Boltzmann distribution law :-

Boltzmann distribution law is very important law in statistical Thermody-
-namics. It deals with the probability of distribution of total energy among the particle of the system and lead to the introduction of the concept of partition function.

Let us consider a system of 'N' identical, independent and distinguishable particles. $\epsilon_1, \epsilon_2, \epsilon_3 \ldots \epsilon_i$ are the discreate set of energy levels. Let n_1 particle at energy state ϵ_1, $n_2 \ldots \epsilon_2$, $\ldots n_i \ldots \epsilon_i$.

If we assume that the system is closed and isolated then each set ~~state~~ ~~of population no~~ must be governed by two conditions-

(1). $E = n_1\epsilon_1 + n_2\epsilon_2 + \ldots n_i\epsilon_i$

i.e. $E = n_i \epsilon_i$

or $E = \sum_i n_i \epsilon_i$ = constant.

(2). $N = n_1 + n_2 + \ldots + n_i$

i.e. $N = \sum_i n_i$ = Constant.

$$\text{Probability } (W) = \frac{N!}{n_1!\, n_2!\, n_3! \ldots n_i!}$$

or $\ln W = \ln N! - \ln \sum_i n_i$ ——— (1)

at. Maximum probability —

$d \ln W = 0$.

$0 = \partial \ln N! - \partial \ln \sum_i n_i!$

or $\partial \ln N! = \partial \ln \sum_i n_i!$ ——— (2)

as $[\partial \ln n_i = 0.]$

Using stirling approximation —

$$\ln N_i = N \ln N - N$$

then from eqs — (2)

$$d \sum_i n_i \ln n_i - d \sum_i n_i = 0$$

as, $d \sum_i n_i = 0$

$$\therefore \sum_i \ln n_i \, dn_i = 0 \qquad \text{——— (3)}$$

Since,

$$E = \sum n_i E_i$$

$$dE = d \sum n_i E_i = 0$$

$$\beta \, dE = \beta \, d \sum n_i E_i = 0$$

and

$$N = \sum n_i$$

$$dN = d \sum n_i = 0$$

$$\alpha \, dN = \alpha \, d \sum n_i = 0$$

Where, α and β are lagrange undetermined multipliers.

Thus, We have —

$$\left.\begin{aligned} \alpha \, dN &= \alpha \, d \sum n_i \\ \& \ \beta dE &= \beta \sum E_i dn_i \end{aligned}\right\} \text{——— (4)}$$

on adding eqs — (3) & eqs — (4)

$$\alpha \sum dn_i + \beta \sum E_i dn_i + \sum \ln n_i dn_i = 0.$$

$$\text{or } (\alpha + \beta E_1 + \ln n_1) dn_1 + (\alpha + \beta E_2 + \ln n_2) dn_2 + \cdots\cdots = 0$$

Each term is seperated to be zero.

$$\therefore (\alpha + \beta E_1 + \ln n_1) dn_1 = 0$$

but $dn_1 \neq 0$

$\therefore \quad \alpha + \beta \varepsilon_1 + \ln n_1 = 0.$

$\ln n_1 = -(\alpha + \beta \varepsilon_1)$

or $n_1 = \exp\{-(\alpha + \beta\varepsilon_1)$

or $n_1 = \exp(-\alpha)\exp(-\beta\varepsilon_1)$

$\therefore \quad n_i = \exp(-\alpha)\exp(-\beta\varepsilon_i)$ ——— (5)

Since, $N_i = \sum n_i$

$N_i = \sum \exp(-\alpha)\exp(-\beta\varepsilon_i)$

$$\boxed{\text{or} \quad N_i = \sum \exp(-\alpha - \beta\varepsilon_i)}$$

or $\exp(-\alpha) = \dfrac{N_i}{\sum \exp(-\beta\varepsilon_i)}$ ——— (6)

Now putting the value of $\exp(-\alpha)$ from eqn (6) in to eqs (5) we get.

$$n_i = \frac{N_i}{\sum \exp(-\beta\varepsilon_i)} \exp(-\beta\varepsilon_i)$$

$$\frac{n_i}{N_i} = \frac{\exp(-\beta\varepsilon_i)}{\sum \exp(-\beta\varepsilon_i)}$$

β has the dimension of energy^{-1} and is evaluated to $1/KT$

$$\therefore \quad \boxed{\frac{n_i}{N_i} = \frac{\exp(-\varepsilon_i/KT)}{\sum \exp(-\varepsilon_i/KT)}} \quad \text{——— (7)}$$

eqs -(7) is the expression of Boltzmann distribution law for non-degenerate state.

But in case of degenerate states —

Eqn — 7 is written as —

$$\boxed{\frac{n_i}{N_i} = \frac{g_i \exp(-\varepsilon_i/kT)}{\sum g_i \exp(-\varepsilon_i/kT)}} \quad \text{—— (8)}$$

where, g_i is statistical weight factor i.e. degeneracy.

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