

16/1/20
Ch-12 - Kinetic Theory

* Behaviour of Gases:-

→ For any gas, relation of pressure, temp & volume is as follows:-

$$PV \propto T$$

$$PV = KT$$

↑ constant which depends on volume of given gas

→ Here $K \propto N$ (no. of atoms of gas)

$$K = Nk_b$$

↑ Boltzmann const.

$$k_b = 1.38 \times 10^{-23}$$

Q80, $PV = Nk_b T$

Q0, for any gas

$$\frac{P_1 V_1}{N_1 T_1} = \frac{P_2 V_2}{N_2 T_2}$$

→ For any gas for equal temp & pressure in equal volume of gas, no. of atoms are equal

} Avogadro's hypothesis.

* Mole Concept:-

$$T = 0^\circ C = 273K$$

$$P_{atm} = 1.013 \times 10^5 Pa$$

STP = Standard temp. & pressure

→ For any gas at STP, mass of gas of 22.4 l is always equal to molecular mass of that gas. And this amount of gas is 1 mole.

$$M = \mu M_0 \rightarrow \mu = \frac{M}{M_0}$$

→ For all gases, no. of molecules in one mole gas is equal & that is $N_A = 6.023 \times 10^{23}$

→ For given gas no. of molecules in given μ mole gas is

$$N = \mu N_A$$

$$\therefore \mu = \frac{N}{N_A}$$

→ We know for any gas,

$$PV = N k_b T$$

from ideal gas eqⁿ,

$$PV = \mu RT$$

from comparing,

$$\mu R = N k_b$$

for 1 mole gas $N = N_A$

$$\therefore, 1 \times R = N_A k_b$$

$$\therefore, \boxed{R = N_A k_b}$$

* Dalton's law of Partial Pressure:-

→ Let consider mixture of different non-reacting gas

→ If mole of gases is $\mu_1, \mu_2, \dots, \mu_n$

→ Here total volume of this mixture is V then for given pressure P & temp T .

$$PV = \mu RT$$

$$PV = (\mu_1 + \mu_2 + \dots + \mu_n) RT$$

$$P = \frac{\mu_1 RT}{V} + \frac{\mu_2 RT}{V} + \dots + \frac{\mu_n RT}{V}$$

Here $\frac{\mu_i RT}{V} = P_i =$ partial pressure of i^{th} gas.

→ Pressure of gas at given temp & volume in absence of other gas

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

⇒ We know that $PV = \mu RT$
 where $\mu = \frac{M}{M_0}$

$$\text{So, } PV = \frac{M}{M_0} RT$$

$$P = \frac{M}{V} \frac{RT}{M_0}$$

$$\therefore \boxed{P = \rho RT} \quad \left. \begin{array}{l} \text{where } \rho = \\ \text{density of gas} \end{array} \right\}$$

⇒ We know, $PV = \mu RT$
 $\mu = \frac{N}{N_A}$

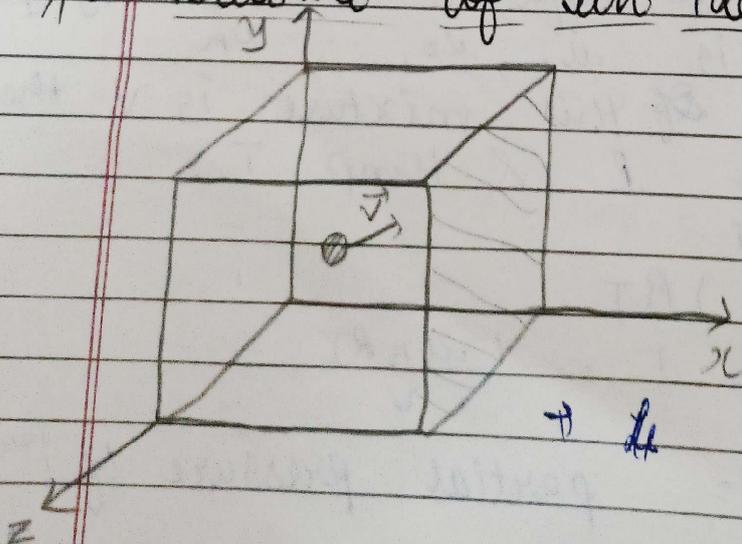
$$PV = \frac{N}{N_A} RT$$

$$P = \frac{N}{V} \frac{RT}{N_A} \quad \text{where } \frac{N}{V} = n \quad \&$$

$n = \text{molar density of gas}$

$$\text{So, } P = \frac{nRT}{N_A}$$

* Pressure of an ideal gas:-



Let consider a particle of ideal gas moving with velocity $\vec{v} = (v_x, v_y, v_z)$

⇒ Let consider this particle collide with wall which is parallel to xy plane after

$$p = mv_x - (-mv_x)$$

- Δt time molecule.
- when particle collide with wall it transfer momentum to wall which is $2mv_x$ where m is mass of ideal gas molecule.
- That means the molecules which are at distance less or equal to $v_x \Delta t$ can collide with wall, which is parallel to XY plane in Δt time.
- If area of plane is A then we can say molecules in $Av_x \Delta t$ can collide with wall in Δt time.
- If no. density of molecules is n , then no. of molecules which may collide with wall is $nAv_x \Delta t$.
- But on avg. we can say half of $nAv_x \Delta t$ move in $+x$ & other half move in $-x$ direction.

→ That means momentum transfer on wall in Δt time is

$$\Delta p = 2mv_x \times \frac{1}{2} nAv_x \Delta t$$

$$\Delta p = nmv_x^2 A \Delta t$$

So, force acting on wall

$$F = \frac{\Delta p}{\Delta t} = \frac{nmv_x^2 A \Delta t}{\Delta t}$$

$$F = nmv_x^2 A$$

→ Due to this force pressure on wall

$$P = \frac{F}{A} = \frac{nmv_x^2 A}{A} = nmv_x^2$$

→ For macroscopic level we can write for all molecules

$$P = nm \langle v_x^2 \rangle$$

Here $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$

$$\text{but } \vec{v} = (v_x, v_y, v_z)$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

$$\langle v^2 \rangle = 3 \langle v_x^2 \rangle$$

$$\text{So, } \langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

$$\text{So, } p = \frac{1}{3} n m \langle v^2 \rangle$$

• extra:

$$\sqrt{\langle v^2 \rangle} = v_{rms}$$

$$\langle v^2 \rangle = v_{rms}^2$$

$$\text{So, } p = \frac{1}{3} n m v_{rms}^2$$

* Kinetic Interpretation of temperature:

→ From kinetic interpretation of pressure,

$$p = \frac{1}{3} n m v_{rms}^2$$

where $p = \frac{nRT}{V}$

& $n = \frac{N}{V}$

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

$$\frac{3nRT}{2} = \frac{Nm}{2} v_{rms}^2$$

$$\frac{3nRT}{2} = \frac{1}{2} (Nm) (v_{rms}^2)$$

$$nR = n N_A K_b$$

$$nR = \frac{N}{N_A} N_A K_b$$

$$\therefore nR = N K_b$$

$$\frac{3}{2} N K_b T = \frac{1}{2} N m V_{rms}^2$$

$$\frac{1}{2} m V_{rms}^2 = \frac{3}{2} K_b T$$

$$E = \frac{3}{2} K_b T$$

Kinetic energy of a molecule

For 1 mole gas

Total energy

$$U = N_A E$$

$$= N_A \times \frac{3}{2} K_b T$$

$$= \frac{3}{2} R T$$

$$P = \frac{1}{3} n m V_{rms}^2$$

$$= \frac{1}{3} \frac{N}{V} m V_{rms}^2$$

$$= \frac{1}{3} \frac{M}{V} V_{rms}^2$$

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

$$V_{rms} = \sqrt{\frac{3P}{\rho}}$$

$$E = \frac{3}{2} K_b T$$

$$\frac{1}{2} m V_{rms}^2 = \frac{3}{2} K_b T$$

$$\frac{m}{M_0} = \frac{N}{N_A} \therefore m = \frac{M_0}{N_A}$$

$$\frac{M_0}{N_A} V_{rms}^2 = 3 K_b T$$

$$V_{rms}^2 = \frac{3 K_b N_A T}{M_0}$$

$$V_{rms} = \sqrt{\frac{3 R T}{M_0}}$$

* Dalton's partial pressure law:-
 → Let us consider mixtures of non-reacting gas.

→ So, total pressure due to this gas

$$P = \frac{1}{3} n m V_{rms}^2$$

$$= \frac{1}{3} (n_1 + n_2 + \dots + n_n) m V_{rms}^2$$

$$= \frac{1}{3} n_1 m v_{rms}^2 + \frac{1}{3} n_2 m v_{rms}^2 + \dots$$

$$= P_1 + P_2 + \dots$$

* Law of equipartition :-

→ Energy of one molecule $E = \frac{3}{2} K_b T$

$$\frac{1}{2} m v_{rms}^2 = \frac{3}{2} K_b T$$

$$v_{rms}^2 = \langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

$$\text{but } \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

$$\therefore v_{rms}^2 = \langle v^2 \rangle = 3 \langle v_x^2 \rangle = 3 \langle v_y^2 \rangle = 3 \langle v_z^2 \rangle$$

So,

$$\frac{1}{2} m v_{rms}^2 = \frac{1}{2} m 3 \langle v_x^2 \rangle = \frac{3}{2} K_b T$$

$$\text{So, } \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} K_b T$$

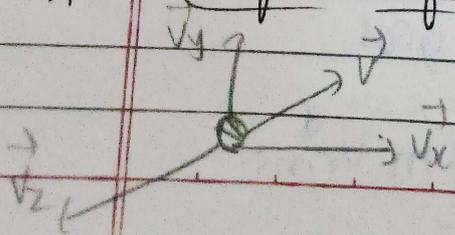
Similarly,

$$\frac{1}{2} m \langle v_y^2 \rangle = \frac{1}{2} K_b T$$

$$\frac{1}{2} m \langle v_z^2 \rangle = \frac{1}{2} K_b T$$

∴ In equilibrium, energy associated with each mode of motion is equal to $\frac{1}{2} K_b T$. And the possible mode of motion is called degree of freedom.

* Degree of freedom for mono atomic gas :-
mono atomic gas has only translational motion.
∴ It has 3 degree of freedom



total energy of a molecule $E = \frac{1}{2} m \langle v_x^2 \rangle + \frac{1}{2} m \langle v_y^2 \rangle + \frac{1}{2} m \langle v_z^2 \rangle$

* Degree of freedom for diatomic gas:-

(i) for rigid rotor (low temp) d.o.f. for trans.

total energy of diatomic gas $E_t = \frac{1}{2} m \langle v_x^2 \rangle + \frac{1}{2} m \langle v_y^2 \rangle + \frac{1}{2} m \langle v_z^2 \rangle + \frac{1}{2} I_x \omega^2 + \frac{1}{2} I_y \omega^2$

→ So, degree of freedom for diatomic gas is 5

(ii) for non-rigid rotor (high temp.) for translational

Total energy $E_t = \frac{1}{2} m \langle v_x^2 \rangle + \frac{1}{2} m \langle v_y^2 \rangle + \frac{1}{2} m \langle v_z^2 \rangle + \frac{1}{2} \langle I_x \omega^2 \rangle + \frac{1}{2} \langle I_y \omega^2 \rangle + \frac{1}{2} m \left(\frac{dx}{dt} \right)^2 + \frac{1}{2} kx^2$

} for rotational
} for vibrational

* C_p & C_v for monoatomic gas:-

→ From 1st law of thermo.,
 $\Delta Q = \Delta U + P \Delta V$
at const. volume.

$$\Delta Q = \Delta U$$

$$\frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T}$$

→ We know for 1 mole gas -

$$\Delta Q = \mu C_v \Delta T \quad (\mu = 1)$$

$$C_v = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T}$$

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→ energy of a monoatomic molecule

but $f = 3$

$$E = \frac{3}{2} K_b T$$

So, total energy of 1 mole gas

$$U = N_A \times E$$

$$= N_A \times \frac{3}{2} K_b T$$

$$\text{but } N_A \times K_b = R$$

$$\text{So, } U = \frac{3}{2} RT$$

$$\text{So, } \frac{dU}{dT} = \frac{3}{2} R$$

$$\text{So, } C_V = \frac{3}{2} R$$

$$\begin{aligned} \text{Now, } C_p &= C_V + R \\ &= \frac{3}{2} R + R \\ &= \frac{5}{2} R \end{aligned}$$

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{5}{2} R}{\frac{3}{2} R} = \frac{5}{3}$$

* Molar specific heat capacity of solid :-
→ For solid body no translational & rotational degree of freedom exist.
→ But it has 3 mode of vibration in 3-D space.
→ So, total degree of freedom $f = 3 \times 2 = 6$

→ So, energy of a molecule,
$$E_T = \frac{f}{2} K_b T = \frac{6}{2} K_b T = 3 K_b T$$

Internal energy of one mole solid = $U = N_A \times E_T$
 $U = N_A \times 3K_B T$
 $U = 3RT$ ($K_B N_A = R$)

\Rightarrow We know solid has fixed volume,
 So, $\frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = C$
 So, $C = 3R$

* Free Mean Path :-

- Free path :- Distance travelled by particle b/w 2 successive collision.

\rightarrow free mean path $\bar{l} = \frac{\text{total free path}}{\text{no. of collision}}$

$$= \frac{l_1 + l_2 + l_3 + \dots + l_n}{n}$$