Classical Statistics (Maxwell Boltzman Distribution):

$$W = N! \prod \left[\frac{g_s^{n_s}}{n_s!} \right]$$

$$n_s = g_s \, e^{\alpha + \beta \epsilon_s} \quad , \quad N = \sum n_s$$

The weight of the most probable configuration W_{max} is obtained as follow :

$$\log W_{max} = \log (N!) + \log \left(\prod \frac{g_s^{n_s}}{n_s!}\right)$$
$$= N \log N - \cancel{N} + \sum (n_s \log g_s - n_s \log n_s + \cancel{n_s})$$
$$= N \log N + \left(\sum n_s \log \frac{g_s}{n_s}\right)$$

$$\log W_{max} = N \log N + \sum n_s \cancel{\log} \, \cancel{e}^{-\alpha - \beta \epsilon_s}$$
$$= N \log N - \alpha \sum n_s - \beta \sum n_s \epsilon_s \quad \text{--- (1)}$$

$$\because \sum n_s \epsilon_s = E \quad , \quad \sum n_s = N$$
$$\therefore \log W_{max} = N \log N - \alpha N - \beta E \quad \text{--- (2)}$$

if $e^{\alpha} = A \quad \therefore \alpha = \log A \quad , \quad \beta = \frac{-1}{KT}$

$\therefore \log W_{max} = N \log N - N \log A + \frac{E}{KT}$

$$\therefore \left[\log W_{max} = N \log \frac{N}{A} + \frac{E}{KT} \right] \quad \text{--- (3)}$$

The ratio $\frac{N}{A} = Z = \frac{\sum n_s}{e^{\alpha}}$

$\therefore Z = \frac{\sum g_s e^{\alpha + \beta \epsilon_s}}{e^{\alpha}}$

$$\therefore \left[Z = \sum g_s e^{-\epsilon_s / KT} \right] \quad \text{--- (4)}$$

Z = the Boltzman partition function of a system assembly

if $g_s = 1$ then $\left[Z = \sum_i e^{-\epsilon_i / KT} \right]$ --- (5)

Substituting for $Z = \frac{N}{A}$ in eq (3)

$$\left[\log W_{max} = N \log Z + \frac{E}{KT} \right] \quad \text{--- (6)}$$

$\because$ $S = K \log W_{max}$ ⇒ the intropy

$\therefore \left[S = NK \log Z + \frac{E}{T} \right]$ --- (7)

$\because$ $F = E - TS$ --- (8) to get the Helmoholtz free energy

Substitute (7) in (8)

$\therefore F = \cancel{E} - TKN \log Z - \cancel{E}$

$\therefore \left[F = -NKT \log Z \right]$

H.W

(1) prove that $\left[E = NKT^2 \left\{ \frac{\partial \log Z}{\partial T} \right\}_V \right]$ by using the expression

$E = -T^2 \left\{ \frac{\partial (F/T)}{\partial T} \right\}_V$.

(2) Prove That the expression of E, S & F in terms of β and Z are:

(a) $E = \frac{N \partial \log Z}{\partial \beta}$ (b) $F = \frac{N \log Z}{\beta}$

(c) $S = NK \left(\log Z - \left\{ \frac{\partial \log Z}{\partial \log \beta} \right\}_V \right)$.

$\because n_i = g_s e^{\alpha + \beta \epsilon_s}$ ---- (1)

$\because e^{\alpha} = A$ & $Z = \frac{N}{A}$

$\therefore A = e^{\alpha} = \frac{N}{Z}$ ---- (2)

substituting (2) in (1)

$\therefore n_i = g_s \frac{N}{Z} e^{\beta \epsilon_s} = g_s \frac{N}{Z} e^{-\epsilon/KT}$

if there is no degeneracy $\Rightarrow g_s = 1$

$$\therefore \left[n_i = \frac{N}{Z} e^{-\epsilon/KT} \right]$$

The distribution of the system over the Various energy sheets in term of (Z).

Ex: N Particles are distributed among (3) states having energy $\epsilon_1 = 0$, $\epsilon_2 = KT$, $\epsilon_3 = 2KT$ and a total equillibrum of energy is (1000KT) What is the Value of N ?

Sol:

$\because N = n_1 + n_2 + n_3$

$\because n_i = \frac{N}{Z} e^{-\epsilon_i/KT}$

$\therefore n_1 = \frac{N}{Z} e^{0} \Rightarrow n_1 = \frac{N}{Z}$

$n_2 = \frac{N}{Z} e^{-KT/KT} \Rightarrow n_2 = \frac{N}{Z} e^{-1}$

$n_3 = \frac{N}{Z} e^{-2KT/KT} \Rightarrow n_3 = \frac{N}{Z} e^{-2}$

$\therefore n_2 = n_1 e^{-1}$, $n_1 = n_2 e^{1}$

$n_3 = n_2 e^{-1}$

$\because E_{TOT} = n_1 \epsilon_1 + n_2 \epsilon_2 + n_3 \epsilon_3$

$$\therefore 1000\,K\cancel{T} = 0 + n_2 K\cancel{T} + \frac{n_2}{e^1} * 2K\cancel{T}$$

$$1000 = n_2 + 2\frac{n_2}{e^1}$$

$$\therefore 1000 = n_2\left(1 + \frac{2}{e^1}\right) \Rightarrow 1000 = n_2\left(\frac{e^1+2}{e^1}\right)$$

$$\therefore n_2 = \frac{1000\,e^1}{(e^1+2)}$$

$$\therefore n_3 = n_2 e^{-1} \Rightarrow n_3 = \left(\frac{1000\,\cancel{e^1}}{e^1+2}\right) * \cancel{e^{-1}}$$

$$\therefore n_3 = \frac{1000}{e^1+2}$$

$$\therefore n_1 = n_2 * e^1 \Rightarrow n_1 = \frac{1000\;e^2}{(e^1+2)}$$

$$\therefore N = n_1 + n_2 + n_3$$

$$\therefore N = \frac{1000\,e^2}{(e^1+2)} + \frac{1000\,e^1}{(e^1+2)} + \frac{1000}{(e^1+2)}$$

$$\therefore N_{TOT.} = \frac{1000}{(e^1+2)}\left(e^2 + e^1 + 1\right)$$

EX: Consider a system of (N) particles of phase space of just three cells (1, 2 & 3) let ($\epsilon_1 = 0$, $\epsilon_2 = \epsilon_3$, $\epsilon_3 = 2\epsilon$), find Z, n_1, n_2, n_3, E and S.

1)

$$\because Z = \sum_{i=1}^{3} e^{-\epsilon_i/KT} = \left(e^{-0/KT} + e^{-2\epsilon/KT} + e^{-2\epsilon/KT}\right)$$

$$= 1 + 2e^{-2\epsilon/KT}$$

2) $$\because n_i = \frac{N}{Z} e^{-\epsilon_i/KT}$$

$$\therefore n_1 = \frac{N}{1+2e^{-2\epsilon/KT}} * e^{-0/KT} = \frac{N}{Z}$$

$$n_2 = \frac{N}{1+2e^{-2\epsilon/KT}} * e^{-2\epsilon/KT}$$

$$= \frac{N}{1+2e^{-2\epsilon/KT}} * \frac{1}{e^{2\epsilon/KT}}$$

$$\therefore n_2 = \frac{N}{e^{2\epsilon/KT}+2} = n_3$$

(3)

$$\therefore E = NKT^2 \frac{d \log Z}{dT} = \frac{NKT^2}{Z} * \frac{dZ}{dT}$$

$$\therefore E = \frac{NKT^2}{1+2e^{-2\epsilon/KT}} * \frac{d\left(1+2e^{-2\epsilon/KT}\right)}{dT}$$

$$E = \frac{NK\cancel{T^2}}{1+2e^{-2\epsilon/KT}} * 2\left(\frac{2\epsilon}{\cancel{KT^2}}\right) e^{-2\epsilon/KT}$$

$$\therefore E = \frac{4N\epsilon}{1+2e^{-2\epsilon/KT}} * e^{-2\epsilon/KT} = \frac{4N\epsilon}{e^{2\epsilon/KT}+2}$$

(4) $\because S = NK \log Z + \frac{E}{T}$

$$\therefore S = NK \log\left(1+2e^{-2\epsilon/KT}\right) + \frac{4N\epsilon}{T} * \frac{1}{e^{2\epsilon/KT}+2}$$

$$= NK \log 2e^{-2\epsilon/KT} + \frac{4N\epsilon}{T} \frac{1}{e^{2\epsilon/KT}+2}$$

$$= NK\left[\log 2 - \frac{2\epsilon}{KT}\right] + \frac{4N\epsilon}{T} * \frac{1}{e^{2\epsilon/KT}+2}.$$

EX: consider a system of (10^6) particles and phase space of (5×10^5) cells in which the energy (ϵ_i) is the same for all cells. what is the thermodynamics probability of:

(a) the most probable distribution.

(b) The less probable distribution.

Solution:

$N = 10^6 \quad , \quad n = 5\times10^5$

a For the most probable distribution

$n_1 = n_2 = n_3$

$$Z = \sum e^{-\beta\epsilon_i} \qquad \Longrightarrow \qquad n \approx \sum$$

$$Z = n\, e^{-\beta\epsilon_i}$$

$$n_i = \frac{N}{Z} e^{-\beta\epsilon_i} \quad \Longrightarrow n_1 = \frac{N}{n\cancel{e^{-\beta\epsilon_1}}} * \cancel{e^{-\beta\epsilon_1}}$$

$$\therefore n_1 = \frac{N}{n} \quad ; \quad \therefore \left(n_i = n_1 = n_2 = n_3 = \frac{N}{n}\right)$$

$$\therefore n_i = \frac{10^6}{5\times10^5} = \frac{1}{5}\times10^6\times10^{-5} = 2$$

$\because \quad W = \frac{N!}{\sum n_i!}$

$\therefore \log W = \log N! - \sum \log n_i!$

$= N\log N - N - \sum [n_i \log n_i - n_i]$

$= N\log N - \cancel{N} - \sum n_i \log n_i - \cancel{\sum n_i}$

$\because \quad \boxed{\sum \approx n}$

$\therefore \log W = N\log N - n * n_i \log n_i$

$\because \quad \boxed{n_i = \frac{N}{n}}$

$\therefore \log W = N\log N - \cancel{n} * \frac{N}{\cancel{n}} \log \frac{N}{n}$

$= N\log N - N(\log N - \log n)$

$\therefore \log W = N \log n$

$\therefore \log W = N \log \frac{N}{n_i} = 10^6 \log \left(\frac{10^6}{2}\right)$

$= 10^6 (\log 10^6 - \log 2) = 10^6 (13.8 - 1)$

$\log W = 10^6 * 12.8 \Rightarrow W = e^{10^6 * 12.8}$

(b) $W = \frac{N!}{\sum n_i!} = \frac{0!}{0!} = 1 \Rightarrow$ less Probable distribution

Ex: The ord (statistic) contains of (9) characters, the character (t) repeats three times, (S) repeats twice and (i) repeats twice. Calculate the number of different words that can be configured from these (9) characters regardless of there meanings (number of possible arrangementes for these characters).

$$W = \frac{N!}{n_1! n_2! n_3!}$$

$$= \frac{9!}{3! 2! 2!} = 15120$$