NEED OF QUANTUM STATISTICS :— or Advantages of Q. St. or Limitations of M.B St.

Classical statistics explained successfully many observed phenomenon like temp., pressure etc. alongwith the behaviour of a system like an ideal gas. But it failed to explain certain phenomenon like black body radiation, photoelectric effect, specific heat at low temp. etc. eg.

Consider a hollow enclosure at temp. T, it is said to be filled with radiation characteristic of temp. T. These radiations are called photons and enclosure is said to be filled with photon gas. These photons move about, collide with each other and with the walls of the enclosure. The energy distribution of this photon gas can't be explained by M-B statistics. Sly it fails to explain the energy distribution of e gas. The electronic theory says that the flow of heat energy in a bar is because of the conduction ēs which move freely inside the bar (ie conductor). These ēs form an ē gas. classical st. supposes that energy of the particles varies from 0 to ∞ whereas quantum st. says that energy of the particles can be quantised. All such problems were resolved by quantum statistics which is further divided into two categories —

(i) Bose-einstein (ii) Fermi-dirac Statistics.

(i) Bose-Einstein (BE) Statistics:- The basic assumptions of BE statistics are as under—

(a) The particles are indistinguishable.

(b) Available volume of the phase space cell can't be less than h^3, h → a plank's const.

(c) Any no. of particles can occupy a phase space cell.

(d) The no of phase space cells is comparable with the no. of particles. That is the occupation index $\frac{n_i}{g_i} \ll 1$ or >1

(e) The particles do not obey Pauli's exclusion principle.

Particles which obey B.E statistics are called Bosons eg. photons, mesons, quanta of sound wave.

Q What are Bosons & Fermions
A → The particles whose energy distributed is studied using BE st. and having 0 or integral spins are k/a Bosons.

(ii) Fermi-Dirac Statistic :- The basic assumptions of FD statistics are as under—

(a) The particles of the system are indistinguishable.

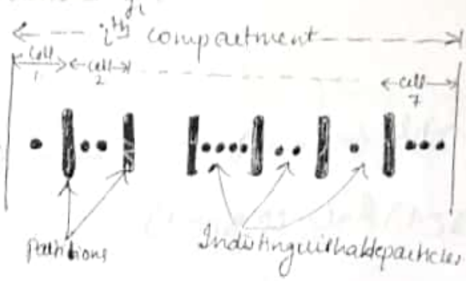
(b) Available volume of the phase space cell can't be less than h^3, h → Plank's const.

(c) A phase space cell can't contain more than one particle.
(d) The no. of phase space cells is large as compared with the no. of particles s.t. the occupation index $\frac{n_i}{g_i} \leq 1$
(e) The particles obey Pauli's exclusion principle.

BOSE EINSTEIN DISTRIBUTION LAW :-

Consider a system of n- bosons. In the most probable macrostate of the system, let $n_1, n_2, n_3, \ldots, n_k$ particles having mean energies $u_1, u_2, u_3, \ldots, u_k$ resp. The phase space can be divided into K- Compartments each corresponding to one energy interval. Then i^{th} compartment contains n_i particles having u_i energy. Let $g_1, g_2, g_3, \ldots, g_k$ be the cells in the compartment numbered 1, 2, 3, ..., k resp. That is the no. of phase space cells in i^{th} compartment is g_i.

Let's place g_i cells in an array (e.g. $g_i = 7$ in fig) and distribute n_i (=13) particles of i^{th} compartment among these cells.



No. of particles $= n_i = 13$
No. of cells, $g_i = 7$
No. of partitions $= 6 = (g_i - 1)$

There are $n_i + g_i$ elements (i.e. the sum of no. of particles + cells, 13+7=20) in the array. Keeping one cell fixed, the rest $(n_i + g_i - 1)$ elements can be arranged in $\lfloor(n_i+g_i-1)$ ways. The selection g_i cells to be kept fixed, it can be done g_i ways as there are g_i cells in all. Hence total no. of ways of distribution are

$$g_i \lfloor(n_i+g_i-1)$$

Since particles are indistinguishable, their arrangement among themselves meaningless. In the similar way, arrangement of g_i cells among themselves is meaningless. Now n_i particles can arrange themselves in $\lfloor n_i$ ways and g_i cells can arrange themselves $\lfloor g_i$ ways. So total no. of meaningless ways are $\lfloor n_i \times \lfloor g_i$

Total No. of arrangements = (Meaningful arrangements) x (No. of meaningless arrangements)

$\Rightarrow$ Meaningful arrangements = $\dfrac{\text{Total no. of arrangements}}{\text{Meaningless arrangements}}$

What are fermions?
The particles whose energy is distributed is studied using FD st. and having $\frac{1}{2}$ integral spins are b/as Fermions

But Meaningful arrangements = Thermodynamic Probability (W)

$$W = \prod_{i=1}^{K} \frac{\lfloor(n_i+g_i-1)\, g_i}{\lfloor g_i \lfloor n_i} = \prod_{i=1}^{K} \frac{g_i \lfloor(g_i+n_i-1)}{g_i \boxed{\lfloor(g_i-1)} \lfloor n_i}$$

$$\Rightarrow \quad W = \prod_{i=1}^{K} \frac{\lfloor(n_i+g_i-1)}{\lfloor(g_i-1) \lfloor n_i}$$

Taking natural logarithm on both sides, we get

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

Applying Stirling's formula $\Rightarrow$ $\underline{\ln \lfloor n = n \ln n - n}$

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

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

$$\Rightarrow \ln W = \sum_{i=1}^{K} \Big[\overbrace{(n_i+g_i-1)}^{u}\, \overbrace{\ln(n_i+g_i-1)}^{v} - (g_i-1)\ln(g_i-1) - n_i \ln n_i \Big]$$

Here $g_i \to$ constt, Diff both sides, we get –

$$d(\ln W) = \sum_{i=1}^{K} \Big[(n_i+g_i-1) \times \frac{dn_i}{(n_i+g_i-1)} + dn_i \ln(n_i+g_i-1) - 0 - n_i \times \frac{1}{n_i} dn_i - dn_i \ln n_i \Big]$$

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

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

Since $n_i >> 1 \Rightarrow \underline{n_i + g_i - 1 \simeq n_i + g_i}$

$\therefore$ eqn (1) can be re-written as

$$d(\ln W) = \sum_{i=1}^{K} \left[\ln(n_i+g_i) - \ln n_i \right] dn_i \longrightarrow (2)$$

for the most probable state, thermodynamic probability is

$$\left[d(\ln W) - \alpha \sum_{i=1}^{k} dn_i - \beta \sum_{i=1}^{k} U_i dn_i = 0 \right] \rightarrow (7)$$

using (2) in (7)

$$\sum_{i=1}^{K} \left[\ln(n_i+g_i) - \ln n_i - \alpha - \beta U_i \right] dn_i = 0$$

Since various dn_i are different for all compartments, thus above eqn is valid only if

$$\ln(n_i+g_i) - \ln n_i - \alpha - \beta U_i = 0$$

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

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

$$\Rightarrow \boxed{n_i = \frac{g_i}{e^{\alpha} \cdot e^{\beta U_i} - 1}} \rightarrow (8)$$

Let $n_U \rightarrow$ the no. of particles per unit energy interval between U and $U+dU$ then

So Writing eq as (8)

$$n_u dU = \frac{g_u}{e^{\alpha} e^{\beta U} - 1} dU \longrightarrow (9)$$

where $g_u \rightarrow$ is the no. of energy levels corresponding to the mean energy state U

But we know $\beta = \frac{1}{kT}$; k → Boltzmann constt. and T → Temperature in kelvin.

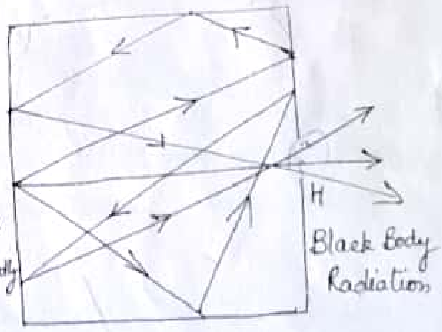
$$\therefore \boxed{n_u dU = \frac{g_u}{e^{\alpha} . e^{U/kT} - 1} dU}$$

This is the expression for Bose-Einstein Distribution of energy law. It gives the distribution of energy among the bosons in the most probable state of the system.

BLACK-BODY RADIATIONS :-

Black-body is a material that absorbs all incident radiation reflecting none. From quantum point of view, a black-body is a material that has many quantized energy levels, spaced over so wide range of energy differences that any photon, whatever its energy is absorbed when incident on it. Since energy absorbed by a material would increase its ~~energy~~ temp. if no energy is emitted, therefore a perfect absorber at a constt. temp. is also a perfect emitter.

A black body that can be achieved in the lab. is a hollow container which is completely closed except for a small hole thro' which radiation can enter or leave as shown in fig.



Any radiation entering the container thro' the hole is absorbed or reflected repeatedly at the inner walls of the container, so all the radiations incident thro' the whole is absorbed in the container.

When the container is maintained at temp. T, the inner walls of the container absorb and emit em radiations at the same rate. These em radiations are in thermal equilibrium with the inner walls and are called black body radiations.

Let $E(\nu)d\nu$ represents the energy per unit volume due to black body radiation having frequencies in the range of ν & $\nu+d\nu$. This is called energy density. The intensity of black body radiations is found to be proportional to the energy density $E(\nu)d\nu$ inside the container. The energy distribution of these radiations is explained by Max-Plank. He used the following assumptions to explain the energy distribution of black body radiations —

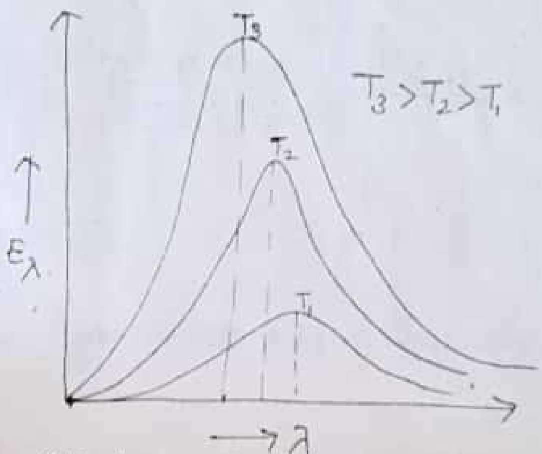
(1) A black-body radiation container is filled up not only with radiation (photon) but also with simple harmonic oscillators of molecular dimensions.

(2) These oscillator absorb or emit energy in quanta of energy $nh\nu$; $n = 1, 2, 3, ---$, $h \rightarrow$ Plank's constt, $\nu \rightarrow$ freq. of oscillator

Let $\lambda \rightarrow$ wavelength and $E_\lambda \rightarrow$ energy corresponding to λ

Then variation of E_λ with λ is shown as below —

It shows that, corresponding to every temp. of the black body radiation, there is a wavelength λ_m for which the emissive power is highest. Also λ_m shifts towards lower values as the temp of the black body is raised.



DERIVATION OF PLANK'S LAW OF RADIATION:—

Max-Plank treated packets of light energy as particles of energy $h\nu$ where $h \rightarrow$ Plank's constt. and ν is the freq. of the radiations and termed them as photons. Bose-Einstein theory is the basis of Plank's law of radiation.

From BE statistics, we know no. of bosons n_u having mean energy U is

$$n_u dU = \frac{g_u}{(e^{\alpha}.e^{U/kT} - 1)} dU \longrightarrow (1)$$

where

$g_u \rightarrow$ is the no. of energy levels corresponding to the mean energy state U.

In case of photon gas, the rest mass of the particle is zero. Photons are continuously absorbed and emitted by the walls of the enclosure, so the no. of photons in the photon gas is not limited. Although the total energy of the photon gas within the enclosure is constt yet the no. of photons may vary.

That is $\sum_{i=1}^{k} n_i = n \neq$ constt

$$\Rightarrow \sum_{i=1}^{k} dn_i \neq 0 \longrightarrow (2)$$

This means that the constraint of constancy of no. of particles does not apply to photon gas. To take this fact into account, we put $\alpha = 0$ in (1), Hence (1) becomes –

$$n_u \, du = \frac{g_u}{e^{u/kT} - 1} du \longrightarrow (3)$$

Since the energy of the photon is quantized and the energy of a photon of frequency ν is given by $u = h\nu \longrightarrow (4)$

using (4) in (1)

$$n_\nu \, d\nu = \frac{g_\nu}{e^{h\nu/kT} - 1} d\nu \longrightarrow (5)$$

$\Rightarrow$ (5) gives the no. of photons or light waves having frequency between ν and $\nu + d\nu$

At any instant, all photons having their momentum between p and $p+dp$ will be within the spherical shell described in momentum space with radii p and $p+dp$. Volume of this shell $= 4\pi p^2 dp$

$\therefore$ Total no. of phase space cells is given by –

$$g_p \, dp = \frac{\text{Volume in position space} \times \text{Vol. in momentum space}}{\text{Vol. of one cell.}}$$

$$\Rightarrow g_p \, dp = \frac{V \times 4\pi p^2 dp}{h^3} \Rightarrow g_p \, dp = \frac{4\pi V p^2 dp}{h^3} \longrightarrow (6)$$

In this derivation, we've assumed that particles are indistinguishable but in case of photons, there are two modes of propagation for each photon. Because of their em nature, they possess polarization. Let's suppose one half of the photons possess right handed polarization and the other half possess left handed polarization. In that case we can say that we are facing two systems in which we have indistinguishable particles. To get exact no. of phase space cells of the whole system, we have to multiply eqn (6) with 2.

$$\therefore g_p dp = 2\,\frac{4\pi V p^2 dp}{h^3} \Rightarrow g_p dp = \frac{8\pi V p^2 dp}{h^3} \longrightarrow (7)$$

for a photon, we know that

$$p = \frac{h\nu}{c} \Rightarrow dp = \frac{h}{c}d\nu \longrightarrow (8)$$

using (8) in (7)

$$g_\nu d\nu = \frac{8\pi V}{h^3}\cdot\frac{h^2\nu^2}{c^2}\cdot\frac{h}{c}d\nu$$

$$\Rightarrow \quad g_\nu d\nu = \frac{8\pi V \nu^2 d\nu}{c^3} \longrightarrow (9)$$

using (9) in (5), we get

$$n_\nu d\nu = \frac{8\pi V \nu^2 d\nu}{c^3}\cdot\frac{1}{e^{h\nu/kT}-1} \longrightarrow (10)$$

If $E_\nu d\nu$ denotes the energy density ie amount of energy per unit volume lying between the frequencies ν and $\nu+d\nu$ then,

$$E_\nu d\nu = h\nu\left(\frac{n_\nu d\nu}{V}\right) \rightarrow (11)$$

using (10) in (11)

$$E_\nu d\nu = \frac{h\nu}{V}\cdot\frac{8\pi V \nu^2 d\nu}{c^3}\cdot\frac{1}{e^{h\nu/kT}-1}$$

$$\Rightarrow \boxed{E_\nu d\nu = \frac{8\pi h}{c^3}\,\frac{\nu^3 d\nu}{e^{h\nu/kT}-1}} \rightarrow (A)$$

This is PLANK'S LAW FOR BLACK-BODY-RADIATION in terms of frequency of the radiation.

Plank's Law in terms of wavelength (λ):-

We know, $c = \nu\lambda \Rightarrow \nu = \frac{c}{\lambda} \Rightarrow d\nu = -\frac{c}{\lambda^2}d\lambda$

$\therefore$ eqn (A) becomes

$$E_\lambda d\lambda = \frac{8\pi h}{\cancel{c^3}}\cdot\frac{\cancel{c^3}}{\lambda^3}\left(-\frac{c}{\lambda^2}d\lambda\right)\times\frac{1}{e^{h\nu/kT}-1}$$

or $$\boxed{E_\lambda d\lambda = +\frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{hc/\lambda kT}-1}} \longrightarrow (B)$$ (magnitude only)

which is plank's law of radiation in terms of wavelength.

For small wavelength $e^{hc/\lambda kT} >> 1$.

$\therefore E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} d\lambda$

or $E_\lambda d\lambda = 8\pi hc \lambda^{-5} e^{-hc/\lambda kT} d\lambda$

$\Rightarrow E_\lambda d\lambda = C_1 \lambda^{-5} e^{-C_2/kT} d\lambda$

where $C_1 = 8\pi hc$, $C_2 = -hc/\lambda$ are constts.

It's called Wein's distribution law.

RAYLEIGH JEAN'S LAW:-

for longer wavelength, $e^{hc/\lambda kT} << 1$ So

$e^{hc/\lambda kT} \simeq 1 + \frac{hc}{\lambda kT}$

(B) becomes $E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{\left(1+\frac{hc}{\lambda kT}\right)-1}$

or $E_\lambda d\lambda = \frac{8\pi \cancel{hc}}{\lambda^5} \cdot \frac{\lambda kT}{\cancel{hc}} d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$

$\Rightarrow \boxed{E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda}$ is called Rayleigh Jean's law.

DEDUCTION OF WEIN'S DISPLACEMEN LAW FROM PLANCK'S LAW:-

According to Wein's displacement law, the wavelength (λ_m) corresponding to maximum energy is inversely proportional to the absolute temp. (T) of the body. i.e

$\lambda_m \propto \frac{1}{T} \Rightarrow \lambda_m T = \text{constt}$

$\Rightarrow \boxed{\lambda_m T = b}$ where $b = 0.2898\,\text{cm K}$ is Wein's constt.

This is wein's displacement law. It is so called because rise in temp. displaces the wavelength towards shorter λ.

This law can be proved from Plank's law as follows—

10

According to Planck's law,

$$E_\lambda d\lambda = -\frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{hc/\lambda kT}-1}$$

for E_λ to be maximum, $\frac{d}{d\lambda}(E_\lambda)=0$

i.e. $$\frac{d}{d\lambda}\left[-\frac{8\pi hc}{\lambda^5}\cdot\frac{1}{e^{hc/\lambda kT}-1}\right]=0$$

$$\Rightarrow -8\pi hc\,\frac{d}{d\lambda}\left[\lambda^{-5}\left(e^{hc/\lambda kT}-1\right)^{-1}\right]=0$$

$$\Rightarrow -8\pi hc\left[-5\lambda^{-6}\left(e^{hc/\lambda kT}-1\right)^{-1}+\lambda^{-5}(-1)\left(e^{hc/\lambda kT}-1\right)^{-2}\left(-\frac{hc}{\lambda^2 kT}\right)e^{hc/\lambda kT}\right]=0$$

$$\Rightarrow -8\pi hc\left[\frac{-5}{\lambda^6\left(e^{hc/\lambda kT}-1\right)}+\frac{hc\,e^{hc/\lambda kT}}{\lambda^7 kT\left(e^{hc/\lambda kT}-1\right)^2}\right]=0$$

$$\Rightarrow \frac{hc\,e^{hc/\lambda kT}}{\lambda^7 kT\left(e^{hc/\lambda kT}-1\right)^2}=\frac{5}{\lambda^6\left(e^{hc/\lambda kT}-1\right)}$$

$$\Rightarrow \frac{hc}{\lambda kT}\frac{e^{hc/\lambda kT}}{\left(e^{hc/\lambda kT}-1\right)}=5 \longrightarrow (12)$$

when $\lambda=\lambda_m$, (12) becomes

$$\frac{hc}{\lambda_m kT}\frac{e^{hc/\lambda_m kT}}{\left(e^{hc/\lambda_m kT}-1\right)}=5$$

Put $\frac{hc}{k}=x \longrightarrow (13)$ & $\lambda_m T=b \longrightarrow (14)$, we get

$$\frac{x}{b}\cdot\frac{e^{x/b}}{\left(e^{x/b}-1\right)}=5 \Rightarrow \frac{x}{b}=\frac{5\left(e^{x/b}-1\right)}{e^{x/b}}=5\left(1-e^{-x/b}\right)$$

$\Rightarrow \frac{x}{b}\simeq 5$ but exact value is 4.9651

$\therefore \frac{x}{b}=4.9651 \Rightarrow b=\frac{x}{4.9651}=\frac{hc}{4.9651\,k}$ (using (13))

$\Rightarrow b=0.2892\text{ cm K} \longrightarrow (15)$

using (15) in (14)

$\lambda_m T=b=0.2898\text{ cm K}.$

which is Wein's displacement law.