

Chapter

Kinetic Theory of Gases

Day - 1

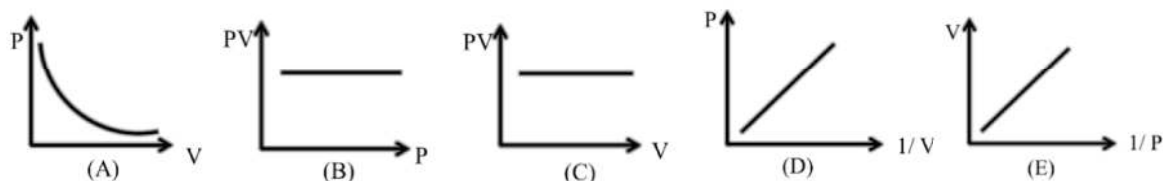
GASSES

In gases the intermolecular forces are very weak and its molecules may fly apart in all directions. So the gas is characterized by the following properties:

- (i) It has no shape and size and can be obtained in a vessel of any shape or size.
- (ii) It expands indefinitely and uniformly to fill the available space.
- (iii) It exerts pressure on its surroundings.
- (iv) Intermolecular forces in gas are minimum.
- (v) They can easily compress and expand.

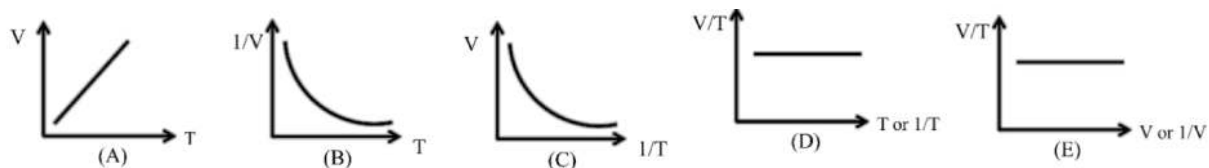
(i) Boyle's law: For a given mass of an ideal gas at constant temperature, the volume of a gas inversely proportional to its pressure.

$$\text{i.e. } V \propto \frac{1}{P} \text{ or } PV = \text{constant} \Rightarrow P_1 V_1 = P_2 V_2$$



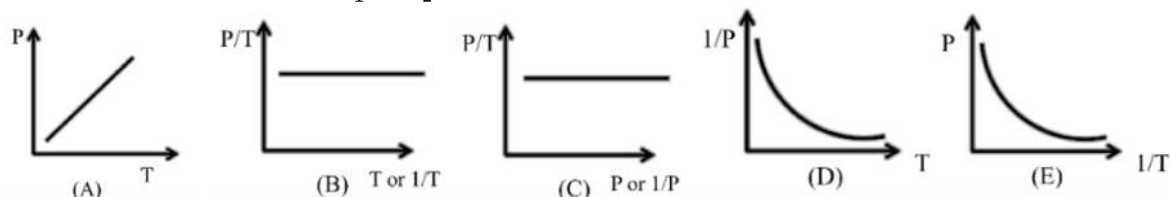
(2) Charles'law : For the pressure remaining constant, the volume of the given mass of a gas is directly proportional to its absolute temperature.

$$\text{i.e., } V \propto T \Rightarrow \frac{V}{T} = \text{constant} \Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$



(3) Gay-Lussac's law or pressure law : The volume remaining constant, the pressure of a given mass of a gas is directly proportional to its absolute temperature.

$$P \propto T \text{ or } \frac{P}{T} = \text{constant} \Rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2}$$



(4) **Avogadro's law:** Equal volume of all the gases under similar conditions of temperature and pressure contain equal number of molecules, i.e., $N_1 = N_2$.

(5) **Graham's law of diffusion:** When two gases at the same pressure and temperature are allowed to diffuse into each other, the rate of diffusion of each gas is inversely proportional to the square root of the density of the gas, i.e., $r \propto \frac{1}{\sqrt{\rho}} \propto \frac{1}{\sqrt{M}}$

M is the molecular weight of the gas) $\Rightarrow \frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_2}{M_1}}$

If V is the volume of gas diffused in t sec then $r = \frac{V}{t} \Rightarrow \frac{r_1}{r_2} = \frac{V_1}{V_2} \times \frac{t_2}{t_1}$

(6) **Dalton's law of partial pressure :** The total pressure exerted by a mixture of non-reacting gases occupying a vessel is equal to the sum of the individual pressure which each gases exert it alone occupied the same volume at a given temperature.

For n gases $P = P_1 + P_2 + P_3 + \dots P_n$

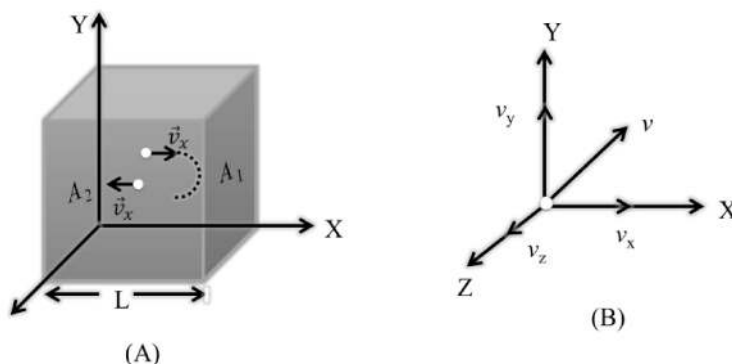
Where P = Pressure exerted by mixture and $P_1, P_2, P_3, \dots P_n$ = Partial pressure of component gases.

EQUATION OF STATE OR IDEAL GAS EQUATION

Quantity of gas	Equation	Constant
1 mole gas	$PV = RT$	R = universal gas constant
μ mole gas	$PV = \mu RT$	
1 molecule of gas	$PV = \left(\frac{R}{N_A}\right)T = kT$	k = Boltzmann's constant
N molecules of gas	$PV = NkT$	
1 g of gas	$PV = \left(\frac{R}{M}\right)T = rT$	r = Specific gas constant
m g of gas	$PV = mrT$	

PRESSURE OF AN IDEAL GAS

Consider an ideal gas (consisting of N molecules each of mass m) enclosed in a cubical box of side L.



(1) **Instantaneous velocity:** Any molecule of gas moves with velocity \vec{v} in any direction

$$\text{where } \vec{v} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k} \Rightarrow v = \sqrt{v_x^2 + v_y^2 + v_z^2}.$$

Due to random motion of molecule $v_x = v_y = v_z \Rightarrow v^2 = 3v_x^2 = 3v_y^2 = 3v_z^2$

(2) **Time during collision:** Time between two successive collision with the wall A_1 .

$$\Delta t = \frac{\text{Distance travelled by molecule two successive collision}}{\text{Velocity of molecule}} = \frac{2L}{v_x}$$

(3) **Collision frequency (n):** It means the number of collisions per second. Hence $n = \frac{1}{\Delta t} =$

$$\frac{v_x}{2L}$$

(4) **Change in momentum:** If a molecules collides with the shaded wall (A_1) with velocity v_x and rebounds with velocity $-v_x$.

The change in momentum of the molecule

$$\Delta p = (-mv_x) - (mv_x) = -2mv_x$$

As the momentum remains conserved in a collision, the change in momentum of the wall A_1 is $\Delta p = 2mv_x$

After rebound this molecule travels towards opposite wall A_2 with velocity $-v_x$, collides to it and again rebounds with velocity v_x towards wall A_1 .

(5) **Force on wall:** Force exerted by a single molecule on shaded wall is equal to rate at which the momentum is transferred to the wall by this molecule.

$$\text{i. e., } F_{\text{single molecule}} = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{(2L/v_x)} = \frac{mv_x^2}{L}$$

The total force on the wall A_1 due to all the molecules

$$F_x = \frac{m}{L} \sum v_x^2 = \frac{m}{L} (v_{x_1}^2 + v_{x_2}^2 + v_{x_3}^2 + \dots) = \frac{mN}{L} \overline{v_x^2}$$

$\overline{v_x^2}$ = mean square of x component of the velocity .

(6) **Pressure:** Now pressure is defined as force per unit area, hence pressure on shaded wall

$$P_x = \frac{F_x}{A} = \frac{mN}{AL} \overline{v_x^2} = \frac{mN}{V} \overline{v_x^2}$$

For any molecule, the mean square velocity $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$;

$$\text{By symmetry } \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \Rightarrow \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{\overline{v^2}}{3}$$

Total pressure inside the container

$$P = \frac{1}{3} \frac{mN}{V} \overline{v^2} = \frac{1}{3} \frac{mN}{V} v_{\text{rms}}^2 \quad (\text{where } v_{\text{rms}} = \sqrt{\overline{v^2}})$$

The motion of molecules in a gas is characterised by any of the following three speeds :

(1) **Root mean square speed:** It is defined as the square root of mean of square of the speed of different molecules

$$\text{i. e., } v_{\text{rms}} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2 + \dots}{N}} = \sqrt{v^2}$$

(i) From the expression of pressure $P = \frac{1}{3} \rho v_{\text{rms}}^2$

$$\Rightarrow v_{\text{rms}} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3PV}{\text{Mass of gas}}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}}$$

where $\rho = \frac{\text{Mass of gas}}{V} = \text{Density of the gas}$, $M = \mu \times (\text{mass of gas})$,

$PV = \mu RT$, $R = kN_A$, $k = \text{Boltzmann's constant}$,

$$m = \frac{M}{N_A} = \text{mass of each molecule.}$$

(ii) With rise in temperature rms speed of gas molecules increases as $v_{\text{rms}} \propto \sqrt{T}$.

(iii) With increases in molecular weight rms speed of gas molecule decreases as $v_{\text{rms}} \propto \frac{1}{\sqrt{M}}$

e.g., rms speed of hydrogen molecules is four times that of oxygen molecules at the same temperature.

(iv) rms speed of gas molecules is of the order of km/s e.g. at NTP for hydrogen gas

$$(v_{\text{rms}}) = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 273}{2 \times 10^3}} = 1840 \text{ m/s.}$$

(2) **Most probable speed:** The particles of a gas have a range of speeds. This is defined as the speed which is possessed by maximum fraction of total number of molecules of the gas. E.g., if speed of 10 molecules of a gas are 1, 2, 2, 3, 3, 3, 4, 5, 6, 6 km/s, then the most probable speed is 3 km/s, as maximum fraction of total molecules possess this speed.

$$\text{Most probable speed } v_{\text{mp}} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2kT}{m}}$$

(3) **Average speed:** It is the arithmetic mean of the speeds of molecules in a gas at given temperature.

$$v_{\text{av}} = \frac{v_1 + v_2 + v_3 + v_4 + \dots}{N}$$

and according to kinetic theory of gases

$$\text{Average speed } v_{\text{av}} = \sqrt{\frac{8P}{\pi\rho}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}$$

MEAN FREE PATH

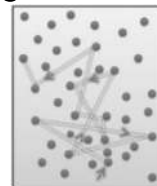
(1) The distance travelled by a gas molecule between two successive collisions is known as free path.

$$\lambda = \frac{\text{Total distance travelled by a gas molecule between successive collisions}}{\text{Total number of collisions}}$$

During two successive collisions, a molecule by a gas moves in a straight line with constant velocity.

Let $\lambda_1, \lambda_2, \lambda_3 \dots$ be the distance travelled by a gas molecule during n collisions respectively, then the mean free path of a gas molecule is given by

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n}{n}$$



$$(2) \lambda = \frac{1}{\sqrt{2} n \pi d^2}$$

where d = Diameter of the molecule,

n = Number of molecules per unit volume

(3) As $PV = \mu RT$

$$= \mu N k T \Rightarrow \frac{N}{V} = \frac{P}{kT} = n = \text{Number of molecule per unit volume so } \lambda = \frac{1}{\sqrt{2}} \frac{kT}{\pi d^2 P}$$

LAW OF EQUIPARTITION OF ENERGY [BOLTZMANN LAW]

According to this law, for any system in thermal equilibrium, the total energy is equally distributed among its various digress of freedom. And each degree of freedom is associated with energy $\frac{1}{2} kT$ (where $k = 1.38 \times 10^{-23}$ J/K, T = absolute temperature of the system).

SPECIFIC HEAT (C_p AND C_v) OF A GAS

(1) **Specific heat at constant volume (C_v)** : The specific heat of a gas at constant volume is defined as the quantity of heat required to raise the temperature of unit mass of gas through 1°C or 1 K when its volume is kept constant, i.e., $c_v = \frac{(\Delta Q)_v}{m\Delta T}$

If instead of unit mass, 1 mole of gas is considered, the specific heat is called molar specific heat a constant volume and is represented by capital C_v .

$$C_v = M_{c_v} = \frac{M(\Delta Q)_v}{m\Delta T} = \frac{1}{\mu} \frac{(\Delta Q)_v}{m\Delta T} \quad \left[\text{As } \mu = \frac{m}{M} \right]$$

(2) **Specific heat at constant pressure (C_p)** : The specific heat of a gas at constant pressure is defined as the quantity of heat required to raise the temperature of unit mass of gas through 1 K when its pressure is kept constant, i.e., $c_p = \frac{(\Delta Q)_p}{m\Delta T}$

If instead of unit mass, 1 mole of gas is considered, the specific heat is called molar specific heat at constant pressure and is represented by C_p .

$$C_p = M_{c_p} = \frac{M(\Delta Q)_p}{m\Delta T} = \frac{1}{\mu} \frac{(\Delta Q)_p}{\Delta T} \quad \left[\text{As } \mu = \frac{m}{M} \right]$$

(iii) **Vander Waal's gas equations**

$$\text{For 1 mole of gas } \left(P + \frac{a}{V^2} \right) (V - b) = RT$$

$$\text{For } \mu \text{ moles of gas } \left(P + \frac{a\mu^2}{V^2} \right) (V - \mu b) = \mu r t$$

Here a and b are constant called Vander Waal's constant.

Dimension : $[a] = [ML^5T^{-2}]$ and $[b] = [L^3]$

Units : $a = N \times m^4$ and $b = m^3$. Real gases obey this equation at high pressure and low temperature.

(iv) **Relation between Vander Waal's constants and T_c , P_c , V_c**

$$T_c = \frac{8a}{27Rb}, P_c = \frac{a}{27b^2}, V_c = 3b,$$

$$a = \frac{27R^2 T_c^2}{64 P_c}, b = \frac{R}{8} \left(\frac{T_c}{P_c} \right) \text{ and } \frac{P_c V_c}{T_c} = \frac{3}{8} R$$

Example:- A closed container of volume 0.02 m^3 contains a mixture of neon and argon gases, at a temperature of 27°C and pressure of $1 \times 10^5 \text{ Nm}^{-2}$. The total mass of the mixture is 28 g . if the molar masses of neon and argon are 20 and 40 g mol^{-1} respectively, find the masses of the individual gases in the container assuming them to be ideal. (Universal gas constant $R = 8.314 \text{ J/mol-K}$).

Solution: Given, temperature of the mixture, $T = 27^\circ\text{C} = 300 \text{ K}$

Let m be the mass of the neon gas in the mixture. Then, mass of argon would be $(28-m)$

Number of gram moles of neon, $n_1 = \frac{m}{20}$

Number of gram moles of argon, $n_2 = \frac{(28-m)}{40}$

From Dalton's law of partial pressure

Total pressure of the mixture (p) = Pressure due to neon (p_1) + Pressure due to argon (p_2)

$$\text{or } p = p_1 + p_2 = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} = (n_1 + n_2) \frac{RT}{V}$$

Substituting the values

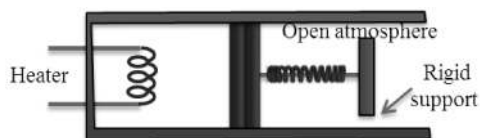
$$1.0 \times 10^5 = \left(\frac{m}{20} + \frac{28-m}{40} \right) \frac{(8.314)(300)}{0.02}$$

Solving this equation, we get

$$28 - m = 23.926 \text{ g} \Rightarrow m = 4.074 \text{ g}$$

Therefore, in the mixture, 4.074 g neon is present and the rest i.e., 23.926 g argon is present.

Example:- An ideal monoatomic gas is confined in a cylinder by a spring –loaded piston of cross –section $8.0 \times 10^{-3} \text{ m}^2$. Initially the gas is at 300 K and occupies a volume of $2.4 \times 10^{-3} \text{ m}^3$ and the spring is in its relaxed (unscratched, uncompressed) state. The gas is heated by a small electric heater until the piston moves out slowly by 0.1 m .



Calculate the final temperature of the gas and the heat supplied (in joules) by the heater. The force constant of the supplied is 8000 N/m, and the atmospheric pressure $2.0 \times 10^5 \text{ Nm}^{-2}$. The cylinder and the piston are thermally insulated. The piston is massless and there is no friction between the piston and the cylinder. Neglect heat loss through the lead wires of the heater coil is negligible. Assume the spring to be massless.

Solution: Final pressure = $p_0 + \frac{kx}{A}$

$$= 1.0 \times 10^5 = \frac{(8000)(0.1)}{8 \times 10^{-3}} = 2 \times 10^5 \text{ N/m}^2$$

Final volume = $2.4 \times 10^{-3} + (0.1)(8 \times 10^{-3})$
 $= 3.2 \times 10^{-3} \text{ m}^3$

Applying, $\frac{p_i V_i}{T_i} = \frac{p_f V_f}{T_f}$

We have, $T_f = \left(\frac{p_f V_f}{p_i V_i} \right) T_i$

$$= \frac{(2 \times 10^5)(3.2 \times 10^{-3})}{(1 \times 10^5)(2.4 \times 10^{-3})} \times 300 = 800 \text{ K}$$

Heat supplied $Q = W_{\text{gas}} + \Delta U$

$$= p_0(\Delta V) + \frac{1}{2} kx^2 + nC_v \Delta T \quad \left(\text{as } n = \frac{p_i V_i}{RT_i} \right)$$

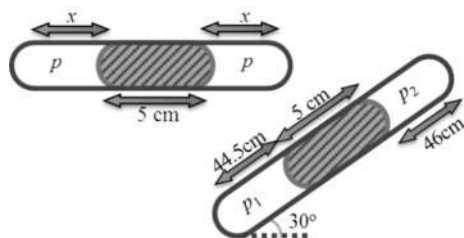
$$= (10^5)(3.2 - 2.4) \times 10^{-3} + \frac{1}{2} \times 8000 \times (0.1)^2$$

$$+ \frac{10^5 \times 2.4 \times 10^{-3}}{8.31 \times 300} \times \frac{3}{2} \times 8.31 \times (800 - 300)$$

$$= 80 + 40 + 600 = 720 \text{ J}$$

Example:- A thin tube of uniform cross-section is sealed at both ends. It lies horizontally, the middle 5 cm containing mercury and the two equal ends containing air at the same pressure p . when the tube is held at an angle of 60° with the vertical direction, the length of the air column above and below the mercury column are 46 cm and 44.5 cm respectively. Calculate the pressure p in centimeter of mercury. (The temperature of the system is kept at 30°C).

Solution: From the two figures we can see that



$$2x + 5 = 44.5 + 5 + 46 \Rightarrow x = 45.25 \text{ cm}$$

Let A be the area of cross –section of the tube. Process is given isothermal. Hence, apply $pV =$ constant in two sides of mercury column.

$$pAx = p_2A (44.5) \text{ or } p (45.25) = p_2(44.5) \quad \dots(i)$$

$$\text{Similarly, } pAx = p_1A (46)$$

$$\text{Or } p (45.25) = p_1(46) \quad \dots(ii)$$

$$\text{From figure (b), } p_2 = p_1 + 5 \sin 30^\circ \quad \dots(iii)$$

Solving these three equations, we get

$$p = 75.4 \text{ cm of Hg}$$

Example:- Two glass bulbs of equal volume are connected by a narrow tube and are filled with a gas at 0°C and a pressure of 76 cm of mercury. One of the bulbs is then placed in melting ice and the other is placed in a water bath maintained at 62°C . What is the new value of the pressure inside the bulbs? The volume of the connecting tube is negligible?

Solution: Let x moles transfer from bulb of higher temperature to lower temperature.

Applying $pV = nRT$ for both the bulbs initially and finally

$$76 \times V = nR \times 273 \quad \dots(i)$$

$$p' \times V = (n + x) R \times 273 \quad \dots(ii)$$

$$p' \times V = (n - x) R \times 335 \quad \dots(iii)$$

Solving these equations, we get $n = \frac{602}{62} x$

Now, dividing Eq. (ii) with Eq. (i) we get

$$\frac{p'}{76} = \frac{n + x}{n} = 1 + \frac{x}{n} = 1 + \frac{62}{602} = 1.103$$

$$P' = 83.83 \text{ cm of Hg}$$

Example:- One gram mole of oxygen at 27°C and one atmospheric pressure is enclosed in a vessel. (a) Assuming the molecules to be moving with v_{rms} , find the number of collisions per second which the molecules make with one square meter area of the vessel wall. (b) The vessel is next thermally insulated and moved with a constant speed v_0 . It is then suddenly stopped. The process results in a rise of the temperature of the gas by 1°C . Calculate the speed v_0 .