Statistical Thermodynamics.

Occupation number-
It is the number of systems in that particular state.

Distribution-
The set of occupation number is called distribution

Configuration-
Various equivalent ways of acheiving a state is called configuration of the system.

Statistical weight factor-
It is the degree of degeneracy of particular energy level and is equal to energy states of an energy level.
It is denoted by 'g'.

Stirling's approximation-
For large 'n' -

$$\ln n! = n.\ln n - n$$

Ensemble-
Ensemble is formed by reproducing the distinct unit many times.

Micro-canonical ensemble-
N, V, E - remains same
No contact with surrounding

Canonical ensemble-
N, V, T - remains same
Thermal contact with surrounding.

Grand canonical ensemble-

μ, V, T - remains same

Thermal and material contact (exchange)

Statistical equilibrium-

An ensemble is said to be in statistical equilibrium if it obeys following conditions-

1. The probabilities of finding phase points in various regions of phase should be independent of time.
2. The average values for properties of system in the ensemble should also be independent of time.

Thermodynamic probability-

The number of microstates which correspond to a macrostate is reffered to as thermodynamic probability.

* Most probable Configuration -

Consider a system containing n particles having total energy E_t.
Thermodynamic probability of this distribution is given by -

$$P = \frac{n!}{n_0!\, n_1!\, n_2! \ldots n_i!} = \frac{n!}{\Pi\, n_i!}$$

Taking log on both sides

$$\log P = \log n! - (\log n_0! + \log n_1! + \ldots + \log n_i!)$$

$$\log P = \log n! - \Sigma \log n_i! \qquad \text{--- (1)}$$

Applying stirling's theorem to eq. (1)

$$\log n! = n \log n - n$$

$$\log P = n.\log n - n - [\Sigma n_i \log n_i - \Sigma n_i]$$

$$= n \log n - n - \Sigma n_i \log n_i + \Sigma n_i$$

(but $\Sigma n_i = n$)

$$= n \log n - n - \Sigma n_i \log n_i + n$$

$$\therefore \log P = n \log n - \Sigma n_i \log n_i \qquad \text{--- (2)}$$

To find most probable disteibution,
system attains equilibrium
↳ probability will be maximum
Hence at equilibrium

$$d \log P = 0.$$

Now,
differentiating eq. (2),

$$d \log P = d\,(n \cdot \log n) - d\,(\Sigma n_i \log n_i) = 0$$

zero

$$d \log P = -\Sigma d\; n_i \log n_i = 0$$

$$\Sigma d n_i \log n_i = 0$$

$$(\Sigma n_i) \cdot d \log n_i + (\Sigma \log n_i) \cdot d n_i = 0$$

$$\Sigma n_i \cdot \frac{d n_i}{n_i} + \Sigma \log n_i \cdot d n_i = 0$$

$$\Sigma d n_i + \Sigma \log n_i \cdot d n_i = 0 \quad \text{—— (3)}$$

But, $\Sigma n_i = n = \text{constant}$

Hence, $\Sigma d n_i = 0$

∴ Equation becomes

$$\Sigma \log n_i \cdot d n_i = 0 \quad \text{—— (4)}$$

For the given system, total energy and total number of particles remains constant.

$$n = \Sigma n_i \quad \text{or} \quad dn = \Sigma d n_i = 0 \quad \text{—— (5)}$$

$$E_t = \Sigma n_i \varepsilon_i \quad \text{or} \quad dE_t = \Sigma \varepsilon_i\, d n_i = 0 \quad \text{—— (6)}$$

Multiply equation (5) and (6) by arbitrary undetermined multipliers α and β respectively and add eq. (4), We get,

$$\Sigma \log n_i \cdot d n_i + \alpha \Sigma d n_i + \beta \Sigma \varepsilon_i\, d n_i = 0$$

$$d n_i (\Sigma \log n_i + \alpha + \beta \Sigma \varepsilon_i) = 0$$

If $d n_i \neq 0$,

$$\log n_i + \alpha + \beta \varepsilon_i = 0$$

$$\log n_i = -\alpha - \beta \varepsilon_i$$

$$\boxed{n_i = e^{-\alpha - \beta \varepsilon_i}} \quad \text{—— (7)}$$

Equation (7) gives number of particles in each energy level.
Equation (7) is the Boltzmann distribution law.

We can write

$$n = \Sigma n_i = e^{-\alpha} . \Sigma e^{-\beta \epsilon_i} \quad \text{——— (8)}$$

Now,

$$\frac{n_i}{n} = \frac{e^{-\alpha} . e^{-\beta \epsilon_i}}{e^{-\alpha} . \Sigma e^{-\beta \epsilon_i}}$$

$$\boxed{\therefore \frac{n_i}{n} = \frac{e^{-\beta \epsilon_i}}{\Sigma . e^{-\beta \epsilon_i}}} \quad \text{——— (9)}$$

Equation (9) is known as Maxwell-Boltzmann distribution law

If there are g_i number of possible distributions of energy in a given energy level 'i', then the state state is said to be 'g_i-degenerate'.

Thus equation (7) and (8) becomes

$$n_i = e^{-\alpha} . g_i . e^{-\beta \epsilon_i} \quad \text{——— (10)}$$

and

$$n_i = e^{-\alpha} . \Sigma g_i e^{-\beta \epsilon_i} \quad \text{——— (11)}$$

$$\boxed{\therefore \frac{n_i}{n} = \frac{g_i . e^{-\beta \epsilon_i}}{\Sigma g_i . e^{-\beta \epsilon_i}}} \quad \text{——— (12)}$$