Kinetic Theory of Gases

Gas

Real Gas	Ideal Gas
→ It follows gas laws only at High T & low P	→ It follows the gas laws at all T & P
→ finite size of molecule	→ Negligible size of molecule
→ Intermolecular attraction exist.	→ No Intermolecular Attraction
→ $E = K + U$	→ $E = K + U = K + 0 = K$
→ $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$	→ $PV = nRT$

Postulates of Kinetic Theory of Gases:

→ Molecules are spherical, identical & rigid.

→ follow zig-zag path.

→ Volume of molecules of gas are negligible in comparision to volume of vessel.

→ Negligible mass of molecules → Collision - Elastic [PE conserved, K.E]

→ No intermolecular interaction. → $E = K.E = f(T)$

→ No Effect of Gravitation.

→ Gas molecules exert pressure on the wall of vessel.

Pressure exerted by molecules of ideal gas

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

$P \rightarrow$ Pressure
$m \rightarrow$ mass of 1 molecule
$n \rightarrow$ no. of molecules
$mn = M =$ Total mass of gas
$V \rightarrow$ Volume
$\bar{v}^2 \rightarrow$ mean square velocity

$$\bar{v}^2 = \frac{v_1^2 + v_2^2 + v_3^2 + \cdots + v_n^2}{n}$$

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

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

$$P = \frac{2}{3}\bar{E} \quad \text{---(2)}$$

$\bar{E} = \frac{\frac{1}{2}m\bar{v}^2}{V}$ = Average Kinetic Energy per unit volume.

From Equation (1)

$$P = \frac{1}{3}\frac{mn}{V}v_{rms}^2$$

$v_{rms} = \sqrt{\bar{v}^2}$ = Root mean square velocity

$$PV = \frac{1}{3}mn\,v_{rms}^2 \quad \text{---(3)}$$

For 1 mole ideal gas:

$n = N_A$

$mn = mN_A = M =$ Molar mass

$PV = RT$

From eqn (3)

$$RT = \frac{1}{3}\cdot M v_{rms}^2$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} \quad \text{---(4)}$$

Average Kinetic Energy :-

for 1 mole:

$$\bar{E} = \frac{1}{2} m \bar{v^2}$$

$$\bar{E} = \frac{1}{2} m v_{rms}^2 = \frac{1}{2} m \cdot \frac{3RT}{m}$$

$$\boxed{\bar{E} = \frac{3}{2} RT} \quad \text{——(5)} \rightarrow 1 \text{ mole}$$

for M mole:

$$\boxed{\bar{E} = \frac{3}{2} MRT}$$

for 1 molecule:

1 mole = N_A molecule

Average K.E of N_A molecule = $\bar{E}$

Average K.E of 1 molecule = $\frac{\bar{E}}{N_A}$

$$= \frac{3RT}{2N_A}$$

$$\boxed{\bar{E} = \frac{3}{2} K_B T} \rightarrow 1 \text{ molecule}$$

$$\boxed{K_B N_A = R}$$

R = Universal Gas Constant = 8.31 J/mol-K ≃ 2 Cal/mol-K

$N_A = 6.023 \times 10^{23}$ = Avogadro Number

$K_B = 1.38 \times 10^{-23}$ J/K = Boltzman's Constant.

Important Point !-

At T=0K ,
$$\left.\begin{aligned} v_{rms} &= 0 \\ \bar{E} &= 0 \\ V &= 0 \\ P &= 0 \end{aligned}\right\}$$

At T=-ive , $\bar{E} = \frac{3}{2}RT$ = -ive = which is impossible

So negative temp. on Kelvin Scale is not possible

At NTP
$$\begin{cases} P = 1\,atm = 1.01 \times 10^5\ Pa \\ T = 0^\circ C = 273K \end{cases}$$

→ Volume of 1 mole gas = 22.4 L = Volume of N_A molecules

Ideal Gas Equation!-

$$P = \frac{1}{3}\frac{mn}{V}\overline{v^2}$$

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

$$PV = \frac{1}{3}mn\,v_{rms}^2$$

$$PV = \frac{1}{\cancel{3}}\cancel{m}n \times \frac{\cancel{3}K_BT}{\cancel{m}}$$

$$\boxed{PV = nK_BT} \longrightarrow \text{for } n \text{ molecule}$$

$$\boxed{PV = K_BT} \longrightarrow \text{for 1 molecule}$$

$n = N_A = 1$ mole

$$\boxed{PV = RT} \longrightarrow \text{for 1 mole}$$

$$\boxed{PV = \mu RT} \longrightarrow \text{for } \mu \text{ mole}$$

Gaseous Law

① Boyle's law:

$$PV = \mu RT$$

At const $T \rightarrow PV =$ Constant $\Rightarrow \boxed{P_1V_1 = P_2V_2}$

At constant T, The Pressure of a definik mass of gas inversely Proportional to its volume.

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

(2) Charle's law:

$$PV = \mu RT$$

At constant Pressure

$$\frac{V}{T} = \text{constant} \Rightarrow \boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$$

→ At constant P, The volume of fixed mass of gas is directly proportioned to it absolute temp.

$$\boxed{V \propto T}$$

Let $t_1 = 0^\circ C \rightarrow V_1 = V_0$

$t_2 = t^\circ C \rightarrow V_2 = V_t$

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} = \frac{0+273}{t+273}$$

$$\frac{V_0}{V_t} = \frac{273}{t+273}$$

$$\boxed{V_t = V_0\left[1 + \frac{t}{273}\right] = V_0\left[1 + \alpha t\right]}$$

Here $\alpha = \frac{1}{273}\ ^\circ C^{-1}$ = coefficient of volume expansion.

(3) Pressure law / Gay-Lussac Law :

$$PV = \mu RT$$

At constant volume

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

→ At constant V, The pressure of fixed mass of gas is directly proportional to its absolute temp.

let $T_1 = 0^\circ C \Rightarrow P_1 = P_0$

$T_2 = t^\circ C \Rightarrow P_2 = P_t$

$$\frac{P_0}{0+273} = \frac{P_t}{t+273}$$

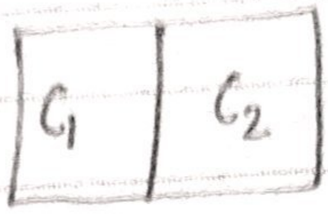
$$P_t = P_0\left(1 + \frac{t}{273}\right)$$

$$\boxed{P_t = P_0(1 + \beta t)}$$

Here $\beta = \frac{1}{273}\,^\circ C^{-1}$ = Coefficient of pressure expansion.

(4) Graham's law of diffusion :-

$C_1 > C_2$



C = concentration

Diffusion :- The movement of gas molecules from high conc. region to low conc. region is called diffusion.

$$P = \frac{1}{3} \frac{mn}{V} \overline{v^2}$$

$$P = \frac{1}{3} \frac{m}{V} v_{rms}^2$$

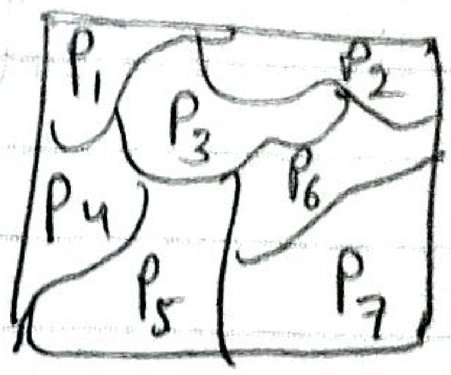
$$P = \frac{1}{3} \rho v_{rms}^2$$

$$\boxed{v_{rms} = \sqrt{\frac{3P}{\rho}}} \quad \text{—— Imp.}$$

$\Rightarrow$ Rate of Diffusion $\propto \frac{1}{\sqrt{\text{molecular density}}}$

(5) Dalton's law of Partial Pressure :—

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



At Constant V & T, the total Pressure of gas is equal to the sum of partial pressure of individual gases.

Maxwell's Law of distribution of Speed :-

(1-) RMS speed :-

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \cdots v_n^2}{n}}$$

for 1 mole

$$v_{rms} = \sqrt{\frac{3RT}{m}}$$

$R = K_B N_A$

or

$$v_{rms} = \sqrt{\frac{3K_BT}{m}}$$

$m = mn = mxN_A$

↓ mass of 1 mole

↓ mass of 1 molecule

for 1 molecule

(2) Average Speed :-

$$\bar{v} = \sqrt{\frac{8RT}{\pi m}} \longrightarrow \text{for 1 mole}$$

or

$$\bar{v} = \sqrt{\frac{8K_BT}{\pi m}} \longrightarrow \text{for 1 molecule}$$

(3) Most Probable speed :-

The speed of most number of molecules

$$v_{mp} = \sqrt{\frac{2RT}{M}} \longrightarrow \text{For 1 mole}$$

or

$$v_{mp} = \sqrt{\frac{2K_BT}{m}} \longrightarrow \text{for 1 molecule}$$

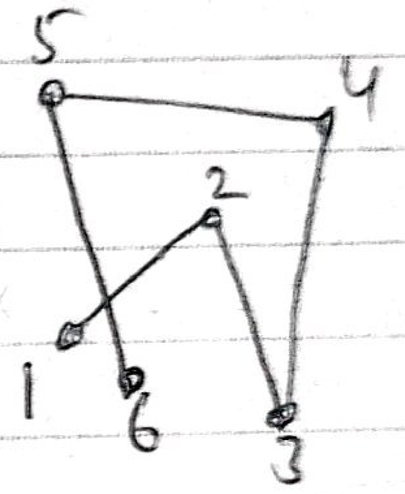
$$v_{rms} : \bar{v} : v_{mp} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2}$$

$$= 1.73 : 1.61 : 1.41$$

$$v_{rms} > \bar{v} > v_{mp}$$

Relaxation Time & Mean Free Path :—

→ The Average time-interval between two successive collision is called Relaxation time (τ)



→ The average/mean distance between two successive collision is called mean free path (λ).

$$\lambda = \frac{1}{\sqrt{2}\pi n d^2} = \frac{K_B T}{\sqrt{2}\pi P d^2} = \frac{m}{\sqrt{2}\pi \rho d^2}$$

$n = \frac{N}{V}$ = number density

$d = \Theta$ = diameter of molecule

T = temp.

ρ = density

m = mass of 1 molecule.

Degree of freedom :—

→ The total number of independent co-ordinate required to completely describe the position & configuration of a system.

Monoatomic
(He, Ne, Ar, ---)

DOF = $\boxed{f = 3T = 3}$

At high temp. vibration mode also activate

Diatomic
(H_2, O_2, N_2 ---)

$\boxed{f = 3T + 2R = 5}$

→ $f = 3T + 2R + 2V = 7$

Polyatomic

H_2O

→ Non Linear
(H_2O, NH_3, ---)

$\boxed{f = 3T + 3R = 6}$

high temp IV = 7

→ Linear
(CO_2, C_2H_2)

$\boxed{f = 3T + 2R = 5}$

high temp IV = 6

T → Translation
R → Rotational
V → Vibrational

Relation between C_p & C_v :—

$$\boxed{\gamma = \frac{C_p}{C_v} = \frac{E_s}{E_T} = 1 + \frac{2}{f}}$$

$$\boxed{C_v = \frac{1}{2} f R = \frac{R}{\gamma - 1}}$$

$$\boxed{C_p - C_v = R}$$ Mayer's formula

$C_v \rightarrow$ molar Specific heat at constant volume

$C_p \rightarrow$ molar Specific heat at constant pressure

$\beta_s \rightarrow$ Adiabatic Bulk modulus

$\beta_T \rightarrow$ Isothermal Bulk modulus

$f \rightarrow$ DOF $\rightarrow$ Degree of freedom.

$$[C_v]_{mix} = \frac{n_1 C_{v_1} + n_2 C_{v_2} + n_3 C_{v_3} + \cdots}{n_1 + n_2 + n_3 + \cdots}$$

$$[C_p]_{mix} = \frac{n_1 C_{p_1} + n_2 C_{p_2} + n_3 C_{p_3} + \cdots}{n_1 + n_2 + n_3 + \cdots}$$

$$[\gamma]_{mix} = \frac{[C_p]_{mix}}{[C_v]_{mix}}$$

$[C_p]_{mix} = R + [C_v]_{mix}$ $\rightarrow$ By Mayer's formula

γ

- Monoatomic: $f = 3$; $\gamma = 1 + \frac{2}{3} = 1 + 0.66$; $\gamma = 1.67$
- Di-atomic: $f = 5$; $\gamma = 1 + \frac{2}{5} = 1 + 0.4$; $\gamma = 1.40$
- Polyatomic: $f = 6$; $\gamma = 1 + \frac{2}{6} = 1 + 0.33$; $\gamma = 1.33$

Law of Equipartition of Energy :—

At Equilibrium —
The total K.E of gas is equally distributed among its all degree of freedom

At temp T —
The K.E associated with each degree of freedom is $\frac{1}{2}K_BT$

This is called law of Equipartition of Energy.

→ K.E associated with 1 molecule & 1 DOf $= \frac{1}{2}K_BT$

K.E associated with 1 molecule & f DOf $= \frac{1}{2}fK_BT$

K.E associated with 1 mole (N_A molecule) & f DOf $= \frac{1}{2}N_AfK_BT$
$= \frac{1}{2}fRT$

K.E associated with μ mole & f DOf $= \frac{1}{2}\mu fRT$

↳ $\boxed{E = \frac{1}{2}\mu fRT}$ — μ mole