

Classical statistics (Maxwell Boltzmann Distribution):

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

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

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

$$\begin{aligned} \log W_{\max} &= \log(N!) + \log\left(\pi \frac{g_s^{n_s}}{n_s!}\right) \\ &= N \log N - N + \sum (n_s \log g_s - n_s \log n_s + n_s) \\ &= N \log N + \left(\sum n_s \log \frac{g_s}{n_s} \right) \end{aligned}$$

$$\begin{aligned} \log W_{\max} &= N \log N + \sum n_s \log e^{-\alpha - \beta E_s} \\ &= N \log N - \alpha \sum n_s - \beta \sum n_s E_s \quad \text{--- (1)} \end{aligned}$$

$$\therefore \sum n_s E_s = E, \quad \sum n_s = N$$

$$\therefore \log W_{\max} = N \log N - \alpha N - \beta E \quad \text{--- (2)}$$

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



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

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

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

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

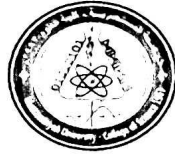
$$\therefore \left[Z = \sum g_s e^{-E_s/kT} \right] \text{--- (4)}$$

Z = the Boltzmann Partition function of a system assembly.

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

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

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



$\therefore S = k \log W_{\max} \Rightarrow$ the entropy

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

$\therefore F = E - TS$ to get the Helmholtz free energy
--- (8)

Substitute (7) in (8)

$$\therefore F = E - TKN \log Z - E$$

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

H.W

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

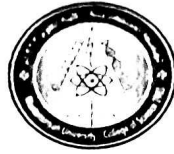
$$E = -T^2 \left\{ \frac{\partial (F/T)}{\partial T} \right\}_V$$

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

$$\textcircled{a} E = \frac{N \partial \log Z}{\partial \beta}$$

$$\textcircled{b} F = \frac{N \log Z}{\beta}$$

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



$$\therefore n_i = g_s e^{\alpha + \beta E_s} \quad \text{--- (1)}$$

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

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

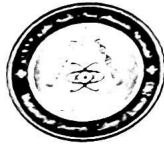
Substituting (2) in (1)

$$\therefore n_i = g_s \frac{N}{Z} e^{\beta E_s} = g_s \frac{N}{Z} e^{-E/kT}$$

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

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

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



EX: N Particles are distributed among (3) states having energy $E_1=0$, $E_2=KT$, $E_3=2KT$ and a total equilibrium of energy is $(1000KT)$. What is the value of N ?

Sol:

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

$$\therefore n_i = \frac{N}{Z} e^{-E_i/KT}$$

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

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

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

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

$$n_3 = n_2 e^{-1}$$

$$\therefore E_{\text{TOT}} = n_1 E_1 + n_2 E_2 + n_3 E_3$$



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

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

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

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

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

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

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

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

$$\therefore N_{\text{Tot.}} = \frac{1000}{(e^1 + 2)} (e^2 + e^1 + 1)$$



EX: Consider a system of (N) particles of phase space of just three cells (1, 2 & 3). let $(E_1=0, E_2=E_3, E_3=2E)$, find Z , n_1, n_2, n_3, E and S .

$$\begin{aligned} \textcircled{1} \quad \therefore Z &= \sum_{i=1}^3 e^{-E_i/KT} = (e^{-0/KT} + e^{-2E/KT} + e^{-2E/KT}) \\ &= 1 + 2e^{-2E/KT} \end{aligned}$$

$$\textcircled{2} \quad \therefore n_i = \frac{N}{Z} e^{-E_i/KT}$$

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

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

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

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



$$\textcircled{3} \therefore E = NKT^2 \frac{d \log Z}{dT} = \frac{NKT^2}{Z} * \frac{dZ}{dT}$$

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

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

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

$$\textcircled{4} \therefore S = NK \log Z + \frac{E}{T}$$

$$\therefore S = NK \log(1+2e^{-2E/KT}) + \frac{4NE}{T} * \frac{1}{e^{2E/KT} + 2}$$

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

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



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

- the most probable distribution.
- The less probable distribution.

Solution:

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

a For the most probable distribution

$$n_1 = n_2 = n_3$$

$$Z = \sum e^{-\beta E_i} \Rightarrow n \approx Z$$
$$Z = \sum n e^{-\beta E_i}$$

$$n_i = \frac{N}{Z} e^{-\beta E_i} \Rightarrow n_1 = \frac{N}{n e^{-\beta E_i}} \times e^{-\beta E_i}$$

$$\therefore n_1 = \frac{N}{n} ; \therefore (n_1 = n_2 = n_3 = \frac{N}{n})$$

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



$$\therefore W = \frac{N!}{\sum n_i!}$$

$$\begin{aligned}\therefore \log W &= \log N! - \sum \log n_i! \\ &= N \log N - N - \sum [n_i \log n_i - n_i] \\ &= N \log N - N - \sum n_i \log n_i + \sum n_i\end{aligned}$$

$$\therefore \boxed{\sum \approx N}$$

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

$$\therefore \boxed{n_i = \frac{N}{n}}$$

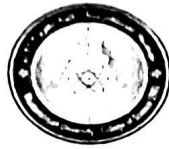
$$\begin{aligned}\therefore \log W &= N \log N - N + \frac{N}{n} \log \frac{N}{n} \\ &= N \log N - N (\log N - \log n)\end{aligned}$$

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

$$\begin{aligned}\therefore \log W &= N \log \left(\frac{N}{n_i} \right) = 10^6 \log \left(\frac{10^6}{2} \right) \\ &= 10^6 (\log 10^6 - \log 2) = 10^6 (13.8 - 1)\end{aligned}$$

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

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



Ex: The word (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 their meanings (number of possible arrangements for these characters).

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

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