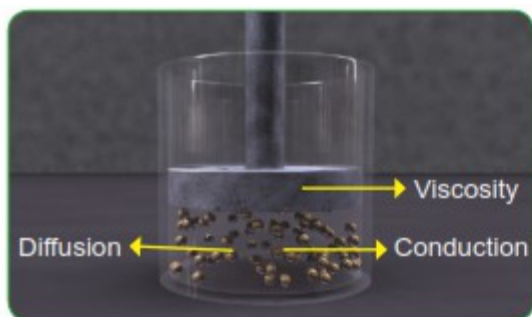


Kinetic theory gives a molecular interpretation of pressure and temperature of a gas.

This theory explains gas laws and Avogadro hypothesis.

It explains specific heat capacities of many gases.

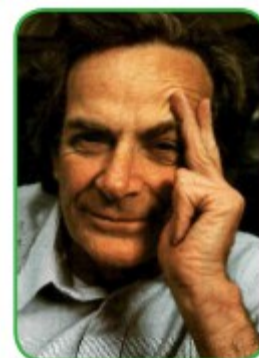
This theory also relates with the measurable properties of gases such as viscosity, conduction and diffusion with molecular parameters to estimate molecular sizes and masses.



Molecular nature of matter:

According to Richard Feynman - Atomic Hypothesis:

All the matter is made of atoms that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling when they are being squeezed into one another.



Richard Feynman

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(Perpetual motion: Moving continuously forever without getting energy from anything else).

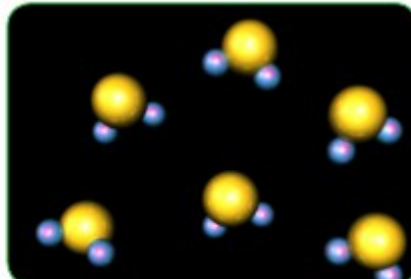
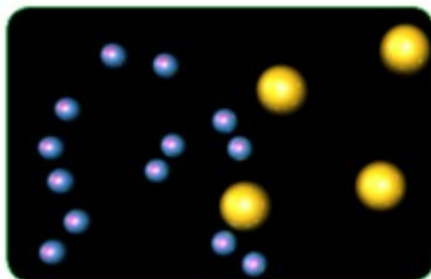
John Dalton proposed the atomic theory to explain the laws of definite and multiple proportions obeyed by elements when they combine into compounds.

Law: *atoms are the smallest constituents of elements. Any given compound has a fixed proportion by mass of its constituents. All atoms of one element are identical but atoms of different elements are different.*

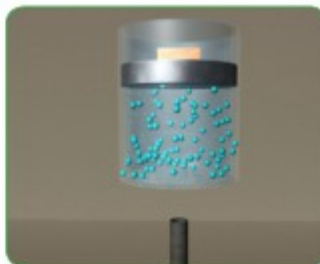
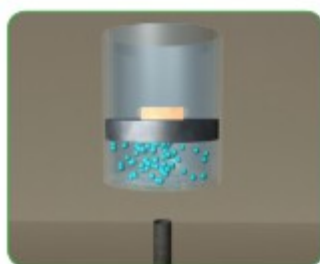
Law: *As small numbers of atoms of each element continue to form a molecule of the compound more than one compound, for a fixed mass of one element, are in the ratio of small integers.*



John Dalton

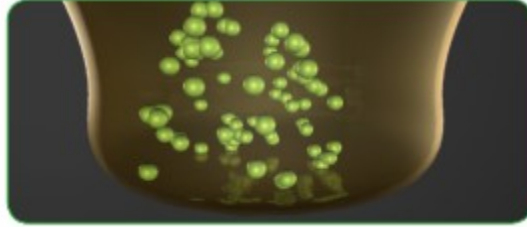


Gay Lussac's law: *When gases combine chemically to yield another gas, their volumes are in the ratio of small integers.*



Avogadro's Law: *Equal volumes of all gases at same temperature and pressure have same number of molecules.*

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BEHAVIOR OF GASES:

- 1) Gas molecules are far from each other as their mutual interactions are negligible.
- 2) Gas molecules occupy entire space which is available to them.
- 3) Gases at low pressure and high temperatures, liquefy or solidify and satisfies the relation between Pressure (P), Volume (V) and Temperature (T) given as

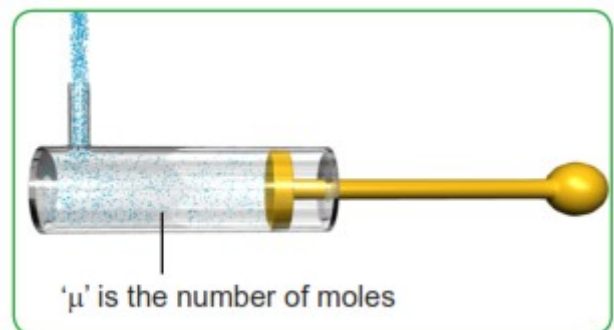
$$PV = RT$$

$$PV = N_A K_B T \quad (\text{Since, Boltzmann constant } K_B =)$$

IDEAL GAS: (Perfect gas)

A gas which obeys Boyle's law and Charles's law strictly at all temperatures and pressures is called a perfect or an ideal gas. Ideal gas satisfies the relation $PV = \mu RT$

Here ' μ ' is the number of moles and ' R ' is the universal gas constant $R = N_A K_B$



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N_A = Avogadro number, K_B = Boltzmann constant. Its value is $1.38 \times 10^{-23} \text{ J/K}$

The value of 'R' is 8.314 Joule/mole-K

Here, =

'M' is the mass of the gas containing 'N' molecules; 'M₀' is the molar mass and

N_A is the Avogadro number.

The ideal gas equation $PV = \mu RT$, , =

We get, $PV = RT = N K_B T$, which implies, $P = n K_B T$

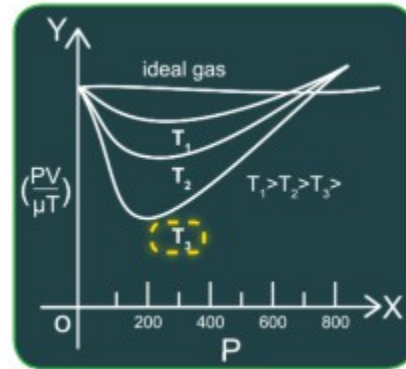
Where, 'n' is number of molecules per unit volume.

REAL GAS: The gas which obeys Boyle's law at low pressure and high temperature is called a real gas.

When a graph is plotted taking gas constant on Y - axis and pressure (P) on X - axis, it is noticed that real gas behaves as an ideal gas at low pressure and high temperature.

At low pressure and high temperatures the molecules are far apart and molecular interactions are negligible, and the gas behaves like an ideal one. But, Ideal gas doesn't exist in practice.

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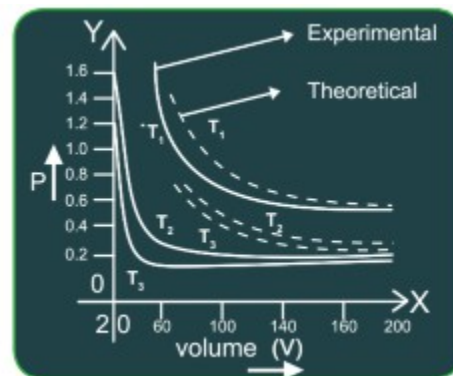
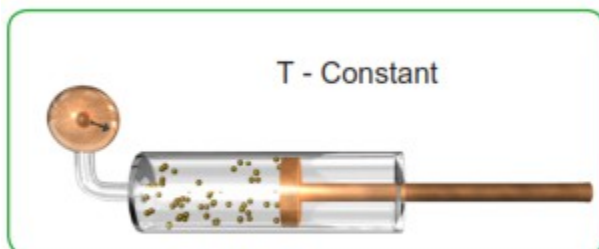
BOYLE'S LAW: We have, ideal gas equation $PV = \mu RT$.

Temperature ' T ' being maintained constant, we get $PV = \text{constant}$

Boyle's law can be stated as 'at constant temperature, pressure of a given mass of gas varies inversely with volume'.

A graph plotted across pressure (P) on Y-axis and volume (V) on x-axis, shows the comparison between experimental and the theoretical PV curves.

Experimental curves are solid curves and theoretical curves are dotted ones. From the graph, Boyle's law holds good at low pressure and high temperature conditions.



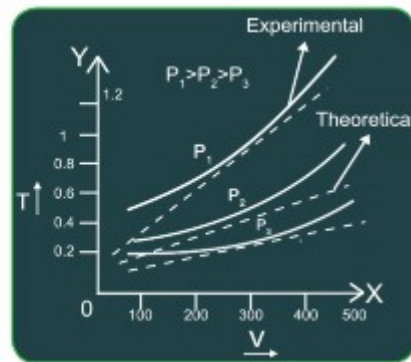
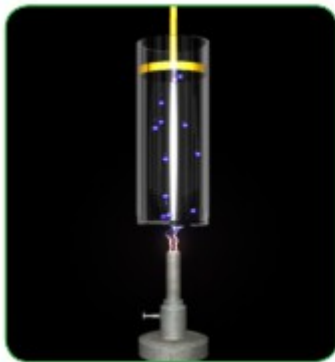
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CHARLE'S LAW: We have, an ideal gas equation $PV = \mu RT$,

At constant pressure, $V = \text{Constant}$

Charle's law can be stated as "At constant pressure, the volume of a given mass of a gas is proportional to its absolute temperature".

When a graph is plotted between volume (V) and absolute Temperature (T), the solid lines represent the experimental and the dotted lines represent theoretical T-V curves.



DALTON'S LAW OF PARTIAL PRESSURES:

Statement: The total pressure of mixture of ideal gases is the sum of partial pressures of them.

Explanation:

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Consider a mixture of non - interacting ideal gases containing μ_1 moles of gas 1, μ_2 moles of gas 2, etc. in a vessel of volume 'V' at temperature 'T' and pressure 'P'. Then,

$PV = \mu_1 RT + \mu_2 RT + \dots$, which is equal to $(\mu_1 + \mu_2 + \dots) RT$.

$P = \mu_1 + \mu_2 + \dots$

$P = P_1 + P_2 + \dots$

Here $P_1 = \mu_1$ is the partial pressure of the gas 1 would exert at the same conditions of volume and temperature, if no other gases were present.

Kinetic theory of gases:

Bernoulli was able to explain for the first time Boyle's law by molecular motions. For this reason he is considered as father of kinetic theory.

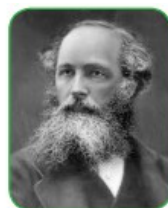
From the middle of 19th century, the kinetic theory of gases was well developed by Clausius, Maxwell, Boltzmann and others.



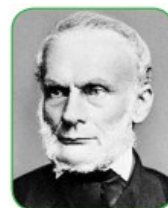
Bernoulli



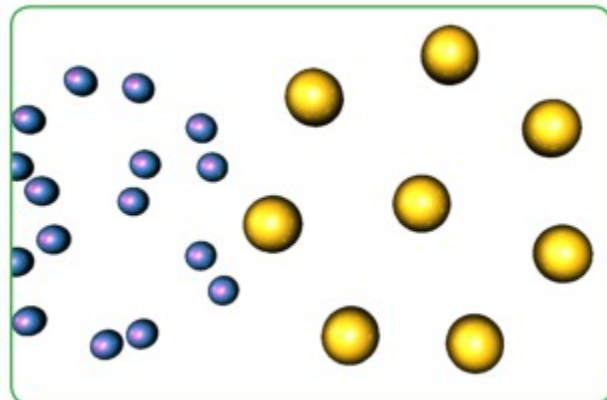
Clausius



Maxwell

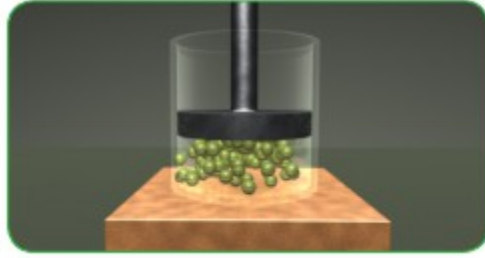


Boltzmann



The study of kinetic theory was first applied to the matter in the gaseous state which is governed by simple definite assumptions which were called as postulates of kinetic theory.

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Postulates of kinetic theory: *The kinetic theory of gases is based on the following assumptions made by Clausius.*

- 1. A given amount of gas is a collection of extremely small particles known as molecules, which are identical, rigid and perfectly elastic point masses whose size is negligible in comparison to the inter molecular distance (10^{-9} meter)*
- 2. Due to weak interaction between the molecules they move randomly in all possible directions with all possible velocities lying in between zero and infinity.*
- 3. The gas molecules occasionally come closer to each other, experience intermolecular forces as a result their velocities, thereby, their linear momenta changes. These interactions are called collisions and these collisions are considered to be elastic in nature.*
- 4. The gas molecules keep on colliding among themselves as well as with the walls of container. As these collisions are perfectly elastic i.e., the total energy of the gas is constant.*
- 5. Molecules move with constant speeds in a straight line during successive collisions. The distance covered by the molecules between any two successive collisions is known as free path and mean of all free paths is known as mean free path.*

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6. The time spent in a collision is negligible (10^{-8} seconds) in comparison to the time between two successive collisions.

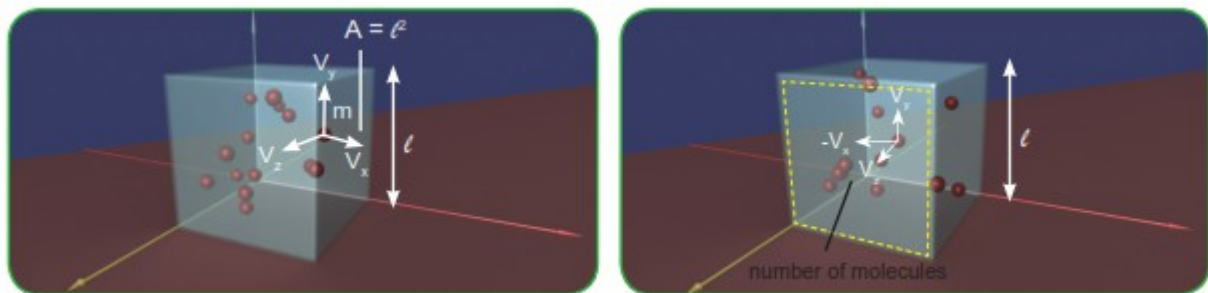
7. The number of collisions per unit volume in a gas remains constant.

8. As the gas molecules collide with their neighbors and with the walls of the container, the change in their momenta is transferred to the walls of the container. Consequently pressure is exerted by the gas molecules on the walls of the container.

With these postulates the bulk properties of matter in gaseous state can be explained by the application of laws of probability to a system in dynamic equilibrium.

Pressure of an Ideal Gas: Consider an ideal gas enclosed in a cubical vessel of side length 'L', parallel to the axes of a co-ordinate system.

A molecule of mass 'm' moving with velocity (v_x, v_y, v_z) hits the planar wall of surface area $A = L^2$ parallel to yz plane, and rebounds with the same velocity, but the x component reverses sign i.e., the velocity of the molecule after the collision is $(-v_x, v_y, v_z)$ {sign of y and z components doesn't change}.



Therefore, the change in momentum of the molecule is equal to

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$m(-v_x) - mv_x = -2mv_x$. As a consequence, the momentum imparted to the wall in the collision is $2mv_x$.

In a small interval of time t , all those molecules within the volume

$Av_x t$ only hit the wall. But, on an average half of these molecules are moving towards the wall and the other half away from the wall. i.e., the number of molecules hitting the wall in time t is $(Av_x t)n$ where n number of molecules per unit volume.

Total momentum transferred to the wall by these molecules in time t is $Q = (2mv_x)(A n v_x t)$.

The force on the wall is the rate of transfer of momentum and pressure is force exerted per unit area, $P = \frac{Q}{At} = n m v_x^2$

As the molecules in a gas possess a range of velocities, the equation for the total pressure is obtained by summing over the contribution due to all groups. $P = n m \overline{v_x^2}$ where $\overline{v_x^2}$ is the average of v_x^2 .

As the gas is isotropic, there is no preferred direction of velocity of the molecules in the vessel.

By symmetry, $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$, therefore, total pressure due to gas molecules is $P = \frac{1}{3} n m \overline{v^2}$

Where $\overline{v^2}$

The above expression for the pressure exerted by an ideal gas is independent of the shape of the vessel. (As the final expression do not contain area 'A' of the surface of the vessel)

KINETIC INTERPRETATION OF TEMPERATURE

The Pressure exerted by a gas made up of n molecules and occupying a volume V is given by the relation $P = \frac{1}{3} n m \overline{v^2}$ or $PV = \frac{1}{3} n m \overline{v^2} V$

$PV =$

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The quantity in the bracket is the average translational kinetic energy of the molecules in the gas. Since the internal energy E of an ideal gas is purely kinetic.

$E =$ Where $N (=nV)$ is the number of molecules in the sample.

Then it gives: $PV = E$

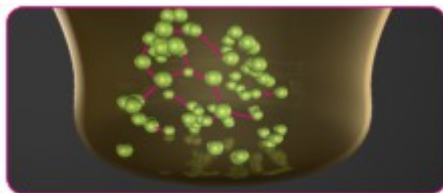
We are now ready for a kinetic interpretation of temperature. Combining equation $PV =$ with ideal gas equation $PV = k_B nT$, we get $E = k_B nT$.

or $\bar{m} = k_B T$

i.e., the average kinetic energy of a molecule is proportional to the absolute temperature of the gas: independent of pressure, volume or the nature of the ideal gas.

Law of equipartition of energy:

Gas molecules are far from each other as their mutual interactions are negligible.

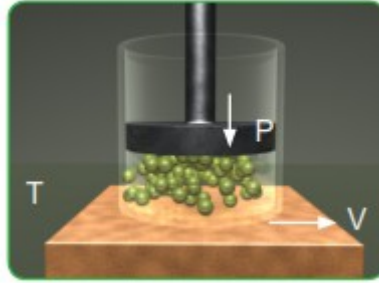


Gas molecules occupy entire space which is available to them.



Gases at low pressure and high temperatures, they liquefy or solidify and satisfies the relation between Pressure (P), Volume (V) and Temperature (T).

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$$PV = RT$$

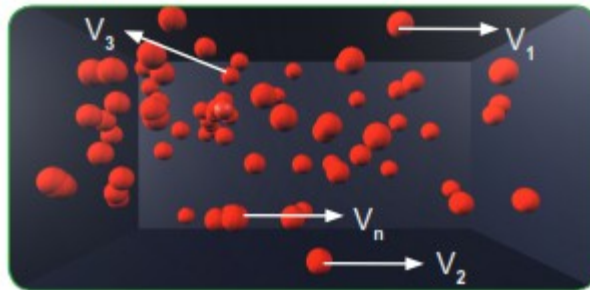
$$PV =$$

Behavior of gases and gas laws:

Various speeds of Gas molecules:- The motion of molecules in a gas can be characterized by any of the following three speeds.

1. Root mean square speed (V_{rms})
2. Most probable speed()
3. Average speed ()

1. **Root mean square speed (V_{rms}):**



It is defined as the square root of mean of squares of instantaneous speeds of different molecules. At given temperature, if v_1, v_2, v_3, v_n are the instantaneous speeds of 'n' different gas molecules at any instant of time, then the RMS speed of the gas molecules is given by,

$$V_{rms} \text{ or } =$$

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Kinetic gas equation for pressure in terms of density is $p = \frac{1}{3} \rho \overline{v^2}$ (Since, $\rho = nm$ as 'n').

Therefore, $\overline{v^2} = \frac{3p}{\rho}$

As ideal gas equation $PV = nRT$,

Therefore, $P = \frac{nRT}{V}$ or $\rho = \frac{nm}{V}$.

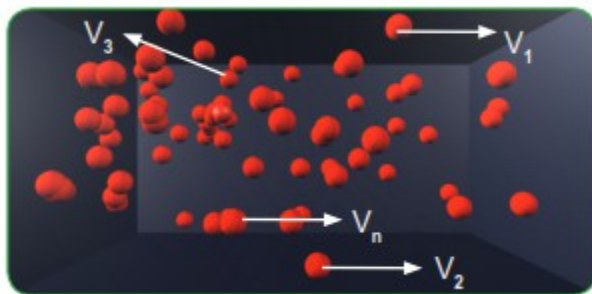
Hence, the rms speed can be also written as $v_{rms} = \sqrt{\frac{3RT}{M}}$

Conclusion:

- RMS speed of gas molecules increases with the absolute temperature (since, $v_{rms} \propto \sqrt{T}$)
- RMS speed of gas molecules decreases with increase in molecular weight (since, $v_{rms} \propto \frac{1}{\sqrt{M}}$)
- At a given temperature, RMS speed of gas molecules is independent of pressure of gas, as according to Boyle's law.
- RMS speed of any gas becomes zero, at absolute zero,

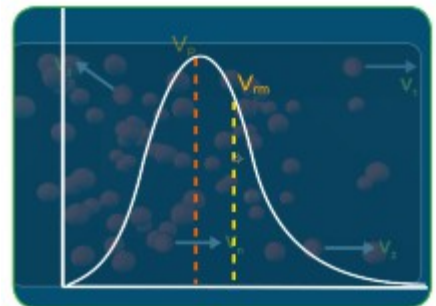
(Since, $v_{rms} \propto \sqrt{T}$)

2. **Most probable speed (v_p):** It is defined as the speed which is possessed by most of gas molecules of total number of molecules of gas.



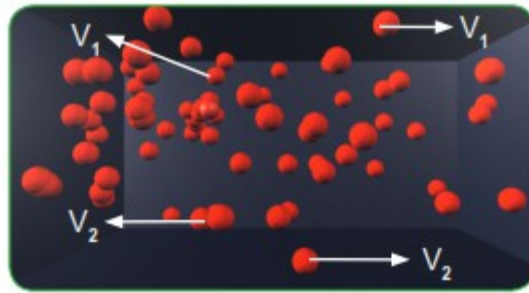
Most probable speed, $v_p = \sqrt{\frac{2RT}{M}}$

Which can be also written as $v_p = \frac{2}{\sqrt{3}} v_{rms}$



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Average speed): The simple arithmetic mean of the speeds of all the molecules in a gas at a given temperature is called average speed.



If $v_1, v_2, v_3, \dots, v_n$ are the instantaneous speeds of n different molecules, at a given temperature, then average speed, =

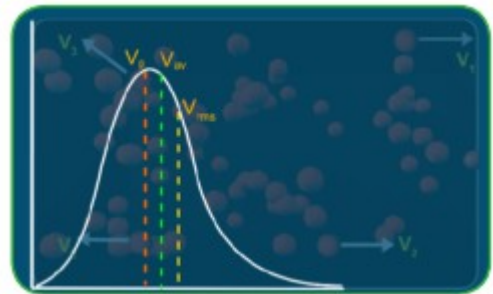
The average speed can be also expressed as

$$= =$$

From the above relations, we notice that

$$: = : :$$

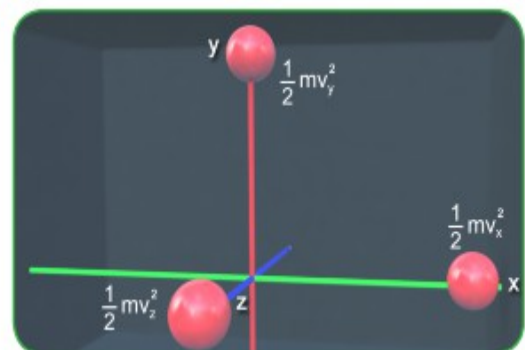
Therefore, $>$.



Maxwell's law of equipartition of energy:-

A molecule free to move in space needs three co-ordinates to specify its location.

Therefore, for a gas in thermal equilibrium at temperature 'T', the average translational kinetic energy denoted by $\langle E_t \rangle = \langle \rangle + \langle \rangle + \langle \rangle =$,

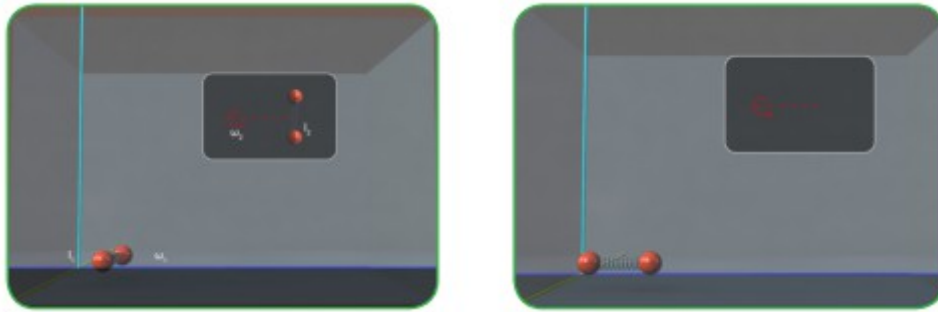


\therefore the average of each term is

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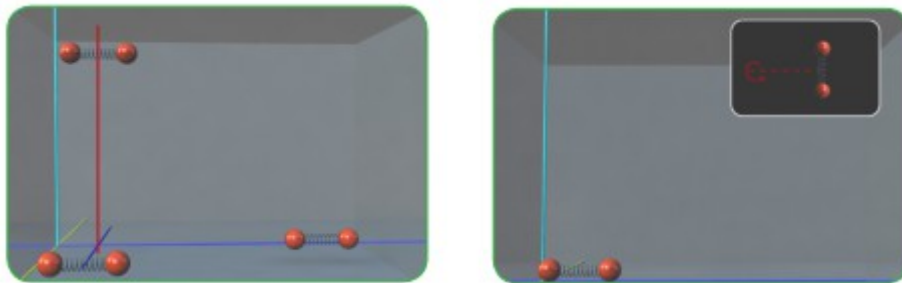
Static Rotar:

A diatomic molecule such as O₂ has three translational degrees of freedom and two rotational degrees of freedom.



∴ the total energy of a diatomic molecule which is a static Rotar is

$$E_t + E_r = + + + +$$



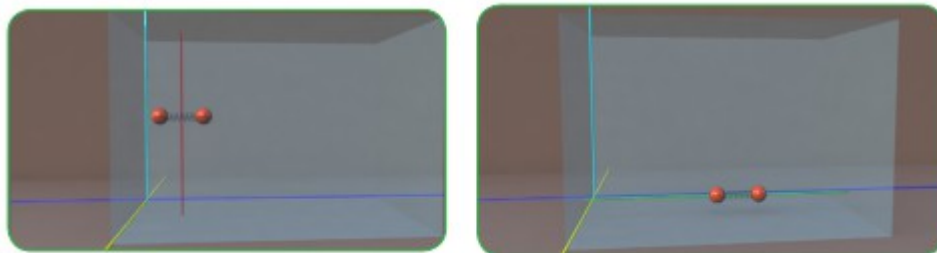
where ω_1 and ω_2 are the angular speeds about the axes (1) and (2) and, I_1 and I_2 are the corresponding moments of inertias.

For the diatomic molecules like CO which is not a static rotar even at moderate temperatures have a mode of vibration i.e, the atoms can vibrate along interatomic axis like a one dimensional oscillator and can contribute a vibrational energy, which is given by,

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$E_v = \frac{1}{2}ky^2 + \frac{1}{2}mv^2$ where k force constant, y vibrational co-ordinate.

From the above equations, it is understood that each translational and rotational degrees of freedom has contributed one squared term of motion, whereas vibrational mode contributes two squared terms related to kinetic and potential energies.



Hence, each translational and rotational degrees of freedom of a molecule can contribute to the total energy, while each vibrational mode contributes 2(). This is the most elegant principle of classical statistical mechanics first proved by Maxwell, called law of equipartition of energy.

Statement: - The total energy of a gas molecule is equally distributed among all degrees of freedom and the energy associated with each degree of freedom at absolute temperature 'T' is

Consequences :- If the no. of degrees of freedom of a gas molecule is 'f' at absolute temperature 'T' then its total mean energy will be $E = U =$

for 1 mole of a gas $E = U =$

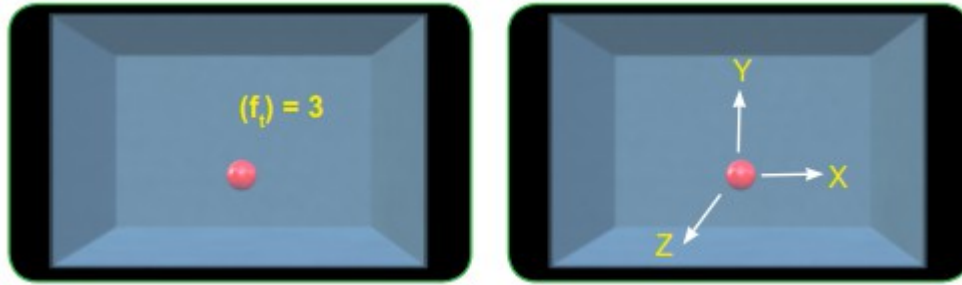
This law is based on the kinetic theory of gas and according to it mean energy of all degrees of freedom is same.

Degrees of freedom :-

Monoatomic gas:- A mono atomic gas molecule can move linearly in any direction along three co-ordinate axes. Hence its degrees of freedom is $(f) = 3$

Examples: Molecules of noble gases like He (helium), Ne (neon), Ar (Argon) etc.

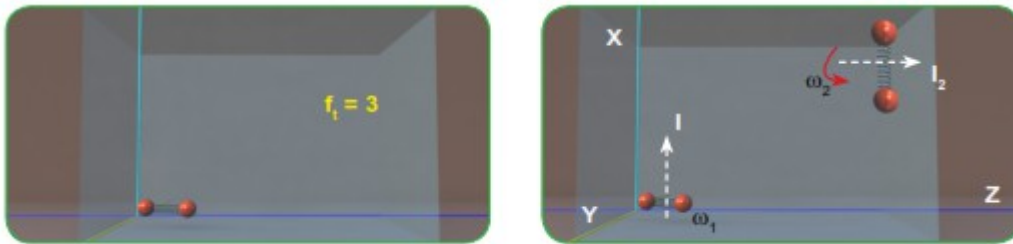
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Diatomic gas: The center of mass of two atoms is free to move along three Co-ordinate axes. Hence its translational degrees of freedom is

$$= 3$$

The molecules of these gases can rotate about a perpendicular axis passing through their center of mass in two directions. Hence its degree of freedom of rotating motion is = 2 , Therefore, total degrees of freedom $f = + = 3 + 2 = 5$



For a tri atomic or polyatomic gas (non linear) :-

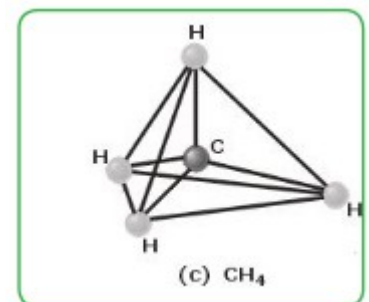
Degrees of freedom of translational motion, = 3 and degrees of freedom of rotational motion, = 3, Therefore, total degree of freedom, $f = + = 3 + 3 = 6$.

Specific heat capacity for gases:

Mono atomic gases :The molecule of a mono atomic gas has three translational

degrees of freedom. Thus, the average energy of a molecule at temperature 'T'

is $\frac{3}{2}kT$. Thus, the total energy of one mole of such a gas is



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$$U = (T) = RT$$



Therefore, the molar specific heat at constant volume, is $= R$

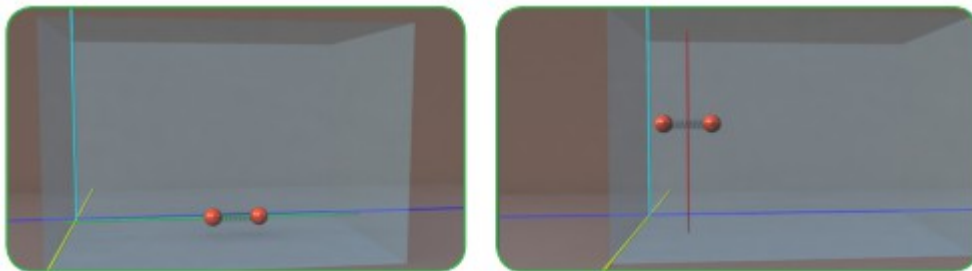
We know that $= R$

$$= +R = R + R$$

Therefore, the molar specific heat at constant pressure, $= R$

The ratio of specific heat for a monoatomic gas is $= =$.

Diatomic gas: If a diatomic molecule is treated as a 'rigid rotator' like a dumbbell, it will have 5 degrees of freedom (3-translational and 2- rotational)



According to law of equipartition of energy, the total energy of a mole of such a gas is $U = (5) = RT$.

Therefore, molar heat capacity of a diatomic molecule at constant volume is,

$$= R$$

$$\therefore +R = R + R = R$$

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Therefore, molar specific heat capacity at constant pressure is $=R$

$= = .$

If a diatomic molecule is not rigid but has in addition a vibrational mode, then it will have 7 degrees of freedom (3 translational, 2 rotational, and 2 vibrational modes).

Total energy of a mole of such a gas will be $U = \{T + 2 (T)\}$

$$= RT$$

$= R$ and $= + R = R, .$

3. Polyatomic gas: In general, a poly atomic gas molecule will have 3 translational, 3 rotational degrees of freedom and certain number (f) vibrational modes.

According to law of equipartition of energy, one mole of such a gas has total internal energy,

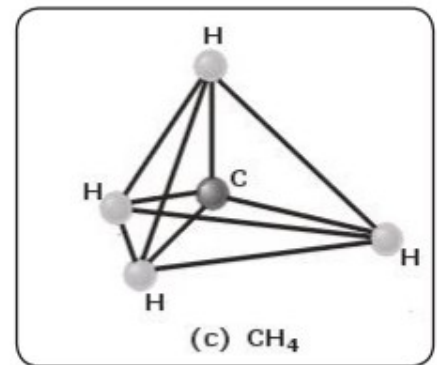
$$U = (T + T + f T) = (3+f) RT$$

Molar specific heat capacity at constant volume is

$$= = (3+f) R$$

$$\text{And, } = +R = (3+f) R + R = (4+f) R$$

And, $= .$



Specific heat capacity of solids: Consider a solid substance, of N atoms, each

atom is vibrating about its mean position. The average energy due to vibration

in one dimension is $2 (= \text{one corresponding to kinetic and other potential energy})$. In three dimensions, the average energy is $3 .$

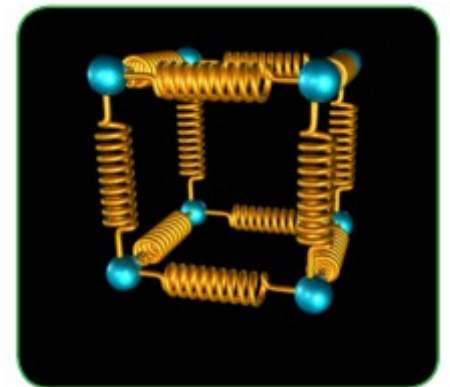
Total internal energy for a mole of a solid substance is $U = (3) = 3RT$.

According to 1st law of thermodynamics

$$= \text{(as } V \text{ is negligible at constant pressure)}$$

Hence, specific heat of a solid substance is

$$C = = = R.$$



Specific heat capacity of water: For each atom of water, the average

KINETICE THEROY OF GASES

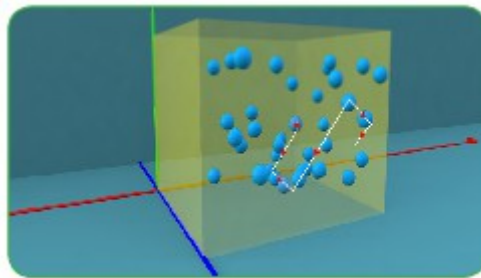
energy is 3 . As the water molecule have three atoms, two hydrogen and one Oxygen, the total internal energy is $U = 3 (3) = 9RT$

And, specific heat capacity, $C = = = 9R$.

MEAN FREE PATH:

Definition:

The distance travelled by a gas molecule between two successive collisions is known as free path and the mean of free paths is called mean free path.



Explanation:

Consider the molecules of a gas are spheres of diameter 'd' moving with average speed 'V'.

The molecules get collide with one another that comes within a distance 'd' between their centers.

In time ' Δt ' it sweeps a volume $\pi d^2 V \Delta t$ and collides with another molecule.

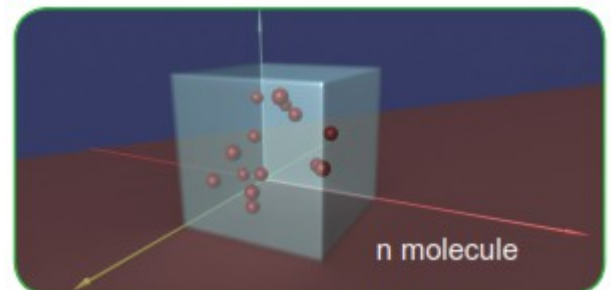
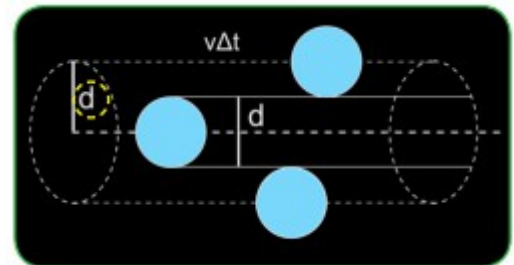
If 'n' is the number of molecules per unit volume, then the molecule suffers ' $n \pi d^2 \langle V \rangle \Delta t$ ' number of collisions in the time Δt second.

The time interval between any two successive collisions is,

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The average distance between two successive collisions is called the mean free path 'L'.

$L = V =$



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As all the molecules are moving, the collision rate is determined by the average relative velocity. (V should be replaced by V_{relative})

Mean free path of gas molecule is $L = \dots$

