Kinetic Theory of gases

1. Write down the assumptions of in developing the Kinetic theory of gases.

2. ~~Deduction of Perfect gas equation~~.

Ans:- (i) A gas consists of large no. of hard minute elastic spherical molecules which are moving in all possible directions with velocity - ∞ to + ∞

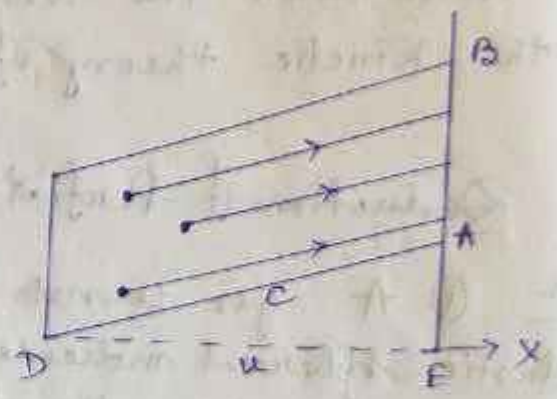
(ii) During motion the molecules collide with one another and also with the walls of the containers. The collision is perfectly elastic so there is no loss in K.E due to collision.

(iii) The molecules exert no force each other except when they are actually collide. So, in between two successive collisions the molecules move with uniform velocity along straight lines.

(iv) The collisions are instantaneous, so, the duration of collision is negligible compared to the time taken between two collisions.

(v) Due to their geometrical mass points structure the molecular volume is negligible compared to the actual volume of the container.

2. Derive the expression for the pressure of an ideal gas.



Consider a perfect gas is enclosed in a container, one if its ~~wall~~ ~~is~~ BAE is perpendicular to the X axis. Let the velocities of any molecules of the gas are u, v, w along X, Y, Z axes. So, we may write any velocity c as

$$c^2 = u^2 + v^2 + w^2 \longrightarrow (1)$$

the limits of u, v, w are from $-\infty$ to $+\infty$ and c from 0 to ∞.

Since, BAE is perpendicular to X axis so 'u' suffer a change in direction due to collision but 'v' and 'w' are remain unchanged in their direction due to this type of reflection.

If the mass of any molecule be m, then the momentum change per collision is = mu - (-mu)

= 2mu

Let nu be the no. of molecules per unit volume moving with velocity u, Now, the no. of molecules which striking unit area in time dt ~~will be~~ would be contained in any cylinder of height udt and unity base area. So, the no. of molecules inside this cylinder is = nu · u dt where where 'udt' is the volume of the said cylinder.

So, the change in momentum by the above molecules in time dt is $= 2mu \times nu\,dt$

The above quantity is only for the molecules moving in positive x-direction.

$\therefore$ Total change in momentum per unit area in time dt is $= 2m \sum_0^\infty nu u^2\,dt$

If the above change in momentum results in an average force δF, then

$$\delta F \cdot dt = 2m \sum_0^\infty nu u^2\,dt$$

$$\therefore \delta F = 2m \sum_0^\infty nu u^2$$

Since the area of the cylinder is unity, so δF is also the pressure p.

$$\therefore p = 2m \sum_0^\infty nu u^2 \longrightarrow (iii)$$

Now, $\overline{u^2}$ can may be expressed as

$$\overline{u^2} = \frac{n_1 u_1^2 + n_2 u_2^2 + \dots + n_i u_i^2 + \dots}{n_1 + n_2 + \dots + n_i + \dots}$$

$$= \frac{\sum nu u^2}{\sum nu} = \frac{\sum nu u^2}{\frac{1}{2} n}$$

$\sum nu = \frac{1}{2} n \Rightarrow$ only positive x axis molecules are considered

$$\therefore \sum_0^\infty nu u^2 = \frac{1}{2} n \overline{u^2}$$ where 'n' be the total no. of molecules per unit volume.

$$\therefore P_x = 2m \times \frac{1}{2} n \overline{u^2} = mn \overline{u^2}$$

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

Since pressure at any particular point in all directions are same. So,

$$p = p_x = p_y = p_z = mn\overline{u^2} = mn\overline{v^2} = mn\overline{w^2}$$

But $c^2 = u^2 + v^2 + w^2$

$$\therefore \overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3}\overline{c^2}$$

Where $\overline{c^2}$ is the mean square velocity

$$\therefore p = \frac{1}{3} mn\overline{c^2} = \frac{1}{3} mnc^2$$

Where $c = \sqrt{\overline{c^2}}$ is the r.m.s velocity

If the density of gas is ρ

$$\therefore \rho = mn$$

$$\therefore p = \frac{1}{3}\rho c^2$$

This is the required expression for pressure of an ideal gas.

3. Deduce R.M.S velocity, Kinetic energy, Boyle's law, Charles law and Avogadro's hypothesis from pressure equation.

(a) $$c^2 = \frac{3p}{\rho} \Rightarrow \boxed{c = \sqrt{\frac{3p}{\rho}}}$$

$$c^2 = \frac{3p}{\rho} = \frac{3pV}{Vp}$$

$$= \frac{3RT}{M} \quad \text{for 1 mole of gas}$$

$$\therefore \boxed{c = \sqrt{\frac{3RT}{M}}}$$

again $c^2 \propto T$ it shows that the K.E of a gas molecule ($\frac{1}{2}mc^2$) is proportional to the temperature. In other words

We can say that Kinetic energy of molecules manifests itself as temperature. This is called Kinetic interpretation of temperature.

(b) K.E

$$p = \frac{1}{3} \rho c^2$$
$$= \frac{2}{3} \times \frac{1}{2} \rho c^2$$
$$= \frac{2}{3} E$$

$E = \frac{1}{2} \rho c^2$ is the mean K.E of the gas per unit volume.

(c) Boyle's law:

$$p = \frac{1}{3} \rho c^2$$
$$\text{or, } p = \frac{1}{3} \left(\frac{M}{V}\right) c^2$$

Where M is the mass of the gas inside a arbitrary volume V.

$$\therefore pV = \frac{1}{3} Mc^2 = \text{Constant when 'T' const}$$

$\therefore pV =$ const when Temperature fixed

this is Boyle's law.

(d) Charles law:

$$p = \frac{1}{3} \rho c^2$$
$$p = \frac{1}{3} \frac{M}{V} c^2$$
$$\text{or } pV = \frac{1}{3} Mc^2$$
$$\text{or, } pV \propto c^2$$

again $c^2 \propto T \quad \therefore pV \propto T$

$\therefore \frac{pV}{T} =$ constant (Says R)

$\therefore pV = RT$ this is charle's law

(e) Avogadro's hypothesis:

Let us consider two gases of same volume unity are separated by two container. let n_1, m_1, c_1 and n_2, m_2 and c_2 are the no. of molecules, molecular mass and r.m.s velocity respectively.

If the pressure of the two containeare are same, then according to pressure expression

$$\frac{1}{3} m_1 n_1 c_1^2 = \frac{1}{3} m_2 n_2 c_2^2 \longrightarrow (i)$$

If the temperature of the two container are same then

$$\frac{1}{2} m_1 c_1^2 = \frac{1}{2} m_2 c_2^2 \longrightarrow (ii)$$

Now, from (i)

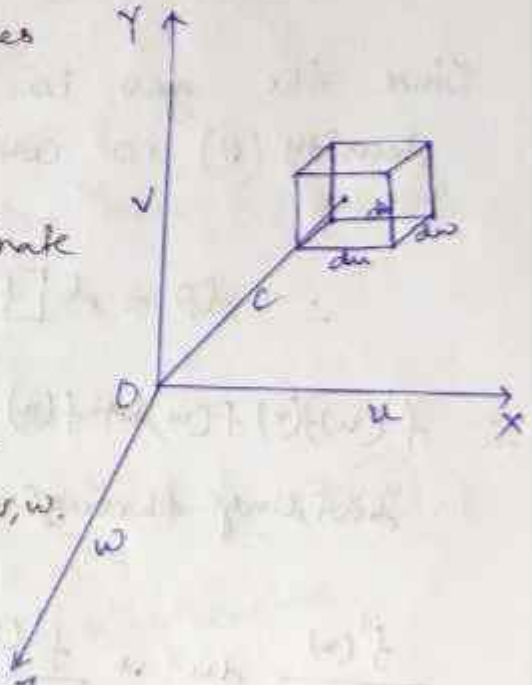
$$\frac{1}{2} m_1 c_1^2 \times \frac{2}{3} n_1 = \frac{1}{2} m_2 c_2^2 \times \frac{2}{3} n_2$$

$$n_1 = n_2$$

So, the no. of molecules of the container two container are same when the temperature, pressure and the volume of the two container are same. This is well known Avogadro's hypothesis.

3. Maxwell Velocity or Speed distribution law :—

Let us consider all the molecules of gas in a velocity diagram. ~~with~~ let ox, oy, oz be the axes of a rectangular co-ordinate system with O as origin.



Now, any velocity C can be expressed ~~by the~~ with the help of component velocities u, v, w.

$$u^2 + v^2 + w^2 = c^2 \longrightarrow (i)$$

Differentiating the above eqn

$$u\,du + v\,dv + w\,dw = 0 \longrightarrow (ii)$$

The above eqn shows that du, dv, dw are dependent to each other.

The probabilities to find a molecule within velocity range u and u+du, v and v+dv and w and w+dw are respectively $f(u)\,du$, $f(v)\,dv$ and $f(w)\,dw$.

Now the probality to find an individual molecule within the velocity range u and u+du, v and v+dv and w and w+dw is the product of of each individual probabilities. i.e

$$f(u)\,f(v)\,f(w)\,du\,dv\,dw$$

If the total no. of molecule in the gas ensemble is N and dN' no. of molecules having the ~~Specified velocity~~ range of velocities then

$$dN' = N f(u) f(v) f(w)\,du\,dv\,dw \longrightarrow (iii)$$

Now, the no. of specified molecules per unit volume is $\rho = \frac{dN'}{du\,dv\,dw} = f(u)f(v)f(w)$ → (iv)

Since the gas is steady, so the molecular density (ρ) is constant i.e $d\rho = 0$

$$\therefore d\rho = d[f(u)f(v)f(w)] = 0$$

$$\therefore f'(u)f(v)f(w)du + f(u)f'(v)f(w)dv + f(u)f(v)f'(w)dw = 0$$

dividing throughout by $f(u)f(v)f(w)$

$$\frac{f'(u)}{f(u)}du + \frac{f'(v)}{f(v)}dv + \frac{f'(w)}{f(w)}dw = 0 \quad \rightarrow (v)$$

Since du, dv, dw are not independent so we cannot equate each of co-efficients to zero. We can solve the above eqn with the help of Lagrange undetermined multipliers.

Multiplying eqn (iv) with α and adding the product with eqn (v), we get

$$\left\{\frac{f'(u)}{f(u)} + \alpha u\right\}du + \left\{\frac{f'(v)}{f(v)} + \alpha v\right\}dv + \left\{\frac{f'(w)}{f(w)} + \alpha w\right\}dw = 0$$

Now, we can equate each co-efficients to 0.

$$\left.\begin{aligned} \frac{f'(u)}{f(u)} + \alpha u &= 0 \\ \frac{f'(v)}{f(v)} + \alpha v &= 0 \\ \frac{f'(w)}{f(w)} + \alpha w &= 0 \end{aligned}\right\} \rightarrow (vi)$$

Now, integrating set of equations (vi) we get

$$f(u) = A e^{-\frac{\alpha u^2}{2}}, \quad f(v) = A e^{-\frac{\alpha v^2}{2}}$$

$$f(w) = A e^{-\frac{\alpha w^2}{2}}$$

Where A is a constant

Now, Putting these values into eqn (iii) we get,

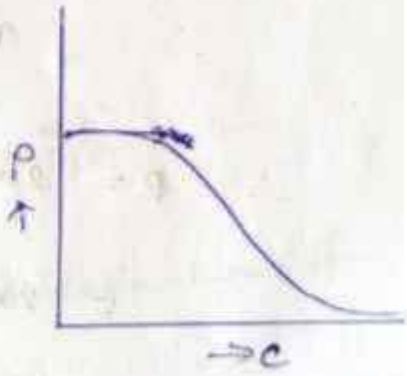
$$dN' = N A^3 e^{-\frac{\alpha}{2}(u^2+v^2+w^2)} du\, dv\, dw$$

$$\therefore dN' = N A^3 e^{-bc^2} du\, dv\, dw$$

$$\therefore \rho = \frac{dN'}{du\, dv\, dw} = N A^3 e^{-bc^2} \longrightarrow (vii)$$

Where, $b = \frac{\alpha}{2}$ and $c^2 = u^2+v^2+w^2$

The above equation shows that molecular density is a function of 'c' only. ρ falls off exponentially with C.



* Evaluation of Constant 'A'

$$\int dN' = N \Rightarrow \text{Since the total no. of molecules in the ensemble is } N$$

$$\int_{-\infty}^{+\infty}\int\int\int N A^3 e^{-b(u^2+v^2+w^2)} du\, dv\, dw = N$$

$$\therefore \int_{-\infty}^{+\infty}\int\int\int A^3 e^{-b(u^2+v^2+w^2)} du\, dv\, dw = \frac{1}{A^3}$$

Let $I = \int_{-\alpha}^{+\alpha} e^{-bu^2} du = \int_{-\alpha}^{+\alpha} e^{-bv^2} dv = \int_{-\alpha}^{+\alpha} e^{-bw^2} dw$

$\therefore I^3 = \frac{1}{A^3}$

$\therefore I = \frac{1}{A}$

We know that $I = \int_{-\alpha}^{+\alpha} e^{-bu^2} du = \sqrt{\frac{\pi}{b}}$

$\therefore A = \sqrt{\frac{b}{\pi}}$

Evaluation of b :-

We know that Pressure

$P = 2m \sum n_u u^2$

Where n_u be the no. of molecules per unit Volume moving with velocity u and u+du, m be the mass of each molecule.

$\therefore n_u = n f(u) du$, n being the no. of molecules per unit Volume

$\therefore P = 2mn \int_0^\infty f(u) u^2 du$

$= 2mn A \int_0^\infty e^{-bu^2} u^2 du \quad [\because f(u) = A e^{-bu^2}]$

$= 2mn A \cdot \frac{1}{2A} \sqrt{\frac{\pi}{b^3}}$

$= \frac{mn}{2} \cdot \sqrt{\frac{b}{\pi}} \cdot \sqrt{\frac{\pi}{b^3}}$

$= \frac{mn}{2b}$

$\therefore b = \frac{mn}{2P} = \frac{mn}{2nKT} \quad [\because P = nKT]$

$= \frac{m}{2KT}$

And $A = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi KT}}$

$$\therefore \quad \rho = N A^3 e^{-bc^2}$$

$$= N \left(\frac{m}{2\pi KT}\right)^{3/2} \cdot e^{-\frac{mc^2}{2KT}} \longrightarrow (iii)$$

This is the expression for molecular density.

So, the no. of molecules having velocity range c and c+dc is ρ times the volume between the two spheres of radius c and c+dc.

$$\therefore \quad dN_c = 4\pi c^2 dc \cdot \rho$$

$$= 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} \cdot c^2 dc$$

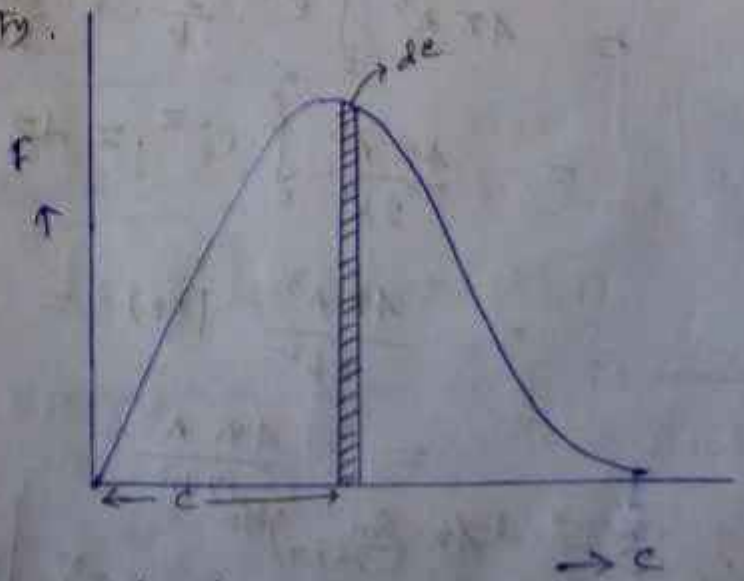
The above equation is known as Maxwell's velocity or speed distribution law.

$$\frac{dN_c}{N} = 4\pi \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} c^2 dc$$

$$= F \cdot dc$$

$$\therefore \quad F = 4\pi \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} \cdot c^2$$

Plot of F vs c gives the distribution curve of molecular velocity.



Distribution Curve

* Most Probable velocity :-

Maximum no. of molecules possess a particulate velocity, is called most probable velocity.

(A) Evaluation of average, mean and r.m.s velocity :-

(a) Average Speed :-

let n_1 molecules have speed c_1, n_2 molecules have speed c_2 and so on.

So, $$\bar{c} = \frac{n_1c_1 + n_2c_2 + \cdots}{n_1 + n_2 + \cdots} = \frac{\sum n_i c_i}{\sum n_i}$$

$$= \frac{1}{N}\int_0^\infty c\, dN_c \qquad [\because \sum n_i = N]$$

$$= \frac{1}{N}\int_0^\infty c\, 4\pi N A^3 e^{-bc^2} c^2\, dc$$

$$= 4\pi A^3 \int_0^\infty e^{-bc^2}\cdot c^3\, dc$$

$$= 4\pi A^3 \int_0^\infty e^{-z}\cdot c^2 \cdot c\, dc \qquad [\text{let } bc^2 = z]$$

$$2bc\,dc = dz$$

$$= 4\pi A^3 \int_0^\infty e^{-z}\cdot \frac{z}{b}\cdot c\cdot \frac{dz}{2bc} \qquad \therefore c^2 = \frac{z}{b}$$

$$= \frac{4\pi A^3}{2b^2}\int_0^\infty e^{-z}\cdot z\, dz$$

$$= \frac{4\pi A^3}{2b^2}\Gamma(2) = \frac{4\pi A^3}{2b^2}\cdot 1\cdot \Gamma(1) \qquad [\because \Gamma(n+1) = n\Gamma(n)]$$

$$= \frac{4\pi A^3}{2b^2} \qquad [\because \Gamma(1) = 1]$$

$$\therefore \bar{c} = \frac{4\pi\left(\frac{m}{2\pi KT}\right)^{3/2}}{2\left(m/2KT\right)^2} \Rightarrow \boxed{\sqrt{\frac{8KT}{\pi m}} = \bar{c}}$$

(b) R.M.S Speed :-

$$C_{r.m.s} = \overline{c^2}$$

$$\overline{c_2} = \frac{n_1 c_1^2 + n_2 c_2^2 + \cdots}{n_1 + n_2 + \cdots} = \frac{\sum n_i c_i^2}{\sum n_i}$$

$$= \frac{1}{N} \int_0^\infty c^2 \, dN_c$$

$$= \frac{4\pi N A^3}{N} \int_0^\infty e^{-bc^2} c^4 \, dc \qquad [\text{Putting the value of } dN_c]$$

$$= \frac{4\pi A^3}{2b^{5/2}} \int_0^\infty e^{-z} z^{3/2} \, dz \qquad [\text{Putting } bc^2 = z]$$

$$= \frac{4\pi A^3}{2b^{5/2}} \Gamma(5/2) = \frac{4\pi A^3}{2b^{5/2}} \cdot \frac{3}{2} \cdot \frac{1}{2} \Gamma(1/2)$$

$$= \frac{4\pi A^3}{2b^{5/2}} \cdot \frac{3}{4} \cdot \frac{1}{2} \cdot \sqrt{\pi} \qquad [\Gamma(1/2) = \sqrt{\pi}]$$

$$= \frac{\pi \left(\frac{m}{2\pi KT}\right)^{3/2} \cdot 3\sqrt{\pi}}{2 \left(\frac{m}{2KT}\right)^{5/2}}$$

$$\boxed{C_{r.m.s} = \frac{3KT}{m}}$$

(c) Most Probable Speed :-

We Know, $F = 4\pi A^3 c^2 e^{-bc^2}$

at most probable speed $c = c_m$, value of F is maximum

i.e; $\frac{dF}{dc} = 0$

or $8\pi c A^3 e^{-bc^2} - 8\pi b c^3 A^3 e^{-bc^2} = 0$

$$8\pi C_m A^3 e^{-bc_m^2} = 8\pi b C_m^3 A^3 e^{-bc_m^2}$$

$$\therefore C_m^2 = \frac{1}{b} = \frac{2KT}{m} \qquad \left[\because b = \frac{m}{2KT}\right]$$

$$\therefore \boxed{C_m = \sqrt{\frac{2KT}{m}}}$$

Ratio of three Speeds :-

$$\bar{c} : C_{r.m.s} : C_m = \sqrt{\frac{8KT}{\pi m}} : \sqrt{\frac{3KT}{m}} : \sqrt{\frac{2KT}{m}}$$

$$= \sqrt{8/\pi} : \sqrt{3} : \sqrt{2}$$

$$\therefore \frac{\bar{c}}{C_{r.m.s}} = \sqrt{\frac{8}{3\pi}} = .921 \quad , \quad \frac{C_m}{C_{r.m.s}} = \sqrt{\frac{2}{3}} = .817$$

$$\therefore \boxed{C_m : \bar{c} : C_{r.m.s} = 1 : 1.128 : 1.224}$$

(5) Energy & momentum distribution of molecules :-

$$E = \frac{1}{2} m c^2 \Rightarrow dE = mc\,dc \longrightarrow (i)$$

$$\therefore dc = \frac{dE}{mc} = \frac{dE}{m\sqrt{\frac{2E}{m}}} = \frac{dE}{\sqrt{2mE}} \longrightarrow (ii)$$

We know Maxwell velocity distribution law

$$dN_c = 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} \cdot e^{-\frac{mc^2}{2KT}} \cdot c^2\,dc$$

Now, the no. of molecules dN_E having energy lying between E and E + dE can be obtained by using (i) and (ii)

$$dN_E = A\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} \cdot e^{-\frac{2E}{2KT}} \cdot \frac{2E}{m} \cdot \frac{dE}{\sqrt{2mE}}$$

$$= 2N \left(\frac{E}{\pi}\right)^{1/2} \cdot \left(\frac{1}{KT}\right)^{3/2} \cdot e^{-\frac{E}{KT}} dE$$

$$\boxed{dN_E = 2N \left(\frac{E}{\pi}\right)^{1/2} \cdot (KT)^{-3/2} e^{-E/KT} dE}$$

This is the no. of molecules with specified energy.

* momentum distribution:-

momentum of a molecule $p = mc$

$$dp = m\,dc \longrightarrow (i)$$

$$dc = \frac{dp}{m} \longrightarrow (ii)$$

Now, with the help of Maxwell's velocity distribution law we can find the no. of molecules with momentum lying between p and p+dp

$$dN_c = A\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} \cdot c^2\,dc$$

Now putting the value of c and dc, we get

$$dN_c = A\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} \cdot e^{-\frac{m^2c^2}{2mKT}} \cdot c^2\,dc$$

$$= A\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} \cdot e^{-\frac{p^2}{2mKT}} \cdot \frac{p^2}{m^2} \cdot \frac{dp}{m}$$

$$= A\pi N \left(\frac{1}{2\pi mKT}\right)^{3/2} \cdot e^{-\frac{p^2}{2mKT}} \cdot p^2\,dp$$

$$\boxed{dN_p = A\pi N (2\pi mKT)^{-3/2} \cdot e^{-\frac{p^2}{2mKT}} \cdot p^2\,dp}$$

This is momentum distribution of molecules having momentum lying between p and p+dp.

(6) Degrees of freedom :-

The no. of independent coordinates necessary to specify the position and configuration of a dynamical system in space.

Or, the no. of independent quadratic variables by which the energy of a system is determined.

* Consider a material system consisting of N - Particles (x_1, y_1, z_1), (x_2, y_2, z_2), ... (x_N, y_N, z_N) and subject to m constraint equations.

If $m < 3N$, then the degrees of freedom of the system

$$f = 3N - m$$

(7) Equipartition of energy :-

If the molecules in their motion obey the laws of mechanics, the mean Kinetic energy of a system of molecules in thermal equilibrium at temperature T, is uniformly distributed among all the degrees of freedom and for each degrees of freedom it equals to $\frac{1}{2}KT$. K is Boltzman's Constant.

(8) Degrees of freedom and ratio of heat capacities:-

We consider a system consist of only free particles having f degrees of freedom.

According to equipartition theorem energy associated per each particle is $= \frac{1}{2}KTf$
$= \frac{1}{2}fKT$

∴ So, the energy per mole $E = \frac{1}{2}fKT \cdot N_A$

$= \frac{1}{2}fN_AKT$

$= \frac{1}{2}fRT \quad [\because N_AK = R]$

∴ Molar heat capacity at constant volume

$$C_V = \left(\frac{dE}{dT}\right)_V = \frac{d}{dT}\left(\frac{1}{2}fRT\right) = \frac{1}{2}fR \longrightarrow (i)$$

But for 1 mole of gas

$$C_p - C_V = R$$

or $C_p = \frac{1}{2}fR + R = R\left(1 + \frac{f}{2}\right) \longrightarrow (ii)$

$$\therefore \gamma = \frac{C_p}{C_V} = \frac{R\left(1+\frac{f}{2}\right)}{\frac{1}{2}fR} = 1 + \frac{2}{f}$$

$$\boxed{\therefore \gamma = 1 + \frac{2}{f}}$$

This is the required relation linking between γ and f.

* For monoatomic gas $f = 3$

$$\therefore \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{3} = 1.67$$

** For diatomic gas $f = 3N - m = 3\times2 - 1$
$= 5$

Of these, 3 are of translation and 2 of rotation.

$\therefore \quad \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{5} = 1.4$

*** For linearly arranged triatomic gas molecule like CO_2 ($O=C=O$) ($m=2$)

$$f = 3N - m = 3\times 3 - 2 = 7$$

$$\therefore \quad \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{7} = 1.28$$

If the atoms are arranged at the vertices of a triangle then ($m=3$)

$$f = 3N - m = 3\times 3 - 3 = 6$$

$$\therefore \quad \gamma = 1 + \frac{2}{f} = 1.33$$

(9) γ for a mixture of two ideal gases :—

Let a container consist of N_1 mole of one type of gas having f_1 degrees of freedom per molecule and another type of N_2 mole of gas having f_2 degrees of freedom per molecule.

$\therefore$ Total energy of the system

$$E = \frac{1}{2} KT \cdot f_1 \cdot N_1 N_A + \frac{1}{2} KT \cdot f_2 \cdot N_2 \cdot N_A$$

$$= \frac{1}{2} N_1 f_1 RT + \frac{1}{2} N_2 f_2 RT \quad [\because N_A K = R]$$

$$= \frac{1}{2} RT (N_1 f_1 + N_2 f_2)$$

$$\therefore C_V = \left(\frac{dE}{dT}\right)_V = \frac{1}{2} R (N_1 f_1 + N_2 f_2)$$

But, for (N_1+N_2) mole of gas

$$C_p - C_v = (N_1+N_2)R$$

$$\therefore C_p = C_v + (N_1+N_2)R$$

$$= \frac{1}{2}R(N_1f_1+N_2f_2) + (N_1+N_2)R$$

$$= \frac{R[(N_1f_1+N_2f_2) + (2N_1+2N_2)]}{2}$$

$$= \frac{R[N_1(2+f_1) + N_2(2+f_2)]}{2}$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{\frac{R[N_1(2+f_1)+N_2(2+f_2)]}{2}}{\frac{1}{2}R(N_1f_1+N_2f_2)}$$

$$\boxed{\gamma = \frac{N_1(2+f_1)+N_2(2+f_2)}{N_1f_1+N_2f_2}}$$

This is the required relation.

*** For N_1, N_2, N_3 mole of gases the above equation can be modified as

$$\gamma = \frac{N_1(2+f_1)+N_2(2+f_2)+N_3(2+f_3)}{N_1f_1+N_2f_2+N_3f_3} \quad (1)$$

Where f_1, f_2, f_3 are the degrees of freedom of each type gases respectively.

(10) Dulong & Petit's law :-

If the temperature is not too low, the molar Sp. heat capacity of all pure substances in solid state are nearly equal to 6 Calorie.

Proof :-

Consider one gm atom of solid so there will be N_A of atoms. The atoms within the solid can vibrate only since they have fixed position. So, the no. of degrees of freedom (vibrational) = $3N_A$. Now an atom can have both Kinetic and potential energy. So, the average Kinetic energy is equal to the average potential energy.

∴ Kinetic energy of the above solid = $\frac{1}{2}KT \times 3N_A$

∴ Total energy (U) = $2 \times \frac{1}{2}KT \times 3N_A$

$= 3N_A KT$

∴ $C_V = \left(\frac{dU}{dT}\right)_V = 3N_A K$

$= 3R$

$= 3 \times 2 = 6$ Calorie.

[∵ $R \simeq 2$ Cal.]

(11) Mean free path :-

The path traversed by a molecule between two successive collisions is called a free path and the average distance traversed by this molecule between two successive collisions is called mean free path. Mean free path always be a straight line.

(12) Distribution of free path (Survival Equation) :-

To determine how the free paths are distributed among the molecules is equivalent to find the probability that molecule moving with a velocity c and ~~describe~~ traverse a distance x without suffering any collision. This is a function of x Say $f(x)$. Now, if the mean free path is λ, then the probability to suffer a collision in traversing a distance dx is dx/λ. So, the probability of no collision to traverse a distance dx is $(1 - dx/\lambda)$.

Now, the probability of that molecule to traverse further distance $x+dx$ with suffering no collision $f(x+dx)$ is the product of $f(x)$ and $(1 - \frac{dx}{\lambda})$

$$\therefore f(x+dx) = f(x)\left(1 - \frac{dx}{\lambda}\right) \longrightarrow (1)$$

Expanding with the help of Taylor series

$$f'(x)\,dx = -f(x)\frac{dx}{\lambda}$$

or, $$\frac{f'(x)}{f(x)}\,dx = -\frac{dx}{\lambda}$$

Integrating we get

$$\ln f(x) = -\frac{x}{\lambda} + \ln A \quad (\text{Const.})$$

$$f(x) = Ae^{-\frac{x}{\lambda}}$$

Now, when $x=0$, $f(x)=1$

$$\therefore A = 1$$

$$\therefore f(x) = e^{-x/\lambda}$$

This is the law of distribution of free paths.

The above law shows that the very long paths probability is very small.

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Now, If N_0 molecules of velocity c are incident on the gas, then only $N_0 e^{-x/\lambda}$ will travel a distance x without suffering any collision, i.e

$$N = N_0 e^{-x/\lambda}$$

This is well known Survival Equation.

(13) Expression for mean free path (Elementary treatment)

Assume at any instant all molecules of a gas are at rest except one. This particular molecule moving with an average velocity $\bar{c}$. We also assume that the molecules are perfectly elastic sphere of diameter σ. So, the centre to centre distance during collision of the colliding molecules is σ. The Centre to centre distance of the colliding molecules remain same if the radius of the moving molecule increase to σ and all the other molecules all shrunk to a geometrical mass point.

So, the effective cross sectional area of the moving molecule i.e Collision cross section ρ is $\rho = \pi \sigma^2$

After an interval t the moving molecule transverses a distance $\bar{c}t$ and sweeps out a cylindrical volume of cross section ρ and length $\bar{c}t$. Plainly the moving molecule collide with those molecule having their centre within this cylindrical volume.

in time t. If n be the number of molecule per unit volume. Then the no. of molecules within the cylindrical volume is $\rho \bar{c} t n$.

$\therefore$ So, the no. of Collision in time $t = \rho n \bar{c} t$

$\therefore$ Collision frequency (no. of collision per unit time)

$$= \rho n \bar{c}$$

$\therefore$ Mean free path $\lambda = \frac{\text{distance covered in time } t}{\text{no. of collision in } t}$

$$= \frac{\bar{c} t}{\rho n \bar{c} t} = \frac{1}{\rho n}$$

$$= \frac{1}{\pi \sigma^2 n} \quad [\because \rho = \pi \sigma^2]$$

This is the expression for mean free path when one molecule is moving and other assume to be in rest.

* But, For more complete calculation for mean free path must take into account the motion of all molecules of the gas, the fact that all molecules are not moving with the same speed and also other factors. After Consider the motion of all molecules the mean free path equation is

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 n}$$