

Probability:-

Def:- Probability is the property or a kind to measure the likelihood of an event.

OR

The probability of an event is defined as the ratio of the number of events occurring to the total no. of cases in an event.

Total Probability:-

————— is the sum of the probabilities taking place in an event.

Zero Probability:-

The ——— of an event which is impossible is called zero probability.

Probability one:-

The probability of a sure or certain event is called probability one.

Principle of equal priori probability:-

The principle of assuming equal probabilities for events which are equally occurring is called

principle of equal prior probability.

Permutation:-

The arrangement of which can be made of given no. of things by taking some of them or all at a time are called permutation.

To denote the permutations of n things taken r at a time then the symbol is ${}^n P_r$ or $P(n, r)$ is given by

$${}^n P_r = \frac{n!}{(n-r)!}$$

where $n! = n(n-1)(n-2) \dots 2 \times 1$

and $(n-r)! = (n-r)(n-r-1) \dots 2 \times 1$.

Combinations:-

The different selections or groups that can be formed out of a given no. of things some or all of them at a time are called as combinations.

The no. of combinations of n things taken r at a time is denoted by ${}^n C_r$ and is given by

$${}^n C_r = \frac{n!}{r!(n-r)!}$$

The permutation and combination can be related to each other by the eqⁿ

$${}^nC_r = \frac{{}^nP_r}{r!} \quad \underline{\text{OR}} \quad {}^nP_r = {}^nC_r \cdot r!$$

The no. of arrangements of n things taking all at a time for both permutation and combination is given by

$${}^nP_n = \frac{n!}{(n-n)!} = n! \quad (0! = 1)$$

$${}^nC_n = \frac{n!}{n!(n-n)!} = \frac{n!}{n! \times 1} = 1$$

* Difference betⁿ permutation & combination. —

- ① In combination group of objects is considered whereas in permutation there arrangement is considered
- ② Consider 3 alphabets a, b, c , for combination a, b, c is same as c, b, a whereas in permutation $a, b, c \neq c, b, a$.

Probability and frequency :-

Consider the tossing of a coin, say 50 times and in that only 10 times the head is occurring then the probability is given by

$$p = \frac{10}{50} = 0.2$$

Defⁿ:- The frequency is defined as the ratio of no. of trials in which head occurs to the no. of trials.

Defining the probability in terms of frequency is given by

$$p = \lim_{n \rightarrow \infty} \frac{M}{N}$$

Where N represents the no. of trials
& M represents the trials in which head occur
OR

The trial in which the event takes place.
The ratio $\frac{M}{N}$ differ from one another by

a very small value then we say that

probability = frequency.

* Macrostate and Microstate :-

Macrostate :-

To understand the macrostructure, consider an example. consider 2 compartments which are equally spaced or similar.

Consider 4 particles denoted by symbol a, b, c, d.

Since both the compartments are similar the particle has priori probability in the compartments.

The 2 compartments are same but differ only in the case of energy, momentum or velocity of the particle. Let us take the property of energy E . For compartment ① energy is E_1 and for compartment ② the energy is E_2 .

The possible ways in which the four particles can be distributed in 2 compartments is given in the table below.

Compartment	No. of particles Distribution				
	I	II	III	IV	V
1	4	3	2	1	0
2	0	1	2	3	4

Here, we get 5 different distributions
i.e. (4,0), (3,1), (2,2), (1,3), (0,4)

The compartmentwise arrangement or distribution of a system of particles is called as macrostate. In general for n no. of particles distributed among 2 compartments is given by

$$(n, 0) \quad (n-1, 1) \quad (n-2, 2) \quad \dots \quad (0, n)$$

Microstate:-

To understand the microstate consider the same example of macrostate. The particles are considered to be distinguishable for the compartmentwise distribution and can have a no. of different arrangements which is as shown in below table.

Macrostate	Possible arrangement		No. of microstates
	comp 1	comp 2	
(4, 0)	a b c d	0	1
(3, 1)	abc	d	4
	bcd	a	
	acd	b	
	abd	c	
(2, 2)	ab	cd	
	bc	da	
	cd	ab	
	da	bc	
	ac	bd	

	ad ba cb	cb dc ad	6
(1,3)	abc abd acd bcd	d c b a	4
(0,4)	0	abcd	

Each distinct arrangement is known as the microstate of the system.

In the distribution table for 1st case i.e. (4,0) we have only one arrangement. Similarly for case ② i.e. (3,1) we have 4 microstates. $\therefore$ considering all the arrangements of 4 particles the total no. of microstate is given by the value 2^4 .

For n no. of particles the microstates is given by the value 2^n .

Constraints :- The condition or the restrictions applied to the distribution of the particles in a given system is called constraints.

As the constraints value is increased the no. of macrostate and microstate reduces.

Types of macrostate and microstate:-

The macrostates or microstates which are allowed under a constraint or condition are called accessible macrostate or accessible microstate.

The macrostates or microstates which are not allowed under the constraints or condition are called inaccessible macrostate or inaccessible microstate.

* Thermodynamic Probability:-

The thermodynamic probability is defined as the no. of microstates corresponding to a particular macrostate.

If we consider n no. of particles to be arranged in 2 cells or compartments, if r is the no. of microstates present in compartment 1 then remaining $n-r$ particles will be present in the compartment 2.

$\therefore$ the no. of microstates in a macrostate $(r, n-r)$ or the thermodynamic probability is given by

$$W(r, n-r) = \frac{n!}{r! (n-r)!}$$

$$W(r, n=0) = {}^nC_r$$

Most Probable State :-

The most probable state of a system is that macrostate which has the maximum no. of probabilities.

Additive law of probability :-

This law is applicable for mutually exclusive events. Two or more events are said to be mutually exclusive if the occurrence of any one of them prevents the occurrence of other. Such events never occur simultaneously.

Then the probability for n no. of particles i.e. $p_1, p_2, p_3, \dots, p_n$ is given by

$$P = p_1 + p_2 + p_3 + \dots + p_n$$

Multiplication rule of probability / Joint Probability :-

The probabilistic calculations can be done for random events, the events may be occurring at the same time such that the probability of occurrence of one event does not effect the other event. For such probabilities, the multiplication

rule is applicable.

The events are said to be independent events. If p_1 and p_2 are the probabilities taking place then the multiplication of these probabilities is given by

$$P = p_1 \times p_2$$

* Statistics :-

It is the branch of science which deals with the collection and calculation of numerical data as the basis of explanation, description and comparison of various phenomena.

Statistical Physics :-

It is the branch of science which deals with the particles which are at rest.

OR

It deals with macroscopic systems i.e. the system containing large no. of individual particles such as atoms, molecules, etc.

The statistical physics is divided into 3 kinds

① Maxwell - Boltzmann Statistics -

This is applicable to the identical distinguishable particles of any spins.

Ex. Molecules of gas comes under this statistics.

② Bose - Einstein statistics :-

This is applicable to identical, indistinguishable particles having zero or integral values.

These particles are called as Bosons.

Ex. He atoms at low temp.

③ Fermi - dirac statistics :-

This is applicable to identical, indistinguishable particles having half integral spin. They obey Pauli's Exclusion Principle and are called as Fermions.

Ex. electrons, protons, neutrons.

Classical & Quantum Statistics

Phase Space :-

The combination of position space and momentum space is called phase space.

Position Space :-

If a particle is considered in 3 dimension and its position is determined w.r.t. 3 co-ordinates x, y, z then it represents position space.

Defⁿ :- The 3 dimensional space in which the position of a particle is determined by the 3 co-ordinates is known as position space.

Momentum Space :-

Consider the particle is having some mass m and moving with velocity V in 3 co-ordinates then the velocity is given by V_x, V_y, V_z . then the momentum of the particle in all 3 co-ordinates is given by $P_x = mV_x, P_y = mV_y, P_z = mV_z$.

The momentum of the particle is completely specified by 3 momentum co-ordinates x, y, z in 3 dimensional space is known as momentum space.

Depending upon phase space the statistics is divided into 2 types.

① Classical Statistics / Maxwell-Boltzmann statistics :-

In this —" — the particles are identical and distinguishable.

② Quantum Statistics :-

It is further divided into 2 types :-

① Bose Einstein Statistics :-

② Fermi dirac —" —

In this, the particles are identical but indistinguishable.

classical Statistics

Quantum Statistics

① The particles are identical and distinguishable.

① The particles are identical and indistinguishable.

② The no. of cells and area of cells can be made as large as possible.

② The no. of cells or the area of cells cannot be made as large as possible.

③ The size of the particles can be made as small as possible or zero with no restriction.

③ The particles size cannot be ^{more} less than h^3 . where h is plank's constant.

④ The particles are obeying the maxwell-Boltzmann statistics.

④ The particles obey the Bose-Einstein and Fermi-dirac statistical.

① The Maxwell-Boltzmann Statistics :-

The particles in this $\rightarrow n \rightarrow$, are distinguishable. They can take any position in the given no. of cells.

The statistics is applicable to the particles having large size.

Two particles or more than 2 particles can occupy the same space.

② Bose-Einstein Statistics :-

The particles are indistinguishable and can take any position in the given no. of cells. Since they do not obey 'Pauli's Exclusion Principle'. Two or more particles can occupy the same space.

③ Fermi-Dirac Statistics:-

The particles are indistinguishable. Since they obey Pauli's exclusion principle, One particle can only be placed in one cell.

* Maxwell-Boltzmann Statistics for distribution of energy :-

Consider $n_1, n_2, n_3 \dots n_i \dots n_k$ the no. of particles having energy $E_1, E_2 \dots E_i \dots E_k$ resp. should be arranged in the cells or compartments numbered as $1, 2, 3 \dots i \dots k$ having the arrangement cells $g_1, g_2, g_3 \dots g_i \dots g_k$

The total no. of particles in the system which are to be arranged in the cells is given by

$$n = n_1 + n_2 + \dots + n_i + \dots + n_k$$

The thermodynamic probability is applied to the n no. of particles which are to be arranged in the different cells is considered. is given by

$$W = \frac{n!}{n_1! n_2! \dots n_i! \dots n_k!} \prod (g_i)^{n_i} \quad (n = \sum n_i)$$

$$W = \frac{n!}{n_1!} \sum (g_i)^{n_i}$$

Taking log on both sides we get,

$$\log W = \log \left[\frac{n! \pi (g_i)^{n_i}}{n_i!} \right] \quad \text{--- ①}$$

$$= \log n! + \log \left[\frac{\pi (g_i)^{n_i}}{n_i!} \right]$$

$$= \log n! + \log \pi (g_i)^{n_i} - \log n_i!$$

$$\log W = \log n! + n_i \log \pi (g_i) - \log n_i!$$

$$\log W = \log n! + \sum_{i=1}^K n_i \log (g_i) - \sum_{i=1}^K \log n_i! \quad \text{--- ②}$$

By using 'stirling theorem' which states that
 $\log n! = n \log n - n$

$$\log W = n \log n - n + \sum_{i=1}^K n_i \log (g_i) - \sum_{i=1}^K n_i \log n_i - n_i$$

$$\log W = n \log n - n + \sum_{i=1}^K n_i \log (g_i) - \sum_{i=1}^K n_i \log n_i - \sum_{i=1}^K n_i$$

$$n = n_1 + n_2 + \dots + n_K \Rightarrow n = \sum_{i=1}^K n_i$$

$$\sum n_i = n$$

$$\log W = n \log n - n + \sum_{i=1}^k n_i \log (g_i) - \sum_{i=1}^k n_i \log n_i$$

$$\log W = n \log n + \sum_{i=1}^k n_i \log (g_i) - \sum_{i=1}^k n_i \log n_i \quad \text{--- (3)}$$

Differentiating eqⁿ (3) by taking n & g_i as constant.

$$d(\log W) = 0 + \sum_{i=1}^k dn_i \log (g_i) - \sum_{i=1}^k \left[dn_i \log n_i + n_i \cdot \frac{1}{n_i} \cdot dn_i \right]$$

$$d(\log W) = \sum_{i=1}^k dn_i \log (g_i) - \sum_{i=1}^k dn_i \log (n_i) - \sum_{i=1}^k dn_i \quad \text{--- (4)}$$

Eqⁿ (4) can be further reduced by taking the term $\sum_{i=1}^k dn_i = 0$.

$$d(\log W) = \sum_{i=1}^k dn_i \log (g_i) - \sum_{i=1}^k dn_i \log (n_i)$$

$$d(\log W) = \sum_{i=1}^k dn_i [\log (g_i) - \log (n_i)] \quad \text{--- (5)}$$

The most probable state is that for which the thermodynamic probability is maximum.

$$\text{i.e. } d(W) = 0$$

$$\text{or } d(\log W) = 0.$$

$$0 = \sum_{i=1}^k [\log(g_i) - \log(n_i)] dn_i \quad \text{--- (6)}$$

$$\sum_{i=1}^k [\log(g_i) - \log(n_i)] = 0.$$

Since the total no. of particles n is constant and the total energy E is constant. Thus we can have ~~a~~ derivative of n and E is $dn=0$, $dE=0$.

$$\sum_{i=1}^k dn_i = 0 \quad \text{--- (7)}$$

$$\sum_{i=1}^k dE = 0 \quad \text{--- (8)}$$

Multiplying eqn (7) by $-\alpha$ and eqn (8) by $-\beta$.
We get

$$\sum_{i=1}^k dn_i (-\alpha) = 0 \quad \text{--- (9)}$$

$$\sum_{i=1}^k dE (-\beta) = 0.$$

The derivative of energy w.r.t. n_i particles is given by

$$\sum_{i=1}^k d n_i E_i (-\beta) = 0 \quad \text{--- ⑩}$$

Adding eqⁿ ⑨ & ⑩ to eqⁿ ⑥, We get

$$\sum_{i=1}^k [\log(g_i) - \log(n_i)] d n_i - \sum_{i=1}^k d n_i \alpha -$$

$$\sum_{i=1}^k d n_i E_i \beta = 0.$$

$$\sum_{i=1}^k [\log g_i - \log n_i - \alpha - E_i \beta] d n_i = 0 \quad \text{--- ⑪}$$

In eqⁿ ⑪ each term must be independently zero.

Therefore,

$$\log g_i - \log n_i - \alpha - E_i \beta = 0.$$

$$\log \left(\frac{g_i}{n_i} \right) - \alpha - E_i \beta = 0.$$

$$\log \left(\frac{g_i}{n_i} \right) = \alpha + E_i \beta.$$

$$\frac{g_i}{n_i} = e^{\alpha + E_i \beta}$$

$$n_i = \frac{g_i}{e^{\alpha + E_i \beta}} \Rightarrow n_i = g_i e^{-(\alpha + E_i \beta)}$$

$$n_i = g_i e^{-\alpha} \cdot e^{-E_i \beta} \quad \text{--- ⑫}$$

Eqⁿ (12) is called as the Maxwell-Boltzmann law of energy distribution in the general form. The value of β given as

$$\beta = \frac{1}{KT}$$

Substituting this value in eqⁿ (12), We get,

$$n_i = g_i e^{-\alpha} e^{\frac{-E_i}{KT}} \quad \text{--- (13)}$$

Where $e^{\frac{-E_i}{KT}}$ is called Boltzmann factor.

We know that $n = \sum_i n_i$

Eqⁿ (13) can be used to substitute the value of n_i ,

$$n = \sum_i g_i e^{-\alpha} e^{\frac{-E_i}{KT}}$$

$$n = e^{-\alpha} \sum_i g_i e^{\frac{-E_i}{KT}}$$

$$e^{-\alpha} = \frac{n}{\sum_i g_i e^{\frac{-E_i}{KT}}} \quad \text{--- (14)}$$

The quantity $\sum_i g_i e^{\frac{-E_i}{KT}}$ is the sum over all the states or cells of the system and is called as the partition function denoted by Z .

$$\sum_i g_i e^{\frac{-E_i}{KT}} = Z$$

$$\bar{e}^x = \frac{n}{Z}$$

$$n_i = g_i \bar{e}^x e^{-\frac{\epsilon_i}{kT}}$$

$$n_i = g_i \frac{n}{Z} e^{-\frac{\epsilon_i}{kT}}$$

$$n_i = \frac{g_i n e^{-\frac{\epsilon_i}{kT}}}{\sum_j g_j e^{-\frac{\epsilon_j}{kT}}}$$

$$n_i = \frac{g_i n}{\sum_j g_j}$$

* Need for the quantum statistics / Drawback of Maxwell-Boltzmann Statistics :-

- ① The metallic conductors contain a large no. of free particles which move freely inside the conductor like the gas molecules. Such particles are called as electron gas. The Maxwell Boltzmann Statistics fails to explain the energy distribution of the particles in electron gas.
- ② Similarly in a hollow system filled with radiations called photons. These photons

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collide and exert the energy on the surface of the hollow system. In this case also the Maxwell Boltzmann Statistics = fail to explain the energy distribution of photons.

③ In this statistics, the size of the cell can be considered as small as possible or as large as possible. In such case the probability of having 2 or more particles occupying the cell cannot be determined as the size of the cell should be ~~more~~ around h^3

④ Since the particles are distinguishable we cannot determine the energy distribution on the particles through maxwell distribution Law.

Base-Einstein Statistics :-

Assumptions of B.E. statistics :-

① The particles in B.E. — " — are indistinguishable and are identical.

② The size of the cells should be less than h^3 , where h is plank's constant.

- ③ Any no. of particles can occupy a single cell.
 ④ The particles are having the spin integral values such as $S=0$ or $S=1$ and so on.

The particles which exhibit the Bose-Einstein statistics are called Bosons.

* Bose Einstein distribution law :-

Consider a n no. of particles obeying Bose-Einstein statistics. Let $n_1, n_2, \dots, n_i, \dots, n_k$ be the no. of particles having energy $E_1, E_2, E_3, \dots, E_i, \dots, E_k$ resp. to be arranged in the compartments $1, 2, 3, \dots, i, \dots, k$ having $g_1, g_2, \dots, g_i, \dots, g_k$ as the cells or compartments resp. in them. Then the total no. of particles in the system is given by

$$n = n_1 + n_2 + \dots + n_i + \dots + n_k.$$

Consider the i th compartment then there are n_i no. of particles which are to be arranged in g_i cells to calculate the no. of ways in which the n_i no. of particles can be distributed in g_i cells. We have to choose a cell in which we can ~~begin~~ begin the arrangements.

Let us consider g_i cell in which the particles are to be arranged then the remaining $(g_i - 1)$ cells are to be used for the n_i particles i.e. $(n_i + g_i - 1)$ particles can be arranged in any order.

Hence the total no. of ways for getting distribution will be $g_i (n_i + g_i - 1)!$

To get the no. of different arrangements the above term is divided by $n_i! \cdot g_i!$ i.e.

$$W = \frac{g_i (n_i + g_i - 1)!}{n_i! g_i!} \quad \text{--- (1)}$$

Since $g_i!$ is given by

$$g_i! = g_i (g_i - 1)!$$

$\therefore$ eqn (1) can be represented as

$$W = \frac{g_i (n_i + g_i - 1)!}{n_i! g_i (g_i - 1)!}$$

$$W = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad \text{--- (2)}$$

The thermodynamic probability can be represented as

$$W = \frac{\pi (n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

$\therefore n_i$ and g_i are very large values and $\therefore$ one can be neglected then we have

$$W = \frac{\pi (n_i + g_i)!}{n_i! g_i!} \quad \text{--- ①}$$

Taking log on both sides of eqⁿ ① we get,

$$\log W = \sum_{i=1}^K \log \left[\frac{(n_i + g_i)!}{n_i! g_i!} \right]$$

$$\log W = \sum_{i=1}^K \left[\log (n_i + g_i)! - (\log n_i!) - (\log g_i!) \right]$$

~~$\log n!$~~ Using Stirling's theorem we get,

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

$$\log W = \sum_{i=1}^K \left[(n_i + g_i) \log (n_i + g_i) - (n_i + g_i) - n_i \log n_i + n_i - g_i \log g_i + g_i \right]$$

$$\log W = \sum_{i=1}^k \left[(n_i + g_i) \log (n_i + g_i) - n_i \log n_i - g_i \log g_i \right] \quad \text{--- (2)}$$

Differentiating eq. (2) where n_i is variable and g_i is constant. We get,

$$d[\log W] = \sum_{i=1}^k \left[d n_i \log (n_i + g_i) + (n_i + g_i) \frac{1}{n_i + g_i} d n_i - d n_i \log n_i - n_i \frac{1}{n_i} d n_i \right]$$

$$d[\log W] = \sum_{i=1}^k \left[d n_i \log (n_i + g_i) + d n_i - d n_i \log n_i - d n_i \right]$$

$$d[\log W] = \sum_{i=1}^k \left[d n_i \log (n_i + g_i) - d n_i \log n_i \right]$$

$$d[\log W] = \sum_{i=1}^k \left[\log (n_i + g_i) - \log n_i \right] d n_i$$

The thermodynamic probability will be maxima when it has the value ~~per~~ as zero.

i.e.

$$\sum_{i=1}^k \left[\log (n_i + g_i) - \log n_i \right] d n_i = 0 \quad \text{--- (3)}$$

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The no. of particles to be arranged is given by

$$d_n = \sum_{i=1}^k d n_i = 0 \quad \text{--- (4)}$$

Similarly, the energy distributed w.r.t. n_i no. of particles, is given by,

$$dE = \sum_{i=1}^k d n_i E_i = 0 \quad \text{--- (5)}$$

Multiplying eqⁿ (4) by $-\alpha$ and eqⁿ (5) by $-\beta$, and adding to eqⁿ (3) we get,

$$\text{(4)} \Rightarrow - \sum_{i=1}^k d n_i \alpha = 0$$

$$\text{(5)} \Rightarrow - \sum_{i=1}^k d n_i E_i \beta = 0$$

$$\sum_{i=1}^k [\log(n_i + g_i) - \log n_i - \alpha - E_i \beta] d n_i = 0$$

$$\log(n_i + g_i) - \log n_i - \alpha - E_i \beta = 0$$

$$\log(n_i + g_i) = \log n_i + \alpha + E_i \beta$$

$$\log \left(\frac{n_i + g_i}{n_i} \right) = \alpha + E_i \beta$$

$$\frac{n_i + g_i}{n_i} = e^{\alpha + E_i \beta}$$

$$1 + \frac{g_i}{n_i} = e^{\alpha + E_i \beta}$$

$$\frac{g_i}{n_i} = e^{\alpha + E_i \beta} - 1$$

$$n_i = \frac{g_i}{e^{\alpha + E_i \beta} - 1} \quad \text{--- (6)}$$

Substitute $\beta = \frac{1}{KT}$ in eqⁿ (6), we get,

$$n_i = \frac{g_i}{e^{\alpha + \frac{E_i}{KT}} - 1} \quad \text{--- (7)}$$

Eqⁿ (7) represents the Bose-Einstein distribution law.

Fermi - Dirac Statistics :-

Assumptions :-

- ① The particles are indistinguishable and identical
- ② The particles obey the Pauli's Exclusion Principle and hence only one particle can occupy a single cell.
- ③ The particles have half integral spin, such particles are called as fermions.
- ④ The no. of cells say g_i should be greater than the no. of particles say n_i

Fermi - Dirac distribution law :-

Consider $n_1, n_2, \dots, n_i, \dots, n_k$ no. of particles having energy $E_1, E_2, \dots, E_i, \dots, E_k$. The compartments are represented as $1, 2, \dots, i, \dots, k$ and named as $g_1, g_2, \dots, g_i, \dots, g_k$ resp.

Consider the i th compartment in which n_i no. of particles are to be arranged. Once this arrangement is completed then we have $(g_i - n_i)$ no. of ways left out.

According to the 4th assumption of Fermi-Dirac statistics i.e. g_i should be greater than n_i . We have the total no. of arrangements given by

$$\frac{g_i!}{n_i! (g_i - n_i)!}$$

This is for the i^{th} compartment similarly we can obtain the values for different compartments. Hence, the total no. of different arrangements of the particles can be represented as

$$W = \pi \frac{g_i!}{n_i! (g_i - n_i)!} \quad \text{--- (1)}$$

Taking log on both sides,

$$\log W = \sum_{i=1}^K \log \left[\frac{g_i!}{n_i! (g_i - n_i)!} \right]$$

$$\log W = \sum_{i=1}^K [\log g_i! - \log n_i! - \log (g_i - n_i)!]$$

By Stirling's theorem,

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

$$\log W = \sum_{i=1}^K [g_i \log g_i - g_i - n_i \log n_i + n_i - (g_i - n_i) \log (g_i - n_i) + (g_i - n_i)]$$

$$\log W = \sum_{i=1}^K [g_i \log g_i - n_i \log n_i - (g_i - n_i) - (g_i - n_i) \log (g_i - n_i) + (g_i - n_i)]$$

$$\log W = \sum_{i=1}^k [g_i \log g_i - n_i \log n_i - (g_i - n_i) \log (g_i - n_i)]$$

————— ②

Differentiating eqn ②, where n_i is variable and g_i is constant. We get,

$$d[\log W] = \sum_{i=1}^k \left[-\cancel{n_i} \frac{1}{\cancel{n_i}} (dn_i) - dn_i \log n_i - \left(\cancel{g_i - n_i} \right) \left(\frac{1}{\cancel{g_i - n_i}} \right) (-dn_i) + dn_i \log (g_i - n_i) \right]$$

$$= \sum_{i=1}^k \left[-\cancel{dn_i} - dn_i \log n_i + \cancel{dn_i} + dn_i \log (g_i - n_i) \right]$$

$$= \sum_{i=1}^k \left[-dn_i \log n_i + dn_i \log (g_i - n_i) \right]$$

$$= \sum_{i=1}^k \left[dn_i \log (g_i - n_i) - dn_i \log n_i \right]$$

$$d[\log W] = \sum_{i=1}^k [\log (g_i - n_i) - \log n_i] dn_i$$

$$0 = \sum_{i=1}^k [\log (g_i - n_i) - \log n_i] dn_i$$

$$dn = \sum_{i=1}^K dn_i = 0$$

$$dE = \sum_{i=1}^K dn_i E_i = 0$$

$$dn = \sum_{i=1}^K -\alpha dn_i = 0$$

$$dE = \sum_{i=1}^K -\beta dn_i E_i = 0$$

$$\sum_{i=1}^K [\log(g_i - n_i) - \log n_i - \alpha - \beta E_i] dn_i = 0$$

$$\log(g_i - n_i) - \log n_i - \alpha - \beta E_i = 0$$

$$\log \frac{g_i - n_i}{n_i} = \alpha + \beta E_i$$

$$\frac{g_i - n_i}{n_i} = e^{\alpha + \beta E_i}$$

$$\frac{g_i}{n_i} - 1 = e^{\alpha + \beta E_i}$$

$$\frac{g_i}{n_i} = e^{\alpha + \beta E_i} + 1$$

$$n_i = \frac{g_i}{e^{\alpha + \beta E_i} + 1}$$

$$n_i = \frac{g_i}{e^{\alpha + \frac{E_i}{kT}} + 1}$$

This eqⁿ represents the Fermi-dirac distribution law.

All the 3 statistics can be summarised in a single eqⁿ given by

$$n_i = \frac{g_i}{e^{\alpha + \frac{E_i}{kT}} + \gamma}$$

Where $\gamma = 0$ for Maxwell-Boltzmann statistics

$\gamma = -1$ for Bose-Einstein

$\gamma = +1$ for Fermi-dirac

* Comparison of MB, BE, FD statistics :-

M.B.	B.E.	F.D.
① Particles are distinguishable.	① Particles are indistinguishable.	① Particles are indistinguishable.
② Will not obey Pauli's exclusion principle.	② do not obey Pauli's exclusion principle.	② Will obey Pauli's exclusion principle.
③ 2 or any no. of particles can occupy a single cell.	③ any no. of particles can occupy a single cell.	③ A single particle can occupy a single cell.

- | | | |
|---|--|--|
| ④ The particles are not dependent on spin value. | ④ The particles have zero/integral spin values. | ④ The particles can have $\frac{1}{2}$ integral spin values. |
| ⑤ The size of cells can take the size as large as possible or as small as possible or zero value. | ⑤ The size of cells should be always less than h^3 . | ⑤ The size of cells should be less than h^3 . |
| ⑥ It can have one microstate from macrostate. | ⑥ It can have only one microstate from macrostate. | ⑥ It can have only one microstate from macrostate. |
| ⑦ $n_i = \frac{g_i}{e^{x + \beta E_i}}$ | ⑦ $n_i = \frac{g_i}{e^{x + \beta E_i} - 1}$ | ⑦ $n_i = \frac{g_i}{e^{x + \beta E_i} + 1}$ |
| ⑧ The energy distribution is continuous. | ⑧ The energy distribution is quantised. | ⑧ The energy distribution is quantised. |
| ⑨ Example for MB statistics are gas molecules. | ⑨ Ex. Bosons i.e. photons. | ⑨ Ex. Fermions. i.e. electrons. |

Photon gas :-

Photon :- Defⁿ :- The describe energy of particle of an electromagnetic radiation or light is called photon.

Defⁿ :- photon gas :- The gas like collection of the photons having same property as that of gas molecules is called photon gas.

The photon gas obey the Bose-Einstein Statistics and hence they are indistinguishable.

The photons can emit or absorb the energy by the containing vessel during collision and hence the total no. of photons donot remain constant.

The photon's total energy remains constant if the temperature remains constant.

This photon gas concept can be used while deriving the black body radiation.

Electron gas :-

The free electrons present in the metal which collide with some fixed atom is called electron gas.

The electron gas have the spin half integer values and hence they obey fermi-dirac statistico. They are ~~indisg~~ indistinguishable particles. They are also called fermi gas. The electron gas are electrically charged particles.

They obey the ~~Pott~~ Pauli's exclusion principle and hence are called as fermions.