PARTITION FUNCTIONS:

For developing the concept of partition function we consider an assembly of ideal gas molecules obeying classical statistics (M-B Statistics)

Let the distribution of gas molecules be such that n_i molecules occupying i^{th} state with energy between ϵ_i & $\epsilon_i + d\epsilon_i$ and degeneracy (g_i) (i.e the no. of energy levels more than One)

Now,

According to Boltzmann distribution law

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

Let $e^{-\alpha} = A$

Then eq^n (1) becomes : $n_i = g_i A e^{-\beta \epsilon_i}$ --- (2)

Let,

Total no. of gas molecules in the assembly $= N$

So that from eq^n (1)

$$N = \sum_i n_i = \sum g_i A e^{-\beta \epsilon_i}$$

Thus $$\frac{N}{A} = \sum g_i e^{-\beta \epsilon_i} = Z \text{ (say)} \quad \text{--- (3)}$$

Where Z is known as Partition function the quantity Z indicates how the gas mole-cules of an assembly are distributed or Partitioned among the various energy levels.

Obviously, the particular functions for different distributions will be different.

Relation between Partition function and Thermodynamical quantities:

The entropy (S, U, γ, ϕ) of an assembly and the probability (W) of an certain state are related by the following equation.

$$S = K \ln W_{max} \quad \text{--- (1)}$$

Where K = Boltzmann Constant.
assuming the distribution of gas molecules such that n_i molecules are in the i^{th} state having energy between ϵ_i & $\epsilon_i + d\epsilon_i$ with degeneracy g_i.
We have

$$W_{max} = \left(\lfloor n \prod_i \frac{g_i^{n_i}}{\lfloor n_i} \right) \quad \text{--- (2)}$$

N is total no. of particles per mole i.e Avogadro's no.

$$\therefore \ln W_{max} = \ln \lfloor n + \sum n_i \ln g_i - \ln \lfloor n_i \quad \text{--- (3)}$$

Stirling's approximation is as follows:-

$$\ln \lfloor n = N \ln N - N$$

So that eq^n (3) becomes

$$\ln W_{max} = \left\{ (N \ln N - N) + \sum_i (n_i \ln g_i - n_i \ln n_i + n_i) \right\}$$

$$= \left\{ N \ln N - N + \sum_i (n_i \ln g_i - n_i \ln n_i) + N \right.$$

$\because \sum n_i = N$

Thus $$\ln W_{max} = \left\{ N \ln N + \sum_i n_i \ln g_i - n_i \ln n_i \right\} \quad \text{--- (4)}$$

Now, According to the M-B distribution

Law.

We have, $n_i = g_i \bar{e}^{\alpha} . \bar{e}^{\beta \epsilon_i}$ — (5)

where α & β are constants.

Substituting from eq^n (5) in (4) for n_i we have

$$\ln W_{max} = \left\{ N \ln N + \sum_i n_i \ln g_i - n_i \ln g_i \, \bar{e}^{\alpha} . \bar{e}^{\beta \epsilon_i} \right\}$$

$$= \left\{ N \ln N + \sum_i \left(n_i \ln g_i - n_i \ln g_i - n_i \ln \bar{e}^{\alpha} - n_i \ln \bar{e}^{\beta \epsilon_i} \right) \right\}$$

$$= \left\{ N \ln N + \sum_i n_i \alpha + n_i \beta \epsilon_i \right\}$$

$$\therefore \ln W_{max} = \left\{ N \ln N + N \alpha + \beta \sum_i n_i \epsilon_i \right\} \text{ — (6)}$$

Again if E = Total energy of gas molecules then :

$$\sum n_i \epsilon_i = E$$

So that eq^n (6) changes to

$$\ln W_{max} = (N \ln N + N\alpha + \beta E) \text{ — (7)}$$

Let $A = e^{-\alpha}$ i.e. $\alpha = -\ln A$ — (8)

Using eq^n (8) in (7) we obtain

$$\ln W_{max} = N \ln N - N \ln A + \beta E$$

$$= N \ln \frac{N}{A} + \beta E$$

But $\frac{N}{A} = Z$ = Partition function.

Thus,

$$\ln W_{max} = N \ln Z + \frac{E}{KT} \text{ — (9)} \quad \left[\because \beta = \frac{1}{KT} \right]$$

from eq^n (1) and (9) we have

i.e $S = NK \ln Z + \frac{E}{T}$ —— (10)

Further,

The energy associated with each degree of freedom of a molecule is $\frac{1}{2} KT$. So that for a molecule of a mono atomic gas the energy is $\frac{3}{2} KT$ (Since degrees of freedom $= 3$) and for a mole we have the energy given by

$$E = \frac{3}{2} KTN \quad \text{—— (11)}$$

From eq^n (10) and (11) we get

$$S = NK \ln Z + \frac{3}{2} NK\cancel{T} \cdot \frac{1}{\cancel{T}}$$

Hence,

$$\boxed{S = \left(NK \ln Z + \frac{3}{2} NK \right)} \quad \text{—— (12)}$$