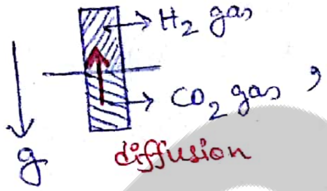
Kinetic Theory of Gases (K.T.)

Rule of thumb: Every material (solid, liquid, gas, plasma, intermedial phases) are made of atoms. They "may" attract or repel & form molecules of liquid or be restricted in definite shape of solid by huge cohesive force.

Experimental hints in favour of K.T.

1. Diffusion and Solution:



when slowly poured Alcohol over water, it spreads throughout.

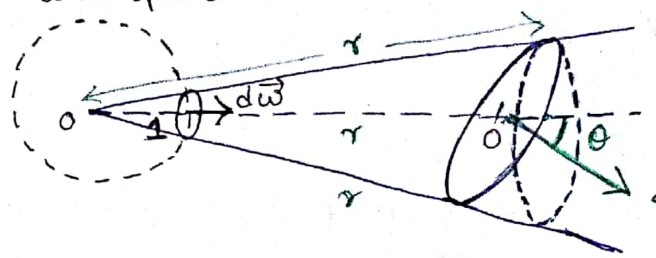
2. Expansion of substance with heat: atoms tend to move away.
3. Phenomena of evaporation & vapour pressure.
4. Brownian motion. 1827 R. Brown → incessant motion of polens on water.

Basic assumptions & postulates of K.T.

1. A gas consists of large number of identical atoms, which are rigid, elastic & equal mass objects.
2. Atoms are in chaos → motion is fully irregular & spans in all three directions.
3. Inevitably the gas molecules collide with each other & surface of container (wall, sphere, cylinder). Total K.E. remains constant, but velocity of each atom continuously changes both in magnitude & direction. In evolving state (intermediate) density in a volume element will change but in steady state, collisions do not affect the density.
4. In between two successive collisions, molecules move in straight line following Newton's law.
5. Collisions are perfectly elastic i.e. no force of attraction/repulsion (P.E. = 0), energy is fully kinetic.

6. Atoms are "point" mass, meaning, their total volume <<<< volume of the container.

Concept of solid angle



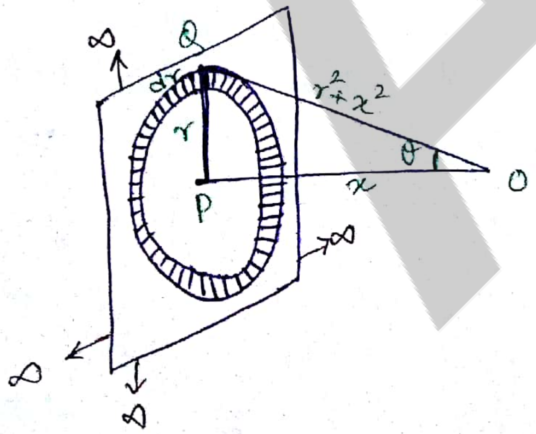
Solid angle subtended by an area at a point is defined as the area intercepted by the cone on a unit sphere (radius = 1) with its centre at the apex of the cone.

If dS is an area that makes a solid angle dω at origin O at a distance $OO' = r$, then from similar figures

$$\frac{d\omega}{1^2} = \frac{dS\cos\theta}{r^2} \quad \therefore \; d\omega = \frac{dS\cos\theta}{r^2}$$

unit of solid angle = steradian.

CW 1. Calculate the solid angle (a) subtended by an infinite plain at a point in front of it, (b) hemisphere and (c) full sphere at its center.



Consider the annular ring, r distance apart from P & thick dr.

Area of this ring $= \pi(r+dr)^2 - \pi r^2$

$= 2\pi r\,dr$

(N.B. we throw $O(dr^2)$ term in limit $dr \to 0$)

So solid angle subtended by that circular annulus

$$d\omega = \frac{dS\cos\theta}{OQ^2} = \frac{2\pi r\,dr\cos\theta}{r^2+x^2}$$

Infinite plain meaning θ going from 0 to $\pi/2$.

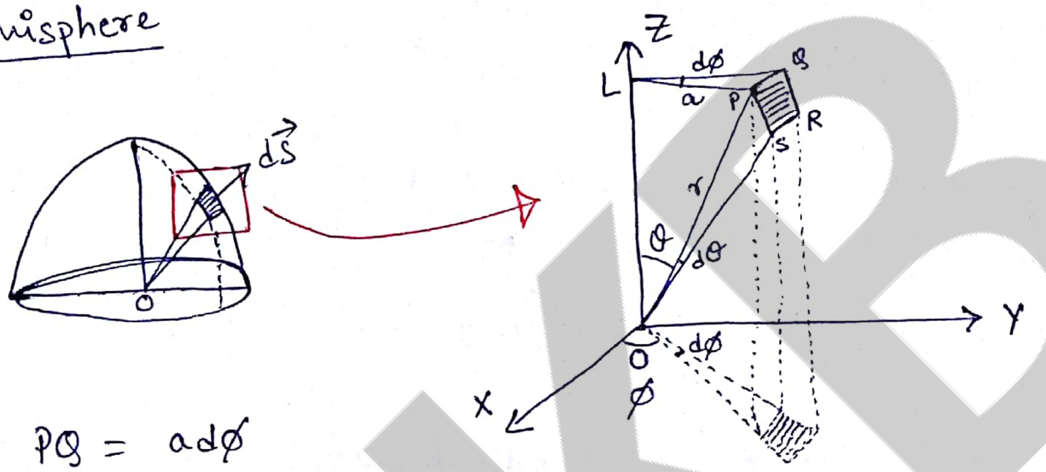
$$\therefore \omega = \int_{\theta=0}^{\pi/2} \frac{2\pi r\, dr \cos\theta}{r^2+x^2}$$

$$\left[r = x\tan\theta \quad dr = x\sec^2\theta\, d\theta \quad \& \; x^2+r^2 = x^2\sec^2\theta \right]$$

$$= 2\pi \int_{\theta=0}^{\pi/2} \frac{x\tan\theta \cdot x\sec^2\theta\, d\theta \cos\theta}{x^2\sec^2\theta}$$

$$= 2\pi \int_0^{\pi/2} \sin\theta\, d\theta = \underline{2\pi}.$$

Hemisphere



$LP = a$
$OP = r$

$$\frac{a}{r} = \sin\theta$$

& $PQ = a\,d\phi$

$PS = r\,d\theta$

$\therefore dS =$ area $PQRS$ $= a\,d\phi \times r\,d\theta = r^2\sin\theta\, d\theta\, d\phi.$

So $d\omega$ at point O $= \dfrac{r^2\sin\theta\, d\theta\, d\phi}{r^2} \times \cos 0 = \sin\theta\, d\theta\, d\phi.$

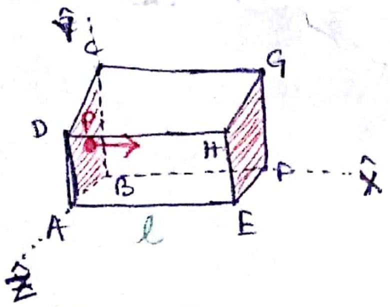
So solid angle subtended $= \int d\omega = \int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} \sin\theta\, d\theta\, d\phi = \underline{2\pi}.$

Full sphere

Solid angle subtended $= \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \sin\theta\, d\theta\, d\phi = \underline{4\pi}.$

We will find out now pressure exerted by a perfect gas from K.T. (a) collisionless atoms in a box moving in 3 directions, (b) collisionless atoms coming from all directions. Collision will be dealt in "mean free path".

Method 1 $\qquad AB = AD = AE = l$



The gas is confined within this cube of volume l^3. P (say) is a gas atom with velocity "c" whose components in 3-direction is (u, v, w).

N = total no. of atoms or molecules.

So each of them have different velocity $c_1, c_2, c_3, c_4, \dots$ etc

so different components $(u_1, v_1, w_1), (u_2, v_2, w_2), (u_3, v_3, w_3), \dots$

Mean square average $$\overline{c^2} = \frac{c_1^2 + c_2^2 + c_3^2 + \dots}{N} = \frac{u_1^2 + u_2^2 + u_3^2 + \dots}{N} + \frac{v_1^2 + v_2^2 + v_3^2 + \dots}{N} + \frac{w_1^2 + w_2^2 + w_3^2 + \dots}{N}$$

$$= \overline{u^2} + \overline{v^2} + \overline{w^2} \quad \text{—— (1)}$$

mean square velocity in X-direction $\qquad$ Y-direction $\qquad$ Z-direction.

Consider particle p with mass m, velocity $\vec{c} = (\vec{u}, \vec{v}, \vec{w})$.

It travels from ABCD to EFGH, makes collision to exert pressure, rebounds elastically, momentum gets changed, comes back to ABCD to make another collision.

Total distance traveled with velocity u is $2l$.

$\therefore$ Time between collision $= \frac{2l}{u}$, meaning

number of collission per second $= \frac{u}{2l}$.

Momentum imparted in +X direction ~~of~~ on EFGH = mu.

Momentum obtained in −X direction after collission = −mu.

$\therefore$ Change of momentum $= mu - (-mu) = 2mu$.

Rate of change of momentum for one atom in X direction

$$= 2mu \times \frac{u}{2l} = \frac{mu^2}{l}.$$

Similarly in Y and Z direction, rate of change of momentum is $\frac{mv^2}{l}$ & $\frac{mw^2}{l}$ for one atom

∴ Total rate of change of momentum for all atoms per unit area along x direction is

$$P_x = \frac{m(u_1^2+u_2^2+u_3^2+\cdots)}{l} \times \frac{1}{l^2} = m\overline{u^2}\frac{N}{l^3} = mn\overline{u^2}$$

(see eqn. ①)

Similarly $P_y = mn\overline{v^2}$, $P_z = mn\overline{w^2}$.

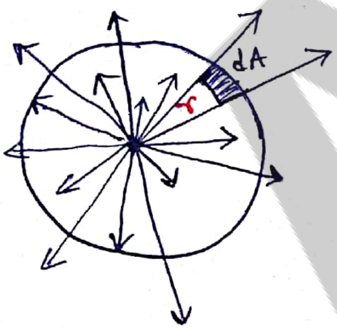
In steady state, molecules move in all directions, so no preference, meaning $\overline{u^2} = \overline{v^2} = \overline{w^2}$ & $P_x = P_y = P_z$.

Meaing $\overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3}\overline{c^2}$ (see eqn. ①)

collecting all pieces together,

$$P_x = P_y = P_z = \frac{1}{3}mn\overline{c^2} \quad \text{or} \quad \boxed{P = \frac{1}{3}mn\overline{c^2}}$$

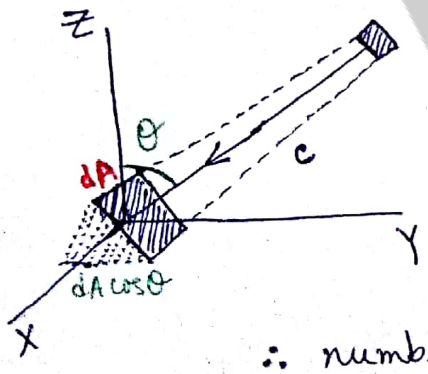
Method 2



N no. of molecules moving in all directions with all possible velocity. How many collide with vessel & insert pressure?

number of vectors per unit area $= \frac{N}{4\pi r^2}$

∴ number of molecules at dA is $\frac{NdA}{4\pi r^2}$



We already learned that $dA = r^2\sin\theta\, d\theta\, d\phi$

$$\frac{NdA}{4\pi r^2} = \frac{N}{4\pi}\sin\theta\, d\theta\, d\phi$$

∴ number of molecules per unit volume within velocity range c & c+dc [dn_c], within direction θ & θ+dθ & φ & φ+dφ

[$d\omega = \sin\theta\, d\theta\, d\phi$]

$$dn_{c,\theta,\phi} = \frac{dn_c}{4\pi}\sin\theta\, d\theta\, d\phi$$

Let's find now, how many of them strike dA of the wall of container. Geometrically, this is the number of molecules within the slanted prism of length $c\,dt$ with edges in the direction θ & ϕ $= \frac{dn_c}{4\pi}\sin\theta\, d\theta\, d\phi \times c\, dA \cos\theta\, dt$

$\therefore$ Total number of collisions at dA per unit time

$$\int_{c=0}^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} \frac{dn_c}{4\pi}\sin\theta\, d\theta\, d\phi \times c\, dA\cos\theta$$

$$= \frac{dA}{4\pi}\int_0^{\infty} c\, dn_c \underbrace{\int_0^{\pi/2}\sin\theta\cos\theta\, d\theta}_{1/2} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} = \frac{dA}{4}\int_0^{\infty} c\, dn_c .$$

If n_1 atoms per unit volume moves with velocity c_1,

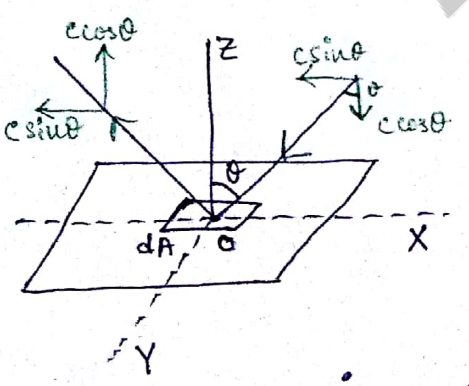
n_2 " " " " " c_2,

n_3 " " " " " c_3, ...

average velocity $\bar{c} = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \cdots}{n_1 + n_2 + n_3 + \cdots}$

$$= \frac{\sum n_i c_i}{\sum n_i} = \frac{1}{n}\int_0^{\infty} c\, dn_c$$

$\therefore$ Number of molecules colliding at dA of the container per unit time $= \boxed{\frac{dA}{4}\, n\bar{c}}$



Now let's compute change in momentum by molecules striking area dA in unit time.

normal component of incident momentum is $mc\cos\theta$ & reflected momentum $-mc\cos\theta$.

So each atom had a change in momentum $2mc\cos\theta$.

$\therefore$ Total change of momentum experienced by all gas atoms/molecules colliding to area dA, per unit time is

$$\int_{c=0}^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} \frac{dn_c}{4\pi}\sin\theta\, d\theta\, d\phi \times c\, dA\cos\theta \times 2mc\cos\theta$$

$$= \frac{m\,dA}{2\pi}\int_{c=0}^{\infty} c^2 dn_c \underbrace{\int_{\theta=0}^{\pi/2}\cos^2\theta\sin\theta\, d\theta}_{=1/3} \underbrace{\int_{\phi=0}^{2\pi} d\phi}_{2\pi} = \frac{1}{3} m\,dA \int_{c=0}^{\infty} c^2 dn_c$$

$$c_{rms}^2 = \bar{c}^2 = \frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \cdots}{n_1 + n_2 + n_3 + \cdots} = \frac{\sum n_i c_i^2}{\sum n_i}$$

$$= \frac{\int_0^{\infty} c^2 dn_c}{n}$$

$\therefore$ Force exerted by gas atoms on dA is

$$F = \frac{1}{3} m\,dA\, n\bar{c}^2$$

Thus, pressure exerted $\boxed{p = \frac{F}{dA} = \frac{1}{3} mn\bar{c}^2}$

Corollary From above, $p = \frac{1}{3}\rho\bar{c}^2 \Rightarrow \bar{c} = \sqrt{\frac{3p}{\rho}}$

For Hydrogen $\rho = 8.9 \times 10^{-5}$ gm/cc.

1 atm pressure $P = h\rho g = 76 \times 13.6 \times 981$ dynes/cm^2

$$\therefore \bar{c} = \sqrt{\frac{3\times 76\times 13.6\times 981}{8.9\times 10^{-5}}} = 1.85 \times 10^5 \text{ cm/sec.}$$

$c_l = 3\times 10^8$ m/s, $c_s = 300$ m/s

$= 3\times 10^{10}$ cm/s. & $= 3\times 10^4$ cm/s.

Kinetic interpretation of temperature

From K.T. $p = \frac{1}{3} m n \bar{c}^2 = \frac{1}{3} m \frac{N}{V} \bar{c}^2$

But we assume!!

$\therefore PV = \frac{1}{3} m N \bar{c}^2 = RT$ [Boyle's law]

$\bar{c} = \sqrt{\frac{3RT}{mN}} = \sqrt{\frac{3RT}{M}}$ where M = molecular weight

$\therefore \bar{c} \propto \sqrt{T}$ RMS velocity of gas atom is proportional to square root of absolute temperature.

As from $T = 0$, $\bar{c} = 0$ ie. absolute zero temperature is where molecule cease to move.

Now $\bar{c}^2 = \frac{3RT}{M} \Rightarrow \frac{1}{2} M \bar{c}^2 = \frac{3}{2} RT$

divide by N, $\underbrace{\frac{1}{2} m \bar{c}^2}_{\text{mean K.E.}} = \frac{3}{2} k_B \underbrace{T}_{\text{abs. tmp.}}$, k_B = Boltzmann's constant.

for a given T, there is always a K.E. & molecular collission lead to uniform T.

Boyle's law from K.T.

$PV = \frac{1}{3} M \bar{c}^2$ & because $\bar{c}^2 \propto T$.

So if T is fixed $\bar{c}^2$ is constant so PV = constant.

Charle's law from K.T.

Again $\bar{c}^2 \propto T$, so $PV \propto T$

i.e. $V \propto T$ when p = constant.

Avogadro's law from K.T.

For same T & P, equal V of gases contain equal number of atoms.

P, V, N_1	P, V, N_2
1	2

$$P = \frac{1}{3} m_1 \frac{N_1}{V} \bar{c}_1^2$$
$$P = \frac{1}{3} m_2 \frac{N_2}{V} \bar{c}_2^2$$
$$\therefore m_1 N_1 \bar{c}_1^2 = m_2 N_2 \bar{c}_2^2$$

But T is equal, so K.E. is equal.

$$\frac{1}{2} m_1 \bar{c}_1^2 = \frac{1}{2} m_2 \bar{c}_2^2 \Rightarrow m_1 \bar{c}_1^2 = m_2 \bar{c}_2^2$$

$$\therefore N_1 = N_2.$$

Clapeyron's equation from K.T.

$$P = \frac{1}{3} m n \bar{c}^2 = \frac{1}{3} \frac{n}{N} m N \bar{c}^2 = \frac{n}{N} \times \frac{1}{3} M \bar{c}^2$$
$$= \frac{n}{N} RT = n k_B T \qquad \left[k_B = \frac{R}{N}\right]$$

$N = 6.023 \times 10^{23}$ atoms/mole.

Universal gas constant R

$PV = RT$.

$$\therefore R = \frac{PV}{T} = \frac{(76 \times 13.6 \times 981) \times 22.4 \times 10^3}{273}$$
$$= 8.31 \times 10^7 \text{ dynes-cm}/^\circ K/\text{mole or erg/degK/mole.}$$

in heat units, $= \frac{8.31 \times 10^7}{4.18 \times 10^7} = 2$ cal/degK/mole

& $k_B = \frac{R}{N} = \frac{8.31 \times 10^7}{6.023 \times 10^{23}} = 1.38 \times 10^{-16}$ ergs/degK/mole

Dalton's law of partial pressure

N no. of gases with density ρ_1, ρ_2, ρ_3 with rms velocities $\bar{c}_1, \bar{c}_2, \bar{c}_3$ etc, $P = \frac{1}{3}\rho_1 \bar{c}_1^2 + \frac{1}{3}\rho_2 \bar{c}_2^2 + \frac{1}{3}\rho_3 \bar{c}_3^2 = P_1 + P_2 + P_3 + \ldots$

Relation between pressure & K.E.

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

so pressure of a gas is 2/3 the translational K.E. of the atoms per unit volume.

CW Compute the r.m.s. velocity of oxygen (O_2) & ~~hydrogen~~ CO_2 atoms at 27°c. Given, density of oxygen at N.T.P. = 1.43 Kg/m^3 & molecular weight of CO_2 = 44 gm, (molecular weight of O_2 = 32 gm).

at N.T.P. $(T_0 = 273K)$ for O_2, $\rho_0 = 1.43\ Kg/m^3$.

[If not this supplied, then molecular weight = 32gm = 0.032 Kg.

at N.T.P. gram molecular volume = 22.4 litre

$= 22.4 \times 10^{-3}\ m^3$

$= 0.0224\ m^3$.

Density $\rho_0 = \frac{0.032}{0.0224} = 1.43\ kg/m^3$]

Similarly for CO_2, density $\rho_0 = \frac{0.044}{0.0224} = 1.96\ Kg/m^3$ at N.T.P.

Using K.T. we have $\rho_0 T_0 = \rho T$.

$$\therefore \rho_{27°} = \frac{\rho_0 T_0}{T} = \frac{1.43 \times 273}{(27+273)} = 1.3\ kg/m^3 \text{ for } O_2$$

$$\rho_{27°} = \frac{\rho_0 T_0}{T} = \frac{1.96 \times 273}{(27+273)} = 1.79\ Kg/m^3 \text{ for } CO_2$$

pressure $P = 0.76 \times 13.6 \times 10^3 \times 9.8 = 1.013 \times 10^5\ N/m^2$.

from K.T. $P = \frac{1}{3}\rho\bar{c}^2$

So r.m.s. velocity $\bar{c}_{O_2} = \sqrt{\frac{3P}{\rho_{O_2}}} = \sqrt{\frac{3 \times 1.013 \times 10^5}{1.3}}$

$= 4.835 \times 10^2$ m/s.

$\bar{c}_{CO_2} = \sqrt{\frac{3P}{\rho_{CO_2}}} = \sqrt{\frac{3 \times 1.013 \times 10^5}{1.79}}$

$= 4.12 \times 10^2$ m/s.

HW

1. Calculate the ~~n~~ number of molecules/cc of an ideal gas at 27°C & at pressure of 20 mm of mercury. Density of mercury = 13.6 gm/cc & mean KE of a molecule at 27°C is 4×10^{-21} Joules.

2. At what temperature will the r.m.s. velocity of a gas will become half its value at 0°C ?