

Position space:

The three dimensional space in which the location of a particle is completely given by the three position co-ordinates, is known as position space.

A small element in position space is given by,

$$dV = dx dy dz.$$

$$\therefore V = \iiint dx dy dz.$$

Momentum space:

If the system is dynamic, its particles move about with various velocities and hence possess momentum.

A complete specification of such a system can not be described in terms of position co-ordinate only. For a dynamic system, we must specify the three components of momentum with the help of three velocity components v_x, v_y and v_z in addition to the three position co-ordinates x, y and z .

The three components of momentum are,

$$p_x = mv_x, \quad p_y = mv_y \quad \& \quad p_z = mv_z.$$

The momentum of the particle is completely specified by the three mutually perpendicular co-ordinates p_x, p_y and p_z in three dimensional space known as momentum space.

A small volⁿ in momentum space is given by,

$$d\Gamma = dp_x dp_y dp_z.$$

$$\therefore \Gamma = \iiint dp_x dp_y dp_z.$$

Phase space:

A combination of the position space and momentum space is known as phase space. Thus, phase space has six dimensions. A point in phase space is, therefore, completely specified by six co-ordinates x, y, z, p_x, p_y, p_z .

A small volⁿ in phase space is given by,

$$d\tau = dx dy dz dp_x dp_y dp_z.$$

$$d\tau = dV d\Gamma.$$

$$\therefore \tau = \iiint dx dy dz \iiint dp_x dp_y dp_z.$$

$\text{Size of a phase space cell} = h_0^3$

Macrostate:

A macrostate the overall description of the system in terms of a few macroscopic variables such as pressure, volume, temperature etc. A single macrostate can correspond to many possible microstates.

Microstates:

A microstate is a specific detailed arrangement of all the particles of a system, consistent with its energy, volume and no. of particles. It describes exactly how each particle is distributed in position and momentum space.

Thermodynamic probability:

The thermodynamic probability of a macrostate is the number of microstates corresponding to that macrostate.

It is denoted by W . It is not a probability in usual sense (0-1) range, ^{but} rather a count (always a positive integer).

Example: 4 identical & distinguishable particles a, b, c, & d distributed into two compartments. List all the macrostates & microstate from this example.

Microstates.		Macrostate	Freq. W	Probability $P = \frac{W}{K^N}$
Comp 1	Comp 2			
abcd	—	(4, 0)	1	$1/16$
bcd	a	(3, 1)	4	$4/16 = \frac{1}{4}$
acd	b			
abd	c			
abc	d			
ab	cd	(2, 2)	6	$6/16$
ac	bd			
ad	bc			
bc	ad			
bd	ac			
cd	ab			
a	bcd	(1, 3)	4	$4/16$
b	acd			
c	abd			
d	abc			
—	abcd	(0, 4)	1	$1/16$

(4, 0) macrostate has 1 microstate

(3, 1) macrostate has 4 microstates.

(2, 2) macrostate has 6 microstates & so on.

No. of micro macrostate = $n+1$ No. of microstates = K^n	n = no. of particles K = compartments
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Q: State the assumptions made in the derivation of velocity distribution of gas molecules.

Ans: To derive the velocity distribution of gas molecules, we use Maxwell-Boltzmann statistics. The main assumptions of Maxwell-Boltzmann statistics are →

- (i) The particles of the system are identical and distinguishable.
- (ii) The available vol^m of the phase space cell can be as small as we please and may even approach zero.
- (iii) The phase space can be divided into a very large number of cells.
- (iv) The state of each particle is specified by giving its instantaneous position and momentum coordinates or by giving its cell number in phase space.
- (v) There is no restriction in the number of particles which can occupy a phase space cell.
- (vi) The system of particles contained in a vessel form an isolated system, i.e. the system satisfies two conditions —
 - (a) The total no. of particles in the system remains constant and
 - (b) The total energy of the system remains constant.

Maxwell-Boltzmann distribution law:

MB distribution law is applicable to identical but-distinguishable particles. It finds the energywise distribution of the particles. To find the distribution law, let us consider a vessel having a volⁿ V . Let we have an ideal (non-interacting) gas having very large no. of molecules n , enclosed in the vessel. These molecules are in motion constantly. They are colliding with each-other and walls of the vessel. The gas molecules possess momentum and energy due to these thermal motions. Due to collisions, the ~~the~~ momentum and energy of any particular molecule goes on continuously changing. If the gas is thermally isolated, the total energy E of all the molecules of the gas taken together remains constant. Hence, the system on the whole, is in a state of equilibrium (most probable state).

Let there are n molecules in the gas. Let the gas molecules have energies ranging from 0 to ϵ_K . Divide the whole energy intervals from 0 to ϵ_K into a very large number of K intervals numbered as 1, 2, 3, ..., K . Let the mean energies corresponding to these intervals are $\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_K$ respectively. As the molecules possess energies ranging from 0 to ϵ_K , a molecule must lie in one of the energy intervals. This case is similar to arranging n particles in K sections with the difference that in this case instead of sections we have energy intervals. Divide each interval into equal sized cells in phase space and $g_1, g_2, \dots, g_K$ be the no. of cells corresponding to

energy intervals marked 1, 2, 3, ..., K respectively. Let $n_1, n_2, \dots, n_K$ represent the no. of molecules in the energy intervals 1, 2, ..., K respectively in most probable state and mean energies of the particles are $\epsilon_1, \epsilon_2, \dots, \epsilon_K$ respectively.

$$\therefore n = n_1 + n_2 + \dots + n_K = \sum_{i=1}^K n_i$$

$$\because n = \text{const}$$

$$\therefore dn = \sum dn_i = 0 \longrightarrow (1)$$

ly, total energy,

$$E = n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_K \epsilon_K = \sum_{i=1}^K n_i \epsilon_i$$

$$\because E = \text{const.}$$

$$\therefore dE = \sum_{i=1}^K dn_i \epsilon_i = 0 \longrightarrow (2)$$

Multiplying eqⁿ (1) & eqⁿ (2) by arbitrary constants α and β and then adding, we get,

$$\alpha dn + \beta dE = 0 \longrightarrow (3)$$

Now, the thermodynamic probability of the macrostate,

$$W = n! \prod \frac{g_i^{n_i}}{n_i!}$$

Taking logarithms on both sides,

$$\ln W = \ln n! + \sum_{i=1}^K n_i \ln g_i - \sum_{i=1}^K \ln(n_i!) \longrightarrow (4)$$

As n & n_i are all large numbers, we can apply Stirling's formula $\longrightarrow$

$$\ln(n!) = n \ln n - n$$

$\therefore \text{Eqn (4)} \Rightarrow$

$$\ln W = n \ln n - n + \sum_{i=1}^K n_i \ln g_i - \sum_{i=1}^K n_i \ln n_i + \sum_{i=1}^K n_i$$

As, $\sum_{i=1}^K n_i = n$

$$\therefore \ln W = n \ln n + \sum_{i=1}^K n_i \ln g_i - \sum_{i=1}^K n_i \ln n_i \longrightarrow (5)$$

The thermodynamic probability is maximum for the most probable state, i.e. in equilibrium.

$$\therefore d(\ln W) = 0.$$

$$\Rightarrow \sum_{i=1}^K dn_i \ln g_i - \sum_{i=1}^K dn_i \ln n_i = 0$$

$$\Rightarrow \sum_{i=1}^K (\ln g_i - \ln n_i) dn_i = 0 \longrightarrow (6)$$

Comparing eqn (3) & eqn (6) $\Rightarrow$

$$\alpha dn + \beta d\varepsilon = \sum_{i=1}^K (\ln g_i - \ln n_i) dn_i$$

$$\Rightarrow \alpha \sum_{i=1}^K dn_i + \beta \sum_{i=1}^K dn_i \varepsilon_i = \sum_{i=1}^K (\ln g_i - \ln n_i) dn_i$$

$$\Rightarrow \sum_{i=1}^K (\ln g_i - \ln n_i - \alpha - \beta \varepsilon_i) dn_i = 0 \longrightarrow$$

$$\therefore dn_i \neq 0.$$

$$\therefore \ln g_i - \ln n_i - \alpha - \beta \varepsilon_i = 0.$$

$$\Rightarrow \ln (g_i / n_i) = \alpha + \beta \varepsilon_i$$

$$\Rightarrow n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i}} \longrightarrow (7)$$

— This is MB law of energy distribution.

Evaluation of g_i , α and β !

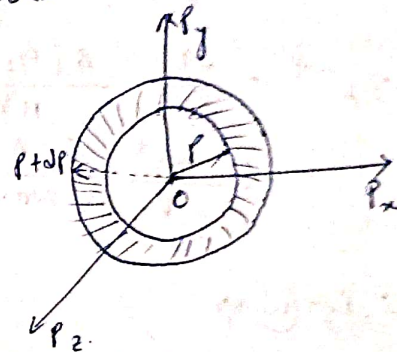
In order to evaluate g_i , α and β , in eqn (7), let us consider a continuous distribution of molecular energies. If $n(\varepsilon)d\varepsilon$ be the no. of molecules whose energies lie betn $\varepsilon \rightarrow \varepsilon + d\varepsilon$; then eqn (7) can be written as,

$$n(\varepsilon)d\varepsilon = g(\varepsilon) e^{-(\alpha + \beta \varepsilon)} d\varepsilon \longrightarrow (8)$$

where, $g(\varepsilon)$ = no. of cells in phase space.

$$\varepsilon = \frac{1}{2} m v^2$$

$$\text{or, } \varepsilon = \frac{p^2}{2m}.$$



$$\therefore \text{Eqn (8)} \Rightarrow n(p) dp = g(p) e^{-\alpha} e^{-\beta p^2 / 2m} dp. \longrightarrow (9)$$

$n(p)dp$ = no. of molecules in the momentum interval $p \rightarrow p + dp$.

$g(p)dp$ = no. of cells in phase space in the momⁿ interval $p \rightarrow p + dp$.

If h^3 = vol^m of a single cell in phase space; then,

$$g(p)dp = \frac{\iiint dx dy dz \iiint dp_x dp_y dp_z}{h^3}$$

$$= \frac{V}{h^3} \iiint dp_x dp_y dp_z.$$

$$= \frac{V}{h^3} 4\pi p^2 dp.$$

$$\therefore n(p)dp = \frac{4\pi V}{h^3} p^2 e^{-\alpha} e^{-\beta p^2 / 2m} dp \longrightarrow (10)$$

Now, we evaluate $e^{-\alpha}$ in eqn (10).

Since, total no. of molecules = n .

$$n = \int_0^{\infty} n(p) dp.$$

$$= \frac{4\pi V}{h^3} e^{-\alpha} \int_0^{\infty} p^2 e^{-\beta p^2/2m} dp.$$

$$= \frac{4\pi V}{h^3} e^{-\alpha} \frac{1}{4} \left[\frac{\pi}{(\beta/2m)} \right]^{1/2} \left[\because \int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}} \right]$$

$$\Rightarrow e^{-\alpha} = \frac{n h^3}{4\pi V} \frac{4 (\beta/2m)^{3/2}}{\pi^{1/2}}$$

$$= \frac{n h^3}{V} \left(\frac{\beta}{2\pi m} \right)^{3/2}.$$

$\therefore$ Eqn (10) $\Rightarrow$

$$n(p) dp = \frac{4\pi V}{h^3} p^2 \frac{n h^3}{V} \left(\frac{\beta}{2\pi m} \right)^{3/2} e^{-\beta p^2/2m} dp.$$

$$\Rightarrow n(p) dp = 4\pi n \left(\frac{\beta}{2\pi m} \right)^{3/2} e^{-\beta p^2/2m} p^2 dp \longrightarrow (11).$$

In order to evaluate β , we compute the total energy E of the system of molecules.

$$p^2 = 2m\epsilon.$$

Differentiating,

$$2p dp = 2m d\epsilon.$$

$$\Rightarrow dp = \frac{m}{\sqrt{2m\epsilon}} d\epsilon.$$

$$= \sqrt{\frac{m}{2\epsilon}} d\epsilon.$$

$\therefore$ Eqn (11) $\Rightarrow$

$$n(\epsilon) d\epsilon = 4\pi n \left(\frac{\beta}{2\pi m} \right)^{3/2} 2m\epsilon e^{-\beta\epsilon} \left(\frac{m}{2\epsilon} \right)^{1/2} d\epsilon.$$

$$\Rightarrow n(\epsilon) d\epsilon = \frac{2n}{\sqrt{\pi}} \beta^{3/2} \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon \longrightarrow (12)$$

This is the no. of molecules lying in the energy interval $\epsilon \rightarrow \epsilon + d\epsilon$ in terms of β .

$\therefore$ Total energy of these molecules = $\epsilon n(\epsilon) d\epsilon$.

$\therefore$ Total energy of the system containing all the n molecules.

$$E = \int_0^{\infty} \epsilon n(\epsilon) d\epsilon.$$

$$= \frac{2n}{\sqrt{\pi}} \beta^{3/2} \int_0^{\infty} \epsilon^{3/2} e^{-\beta\epsilon} d\epsilon.$$

$$= \frac{2n}{\sqrt{\pi}} \beta^{3/2} \frac{3}{4\beta^2} \sqrt{\frac{\pi}{\beta}} \left[\because \int_0^{\infty} x^{3/2} e^{-ax} dx = \frac{3}{4a^2} \sqrt{\frac{\pi}{a}} \right]$$

$$E = \frac{3n}{2\beta} \longrightarrow (13)$$

According to kinetic theory of gases, the total energy of n molecules of an ideal gas at absolute temperature T is given by,

$$E = \frac{3}{2} nKT \longrightarrow (14)$$

$\therefore K = \text{Boltzmann const.}$

Comparing (13) & (14) $\Rightarrow$

$$\beta = \frac{1}{KT}.$$

Substituting the value of β in eqn (12); we have,

$$n(\epsilon) d\epsilon = \frac{2n}{\sqrt{\pi}} \left(\frac{1}{KT} \right)^{3/2} \epsilon^{1/2} e^{-\epsilon/KT} d\epsilon \quad \rightarrow (15)$$

↳ This is law of distribution of energies. It gives the no. of molecules having energies betn ϵ & $\epsilon + d\epsilon$ in terms of total no. of molecules n , absolute temp (T) & Boltzmann const. (K).

Eqn (11) $\Rightarrow$

$$n(p) dp = 4\pi n \left(\frac{1}{2\pi mKT} \right)^{3/2} p^2 e^{-\frac{p^2}{2mKT}} dp \quad \rightarrow (16)$$

↳ This gives the no. of molecules having momentum betn p and $p + dp$.

Substituting $p = mv$ & $dp = m dv$;

Eqn (16) $\Rightarrow$

$$n(v) dv = 4\pi n \left(\frac{1}{2\pi mKT} \right)^{3/2} e^{-\frac{mv^2}{2KT}} m^2 v^2 m dv$$

$$\Rightarrow n(v) dv = 4\pi n \left(\frac{m}{2\pi KT} \right)^{3/2} e^{-\frac{mv^2}{2KT}} v^2 dv \quad \rightarrow (17)$$

↳ This gives the no. of molecules having velocity betn v and $v + dv$ and is known as MB law of distribution of velocities.

** Probability that molecules possess the speed betn v and $v + dv$ is;

$$P(v) dv = \frac{n(v) dv}{n}$$

$$\Rightarrow P(v) dv = 4\pi \left(\frac{m}{2\pi KT} \right)^{3/2} e^{-\frac{mv^2}{2KT}} v^2 dv \quad \rightarrow (18)$$

Expression for Average speed:

We have, the no. of molecules in the velocity range v and $v + dv$ is given by,

$$n(v) dv = 4\pi n \left(\frac{m}{2\pi KT} \right)^{3/2} e^{-\frac{mv^2}{2KT}} v^2 dv$$

The average speed of gas molecules is given by,

$$V_{av} = \frac{\int_0^\infty v n(v) dv}{\int_0^\infty n(v) dv}$$

$$\because \int_0^\infty n(v) dv = n$$

$$\therefore V_{av} = \frac{1}{n} \int_0^\infty v n(v) dv$$

$$= \frac{4\pi n}{n} \left(\frac{m}{2\pi KT} \right)^{3/2} \int_0^\infty v^3 e^{-\frac{mv^2}{2KT}} dv$$

$$= 4\pi \left(\frac{m}{2\pi KT} \right)^{3/2} \frac{4K^2 T^2}{2m^2} \left[\because \int_0^\infty v^3 e^{-\frac{mv^2}{2KT}} dv = \frac{1}{2K^2} \right]$$

$$= \sqrt{\frac{2}{\pi}} 4\pi \left(\frac{m}{2\pi KT} \right) \sqrt{\frac{m}{2\pi KT}} \frac{4K^2 T^2}{2m^2}$$

$$= \sqrt{\frac{8KT}{\pi m}}$$

$$\therefore V_{av} = \sqrt{\frac{8KT}{\pi m}}$$

Expression for Root Mean Square Speed:

We have, the no. of molecules within the velocity range $v \rightarrow v+dv$ is given by,

$$n(v)dv = 4\pi n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT} v^2 dv$$

$$\text{Now, } v_{rms}^2 = \frac{\int_0^\infty v^2 n(v) dv}{\int_0^\infty n(v) dv}$$

$$= \frac{1}{n} \int_0^\infty v^2 n(v) dv$$

$$= \frac{1}{n} 4\pi n \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty v^4 e^{-mv^2/2kT} dv$$

Using standard integral;

$$\int_0^\infty x^4 e^{-ax^2} dx = \frac{3}{8a^2} \sqrt{\frac{\pi}{a}}; \text{ we get,}$$

$$v_{rms}^2 = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{3 \times 4 k^2 T^2}{8 m^2} \sqrt{\frac{2\pi kT}{m}}$$

$$= 4 \cdot \frac{6\pi k^2 T^2}{m^2} \frac{m}{2\pi kT} \sqrt{\frac{m 2\pi kT}{m}}$$

$$= \frac{3kT}{m}$$

$$\Rightarrow v_{rms} = \sqrt{\frac{3kT}{m}}$$

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

Expression for the Most-Probable Speed:

No. of molecules lying within the velocity range v and $v+dv$ is given by,

$$n(v)dv = 4\pi n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT} v^2 dv$$

Probability that molecules possess velocity between v and $v+dv$ is,

$$P(v)dv = \frac{n(v)dv}{n}$$

$$\Rightarrow P(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$

At the most probable speed;

$$\frac{dP(v)}{dv} = 0$$

$$\Rightarrow 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \left[2v e^{-mv^2/2kT} + v^2 e^{-mv^2/2kT} \left(-\frac{2mv}{2kT} \right) \right] = 0$$

$$\Rightarrow e^{-mv^2/2kT} \left[2v - \frac{mv^3}{kT} \right] = 0$$

$$\Rightarrow \frac{mv^3}{kT} = 2v$$

$$\Rightarrow v^2 = \frac{2kT}{m}$$

$$\Rightarrow v_{mp} = \sqrt{\frac{2kT}{m}}$$

$$v_{mp} = \sqrt{\frac{2kT}{m}}$$

Experimental verification of Maxwell velocity distribution:

Experimental evidences of Maxwell law of velocity distribution were explained by using molecular beam methods given as —

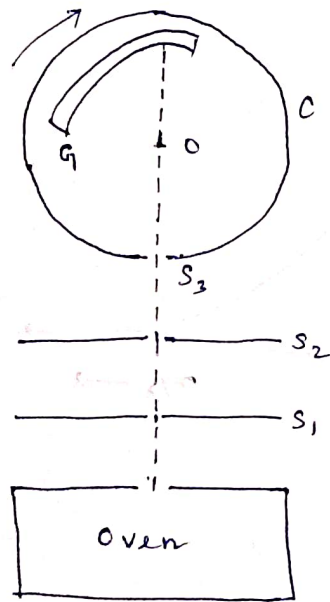
- ① Zartmann & Ko method.
- ② Estermann, Simpson & Stern method.

① ZARTMANN & KO'S METHOD:

The direct experimental verification was given by Zartmann and Ko in 1930-34.

Principle: Density of molecules deposited is directly proportional to the molecular speed.

Construction:



Oven: An oven is taken in which silver is heated to convert into gaseous state.

Collimator: Slits S_1 and S_2 are taken to provide a fine beam of silver molecules.

Cylinder: C is an cylindrical drum which can be rotated with a speed of 100 revolutions per second about an axis O and a hole on the drum, use as slit S_3 .

Glass plate: A glass plate G is connected with the drum C opposite to the slit S_3 .

Microphotometer: The no. of molecules falling on a certain part of glass plate G , is estimated by measuring the thickness with a microphotometer.

Working: Whenever the oven is switched on, as soon as the silver molecules evaporate & reached to the glass plate by the slit S_1 and S_2 and they start deposited on the glass plate G through the slit S_3 . The drum is kept rotating continuously and only one single time S_1, S_2 and S_3 are in a straight line and silver ions are deposited on the plate. Every gas molecules moves with different speed and fastest moving silver ions reached first on the plate and slower reached later on the plate. Thus less is the speed of molecules, they deposited left to the glass plate G from the reference point. Thus, the measurement of density or number of molecules is the measure of velocity spectrum.

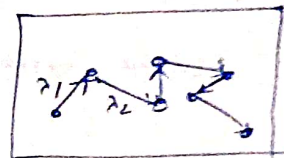
Mean free path :

It is defined as the average distance traversed by a molecule betⁿ two successive collisions. It is denoted by λ . If $\lambda_1, \lambda_2, \lambda_3, \dots$ are the successive free paths traversed by a molecule in real time t and N_0 is no. of collisions suffered by gas molecule during this time, then mean free path is

given by;

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots}{N_0}$$

$$= \frac{C_{av} \times t}{N_0} \quad \text{--- (1)}$$



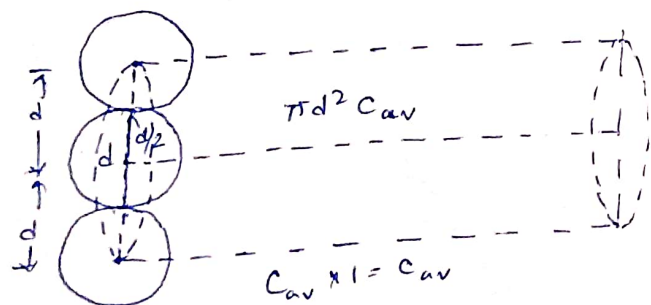
where, C_{av} is average speed of the gas molecules.

Expression for mean free path:

To obtain expression for mean free path (λ);
Let us assume that all the molecules except one are at rest. Let n be the no. of gas molecules per unit vol^m and d be diameter of gas molecule. The moving molecule will collide with all the molecules whose centres lie within distance d from its centre.

Distance covered by moving molecule in one second
 $= C_{av} \times 1 = C_{av}$.

In one second, the moving molecule will collide with all the molecules whose centres lie within the cylinder of vol^m $\pi d^2 C_{av}$.



The no. of collisions made by moving molecule in unit time is given by;

$$N_0 = \pi d^2 C_{av} \times n \longrightarrow (2) \quad ; \text{ no. of molecules per unit vol^m }$$

$$\text{Mean free path} = \frac{\text{Total distance traversed in 1 sec.}}{\text{Total no. of collisions made by molecule in 1 sec.}}$$

$$\lambda = \frac{C_{av}}{\pi d^2 C_{av} \times n}$$

$$\lambda = \frac{1}{\pi d^2 n} \longrightarrow (3)$$

The above expression has been derived on the basis of an assumption that - all molecules except one are at rest. In reality all the gas molecules are moving in random directions with all possible speeds. Maxwell modified above expression by considering actual behaviour of gases;

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

Mean free path in terms of temp^r and pressure^s

We know that pressure exerted by gas on the walls of container is given by;

$$P = \frac{1}{3} f c^2 \quad ; c = \text{rms speed of a gas molecule.}$$

$$c = \sqrt{\frac{3KT}{m}}$$

$$\therefore P = \frac{1}{3} f \frac{3KT}{m}$$

$$P = \frac{fKT}{m}$$

Here, $f = n \times m$; where m is mass of a gas molecule.

$$\therefore P = \frac{n m K T}{m}$$

$$\Rightarrow n = \frac{P}{KT}$$

$$\lambda = \frac{KT}{\sqrt{2} \pi d^2 P}$$

Show that mean free path directly proportional to temp^r or inversely proportional to pressure.

Transport of mass: Diffusion:

A gas may be assumed to be consisting of large no. of parallel layers, each layer having different molecular concentrations. In such case, the gas molecules will move from the layers having higher concentrations towards the layers having lower concentrations so as to bring about the eqm state. This phenomenon is known as diffusion in gases.

If we consider two parallel gas layers having molecular concentration $n + dn$ and n respectively, then no. of molecules flowing per unit area from layer ① towards layer ② are given

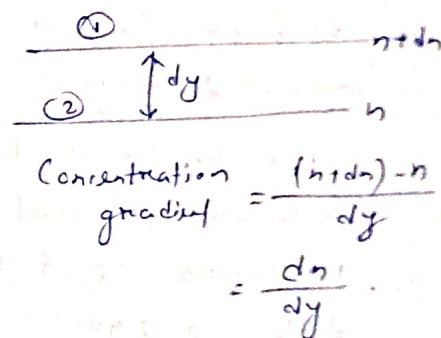
by;

$$N \propto \frac{dn}{dy}$$

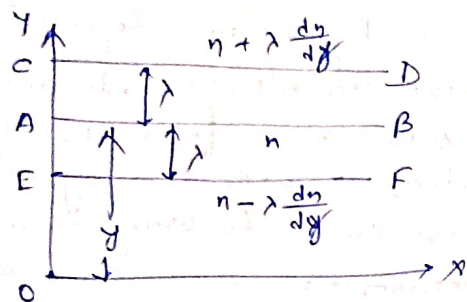
$$\Rightarrow N = D \frac{dn}{dy}$$

D = coefficient of diffusion.

$\frac{dn}{dy}$ = concentration gradient (Rate of change of molecular concentration with distance).



Expression for co-efficient of diffusion of a gas on the basis of kinetic theory of gases:



Consider a gas flowing in parallel layers to a fixed axis ox . Consider a gas layer AB situated at a normal distance y from ox .

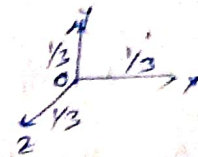
Let n be the molecular concentration (i.e. no. of molecules per unit vol^m) in layer AB . Consider two layers CD & EF above and below AB at a distance λ equal to mean free path of gas molecules.

Molecular concentration in layer $CD = n + \lambda \frac{dn}{dy} \rightarrow \textcircled{2}$

Molecular concentration in layer $EF = n - \lambda \frac{dn}{dy} \rightarrow \textcircled{3}$.

A/c to postulates of kinetic theory of gases, the gas molecules can have equal probability to move in all the possible direction (x, y, z).

No. of molecules moving along y -axis = $\frac{1}{3}$.



Out of these, $\frac{1}{6}$ th molecules are moving upwards and $\frac{1}{6}$ th molecules are moving downwards. If $\bar{c}$ is average speed of these gas molecules, then, the no. of molecules crossing layer AB downwards per unit area per unit time = $\frac{1}{6} \bar{c}$

No. of molecules coming from the layer CD and crossing layer AB downwards per unit area per unit time is given by,

$$= \frac{1}{6} \bar{c} \left(n + \lambda \frac{dn}{dy} \right)$$

Similarly, no. of molecules coming from the layer EF and crossing the layer AB upwards per unit area per unit time is given

$$\text{by, } \frac{1}{6} \bar{c} \left(n - \lambda \frac{dn}{dy} \right) = \frac{1}{6} \bar{c} \left(n - \lambda \frac{dn}{dy} \right)$$

Net no. of molecules crossing layer AB downwards per unit area per unit time

$$N = \frac{1}{6} \bar{c} \left(n + \lambda \frac{dn}{dy} \right) - \frac{1}{6} \bar{c} \left(n - \lambda \frac{dn}{dy} \right)$$

$$= \frac{1}{6} \bar{c} \left[n + \lambda \frac{dn}{dy} - n + \lambda \frac{dn}{dy} \right]$$

$$= \frac{1}{6} \bar{c} \left(2\lambda \frac{dn}{dy} \right)$$

$$= \frac{1}{3} \bar{c} \lambda \frac{dn}{dy}$$

$$N = \frac{1}{3} \bar{c} \lambda \frac{dn}{dy} \rightarrow (4)$$

$$\text{And } N = D \frac{dn}{dy} \rightarrow (1)$$

Comparing (1) & (4); we get;

$$D \frac{dn}{dy} = \frac{1}{3} \bar{c} \lambda \frac{dn}{dy}$$

$$\Rightarrow D = \frac{1}{3} \bar{c} \lambda \rightarrow (5)$$

$$\left. \begin{array}{l} \bar{c} \propto \sqrt{T} \\ \lambda \propto \frac{1}{P} \end{array} \right\} \rightarrow (6)$$

Using (6) in (5);

$$D \propto \frac{\sqrt{T} \cdot T}{P}$$

$$D \propto \frac{T^{3/2}}{P}$$

Degree of Freedom:

The total number of independent variables required to describe completely the state of motion of a body are called its degree of freedom.

- Monoatomic molecule, e.g. Neon (Ne), Helium (He) etc., has 3 degree of freedom (all are translational).
- Diatomic molecule having a dumb-bell shape, e.g., HCl, Cl₂, O₂, CO etc. has 5 degree of freedom (3 translational + 2 rotational).
- A triatomic molecule, if it is linear e.g. CO₂, CH₂, etc., has 5 degree of freedom (3 translation + 2 rotational).
if it is non-linear, e.g. H₂O, SO₂ etc. has 6 degree of freedom (3 translational + 3 rotational).

Relation betn molar specific heats and degree of freedom:

For an ideal gas, there is no force of attraction betn the molecules, hence the internal energy U of the gas is wholly kinetic. If f is the number of degree of freedom, then according to the law of equipartition of energy,

$$\text{Average energy per molecule} = \frac{1}{2} f K T.$$

$$\therefore \text{Total energy; } U = \frac{1}{2} N f K T.$$

$$= \frac{1}{2} f R T.$$

$$\left[\because \frac{R}{N} = K \right]$$

$\therefore$ The molar specific heat of the gas at constant volume,

$$C_V = \frac{dU}{dT}$$

$$= \frac{1}{2} f R$$

& the molar specific heat of the gas at constant pressure,

$$C_P = C_V + R$$

$$= \left(1 + \frac{f}{2}\right) R.$$

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

① Monoatomic gas:

$$f = 3.$$

$$\therefore U = \frac{3}{2} R T.$$

$$C_V = \frac{3}{2} R \quad \& \quad C_P = \left(\frac{3}{2} R + R\right) = \frac{5}{2} R.$$

$$\& \quad \gamma = \frac{C_P}{C_V} = \frac{5}{3} = 1.67.$$

② Diatomic gas:

$$f = 5$$

$$\therefore U = \frac{5}{2} R T$$

$$C_V = \frac{5}{2} R \quad \& \quad C_P = \left(\frac{5}{2} R + R\right) = \frac{7}{2} R$$

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{7}{5} = 1.40$$

<u>Monoatomic</u>
$\gamma = 1 + \frac{2}{f}$
$= 1 + \frac{2}{3}$
$= \frac{5}{3}$
$= 1.67$
<u>Diatomic</u>
$\gamma = 1 + \frac{2}{f} = 1 + \frac{2}{5}$
$= \frac{7}{5} = 1.4$

Variation of γ with temp:

At high temp, vibrational degree of freedom is also become prominent. (3 translational + 2 rotational + 2 vibrational)

$$\begin{aligned}\therefore \gamma &= \frac{C_p}{C_v} = 1 + \frac{2}{f} \\ &= 1 + \frac{2}{7} \\ &= \frac{9}{7} \\ &= 1.29\end{aligned}$$

(3) Triatomic molecule:

(a) Non-linear molecule:

$$\begin{aligned}f &= 6. \\ \gamma &= 1 + \frac{2}{6} = \frac{4}{3} = 1.33.\end{aligned} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{ordinary temp.}$$

$$\begin{aligned}\text{At high temp; } f &= 7. \\ \gamma &= 1 + \frac{2}{7} = \frac{9}{7} = 1.29\end{aligned} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{high temp.} \quad (1)$$

(b) Linear molecule:

~~f = 5~~

A triatomic linear gas molecule has 5 degrees of freedom. This is similar to diatomic molecule & possess $\gamma = 1.40$.

Taking into consideration vibrational degrees of freedom, a triatomic linear molecule possesses in all 6 degrees of freedom.

$$\gamma = 1 + \frac{2}{6} = 1.33.$$

Law of equipartition of energy:

Statement:

It states that, for any system in thermal equilibrium, the total energy is equally distributed among all the degrees of freedom and energy associated with each degree of freedom is $\frac{1}{2} kT$.

Proof:

According to kinetic theory of gases, the average translational kinetic energy of gas molecules at tempⁿ T is given by,

$$\frac{1}{2} m \bar{c}^2 = \frac{3}{2} kT \rightarrow (1)$$

where, m = mass of gas molecule.

k = Boltzmann const.

$$c = \sqrt{\frac{c_1^2 + c_2^2 + \dots + c_n^2}{n}}$$

$\rightarrow$ root mean square speed of gas molecules.

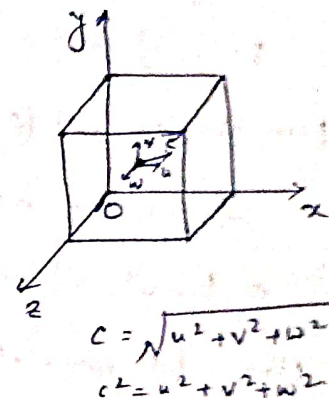
$$\text{Now, } c^2 = u^2 + v^2 + w^2 \rightarrow (2)$$

where, u , v and w are the components of c along x , y and z axis directions respectively.

In a container, gas molecules have no preference to move in any particular direction. Thus, we can write,

$$u = v = w$$

$$\Rightarrow \frac{1}{2} m u^2 = \frac{1}{2} m v^2 = \frac{1}{2} m w^2 \rightarrow (3)$$



Using ② in ① $\Rightarrow$

$$\frac{1}{2} m (u^2 + v^2 + w^2) = \frac{3}{2} K T$$

$$\Rightarrow \frac{1}{2} m (u^2 + w^2 + u^2) = \frac{3}{2} K T.$$

$$\Rightarrow \frac{1}{2} m (3u^2) = \frac{3}{2} K T$$

$$\Rightarrow \frac{3}{2} m u^2 = \frac{3}{2} K T \longrightarrow \textcircled{4}$$

$$\text{Similarly, } \frac{3}{2} m v^2 = \frac{3}{2} K T \longrightarrow \textcircled{5}$$

$$\& \quad \frac{3}{2} m w^2 = \frac{3}{2} K T \longrightarrow \textcircled{6}$$

From ④, ⑤ and ⑥

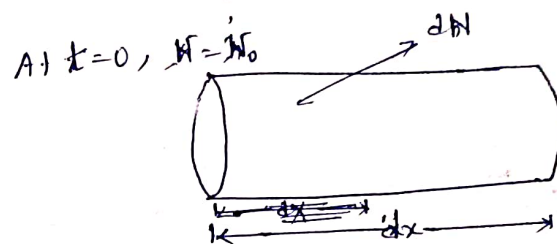
$$\frac{3}{2} m u^2 = \frac{3}{2} m v^2 = \frac{3}{2} m w^2 = \frac{3}{2} K T.$$

$$\Rightarrow \frac{1}{2} m u^2 = \frac{1}{2} m v^2 = \frac{1}{2} m w^2 = \frac{1}{2} K T$$

Thus, KE associated with each degree of freedom is $\frac{1}{2} K T$.

Collision Probability:
(Distribution of free paths):

Distribution of free paths means how many molecules have a specified free path length betn x and $x + dx$ out of a large no. of free paths.



Let us consider a system of N_0 molecules at a given instant as a group and they move along a certain direction and during motion they collide among them. In each collision some molecules are knocked out of this group. Let us consider N molecules are able to cross the distance x without collision. Now out of these N molecules say dN molecules are again knocked out due to collision on their forward additional journey through a short distance dx . Thus, we can write,

$$dN \propto N$$

$$dN \propto dx$$

$$\therefore dN = -P_c N dx \longrightarrow \textcircled{1}$$

Here, the constant of proportionality P_c is called collision probability. The negative sign is because each collision removes a molecule from the group and dN decreases.

$$dN = -P_c N dx$$

$$\Rightarrow \frac{dN}{N} = -P_c dx \quad \rightarrow (2)$$

Integrating both sides,

$$\ln N = -P_c x + \text{const.} \quad \rightarrow (3)$$

$$\text{At } x=0, N=N_0$$

$$\therefore (3) \Rightarrow \ln N_0 = 0 + \text{const.}$$

$$\therefore \ln N = -P_c x + \ln N_0$$

$$\Rightarrow \ln N - \ln N_0 = -P_c x$$

$$\Rightarrow \ln \left(\frac{N}{N_0} \right) = -P_c x$$

$$\Rightarrow \frac{N}{N_0} = e^{-P_c x}$$

$$\Rightarrow N = N_0 e^{-P_c x} \quad \rightarrow (4)$$

$$\therefore \text{Eqn (1)} \Rightarrow dN = -N_0 P_c e^{-P_c x} dx \quad \rightarrow (5)$$

From Eqn (5), we get the no. of molecules which have free paths at least equal to x (between x and $x+dx$).

The mean free path λ can thus be written as,

$$\lambda = \frac{x_1 dN_1 + x_2 dN_2 + \dots}{N_0}$$

$$= \frac{1}{N_0} \int_0^\infty x dN$$

$$= \frac{1}{N_0} \int_0^\infty x N_0 P_c e^{-P_c x} dx$$

$$\Rightarrow \lambda = P_c \int_0^\infty x e^{-P_c x} dx$$

$$= P_c \frac{1}{P_c^2} \Gamma(2)$$

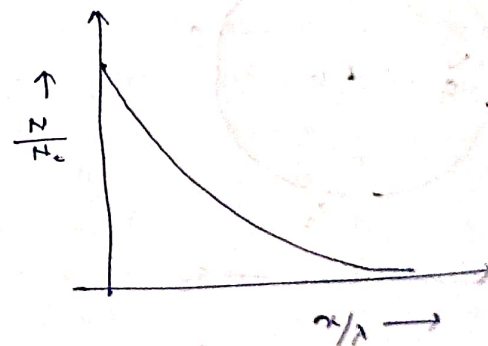
$$= P_c \cdot \frac{1}{P_c} (1)$$

$$= \frac{1}{P_c}$$

$$\therefore P_c = \frac{1}{\lambda}$$

$$\therefore \text{Eqn (4)} \Rightarrow N = N_0 e^{-x/\lambda} \quad \rightarrow (6)$$

Eqn (6) is known as the survival eqn. It gives the no. of molecules N (out of N_0) having free paths greater than x , i.e. molecules that survived over a path length x . It also shows that molecules falls off exponentially with distance x .



Gamma function

$$\Gamma(n) = \int_0^\infty e^{-x} x^{n-1} dx$$

$$\Gamma(n+1) = n \Gamma(n)$$

$$\Gamma(n+1) = n!$$

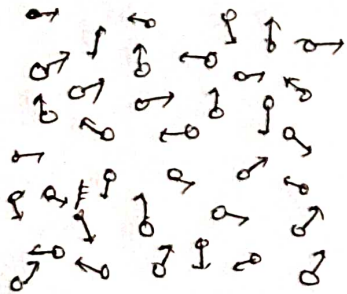
$$\Gamma(1) = 1$$

$$\Gamma(1/2) = \sqrt{\pi}$$

Brownian motion:

Brownian motion was first observed in 1827 by Brown, a botanist. The phenomenon of Brownian movement can easily be observed in a laboratory if a colloidal solution is examined under an ultramicroscope. As the direction of illumination is $\perp$ to the axis of microscope, the suspended particles in the solution look like bright-illuminated spots. These illuminated particles continuously move to and fro in a random haphazard way. The particles spin, rise, sink and rise again. The movement of the particles is continuous and spontaneous. This non-stop random and haphazard motion of the particles is called Brownian motion.

The motion of the particles becomes more violent with increase in temperature and more noticeable in a liquid of lower viscosity.



Brownian motion.

Essential features:

- (i) The motion of each particle is completely irregular and random. No two particles are found to execute the same motion.
- (ii) The motion is continuous and takes place forever.
- (iii) The motion is independent of the nature of the suspended particles.
- (iv) The motion becomes more violent on increasing the tempⁿ.
- (v) The smaller particles appear to be more agitated than the larger ones.
- (vi) The motion is more noticeable in a liquid of lower viscosity.
- (vii) The motion is not modified due to the staking of colloidal solution.
- (viii) The laws of kinetic theory of gases are applicable to Brownian motion too.

Q¹ Calculate the diameter of a molecule of benzene if the mean free path, $\lambda = 2.2 \times 10^{-6}$ cm and $n = 2.79 \times 10^{19}$ molecule/cm³ at normal temp^r and pressure.

Solⁿ: $\lambda = \frac{1}{\sqrt{2} \pi d^2 n}$

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

$$= \frac{1}{1.41 \times 3.14 \times 2.2 \times 10^{-6} \times 2.79 \times 10^{19}}$$

$$= 36.80 \times 10^{-16}$$

$$d = 6.06 \times 10^{-8} \text{ cm}$$

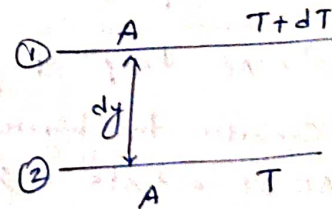
$$= 6.06 \text{ \AA}$$

Thermal conduction in gases? (Transport of energy)

A gas may be assumed to be consists of large no. of parallel layers which may be at different temp^s. In such a case, the gas molecules will carry kinetic energy from regions of higher temp^r to the regions of lower temp^r, so as to bring about thermal eqm state. This phenomenon is known as thermal conduction. If we consider two parallel gas layers separated by normal distance dy and having temp^r T and $T+dT$, then amount of heat energy flowing from layer ① ($T+dT$) to layer ② (T) is given by:

$$E \propto A \frac{dT}{dy}$$

$$E = K A \frac{dT}{dy} \rightarrow \text{①}$$



where,

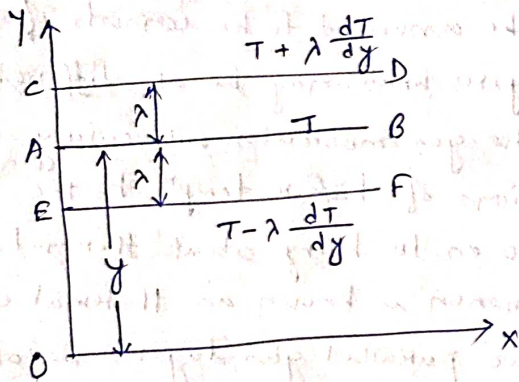
A = area of cross-section of each layer.

K = coefficient of thermal conductivity of gas.

$$\frac{dT}{dy} = \text{Temp^r gradient}$$

(rate of change of temp^r with distance).

Expression for co-efficient of thermal conductivity of gas:



Consider a gas at rest in the form of layers parallel to ox . Let AB be a layer at a normal distance y from ox .

Let, AB = tempⁿ of gas molecules in layer AB .

Consider two layers CD and EF above and below AB at a distance λ equal to mean free path of gas molecules.

Tempⁿ of gas molecules in layer $CD = T + \lambda \frac{dT}{dy}$

Tempⁿ of gas molecules in layer $EF = T - \lambda \frac{dT}{dy}$

A/c to postulates of kinetic theory of gases, gas molecules move in all possible directions x, y, z , so if n be the no. of gas molecules per unit vol^m; then;

No. of gas molecules moving along y -axis = $\frac{n}{3}$

Out of these, $\frac{n}{6}$ molecules ^{are} moving downwards and $\frac{n}{6}$ molecules are moving upwards.

Let $\bar{c}$ be avg. speed of gas molecules

No. of molecules crossing the layer AB downward per unit area per unit time = $\frac{n}{6} \bar{c}$

Total thermal energy carried by all the molecules crossing the layer AB downward per unit area per unit time = $m \left(\frac{n\bar{c}}{6} \right) c_v \left[T + \lambda \frac{dT}{dy} \right]$

Similarly, total thermal energy carried by all the molecules crossing the layer AB upwards per unit area per unit time = $m \left(\frac{n\bar{c}}{6} \right) c_v \left(T - \lambda \frac{dT}{dy} \right)$

Net transfer of ~~total~~ thermal energy across layer AB per unit area per unit time

$$E = m \left(\frac{n\bar{c}}{6} \right) c_v 2\lambda \frac{dT}{dy}$$

$$= \frac{1}{3} m n \bar{c} c_v \lambda \frac{dT}{dy}$$

$$E = \frac{1}{3} \rho \bar{c} c_v \lambda \frac{dT}{dy} ; \quad [\because \rho = mn] \quad \text{--- (3)}$$

Again;

$$E = KA \frac{dT}{dy}.$$

For unit area; $E = K \frac{dT}{dy} \quad \text{--- (4)}$

Comparing (3) & (4)

$$K = \frac{1}{3} \rho \bar{c} c_v \lambda$$

Now, $\bar{c} = \sqrt{\frac{8KT}{\pi m}}$

$$\therefore K = \frac{1}{3} \rho \sqrt{\frac{8KT}{\pi m}} c_v \lambda$$

$$\therefore K \propto \sqrt{T}$$

$$K \propto \frac{1}{\sqrt{m}}$$

Q. Calculate the radius of an oxygen molecule if its co-efficient of viscosity thermal conductivity;

$K = 24 \times 10^{-3} \text{ dm-sec-K at } 0^\circ\text{C}$ and specific heat at const. volm, $c_v = 20.9 \times 10^3 \text{ Joule/Kilomole/K}$.

Given, $K_B = 1.38 \times 10^{-23} \text{ J/K}$ and mass of an oxygen molecule; $= 5.31 \times 10^{-26} \text{ kg}$.

Soln:

$$K = \frac{1}{3} \rho \bar{c} c_v \lambda.$$

$$= \frac{1}{3} mn \sqrt{\frac{8KT}{\pi m}} \frac{c_v}{\sqrt{2} \pi d^2 n}.$$

$$= \frac{1}{3\sqrt{2}} mn \bar{c} \frac{c_v}{\pi d^2 n}.$$

$$\bar{c} = \sqrt{\frac{8KT}{\pi m}} = \sqrt{\frac{8 \times 1.38 \times 10^{-23} \times 273}{3.14 \times 5.31 \times 10^{-26}}}$$

$$= 424 \text{ m/sec.}$$

$$\therefore K = \frac{1}{3\sqrt{2}} \frac{m \bar{c} c_v}{\pi d^2}$$

$$\Rightarrow d^2 = \frac{1}{3\sqrt{2}} \frac{m \bar{c}}{\pi K}$$

$$= \frac{1}{3\sqrt{2}} \frac{5.31 \times 10^{-26} \times 424}{\pi \times 24 \times 10^{-3}} \times \frac{20.9 \times 10^3}{32} \text{ m}^2$$

$$= 4.6 \times 10^{-20}$$

$$\Rightarrow d = 2.14 \times 10^{-10}$$

$$\Rightarrow d = 2.14 \text{ \AA}.$$

$$\therefore r = d/2 = 1.07 \text{ \AA}.$$

$$c_v = 20.9 \times 10^3 \text{ Joule/Kilomole/K}$$

$$= \frac{20.9 \times 10^3 \text{ J/kg/K}}{\left(\frac{\text{molecular weight of oxygen}}{32} \right)}$$

$$c_v = 20.9 \times 10^3 \text{ J/Kilomole/K}$$

Transport of momentum: VISCOSITY:

Viscosity is the property of a fluid by which it tends to resist relative motion between them.

If different layers of a fluid are moving with different velocities, viscous forces come into play, tending to slow down the faster moving layers and to increase the velocity of slow moving layers.

If we consider two parallel fluid layers separated by a normal distance ' dy ' and having velocities ' v ' and ' $v+dv$ ', then viscous force F is given by,

$$F = -\eta A \frac{dv}{dy} \quad \text{--- (1)}$$

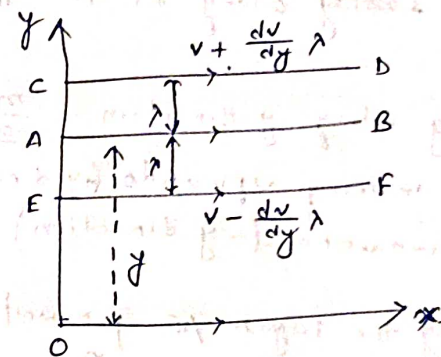
where, A = surface area of the layers

η = coefficient of viscosity of given fluid

$\frac{dv}{dy}$ = velocity gradient - (rate of change of velocity with distance).

The negative sign indicates that the viscous force is opposing the relative motion.

Expression for coefficient of viscosity of a gas on the basis of kinetic theory of gases:



Let a gas flows over a fixed horizontal surface Ox . The velocity of gas in contact with Ox is zero and increases along y -axis. AB at a normal distance ' y ' from Ox .

Let ' v ' be the velocity of gas in layer AB . Consider two layers CD and EF above and below the layer AB at a distance equal to mean free path ' λ ' of the molecules.

Let, $\frac{dv}{dy}$ = velocity gradient.

$$\text{Velocity of gas in layer } CD = v + \lambda \frac{dv}{dy} \quad \text{--- (2)}$$

$$\text{Velocity of gas in layer } EF = v - \lambda \frac{dv}{dy} \quad \text{--- (3)}$$

Let, n = no. of molecules per unit vol^m of gas.
 $\bar{c}$ = average speed of gas molecules.

A/c to postulates of kinetic theory of gases, the gas molecules can move ~~simultaneously~~ along all the three (x, y, z) directions; so

No. of molecules moving along y-direction = $\frac{n}{3}$. $\rightarrow$ (4)

Out of these $\frac{n}{3}$ are moving upwards (+y direction) and $\frac{n}{3}$ are moving downward (-y direction).

No. of molecules crossing the layer AB per unit area per unit time in downward direction = $\frac{n}{3} \bar{c}$ $\rightarrow$ (5)

Downward momentum carried by the molecules from layer CD crossing layer AB per unit area per unit time

$$= \text{num of molecules} \times \text{speed of a gas molecule}$$

$$= m \left(\frac{n\bar{c}}{3} \right) \times \left(v + \frac{dv}{dy} \lambda \right) \rightarrow (6)$$

lly, upward momentum carried by the molecules from layer EF crossing layer AB per unit area per unit time

$$= m \left(\frac{n\bar{c}}{3} \right) \times \left(v - \frac{dv}{dy} \lambda \right) \rightarrow (7)$$

Net transfer of momentum to layer AB per unit area per unit time

$$= m \left(\frac{n\bar{c}}{3} \right) \left[\left(v + \frac{dv}{dy} \lambda \right) - \left(v - \frac{dv}{dy} \lambda \right) \right]$$

$$= \frac{2mn\bar{c}}{3} \frac{dv}{dy} \lambda$$

$$= \frac{1}{3} mn\bar{c} \lambda \frac{dv}{dy} \rightarrow (8)$$

A/c to Newton's ^{2nd} law of motion, force is defined as the rate of change of momentum; so eqn (8) gives force on layer AB per unit area; i.e;

$$F = \frac{1}{3} mn\bar{c} \lambda \frac{dv}{dy} \rightarrow (9)$$

Again; viscous force is given by;

$$F = -\eta A \frac{dv}{dy} \rightarrow (10)$$

For unit area; ⁽¹⁰⁾ can be written as;

$$F = -\eta \frac{dv}{dy} \rightarrow (11)$$

Comparing (9) & (11); we get;

$$\eta = \frac{1}{3} mn\bar{c} \lambda$$

$$= \frac{1}{3} \rho \bar{c} \lambda, \text{ where } \rho = mn = \text{density of gas}$$

$$\rightarrow (12)$$

$$\text{As, } \tau \propto \sqrt{T}$$

$$\therefore \eta \propto \sqrt{T}$$

Hence, co-efficient of viscosity of gas is directly proportional to square root of its tempⁿ.

From (12); co-efficient of viscosity of gas is independent of pressure of gas.