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PHYSICS UNIT # 15

MOLECULAR THEORY OF GASES

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MOLECULAR THEORY OF GASES

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15.1 HEAT:

Conventional Definition:

"Heat is the sensation of hotness or coldness in a body."

Modern Definition:

"Heat is the energy in transit between the two bodies of different temperature (from high temperature body to low temperature body)"

Microscopic view:

According to microscopic theory, every substance consists of molecules or atoms. These move all the time and have kinetic energy. When the temperature of substance is increased then the molecules or atoms move rapidly. It is known as thermal agitation due to which kinetic energy of molecules or atoms increases.

The sum of all kinetic energies of all the molecule present in a substance is called "heat energy or thermal energy" in that substance.

Internal Energy:

The sum of all types of energies possessed by a body is called internal energy of the body. For a mono-atomic or an ideal gas, microscopically, it is defined as *the sum of Translatory Kinetic energies of molecules.*

Units of Heat:

- (i) Joule (In S.I. System).
- (ii) Calorie (in C.G.S. system)
- (iii) British Thermal unit (BTU) in British Eng. System.

Conversion of units

- (i) 1 Calorie = 4.186 Joule
- (ii) 1 BTU = 1055 J
- (iii) 1 BTU = 252 calorie

15.2 Temperature:

Conventional Definition:

Temperature is the property which determines the direction of flow of heat when two bodies are brought in thermal contact with each other. Conventionally it was define as:

"The measure of the degree of hotness or coldness of a body is called Temperature."



Modern Definition:

"The average kinetic energy of a molecule present in a body is called temperature of the body."

15.3 Thermometer:

The temperature of a body is measured by a device called thermometer.

Construction of thermometer:

Thermometer consists of following to characteristics:

Thermometric property of matter

Thermometric scale

i) Thermometric property of matter:

The property of a matter which changes uniformly with the change of temperature is called thermometric property.

For example length, volume, pressure and electrical resistance are change due to change of temperature therefore they are called thermometric properties of matter.

ii) Thermometric scale:

The three scales commonly used to measure temperature:

- i) Centigrade or Celsius Scale ($^{\circ}\text{C}$) ii) Fahrenheit Scale ($^{\circ}\text{F}$) iii) Kelvin or Absolute Scale (K)

Centigrade or Celsius Scale

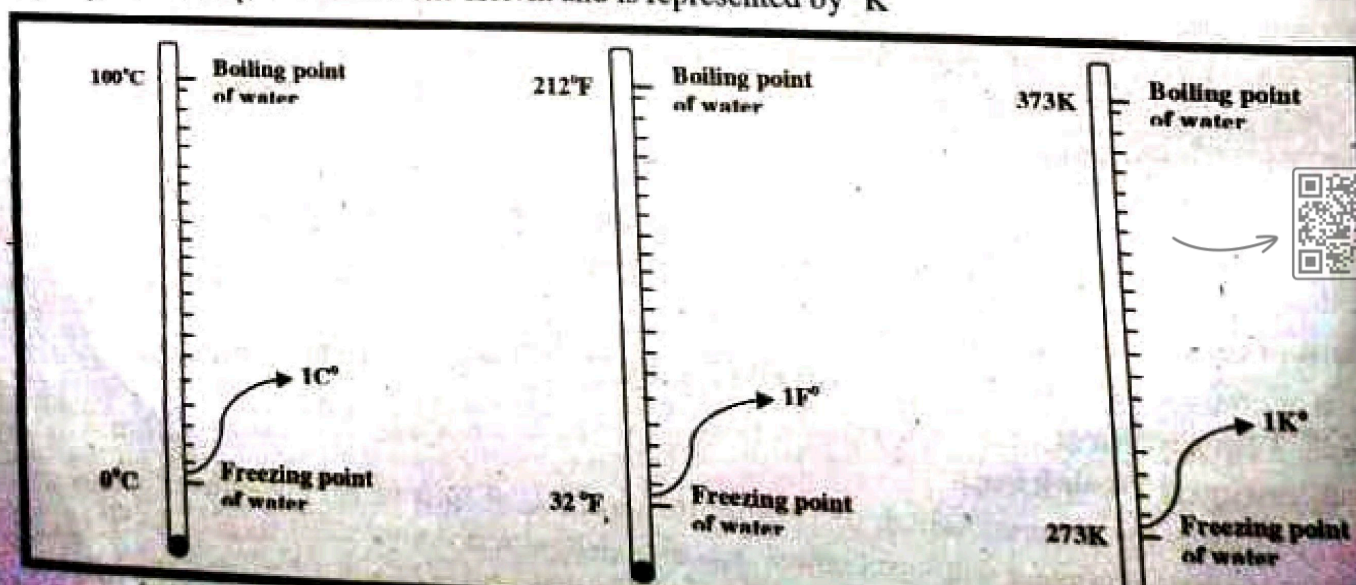
In this scale, the freezing point of water is marked as 0 and the boiling point of water is marked as 100. The distance between the freezing point of water and the boiling point of water is divided into 100 equal parts. Each part is called one degree centigrade and is represented by $^{\circ}\text{C}$.

Fahrenheit Scale

In this scale the freezing point of water is marked as 32 and the boiling point of water is marked as 212. The distance between the freezing point and the boiling point of water is divided into 180 equal parts. Each part is called one degree Fahrenheit and is represented by $^{\circ}\text{F}$.

Kelvin or Absolute Scale

In this scale the freezing point of water is marked as 273 and the boiling point of water is marked as 373. The distance between the freezing point and the boiling point of water is divided in 100 equal parts. Each part is called one Kelvin and is represented by 'K'.

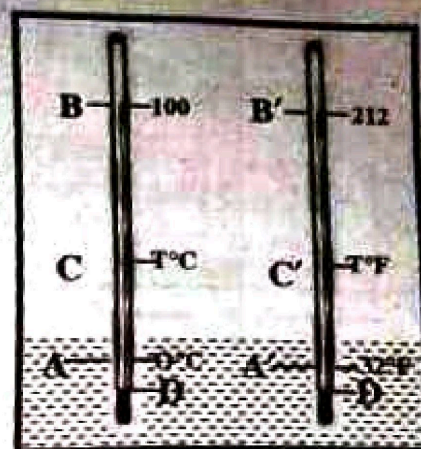


15.4- Relation between different temperature Scales:

1) Relation between Celsius and Fahrenheit Scales:

Let us consider that both, a Celsius and a Fahrenheit, thermometers are dipped in the same water bath placed at room temperature, as shown in the figure. The final and initial points in Celsius thermometer are labelled as A and B, and those are in the Fahrenheit thermometer as A' and B' respectively, whereas the mercury levels in both are labelled as C and C'. The general relation between two scales of temperature can be written as:

$$\frac{\text{Temp. on 1st scale} - \text{Freezing point}}{\text{Boiling point} - \text{Freezing point}} = \frac{\text{Temp. on 2nd scale} - \text{Freezing point}}{\text{Boiling point} - \text{Freezing point}}$$



$$\frac{T^{\circ}\text{C} - 0}{100 - 0} = \frac{T^{\circ}\text{F} - 32}{212 - 32}$$

$$\frac{T^{\circ}\text{C}}{100} = \frac{T^{\circ}\text{F} - 32}{180}$$

OR

$$\frac{T^{\circ}\text{C}}{5} = \frac{T^{\circ}\text{F} - 32}{9}$$

$$T^{\circ}\text{C} = \frac{5}{9} (T^{\circ}\text{F} - 32)$$

OR

$$T^{\circ}\text{F} = \frac{9}{5} T^{\circ}\text{C} + 32$$

2) Relation between Kelvin and Fahrenheit Scales:

$$\frac{\text{TK} - 273}{5} = \frac{T^{\circ}\text{F} - 32}{9}$$

3) Relation between Celsius and Kelvin Scales:

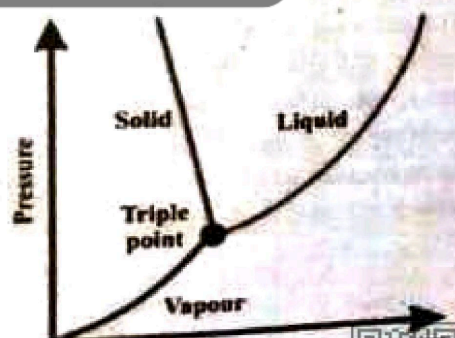
$$T^{\circ}\text{C} = \text{TK} - 273$$

$$\text{TK} = T^{\circ}\text{C} + 273$$

15.5 THE TRIPLE POINT OF WATER

The specific temperature and pressure, where all three states or phases (liquid, solid and vapour or gas) are coexist in thermal equilibrium is called Triple Point of Water.

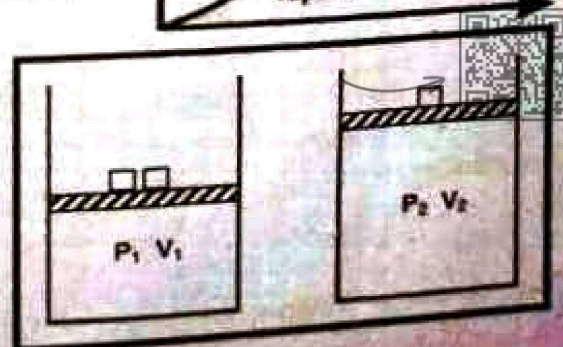
This particular temperature is 273.16K, 0.01°C and 32.02°F while the pressure is 4.58 mm of Hg and 611.73 Pascal (N/m²).



15.6 GAS LAWS

Boyles' Law:

The relation between the Volume and Pressure of a gas was studied by Robert Boyle and formulated in the form of a law known as **Boyles' law**, which states that "For a given mass of a gas, the volume of the gas is inversely proportional to the pressure of the



gas provided the temperature of the gas remains constant". Mathematically,

$$V \propto \frac{1}{P}$$

$$V = \text{Constant} \frac{1}{P}$$

OR

For different states of the gas, it can be written as

The Pressure - Volume graph of Boyle's law is a hyperbola.

Graph of P plotted against $\frac{1}{V}$ is a straight line passing through the origin.

The inverse relation of volume and pressure of a gas remains valid until the mass of the gas remains constant. If, however, the mass of the gas varies, then the product PV will be directly proportional to the mass of the gas.

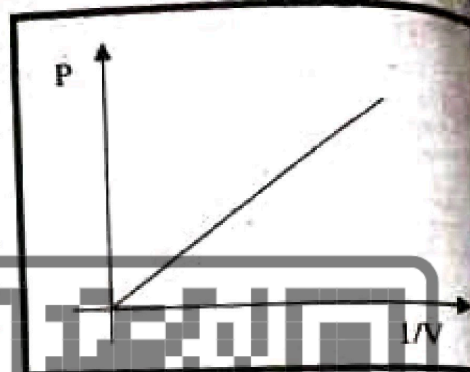
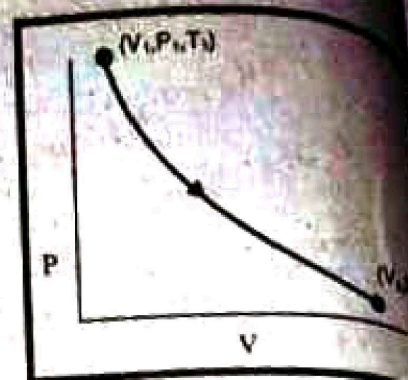
$$PV \propto m$$

$$\text{OR } \frac{PV}{m} = \text{Constant}$$

For different states of gas,

$$\text{OR } \frac{P_1 V_1}{m_1} = \frac{P_2 V_2}{m_2} = \text{Constant}$$

Real gases obey Boyle's law at low pressure



Charles' Law:

The relation between the volume of a gas and its absolute temperature was first studied by Charles called **Charles' Law**, which states that "for the given mass of a gas, the volume of a gas is directly proportional to the absolute temperature of the gas, provided the pressure of the gas remains constant". Mathematically,

$$V \propto T$$

$$V = \text{Constant } T$$

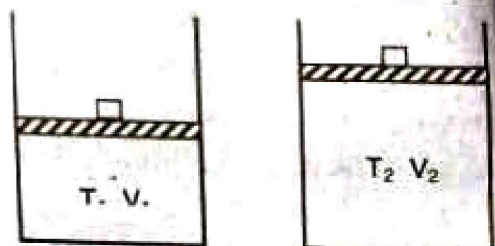
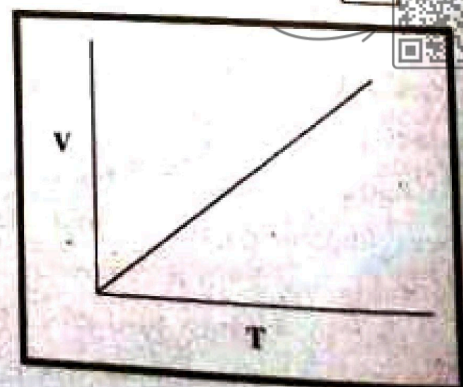
OR

$$\frac{V}{T} = \text{Constant}$$

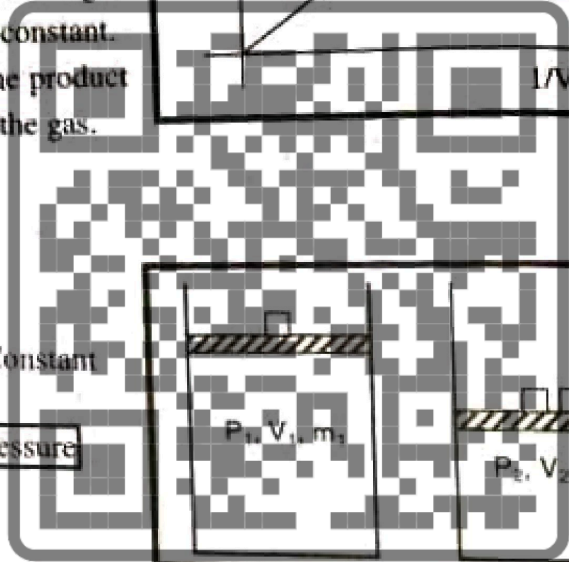
For different states of gas, it can be written as

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

The Volume - Temperature graph of Charles' Law is a



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The direct relation of volume and temperature of a gas remains valid until the mass of the gas remain constant. If, however, the mass of the gas varies, then the ratio will be directly proportional to the mass of the gas.

$$\frac{V}{T} \propto m$$

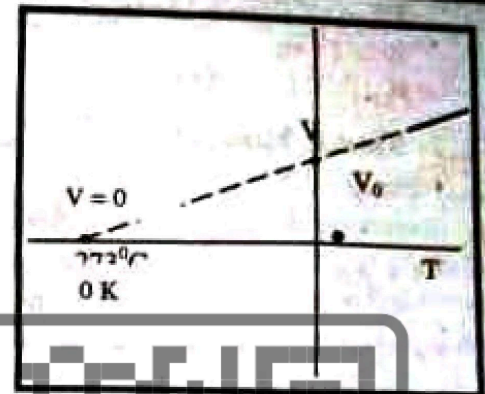
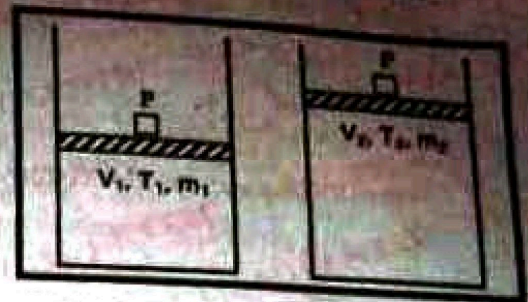
$$\frac{V}{mT} = \text{Constant}$$

OR

For different states of gas,

$$\frac{V_1}{m_1 T_1} = \frac{V_2}{m_2 T_2} = \text{Constant}$$

Real gases obey Charles' law at high temperature



Absolute Zero:

According to Charles' Law, the volume of a gas at constant pressure is directly proportional to its absolute temperature, and the graph of volume and temperature is a straight line. From the graph, it is found that at 0°C , the gas still possesses a volume " V_0 ". When the straight line of a graph is extrapolated to lower temperature as shown in the figure, it intersects the temperature axis at -273°C . This implies that if a gas could be cooled off to -273°C , it would have no volume. Lord Kelvin suggested this point as zero of Kelvin Scale which is called **Absolute Zero**. Thus, absolute zero is the theoretical limit of least possible temperature.

Avogadro's Law:

The volume of a gas is directly proportional to the volume of moles of the gas at constant temperature and pressure. Mathematically it can be written as,

$$V \propto n$$

Or

$$V = (\text{constant})n$$

$$\frac{V}{n} = \text{Constant}$$

For different states of gas,

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

General Gas Law:

The interaction between the Pressure, Volume, Temperature and number of moles of a given sample of a gas is called General Gas Law. Which can be derived by the combination of different gas laws as follows:

From Boyle's law $V \propto \frac{1}{P}$ ----- (1)

from Charles' law $V \propto T$ ----- (2)

And from Avogadro's law $V \propto n$ ----- (3)



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From combination of above three

$$V \propto \frac{1}{P} \times T \times n$$

$$V = (\text{Constant}) \frac{nT}{P}$$

Where this constant proportionality is called universal gas constant, denoted by R .

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

Or

$$PV = nRT$$

In S. I unit

$$R = 8.314 \text{ J/mole K}$$

15.7- Kinetic Molecular Theory of Gases:

Kinetic molecular theory of gases explains the physical behavior of gases in terms of the energy and interaction of gas molecules. Assumptions of this theory are made up of ideas put forward by Maxwell, Boltzmann, Clausius, Kelvin, etc. which are as follows:

- (1) All gases are composed of molecules, which possess similar physical behavior. A finite volume of a gas contains a large number of molecules. (about 3×10^{25} molecules of air in 1 m^3 at S.T.P.).
- (2) Sizes of molecules are considered negligible as compared to the distances between them.
- (3) Molecules of a gas always remain in random motion, which follows the laws of mechanics.
- (4) There is no interaction between the molecules of a gas except when they collide with each other, the collisions are perfectly elastic.
- (5) The collisions of molecules with the walls of container are regarded as the pressure of the gas.
- (6) The average translatory Kinetic energy of the molecules is directly proportional to the absolute temperature of the gas.
- (7) Law of mechanics are assumed to be applicable to the motion of molecules.

Interpretation of the Pressure of a Gas on the Basis of Kinetic Molecular Theory of Gases:

OR

Q. Prove that $P = \frac{1}{3} \rho \bar{V}^2$

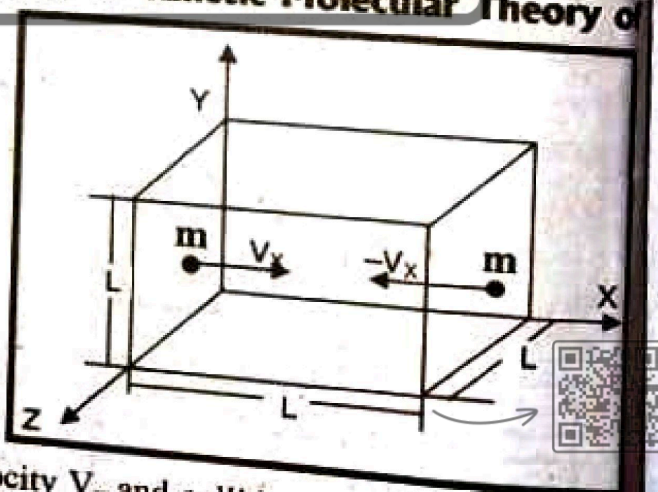
Let us consider " n " moles of a perfect gas, contained in a cubical vessel of equal dimensions each of length L . As gas molecules move randomly, therefore, for the sake of simplicity, we first consider only one molecule of mass " m " moving along x -direction only. The molecule from the left face of the cube moves with velocity V_x and collides with the right face of the cube and rebounds back with the velocity $-V_x$.

Initial momentum of molecule = $P_i = mV_x$

Final momentum of molecules = $P_f = m(-V_x) = -mV_x$

Force = Rate of change of momentum

$$F_x = \frac{P_f - P_i}{t}$$



$$F_x = \frac{-mv_x - (-mv_x)}{t}$$

$$F_x = \frac{-2mv_x}{t}$$

$$\text{OR } F_x = -2mv_x \times \frac{1}{t} \quad (2)$$

The distance travelled by the molecule during one collision or complete trip is:

$$S = 2L$$

From

$$S = vt$$

We have

$$2L = v_x \times t$$

OR

$$\frac{1}{t} = \frac{v_x}{2L}$$

$$\text{Equation. (2)} \Rightarrow F_x = -2mv_x \times \frac{v_x}{2L}$$

$$F_x = \frac{-mv_x^2}{L}$$

According to the third law of motion, the force of the molecule on the wall will be:

$$F_x = \frac{2mv_x^2}{L}$$

The above equation is for the force applied by a single molecule on the face of the cube, the force applied by "N" molecules is

$$F = F_{1x} + F_{2x} + F_{3x} + \dots + F_{Nx}$$

$$F = \frac{mv_{1x}^2}{L} + \frac{mv_{2x}^2}{L} + \dots + \frac{mv_{Nx}^2}{L}$$

$$F = \frac{m}{L} (V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \dots + V_{Nx}^2)$$

Using the definition of Pressure,

$$P = \frac{F}{A} \quad (\text{where } A = L^2)$$

OR

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

OR

$$P = \frac{m}{L^3} (V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \dots + V_{Nx}^2) \quad (3)$$

If n_v is the number of molecules per volume, then

$$n_v = \frac{N}{L^3} \quad \text{OR} \quad L^3 = \frac{N}{n_v}$$

Equation (3) \Rightarrow

$$P = \frac{m}{N/n_v} (V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \dots + V_{Nx}^2)$$

OR

$$P = nm_v \frac{(V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \dots + V_{Nx}^2)}{N}$$

Where

$$\frac{V_{1x}^2 + V_{2x}^2 + V_{3x}^2 + \dots + V_{Nx}^2}{N} = \bar{V}_x^2$$

and

$n_v m = \rho$, the density of the gas

$$P = \frac{1}{3} \rho \bar{V}^2 \quad \text{----- (4)}$$

The total velocity of molecules could be expressed as

$$\bar{V}^2 = \bar{V}_x^2 + \bar{V}_y^2 + \bar{V}_z^2$$

But where

$$\bar{V}_y^2 = \bar{V}_z^2 = \bar{V}_x^2$$

Therefore

$$\bar{V}^2 = \bar{V}_x^2 + \bar{V}_x^2 + \bar{V}_x^2$$

OR

$$\bar{V}^2 = 3\bar{V}_x^2$$

$$\bar{V}_x^2 = \frac{\bar{V}^2}{3} \quad \text{----- (5)}$$

Now, equation (4) becomes \Rightarrow

$$P = \frac{1}{3} \rho \bar{V}^2$$

Proved

Q. Prove that the Average Translatory Kinetic Energy of Gas Molecules is directly Proportional to the Absolute Temperature of The Gas:
OR Prove that $T \propto (K.E.)_{av}$ OR On the basis of KMT OF Gases, Show that $\frac{1}{2} m \bar{V}^2 = \frac{3}{2} KT$.

Proof:

According to the kinetic molecular theory, the pressure of an ideal gas is given by:

$$P = \frac{1}{3} \rho \bar{V}^2$$

Where

$\rho = n_v m$, the density of the gas

And

$n_v = \frac{N}{V}$, the number of molecules per unit volume of the gas,

therefore,

$$\rho = \frac{Nm}{V}$$

\therefore

$$P = \frac{1}{3} \frac{Nm \bar{V}^2}{V}$$

OR

$$PV = \frac{1}{3} Nm \bar{V}^2$$

Multiplying and dividing R.H.S. by 2, we get.

$$PV = \frac{2}{3} N \left(\frac{1}{2} m \bar{V}^2 \right) \quad \text{----- (1)}$$

According to the general gas law,
 $PV = nRT$

As avagadro's number is the number of molecules present in a mole of a gas, therefore,

OR

$$N_A = N/n$$

$$n = N/N_A$$

$$\therefore PV = \frac{NRT}{N_A}$$

Where $\frac{R}{N_A} = K$; the Boltzman constant

$$\therefore PV = NKT \quad \dots\dots\dots (2)$$

By equating equation (1) and (2), we get

$$\frac{2}{3} N \left(\frac{1}{2} m \bar{V}^2 \right) = N K T$$

$$\frac{1}{2} m \bar{V}^2 = \frac{3}{2} K T$$

$$(K.E.)_{ave} = \frac{3}{2} K T$$

Since the factor

$$\frac{3}{2} K = \text{Constant}$$

$$\therefore K.E. = \text{Constant} \times T$$

OR

Note:

$$(K.E.)_{ave} \propto T$$

Proved

Average translational kinetic energy is also called kinetic energy per molecule of the gas i.e.

$$K.E. \text{ per molecule} = (K.E.)_{ave} = \frac{3}{2} K T$$

While the kinetic energy of per mole of a gas can be written as:

$$K.E \text{ per mole} = \frac{3}{2} R T$$

