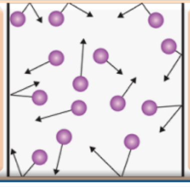


UNIT-15 MOLECULAR THEORY OF GASES

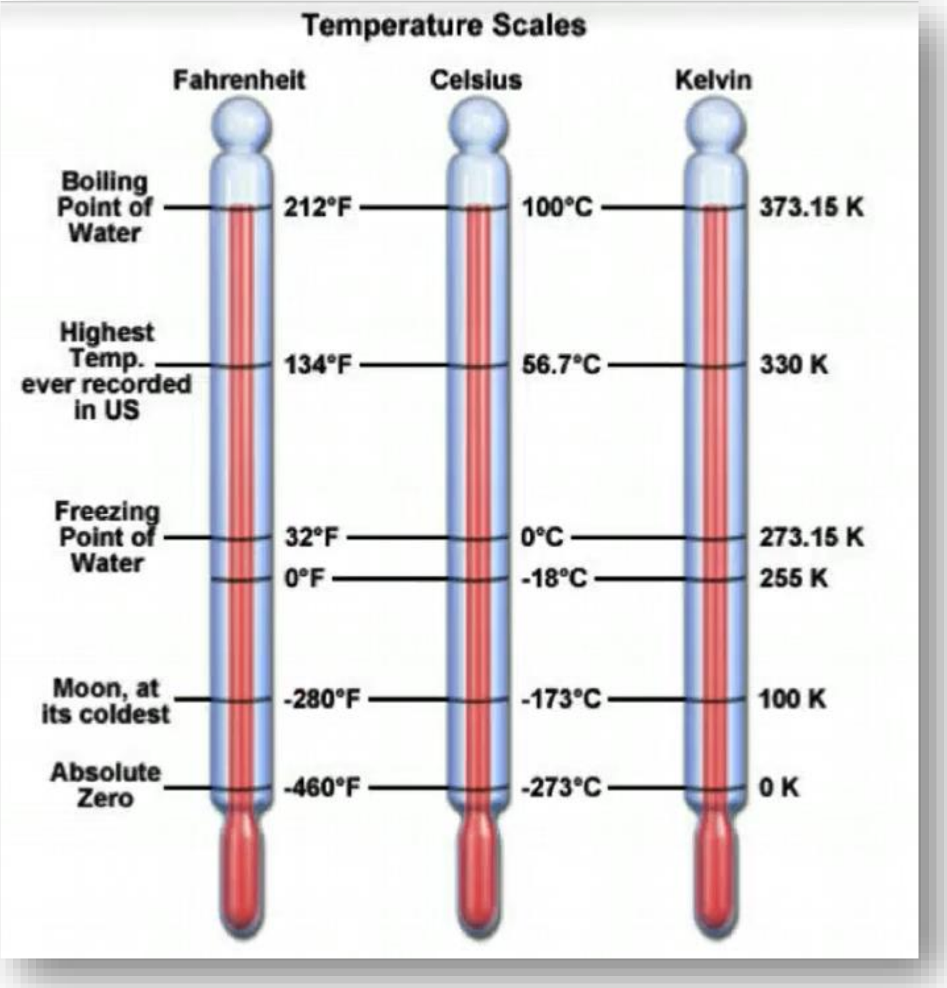
TEMPERATURE

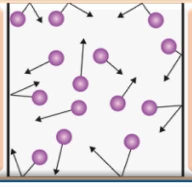
Temperature measures the average translational kinetic energy of the molecules of the body.

SCALES OF TEMPERATURE

A temperature scale is used to measure the temperature quantitatively. To measure temperature quantitatively, we must put some numbers on the capillary tube, for constructing a scale of temperature, it is necessary to choose reference points that are fixed. That is the value of the fixed points. The melting point of ice and boiling point of water at standard pressure (76cm of Hg) are the two fixed points and the difference between these two points is divided in different ways, called scales of graduation. There are three scales of temperature

(i) Centigrade or Celsius scale
(ii) Fahrenheit scale
(iii) Kelvin or absolute scale are commonly used these days





CENTIGRADE SCALE OR CELSIUS SCALE

Celsius is a more scientific scale. A Swedish astronomer, Anders Celsius, is credited with being the first to conduct and publish the scientific definition of an international temperature scale through experiments.

In the Celsius scale, the freezing point (Melting point of ice) is marked 00C and the boiling point is 100 ^{0}C. The interval between these two points is divided into hundred equal parts. Each part thus represents one degree Celsius (1°C).

FAHRENHEIT SCALE

Daniel Gabriel developed the Fahrenheit scale in 1744 when he was inventing alcohol and mercury thermometers.

In the Fahrenheit scale, the freezing temperature of the water is 32^0 F, the lower point. The boiling temperature of the water is taken as 212^0 F and is fixed as the upper point. The division of the Fahrenheit scale takes place into 180 equal parts. Each part represents 1°F.

KELVIN SCALE

Lord Kelvin developed the Kelvin scale in 1848. The derivation of the Kelvin scale is from the Celsius scale only. Kelvin scale does not use degrees and its writing form is as Kelvin or K.

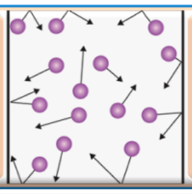
In this scale, the melting point of ice is 273K and the boiling point of water is 373K of water. The temperature is given in units called Kelvin instead of degrees. The lowest temperature is –273°C.

The relationship among centigrade, Fahrenheit, and Kelvin scales are.

$$\frac{\text{Temperature on one scale} - \text{freezing point}}{\text{boiling point} - \text{freezing point}} = \frac{\text{Temperature on second scale} - \text{F.P}}{\text{B.P} - \text{F.P}}$$

$$\frac{T_{^\circ\mathrm{C}} - 0}{100} = \frac{T_{^\circ\mathrm{F}} - 32}{180} = \frac{T_k - 273}{100}$$

$$\frac{T_{^\circ\mathrm{C}}}{100} = \frac{T_{^\circ\mathrm{F}} - 32}{180} = \frac{T_k - 273}{100}$$



Temperature on this scale can be converted using the following equations

To convert from	*Use the equation*
Celsius to Fahrenheit	$T_{°F} = \frac{9}{5} T_{°C} + 32$
Fahrenheit to Celsius	$T_{°C} = \frac{5}{9} (T_{°F} - 32)$
Celsius to kelvin	$T_K = T_{°C} + 273.15$
Kelvin to Celsius	$T_{°C} = T_K - 273.15$
To convert from	Use the equation
Fahrenheit to Kevin	$T_K = \frac{5}{9} (T_{°F} - 32) + 273.15$
Kelvin to Fahrenheit	$T_{°F} = \frac{9}{5} (T_K - 273.15) + 32$

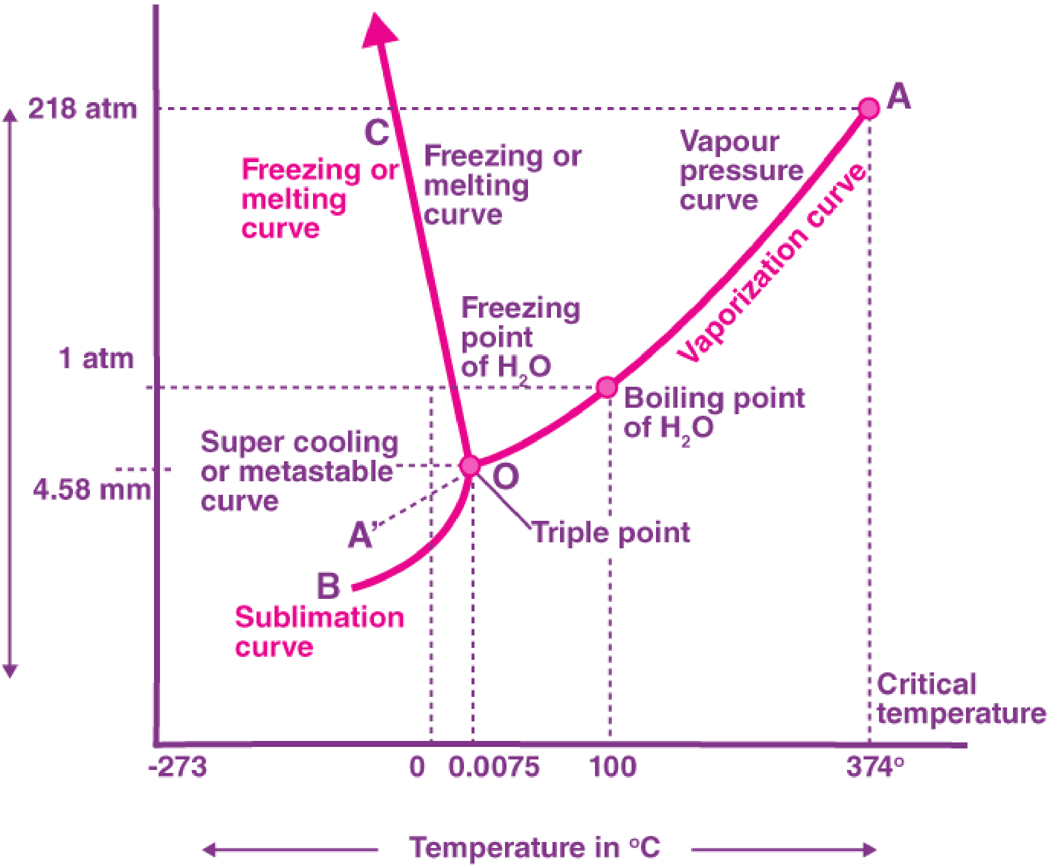
THE TRIPLE POINT OF WATER.

Water's liquid, solid and vapor states can co-exist in thermal equilibrium, at only one set of pressure and temperature values.

"The particular temperature and pressure at which the solid, liquid, and gaseous phases of a given substance co-exist in thermal equilibrium is called Triple point water."

The triple point of water defines the Kelvin(K), the base unit of thermodynamic temperature in the International System of Units (SI). The triple point of water is 273.16 K, (0.01 0C), or 32.018 0F.

In the following figure, The triple point is represented as the point where the lines separating the solid, liquid, and gas phases meet. This diagram visually demonstrates the relationship between temperature and pressure for the different phases of water.



GAS LAWS

The behavior of a gas can be described by four variables i.e., pressure, volume, mass, and temperature. The relation between any two variables is found experimentally while keeping the other constant.

BOYLE'S LAW

In 1660 an English Scientist Robert Boyle presented the following law, which relates pressure & volume.

STATEMENT

volume of a given mass of a gas is inversely proportional to pressure provided the temperature of the gas remains constant.

MATHEMATICAL FORM

According to Boyle's law

$$V \ \alpha \ \frac{1}{P} \qquad (At\ constant\ temperature)$$

or

$$V = (constant)\ \frac{1}{P}$$

$$PV = (constant)$$

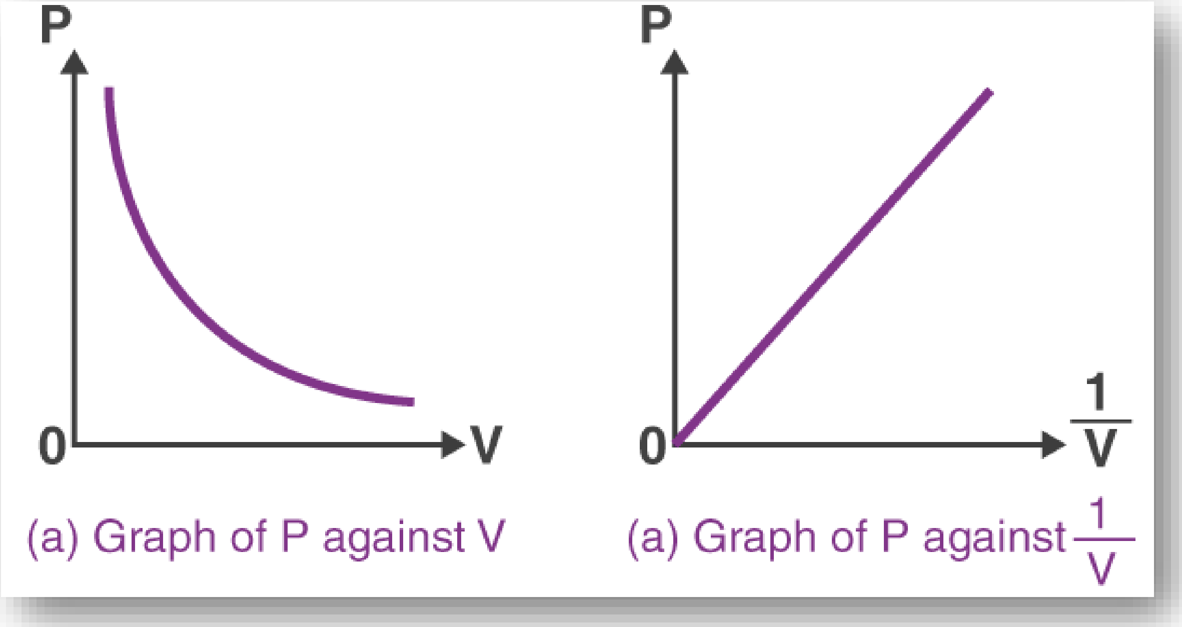
where,

P= pressure

V = volume of a gas

THE GRAPH BETWEEN P AND V AT CONSTANT TEMPERATURE

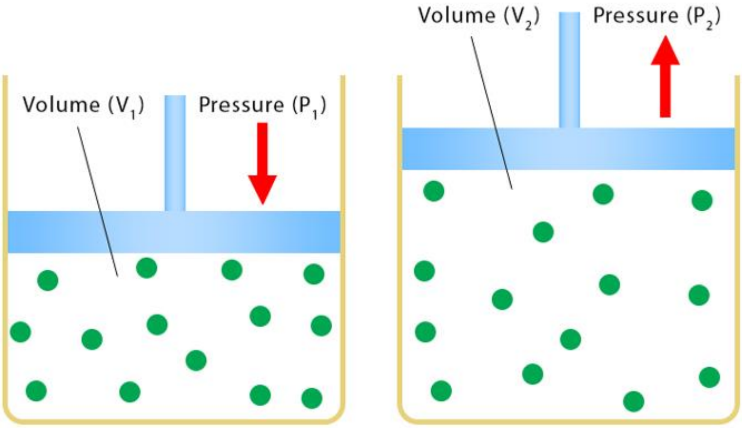
The graph between P and V at constant temperature is a curve called a hyperbola showing the inverse relation between them for two different states, the Second graph of P plotted against 1/V is a straight line passing through the origin.



(a) Graph of P against V

(a) Graph of P against $\frac{1}{V}$

If pressure is changed from P_1 to P_2 and a change in volume is V_1 to V_2 then,



P_1V_1 = constant ………..(i) (at constant temperature)

P_2V_2 = constant ………..(ii) (at constant temperature)

Comparing equations (i) and (ii), we get

$$P_1V_1 = P_2V_2$$

EFFECT OF MASS

The mass of a gas affects the pressure, and experiments show that:

$$PV \propto m$$

$$PV = (constant)\ m$$

$$\frac{PV}{m} = constant$$

And $$\frac{P_1 V_1}{m_1} = \frac{P_2 V_2}{m_2} \quad at\ constant\ \ temperature$$

CHARLE'S LAW

In 1787 Jacques Charles presented the following law which relates volume and temperature.

STATEMENT

volume of a given mass of a gas is directly proportional to the temperature measured in Kelvin. provided its pressure is kept constant.

MATHEMATICAL FORM

According to Charle's law:

$$V \ \alpha \, T$$

$$V = (constant)\, T$$

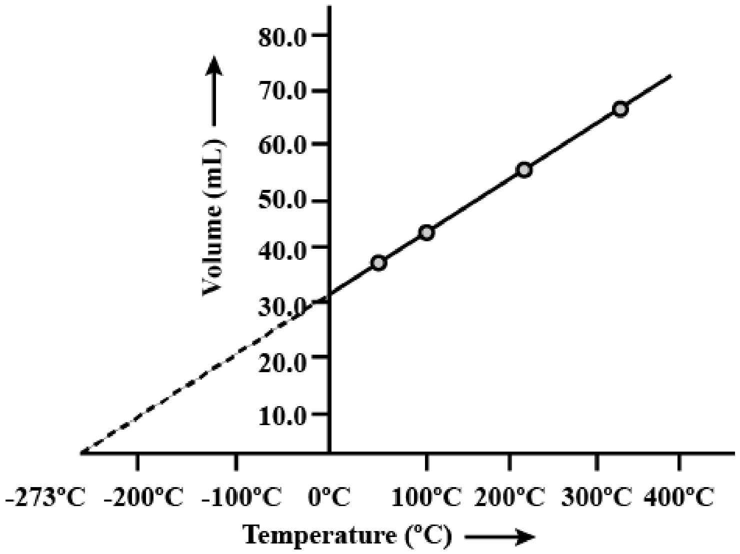
$$\frac{V}{T} = \mathbf{constant} \qquad (constant\ pressure)$$

If temperature is changed from T_1 to T_2 and its volume will change from V_1 to V_2, then

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

ABSOLUTE ZERO

The temperature at which the volume of an ideal gas is considered to be zero is known as absolute zero.



A graph of the volume of gas against its temperature is a straight line. It shows that at O °C the gas possesses a volume called V_o. Now if the graph is extra plotted, it intersects

the temperature axis at $-273.15\,^{o}C$. This shows that if a gas could be cooled to $-273^{o}C$ its volume would be zero. Hence $-273.15\,^{o}C$ is called absolute zero.

AVOGADRO'S LAW

In 1811, Italian scientist Amedeo Avogadro suggested his hypothesis regarding the relationship between the volume and number of molecules of a gas. This hypothesis now called Avogadro's law

STATEMENT

Avogadro's law states that "***An equal volume of all gases contains the same number of molecules at the same temperature and pressure".*** Thus, the volume of a gas is directly proportional to the number of moles of the gas at constant temperature and pressure.

AVOGADRO'S LAW FORMULA

Avogadro's law can be written as:

$$V \propto n \text{ (at constant temperature and pressure)}$$

$$\frac{V}{n} = \mathrm{K}$$

the volume V to the number of gas particles **n** ratio equals a proportionality constant k. Thus,

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

This equation says that when the number of particles in a gas changes from n_1 to n_2, the volume also changes from V_1 to V_2.

GENERAL GAS LAW:

In order to derive general gas law, we make use of Boyle's law, Charles's law, and Avogadro's law.

According to Boyle's law

$$V \propto \frac{1}{P} \text{ (when n number of mole and temperature T are kept constant)}$$

According to Charles's law

$$V \propto T \quad \text{(when n and pressure P are kept constant)}$$

According to Avogadro's law

$$V \propto n \text{ (when T and P are kept constant)}$$

Consider for a moment that none of the variables are to be kept constant, then all the above three relationships can be joined together.

$$V \propto \frac{nT}{P}$$

$$V = R\,\frac{nT}{P}$$

$$V = \frac{n\,R\,T}{P}$$

Where **R** is a constant of proportionally and is called a General gas constant or universal gas constant and does not depend on the quantity of gas in the sample. If P is measured in Nm^{-2}, V in $m^{3,}$ and T in Kelvin, then the volume of the universal gas constant is **R = 8.314J mol^{-1} k^{-1}.** The above equation is written as

$$PV = nRT$$

This is known as the general gas law or equation of state. Where R is called the universal gas constant. in the SI system, its value is R = 8.31 J mol^{-1} K^{-1}.

IDEAL GAS	NON-IDEAL GAS
1 A gas which obeys all the laws at all temperatures and pressure is called an ideal or perfect gas.	Non-ideal or Real gases do not obey all the gas laws at all temperatures and pressure. .
2 An ideal gas consists of infinitely small, elastic molecules.	Non-ideal or Real gas molecules have definite size.
3 The molecules exerts no force of attraction on each other.	Non-ideal or Real gas molecules attract each other

NOTE **Real gases become ideal or perfect at low pressure and high temperature**.

KINETIC THEORY OF GASES

We discussed the properties of an ideal gas by using such macroscopic variables such as pressure, volume and temperature. Such large-scale properties can be related to a description on a microscopic scale, where matter is treated as collection of molecules. Now we begin by developing a microscopic model of an ideal gas called Kinetic Theory of gas.

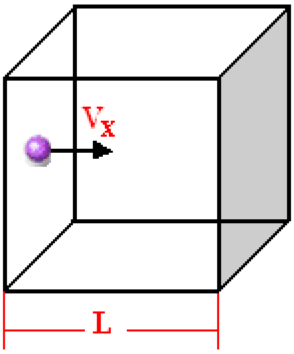
THE BASIC POSTULATES OF KINETIC THEORY OF GASES

1. A gas contains a very large number of spherical particles called molecules. Depending on the gases each molecule consists of an atom or a group of atoms.
2. A finite volume of a gas consists of very large number of molecules. This assumption is justified by experiments. At standard conditions there are 3x1025 molecules per cubic meter.
3. The size of the molecules is much smaller than separation between sphere, it is about $3x10^{-10}$ m.

4. The molecules move in all directions with various speeds making elastic collision with one another and with walls of the container.
5. The molecules exert no forces on one another except during collisions. In the absence of the external forces, they move freely in straight lines.
6. Laws of mechanics are assumed to be applicable to the motion of molecules

DERIVATION OF PRESSURE BASED ON THE KINETIC THEORY OF GASES

To derive an expression for the pressure of an ideal gas consisting of **N** molecules in a container of volume V. The container is a cube with edges of length 'L'.



The pressure of a gas is due to collisions of molecules with the walls of a container is;

$$\boldsymbol{pressure = \frac{force}{area}}$$

Consider the collision of one molecule moving with the velocity $\boldsymbol{v}$ toward the right-hand face of the box. A molecule that has a velocity $\boldsymbol{v}$ can be resolved into three components $\boldsymbol{v_x, \ v_y, \ v_z}$. A molecule collides with the wall of the cube, it will rebound elastically in the opposite direction, such that the x-component of velocity is reversed, while its $\boldsymbol{v_y \ and \ v_z}$ components of velocity remain unaffected. Because the x component of the momentum of the molecule is $-mv_x$ before the collision and mv_x after the collision, the change of momentum of the molecule is

Change in momentum = $\boldsymbol{mv_x - (-m\,v_x)}$

Change in momentum = $\boldsymbol{mv_x + (m\,v_x) = 2\,m\,v_x}$

For one collision, the molecule covers a distance = L + L = 2L

For one collision, the molecule takes a time $= \boldsymbol{\frac{distance}{velocity} = \frac{2L}{v_x}}$

Now,

rate of change of momentum per collision $= \boldsymbol{\frac{change\ in\ momentum}{time\ taken}}$

$$= \boldsymbol{\frac{2mV_x}{\frac{2L}{v_x}}}$$

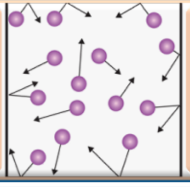
rate of change of momentum per collision $= \boldsymbol{\frac{m\,v_x^2}{L}}$

But, force exerted by molecule = of change of momentum

$$F = \frac{mV_x^2}{L}$$

Similarly, The force due to all molecules can be determined

$$F = F_1 + F_2 + F_3 \ldots\ldots\ldots\ldots.. + F_N$$



$$F_x = \frac{mV_{1x}^2}{L} + \frac{mV_{2x}^2}{L} + \cdots\cdots\cdots\cdots + \frac{mV_{nx}^2}{L}$$

$$F_x = \frac{m}{L}(V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \cdots\cdots\cdots + V_{1x}^2)$$

As pressure is normal force per unit area, hence pressure p on the face perpendicular to the x-axis is

$$P = \frac{F_x}{A} = \frac{F_x}{L^2}$$

$$P = \frac{1}{L^2}\,(F_x)$$

$$P = \frac{1}{L^2}\,\frac{m}{L}(V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \cdots\cdots\cdots + V_{1x}^2)$$

$$P = \frac{m}{L^3}\,(V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \cdots\cdots\cdots + V_{1x}^2) \ldots\ldots..(i)$$

Let N = total number of molecules
L^3 = volume of cubical container
n_v = number of molecules per unit volume.

$\therefore \quad n_v = \frac{m}{L^3} \quad$ or $\quad L^3 = \frac{N}{n} \quad$ substituting this value in equation (i)

$$P = \frac{m}{\frac{N}{n_v}}\,(V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \cdots\cdots\cdots + V_{1x}^2)$$

$$P = \frac{m\,n_v}{N}\,(V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \cdots\cdots\cdots + V_{1x}^2)$$

$$P = m\,n_v\left(\frac{V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \cdots\cdots\cdots + V_{1x}^2}{N}\right)$$

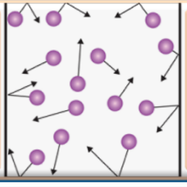
Where $m\,n_v$ is the mass per unit volume which we call density $\boldsymbol{\rho = m\,n_v}$ The average value of the square of the x-component of velocity is

$$\overline{v_x^2} = \frac{({V_{1x}}^2 + {V_{2x}}^2 + - - - - - - - - - - + {V_{nx}}^2)}{N}$$

thus, we can write the pressure as

$$P = \rho\,\overline{v_x^2} \ldots\ldots\ldots\ldots(ii)$$

The term $\overline{v_x^2}$ is only one component of total velocity.



We know that the square of any velocity is equal to the sum of the square of velocity component. Thus

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

Since the velocities of the molecules in our gas are assumed to be random,

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

$$\overline{v^2} = \overline{v_x^2} + \overline{v_x^2} + \overline{v_x^2}$$

$$\overline{v^2} = 3\,\overline{v_x^2}$$

$$\frac{1}{3}\,\overline{v^2} = \overline{v_x^2}$$

Substituting this value in equation (ii), we get

$$P = \frac{1}{3}\rho\,\overline{v^2}$$

Where $\overline{v^2} =$ mean square speed

$$\sqrt{\overline{v^2}} = v_{rms} = root\ mean\ square\ velocity$$

THE RELATION BETWEEN KINETIC ENERGY OF MOLECULES AND TEMPERATURE

From the kinetic theory of gases, pressure is given by

$$\boldsymbol{P = \frac{1}{3}\rho\,\overline{v^2}}$$

$$\boldsymbol{P = \frac{1}{3} m\, n_v\,\overline{v^2}}$$

$$\boldsymbol{P = \frac{1}{3} m \left(\frac{N}{V}\right)\overline{v^2}}$$

$$\boldsymbol{P\,V = \frac{1}{3} m\,N\,\overline{v^2}}$$

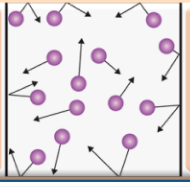
Now, we can compare the above equation with ideal gas equation, PV = nRT

$$\boldsymbol{n\,R\,T = \frac{1}{3} m\,N\,\overline{v^2}}$$

Substituting $n = \frac{N}{N_A}$ and multiplying both the sides by $\frac{3}{2}$

$$\boldsymbol{\frac{3}{2}\left(\frac{N}{N_A}\right) R\,T = \frac{3}{2}\times\frac{1}{3} m\,N\,\overline{v^2}}$$

$$\boldsymbol{\frac{3}{2}\left(\frac{R}{N_A}\right) N\,T = \frac{1}{2} m\,N\,\overline{v^2}}$$



$$\frac{1}{2}\, m\, N\, \overline{v^2} = \frac{3}{2}\left(\frac{R}{N_A}\right) N\, T$$

$$\frac{1}{2}\, m\, \overline{v^2} = \frac{3}{2}\left(\frac{R}{N_A}\right)\, T$$

Since $\frac{R}{N_A} = k\ (boltzmaan\ constant)$

$$k = 1.38 \times 10^{-23}\, \frac{J}{K}$$

$$\frac{1}{2}\, m\, \overline{v^2} = \frac{3}{2} k\, T$$

This is known as the kinetic interpretation of temperature. It indicates that the mean translational kinetic energy of a molecule of an ideal gas is directly proportional to the absolute temperature.

$$\frac{1}{2}\, m\, \overline{v^2} \quad \alpha \quad T$$