

Q. What is Fermi-Energy? Calculate the value of Fermi-energy of a metal. Does the Fermi-energy depend upon size or volume of a conductor.

Ans: The energy values up to which all the energy states are full at  $0^\circ\text{K}$  and above which all the energy states are empty is known as Fermi-energy.

Value of Fermi-energy:-

At the temperature  $T=0\text{K}$ , the number of electrons is equal to the total number of energy states occupied by the electrons from zero to  $u_f$ , since each energy state can have one electron.

i.e

$$\begin{aligned}
 n &= \int_0^{u_f} g(u) du = \frac{8\sqrt{2} \pi V m^{3/2}}{h^3} \int_0^{u_f} u^{1/2} du \\
 &= \frac{8\sqrt{2} \pi V m^{3/2}}{h^3} \left[ \frac{2}{3} u^{3/2} \right]_0^{u_f} \\
 &= 16\sqrt{2} \pi V \frac{m^{3/2}}{3h^3} u_f^{3/2}
 \end{aligned}$$

$$\therefore \boxed{u_f = \frac{h^2}{2m} \left( \frac{3n}{8\pi V} \right)^{2/3}}$$

It is clear from the <sup>above</sup> expression of Fermi energy that it is independent of the size and volume of the conductor as it only depends upon  $\left(\frac{n}{V}\right)$ , the number of electron per unit volume.

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✓ Q. 5.2. What is Bose-Einstein statistics? What difficulties were met with M.B. statistics and how they were explained? Write basic assumptions of Bose-Einstein quantum statistics and derive the expression  $n_i = \frac{g_i}{e^\alpha e^{u_i/kT} - 1}$  for the most probable distribution of a system of particles obeying B.E. statistics

(Pbi. U. 2007; K.U., 2002, 2001, 2000; H.P.U. 2001, 1994; Madurai.U., 2003; M.D.U., 2005, 2000; P.U., 1999, 1994; G.N.D.U., 2004, 1996, 1995)

**Ans. Bose-Einstein statistics.** Bose-Einstein statistics is obeyed by those particles which are identical, indistinguishable and have integral spin. These particles are known as *Bosons*.

Bose used Planck's hypothesis according to which radiation in a temperature enclosure are composed of light quanta or photons of energy  $h\nu$ . These photons in the enclosure are indistinguishable.

**Difficulties with M.B. statistics.** See need for quantum statistics Q. 5.1.

**Assumptions.** In Bose-Einstein statistics following assumptions are made:

- (i) The particles of the system are *identical* and *indistinguishable*.
- (ii) *Any number of particles can occupy a single cell in the phase space.*
- (iii) The size of the cell cannot be less than  $h^3$  where  $h$  is Planck's constant having a value  $6.63 \times 10^{-34}$  Joule sec.
- (iv) The number of phase space cells is comparable with the number of particles *i.e.*, occupation index  $\frac{n_i}{g_i} = 1$ .
- (v) Bose-Einstein statistics is applicable to particles with *integral spin* angular momentum in units of  $\frac{h}{2\pi}$ . All particles which obey B.E statistics one known as *Bosons*.

**Bose-Einstein distribution law.** Consider a system consisting of  $n$  independent identical particles. The particles have definite energies or *momenta* as well as occupy definite *positions* and hence can be represented by *phase points* in the phase space. In order to determine the energy or momentum distribution of these particles in the *most probable* or *equilibrium state* we divide the available volume in the phase space into a large number (say  $k$ ) compartments (*quantum group* or *energy levels*) each compartment representing a small interval of energy (or momentum). Further we divide each compartment into elementary cells of size  $h^3$  where  $h$  is Planck's constant. We further suppose that the size of the compartment is very large as compared to the size of the cell so that each compartment contains a *very large number* of elementary cells.

Let there be  $n_1, n_2, \dots, n_i, \dots, n_k$  particles having mean energy values  $u_1, u_2, \dots, u_i, \dots, u_k$  respectively in compartments numbered as 1, 2,  $\dots, i, \dots, k$  containing  $g_1, g_2, \dots, g_i, \dots, g_k$  cells respectively in them.

The total number of particles in the system  $n = n_1 + n_2 + \dots + n_i + \dots + n_k$

Now consider the  $i$ th compartment. It has  $n_i$  indistinguishable particles distributed among its  $g_i$  cells. Let us calculate the number of ways in which these  $n_i$  identical particles can be distributed among  $g_i$  cells. To do this, we first choose the cell with which to begin the sequence. This choice can be made in  $g_i$  ways since there are  $g_i$  cells. Once this has been done, the remaining  $(g_i - 1)$  cells and  $n_i$  particles i.e., total  $(n_i + g_i - 1)$  elements can be arranged in order. The number of ways of doing this  $= (n_i + g_i - 1)!$

Thus the total number of ways for realising the distribution will be  $g_i (n_i + g_i - 1)!$

As the particles are indistinguishable, the re-arrangement of particles among themselves will not give rise to any new distribution. The number of such meaningless permutations is  $n_i!$  Hence the above result should be divided by  $n_i!$

Secondly, the distribution which can be derived by mere permutation of  $g_i$  cells among themselves  $= g_i!$  These permutations also do not produce different states and are hence meaningless. The above result should, therefore, be further divided by  $g_i!$

Thus the number of different arrangements or meaningful microstates for the  $i$ th compartment having  $n_i$  indistinguishable particles to be distributed among its  $g_i$  cells, is given by

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

Now since  $g_i! = g_i (g_i - 1)!$  we can write the above relation as

$$W_i = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad \dots(i)$$

Equation (i) gives the number of different arrangements of distributing  $n_i$  distinguishable particles among  $g_i$  cells in the  $i$ th compartment.

Similar expressions will be obtained for other compartments. Therefore, the total number of different arrangements for all the  $n$  particles of the system gives thermodynamic probability

$$\begin{aligned} W(n_1, n_2, \dots, n_i, \dots, n_k) &= \frac{(n_1 + g_1 - 1)!}{n_1! (g_1 - 1)!} \times \frac{(n_2 + g_2 - 1)!}{n_2! (g_2 - 1)!} \dots \times \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \dots \times \frac{(n_k + g_k - 1)!}{n_k! (g_k - 1)!} \\ &= \prod_{i=1}^k \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad \dots(ii) \end{aligned}$$

where  $\prod$  denotes multiplication of terms stated above for various values of  $i$ .

**Most probable macrostate.** The most probable macrostate corresponds to the state of maximum thermodynamic probability.

In Eq. (ii)  $n_i$  and  $g_i$  are both very large numbers so that neglecting 1 as compared to  $(n_i + g_i)$  and  $g_i$ , we get

$$W(n_1, n_2, \dots, n_i, \dots, n_k) = \prod_{i=1}^k \frac{(n_i + g_i)!}{n_i! g_i!}$$

Taking natural logarithms on both sides, (and representing  $W(n_1, n_2, \dots, n_i, \dots, n_k)$  simply as  $W$ , we have

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

Applying Stirling's approximation we get

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

To get the state of *maximum thermodynamic probability*, we differentiate the expression for  $\ln W$  and equate it to zero.

$$\begin{aligned} \therefore d(\ln W) &= \sum_{i=1}^k \left[ dn_i \ln (n_i + g_i) + (n_i + g_i) \frac{1}{(n_i + g_i)} dn_i - dn_i \ln n_i - n_i \cdot \frac{1}{n_i} dn_i \right] \\ &= \sum_{i=1}^k dn_i \ln (n_i + g_i) - dn_i \ln n_i \quad [ \because g_i \text{ is a mere number } d(g_i) = 0 ] \end{aligned}$$

$$\text{or } d(\ln W) = \sum_{i=1}^k \left[ \ln \frac{(n_i + g_i)}{n_i} \right] dn_i = 0 \quad \dots(iii)$$

In addition our system must satisfy two auxillary conditions.

(i) Conservation of total number of particles i.e.,  $n = \text{a constant}$ .

$$\therefore dn = \sum_{i=1}^k dn_i = 0 \quad \dots(iv)$$

(ii) Conservation of total energy of the system i.e.,  $U = \text{a constant}$

$$\therefore dU = \sum_{i=1}^k u_i dn_i = 0 \quad \dots(v)$$

Multiplying equation (iv) with  $\alpha$  and equation (v) with  $\beta$  and adding, we get

$$\alpha \sum_{i=1}^k dn_i + \beta \sum_{i=1}^k u_i dn_i = 0 \quad \dots(vi)$$

Equating relation (iii) and (vi) we get

$$\begin{aligned} \sum_{i=1}^k \left[ \ln \frac{(n_i + g_i)}{n_i} \right] dn_i &= \alpha \sum_{i=1}^k dn_i + \beta \sum_{i=1}^k u_i dn_i \\ \text{or } \sum_{i=1}^k \left[ \ln \frac{(n_i + g_i)}{n_i} - \alpha - \beta u_i \right] dn_i &= 0 \end{aligned}$$

As the various  $dn_i$ 's are independent of one another, the above sum is equal to zero if the expression within the brackets vanishes separately for each value of  $i$

$$\therefore \ln \frac{n_i + g_i}{n_i} = \alpha + \beta u_i = \alpha + \frac{u_i}{kT} \quad [ \because \beta = \frac{1}{kT} ]$$

$$\text{or } \frac{n_i + g_i}{n_i} = e^\alpha e^{\frac{u_i}{kT}} \quad \text{or} \quad 1 + \frac{g_i}{n_i} = e^\alpha e^{\frac{u_i}{kT}}$$

$$\therefore \frac{g_i}{n_i} = e^\alpha e^{\frac{u_i}{kT}} - 1 \quad \text{or} \quad n_i = \frac{g_i}{e^\alpha e^{\frac{u_i}{kT}} - 1} \quad \dots(vii)$$