Maxwell- Boltzmann Distribution Law:-

As we know that the M-B statistics is applied to those particles which are distinguishable, no restriction to occupy the energy states and the particles have definite position and momenta. Now let us consider a system of 'N' identical but distinguishable particles at temperature T. Let the total volume of the system is V and total energy is E. N is very large and all the particles (molecules) do not have same energy. ~~Let n_0~~ Let

n_0 molecules are in energy level with energy $\epsilon_0 \Rightarrow n_0\epsilon_0$ — Energy
n_1 " .... $= \epsilon_1 \Rightarrow n_1\epsilon_1$
n_2 " .... $= \epsilon_2 \Rightarrow n_2\epsilon_2$

The energy levels are fixed by quantum mechanical principles. Then

$$\text{Total energy } E = n_0\epsilon_0 + n_1\epsilon_1 + n_2\epsilon_2 + \cdots n_i\epsilon_i = \sum n_i\epsilon_i$$

$$\text{and } N = n_0 + n_1 + \cdots n_i = \sum n_i$$

The thermodynamic Probability (W) of the a given distribution is

$$W = \frac{N!}{n_0!\,n_1!\,n_2!\cdots} = \frac{N!}{\pi n_i!}$$

taking logarithm

$$\ln W = \ln N! - \sum \ln n_i!$$

Applying Stirling approximation [as N is very large]

$$\ln W = N\ln N - N - \sum(n_i\ln n_i - n_i)$$

$$= N\ln N - N - \sum n_i\ln n_i + \sum n_i$$

$$= N\ln N - N - \sum n_i\ln n_i + N$$

$$= N\ln N - \sum n_i\ln n_i$$

Differentiating both sides.

$$d \ln W = d(N \ln N) - \sum d\, n_i \ln n_i$$

$$= 0 - \sum \left[n_i \times \frac{1}{n_i} + \ln n_i \times 1 \right] dn_i$$

$$= -\sum (\ln n_i + 1) dn_i$$

According to Principles of statistical mechanics, the most Probable distribution is one that makes W the maximum. So for maximum probability $d \ln W = 0$.

Thus $\quad 0 = -\sum (\ln n_i + 1) dn_i$

$\Rightarrow \sum (\ln n_i + 1) dn_i = 0$ — (A)

Now we have

$\sum n_i = N =$ costant or, $\sum dn_i = 0$. (B)

and $\sum n_i \epsilon_i = E =$ Constant, or $\sum \epsilon_i dn_i = 0$. — (C)

Multiplying (B) and (C) by α' and β and adding with (A). We have

$$\sum (\ln n_i + 1 + \alpha' + \beta \epsilon_i) dn_i = 0 \quad \text{— (D)}$$

~~This method is called method of Lang~~

This is called method of Langrange undetermined multipliers.

Putting $\alpha' + 1 = \alpha$ we have

$$\sum (\ln n_i + \alpha + \beta \epsilon_i) dn_i = 0 \quad \text{— (E)}$$

According to Langrange undetermined the constraints (restrictions/ conditions) are mutiplyed, Within the restrictions imposed on the system for constant volume (V) and energy (E) values, the veriations are independent of each other and need not be zero. i.e $dn_i \neq 0$. This relation is true for any energy-level or cell. Hence

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

$$\text{or, } \ln n_i = -\alpha - \beta\epsilon_i \longrightarrow (\Upsilon\Upsilon)$$

$$\text{or, } n_i = e^{-(\alpha+\beta\epsilon_i)}$$

This expression is called Maxwell-Boltzmann distribution law

$$\text{Again } N = \sum n_i = \sum e^{-(\alpha+\beta\epsilon_i)}$$

$$= e^{-\alpha}\sum e^{-\beta\epsilon_i}$$

$$\text{or, } \frac{n_i}{N} = \frac{e^{-\alpha} \cdot e^{-\beta\epsilon_i}}{e^{-\alpha}\sum e^{-\beta\epsilon_i}}$$

$$\text{or, } n_i = \frac{N e^{-\beta\epsilon_i}}{\sum e^{-\beta\epsilon_i}} \longrightarrow (F)$$

From energy of an ideal gas we have $\beta = \frac{1}{KT}$ [Where K = Boltzmann constant, T = temperature]. Thus

$$\boxed{n_i = \frac{N e^{-\epsilon_i/KT}}{\sum e^{-\epsilon_i/KT}}}$$

This expression is for ~~dege~~ non-degenerate state i.e, there is a single energy level. But the energy may be arrayed in different ways for different particles. If so there comes the term degeneracy. If there be 'g_i' number of possible distribution of energy in a given energy-level 'i', then the state is said to be g_i-degenerate where 'g_i' is called the statistical weight factor. Introducing this, we have,

$$\boxed{\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/KT}}{\sum g_i e^{-\epsilon_i/KT}}}$$ — This is M-B distribution Law.

We have for i' th level

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

then for 'j' th level

$$n_j = g_j e^{-\alpha} e^{-\beta\epsilon_j} \quad \text{—— (2)}$$

Thus
$$\frac{n_i}{n_j} = \frac{g_i e^{-\alpha} e^{-\beta\epsilon_i}}{g_j e^{-\alpha} e^{-\beta\epsilon_j}}$$

$$= \boxed{\frac{g_i}{g_j} \times e^{-\beta(\epsilon_i - \epsilon_j)}} \quad \text{—— (3)}$$

This equation gives the relative populations of any two levels. If n_j is the ground state then

$$\frac{n_i}{n_0} = \frac{g_i}{g_0} e^{-\beta(\epsilon_i - \epsilon_0)} = \frac{g_i}{g_0} e^{\frac{-(\epsilon_i - \epsilon_0)}{KT}} = \frac{g_i}{g_0} e^{-\Delta\epsilon_i/KT}$$

For ground-state $g_0 = 1$, Thus

$$\boxed{\frac{n_i}{n_0} = g_i e^{-\Delta\epsilon_i/KT}} \quad \text{—— (4)}$$

Now, (1) if the energy of the i-th level is much more than the thermal energy of the system i.e, $\epsilon_i >> KT$, the 'i'-th level will be having no molecules, i.e, all the molecules will be in ground-state level, i.e, $n_i = 0$.

(2) When $\epsilon_i << KT$, then eq^n(4) reduced to

$n_i \simeq n_0 g_i$ i.e, the number of molecules in the i'-th level is the g_i-th multiple of the number of molecules in the ground state.

Calculation of β :

The entropy (S) and thermodynamic probability (W) are related as

$$S = K \ln W \quad [K = \text{Boltzmann constant}]$$

or $S = K\left(N\ln N - \sum n_i \ln n_i\right) \rightarrow$ (for non-degenerate)

$\Rightarrow K\left(N\ln N - \sum n_i \ln n_i/g_i\right) \rightarrow$ (for g_i-degeneracy) $\rightarrow$ ①

Again $\ln(n_i/g_i) = -\alpha - \beta\epsilon_i$ (from eqn YY)

Thus

$$S = K\left[N\ln N - \sum n_i(-\alpha - \beta\epsilon_i)\right]$$

$$= K\left[N\ln N - \alpha\sum n_i + \beta\sum n_i\epsilon_i\right]$$

$$= K\left[N\ln N + \alpha N + \beta E\right]$$

$$= KN\ln N + K\alpha N + K\beta E$$

The energy E is purely internal energy, thus $E = U$

$\therefore S = KN\ln N + K\alpha N + K\beta U$

Differentiating

$$\left(\frac{\partial S}{\partial U}\right)_V = K\beta$$

For an isolated system, $dS = \frac{\partial q_{rev}}{T} = \frac{dU + PdV}{T}$

or, $\left(\frac{dS}{dU}\right)_V = \frac{1}{T}$

Thus $\frac{1}{T} = K\beta$, or $\boxed{\beta = \frac{1}{KT}}$

+ Condition for applicability of M-B Statistics:

The Maxwell-Boltzmann statistics is applicable for the following types of systems:

① If the system is independent and localised. i.e, the system consists of independent, identical but distinguishable particles, the equilibrium sites around which molecules vibrate are distinguishable.

② The system is applicable for the molecular states with energy about $\sim 10KT$ above the ground state level. That is why this statistics fails in the case of very light system like H_2, He etc at very low temperatures.

③ This system is valid for such cases where there is no force of attraction between systems or molecules present in the same energy state.

④ This statistics can not be applied to assembly of charged particles like electrons, protons etc.

Applications:

i) Different molecular thermodynamic properties can be evolved.

ii) Barometric distribution formula can be derived.

iii) Different translational kinetic energies, vibrational, rotational energies, partition functions can also be derived from Boltzmann-Maxwell statistics