1. **Molecular Nature of Matter**

   From recent theories it is proved that molecules (made up of one or more atoms) constitute matter. Atoms are not indivisible or elementary. They consist of a nucleus and electrons. The nucleus itself is made up of protons and neutrons. The protons and neutrons are again made up of quarks. Even quarks may not be the end of the story. There may be string like elementary entities.

2. **Behaviour of Gases.** At low pressures and high temperatures, gases behave like ideal gases and obey,

   > $PV = RT$ for 1 mole
   > $PV = n\,RT$ for n-moles
   > $PV = kT$ for one molecule
   > $PV = NkT$ for N molecules

   where, N = no. of molecules

   k = Boltzmann Constant

   $= 1.38 \times 10^{-23}$ JK^{-1}

   n = no. of moles

   R = Universal Gas Constant

   $= 8.314$ JK^{-1} mol^{-1}

   T = Absolute temperature in kelvin

   Also, $n = \dfrac{M}{M_0} = \dfrac{N}{N_A}$

   where, M = total mass of the gas containing N molecules

   M_0 = Molar mass

   N_A = Avogadro's Number

   Another useful form is

   $P = \dfrac{\rho RT}{M_0}$

   where, ρ = mass density of gas

   Finally, it n_1 moles of one gas, n_2 of second gas etc. are all contained in the same vessel (while all these gases are non-interactive) at the same temperature T, then equation of state of the mixture is

   $PV = (n_1 + n_2 + n_3 + \ldots)\,RT$

   where, P is their total pressure.

   Clearly, $P_1 = n_1 RT/V$, etc.

3. **Kinetic theory of gases.** Some basic assumptions of the kinetic theory are :

   1. Every gas is composed of a large number of tiny, perfectly elastic particles, called molecules.

   2. The distance between the molecules is so large that they do not exert any appreciable attraction on one another.

   3. The total volume of molecules is negligible compared to the volume of the container vessel.

   4. The molecules are in a state of continuous random motion with different velocities such that the average velocity of molecules is zero and the average speed of thermal agitation depends on temperature.

   5. The molecules in their random motion collide with one another and with the walls of the container vessel. These collisions are perfectly elastic. The molecules move in straight lines between any two consecutive collisions.

   6. The duration of collision is negligible as compared to the time spent to travel the free path between consecutive collisions.

   7. The molecules exert pressure on the walls of the container vessel. This pressure is the rate of change of momentum of the molecules striking per unit area of the walls of the container vessel. The pressure exerted by the molecules on the walls is same in all directions.

4. **Concept of Pressure Exerted by a Gas.** The pressure exerted by the gas is due to the continuous collisions of gas molecules against the walls of the container. Due to these collisions the walls of the container experiences a continuous force which is equal to the total momentum imparted to the walls

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per second. The force experienced per unit area of the walls of the container gives us the idea of pressure exerted by the gas.

5. **Expression for pressure due to an ideal gas.** The molecules of a gas contained in a vessel frequently collide against the walls of the vessel. As the collisions are perfectly elastic, the molecules rebound with exactly the same speed with which they strike against the walls of the container. The momentum delivered by these bombarding molecules produces force on each wall of the vessel whose value per unit area gives the pressure exerted by the gas.

Consider a cubical vessel containing an ideal gas.

Imaginary box of length ut
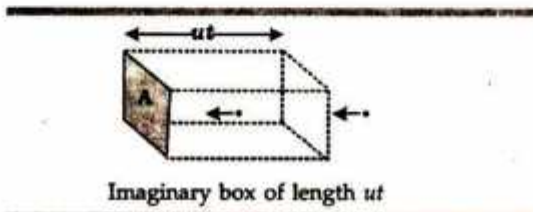
Let l = length of each side of the vessel

$V = l^3$, volume of vessel

= volume of gas

m = mass of each molecule

N = number of molecules in the gas

Assuming that molecules in a gas are travelling with a speed of u. Let a molecule travelling in a certain direction strike a face of the vessel with velocity = u and after collision, is turned back with a velocity $-u$.

Initial momentum of the molecule = mu

Final momentum of the molecule = $-mu$

Change of momentum = $-mu - (mu)$

$= -2mu$

Between two successive collisions against the same wall, the molecule shall first reach the opposite wall and from there, get turned back to again reach the first wall. Thus, time taken between two successive collisions with the same wall, t

= Distance / Velocity = $2l/u$

Number of collisions per sec = $1/t = u/2l$

Change in momentum/sec of wall of vessel due to collisions made by a molecule

= Change in momentum × Number of collisions per sec

$= -2mu \times u/2l = -mu^2/l$

From Newton's second law of motion, this change in momentum/sec represents the force F applied by a molecule on any wall. For N number of gas molecules in the vessel, force on the wall = Nmu^2/l

∴ Force = Nmu^2/l

Pressure = $P_i = F/l^2 = Nmu^2/l^3 = N/V mu^2$

Pressure exerted by gas molecules is same in all the direction, i.e., $P_x = P_y = P_z = P_i$

Thus $P_x + P_y + P_z = 3P_i$

or $P = P_i/3 = \dfrac{1}{3}\dfrac{N}{V} mu^2$

As the molecules don't travel with the same speed, the change in momentum and pressure they exert should all be average. Let C^2 be the average value of u^2. The equation for pressure of an ideal gas would be

$P = \dfrac{1}{3}\dfrac{N}{V} mC^2$ where C^2 is the square of the

root mean square speed.

Let M be the total mass of the gas enclosed in the container. Then

$M = m \times N$

Thus $\boxed{P = \dfrac{M}{3V} C^2}$

Substituting $M/V = \rho$, the density of the gas,

$\boxed{P = \dfrac{1}{3}\rho C^2}$

Thus $C = \sqrt{3P/\rho}$

6. **Relation between Pressure and Kinetic energy of the gas**

$P = \dfrac{1}{3}\rho C^2$

Mass of unit volume of the gas = $1 \times \rho = \rho$. Mean kinetic energy of translation per unit volume of the gas is

$E = \dfrac{1}{2}\rho C^2$

$$\therefore \quad \frac{P}{E} = \frac{(1/3)\rho C^2}{(1/2)\rho C^2} = \frac{2}{3}$$

or $\boxed{P = \frac{2}{3}E}$ ... (a)

Because energy E is due to the translatory motion of the molecules, it is called *kinetic energy of translation of the gas molecules*. From (a), we find that, *the pressure exerted by an ideal gas is numerically equal to two third of the mean kinetic energy of translation per unit volume of the gas.*

7. **Average Kinetic energy per Molecule of the Gas.** Consider one mole of an ideal gas at absolute temperature T, of volume V and molecular weight M. N being the Avogadro's number and m the mass of each molecule of the gas, we have

$$M = m \times N$$

$$P = \frac{1}{3}\frac{M}{V}C^2 \text{ or } PV = \frac{1}{3}MC^2$$

From perfect gas equation, PV = RT.

$$\therefore \frac{1}{3}MC^2 = RT \text{ or } \frac{1}{2}MC^2 = \frac{3}{2}RT$$

$\therefore$ Average K.E. of translation of one mole of the gas is

$$= \frac{1}{2}MC^2 = \frac{3}{2}RT$$

or $\frac{1}{2}mNC^2 = \frac{3}{2}RT$ $(\because M = mN)$

or $\frac{1}{2}mC^2 = \frac{3}{2}\left(\frac{R}{N}\right)T$

$$= \frac{3}{2}kT \qquad \left(\because \frac{R}{N} = k\right)$$

where k is called Boltzmann's constant.

R is gas constant per *mole* of the gas and k, called Boltzmann's constant, is gas constant per *molecule* of the gas, n stands for number of molecules while N for number of moles.

$\therefore$ Average K.E. of translation *per molecule* of a gas

$$KE_{avg} = \frac{1}{2}mC^2 = \frac{3}{2}kT$$

Thus average K.E. of translation per molecule of the gas does not depend upon the mass of the molecule, but depends entirely upon the temperature of the gas.

8. **Kinetic interpretation of temperature.** Average kinetic energy per molecule

$$KE_{avg} = \frac{3}{2}kT$$

Thus average translational kinetic energy per molecule is directly proportional to the absolute temperature.

As $\frac{1}{2}mc^2 = \frac{3}{2}kT$

or $\frac{1}{2}mc^2 \propto T$

when $T = 0$, $c = 0$

Hence absolute zero of temperature may be defined as that temperature at which the root mean square velocity of the gas molecules reduces to zero.

9. **Degrees of freedom.** The number of ways in which a gas molecule can absorb energy is called degrees of freedom. $(f = 3N - k)$

A gas molecule can have degree of freedom due to its linear motion (f_t), or rotational motion (f_r) or vibrational motion (f_v). So, the total number of degrees of freedom (f) is given by:

$$\boxed{f = f_t + f_r + f_v}$$

f_t are present at all temperatures, f_r at ordinary temperatures and f_v at high temperatures.

Gas	f_t	f_r	f_v	$f = f_t + f_r + f_v$
Monoatomic gases (He + noble gases: Ne, Ar, Kr, Xe, Rn)	3	0	0	3
Diatomic gases (e.g. H_2, N_2, O_2, HCl etc.)	3	2	0	5
Linear triatomic gases (e.g. CO_2, etc.)	3	2	2	7
Non-linear triatomic gases (e.g. H_2O, O_3 etc.)	3	2	1	6

10. **Law of equipartition of energy** states that in equilibrium, the total kinetic energy of a dynamical system is equally distributed among its various Degrees of freedom and the kinetic energy associated with each degree of freedom is $(\frac{1}{2}kT)$.

Accordingly, each translational and rotational degree of freedom of a molecule contributes $\frac{1}{2} kT$ to the energy while each vibrational frequency contributes $2 \times \frac{1}{2} kT = kT$, since a vibrational mode has both kinetic and potential energy modes.

In case of a gas whose molecules have f Degrees of freedom,

A. **KE per molecule per degree of freedom**

$$= \frac{1}{2} kT$$

B. **Total KE of each molecule**

$$= f \times \frac{1}{2} kT = \frac{1}{2} f kT$$

C. **KE per mole**

$$= N_A \times (f \times \frac{1}{2} kT) = \frac{1}{2} f RT$$
$$(\because k = R / N_A)$$

D. **Total KE of the gas in the container, U**

$$= \frac{1}{2} N f RT$$

E. **Total KE of the gas, $U \propto T$**

F. **Molar sp. heat at constant volume, (C_v)**

$$C_v = \frac{1}{2} f R$$

G. **Molar sp. heat at constant pressure (C_p)**

$$C_p - C_v = R$$
$$\therefore \quad C_p = C_v + R$$
$$= \frac{1}{2} f R + R = R \left(\frac{f}{2} + 1 \right)$$

H. $\gamma = \dfrac{C_p}{C_v} = \dfrac{R \left(\frac{f}{2} + 1 \right)}{\frac{1}{2} f R} = 1 + \dfrac{2}{f}$

I. f, r, C_v, C_p of various gases

	for monoatomic gases	for diatomic gases	for polyatomic gases	
f	3	5	6	7
C_v	3/2 R	5/2 R	3R	7/2 R
C_p	5/2 R	7/2 R	4R	9/2 R
γ	5/3	7/5	4/3	9/7

$R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$

11. **Specific Heat Capacity of Solids.** Consider a solid of N atoms, each vibrating about its mean position. An oscillation in one dimension has average energy of

$2 \times \frac{1}{2} k_B T = k_B T$.

In three dimensions, the average energy is $3 k_B T$. For a mole of solid, $N = N_A$, and the total energy is

$U = 3 k_B T \times N_A = 3 RT$

At constant pressure, $\Delta Q = \Delta U + P \Delta V = \Delta U$, since for a solid ΔV is negligible. Hence,

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

12. **Specific Heat Capacity of Water.** Treating water like a solid, for each atom, average energy is $3 k_B T$. Water molecule has three atoms, two hydrogen and one oxygen. So it has

$U = 3 \times 3 k_B T \times N_A = 9 RT$

and $C = \Delta Q / \Delta T = \Delta U / \Delta T = 9R$.

This is in agreement with the observed value.

13. **Boyle's Law.** At constant temperature, the volume of a given mass of a gas is inversely proportional to its pressure i.e.

$V \propto 1/P \quad$ or

$$\boxed{PV = \text{constant}}$$

14. **Charle's Law.** At constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature i.e.

$V \propto T \quad$ or

$$\boxed{\frac{V}{T} = \text{constant}}$$

15. **Avogadro's Law.** It states that at the same temperature and pressure, equal volumes of *all* gases contain the same number of molecules.

Further, 22.4 litres i.e. $22.4 \times 10^{-3} \text{ m}^3$ of every gas at NTP weighs 1 gram mole (gram-mole is molecular weight in a.m.u. but a.m.u. is read as gram).

16. **Dalton's Law of Partial Pressures.** If an enclosure contains a number of non-reacting gases, each gas behaves independent of the

other and the total pressure exerted by gases on the walls of enclosure is the sum of the pressures exerted by individual gases i.e.

$$P = P_1 + P_2 + P_3 + \dots$$

The *partial pressure* of a gas in a mixture of gases occupying a fixed volume is the pressure that the gas would exert if it alone had occupied the total volume.

17. **Gay Lussac's law.** It states that whenever gases take part in a reaction (either as reactants or products), they do so in simple ratio of their volumes measured under similar conditions of temperature and pressure.

18. **Graham's Law of Diffusion.** It states that under similar conditions of temperature and pressure, the rates of diffusion of gases (by volume) are inversely proportional to the square root of their densities.

Rate of diffusion,

$$r = \frac{\text{Volume of gas diffused, V}}{\text{Time taken to diffuse, t}}$$

$$\therefore \quad \frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{m_2}{m_1}}$$

If volumes diffused of two gases are same i.e. $V_1 = V_2$, in time t_1 and t_2 respectively, then

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{\rho_2}{\rho_1}}$$

If $t_1 = t_2$,

$$\frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

19. **Mean free Path.** It is the average distance between two successive collisions of gas molecules

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

where
l = mean free path
n = number of molecules per unit volume
d = diameter of each molecule

l can also be defined as

$$l = \frac{kT}{\sqrt{2}\pi d^2 p}$$

where
p is pressure of the gas
T is temperature of the gas
k is Boltzmann constant

The value of l is of the order of a micron.

20. **Brownian motion** is the random motion of small suspended particles in a fluid by continuous bombardment by the surrounding molecules of the fluid.

Brownian motion increases if:
1. the size of suspended object decreases
2. the density of medium decreases
3. temperature increases
4. viscosity of the medium decreases.