

General Statistical Distribution Law :-

Before considering the general statistical distribution law, we would like to define probability, that is defined as the ratio of number of cases in which the event occurs to the total number of cases i.e.

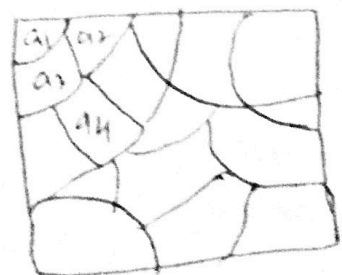
$$\begin{aligned} \text{Probability of an event} \\ = \frac{\text{No. of cases in which event occurs}}{\text{Total no. of cases}} \end{aligned}$$

Let us consider that an event happens in x ways and fails to happen in y ways, then

$$\begin{aligned} \text{Probability of happening the event} \\ = \frac{x}{x+y} \end{aligned}$$

because total number of cases is $(x+y)$

Considering the case of large flat box having compartments or cells of size $a_1, a_2, \dots, a_i, a_n$ shown in figure, so that particles or marbles among the compartments.



The distribution is defined by stating the number of particles in each cell as n_1, n_2, \dots, n_i .

The total number of particles N is fixed i.e.

$$n_1 + n_2 + \dots + n_i = N$$

Mathematically, the probability of a given distribution

W is given the product of two function. The 1st the number of ways the particles may be rearranged & till leave the distribution same i.e. the total number of particles in each cell left as before.

Let we choose n_1 particles which are to be placed in first cell. This can be done in $n C_{n_1}$ ways i.e.

$$\frac{n!}{n_1! (n-n_1)!}$$

Now remaining number $(n-n_1)$ and we want n_2 particles in second cell, which can be done in $n-n_1 C_{n_2}$ ways i.e.

$$\frac{(n-n_1)!}{n_2! (n-n_1-n_2)!}$$

Therefore, the number of ways in which the particles in different cells may be exchanged, leaving cell total number in each cell fixed is

$$\frac{n!}{n_1! (n-n_1)!} \times \frac{(n-n_1)!}{n_2! (n-n_1-n_2)!} \times \dots \times \frac{n!}{n_1! n_2! n_3! \dots n_r!}$$

The second factor is a priori probability of a particle falling into given cell. The

Probability certain that cell $g_i =$

The number of particles falling in

is g_i

$$\therefore \omega$$

Now we the largest corresponds of each

$\delta(L)$
The n_i 's
 $n_1 + n_2 + \dots$

action. The rest
 rearranging &
 same in the
 cell left

Probability, g_i , of any one particle falling in
 certain cell is given by the ratio of the size of
 that cell to the size of the box

$$g_i = \frac{a_i}{a}, \text{ where } a = a_1 + a_2 + \dots + a_z,$$

which are to be
 done in

The sum of the ~~Relative~~ Probabilities for all cells
 is, of course unity: the probability of n_i particles
 falling in the i th cell is $g_i^{n_i}$.

Therefore a priori probability of the distribution

we want n_2
 done in

is

$$g_1^{n_1} g_2^{n_2} g_3^{n_3} g_4^{n_4} \dots g_z^{n_z}$$

$$\therefore \omega = \frac{n!}{n_1! n_2! n_3! \dots n_z!} g_1^{n_1} g_2^{n_2} \dots g_z^{n_z}$$

Most Probable distribution :-

the particles
 in cell

Now we must select the distribution which has
 the largest value of ω . It $\log \omega$, which obviously
~~corresponding to~~ w.r. to the independent variables
 of each n_i separately all its partial derivatives

$$\frac{\partial}{\partial n_i} (\log \omega)$$

would have to be zero. Actually
 the n_i 's must satisfy an auxiliary condition

Probability
 The

$$n_1 + n_2 + \dots + n_z = n, \text{ such a condition may be formulated as } f(n_1, \dots, n_z) = \text{const.}$$

$$ic \quad f = \sum_{i=1}^z n_i$$

using Lagrange's method & Stirling approximation

we have $\frac{n_i}{n} = g_i$

Means that the most probable number of particles in each cell is proportional to the size of cell.



division of phase space into cells:-

A element of volume in the phase space is represented by

$$\delta q_1 \dots \delta q_f \delta p_1 \dots \delta p_f$$

The dimensions of this volume elements are those of (length x momentum). If a finite volume of the phase space is divided into a large number of cells, then the size of each cell will be h^f , where h is any arbitrary const, then

$$h = \delta q_i \delta p_i$$

Number

* Maxwell usually a type of par

(1) Ident are the pa distribution

(2) Ident or

obey

Bose-

(3) Ident

Spin

Pauli's

stat's

Number of phase cells in the volume elements is

$$= \frac{\delta q_1 \delta q_2 \dots \delta q_f \quad \delta p_1 \delta p_2 \dots \delta p_f}{h^f}$$

~~Number of phase cells in the volume elements is~~

* Maxwell-Boltzmann distribution Law :-

usually assemblies, in general, consist of three type particles -

(1) Identical but distinguishable :- Molecules of a gas are the particles of this kind. obey Maxwell-Boltzmann distribution law.

(2) Identical but indistinguishable particles of zero or integral spin → (neutrons, photons) and they obey Bose-Einstein statistics and hence known as Bose-particles (Boson)

(3) Identical but indistinguishable particles of spin $\frac{1}{2}$ namely electrons, protons, neutrons, follows Pauli's exclusion principle and Fermi-Dirac statistic. (particles name Fermion)

Maxwell-Boltzmann Distribution Law

The assemblies consist of - three kinds of particles -

- (i) Identical, but distinguishable particles of any spin, The molecules of a gas are the particles of this kind.
- (ii) Identical and indistinguishable particles of zero or integral spin. - particles \rightarrow helium at low temperature and photons - named Bose - particles and don't obey the Pauli's exclusion principle.
- (iii) Identical and indistinguishable particles of spin $\frac{1}{2}$, These particles obey Pauli's exclusion principle - named as \rightarrow e , p , neutrons etc, named Fermi-

The particles of the first kind obey Maxwell-Boltzmann distribution law, providing the total fixed amount of energy is distributed among the various members of an assembly of identical particles in the most probable distribution -

Let a system of N similar, distinguishable molecules of a gas, having instantaneous state phase point in the phase space. The phase space divided into cells of $1, 2, 3, \dots, k,$

and $n_1, n_2, \dots, n_i, \dots, n_k$ be the number of gas molecules, whose phase points lie in cell 1, 2, \dots , i , \dots , k respectively in the equilibrium state.

As the gas molecules are moving continuously; therefore n_i 's will change continuously in many different ways; but will always keep values close to those for the state of equilibrium i.e. the most probable state.

Let us suppose n_i 's change obeying the fundamental postulate of Statistical mechanics

(i) The total number of molecules is constant i.e.

$$N = n_1 + n_2 + \dots + n_i + \dots + n_k = \text{constant}$$

$$\delta N = \delta n_1 + \delta n_2 + \dots + \delta n_i + \dots + \delta n_k = 0$$

$$\text{i.e. } \sum_i \delta n_i = 0 \quad \text{--- --- --- --- ---} \quad \textcircled{A}$$

(ii) The total energy of the system is constant

$$E = E_1 n_1 + E_2 n_2 + \dots + E_i n_i + \dots + E_k n_k = \text{constant}$$

$$\Rightarrow \delta E = E_1 \delta n_1 + E_2 \delta n_2 + \dots + E_i \delta n_i + \dots + E_k \delta n_k = 0$$

$$\text{i.e. } \sum_i E_i \delta n_i = 0 \quad \text{--- --- --- --- ---} \quad \textcircled{B}$$

(iii) when gas is in equilibrium, the probability is max^m

$$\delta P = 0$$

i.e. when P is max^m , $\log P$ is max^m ,

$$\delta(\log P) = 0$$

$$\text{But } P = \frac{N!}{n_1! n_2! \dots n_i! \dots n_k!} (g_1)^{n_1} (g_2)^{n_2} \dots (g_i)^{n_i} \dots (g_k)^{n_k}$$

where g_i is the a priori probability for a molecule to have the energy ϵ_i

Taking natural logarithm of above eq, we get

$$\log P = \log N! - \sum_i \log(n_i!) + \sum_i n_i (\log g_i)$$

using Stirling's formula, we get

$$\log P = N \log N - N - \sum_i n_i \log n_i + \sum_i n_i + \sum_i n_i \log g_i \quad \text{--- (1)}$$

$$\text{But } \sum_i n_i = N$$

$$\log P = N \log N - \sum_i n_i \log n_i + \sum_i n_i \log g_i$$

Therefore, acc to eqn (1), we get

$$\delta(\log P) = - \sum_i n_i \delta(\log n_i) + \sum_i \log g_i \delta n_i + \sum_i \log g_i \delta n_i = 0 \quad \text{--- (2)}$$

$$\text{But } \delta(\log n_i) = \frac{1}{n_i} \delta n_i$$

$$\Rightarrow n_i \delta(\log n_i) = \delta n_i$$

$$\Rightarrow \sum_i n_i \delta(\log n_i) = \sum_i \delta n_i = 0$$

$\therefore [\delta N \log N \text{ is constant}]$

ans.

$$\log g_i \delta n_i = 0 \quad (3)$$

Method of Lagrangian
implies. For the purpose

(3) by α & β respectively
entirely independent of n_i 's
eqn (3), we get

$$\log g_i \delta n_i + \sum \alpha \delta n_i + \beta \delta n_i = 0$$

$$(\alpha + \beta \epsilon_i) \delta n_i = 0 \quad (4)$$

we.

$$\alpha + \beta \epsilon_i = 0$$

$$-(\alpha + \beta \epsilon_i)$$

- log g_i

$$\beta \epsilon_i$$

the most probable, therefore
occurrences among the various
states and is known as
Boltzmann distribution law.

Energy

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$\sum n_i + \dots$

$n_i = 0$ — (4)

Boole, that
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is known as
distribution law.

Next.

Evaluation of constant e & β

To evaluate e & β considering continuous distribution of molecular energies rather than discrete energies $\epsilon_1, \epsilon_2, \dots, \epsilon_i, \dots, \epsilon_k$, then eqn

$$n_i = g_i e^{-\alpha} e^{-\beta \epsilon_i} \quad \text{--- (1)}$$

$$\Rightarrow n(\epsilon) d\epsilon = g(\epsilon) e^{-\alpha} e^{-\beta \epsilon} d\epsilon \quad \text{--- (2)}$$

Here $n(\epsilon)$ represents the number of molecules having energies between ϵ and $\epsilon + d\epsilon$ and if p be the molecular momentum, then

$$\epsilon = \frac{p^2}{2m}$$

Then eqn (2), $\Rightarrow n(p) dp = g(p) e^{-\alpha} e^{-\beta p^2 / 2m} dp \quad \text{--- (3)}$

$n(p) dp$ no. of molecules having momentum p and dp and a priori probability $g(p)$ that a molecule have momentum between p and dp is equal to the number of cells in the phase space for infinitesimal volume h^3 , then

$$g(p) dp = \frac{\iiint dxdydz dp_x dp_y dp_z}{h^3} \quad \text{--- (4)}$$

If V is the volume occupied by the gas in ordinary position, space then, $\iiint dxdydz = V \quad \text{--- (5)}$

Let us imagine that x, y, z are along three coordinate axes and if draw a sphere of radius f and the about the origin, then

$$x^2 + y^2 + z^2 = f^2$$

Again drawing a sphere of radius $f + df$ and the volume between two spheres of radii f and $f + df$ having momentum p to $p + dp$ all molecules too with momentum p & $p + dp$

The volume between two spheres is given

$$\begin{aligned} \int \int \int dV &= \frac{4}{3}\pi (r+dr)^3 - \frac{4}{3}\pi r^3 \\ &= 4\pi r^2 dr \quad \left[\text{Neglecting terms containing } dr^2 \text{ and } dr^3 \right] \end{aligned}$$

Hence eqn (4)

$$g(r) dr = \frac{\sqrt{4\pi r^2} dp}{h^3} e^{-\beta \epsilon^2/2m}$$

$$\therefore \lambda(r) dr = \frac{\sqrt{4\pi r^2} e^{-\beta \epsilon^2/2m}}{h^3} dp \quad \text{--- (7)}$$

Since total number of molecules is N i.e.

$$\int_0^\infty \lambda(r) dr = N \quad \text{--- (8)}$$

$$\text{Hence } N = \frac{4\pi V e^{-\alpha}}{h^3} \int_0^\infty r^2 e^{-\beta \epsilon^2/2m} dp \quad \text{--- (9)}$$

Since $\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}}$

$$\begin{aligned} \int_0^\infty r^2 e^{-\beta \epsilon^2/2m} dp &= \frac{1}{4} \left[\frac{\pi}{(\beta/2m)^3} \right]^{1/2} \\ &= \frac{1}{4} \left[\frac{8m^3 \pi}{\beta^3} \right]^{1/2} \end{aligned}$$

$$\therefore N = \frac{4\pi V e^{-\alpha}}{h^3} \cdot \frac{1}{4} \left[\frac{8m^3 \pi}{\beta^3} \right]^{1/2}$$

$$= \frac{V e^{-\alpha}}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2}$$

$$\therefore e^{-\alpha} = \frac{N h^3}{V} \times \left(\frac{\beta}{2\pi m} \right)^{3/2}$$

$$\therefore \text{all } dp = 4\pi N \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta p^2/2m} p^2 dp \quad \text{--- (10)}$$

To compute the value of β , then total energy (E) of the system of molecules,

$$p^2 = 2mE \text{ and } dp = \frac{m dE}{\sqrt{2mE}}, \text{ then eqn (10)}$$

$$\Rightarrow \text{all } n(E)dE = 4\pi N \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta E} \frac{m dE}{\sqrt{2mE}}$$

$$\Rightarrow n(E)dE = 2\pi N \left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta E} E^{1/2} dE \quad \text{--- (11)}$$

Again total energy

$$E = \int_0^\infty E n(E) dE = \int_0^\infty 2\pi N \left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta E} E^{3/2} dE$$

$$= 2\pi N \left(\frac{\beta}{\pi}\right)^{3/2} \cdot \frac{3}{4} \sqrt{\frac{\pi}{\beta^5}}$$

$$E = \frac{3}{2} \frac{N}{\beta} \quad \text{--- (12)} \quad \left| \because \int_0^\infty e^{-\beta E} E^{3/2} dE = \frac{3}{4} \sqrt{\frac{\pi}{\beta^5}} \right.$$

For ideal gas,

$$E = \frac{3}{2} NKT \quad \text{--- (13)} \quad K \rightarrow \text{Boltzmann's Constant}$$

Comparing eqn (12) & (13), we

$$\frac{3}{2} \frac{N}{\beta} = \frac{3}{2} NKT$$

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

Use eqn (10) \Rightarrow

$$n(f)df = 4\pi N \left(\frac{1}{2\pi mKT}\right)^{3/2} e^{-\frac{mv^2}{2mKT}} f^2 df \quad (14)$$

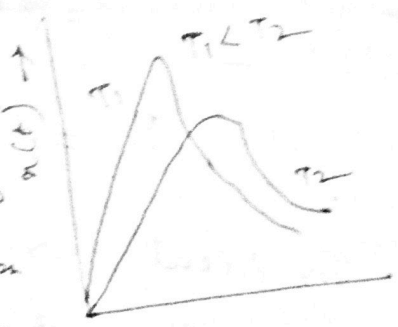
and eqn (14) \Rightarrow

$$n(E)dE = 2\pi N \left(\frac{1}{\pi KT}\right)^{3/2} e^{-E/KT} E^{1/2} dE \quad (15)$$

The eqn (14) known as Maxwell-Boltzmann distribution law of microstates and eqn (15) known as Maxwell-Boltzmann distribution law of energies.

For small values of E the term $e^{-E/KT}$ is nearly unity and hence $n(E)$ is the number of molecules with energy E is proportional to $E^{1/2}$ and so for $E=0$, $n(E)=0$.

For large values of E the term $e^{-E/KT}$ dominates over $E^{1/2}$, therefore $n(E)$ is proportional to $e^{-E/KT}$. Thus, if $n(E)$ is plotted against E , the curve distribution curve first rises due to term $E^{1/2}$, reaches a maximum and then falls due to $e^{-E/KT}$. The M-B energy distribution at two different Temp T_1 & T_2 is shown in fig.



In order to find M-B distribution law of speeds we put $f = mv$, $df = m dv$

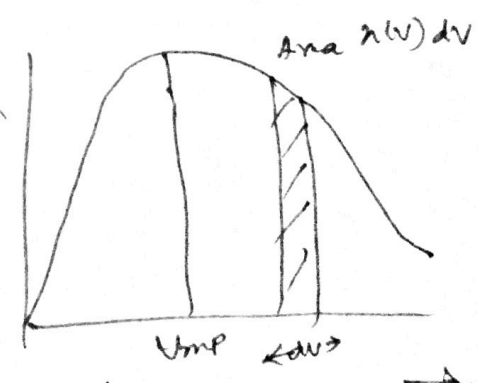
Substituting (14) \Rightarrow

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

$$= 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} v^2 dv \quad (16)$$

This eqn is known as M-B distribution law of speeds of the molecules depending on $e^{-\frac{mv^2}{2m kT}}$. For small value of v , $\ln e^{-\frac{mv^2}{2m kT}}$ is nearly unity and hence $n(v)$ i.e. the number of molecules with speed v , is proportional to v^2 . For large value of v , the exponential term $e^{-\frac{mv^2}{2m kT}}$ dominates over v^2 , and hence $n(v)$ is proportional to $e^{-\frac{mv^2}{2kT}}$. Thus curve $n(v)$ vs v , the speed distribution curve, first rises parabolically, reaches a maximum and then falls exponentially to zero as shown in fig.

The maximum corresponds to the most probable speed v_{mp} .



The ~~small~~ number of molecules

lying in speed range v to $v+dv$,

is given by

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

Thus, the probability that a molecule will possess the speed between v and $v+dv$ is

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

Hence the probability that a molecule possess speed v , is the probability, $P(v)$.

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

