Molecular Nature of Matter

- **Atomic hypothesis**: All things are made of atoms − little particles that move around in perpetual motion, attracting each other when they are at a little distance apart and repelling when squeezed into one another.

- **Atomic theory**: Proposed by John Dalton to explain the laws of definite and multiple proportions.

- First law states that any given compound has fixed proportion by mass of its constituents.

- Second law states that when two elements form more than one compound, for a fixed mass of one element, the masses of the other elements are in the ratio of small integers.

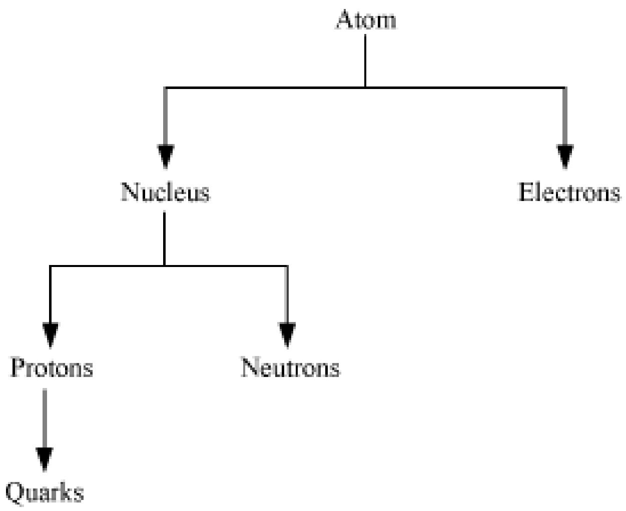
- **Gay-Lussac's law**: When gases combine chemically to yield another gas, their volumes are in the ratio of small integers.

- **Avogadro's law**: Equal volumes of all gases at equal temperature and pressure have the same number of molecules.

- Dalton's atomic theory is referred to as the molecular theory of matter.

- Atoms in gases are freer than those in liquid and solids.

- Atoms are not elementary; they can be further sub divided into their constituents.



The chain of sub division does not end here.

Behaviour of Gases

- Gases at low pressures and high temperatures satisfy the relation

  $PV = KT$, where

  P = Pressure

  V = Volume

  T = Temperature

  $K = Nk_B$

  k_B = Boltzmann constant

  N = Number of molecules

- 22.4 litres of any gas contain 6.02×10^{23} number of molecules. This is called Avogadro's number.

- Perfect gas equation is

  $PV = \mu RT$

  An ideal gas satisfies the above equation at all pressures and temperatures.

  Here, μ = Number of moles

  R = Universal gas constant

  $R = N_A k_B$

  $$\mu = \frac{M}{M_0} = \frac{N}{N_A}$$

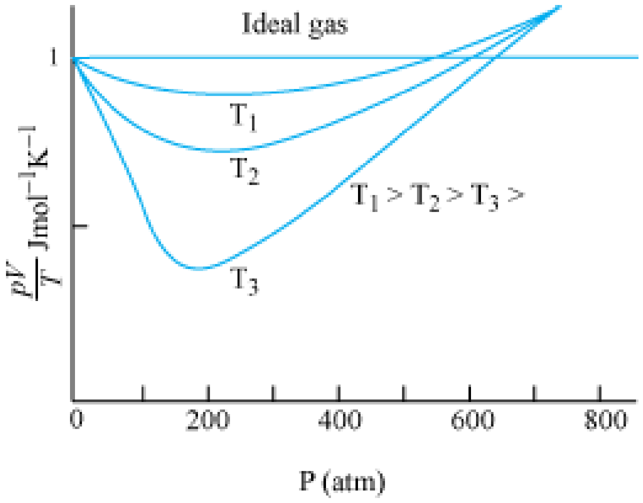
  Here,

  M = Mass of the gas containing N molecules

  M_0 = Molar mass

N_A = Avogadro's number

- A real gas approaches ideal gas behaviour only at low pressures and high temperatures.



This is because at low pressures or high temperatures, the molecules are far apart and molecular interaction is negligible. Without molecular interactions, a gas behaves like an ideal one.

- **Boyle's Law**: At constant temperature, the pressure of a given mass of gas varies inversely with volume.

- **Charles' Law**: At constant pressure, the volume of a gas is proportional to its absolute temperature.

- Consider a mixture of non-reacting ideal gases.

The equation of state is

$$PV = (\mu_1 + \mu_2 + \ldots)\mathrm{R}T$$

$$P = \mu_1 \frac{\mathrm{RT}}{\mathrm{V}} + \mu_2 \frac{\mathrm{R}T}{V} + \ldots$$

$$P = P_1 + P_2$$

Here,

μ_1 = Number of moles of gas 1

μ_2 = Number of moles of gas 2

P_1, P_2 = Partial pressures of the gases

Therefore, the total pressure of a mixture of ideal gases is the sum of the partial pressures of the gases. This is Dalton’s Law of Partial Pressure.

Assumptions of Kinetic Theory of Gases

- Gases are made up of a large number of tiny molecules.
- Molecules in a gas have much space between them such that the actual volume occupied by the gas is very small compared to the total volume of the gas.
- Molecules are perfectly rigid and perfectly elastic spheres of very small diameters.
- All the molecules have same size, shape and mass.

Random motion of gas molecules

- Gas molecules are in constant random motion. At any given time, the molecules are moving in many different directions at many different speeds.
- Due to their random motion, the molecules constantly collide with each other and also with the walls of the container. Molecular collisions are perfectly elastic.
- Between two successive collisions, a molecule travels in a straight line with steady velocity. This is known as the mean free path.
- The time taken for the collision is very small compared to the time required to cover the free path between two collisions.

Boyle's Law

According to Boyle's Law, at constant temperature, the pressure exerted by a fixed mass of a gas is inversely proportional to the volume occupied by the gas.
$P \propto 1VP \propto 1V$

$\Rightarrow PV$ = constant, where
P = pressure of an enclosed gas
V = volume of an enclosed gas

This relation can be derived on the basis of the kinetic theory of gases. Consider a gas of volume V with N molecules, each of mass m. Mass of the gas, $M = Nm$.

According to the kinetic theory of gases, the expression for pressure is given by the following equation:

$$P = \frac{1}{3}\rho C^2{}_{Rms}$$
$$P = \frac{1}{3}\frac{M}{V}C^2{}_{Rms}$$
$$PV = \frac{1}{3}NmC^2{}_{Rms}$$
$$PV = \frac{2}{3}N\left(\frac{1}{2}mC^2{}_{Rms}\right)$$

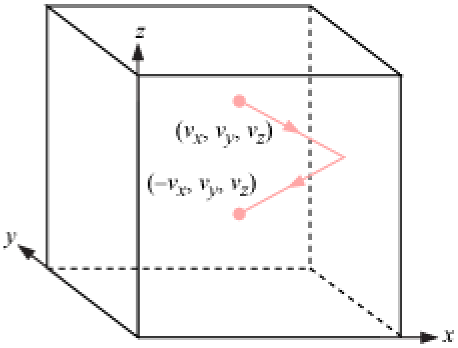
Since N is constant, the quantity $\frac{1}{2}mNC^2{}_{Rms}$, which is the average kinetic energy of the gas molecules, remains constant at constant temperature. Therefore,
PV = constant or $P \propto 1/V$

This equation is known as Boyle's Law.

Kinetic Interpretation of Pressure of an Ideal Gas

- Gas is a collection of large number of molecules, and they are in random motion at ordinary pressure and temperature.
- Molecules come close to each other due to inter molecular forces, and these forces change the velocities of molecules.
- Collisions between molecules or those between molecules and the walls of the container are elastic.

Pressure of an Ideal Gas



- A gas is enclosed in a cube of length l.
- Velocity of the particle is (v_x, v_y, v_z). It hits the wall parallel to the yz-plane of area, $A = (l^2)$.
- Velocity of the particle after collision is ($-v_x$, v_y, v_z). Since the collision is elastic, its y and z components of velocity do not change.

- Change in momentum of the particle is $-mv_x - (mv_x) = -2mv_x$, and the momentum imparted to the wall is $2mv_x$.
- Half of the molecules within a volume move towards the wall and the rest of the molecules move away from it.
- So the number of molecules hitting the wall in time, Δt is $\frac{1}{2} A v_x \Delta t n$

  Where, n = Number of molecules per unit volume
- Total momentum (Q) transferred to the wall in time, Δt is $(2mv_x)\frac{1}{2} n A v_x \Delta t$.
- Force on the wall is the rate of change of momentum. Therefore, we get $Q/\Delta t$.
- Pressure is the force acting per unit area, i.e.,

  $$P = \frac{Q}{A\Delta t} = nmv_x^2$$
- Pressure due to the group of molecules with speed v_x is, $P = nm\left(\overline{v}_x\right)^2$

  Where, $\left(\overline{v}_x\right)^2$ = Average of v_x^2
- By the symmetry, we get

  $$\left(\overline{v}_x\right)^2 = \left(\overline{v}_y\right)^2 = \left(\overline{v}_z\right)^2 = \frac{1}{3}\left[\left(\overline{v}_x\right)^2 + \left(\overline{v}_y\right)^2 + \left(\overline{v}_y\right)^2\right]$$
  $$= \frac{1}{3}\overline{v^2}$$
  $$\boxed{\therefore P = \frac{1}{3} nm\left(\overline{v}\right)^2}$$

  Where, $\left(\overline{v}\right)^2$ denotes the mean of the squared speed

  ## Kinetic Interpretation of Temperature
- Pressure, $P = \frac{1}{3} nm\left(\overline{v}\right)^2$

On multiplying both sides by V (volume), we get

$$PV = \frac{1}{3} nVm\overline{v}^2$$

OR

$$PV = \frac{2}{3} N(\frac{1}{2}\ m\overline{v}^2) \qquad ....(i)$$

$nV = N$ = Number of molecules

$\overline{v}^2$ = Mean of the squared speed

P =Pressure of the gas

V = Volume of the gas

Internal energy (E) of an ideal gas is purely kinetic. Therefore,

$$E = N \times \frac{1}{2} m\overline{v}^2$$

So, $PV = \frac{2}{3} E \qquad$ [From (i)]

We know that $PV = NK_BT$

$$\therefore E = \frac{3}{2} K_B NT$$

$$\Rightarrow \frac{E}{N} = \frac{3}{2} K_B T$$

This implies that the average kinetic energy of a molecule is directly proportional to the absolute temperature of the gas.

Law of Equipartition of Energy

- Total number of co-ordinates or independent quantities required to describe the configuration of a system completely is called degree of freedom.

- **Law of Equipartition of Energy −** A dynamic system in thermal equilibrium has the energy system equally distributed amongst the various degrees of freedom and the energy associated with each degree of freedom per molecule is $\frac{1}{2}\mathrm{k}_{\mathrm{B}}T$.

  Where,

  k_{B} − Boltzmann constant

  T − Temperature

- Monoatomic gas

- It has three degrees of freedom for translational motion. Mean kinetic energy of translational motion of gas is $\frac{1}{2}mv^2 = \frac{3}{2}\mathrm{k}_B T$

- Components along 3 axes:

  $$\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{3}{2}\mathrm{k}_{\mathrm{B}}T$$

- Average kinetic energy for each degree of freedom is

  $$\frac{1}{2}mv_x^2 = \frac{1}{2}mv_y^2 = \frac{1}{2}mv_z^2 = \frac{1}{2}\mathrm{k}T$$

- Translational and rotational degree of freedom of molecule contributes $\frac{1}{2}\mathrm{k}_{\mathrm{B}}T$ to the energy.

- Vibrational mode has both kinetic and potential energy. Therefore, each vibrational frequency contributes $2 \times \frac{1}{2}\mathrm{k}_{\mathrm{B}}T = \mathrm{k}_{\mathrm{B}}T$

Specific Heat Capacity

Monatomic Gas

- It has three translational degrees of freedom.

- Average energy of a molecule is $\frac{3}{2}k_{\mathrm{B}}T$.
- Total internal energy (U) of a mole of each gas is

$$U=\frac{3}{2}k_{\mathrm{B}}T\times N_{\mathrm{A}}=\frac{3}{2}RT \quad [\because k_B N_A = R]$$

k_{B} → Boltzmann constant

T → Temperature

N_A → Avogadro's number

R → Gas constant

- Molar specific heat at constant volume (C_V) is

$$C_{\mathrm{V}}=\frac{dU}{dt}=\frac{3}{2}R$$

- $C_{\mathrm{P}}-C_{\mathrm{V}}=R$

$$\therefore C_{\mathrm{P}}=R+\frac{3}{2}R$$
$$=\frac{5}{2}R$$

- Ratio of specific heats:

$$\gamma=\frac{C_{\mathrm{P}}}{C_{\mathrm{V}}}=\frac{5}{3}$$

Diatomic Gases or Rigid Rotator

- **For Rigid Rotator:**
- It has 5 degrees of freedom, out of which 3 are transitional and 2 are rotational.
- Internal energy of the gas is $U=\frac{5}{2}k_{\mathrm{B}}T\times N_{\mathrm{A}}=\frac{5}{2}RT$.

- Molar specific heat at constant volume C_V is

$$C_V = \frac{dU}{dT} = \frac{5}{2}R$$

- $C_P - C_V = R$

$$\therefore C_P = R + \frac{5}{2}R = \frac{7}{2}R$$

Ratio of specific heat:

$$\gamma = \frac{7}{5}$$

- **For Non-Rigid Rotator:**
- It has 6 degrees of freedom, out of which 3 are translational, 2 are rotational and 1 is vibrational.
- Internal energy is

$$U = \frac{5}{2}k_B T N_A + k_B T N_A = \frac{7}{2}k_B T N_A$$
$$= \frac{7}{2}RT$$

- Molar specific heat at constant volume (C_V) is

$$C_V = \frac{dU}{dT} = \frac{7}{2}R$$

- $C_P - C_V = R$

$$\therefore C_P = R + \frac{7}{2}R = \frac{9}{2}R$$

- Ratio of specific heat:

$$\gamma = \frac{C_P}{C_V} = \frac{9}{7}$$

Polyatomic Gas

- It has 3 translational and 3 rotational degrees of freedom and a certain number (*f*) of vibrational modes.
- Internal energy or a mole of the gas is

$$U = \frac{3}{2}k_B T N_A + \frac{3}{2}k_B T N_A + f k_B T N_A$$

- Molar specific heat at constant volume is

$$C_V = \frac{dU}{dT} = (3 + f)R$$

- $C_P - C_V = R$

$$C_P = (3 + f)R + R = (4 + f)R$$

- Ratio of specific heat:

$$\gamma = \frac{C_P}{C_V} = \frac{4 + f}{3 + f}$$

Specific Heat Capacity of Solids

It can be determined by using the Law of Equipartition of Energy.

Take a solid consisting of *N* atoms, each vibrating about its mean position. According to the Law of Equipartition, average energy of an oscillation in one dimension,

$$2 \times \frac{1}{2} K_B T = K_B T$$

For one mole of the given solid,
$N = N_A$ (Avogadro's number)
∴ Total energy,

$$U = 3K_B T \times N = 3RT$$

At constant pressure, the First Law of Thermodynamics can be written as

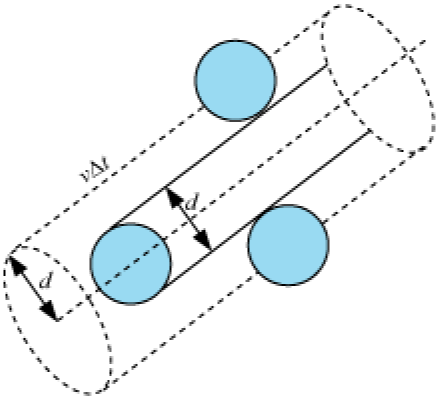
$$\Delta Q = \Delta U + P\Delta V$$

For solids, $\Delta V = 0$.

$$\therefore C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 3R$$

Mean Free Path

- A gas consists of a large number of molecules which are in random motion; this leads to collisions.
- Distance covered between two successive collisions is called the free path.
- Average distance travelled by a molecule between two successive collisions, and measured as the mean of the large number of free paths, is called the mean free path.



d = Diameter of a gaseous molecule

v = Average speed of the molecule

n = Number of molecules per unit volume

  - Molecules suffer collision when their centres are separated by a distance, d.
  - Volume (swept in time, Δt) in which any other molecules collide = $\pi d^2 v\Delta t$

Rate of collision is $n\,\pi d^2 v$

Average time between two successive collisions,

$$\tau = \frac{1}{n\pi v d^2}$$

Mean free path,

$$l = v\tau = \frac{1}{n\pi d^2} \qquad \text{(Other molecules are at rest)}$$

In this derivation, we assumed that the other molecules are at rest. But, actually, all the molecules are moving and the collision rate is determined by the average relative velocity of the molecules.

A more exact treatment leads to the following relation:

$$\boxed{l = \frac{1}{\sqrt{2}n\pi d^2}}$$

Mean Velocity (Average velocity) $\overline{C}$:

For N molecules of an ideal gas enclosed in a container, if the molecules of the ideal gas have velocities C_1, C_2 ....C_N , then their mean velocity,

$$\overline{C} = \frac{C_1 + C_2 + \ldots . C_N}{N}$$

Mean Square Velocity ($\overline{C^2}$)

The average value of the squares of the velocities of all the molecules of an ideal gas is known as mean square velocity.

If the molecules have velocities C_1, C_2 ....C_N, then their mean square velocity,

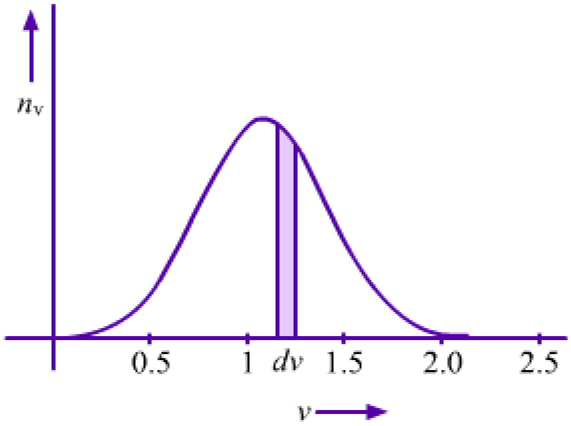
$$\overline{C^2} = \frac{{C_1}^2 + {C_2}^2 + \ldots \ldots . {C_N}^2}{N}$$

Root Mean Square Velocity ($\sqrt{\overline{C^2}}$)

It is defined as the square root of the mean square velocity. If 'N' molecules of an ideal gas are enclosed in a container of volume 'V' and the molecules have velocities C_1, C_2 ....C_N, then the root mean square velocity,

$$C_{RMS} = \sqrt{C^2}$$
$$= \sqrt{\frac{{C_1}^2+{C_2}^2+......{C_N}^2}{N}}$$

Maxwell's Speed Distribution:



In the given mass of a gas, the velocities of all the molecules are different, even if the bulk parameters like pressure, volume and temperature are fixed. The speed of molecules and their directions of motion are changed due to collisions between them.

But, in a state of equilibrium, the distribution of speeds is found to be constant. The molecular speed distribution gives the number of molecules between the speeds v and v + dv. This is proportional to dv or

$$dn = n\left(v\right)dv = 4\pi na^3 e^{-bv^2} v^2 \, dv$$

where, $a = \sqrt{\frac{m}{2\pi k_B T}}$ and $b = \frac{m}{2k_B T}$

This is known as Maxwell's speed distribution.

The given plot is a graph between η_v and v. The fraction of the molecules with speeds v and v + dv is equal to the area of the strip shown.