



In classical mechanics, we can describe the motion of a particle by finding its position, velocity, etc. employing the laws of motion. But for the macroscopic system that contains an enormous number of microparticles (such as atoms, molecules) it is too much rigorous job to determine the motion of each particle. For example, if we want to know the actual description of motion of a gaseous system confined in a box and containing  $10^{23}$  molecules/cm<sup>3</sup> with 3 degrees of freedom, then for each molecule under normal temperature and pressure we have to solve  $3 \times 10^{23}$  equations of motion.

In this case thermodynamics helps us to solve number of specific problem without having any knowledge of atomic and molecular structure of a system. Here we are not considering detail calculation of position, velocity of individual particles. Instead of observing these physical parameter of each particle we only use some variables such as temperature, pressure, volume and number of moles for specifying the physical properties of the system. But the results of thermodynamical method can not give us any information about the process which arises due to atomic and molecular structure and do not explain why a particular substance has certain properties. Even it can not provide a complete link between the position, velocity, energy of each molecule and their thermodynamic variables such as pressure, temperature, entropy, etc. Under such circumstances statistical mechanics are applied.

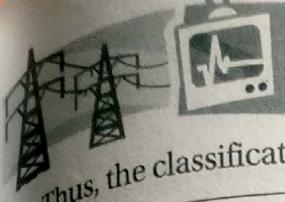
Statistical mechanics develops a relation between the macroscopic behaviours (i.e., bulk properties) of system in terms of microscopic behaviours (individual property) using the law of probability and distribution function.

Statistical mechanics can be classified into two types—

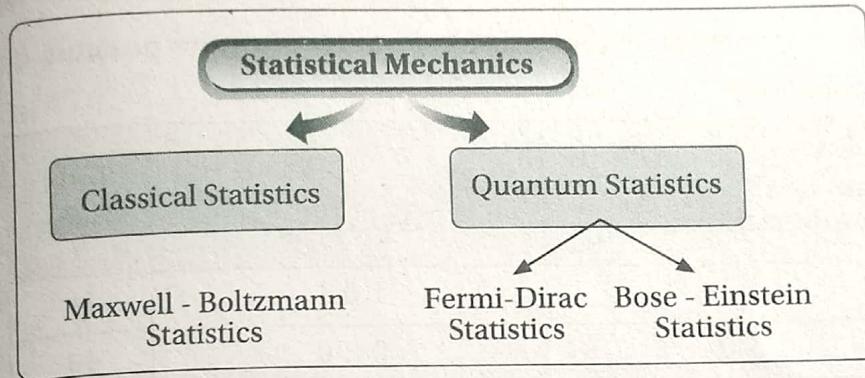
- i** Classical statistics and    **ii** Quantum statistics.

**Classical statistics:** If the properties and laws of motion of individual microparticles can be explained by classical mechanics, we call it classical statistics. Maxwell-Boltzmann statistics is classical statistics.

**Quantum statistics:** If the properties and laws of motion of individual micro particles can be explained by quantum mechanics, we call it quantum statistics. Fermi-Dirac and Bose-Einstein statistics are quantum statistics.



Thus, the classification of statistical mechanics can be shown on the following diagram:



The classical statistics explains successfully many physical phenomena (like as temperature, pressure, energy, etc.) of a system. But it fails to explain adequately several other physical phenomena such as black body radiation or specific heat at low temperature of a system. These phenomena can be explained with the help of quantum statistics. The three statistics M-B, B-E and F-D will practically give the same result at higher temperature and low pressure.

7.2



## ENERGY LEVELS AND ENERGY STATES

A thermodynamic system is always associated with some discrete energy levels in which a large number of particles can be accommodated. Any **energy level of a system is characterized by principal quantum number  $n$** . Generally, each and every energy level is associated with a large number of particles and all the quantum numbers ( $n, l, m_l, m_s$ ) for any two particles are not identical. Thus, there are several states for a given energy level. The several states corresponding to a given energy level are called energy states.

**The number of quantum states for a given energy level is called the degeneracy of the level.**

### 7.2.1 Macrostate and Microstate

**Macrostate:** An isolated system<sup>①</sup> consisting of a fixed number ( $N$ ) of non-interacting identical particles, having a fixed internal energy ( $E$ ) and occupying a fixed space of volume ( $V$ ) is said to be macroscopic state or macrostate (or, thermodynamic state) of the system.

**Microstate:** Generally, each and every specified energy level is associated with a large number of particles. The number of different meaningful ways (of the various particles in the macrostates) in which the total energy ( $E$ ) of the system can be distributed among its constituent particles are called microstate.

*Thus a large number of microstates may lead to the same macrostates.*

<sup>①</sup> Isolated system is a system of particles which does not interact with any other system so that its total energy is constant.



**Explanation with example:** For 2 distinguishable particles each of which can be in one of the  $\epsilon$ ,  $2\epsilon$ ,  $3\epsilon$  energy states with total energy  $4\epsilon$ , the possible combinations of particles are given below:

No. of combinations ↓	$E_k \rightarrow$	$\epsilon \ 2\epsilon \ 3\epsilon$	Total energy
	$N_k \rightarrow$	$N_1 \ N_2 \ N_3$	
1		1 0 1	$4\epsilon$
2		0 2 0	$4\epsilon$

So, the total number of macrostates = the possible number of combinations of particles = 2. They are (1, 0, 1) and (0, 2, 0).

Let the particles be  $a$  and  $b$ .

So, the possible microstates of the various particles in the macrostates can be evaluated from the following methods :

Macrostates	$\epsilon$	$2\epsilon$	$3\epsilon$	No. of microstates
(1, 0, 1)	$a \ b$	0 0	$b \ a$	2
(0, 2, 0)	0	$ab$	0	1

So, the total number of microstates = 3 and the total number of macrostates = 2.

## 7.2.2 Ensemble

The ensemble approach was developed by French scientist Gibbs in 1902. It means **assembly of systems**.

A very large number of identical entities are called an assembly. If the entities are single particles, the assembly is simply called system.

We know, there are a very large number of states corresponds to a given identical macroscopic system. **In general, the collection of very large number of identical interacting macroscopic systems is called an ensemble.**

The classification of ensembles depends on the manner in which the system will interact. There are three types of ensemble.

- ① **Canonical ensemble** : If physical systems exchange energy but not matter with each other, the corresponding ensemble is called canonical ensemble.
- ② **Grand canonical ensemble** : If physical systems exchange both energy and matter with each other, the corresponding ensemble is called grand canonical ensemble.
- ③ **Microcanonical ensemble** : The ensemble which can not exchange neither energy nor matter with each other is called microcanonical ensemble.

## 7.3 THERMODYNAMIC PROBABILITY AND ENTROPY

The total number of possible microstates of a system corresponding to a given macrostate is called **thermodynamic probability** (or thermodynamic frequency or statistical weight). It is represented by  $W$ .

For  $n$  particles, the number of microstates for its  $(n_1, n - n_1)$  macrostates is

$$W_{n_1, n-n_1} = \frac{n!}{n_1!(n-n_1)!}$$

Example: For 4 distinguishable particles, for its (3,1) macrostate the number of microstates (i.e., thermodynamic probability  $W$ ),

$$W_{3,1} = \frac{4!}{3!1!} = 4$$

It is known to us that the entropy of an isolated system always increases when the system undergoes an irreversible process. When the system reaches an equilibrium, the entropy becomes maximum. In equilibrium, all the microstates of a system are equally probable. Hence, all the microstates i.e., the arrangement ( $W$ ) of atoms in the energy states of the system should also come to a maximum value. Let  $S$  be the entropy of the system. So, there must be a co-relation between  $S$  and  $W$ . To co-relate  $S$  and  $W$  we consider two identical systems  $A$  and  $B$  in thermal contact with each other. Let entropy of the systems  $A$  and  $B$  be  $S_A$  and  $S_B$  and thermodynamic probabilities be  $W_A$  and  $W_B$  respectively.

The total entropy of the composite system

$$S = S_A + S_B \quad \dots (7.3.1)$$

If we think that  $S$  is some functionally related to  $W$  then we can write,

$$S = f(W) \quad \dots (7.3.2)$$

Thus, we can write from equation (8.3.1),

$$f(W) = f(W_A) + f(W_B)$$

This is possible only if the functional form is in logarithmic form

$$\dots (7.3.3)$$

$$S = K \ln W$$

where  $K$  is an arbitrary constant.

## 7.4 PHASE SPACE

To describe both the position and the state of motion of the particle, it is required to set up a six dimensional space in which a point has six co-ordinates  $x, y, z$  (position co-ordinates) and  $p_x, p_y, p_z$  (momentum co-ordinates) along six mutually perpendicular axes in space. A point in this space describes both the position and momentum of the particle at some particular instant. This combined position and momentum space for a single particle is called a phase space.

Examples: **Phase space of a Simple Harmonic Oscillator**

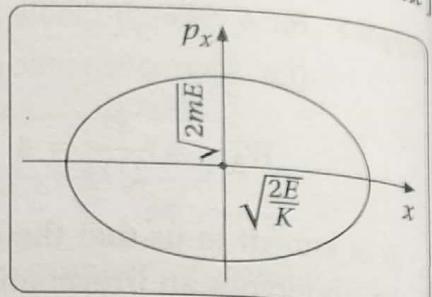
For a one dimensional simple harmonic oscillator of mass  $m$  and spring constant  $K$ , the total energy at any instant for its displacement ' $x$ ' from its equilibrium position can be written as

$$E (= \text{K.E} + \text{P.E}) = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}Kx^2 = \frac{p_x^2}{2m} + \frac{1}{2}Kx^2$$

[ $\therefore$  momentum of the harmonic oscillator,  $p_x = m\dot{x}$ ]

$$\text{or, } \frac{x^2}{(2E/K)} + \frac{p_x^2}{2mE} = 1 \quad \dots (7.4.1)$$

It is the equation of an ellipse. So, the phase space is two dimensional and the  $x-p_x$  plane forms a curve known as phase trajectory. Here, the phase trajectory of a simple harmonic oscillator is an ellipse with semi-major and semi-minor axes  $\sqrt{2E/K}$  and  $\sqrt{2mE}$  respectively [Fig. 1].



**Fig. 1** ▷ Phase space ( $p_x, x$ ) of a simple harmonic oscillator

## 7.5



## NUMBER OF QUANTUM STATES (OR UNIT CELLS) WITHIN ENERGY RANGE $E$ AND $E + dE$ IN THE PHASE SPACE OR DENSITY OF STATES

Let us consider a phase space of volume containing a system of particles. A small volume element in phase space is given by

$d\tau = dx dy dz dp_x dp_y dp_z$  [where  $(x, y, z, p_x, p_y, p_z)$  are the coordinates of a point in phase space.]

So, the finite volume of the phase space available for a particle is

$$\tau = \iiint dx dy dz dp_x dp_y dp_z \quad \dots (7.5.1)$$

$$\text{or, } \tau = \iiint dx dy dz \iiint dp_x dp_y dp_z \quad \dots (7.5.2)$$

It is possible to divide the phase space into a large number of elementary cells of equal volume (i.e., size).

For quantum mechanical system, we can write using Heisenberg's uncertainty principle the minimum possible value of  $dx \cdot dp_x \cong h$ , where  $h$  is planck's constant.

So, the minimum size or volume of a unit cell for a quantum mechanical system

$$d\tau = dx dp_x dy dp_y dz dp_z \cong h^3 \quad \dots (7.5.3)$$

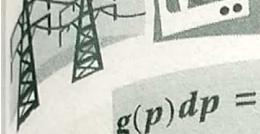
Now, the *number of cells in the phase space* corresponding to momentum  $p$  and  $p + dp$  is

$$g(p)dp = \frac{\text{Volume in phase space corresponding to momentum } p \text{ and } p + dp}{h^3}$$

$$\text{or, } g(p)dp = \frac{\iiint dx dy dz \iiint dp_x dp_y dp_z}{h^3} \quad \dots (7.5.4)$$

Now, the volume of the system of particles

$$V = \iiint dx dy dz \quad \dots (7.5.5)$$



therefore,

$$g(p)dp = \frac{V}{h^3} \cdot \iiint dp_x dp_y dp_z \quad \dots (7.5.6)$$

To evaluate, the volume of the system ( $\iiint dp_x dp_y dp_z$ ) in momentum space corresponding to momentum interval  $p$  and  $p + dp$ , let us draw a sphere [Fig. 2] of radius  $p$  such that all the points lying on the sphere have a momentum  $p$  and it is given by the equation of sphere in momentum space ( $p_x, p_y, p_z$ ) as

$$p^2 = p_x^2 + p_y^2 + p_z^2 = 2mE \quad \dots (7.5.7)$$

where  $E$  is the energy of a particle of mass  $m$ .

If we draw another concentric sphere of radius  $p + dp$ , the volume of the spherical shell enclosed between the two spheres of radius  $p$  and  $p + dp$  is given by

$\iiint dp_x dp_y dp_z$  = surface area of the sphere of radius  $p$   $\times$  thickness of the cell

$$\iiint dp_x dp_y dp_z = 4\pi p^2 dp \quad \dots (7.5.8)$$

Substituting this value in equation (7.5.6), we can write

$$g(p)dp = \frac{V}{h^3} 4\pi p^2 dp \quad \dots (7.5.9)$$

For particles having two allowed values of the spin quantum number  $m_s = \pm \frac{1}{2}$ , the number of available quantum states (i.e., cells) is two times of that given by equation (7.5.9). So,

$$g(p)dp = \frac{2V}{h^3} 4\pi p^2 dp \quad \dots (7.5.10)$$

$$g(P)dp = \frac{8\pi V p^2}{h^3} dp \quad \dots (7.5.11)$$

Again  $p^2 = (2mE)$ , where  $E$  is the energy of the particle mass  $m$ .

Differentiating both sides, we get,

$$2p dP = 2m dE \quad \dots (7.5.12)$$

$$p dp = m dE$$

Substitute,  $p = \sqrt{2mE}$  and  $p dp = m dE$  in equation (7.5.11), we get the number of quantum states available in the phase space corresponding to energy  $E$  and  $E + dE$  is

$$g(E)dE = \frac{8\pi V}{h^3} (2mE)^{1/2} m dE \quad \dots (7.5.13)$$

$$g(E)dE = \frac{8\sqrt{2}\pi V}{h^3} m^{3/2} E^{1/2} dE$$

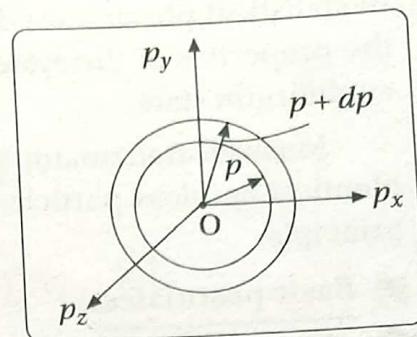


Fig. 2 ▷ Spherical shell in momentum space



In statistical physics, we deal with the systems having a large number of particles and all the properties of the system can be deduced from a knowledge of the most probable or equilibrium state.

Maxwell-Boltzmann statistics gives the statistical behaviour of distinguishable and identical spinless particles of ideal gases. These particles do not obey Pauli's exclusion principle.

### Basic postulates:

- 1 The particles are weakly interacting identical and distinguishable.
- 2 They do not obey Pauli's exclusion principle. So each quantum (energy) state can accommodate any number of particles.
- 3 The particles are spinless.

**Boltzons:** The particles those obey Maxwell-Boltzmann statistics are called Boltzons.



### 7.6.1 Maxwell-Boltzmann Distribution Law

Let  $N$  be the total number of distinguishable particles in an assembly. Out of these  $N$  particles, we consider  $N_1, N_2, N_3 \dots N_k$  number of particles have energies  $E_1, E_2, E_3, \dots, E_k$  respectively and they can be distributed in  $g_1, g_2, g_3, \dots, g_k$  number of quantum states associated with the corresponding energy levels. Since, the total energy  $E$  of the assembly of  $N$  numbers of distinguishable particles is constant we can write,

$$N_1 E_1 + N_2 E_2 + N_3 E_3 + \dots + N_k E_k = \sum_{i=1}^k N_i E_i = E \quad \dots (7.6.1.1)$$

and

$$N_1 + N_2 + N_3 + \dots + N_k = \sum_{i=1}^k N_i = N \quad \dots (7.6.1.2)$$

If  $g_i$  is the probability of locating a particle in a certain energy state  $E_i$ , the probability of locating 2 particles in the same state is  $g_i \times g_i = g_i^2$ . Therefore, the probability for  $N_i$  distinguishable particles to distribute in  $g_i$  states (cells) is  $(g_i)^{N_i}$ . Hence, the total probability, for a given distribution is given by

$$W = \frac{N!}{N_1! N_2! N_3! \dots N_k!} \cdot g_1^{N_1} \cdot g_2^{N_2} \cdot g_3^{N_3} \dots (g_k)^{N_k} = N! \prod_i \frac{(g_i)^{N_i}}{N_i!} \quad \dots (7.6.1.3)$$

where  $\Pi$  denotes the product.

Taking natural logarithm on both sides, we have,

$$\ln W = \ln N! + \ln \left[ \prod_i \frac{(g_i)^{N_i}}{N_i!} \right]$$

$$\ln W = \ln N! + \sum_i N_i \ln g_i - \sum_i \ln N_i! \quad \dots (7.6.1.4)$$

Applying Stirling's approximation,  $\ln x! = x \ln x - x$  (where  $X$  is very large) we get

$$\begin{aligned}
 \ln W &= N \ln N - N + \sum_i N_i \ln g_i - \left[ \sum_i (N_i \ln N_i - N_i) \right] \\
 &= N \ln N - N + \sum_i N_i \ln g_i - \sum_i N_i \ln N_i + \sum_i N_i \\
 &= N \ln N + \sum_i N_i \ln g_i - \sum_i N_i \ln N_i \quad \left[ \because \sum_i N_i = N \right] \\
 &= N \ln N - \sum_i (N_i \ln N_i - N_i \ln g_i)
 \end{aligned}$$

$$\ln W = N \ln N - \sum_i N_i \ln \frac{N_i}{g_i} \quad \dots (7.6.1.5)$$

The **most probable distribution** can be obtained by evaluating the maximum value of  $W$  and then equate it to zero. Differentiating equation (7.6.1.5) w.r.t.  $N_i$ , we get from equation (7.6.1.5),

$$\begin{aligned}
 d[\ln W] &= d(N \ln N) - \sum_i dN_i \ln \frac{N_i}{g_i} - \sum_i N_i d\left(\ln \frac{N_i}{g_i}\right) \\
 &= - \sum_i dN_i \ln \frac{N_i}{g_i} - \sum_i N_i \frac{dN_i}{N_i} \\
 &= - \sum_i dN_i \ln \frac{N_i}{g_i} - \sum_i dN_i
 \end{aligned}$$

$$d[\ln W] = -\sum dN_i \ln \frac{N_i}{g_i} \quad \left[ \begin{array}{l} \because \sum N_i = \text{constant} \\ \therefore \sum dN_i = 0 \end{array} \right] \quad \dots (7.6.1.6)$$

Thus for most probable distribution,  $d(\ln W) = 0$

$$\sum_i \ln \left( \frac{N_i}{g_i} \right) dN_i = 0 \quad \dots (7.6.1.7)$$

The solution of this equation is subjected to the conditions represented by equations (7.6.1.1) and (7.6.1.2)—

$$\sum_i N_i E_i = \text{constant} \quad \text{i.e.,} \quad \sum_i E_i dN_i = 0 \quad \dots (7.6.1.8)$$

and

$$\sum_i N_i = \text{constant} \quad \text{or,} \quad \sum_i dN_i = 0 \quad \dots (7.6.1.9)$$

Multiplying equation (7.6.1.9) by  $\alpha$  and equation (7.6.1.8) by  $\beta$  and then adding to equation (7.6.1.7) we get,

$$\sum_i \left[ \ln \left( \frac{N_i}{g_i} \right) + \alpha + \beta E_i \right] dN_i = 0$$

As the various  $dN_i$  states are independent to one another, the above summation is equal to zero if,

$$\ln \frac{N_i}{g_i} + \alpha + \beta E_i = 0 \text{ or, } \frac{N_i}{g_i} = e^{-\alpha - \beta E_i} \text{ or, } N_i = g_i e^{-(\alpha + \beta E_i)}$$

**This equation is known as the Maxwell-Boltzmann distribution law.** This equation gives the maximum probability of distribution of particles in  $g_i$ -number of states where values of  $\alpha$  and  $\beta$  depend upon the physical property of the system.

Now, the total number of particles

$$\begin{aligned} N &= N_1 + N_2 + N_3 + \dots \\ &= g_1 e^{-\alpha - \beta E_1} + g_2 e^{-\alpha - \beta E_2} + g_3 e^{-\alpha - \beta E_3} + \dots \\ &= e^{-\alpha} \left[ \sum_i g_i e^{-\beta E_i} \right] \end{aligned}$$

or,

$$N = e^{-\alpha} Z \quad \dots (7.6.1.12)$$

where  $Z \left( = \sum_i g_i e^{-\beta E_i} \right)$  is called **the partition function.**

Therefore, we get from equation (7.6.1.12)  $e^{-\alpha} = \frac{N}{Z}$ . Thus we can write from equation (7.6.1.11) after substituting the value of  $e^{-\alpha}$ ,

$$N_i = \left( \frac{N}{Z} \right) g_i e^{-\beta E_i} \quad \dots (7.6.1.13)$$

This equation is also known as Maxwell-Boltzmann distribution law.



## 7.6.2 The Maxwell-Boltzmann Distribution Function

It gives the probability of a particle to occupy an energy state  $E_i$  and is expressed as

$$\frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)}} \quad \dots (7.6.2.1)$$

where  $\alpha$  and  $\beta$  are constants depending upon the physical property of the system.

**PROBLEM**

- A gas has two distinguishable identical particles in  $k$  th energy level in which there are three quantum states according to M-B statistics.
- Find the possible number of microstates,
  - Find also the number of microstates in tabular form.

**Solution**

i) Since the particles are distinguishable, we can apply Maxwell-Boltzmann statistics. In that case, the total probability for this given distribution i.e., the total number of microstates,

$$W = \frac{N! g_k^{N_k}}{N_k!} = 2! \cdot \frac{3^2}{2!} \quad [ \because N = 2, N_k = 2, g_k = 3 ] = 9 \text{ microstates.}$$

ii) If the distinguishable two particles are  $A$  and  $B$ , the number of microstates can be obtained in a tabular form as below (considering each quantum state can accommodate one or more than one particles):

Micro-states	Q-states		
	→ 1	2	3
1	AB	×	×
2	×	AB	×
3	×	×	AB
4	A	B	×
5	B	A	×
6	A	×	B
7	B	×	A
8	×	A	B
9	×	B	A

So, the number of microstates are 9.

### 7.6.3 Disadvantages of Maxwell-Boltzmann Statistics

In the Maxwell-Boltzmann statistics, it is considered that the particles of a system (e.g., ideal gas) are distinguishable. So, it can explain the energy distribution of the molecules of ideal gas to a fair degree of accuracy. But *this statistics is failed to explain the energy distribution of indistinguishable particles like electrons (so called electron gas) or photons (so called photon gas)*.

These problems can be solved with the help of quantum statistics.

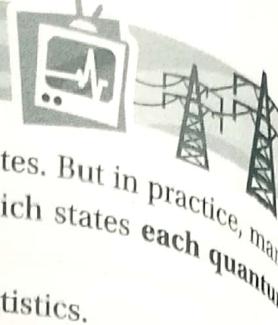
7.7



### NEEDS OF QUANTUM STATISTICS

In Maxwell-Boltzmann distribution it has been assumed that

- the particles are distinguishable, but it fails to explain the energy distribution of many indistinguishable elementary particles like electrons (so called electron gas) and that of photon (so called photon gas).



- 2 any number of particles can occupy the same quantum states. But in practice, many particles like electrons obey Pauli's exclusion principle which states **each quantum state can accommodate only one particle.**

All these difficulties are overcome by the use of quantum statistics.

### Special Note

Degenerate and non-degenerate states :

If  $N_i$  is the number of identical particles in  $g_i$  quantum states (i.e., cells) of  $i$  th energy level (i.e., compartment)  $E_i$  of the phase-space, the ratio of  $\frac{N_i}{g_i}$  is called **occupation index**.

- ① If now,  $\frac{N_i}{g_i} \ll 1$  (i.e.,  $N_i \ll g_i$ ), the system is called non-degenerate.
- ② If  $\frac{N_i}{g_i} > 1$  (i.e.,  $N_i > g_i$ ), the system is called degenerate.
- ③ If  $\frac{N_i}{g_i} \gg 1$ , the system is called strongly degenerate. It is seen for Boltzons particles.

## 7.8 TYPES OF QUANTUM STATISTICS

Quantum statistics is classified into two types—

- 1 Fermi-Dirac (F-D) statistics,
- 2 Bose-Einstein (B-E) statistics.

It is to be noted that the **particles are indistinguishable and identical** in both statistics.

## 7.9 FERMI-DIRAC STATISTICS

It provides the statistical behaviour of indistinguishable and identical particles with  $\frac{1}{2}$  integral spin. These particles obey Pauli's exclusion principle.

### Basic postulates:

- 1 The particles are indistinguishable and identical.
- 2 They obey Pauli's exclusion principle. So, each energy state can accommodate either no particle or only one particle.
- 3 These particles have  $\frac{1}{2}$  integral spin (e.g. spin angular momentum  $m_s \hbar = \frac{1}{2}\hbar, \frac{3}{2}\hbar, \frac{5}{2}\hbar, \dots$ ; where  $m_s$  = spin quantum number).
- 4 The particles have antisymmetric wave function (as no two particles have same quantum state).

**Fermions:** The particles those are indistinguishable, identical having  $\frac{1}{2}$  integral spin and obey Fermi-Dirac statistics are called fermions.

**Examples:** Electrons ( $m_s = \pm \frac{1}{2}$ ), positrons ( $m_s = \pm \frac{1}{2}$ ), neutrons ( $m_s = \pm \frac{1}{2}$ ), protons ( $m_s = \pm \frac{1}{2}$ ),  $\mu$  mesons ( $m_s = \pm \frac{1}{2}$ ) are the examples of fermions. It has also been observed, if the total number of nucleons of atom is odd, the atoms or molecules obey F-D statistics. So,  ${}^1\text{H}^3$ ,  ${}^2\text{He}^3$ ,  ${}^3\text{Li}^7$ ,  ${}^6\text{C}^{13}$  are also the examples of fermions.

## 7.9.1 Fermi-Dirac Distribution Law

Fermi-Dirac statistics is applicable for the particles those are identical, indistinguishable and obey Pauli's exclusion principle.

In order to determine the energy distribution of a system, we divide the available volume in the phase-space into a large number of quantum states. Each quantum state corresponds to a particle wave function.

Let us consider the total number of possible ways (permutations) in which ' $N_i$ ' number of identical and indistinguishable particles can be distributed among the  $g_i$  quantum states of energy  $E_i$  such that each quantum state can accommodate only one particle. In this case,  $g_i$  must be greater than  $N_i$  as there must be at least one cell (quantum state) available for every particle. The number of distinguishable (or, independent) ways in which  $N_i$  particles can be arranged among  $g_i$  quantum states is given by

$$W_i = \frac{g_i!}{N_i! (g_i - N_i)!} \quad \dots (7.9.1.1)$$

So, the total number of independent ways,  $W$ , (i.e., thermodynamic probability) of arranging  $N_1, N_2, \dots, N_n$  particles in various energy levels (say, ' $n$ ') is the product of the term given by equation (7.9.1.1). Thus the probability of the entire distribution of the particles is given by

$$W = \prod_{i=1}^n W_i = \prod_{i=1}^n \frac{g_i!}{N_i! (g_i - N_i)!} \text{ where } \prod \text{ denotes the product.} \quad \dots (7.9.1.2)$$

### Special Note

The number of ways for placing a first of  $N_i$  number of particles in one of the  $g_i$  quantum state =  $g_i$

The remaining number of quantum states after placing the first particle in a particular quantum state is  $(g_i - 1)$ .

So, the number of ways of placing a second particle in  $(g_i - 1)$  states =  $(g_i - 1)$

Thus, the number of ways for placing  $N_i$  th particle in the remaining  $[g_i - (N_i - 1)]$  states =  $g_i - (N_i - 1) = g_i - N_i + 1$

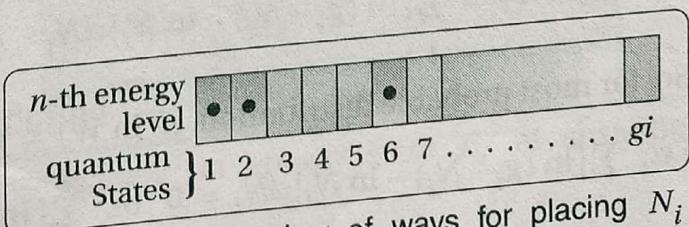


Fig. 3 ▷ The number of ways for placing  $N_i$  number particles in one of the  $g_i$  quantum state

So, the total number of ways for placing  $N_i$  particles among  $g_i$  states of energy  $E_i$  (keeping in mind that there is only one particle in each quantum state)

$$\begin{aligned}
 &= g_i (g_i - 1)(g_i - 2) \cdots (g_i - N_i + 1) \\
 &= \frac{g_i (g_i - 1)(g_i - 2) \cdots (g_i - N_i + 1) \cdot (g_i - N_i)!}{(g_i - N_i)!} \\
 &= \frac{g_i!}{(g_i - N_i)!}
 \end{aligned}$$

For each of these arrangements, the number of permutations of  $N_i$  particles among themselves is  $N_i!$  Again these permutations do not give independent arrangements of these particles due to their indistinguishable properties. So, the number of independent permutations of  $N_i$  particles among  $g_i$  quantum states

$$= \frac{g_i!}{N!(g_i - N_i)!}$$

Taking natural logarithm on both sides, we have

$$\ln W = \sum_{i=1}^n [\ln g_i! - \ln N_i! - \ln (g_i - N_i)!] \quad \dots (7.9.1.3)$$

Applying Stirling's approximation,  $\ln x! = x \ln x - x$ , (when,  $x$  is large), we get from equation (7.9.1.3).

$$\ln W = \sum_i [(g_i \ln g_i - g_i) - (N_i \ln N_i - N_i) - \{(g_i - N_i) \ln (g_i - N_i) - (g_i - N_i)\}]$$

$$\text{or, } \ln W = \sum_i [g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln (g_i - N_i)] \quad \dots (7.9.1.4)$$

The **most probable distribution** can be obtained by evaluating the maximum value of  $\ln W$ . Hence differentiating equation (7.9.1.4) partially w.r.t.  $N_i$  we get,

$$\begin{aligned}
 d(\ln W) &= \sum_i [-N_i \cdot \frac{1}{N_i} dN_i - \ln N_i dN_i + (g_i - N_i) \frac{1}{(g_i - N_i)} dN_i \\
 &\quad + \ln (g_i - N_i) dN_i] \quad [\because g_i \text{ is mere number, } d(g_i) = 0]
 \end{aligned}$$

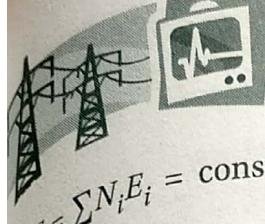
$$\text{or, } d(\ln W) = \sum_i [\ln (g_i - N_i) - \ln N_i] dN_i \quad \dots (7.9.1.5)$$

So, for most probable distribution,  $d(\ln W) = 0$

$$\text{i.e., } \sum_i [\ln (g_i - N_i) - \ln N_i] dN_i = 0 \quad \text{or, } \sum_i [\ln N_i - \ln (g_i - N_i)] dN_i = 0 \quad \dots (7.9.1.6)$$

In addition to it the system must satisfy **conservation of total number of fermions  $N$**  (as no particles leave or enter into the system) and **conservation of total energy  $E$**  (as the system of fermions is isolated)

$$\therefore N = \sum_i N_i = \text{constant} \quad \text{or, } \sum_i dN_i = 0 \quad \dots (7.9.1.7)$$



$$\text{and } E = \sum_i N_i E_i = \text{constant} \quad \text{or, } \sum_i E_i dN_i = 0 \quad \dots (7.9.1.8)$$

Multiplying equation (7.9.1.7) by  $\alpha$  and equation (7.9.1.8) by  $\beta$  and then adding them to equation (7.9.1.6) we have,

$$\sum_i [\ln N_i - \ln(g_i - N_i) + \alpha + \beta E_i] dN_i = 0 \quad \dots (7.9.1.9)$$

where  $\alpha$  and  $\beta$  are Lagrange's undetermined multiplier.

As various  $dN_i$  states are independent of one another, the above summation is equal to zero if

$$\ln N_i - \ln(g_i - N_i) + \alpha + \beta E_i = 0$$

$$\ln \frac{g_i - N_i}{N_i} = \alpha + \beta E_i \quad \text{or, } \frac{g_i - N_i}{N_i} = e^{\alpha + \beta E_i}$$

$$\frac{g_i}{N_i} - 1 = e^{\alpha + \beta E_i} \quad \text{or, } \frac{g_i}{N_i} = 1 + e^{\alpha + \beta E_i}$$

$$N_i = \frac{g_i}{e^{\alpha + \beta E_i} + 1} \quad \dots (7.9.1.10)$$

This equation is Fermi-Dirac distribution law.

For fermions in statistical equilibrium at temperature  $T$ ,  $\alpha = -\frac{E_f}{kT}$  (i.e., the value of  $\alpha$  is negative) and  $\beta = \frac{1}{kT}$  where  $E_F$  = Fermi energy of the system and

$$k = \text{Boltzmann's constant} = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$$

$$\dots (7.9.1.11)$$

$$N_i = \frac{g_i}{e^{(E_i - E_f)/kT} + 1}$$

So, the F-D distribution function thus becomes

$$f(E) = \frac{N_i}{g_i} = \frac{1}{1 + e^{(E_i - E_f)/kT}} \quad \dots (7.9.1.12)$$

## 7.9.2 Fermi-Dirac Distribution Function

This gives the probability of a fermion to occupy an energy state  $E_i$  at absolute temperature  $T$  and is expressed as

$$f(E) = \frac{1}{1 + e^{(E_i - E_f)/kT}} \quad \dots (7.9.2.1)$$

where  $E_f$  = the Fermi energy and  $k$  = Boltzmann's constant =  $8.62 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$

$$= 1.3805 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$$



### 7.9.3 Fermi Distribution at Zero and Non-zero Temperature

If we draw a graph between  $f(E)$  against  $E_i$  at different temperature we get the adjacent graph [Fig. 4]. At  $T = 0\text{K}$ , we get a curve as shown by full line whereas at higher temperature  $T > 0\text{K}$ , the corresponding Fermi distribution curve is shown in Fig. 4. We find from equation, (7.9.1.11),  $N_i$  decreases rapidly for  $E_i > E_f$  at low temperature.

Analyzing this curve the following cases are observed.

**Case 1** If  $T > 0\text{ K}$  and  $E_i = E_f$ ,

$$f(E) = \frac{1}{1 + e^{(E_f - E_i)/kT}} = \frac{1}{1 + e^0} = \frac{1}{2}$$

Thus, for Fermi energy level the probability of occupation of a fermion is  $\frac{1}{2}$  for any temperature greater than 0 K.

**Case 2**

① If  $T = 0$ ,  $E_i < E_f$ ;  $f(E) = \frac{1}{1 + e^{-\infty}} = \frac{1}{1 + 0} = 1$

i.e., All energy states having  $E_i < E_f$  are occupied by a single fermion (i.e., electron).

② if  $T = 0$ ,  $E_i > E_f$ ;  $f(E) = \frac{1}{1 + e^{\infty}} = \frac{1}{1 + \infty} = 0$

i.e., All energy states having  $E_i > E_f$  are unoccupied.

At  $T = 0\text{ K}$ , Fermi energy ( $E_f = \epsilon_f$ , say) is that energy level upto which all the energy states are filled up by fermions and all the energy states above it are empty. The Fermi energy level is the highest occupied energy level of fermions at  $T = 0\text{ K}$ . Thus, **Fermi energy is the maximum energy that can be occupied by a fermion (i.e., electron) at 0 K.**



### 7.9.4 Fermi Temperature ( $\theta_f$ )

It may be defined as the ratio of the fermi energy ( $\epsilon_f$ ) at absolute zero to Boltzmann's constant  $k$  and its corresponding absolute temperature.

So, Fermi temperature  $\theta_f = \epsilon_f/kT$ .

#### PROBLEM

1 A gas has two indistinguishable identical particles in  $k$  th energy level in which there are three quantum states according to F-D statistics.

- (i) Find the possible number of microstates, and
- (ii) Show the number of microstates in tabular form.

#### Solution

- i The total number of microstates considering each indistinguishable quantum state can accomodate only one particle.

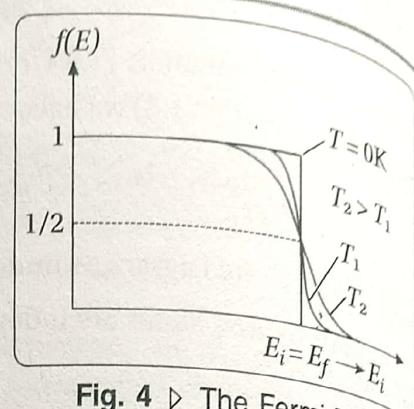


Fig. 4 ▷ The Fermi-Dirac distribution function

$$W = \frac{g_k!}{N_k! (g_k - N_k)!} = \frac{3!}{2! (3-2)!}$$

$$= 3 \text{ microstates } [\because g_k = 3, N_k = 2].$$

Let each indistinguishable particle be  $A$ . Therefore, the number of microstates can be given in the following table:

Micro-states	Q-states		
	1	2	3
1	A	A	X
2	A	X	A
3	X	A	A

Since, the number of microstates are 3.

**BLEM** Find the probability of an electron to occupy an energy state of 6.125 eV at temperature  $991^\circ\text{C}$  (Given : The Fermi energy level of the atom is 5.6 eV).

**Solution** The probability of an electron to occupy an energy state  $E$  is given by,

$$f(E) = \frac{1}{1 + e^{(E - E_f)/kT}}$$

Here  $E = 6.125 \text{ eV}$ ,  $E_f = 5.6 \text{ eV}$ ,

$$k = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} = 8.62 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$$

$$T = 991 + 273 = 1264 \text{ K}$$

$$f(E) = \frac{1}{1 + e^{(6.125 - 5.6)/8.62 \times 10^{-5} \times 1264}}$$

$$= \frac{1}{1 + e^{4.818}} = \frac{1}{1 + 123.77} = \frac{1}{124.77}$$

So, the probability to occupy an energy state with energy 6.125 eV is 0.008 (0.8%  $\approx$  1%).

**BLEM** The probability of an electron to occupy an energy state of 6.125 eV is 1% at temperature  $991^\circ\text{C}$ . Find the Fermi energy.

**Solution** Here  $f(E) = \frac{1}{e^{(E - E_f)/(kT)} + 1}$

$$\frac{1}{100} = \frac{1}{e^{(6.125 - E_f)/8.62 \times 10^{-5} \times 1264} + 1} \quad [991^\circ\text{C} = 1264 \text{ K}]$$

$$E_f = 5.625 \text{ eV}$$

Since, the Fermi energy is 5.625 eV.



### 7.9.5 Electron Gas in Metal

In metal, there is an overlapping between valence band and conduction band. Due to this reason, a large no of free electrons are observed in metals. Thus metal becomes a very good conductor. These free electrons move freely in the metal and continuously collide with the atoms. So they behave like a gas, called electron gas.

Electrons are elementary particles with  $\frac{1}{2}$  integral spin. In a metal electrons have their quantised energy level and obeys Pauli's exclusion principle. So, they are called fermions as they obey Fermi-Dirac statistics.

If we consider a continuous distribution of energy among ' $N$ ' number of free electrons in electron gas then for the electrons with their energy range  $E$  and  $E + dE$ ,  $g_i$  is replaced by  $g(E) dE$  and  $n_i$  is replaced by  $n(E) dE$  in equation (7.9.1.11).

So, the total number of electrons in metal within the energy range  $E$  and  $E + dE$  can be written from equation (7.9.1.12) as,

$$n(E) dE = \frac{g(E) dE}{e^{(E - E_f)/kT} + 1} \quad \dots(7.9.5.1)$$



### 7.9.6 Fermi-Dirac Law of Energy Distribution for Free Electrons in Metal

If  $n(E) dE$  is the total number electrons within the energy range  $E$  and  $E + dE$ , then we can write from equation (7.9.5.1)

$$n(E) dE = \frac{g(E) dE}{e^{(E - E_f)/kT} + 1} \quad \dots(7.9.6.1)$$

where  $g(E) dE$  is the number of energy states within the energy range  $E$  and  $E + dE$ . If  $V$  is the volume of the Fermi-phase space of conductor, the value of  $g(E) dE$  can be written in terms of momentum as

$$g(p) dp = \frac{8\pi V}{h^3} \cdot p^2 dp = \frac{8\pi V}{h^3} \cdot p(p dp) \quad \dots(7.9.6.2)$$

Now, for non-relativistic case, the energy of an electron moving with velocity  $v$ ,

$$E = \frac{1}{2} m v^2 = \frac{p^2}{2m} \quad (\text{since } p = mv) \quad \dots(7.9.6.3)$$

or,  $p^2 = 2mE$

Differentiating,  $2p dp = 2m dE$  or,  $p dp = m dE$  ...(7.9.6.4)

Substituting the value of  $p$  and  $p dp$  we get from equation (7.9.6.2)

$$g(E) dE = \frac{8\pi V}{h^3} (2mE)^{1/2} m dE \quad \dots(7.9.6.5)$$

From equation (7.9.6.1) we can write

$$n(E) dE = \frac{8\sqrt{2}\pi V}{h^3} = \frac{m^{3/2} E^{1/2} dE}{e^{(E - E_f)/kT} + 1} \quad \dots(7.9.6.6)$$

This is the Fermi-Dirac law of energy distribution for free electrons in metals.

### 7.9.7 Value of Total Energy (Fermi Energy) and Total Number of Electrons in Metal at Absolute Zero

At absolute temperature ( $T = 0 \text{ K}$ ), the total number of electrons is equal to the total number of energy states occupied by the electrons from the energy range 0 to  $\varepsilon_f$  (Fermi energy).

Electrons are fermions. Therefore, each energy state has only one electron. Thus, at temperature  $T = 0 \text{ K}$ , the number of electrons ( $N$ ) is equal to the total number of energy states occupied by the electrons for the energy from 0 to  $\varepsilon_f$ . Thus from equation (7.9.6.5) we get,

$$N = \int_0^{\varepsilon_f} g(E) dE = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^{\varepsilon_f} E^{1/2} dE = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \varepsilon_f^{3/2} \times \frac{2}{3}$$

$$N = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} \varepsilon_f^{3/2} \quad \dots (7.9.7.1)$$

This is the expression of total number of electrons in a metal at absolute zero.  
So, the Fermi energy at absolute zero can be written from equation (7.9.7.1).

$$\varepsilon_f = \frac{h^2}{8m} \left( \frac{3N}{\pi V} \right)^{2/3} \quad \dots (7.9.7.2)$$

So Fermi energy depends only on electrons concentration  $\left(\frac{N}{V}\right)$  and it is independent on the size and volume of the conductor.

**PROBLEM 1** For silver, the electron concentration  $\left(\frac{N}{V}\right)$  is  $5.86 \times 10^{28} \text{ m}^{-3}$ . Find its Fermi energy.

**Solution** Given, electron concentration of silver,  $\frac{N}{V} = 5.86 \times 10^{28} \text{ m}^{-3}$

So, the Fermi energy at,  $T = 0 \text{ K}$

$$\begin{aligned} \varepsilon_f &= \frac{h^2}{8m} \left( \frac{3}{\pi} \frac{N}{V} \right)^{2/3} = \frac{(6.624 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31}} \left[ \frac{3}{3.14} \times (5.86 \times 10^{28}) \right]^{2/3} \text{ J} \\ &\simeq 9 \times 10^{-19} \text{ J} = \frac{9 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = 5.625 \text{ eV} \end{aligned}$$

So, the maximum kinetic energy of free electrons in silver at absolute zero temperature is 5.625 eV.

**PROBLEM 2** If the atomic weight and density of silver is  $108 \text{ g} \cdot \text{mol}^{-1}$  and  $10.50 \text{ g} \cdot \text{cm}^{-3}$  respectively, find the Fermi energy level of silver at  $0 \text{ K}$  (considering there is 1 free electron per atom).

**Solution** We know, Fermi energy at  $T = 0 \text{ K}$ ,  $\varepsilon_f = \frac{h^2}{8m} \left( \frac{3N}{\pi V} \right)^{2/3}$

At absolute zero, the highest energy occupied by valence electron is equal to Fermi energy.

Here, electron concentration of silver can be written as

$$\frac{N}{V} = \frac{\text{Avogadro number}}{\text{atomic weight}} \times \text{density}$$

$$= \left( \frac{6.023 \times 10^{23} \text{ atom mole}^{-1}}{108 \text{ g mol}^{-1}} \right) \times (10.50 \text{ g cm}^{-3}) = 5.86 \times 10^{28} \text{ m}^{-3}$$

$$\therefore \varepsilon_f = \frac{h^2}{8m} \left( \frac{3}{\pi} \cdot \frac{N}{V} \right)^{2/3} = \frac{(6.624 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31}} \left[ \frac{3}{3.14} (5.86 \times 10^{28}) \right]^{2/3}$$

$$\simeq 9 \times 10^{-19} \text{ J} = \frac{9 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = 5.625 \text{ eV}.$$

### PROBLEM

- 3** If the Fermi energy at 0 K of metallic silver is 5.5 eV, find the electron concentration of silver atom. Given, the atomic weight of silver is 108 and the number of free electron per atom is 1.

**Solution** We know, Fermi energy at absolute zero

$$\varepsilon_f = \frac{h^2}{8m} \left( \frac{3N}{\pi V} \right)^{2/3}; \quad \text{where } \frac{N}{V} = \text{electron concentration}$$

$$\text{or, } 5.5 \times 1.6 \times 10^{-19} = \frac{(6.6 \times 10^{-34} \text{ J s})^2}{8 \times 9.1 \times 10^{-31} \text{ kg}} \left( \frac{3}{3.14} \right)^{2/3} \cdot \left( \frac{N}{V} \right)^{2/3}$$

$$\text{or, } \frac{640.64 \times 10^{-50}}{(6.6 \times 10^{-34})^2} = \left( \frac{3}{3.14} \right)^{2/3} \cdot \left( \frac{N}{V} \right)^{2/3}$$

$$\text{or, } (14.70 \times 10^{18})^{3/2} = \frac{3}{3.14} \times \frac{N}{V}$$

$$\text{or, } \frac{N}{V} = 5.89 \times 10^{28} \times \frac{3.14}{3} = 5.89 \times 10^{28} \text{ m}^{-3}$$

So, the free electron concentration (or density) =  $5.86 \times 10^{28} \text{ m}^{-3}$ .



### 7.9.8 Mean Internal Energy ( $\bar{\varepsilon}$ ) of Free Electrons of a Metal at Absolute Zero

If  $n(E) dE$  is the total number of electrons in a metal within the energy range  $E$  to  $E + dE$ , the mean internal energy of free electrons of a metal at absolute zero is

$$\bar{\varepsilon} = \frac{1}{N} \int_0^\infty E n(E) dE$$

where,  $N$  = the total number of free electrons in a metal of volume  $V$ .

So,  $\bar{\varepsilon} = \frac{1}{N} \int_0^\infty E [f(E) g(E) dE]$   $[\because n(E) dE = f(E) g(E) dE, \text{ where } g(E) dE$  indicates the number of energy states within the energy range  $E$  and  $E + dE$ .]

$$\text{or, } \bar{\varepsilon} = \int_0^{\varepsilon_f} E f(E) g(E) dE + \int_{\varepsilon_f}^\infty E f(E) g(E) dE$$

... (7.9.8.1)

where  $\epsilon_f$  is the Fermi energy of free electrons at absolute zero.  
at  $T = 0 \text{ K}$ ,

$E \leq \epsilon_f$ , the Fermi distribution function  $f(E) = 1$

at  $T = 0 \text{ K}$

$E \geq \epsilon_f$ , the Fermi distribution function  $f(E) = 0$

thus the 2nd part of equation (7.9.8.1) is zero. So we get from the first part of equation (7.9.8.1)

$$\bar{\epsilon} = \frac{1}{N} \int_0^{\epsilon_f} E g(E) dE \quad [\because f(E) = 1] \quad \dots (7.9.8.2)$$

know, the number of energy states within the energy range  $E$  and  $E + dE$ ,

$$g(E) dE = 4\pi V \left( \frac{2m}{h^2} \right)^{3/2} E^{1/2} dE \quad [\text{from equation (7.9.6.5)}]$$

$$\bar{\epsilon} = \frac{1}{N} \int_0^{\epsilon_f} E 4\pi V \left( \frac{2m}{h^2} \right)^{3/2} E^{1/2} dE = \frac{4\pi V}{N} \left( \frac{2m}{h^2} \right)^{3/2} \int_0^{\epsilon_f} E^{3/2} dE$$

$$\bar{\epsilon} = \frac{4\pi V}{N} \left( \frac{2m}{h^2} \right)^{3/2} \cdot \frac{2}{5} \epsilon_f^{5/2} = \left[ \frac{8\pi V}{5N} \left( \frac{2m}{h^2} \right)^{3/2} \epsilon_f^{3/2} \right] \epsilon_f \quad \dots (7.9.8.3)$$

the Fermi energy at absolute zero (i.e.,  $T = 0 \text{ K}$ ),

$$\epsilon_f = \frac{h^2}{2m} \left( \frac{3N}{8\pi V} \right)^{2/3} \quad \dots (7.9.8.4)$$

$$\epsilon_f^{3/2} = \left( \frac{h^2}{2m} \right)^{3/2} \frac{3N}{8\pi V} \quad \dots (7.9.8.5)$$

substituting the value of  $\epsilon_f^{3/2}$  in equation (7.9.8.3), we get

$$\bar{\epsilon} = \left[ \frac{8\pi V}{5N} \left( \frac{2m}{h^2} \right)^{3/2} \left( \frac{h^2}{2m} \right)^{3/2} \frac{3N}{8\pi V} \right] \epsilon_f \quad \dots (7.9.8.6)$$

$$\bar{\epsilon} = \frac{3}{5} \epsilon_f$$

This is the relation between the mean internal energy  $\bar{\epsilon}$  of a free electron of metal (at  $T = 0 \text{ K}$ ) to its Fermi energy at absolute zero.

PROBLEM

If the Fermi energy of a metal at thermal equilibrium  $T = 0 \text{ K}$  is 12 eV, find

(i) the average energy of free electrons in the metal,

(ii) the speed of the electron corresponding to the above average energy.

Solution

Average energy,

$$\bar{\epsilon} = \frac{3}{5} \epsilon_f = \frac{3}{5} \times 12 \text{ eV} = 7.2 \text{ eV}.$$



ii If  $v$  is the velocity of the electron (in SI unit), its K.E =  $\frac{1}{2}mv^2$

$$\therefore \frac{1}{2}mv^2 = 1.6 \times 10^{-19} \times 7.2$$

$$\text{or, } v = \left( \frac{2 \times 7.2 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}} \right)^{1/2} \text{ m}\cdot\text{s}^{-1} = 1.59 \times 10^6 \text{ m}\cdot\text{s}^{-1}.$$

### 7.10



### BOSE-EINSTEIN STATISTICS

It gives the statistical behaviour of indistinguishable and identical particles with integral spin. These particles do not obey Pauli's exclusion principle.

#### Basic postulates:

- 1 The particles are indistinguishable and identical.
- 2 They do not obey Pauli's exclusion principle. So, each quantum (energy) state can accommodate any number of particles.
- 3 These particles have zero or integral spin (i.e., spin angular momentum  $m_s\hbar = \hbar, 2\hbar, 3\hbar, \dots$ , where  $m_s$  = spin quantum number).
- 4 These particles have symmetric wave function.

**Bosons:** The particles those are indistinguishable, identical having integral spin (i.e.,  $m_s\hbar = 0, \hbar, 2\hbar, \dots$ ) and obey Bose-Einstein statistics are called as bosons.

**Examples:** phonons, photons ( $m_s = 1$ ),  $\pi$ -mesons ( $m_s = 0$ ),  $\alpha$ -particles ( $m_s = 0$ ), mesons,  $\eta$ -mesons.

If the total number of nucleons of atom is even, the atoms or molecules obey Bose-Einstein statistics. So,  ${}_1\text{H}^2$ ,  ${}_2\text{He}^4$ ,  ${}_6\text{C}^{12}$ ,  ${}_8\text{O}^{16}$ , etc. atoms are also the examples of bosons.



#### 7.10.1 Bose-Einstein Distribution Law

Bose-Einstein theory is applicable for the particles those are identical, indistinguishable and each quantum state can be occupied by any number of particles.

In order to find the energy distribution among indistinguishable identical particles (each having spin angular momentum  $m_s\hbar = 0, \frac{1}{2}\hbar, \frac{3}{2}\hbar, \dots$ ), we divide the available volume in the phase space into a large number of quantum states.

Let us consider the total number of ways in which  $N_i$  number of identical indistinguishable particles can be distributed among  $g_i$  quantum states of energy  $E_i$  such that each quantum state (cell of the phase space) can be occupied by any number of particles.

③  $m_s$  = spin quantum number and  $m_s\hbar$  = spin angular momentum.

Suppose,  $N_i$  identical particles are arranged in a row and distributed among  $g_i$  quantum states with  $(g_i - 1)$  partitions in between to give the distinct arrangements [Fig. 5].  
The number of possible distinguishable and distinct arrangements of  $N_i$  particles with  $(g_i - 1)$  partitions can be given as

$$W_i = \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!}$$

So, the total number of distinguishable and distinct ways ( $W$ ) of arranging  $N_1, N_2, \dots, N_n$  particles in ' $n$ ' energy level is the product of expression given in equation (7.10.1.1) for  $i = 1, 2, \dots, n$ .

$$W = \prod_{i=1}^n W_i = \prod_{i=1}^n \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!}$$

where  $\prod$  denotes the product.  
... (7.10.1.2)

**Most probable macrostate:** It corresponds to the state of maximum thermo-dynamic probability. We know,  $N_i$  and  $g_i$  are very large numbers compared to unity. Hence, the equation (7.10.1.2) can be written as

$$W = \frac{\prod_{i=1}^n (N_i + g_i)!}{N_i! g_i!} \quad \dots (7.10.1.3)$$

taking natural logarithm on both sides, we have

$$\ln W = \sum_i \ln(N_i + g_i)! - \ln N_i - \ln g_i! \quad \dots (7.10.1.4)$$

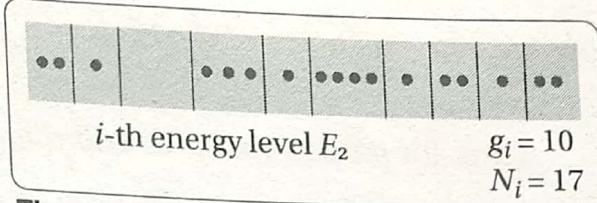
Applying Stirling's approximation,  $\ln x! = x \ln x - x$  (where  $x$  is very large)  
we get from equation (7.10.1.4),

$$\begin{aligned} \ln W &= \sum_i [(N_i + g_i) \ln(N_i + g_i) - (N_i + g_i)] \\ &\quad - \{N_i \ln N_i - N_i\} - \{g_i \ln g_i - g_i\} \end{aligned}$$

$$\ln W = \sum_i [(N_i + g_i) \ln(N_i + g_i) - N_i \ln N_i - g_i \ln g_i] \quad \dots (7.10.1.5)$$

The most probable distribution can be obtained by evaluating the maximum value of  $\ln W$ . Hence, differentiating the equation (7.10.1.5), we get,

$$\begin{aligned} d(\ln W) &= \sum_i [\ln(N_i + g_i) dN_i + (N_i + g_i) \frac{1}{(N_i + g_i)} dN_i] \\ &\quad - N_i \frac{1}{N_i} dN_i - \ln N_i dN_i \quad [g_i \text{ is mere number } d(g_i) = 0] \end{aligned}$$



**Fig. 5** ▷ A possible arrangement of  $N_i$  particles among  $g_i$  number of degenerate quantum states of energy  $E_i$  (i.e., in the  $i$ -th energy state)

... (7.10.1.1)

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or,

$$d(\ln W) = \sum_i [\ln(N_i + g_i) dN_i - \ln N_i dN_i]$$

...(7.10.1.6)

Thus, for *most probable distribution*,  $d(\ln W) = 0$

i.e.,

$$\sum_i [\ln(N_i + g_i) dN_i - \ln N_i dN_i] = 0$$

or,

$$\sum_i [\ln N_i - \ln(N_i + g_i)] dN_i = 0$$

...(7.10.1.7)

As the system must satisfy (i) conservation of total number of bosons  $N$  and (ii) conservation of total energy of the system,

∴

$$N = \sum_i N_i = \text{constant} \quad \text{or, } \sum_i dN_i = 0$$

...(7.10.1.8)

and

$$E = \sum_i N_i E_i = \text{constant} \quad \text{or, } \sum_i E_i dN_i = 0$$

...(7.10.1.9)

Multiplying equation (7.10.1.8) by  $\alpha$  and equation (7.10.1.9)  $\beta$  and then adding to equation (7.10.1.7), we have

$$\sum_i [\ln N_i - \ln(N_i + g_i) + \alpha + \beta E_i] dN_i = 0$$

...(7.10.1.10)

As the variation  $dN_i$  are independent to one another, the above summation is equal to zero if

$$\ln N_i - \ln(N_i + g_i) + \alpha + \beta E_i = 0$$

or,

$$\ln \frac{N_i + g_i}{N_i} = \alpha + \beta E_i \quad \text{or, } \frac{N_i + g_i}{N_i} = e^{\alpha + \beta E_i}$$

or,

$$1 + \frac{g_i}{N_i} = e^{\alpha + \beta E_i} \quad \text{or, } \frac{g_i}{N_i} = e^{\alpha + \beta E_i} - 1$$

or,

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

...(7.10.1.11)

This **equation is Bose-Einstein distribution law**. Thus, it gives the most probable distribution of bosons among the various energy levels (i.e., compartments).

In thermal equilibrium for bosons at temperature  $T$ , if  $\mu$  is the chemical potential of the system and  $k$  is the Boltzmann's constant, we can write

$$\alpha = -\frac{\mu}{kT} \quad \text{and} \quad \beta = \frac{1}{kT}$$

Thus, we get from equation (7.10.1.11),

$$N_i = \frac{g_i}{e^{(E_i - \mu)/kT} - 1}$$

...(7.10.1.12)

So, the Bose-Einstein distribution function becomes

$$f(E) = \frac{N_i}{g_i} \quad \text{or, } f(E) = \frac{1}{e^{\frac{(E_i - \mu)/kT}{-1}}} \quad \dots (7.10.1.13)$$

If  $E_i \gg kT$ , the B-E distribution reduces to M-B distribution.

## 7.10.2 Bose-Einstein Distribution Function

This gives the probability of a boson to occupy an energy state ( $E_i$ ) at absolute temperature ( $T$ ) and is expressed as

$$f(E) = \frac{1}{e^{\frac{(E_i - \mu)/kT}{-1}}} \quad \dots (7.10.2.1)$$

where

$\mu$  = chemical potential of the gas

$k$  = Boltzmann's constant =  $8.62 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$  ( $= 1.3805 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ )

**PROBLEM**  
**1** A gas has two indistinguishable identical particles in  $k$  th energy level in which there are three separate quantum states according to B-E statistics.

(i) Find the possible number of microstates.

(ii) Show the individual microstates in a tabular form.

**Solution**  
**i** In B-E statistics each quantum state can accommodate one or more than one indistinguishable identical particles.

According to B-E statistics, the total number of microstates considering the two particles are in  $k$  th energy level and the other levels are empty

$$W = \frac{(N_k + g_k - 1)!}{N_k! (g_k - 1)!} = \frac{(2 + 3 - 1)!}{2! (3 - 1)!} \quad [\because N_k = 2, g_k = 3]$$

$$= \frac{4!}{2! 2!} = \frac{4 \cdot 3 \cdot 2 \cdot 1}{2 \cdot 2} = 6 \text{ microstates}$$

**ii** If the two indistinguishable identical particles are represented by  $A$ , the number of microstates can be given below in tabular form :

Q-states		1	2	3
Micro-states	↓	AA	×	×
1		AA	×	×
2		×	AA	×
3		×	×	AA

If the energy levels of the system is very closely packed, the number of bosons having energy range  $E$  and  $E + dE$  is given by

$$n(E) dE = \frac{g(E) dE}{(E_i - \mu)/kT}$$

where  $n(E)$  represents the number of quantum states of energies between  $E$  and  $E + dE$ .

Micro-states	Q-states	1	2	3
↓ 4		A	A	×
5		A	×	A
6		×	A	A

So, there are six microstates.

### 7.10.3 Distribution of the Boson Particles for Different Energy Levels at Low and High Temperature

The distribution of the boson particles for different energy level at higher and lower temperature is shown on adjacent figure [Fig. 6].

**It is seen that B-E distribution will give more emphasis on the lower energy levels.**

### 7.10.4 Applications of B-E Statistics : Derivation of Planck's Law of Radiation

According to **Planck's radiation** law, the amount of energy radiation per unit volume of a black body lying between the frequency range  $\nu$  and  $(\nu + d\nu)$  at absolute temperature  $T$  is given by

$$E(\nu)d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1}$$

**Derivation of the law from B-E statistics:** In 1905, Einstein developed that the electromagnetic radiations due to emission or absorption by a blackbody are composed of discrete energy particles called photons. In 1924, Prof. S. N. Bose developed a new statistics to suit the system of photons. The radiation inside an enclosure maintained at constant temperature (i.e., at thermal equilibrium) may be considered as photon gas. The walls of a blackbody can absorb or emit photons of different energies. These photons are indistinguishable and many photons can have the same energy. The photons can interact only with the atoms of the walls of the cavity. They have integral spin and obey Bose-Einstein Statistics. Hence, **we use the Bose-Einstein distribution law to derive Planck's law of radiation.**

In black body radiation, the photons of different energies are absorbed or emitted by the atoms of the walls of the enclosure. Thus the total number of photons present in the enclosure is not constant.

Therefore,  $\sum_i N_i = \text{constant}$  or  $\sum_i dN_i = 0$ , is no longer valid though the total energies

remain constant. Hence, the multiplier  $\alpha = 0$ .

Thus, we have from Bose-Einstein distribution law [i.e., equation (7.10.1.11)]

$$N_i = \frac{g_i}{\beta E_i - 1} \quad \text{or, } N_i = \frac{g_i}{e^{E_i/kT} - 1} \quad \dots (7.10.4.1)$$

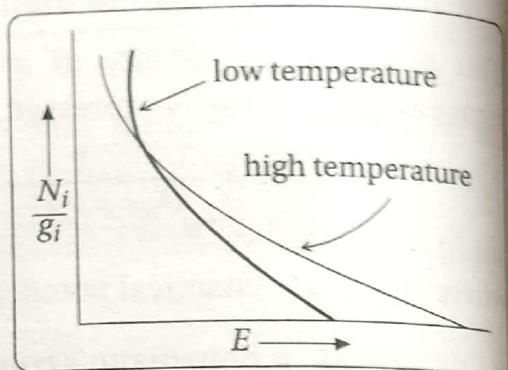


Fig. 6 ▷ Distribution of the boson particles for different energy levels for higher and lower temperature

Therefore, the number of photons (bosons) in the frequency range  $\nu$  and  $\nu + d\nu$  is obtained replacing  $g_i$  by  $g(\nu)d\nu$  and  $N_i$  by  $n(\nu)d\nu$ . Thus we get from the above equation

$$n(\nu)d\nu = \frac{g(\nu)d\nu}{e^{h\nu/kT} - 1} \quad \dots (7.10.4.2)$$

where  $g(\nu)d\nu$  is the number of quantum states in the frequency range  $\nu$  and  $\nu + d\nu$ .

If  $V$  is the volume of Bosons phase space (i.e., volume of the enclosure), the number of quantum states corresponding to the momentum in the range between  $p$  and  $p + dp$  (for the two allowed spin quantum states of each photon)

$$g(p)dp = 2 \times \frac{4\pi V p^2 dp}{h^3} = \frac{8\pi V p^2 dp}{h^3} \quad \dots (7.10.4.3)$$

The energy and frequency of a photon are related by

$$E(=mc^2) = h\nu$$

and momentum of the photon  $p = \frac{h\nu}{c}$

$$\text{or, } dp = \frac{h}{c} d\nu$$

Therefore, the number of quantum states in the frequency range  $\nu$  and  $\nu + d\nu$  can be written from equation (7.10.4.3) as

$$g(\nu)d\nu \frac{8\pi V}{h^3} \left(\frac{h\nu}{c}\right)^2 \left(\frac{h\nu}{c}\right)^2 = \left(\frac{8\pi V}{c^3}\right) \nu^2 d\nu \quad \dots (7.10.4.4)$$

Hence, substituting the value of  $g(\nu)d\nu$  in equation (7.10.4.2), we have

$$n(\nu)d\nu = \frac{8\pi V}{c^3} \nu^2 \frac{1}{e^{h\nu/kT} - 1} d\nu \quad \dots (7.10.4.5)$$

The energy of a photon =  $h\nu$ . Therefore, the amount of energy per unit volume of the enclosure (i.e., energy density or radiation) within the frequency range  $\nu$  and  $\nu + d\nu$  is given by

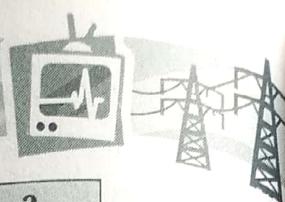
$$E_\nu d\nu = \left(\frac{h\nu}{V}\right) n(\nu) d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} d\nu \quad \dots (7.10.4.6)$$

This is the **Planck's radiation law for blackbody radiation**.

**Planck's law in terms** of wavelength can be obtained by substituting

$$\nu = \frac{c}{\lambda} \text{ and } d\nu = \left| \frac{c}{\lambda^2} \right| d\lambda \text{ (neglecting negative sign) in equation (7.10.4.6) as,}$$

$$E_\lambda d\lambda = \frac{8\pi h}{c^3} \frac{\left(\frac{c}{\lambda}\right)^3 \left(\frac{c}{\lambda^2} d\lambda\right)}{e^{\frac{hc}{\lambda kT}} - 1} = \frac{8\pi hc}{\lambda^5} \left[ \frac{1}{e^{\frac{hc}{\lambda kT}}} \right] d\lambda \quad \dots (7.10.4.7)$$



Micr-states	Q-states →	1	2	3
4		A	A	×
5		A	×	A
6		×	A	A

So, there are six microstates.

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Thus, we have from Bose-Einstein distribution law [i.e., equation (7.10.1.11)]

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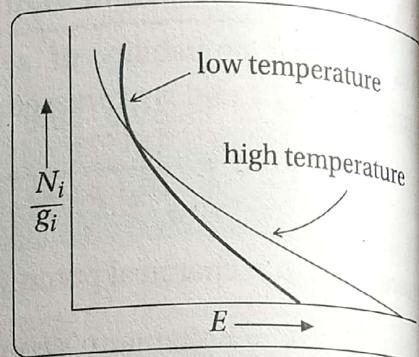


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Hence, substituting the value of  $g(\nu)d\nu$  in equation (7.10.4.2), we have

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$$E_\nu d\nu = \left(\frac{h\nu}{V}\right) n(\nu) d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} d\nu \quad \dots (7.10.4.6)$$

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Planck's law in terms of wavelength can be obtained by substituting

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$$E_\lambda d\lambda = \frac{8\pi h}{c^3} \frac{\left(\frac{c}{\lambda}\right)^3 \left(\frac{c}{\lambda^2} d\lambda\right)}{e^{\frac{hc}{\lambda kT}} - 1} = \frac{8\pi hc}{\lambda^5} \left[ \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \right] d\lambda \quad \dots (7.10.4.7)$$

**PROBLEM**

- 1** Find the number of possible arrangements of two particles in three cells. In each case assuming that the particles obey (i) M-B statistics (ii) B-E statistics [W.B.U.T. '09] (iii) F-D statistics

**Solution**

- i In **M-B statistics**: the particles are distinguishable (we call them  $a$  and  $b$ ) and any number of particles can be accommodated in one quantum state (cell).
- ii In **B-E statistics**: the particles are indistinguishable (we call them  $a, a$ ) and any number of particles can be accommodated in one quantum state (cell).
- iii In **F-D statistics**: the particles are indistinguishable (we call them  $a, a$ ) and only one particle can be accommodated in one quantum state (cell).

Considering, the above properties, the possible arrangements are given below:

M-B Statistics			B-E Statistics			F-D Statistics		
Cell 1	Cell 2	Cell 3	Cell 1	Cell 2	Cell 3	Cell 1	Cell 2	Cell 3
$ab$	$\times$	$\times$	$aa$	$\times$	$\times$	$a$	$a$	$\times$
$\times$	$ab$	$\times$	$\times$	$aa$	$\times$	$a$	$\times$	$a$
$\times$	$\times$	$ab$	$\times$	$\times$	$aa$	$\infty$	$a$	$a$
$a$	$b$	$\times$	$a$	$a$	$\times$			
$b$	$a$	$\times$	$a$	$\times$	$a$			
$a$	$\times$	$b$	$\times$	$a$	$a$			
$b$	$\times$	$a$	$\times$	$a$	$a$			
$\times$	$a$	$b$	$\times$	$a$	$b$			
$\times$	$b$	$a$	$\times$	$a$	$a$			

Total no. of possible ways  
= 9 in which 2 particles  
can be arranged in 3 cells

Total no. of possible ways  
= 6 in which 2 particles  
can be arranged in 3 cells

Total no. of possible ways  
= 3 in which 2 particles  
can be arranged in 3 cells

**PROBLEM**

- 2** Find out the number of possible arrangements of three particles in two cells for (i) M-B statistics, (ii) B-E statistics and (iii) F-D statistics.

**Solution**

- i In **M-B statistics**: the particles are distinguishable (we call them  $a, b$  and  $c$ ) and any number of particles can be accommodated in one quantum state (cell).

Cell 1	$abc$	$\times$	$ab$	$bc$	$ac$	$a$	$b$	$c$
Cell 2	$\times$	$abc$	$c$	$a$	$b$	$bc$	$ac$	$ab$

So, there are 8 possible arrangements for M-B distribution.

- ii In **B-E statistics**: the particles are indistinguishable (we call them  $a, a$  and  $a$ ) and any number of particles can be accommodated in one quantum state (cell).

Cell 1	$aaa$	$\times$	$aa$	$a$
Cell 2	$\times$	$aaa$	$a$	$aa$

So, there are 4 possible arrangements for B-E distribution.

**In F-D statistics :** In F-D statistics, the particles are indistinguishable (we call them  $a, a, a$ ) and only one particle can be accommodated in one cell. Since the number of cell is less than the number of particles, no arrangement is possible.

**PROBLEM**  
**3** Find out the numbers of possible arrangements of 3 particles in 3 cells according to (i) M-B statistics, (ii) B-E statistics and (iii) F-D statistics.

[W.B.U.T 2009]

**Solution**

**i** In M-B statistics : the particles are distinguishable (we call them  $a, b$  and  $c$ ) and any number of particles can be accommodated in one quantum state (cell). The total number of possible arrangements

$$W = \frac{N! g_i^{N_i}}{N_i!} = \frac{3! 3^3}{3!} = 27$$

Cell 1	Cell 2	Cell 3	No. of possible arrangements
$abc$	0	0	
0	$abc$	0	3
0	0	$abc$	
$ab$	$c$	0	
$ab$	0	$c$	
0	$ab$	$c$	
0	$c$	$ab$	
$c$	$ab$	0	
$c$	0	$ab$	
$ac$	$b$	0	
$ac$	0	$b$	
0	$ac$	$b$	18
0	$b$	$ac$	
$b$	0	$ac$	
$b$	$ac$	0	
$bc$	$a$	0	
$bc$	0	$a$	
0	$bc$	$a$	
0	$a$	$bc$	
$a$	0	$bc$	
$a$	$bc$	0	

Cell 1	Cell 2	Cell 3	No. of possible arrangements
<i>a</i>	<i>b</i>	<i>c</i>	
<i>a</i>	<i>c</i>	<i>b</i>	
<i>b</i>	<i>a</i>	<i>c</i>	
<i>b</i>	<i>c</i>	<i>a</i>	
<i>c</i>	<i>a</i>	<i>b</i>	
<i>c</i>	<i>b</i>	<i>a</i>	
			<b>Total 27</b>

**ii In B-E statistics :** the particles are indistinguishable (we call them *a*, *a* and *a*) and any number of particles can be accommodated in one quantum state (cell). The total number of possible arrangements,

$$W = \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} = \frac{(3 + 3 - 1)!}{3!(3 - 1)!} = \frac{5!}{3!2!} = 10$$

Cell 1	Cell 2	Cell 3	No. of possible arrangements
<i>aaa</i>	0	0	
0	<i>aaa</i>	0	3
0	0	<i>aaa</i>	
<i>aa</i>	<i>a</i>	0	
<i>aa</i>	0	<i>a</i>	
<i>a</i>	<i>aa</i>	0	
<i>a</i>	0	<i>aa</i>	6
0	<i>aa</i>	<i>a</i>	
0	<i>a</i>	<i>aa</i>	
<i>a</i>	<i>a</i>	<i>a</i>	1
			<b>Total 10</b>

**iii In F-D statistics :** the particles are indistinguishable (we call them *a*, *a* and *a*) and only one particle can be accommodated in one quantum state (cell). The total number of possible arrangements,

$$W = \frac{g_i!}{N_i!(g_i - N_i)!} = \frac{3!}{3!(3 - 3)!} = 1$$

Cell 1	Cell 2	Cell 3	No. of possible arrangements
<i>a</i>	<i>a</i>	<i>a</i>	1

**PROBLEM**  
 3 distinguishable particles each of which can be in one of the  $\epsilon$ ,  $2\epsilon$ ,  $3\epsilon$ ,  $4\epsilon$  energy states have total energy  $6\epsilon$ . Find all possible number of distributions of all particles in the energy states. Find the number of microstates in each case.

[W.B.U.T. 2007]

Solution

No. of combinations	$E_k \rightarrow$	$\epsilon$	$2\epsilon$	$3\epsilon$	$4\epsilon$	Total energy
	$N_k \rightarrow$	$N_1$	$N_2$	$N_3$	$N_4$	
1		2	0	0	1	$6\epsilon$
2		0	3	0	0	$6\epsilon$
3		1	1	1	0	$6\epsilon$

So, the number of macrostates = The possible number of combination of particles = 3; They are  $(2, 0, 0, 1)$ ,  $(0, 3, 0, 0)$  and  $(1, 1, 1, 0)$ .

Let the particles be  $a$ ,  $b$  and  $c$ .

So, the possible microstates of the various particles in the macrostates can be evaluated as follows :—

Macrostates	$\epsilon$	$2\epsilon$	$3\epsilon$	$4\epsilon$	Number of microstates
$(2, 0, 0, 1)$	$ab$	0	0	$c$	3
	$ac$	0	0	$b$	
	$bc$	0	0	$a$	
$(0, 3, 0, 0)$	0	$abc$	0	0	1
$(1, 1, 1, 0)$	$a$	$b$	$c$	0	6
	$b$	$c$	$a$	0	
	$c$	$a$	$b$	0	
	$b$	$a$	$c$	0	
	$a$	$c$	$b$	0	
	$c$	$b$	$a$	0	

Hence, the total number of macrostates = 3 and the total number of microstates = 10

**PROBLEM**

5 Consider a two particles system each of which can exist in states  $\epsilon_1$ ,  $\epsilon_2$  and  $\epsilon_3$ . What are the possible states if the particles are (i) bosons, (ii) fermions?

[W.B.U.T. 2006]

Solution

i In B-E statistics : The boson particles are indistinguishable (we call them  $a$ ,  $a'$ ) and any number of particles can be accommodated in one quantum cell. Therefore, the possible states are given below :

Microstates	Q-states	$\epsilon_1$	$\epsilon_2$	$\epsilon_3$
↓ 1		$aa$	x	x

Q-states		$\epsilon_1$	$\epsilon_2$	$\epsilon_3$
Microstates				
↓ 2		x	aa	x
3		x	x	aa
4		a	a	x
5		a	x	a
6		x	a	a

So, there are 6 possible distributions.

- ii In F-D statistics : The fermions are indistinguishable (we call them  $a, a$ ) and one particle can be accommodated in one cell. Therefore, considering the property of fermions the arrangement is given below :

Q-states		$\epsilon_1$	$\epsilon_2$	$\epsilon_3$
Microstates				
↓ 1		a	a	x
2		a	x	a
3		x	a	a

So, the total number of arrangements are 3 .

7.11



## COMPARISON OF M-B STATISTICS, B-E STATISTICS AND F-D STATISTICS

		M-B	B-E	F-D
1.	Nature of particles	distinguishable, called boltzons	indistinguishable, called bosons	indistinguishable, called fermions
2.	Spin of particles	—	0 or integral spin (i.e., 0, 1, 2 ... )	half integral spin (i.e., $\frac{1}{2}, \frac{3}{2}, \frac{5}{2} \dots$ )
3.	Number of particles per energy state	no upper limit to the number of particle per quantum state	Boson particles do not obey Pauli's exclusion principle. So, any number of particles can be accommodated per quantum state.	Fermions obey Pauli's exclusion principle. So, only one particle can be accommodated per quantum state.
4.	Distribution function $f(E) = \frac{N_i}{g_i}$	$\frac{1}{e^{\alpha + \beta E_i}}$	$\frac{1}{e^{(\alpha + \beta E_i)} - 1}$ where $\alpha = -\frac{\mu}{kT}$ ; $\beta = \frac{1}{kT}$	$\frac{1}{e^{(\alpha + \beta E_i)} + 1}$ where $\alpha = -\frac{E_f}{kT}$ ; $\beta = \frac{1}{kT}$
5.	Nature of applications	applicable ideal gas.	applicable to photon, phonon with symmetric wave function.	applicable to electron, proton with antisymmetric wave function.

**Special Note** These three statistics can be represented by a single equation as  

$$g_i = e^{\alpha + \beta E_i + \delta},$$
 where for M-B, B-E and F-D statistics, the value of  $\delta = 0, -1$  and  $+1$  respectively.

For higher temperature, since  $\frac{g_i}{n_i} \gg 1$ , we can neglect the value of  $\delta$ . It concludes that **these two statistics will give the same result at higher temperature.**

② When  $e^\alpha e^{E_i/kT} \gg 1$ , the B-E distribution as well as F-D distribution approach to the classical M-B statistics.

# **EXERCISE**

## MULTIPLE CHOICE QUESTIONS

1. The degrees of freedom of a phase space are  
Ⓐ 6 Ⓑ 3 Ⓒ 2 Ans. A

2. A coin and a six-faced dice are thrown. The probability that the coin shows tail and the dice shows 5 is  
Ⓐ  $\frac{7}{12}$  Ⓑ  $\frac{1}{8}$  Ⓒ  $\frac{1}{12}$  Ans. C

Hint:  $\frac{1}{2}$  for coin and  $\frac{1}{6}$  for dice,  $\therefore$  total probability =  $\frac{1}{2} \times \frac{1}{6} = \frac{1}{12}$

3. The number of macrostates for  $N$  particles in M-B distribution are  
Ⓐ  $N+1$  Ⓑ  $N$  Ⓒ  $N-1$  Ans. A

4. The numbers of macrostates for 4 particles in M-B distribution are  
Ⓐ 5 Ⓑ 3 Ⓒ 4 Ans. A

5. The numbers of microstates for  $N$  particles in two compartments (i.e., quantum

states) obeying M-B statistics are  $\textcircled{C} 2^N$

(a, 1), the numbers of possible

6. For 4 distinguishable particles for the macrostates (3, 1), the numbers of

arrangements are  
Ⓐ 2 Ⓡ 3 Ⓢ 4

⑧ 2      ⑨ 3

**Hint:**  $W = \frac{4!}{(4-4)!} = 4$

$$\text{Hint: } W = \frac{4!}{(4-4)!} = 4$$

$$\text{Hint: } W = \frac{4!}{(4-4)!} = 4$$

7. The M-B statistics is applicable for

- ④ distinguishable particles  
⑤ indistinguishable particles

⑥ none

**Ans. A**

**8. In M-B statistics**

- (A) any number of particles can be accommodated in a given quantum state  
 (B) only one particle can be accommodated in a given quantum state  
 (C) none

**9. M-B statistics**

- (A) obeys Pauli's exclusion principle  
 (B) does not obey Pauli's exclusion principle      (C) none

**10. Each energy level has**

- (A) only one quantum state  
 (B) several number of quantum states      (C) none

**11. If a gas has 2 distinguishable particles with 3 separate quantum states the possible number of microstates are**

- (A) 2      (B) 4      (C) 9

**Hint:**  $W = \frac{N! g_k^{N_k}}{N_k!} = \frac{2! 3^2}{2!} = 9$

**12. M-B statistics is applicable for**

- (A) ideal gas      (B) photon      (C) electron

**13. Bose-Einstein statistics is applicable for**

- (A) distinguishable particles  
 (B) indistinguishable particles      (C) both

**14. In B-E statistics each quantum state can accommodate**

- (A) only one particle      (B) one or more particles  
 (C) none

**15. B-E statistics is applicable for**

- (A) photon      (B) electron      (C) ideal gas

**16. Helium  ${}^2\text{He}^4$  atom is under**

- (A) M-B statistics      (B) B-E statistics      (C) F-D statistics

**17. The spin ( $m_s$ ) of photon is**

- (A) 1      (B) 0      (C)  $\hbar$

**18. The spin angular momentum of photon**

- (A) 0      (B)  $2\hbar$       (C)  $\hbar$

**19. If the occupation index  $\left(\frac{n_i}{g_i}\right)$  is too much less than 1, the system is called**

- (A) degenerate      (B) non-degenerate      (C) none

**20. If the occupation index  $\left(\frac{n_i}{g_i}\right)$  is too much less than 1 then the particle is**

- (A) distinguishable      (B) indistinguishable      (C) none

**21. If the occupation index  $\frac{n_i}{g_i} > 1$ , the system is called**

- (A) degenerate      (B) non-degenerate      (C) none

22. Classical statistics can be applied if occupation index  $\frac{n_i}{g_i}$  is

- (A) equal to 1      (B) too much less than 1  
(C) too much greater than 1

Ans. (C)

23. A gas has two indistinguishable particles in 3 separate quantum states obeying B-E statistics. The numbers of microstates are

- (A) 6      (B) 9      (C) 3

Ans. (A)

24. F-D statistics is applicable for

- (A) distinguishable particles  
(B) indistinguishable particles      (C) none

Ans. (B)

25. In F-D statistics each quantum state can accommodate

- (A) only one particle  
(B) more than one particle      (C) none

Ans. (A)

26. F-D statistics is applicable for

- (A) photon      (B) electron      (C) ideal gas

Ans. (B)

27. Helium ( ${}^3\text{He}$ ) atom is under

- (A) M-B statistics      (B) B-E statistics      (C) F-D statistics

Ans. (C)

28. The spin ( $m_s$ ) of an electron is

- (A) 1      (B) 0      (C)  $\frac{1}{2}$

Ans. (C)

29. The spin angular momentum ( $m_s \hbar$ ) of an electron is

- (A)  $\hbar$       (B)  $2\hbar$       (C)  $\frac{\hbar}{2}$

Ans. (C)

30. The Fermi-Dirac distribution function is expressed as

$$\text{(A) } f(E) = \frac{1}{1 + e^{(E - E_f)/kT}}$$
$$\text{(B) } f(E) = \frac{1}{1 - e^{(E - E_f)/kT}} \quad \text{(C) none}$$

Ans. (A)

31. The Bose-Einstein distribution function is expressed as

$$\text{(A) } f(E) = \frac{1}{e^{(E_i - \mu)/kT} + 1}$$
$$\text{(B) } f(E) = \frac{1}{e^{(E_i - \mu)/kT} - 1} \quad \text{(C) none}$$

Ans. (B)

32. For  $T > 0\text{K}$ , the probability of occupancy of an electron at Fermi energy level is

- (A)  $\frac{1}{2}$       (B) 0      (C) 1

Ans. (A)

33. The maximum energy that can be occupied by an electron  $T = 0\text{K}$  is called

- (A) Fermi energy  
(B) chemical potential energy      (C) none

Ans. (A)

34. The Fermi temperature  $\theta_f$  is

(A)  $\frac{\varepsilon_f}{k}$

(B)  $k\varepsilon_f$

(C)  $\frac{k}{\varepsilon_f}$

[where  $\varepsilon_f$  = Fermi energy at absolute zero,  $k$  = Boltzmann's constant]

35. Average energy  $\bar{\varepsilon}$  of an electron in a metal at  $T = 0K$  is

(A)  $\frac{5}{2}\varepsilon_f$

(B)  $\frac{\varepsilon_f}{2}$

(C)  $\frac{3}{5}\varepsilon_f$

36. The possible arrangement of 3 particles obeying F-D statistics in 2 cells is

(A) 0

(B) 1

(C) 2

37. If the Fermi energy of a metal at thermal equilibrium is 15 eV then the average energy of the electron

(A) 9 eV

(B) 10 eV

(C) 5 eV

38. The thermodynamic probability  $\Omega$  can be expressed as

(A)  $S = k \ln \Omega$

(B)  $S = \ln \Omega$

(C)  $S = k \Omega$

[where  $S$  is the entropy of the thermodynamic system]

39. Wein's displacement law is a special case of

(A) Stefan's law

(B) Planck's radiation law

(C) Newton's laws of motion

40. Planck's radiation law for blackbody radiation can be derived from

(A) M-B statistics

(B) B-E statistics

(C) F-D statistics

41. A perfect blackbody is one that

(A) transmits all radiations

(B) absorbs all incident radiations

(C) reflects all incident radiations

## SHORT ANSWER TYPE QUESTIONS

1. Define macrostate and microstate with example.

[See article 7.2]

2. Define thermodynamic probability. Obtain a relation between entropy and thermodynamic probability. [See article 7.3 (for thermodynamic probability)]

3. [a] What is phase space ?

[b] Draw the phase space of a linear harmonic oscillator.

[See article 7.4]

4. State the characteristics of Maxwell-Boltzmann statistics ?

[See article 7.5]

5. Why was quantum statistics introduced ?

[See article 7.6]

6. State the characteristics of B-E and F-D statistics ?

[See article 7.10 and 7.11]

7. Find the possible arrangements of 3 indistinguishable particles in 4 quantum states according to B-E and F-D statistics.

Draw the Fermi distribution function at (i)  $T = 0K$  and (ii)  $T > 0K$ . Explain the physical significances. [See article 7.9]

What are bosons and fermions? Give examples.

[See article 7.9 (for fermions) and 7.10 (for bosons)]

State a comparative study among M-B, B-E and F-D statistics.

[See article 7.11]

Show that at  $T = 0K$ , the average energy of free electrons in the metal is  $\bar{\epsilon} = \frac{3}{5}\epsilon_f$ , where  $\epsilon_f$  is the Fermi energy at  $T = 0K$ .  
[See article 7.9.8]

## LONG ANSWER TYPE QUESTIONS

[a] Define (i) microstate and (ii) macrostate with suitable examples.

[See article 7.2.1] [C.U. (Hons) 1996, 1993]

[b] Define thermodynamic probability and obtain the relation between entropy and probability making reasonable assumptions.  
[See article 7.3]

[B.U. (Hons) '98, '03 ; W.B.U.T. 2005]

[a] What do you mean by phase space ?  
[See article 7.4]

[b] Find the numbers of energy states in energy range  $E$  and  $E + dE$  in phase space and also find the number of states in the momentum range  $p$  and  $p + dp$ .  
[See article 7.5]

[a] State the postulates of Maxwell-Boltzmann statistics.  
[See article 7.6]

[b] Define Maxwell-Boltzmann distribution function.  
[See article 7.6.2]

[c] What are the disadvantages of M-B statistics ?  
[See article 7.6.3]

[d] Derive the M-B distribution law.  
[See article 7.6.1] [B.U. 2003]

[e] Discuss the necessity of quantum statistics.  
[See article 7.7]

[f] What are the different types of quantum statistics ?  
[See article 7.8]

[g] What are fermions and bosons ? Give two examples of each.  
[See article 7.9 (for fermions) and article 7.10 (for bosons)] [W.B.U.T. 2004]

[h] Consider a two particles system each of which can exist in states  $\epsilon_1, \epsilon_2, \epsilon_3$ . What are the possible states, if the particles are (i) bosons, (ii) fermions?  
[W.B.U.T. 2006]

[i] State the basic postulates of F-D statistics and derive an expression for the probability distribution of particles obeying F-D statistics.  
[See article 7.9 and article 7.9.1]

[b] Which statistics will be applicable for

- (i)  ${}_1^1H$  (ii)  $e^-$  (iii)  $\pi^0$  (iv) photon.

Hint: (i) F-D, (ii) F-D, (iii) B-E, (iv) B-E

[See article 7.9.2]

[a] Write down F-D distribution function.

[W.B.U.T. 2009]

[b] Write down the postulates of Fermi-Dirac statistics.

[c] Plot electron distribution function governed by Fermi-Dirac statistics in metal at (i)  $T = 0K$  (ii)  $T > 0K$ .

Explain their physical significance.

[See article 7.9.3] [C.U. (Hons) '95, '97 ; W.B.U.T. 2005, 2009]

or, Write down F-D distribution function and define Fermi level at absolute zero and at a finite temperature.

[d] Compare M-B, F-D, B-E statistics mentioning at least 3 characteristics.

7. [a] Calculate the total number of particles in a fermionic gas in terms of the Fermi level at absolute zero. [See article 7.9.7] [B.U. (H) 01, 05, W.B.U.T. '07]
8. Find how the Fermi energy of a free electron gas varies with electron density  $n$ . [See article 7.9.8] [B.U.(Hons) 2007]
- or, Deduce the expression of Fermi energy at absolute zero and prove that it depends only on electron concentration and it is independent on the size of the conductor. [See article 7.9.9] [B.U(Hons) 2008]
9. [a] Prove that at absolute zero the average energy of free electrons in the metal [See article 7.9.10] is  $\bar{\varepsilon} = \frac{3}{5} \varepsilon_f$ , where  $\varepsilon_f$  = Fermi energy at  $T = 0\text{K}$ .

[b] If the Fermi energy of metal in thermal equilibrium is 25 eV, find (i) the average energy of free electrons in metal and (ii) the speed of electrons corresponding to the above average energy.

10. [a] Write down the B-E distribution function. [See article 7.10.1]
- [b] What are bosons ? Give two examples. [See article 7.10.2]
- [c] Give an expression of B-E statistics and hence obtain Planck's formula for black body radiation. [See article 7.10.4] [W.B.U.T. 2008]
11. [a] Give the basic postulates of B-E statistics. [See article 7.10.5]
- [b] Derive the expression for B-E distribution law. [See article 7.10.6]
- [c] Draw a suitable diagram to show the distribution of boson particles for different energy levels at low and high temperature. [See article 7.10.7]
12. 3 distinguishable particles each of which can be in one of the  $\varepsilon, 2\varepsilon, 3\varepsilon, 4\varepsilon$  energy states have total energy  $6\varepsilon$ . Find all possible distributions of particles in energy states. Find the number of microstates in each case. [W.B.U.T. 2008]
13. A gas has 2 distinguishable identical particles in  $k$  th energy level in which there are separate quantum states. Find the possible number of microstates.
14. Find the possible arrangement of 3 particles in 3 cells according to F-D statistics.

**Hint :** Cell 1 2 3

a a a

15. If the Fermi energy at 0K of metallic silver is 5.6 eV find the electron concentration per silver atom. [Given : The atomic weight of silver is 108 and the number of free electrons per atom is 1 ]

