

Unit-4: Bose – Einstein Statistics

INTRODUCTION:

The B-E statistics determines the statistical distribution of the identical & indistinguishable particles which do not obey the Pauli's exclusion principle. The particles which obey the Bose – Einstein's statistics are known as Bosons.

Bosons are the particles which are identical, indistinguishable and do not obey the Pauli's exclusion principle i.e. two or more particles (Bosons) can occupy the same quantum state, at the same time. They can occupy any number of quantum states. Photons, π – Meson's, Kaon's etc. are some examples of Bosons. A collection of non-interacting Bosons is called Bose gas.

The Bosons have zero or integral spin because these particles are not obeying the Pauli's exclusion principle. Bose used Planck's hypothesis, according to which radiation in a temperature enclosure is composed of light quanta's known as photons each of energy $E = h\nu$. These photons in the enclosure are indistinguishable.

Need of Quantum statistics:

The classical statistics or Maxwell Boltzmann statistics explained the energy and velocity distribution of the molecules of an ideal gas to a fair degree of accuracy, but it failed to explain the energy distribution of electrons in the system of electron gas and that of photons in the photon gas. For example, take the case of the conduction of electrons in a metal. These conducting electrons are free to move within the volume of the metal, like molecules of a gas, confined to the volume of the containing vessel. But when M-B statistics applied to this electron gas, it is unable to explain the observed facts. Another example is that of a photon gas. A hollow enclosure at constant temperature T is filled with radiations (Photons). These photons move around, colliding with one another and with the walls. They exert pressure on the walls and behave like a gas. When M-B statistics applied to this photon gas, it is unable to explain the observed energy distribution of these photons. There are many other systems where classical statistics fails to explain and interpreted the observed facts.

These difficulties have been resolved by the use of quantum statistics. We shall see later that quantum statistics includes M-B statistics as a limiting case. Quantum statistics is of two types: Bose Einstein statistics and Fermi Dirac statistics. In this chapter we will discuss about Bose Einstein statistics and in next chapter we will discuss about Fermi Dirac statistics.

Basic postulates (Assumptions) of quantum statistical mechanics:

In B-E statistics following assumptions are made:

1. The particles of the system are identical and indistinguishable.
2. Any number of particles can occupy a single cell in the phase space.
3. The size of the cell cannot be less than h^3 , where h is a Planck's constant having a value 6.63×10^{-34} joule.sec.
4. The number of phase space cells is comparable with the number of particles i.e. the occupation

$$\text{index } \frac{n_i}{g_i} = 1.$$

5. B-E statistics is applicable to particles with integral spin angular momentum in units of $\frac{h}{2\pi}$. All particles which obey B-E statistics are known as Bosons.

Bose – Einstein distribution law:

Let us consider a box divided into g_i sections by $(g_i - 1)$ partitions and n_i indistinguishable particles to be distributed among these sections. The permutations of n_i particles and $(g_i - 1)$ partition simultaneously is given by $(n_i + g_i - 1)!$. But this includes also the permutations of n_i particles among

themselves and also $(g_i - 1)$ partitions among themselves, as both these groups are internally indistinguishable. Hence the actual number of ways in which n_i particles are to be distributed in g_i cells (sublevels) is given by

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

Therefore, the total number of distinguishable and distinct ways of arranging N particles in all the variable energy states is given by

$$w = \frac{(n_1 + g_1 - 1)!}{n_1! (g_1 - 1)!} \times \frac{(n_2 + g_2 - 1)!}{n_2! (g_2 - 1)!} \times \dots \dots \dots$$

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

Since, n_i and g_i are large numbers. Hence we may neglect 1 in the above equation (1).

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

According to Stirling's approximation

$$\log n_i! = n_i \log n_i - n_i$$

Also, $\sum_i n_i = N$ and $\sum_i n_i E_i = U$

Taking log in equation (2), we have

$$\log w = \sum [\log(n_i + g_i)! - \log n_i! - \log g_i!]$$

Applying Stirling's approximation we get

$$\log w = \sum [(n_i + g_i) \log(n_i + g_i) - (n_i + g_i) - \{n_i \log n_i - n_i\} - \{g_i \log g_i - g_i\}]$$

$$= \sum [(n_i + g_i) \log(n_i + g_i) - n_i - g_i - n_i \log n_i + n_i - g_i \log g_i + g_i] \quad \text{----- (3)}$$

Here, g_i is not subject to variation and n_i varies continuously.

For most probable distribution, $\delta \log w_{\max} = 0$, hence, if the w of equation (3) represents a maximum, then

$$\delta \log w_{\max} = \sum [\log(n_i + g_i) - \log n_i] \delta n_i = 0 \quad \text{--- (4)}$$

As the total number of particles and total energy are constant, we have

$$\sum_i \delta n_i = 0 \quad \text{and} \quad \text{---- (5)}$$

$$\sum_i E_i \delta n_i = 0 \quad \text{----- (6)}$$

Now, applying Lagrange method of undetermined multiplier i.e. multiplying equation (5) by $-\alpha$ and equation (6) by $-\beta$ and adding to equation 4, we get

$$\sum [\log(n_i + g_i) - \log n_i - \alpha - \beta E_i] \delta n_i = 0$$

The variations δn_i are independent of each other. Hence we get

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

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

$$\Rightarrow \left(1 + \frac{g_i}{n_i} \right) = e^{\alpha + \beta E_i}$$

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

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

$$\text{Since, } \beta = \frac{1}{kT}$$

$$\therefore n_i = \frac{g_i}{e^{\alpha + \frac{E_i}{kT}} - 1} \quad \text{---- (8)}$$

The relation (7) or (8) gives the most probable distribution of particles for a system obeying B-E statistics and is known as B-E distribution law. In other words equation (8) determines the most probable distribution of bosons among various energy levels (compartments).

Bose – Einstein Gas and Degeneracy of Bose – Einstein Gas:

An assembly of bosons (i.e. indistinguishable elementary particles of zero or integral spin) is termed as Bose – Einstein gas.

Let us consider a perfect Bose – Einstein gas of n bosons. Let these particles be distributed among quantum states such that n_1, n_2, n_3, \dots, n particles are distributed in quantum states of energies $E_1, E_2, E_3, \dots, E_n$ respectively.

As the gas assumed to be perfect gas, the interaction between the particles is negligible so that the energy may regarded as entirely translational in character. Therefore the result obtained in this case will be particularly applicable to the mono-atomic gas.

If g_i is the degeneracy or statistical weight of i^{th} quantum state then according to the Bose – Einstein distribution law, the most probable distribution is

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

Let, $D = e^{\alpha}$ then above expression will be

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

We know that, for a single particle, the number of eigen states lying between momentum p and $p + dp$ is

$$g(p)dp = g_s \cdot \frac{4\pi V p^2 dp}{h^3} \quad \text{---- (2)}$$

Where, $g_s = (2S + 1)$ is the spin degeneracy factor caused by the particle of spin S .

$$\begin{aligned} \therefore \epsilon &= \frac{p^2}{2m} \\ \Rightarrow p &= \sqrt{2m\epsilon} \\ \Rightarrow dp &= \sqrt{2m} \times \frac{1}{2} \frac{1}{\sqrt{\epsilon}} d\epsilon \end{aligned}$$

Hence,

$$p^2 dp = 2m\epsilon \times \sqrt{2m} \times \frac{1}{2\sqrt{\epsilon}} d\epsilon$$

Now, the number of eigen states in energy range ϵ and $\epsilon + d\epsilon$ is given by (from equation 2)

$$g(\epsilon)d\epsilon = g_s \cdot \frac{4\pi V}{h^3} \times 2m\epsilon \times \sqrt{2m} \times \frac{1}{2\sqrt{\epsilon}} d\epsilon \quad \text{--- (3)}$$

Where, $g(\epsilon)$ is density of states functions. Equation (3) represents the number of quantum states in between ϵ and $\epsilon + d\epsilon$.

From equations (1) & (3) we can get the number of particles in the energy range between ε and $\varepsilon + d\varepsilon$ will be (in the equation 1, we have to put the value of $g(\varepsilon)d\varepsilon$ instead of g_i)

$$\begin{aligned}
 dn(\varepsilon) &= g_s \cdot \frac{4\pi V}{h^3} \times 2m\varepsilon \times \sqrt{2m} \times \frac{1}{2\sqrt{\varepsilon}} d\varepsilon \times \frac{1}{De^{\beta\varepsilon} - 1} \\
 \Rightarrow dn(\varepsilon) &= g_s \cdot \frac{4\pi Vm}{h^3} \times \sqrt{2m} \times \frac{\varepsilon^{1/2} d\varepsilon}{De^{\beta\varepsilon} - 1} \\
 \Rightarrow dn(\varepsilon) &= g_s \cdot \frac{4\pi Vm}{h^3} \times \sqrt{2m} \times \frac{\varepsilon^{1/2} d\varepsilon}{De^{\frac{\varepsilon}{kT}} - 1} \quad \text{---- (4)} \quad \because \beta = \frac{1}{kT}
 \end{aligned}$$

Let us put $\frac{\varepsilon}{kT} = x \Rightarrow dx = \frac{d\varepsilon}{kT}$. Now equation (4) will be

$$\begin{aligned}
 \Rightarrow dn(\varepsilon) &= g_s \cdot \frac{4\pi Vm}{h^3} \times \sqrt{2m} \times \frac{(xkT)^{1/2} kT dx}{De^x - 1} \\
 \Rightarrow dn(\varepsilon) &= g_s \cdot \frac{4\pi mV}{h^3} \times \sqrt{2m} \times \frac{(kT)^{3/2} x^{1/2} dx}{De^x - 1} \\
 \Rightarrow dn(\varepsilon) &= g_s \cdot \frac{2}{\sqrt{\pi}} \sqrt{\pi} \frac{2\pi mV}{h^3} \times \sqrt{2m} \times \frac{(kT)^{3/2} x^{1/2} dx}{De^x - 1} \\
 \Rightarrow dn(\varepsilon) &= g_s \cdot \frac{2}{\sqrt{\pi}} \cdot \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V \cdot \frac{x^{1/2} dx}{De^x - 1}
 \end{aligned}$$

But, previously, from the thermodynamic properties of gas molecule we found the translational partition function is

$$Z_t = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V$$

Hence,

$$dn(\varepsilon) = \frac{2g_s}{\sqrt{\pi}} \cdot Z_t \cdot \frac{x^{1/2} dx}{De^x - 1}$$

Therefore total number of particles will be;

$$n = \int_0^\infty dn(\varepsilon) = \frac{2g_s}{\sqrt{\pi}} \cdot Z_t \cdot \int_0^\infty \frac{x^{1/2} dx}{De^x - 1} \quad \text{--- (5)}$$

Hence, total energy of Bose – Einstein gas will be;

$$\begin{aligned}
 E = \varepsilon n &= xkT \cdot \frac{2g_s}{\sqrt{\pi}} \cdot Z_t \cdot \int_0^\infty \frac{x^{1/2} dx}{De^x - 1} \\
 \Rightarrow E &= kT \cdot \frac{2g_s Z_t}{\sqrt{\pi}} \int_0^\infty \frac{x^{3/2} dx}{De^x - 1} \quad \text{---- (6)}
 \end{aligned}$$

Now we have to evaluate the integrals in equations (5) and (6).

$$\begin{aligned}
\frac{1}{D e^x - 1} &= \frac{1}{D e^x \left[1 - \frac{1}{D e^x} \right]} \\
&= \frac{e^{-x}}{D} \frac{1}{\left[1 - \frac{e^{-x}}{D} \right]} \quad \because \frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots \\
&= \frac{e^{-x}}{D} \left[1 + \frac{e^{-x}}{D} + \left(\frac{e^{-x}}{D} \right)^2 + \left(\frac{e^{-x}}{D} \right)^3 + \dots \right] \\
&= \frac{e^{-x}}{D} \left[1 + \frac{e^{-x}}{D} + \frac{e^{-2x}}{D^2} + \frac{e^{-3x}}{D^3} + \dots \right] \quad \text{--- (7)} \\
\therefore \int_0^\infty \frac{x^{\frac{1}{2}} dx}{D e^x - 1} &= \int_0^\infty x^{\frac{1}{2}} \frac{e^{-x}}{D} \left[1 + \frac{e^{-x}}{D} + \frac{e^{-2x}}{D^2} + \frac{e^{-3x}}{D^3} + \dots \right] dx \\
&= \frac{1}{D} \int_0^\infty x^{\frac{1}{2}} e^{-x} dx + \frac{1}{D^2} \int_0^\infty x^{\frac{1}{2}} e^{-2x} dx + \frac{1}{D^3} \int_0^\infty x^{\frac{1}{2}} e^{-3x} dx + \frac{1}{D^4} \int_0^\infty x^{\frac{1}{2}} e^{-4x} dx + \dots \\
&= \frac{1}{D} \frac{\sqrt{\pi}}{2} + \frac{1}{D^2} \frac{\sqrt{\pi}}{2} \frac{1}{2^{\frac{3}{2}}} + \frac{1}{D^3} \frac{\sqrt{\pi}}{2} \frac{1}{3^{\frac{3}{2}}} + \frac{1}{D^4} \frac{\sqrt{\pi}}{2} \frac{1}{4^{\frac{3}{2}}} + \dots \\
&= \frac{\sqrt{\pi}}{2} \left[\frac{1}{D} + \frac{1}{D^2} \frac{1}{2^{\frac{3}{2}}} + \frac{1}{D^3} \frac{1}{3^{\frac{3}{2}}} + \frac{1}{D^4} \frac{1}{4^{\frac{3}{2}}} + \dots \right]
\end{aligned}$$

(Using Gama function $\int_0^\infty e^{-x} x^{n-1} dx = \Gamma(n)$)

$$\int_0^\infty e^{-x} x^{\frac{1}{2}} dx = \int_0^\infty e^{-x} x^{\frac{3}{2}-1} dx = \Gamma\left(\frac{3}{2}\right) = \Gamma\left(\frac{1}{2} + 1\right) = \frac{1}{2} \Gamma\left(\frac{1}{2}\right) = \frac{1}{2} \sqrt{\pi}$$

And for 2nd integration, let $2x = t \Rightarrow x = \frac{t}{2} \Rightarrow dx = \frac{1}{2} dt$

$$\int_0^\infty x^{\frac{1}{2}} e^{-2x} dx = \int_0^\infty \left(\frac{t}{2}\right)^{\frac{1}{2}} e^{-t} \frac{1}{2} dt = \frac{1}{2^{\frac{3}{2}}} \int_0^\infty e^{-t} (t)^{\frac{1}{2}} dt = \frac{1}{2^{\frac{3}{2}}} \Gamma\left(\frac{3}{2}\right) = \frac{1}{2^{\frac{3}{2}}} \frac{1}{2} \sqrt{\pi} = \frac{\sqrt{\pi}}{2} \frac{1}{2^{\frac{3}{2}}}$$

And so on) No need to write in the exam

Now, equation (5) will be

$$\begin{aligned}
n &= \frac{2g_s}{\sqrt{\pi}} \cdot Z_t \cdot \frac{\sqrt{\pi}}{2} \left[\frac{1}{D} + \frac{1}{D^2} \frac{1}{2^{\frac{3}{2}}} + \frac{1}{D^3} \frac{1}{3^{\frac{3}{2}}} + \frac{1}{D^4} \frac{1}{4^{\frac{3}{2}}} + \dots \right] \\
\Rightarrow n &= g_s Z_t \left[\frac{1}{D} + \frac{1}{D^2} \frac{1}{2^{\frac{3}{2}}} + \frac{1}{D^3} \frac{1}{3^{\frac{3}{2}}} + \frac{1}{D^4} \frac{1}{4^{\frac{3}{2}}} + \dots \right] \quad \text{--- (8)}
\end{aligned}$$

Similarly, from equation (6), we have

$$\begin{aligned}
\int_0^\infty \frac{x^{\frac{3}{2}} dx}{D e^x - 1} &= \int_0^\infty x^{\frac{3}{2}} \left[\frac{e^{-x}}{D} \left(1 + \frac{e^{-x}}{D} + \frac{e^{-2x}}{D^2} + \frac{e^{-3x}}{D^3} \right) \right] dx \\
&= \frac{1}{D} \int_0^\infty x^{\frac{3}{2}} e^{-x} dx + \frac{1}{D^2} \int_0^\infty x^{\frac{3}{2}} e^{-2x} dx + \frac{1}{D^3} \int_0^\infty x^{\frac{3}{2}} e^{-3x} dx + \dots
\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{D} \frac{3}{4} \sqrt{\pi} + \frac{1}{D^2} \frac{3}{4} \sqrt{\pi} \frac{1}{2^{5/2}} + \frac{1}{D^3} \frac{3}{4} \sqrt{\pi} \frac{1}{3^{5/2}} + \dots \\
&= \frac{3\sqrt{\pi}}{4} \left[\frac{1}{D} + \frac{1}{D^2} \frac{1}{2^{5/2}} + \frac{1}{D^3} \frac{1}{3^{5/2}} + \dots \right]
\end{aligned}$$

Now equation (6) will be

$$\begin{aligned}
E &= kT \cdot \frac{2g_s Z_t}{\sqrt{\pi}} \frac{3\sqrt{\pi}}{4} \left[\frac{1}{D} + \frac{1}{D^2} \frac{1}{2^{5/2}} + \frac{1}{D^3} \frac{1}{3^{5/2}} + \dots \right] \\
\Rightarrow E &= \frac{3}{2} g_s Z_t kT \left[\frac{1}{D} + \frac{1}{D^2} \frac{1}{2^{5/2}} + \frac{1}{D^3} \frac{1}{3^{5/2}} + \dots \right] \quad \text{--- (9)}
\end{aligned}$$

Now dividing equation (9) by (8), we get:

$$\begin{aligned}
\frac{E}{n} &= \frac{\frac{3}{2} g_s Z_t kT \left[\frac{1}{D} + \frac{1}{D^2} \frac{1}{2^{5/2}} + \frac{1}{D^3} \frac{1}{3^{5/2}} + \dots \right]}{g_s Z_t \left[\frac{1}{D} - \frac{1}{D^2} \frac{1}{2^{3/2}} + \frac{1}{D^3} \frac{1}{3^{3/2}} - \frac{1}{D^4} \frac{1}{4^{3/2}} + \dots \right]} \\
\frac{E}{n} &= \frac{3}{2} kT \frac{\frac{1}{D} \left[1 + \frac{1}{D} \frac{1}{2^{5/2}} + \frac{1}{D^2} \frac{1}{3^{5/2}} + \dots \right]}{\frac{1}{D} \left[1 - \frac{1}{D} \frac{1}{2^{3/2}} + \frac{1}{D^2} \frac{1}{3^{3/2}} - \frac{1}{D^2} \frac{1}{4^{3/2}} + \dots \right]} \\
\Rightarrow \frac{E}{n} &= \frac{3}{2} kT \left[1 + \frac{1}{D} \frac{1}{2^{5/2}} + \frac{1}{D^2} \frac{1}{3^{5/2}} + \dots \right] \times \left[1 - \frac{1}{D} \frac{1}{2^{3/2}} + \frac{1}{D^2} \frac{1}{3^{3/2}} - \frac{1}{D^2} \frac{1}{4^{3/2}} + \dots \right]^{-1} \\
\Rightarrow \frac{E}{n} &= \frac{3}{2} kT \left[1 + \frac{1}{D} \frac{1}{2^{5/2}} + \frac{1}{D^2} \frac{1}{3^{5/2}} + \dots \right] \times \left[1 - \frac{1}{D} \frac{1}{2^{3/2}} + \frac{1}{D^2} \frac{1}{3^{3/2}} - \frac{1}{D^2} \frac{1}{4^{3/2}} + \dots \right] \quad \text{(Using Binomial theorem)} \\
\Rightarrow E &= \frac{3}{2} nkT \left[1 - \frac{1}{D} \frac{1}{2^{3/2}} + \frac{1}{D} \frac{1}{2^{5/2}} + \frac{1}{D^2} \frac{1}{3^{3/2}} + \frac{1}{D^2} \frac{1}{3^{5/2}} + \dots \right]
\end{aligned}$$

The value of α or D can be determined by equation (8), i.e.

$$\begin{aligned}
\Rightarrow n &= g_s Z_t \left[\frac{1}{D} + \frac{1}{D^2} \frac{1}{2^{3/2}} + \frac{1}{D^3} \frac{1}{3^{3/2}} + \frac{1}{D^4} \frac{1}{4^{3/2}} + \dots \right] \\
\Rightarrow n &= g_s \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \cdot V \left[\frac{1}{D} + \frac{1}{D^2} \frac{1}{2^{3/2}} + \frac{1}{D^3} \frac{1}{3^{3/2}} + \frac{1}{D^4} \frac{1}{4^{3/2}} + \dots \right] \quad \text{--- (9.a)}
\end{aligned}$$

For $D \gg 1$; the terms $\frac{1}{D^2}, \frac{1}{D^3}, \frac{1}{D^4}, \dots$ can be neglected

$$\therefore n = g_s \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \cdot V \times \frac{1}{D} \quad \text{--- (9.b)}$$

$$\Rightarrow n = g_s \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \cdot V \times e^{-\alpha} \quad \therefore D = e^{\alpha}$$

$$\therefore e^{-\alpha} = \frac{1}{D} = \frac{1}{g_s} \frac{n}{V} \frac{h^3}{(2\pi mkT)^{\frac{3}{2}}} \quad \text{--- (10)}$$

Here, $\frac{n}{V}$ is the particle density.

This equation (10) is very much essential to understand the degeneracy of Bose – Einstein gas.

Degeneracy of Bose – Einstein Gas:

From equation (10) we found;

$$e^{-\alpha} = \frac{1}{D} = \frac{1}{g_s} \frac{n}{V} \frac{h^3}{(2\pi mkT)^{\frac{3}{2}}}$$

This expression we found when we have considered $D \gg 1$. The above equation can be written as

$$n = g_s \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \cdot V \times \frac{1}{D} \quad (\text{From equation 9.b})$$

Similarly for $D \gg 1$, the equation (9) will be

$$\Rightarrow E = \frac{3}{2} g_s \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \cdot V \times \frac{1}{D} \times kT$$

Now dividing above two equations, we get

$$\frac{E}{n} = \frac{3}{2} kT$$

$$\Rightarrow E = \frac{3}{2} nkT$$