Dr Sanjeet Kumar, HOD Physics, HDJC, VKSU, Ara

# Maxwell-Boltzmann Distribution Law

This law describes how a fixed total amount of energy is distributed among the various members of an assembly of identical but distinguishable particles (such as the molecules of a gas) in the most probable distribution.

Say we have an assembly of $N$ molecules whose energies are limited to the k-values $\epsilon_1, \epsilon_2, \ldots \epsilon_i, \epsilon_k$ arranged in the order of increasing energy. These energies may represent either discrete energy states or average energies within a sequence of energy intervals. If there are $n_1$ molecules of energy $\epsilon_1$, $n_2$ molecules of energy $\epsilon_2$, and so on, then the most probable distribution of molecules among these k-energies is subject to two conditions:

(I) The total number of molecules $N$ is constant, i.e.

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

or, $\delta N = \delta n_1 + \delta n_2 + \ldots + \delta n_i + \ldots + \delta n_k = 0$

or, $$\boxed{\sum_i \delta n_i = 0.} \quad \text{--- (i)}$$

(II) The total energy $E$ of the assembly is constant, i.e.

$$E = \epsilon_1 n_1 + \epsilon_2 n_2 + \ldots + \epsilon_i n_i + \ldots + \epsilon_k n_k = \text{constant}.$$

or, $\delta E = \epsilon_1 \delta n_1 + \epsilon_2 \delta n_2 + \ldots + \epsilon_i \delta n_i + \ldots + \epsilon_k \delta n_k = 0.$

or, $$\boxed{\sum_i \epsilon_i \delta n_i = 0.} \quad \text{--- (ii)}$$

If the a priori probability for a molecule to have energy $\epsilon_i$ is $g_i$, the probability $P$ for any distribution is;

$$P = \frac{\lfloor N}{\lfloor n_1 \lfloor n_2 \ldots \lfloor n_k} (g_1)^{n_1} (g_2)^{n_2} \ldots (g_k)^{n_k}.$$

Taking natural logarithm of the above equation and using Stirling's approximation, we can observe that the most probable distribution must obey the following equation:

$$-\sum_i \delta n_i (\log_e n_i) + \sum_i \delta n_i (\log_e g_i) = 0. \quad \text{--- (iii)}$$

Now using the method of Lagrange's multiplier; we may multiply eqn. (i) and eqn. (ii) by quantities $-\alpha$ and $-\beta$ respectively (which do not depend upon any of $n_i$'s) and adding the resulting expressions to eqn. (iii); we will get;

$$-\sum_i \delta n_i (\log_e n_i) + \sum_i \delta n_i (\log_e g_i)$$
$$-\sum_i \alpha \delta n_i - \sum_i \beta \epsilon_i \delta n_i = 0.$$

or, $\sum_i (-\log_e n_i + \log_e g_i - \alpha - \beta \epsilon_i)\delta n_i = 0.$

As $\delta n_i$'s are independent variables, therefore, for the validity of the last equation, the quantity in parentheses must always be zero for each value of $i$. Hence;

$$-\log_e n_i + \log_e g_i - \alpha - \beta \epsilon_i = 0$$

or, $$\boxed{n_i = g_i e^{-\alpha} e^{-\beta \epsilon_i}} \quad \text{(iv)}$$

This result determines the most likely probable distribution of molecules among the various energy states and is known as "Maxwell-Boltzmann distribution law". Hence from M.B. distribution the general rule for distinguishable particles (Classical distribution) the general rule will be that the higher the state (higher the value of $\epsilon_i$); the less is the population (less is the value of $n_i$).

Teacher's Signature