Illustration

greater *i.e.*, good emitters of radiation are

If a polished metal ball with a spot of a platinum black

and taken to a dark room, then it is found that the dark spot being a good

If a piece of red glass is heated in an electric furnace and then taken out, it will glow emitting green light. The reason is that, in white light, red glass appears red because it absorbs green light (red and green being complementary colours) and therefore, from Kirchhoff's law it would emit green light when heated.

The best-known illustration of Kirchoff's law is the famous line reversal experiment of Kirchhoff's and Bunsen. A source of white light is viewed through a sodium flame by means of a spectroscope. Two fine dark lines are observed in the continuous spectrum in exactly the same position in the spectrum as the bright yellow lines emitted by sodium. As the sodium source emits only these two lines hence e_λ is larger for these lines only and for other wavelengths $e_\lambda = 0$. Thus a_λ is large for these two lines for the sodium source and when white light is passed through the sodium flame then absorption of these lines occurs while other wavelengths pass because a_λ for them is zero.

The most striking application of Kirchhoff's law was made in the explanation of Fraunhofer lines. He assumed that the sun consists of glowing mass (giving the continuous spectrum) surrounded by a cooler atmosphere which contains elements like hydrogen, nitrogen, sodium, cesium, copper etc. in the gaseous state. When radiation from the central mass passes through the surrounding atmosphere, the elements, present there absorb those wavelength which they can emit at a higher temperature. As a result, these wavelengths are missing from the sun spectrum and we see dark lines in their place. In this way Kirchhoff's law established *that atoms of each element give a spectrum which is characteristic of that element alone.*

B–5. BLACK BODY RADIATION :

When radiant energy falls on a body, a part of it is reflected, a part continues into the interior of the body and is absorbed, and the third part is transmitted by the body. A *body whose absorptivity is unity for all wavelengths is called an ideal black body or simply a black body* or we can say that a *body which absorbs all the incident radiations completely, irrespective of wavelength falling on it, reflecting none and transmitting none is called a black body*. The other characteristic of such a body is that when heated to a suitable high temperature it emits total radiation. A black body is only an ideal conception and Lamp black is the nearest approach to such a body (Lamp black reflects about 1% of the incident radiation). Platinum black is another such a body.

It is found that *as the temperature of a body is raised, the colour emitted by it becomes richer in waves of shorter length*. For example, the colour of blackened platinum appears dull red at about 525°C, cherry red at about 900°C, orange red at 1100°C, yellow 1250°C and white at about 1600°C. The problem of distribution of energy among the wavelengths emitted by black body, when heated to different temperatures, was investigated by Lummer and Pringsheim in 1899. They used an electrically heated chamber with a small aperture as black body whose temperature was measured by a thermocouple. The arrangement is shown in figure 3. S is a slit placed at the focal plane of concave mirror M_1. Hence radiation from a black body was reflected as a parallel beam from this mirror. Radiations are dispersed by a prism P of rock salt or fluorspar placed on the turn table of a spectrometer. They are now focused on the bolometer with the help of another cancave mirror M_2. The bolometer is connected to a sensitive galvanometer. The turn table is rotated slowly so that each part of the spectrum is focused successively on the bolometer and *the deflection of the galvanometer is proportional to the intensity of each line.*

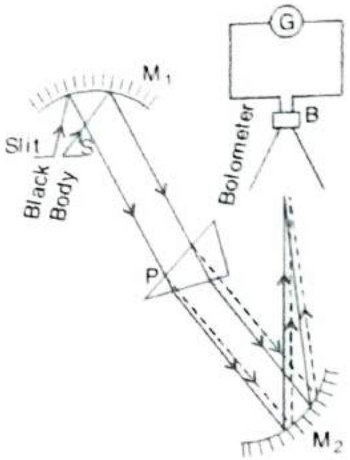

Fig. 3.

The wavelength at different portions of the spectrum was calculated by the formula for the dispersion of the material of the prism. By determining the intensity for various wavelengths in the whole spectrum of black body radiation, a graph is drawn between intensity and wavelength. The body was raised to different temperatures and the distribution curve for each was drawn. The results are shown in fig. 4. It is observed that :

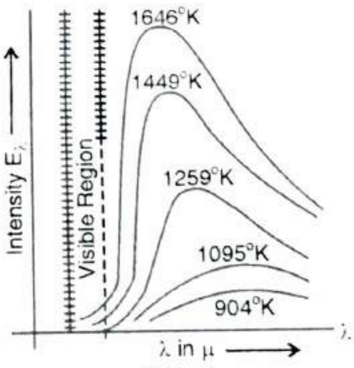

Fig. 4.

(i) as the temperature of the body rises, the intensity of radiation for each wavelength increases.

(ii) for any one temperature, energy is distributed continuously among the various wavelengths and is maximum for a particular wavelength. *The point of maximum energy shifts towards the shorter wavelengths as the temperature increased.*

(iii) the total energy of radiation for given temperature is represented by the area between the curve and the horizontal axis. *The area increases according to the fourth power of absolute temperature.*

B–6. STEFAN BOLTZMANN LAW :

According to Stefan's law, the total amount of heat radiated by a perfectly black body per second per unit area is directly proportional to the fourth power of its absolute temperature,

i.e., $$E \propto T^4 \qquad \text{or} \qquad E = \sigma T^4,$$

where σ is a constant, called the Stefan's constant. This law is sometimes also called as Stefan's fourth power law.

In the above form, this law refers only to the emission and not to the net loss. If a black body A at absolute temperature T is surrounded by another black body B at absolute temperature T_0, then

amount of heat lost by black body $A = \sigma T^4$

amount of heat absorbed by black body A from black body $B = \sigma T_0^4$

so net amount of heat lost by A per second per unit area $= \sigma(T^4 - T_0^4)$

This is also known as *Stefan Boltzmann law.*

Thermodynamic Proof : Suppose the radiation is enclosed in an evacuated cylinder with perfectly reflecting walls and perfectly reflecting moving piston. The object of assuming perfectly reflecting walls is to avoid heat exchange between the walls and the radiation otherwise the thermal capacity of walls will come in the calculation.

Let u = energy density (energy per unit volume) of the radiation inside the cylinder
V = volume of the cylinder
P = pressure of radiations

$\therefore$ Total energy of radiation = energy per unit volume × volume

$$U = u \times V \quad \ldots(1)$$

According To Maxwell's electromagnetic theory of radiation, the pressure p exerted by radiation is given by

$$p = \frac{1}{3}u \quad \ldots(2)$$

Let us suppose that a small amount of heat dQ is brought into the cylinder and at the same time the volume is changed by an amount dV. If dU is the change in the internal energy of radiation and dW the external work done, then according to first law of thermodynamics,

$$\begin{aligned} dQ &= dU + dW \\ &= dU + p\,dV. \end{aligned} \quad \ldots(3)$$

From equations (1) and (2) substituting the values of U and p in equation (3), we have

$$\begin{aligned} dQ &= d(uV) + \frac{1}{3}u\,dV \\ &= u\,dV + V\,du + \frac{1}{3}u\,dV \\ &= \frac{4}{3}u\,dV + V\,du. \end{aligned}$$

According to second law of thermodynamic, we get

$$dQ = T\,dS$$

so that

$$T\,dS = \frac{4}{3}u\,dV + V\,du$$

or

$$dS = \frac{4}{3}\cdot\frac{u}{T}\,dV + \frac{V}{T}du. \quad \ldots(4)$$

Considering S as a function of (V, u) *i.e.*, $S = f(V, u)$, we have

$$dS = \left(\frac{\partial S}{\partial V}\right)dV + \left(\frac{\partial S}{\partial u}\right)du. \quad \ldots(5)$$

Comparing equations (4) and (5), we have

$$\left(\frac{\partial S}{\partial V}\right) = \frac{4}{3}\cdot\frac{u}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial u}\right) = \frac{V}{T}.$$

Again

$$\frac{\partial^2 S}{\partial u.\partial V} = \frac{\partial^2 S}{\partial V.\partial u}$$

i.e.,

$$\frac{\partial}{\partial u}\left(\frac{\partial S}{\partial V}\right)=\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial u}\right)$$

$$\frac{\partial}{\partial u}\left(\frac{4}{3}\cdot\frac{u}{T}\right)=\frac{\partial}{\partial V}\left(\frac{V}{T}\right)$$

$$\frac{4}{3}\cdot\frac{1}{T}-\frac{4}{3}\cdot\frac{u}{T^2}\cdot\frac{\partial T}{\partial u}=\frac{1}{T}$$

$$\frac{1}{3}\cdot\frac{1}{T}=\frac{4}{3}\cdot\frac{u}{T^2}\cdot\frac{\partial T}{\partial u}.$$

$$\frac{\partial u}{u}=4\frac{\partial T}{T}.$$

Integrating

$$\log u = 4\log T + a$$

or

$$u = aT^4,$$

where a is the integration constant.

We know that the energy E radiated per second per unit area from a perfectly black body at absolute temperature T, and the energy of radiation u inside an enclosure at the same temperature, are related by

$$E=\frac{1}{4}uc,$$

where c is velocity of light.

Substituting the value of u in this expression

$$E=\frac{1}{4}acT^4$$

$$E=\sigma T^4.$$

where $\sigma=\frac{1}{4}ac$ and is called Stefan's constant. This is Stefan's law.

Ex. 1. *A black body at* 500°C *has a surface area of* $0.5\,\text{m}^2$ *and radiates heat at the rate of* 1.02×10^4 J/s. *Calculate Stefan's constant.*

According to Stefan's law, the total heat radiated per second by a black body of surface area A and at temperature T K is given by

$$u=\sigma AT^4 \quad \text{or} \quad \sigma=\frac{u}{AT^4}$$

Substituting the given values, we get

$$\sigma=\frac{1.02\times10^4\ \text{joule/sec}}{0.5\ \text{m}^2\times(773\ \text{K})^4}$$

$$=5.7\times10^{-8}\,\text{joule}\,(\text{m}^2\text{-sec.K}^4)$$

B–7. WIEN'S DISPLACEMENT LAW :

When radiation from a black body is passed through a prism, a continuous spectrum is obtained in which the intensity of radiation in different parts of the spectrum is different. The energy is distributed in various wavelengths varying from zero to infinity. The law that connects the intensity with wavelength is known as the law of distribution of intensity of black body

B–8. PLANCK'S RADIATION LAW :

Planck's quantum hypothesis : Wien displacement law and Rayleigh Jeans formula could not explain the entire shape of the curves giving the energy distribution in black body radiation. To explain the entire shape, Planck, in the beginning imagined that a black radiation chamber is filled up not only with radiation, but also with the molecules of a perfect gas. This time he assumed that the exchange of energy can not take place between radiation and gas molecules and hence introduced the idea of resonator of molecular dimension as *via* media between radiation and gas molecules. The resonators absorb energy from radiation and transfer partly or wholly to the molecules when they collide with them. These resonators were supposed to be responsible for the emission of radiation. They could have all possible values of energy and their number is determined by Maxwell Boltzmann distribution law. The distribution law thus derived comes to be the same as given by Rayleigh and Jeans. Planck therefore, gave a new revolutionary idea which laid the foundation of the modern quantum theory.

According to quantum theory, the exchange of energy by resonators does not take place continuously but discontinuously and *discretely* as an integral multiple of small unit of energy called the quantum or we can say that the resonators will emit energy only when the energy absorbed is a certain minimum quantity ε or integral multiple of ε. Thus a resonator which has an energy $(r + p)\ \varepsilon$ [r = whole number, $p = a$ fraction] will remain quiescent until the energy absorbed amounts to $(r + 1)\ \varepsilon$ when the energy ε may be emitted and resonator may revert back to the state with the energy $r\ \varepsilon$. Thus the resonator can vibrate with integral energy $0, \varepsilon, 2\ \varepsilon \ldots n\varepsilon$. On this basis the law of thermal radiation was derived.

Number of resonators per unit volume lying in the frequency range ν and $\nu + d\nu$: In accordance with the electromagnetic theory, the radiation is supposed to consist of a number of waves. If we consider the radiation to be enclosed in a box then the waves in the box travel in all possible directions and undergo multiple reflections from the various walls of the box. A reflected wave interferes with the corresponding incident one to form stationary waves with walls as nodal planes. The formation of stationary waves can be understood by an analogy with the vibrations of a stretched string with fixed end points. As we know that, in this case, only certain discrete frequencies of vibration are followed. The end points of the string are two nodes of the stationary vibrations. If L be the length of the string then allowed wavelengths are

$$\lambda = \frac{2L}{n};\ n = 1, 2, 3, \ldots\ldots \infty$$

Correspondingly, the allowed frequencies are

$$\nu = \frac{c}{\lambda} = \frac{nc}{2L};\ n = 1, 2, 3, \ldots \infty$$

where c is the speed of the waves.

Every allowed frequency is called a mode of vibration. We can calculate the allowed modes of vibration inside the cube (of volume L^3) just as in the case of string for which the analysis is to be extended to three dimensions. The wave equation in one dimension is

$$\frac{\partial^2 u^*}{\partial x^2} = \frac{1}{c^2} \cdot \frac{\partial^2 u^*}{\partial t^2}, \qquad \ldots(1)$$

where $u^*(x, t)$ represents the displacement of the string at a distance x at any instant t and c is the velocity of wave propagation. The solution of above equation (1) is given by

$$u^*(x,t) = A \sin\left(\frac{n\pi x}{L}\right) \cos 2\pi \nu_n t, \qquad \ldots(2)$$

where L be the length of the string between fixed ends and let n be positive integer greater than or equal to 1. The wavelengths and frequencies are given by

$$\lambda_n = \frac{2L}{n} \quad \text{and} \quad \nu_n = \frac{c}{\lambda_n} = \frac{nc}{2L}.$$

The number of possible modes of vibration in frequency interval $d\nu$ is given by

$$dn = \left(\frac{2L}{c}\right) d\nu. \qquad \text{...(3)}$$

Extending the above case to three dimensions, the wave equation is

$$\frac{\partial u^*}{dx^2} + \frac{\partial^2 u^*}{\partial y^2} + \frac{\partial^2 u^*}{\partial z^2} = \frac{1}{c^2} \cdot \frac{\partial^2 u^*}{\partial t^2}, \qquad \text{...(4)}$$

then its solution will be

$$u^*(x, y, z, t) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y xy}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \cos 2\pi \nu t \qquad \text{...(5)}$$

where n_x, n_y and n_z are greater than or equal to 1.

Substituting equation (5) into equation (4), we get

$$\left(\frac{\pi^2}{L^2}\right)\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{4\pi^2 \nu^2}{c^2}$$

or

$$n_x^2 + n_y^2 + n_z^2 = \frac{4L^2 \nu^2}{c^2}. \qquad \text{...(6)}$$

From equation (6) it is obvious that in three-dimensional cases the wavelengths and frequencies are determined by three integers n_x, n_y and n_z. Each choice of n_x, n_y and n_z corresponds to a particular mode of vibration (frequency). The total number of frequencies is the total number of possible sets of n_x, n_y and n_z. The number of modes of vibration within frequency interval ν and $\nu + d\nu$ can be found with the help of equation (6).

It can be shown that the number of modes within the frequency range ν to $\nu + d\nu$ is the volume of an octant $\left(\frac{1}{8}\text{th}\right)$ of spherical shell with radii equal to

$$\frac{2L\nu}{c} \quad \text{and} \quad \frac{2L(\nu + d\nu)}{c}.$$

This volume is

$$\frac{1}{8} \cdot 4\pi r^2 dr = \frac{1}{8} \cdot 4\pi \left(\frac{2L\nu}{c}\right)^2 \frac{2L d\nu}{c}$$

$$= \frac{4\pi L^3 \nu^2}{c^3} d\nu.$$

But L^3 is the volume V of the cube. Therefore the number of mod inside the cubical enclosure is

$$= \frac{4\pi V \nu^2}{c^3} d\nu \cdot$$

Since electromagnetic waves are transverse waves, there are two possible polarizations for each mode. Therefore, for radiation, total number of modes of vibration (or frequencies) between ν and $\nu + d\nu$ is

$$= 2 \times \frac{4\pi V \nu^2}{c^3} d\nu$$

$$= \frac{8\pi V \nu^2}{c^3} d\nu. \qquad \text{...(7)}$$

Derivation of law : Using the laws of probability the average energy for resonator can be estimated as follows :

According to the laws of probability, the modes of vibration associated with resonators having energies 0, ε, 2ε,..... $n\varepsilon$ are in proportion

$$e^{-0\varepsilon/E_0},\ e^{-\varepsilon/E_0},\ e^{-2\varepsilon/E_0}, e^{-3\varepsilon/E_0} \text{....... etc.}$$

that is $$1,\ e^{-\varepsilon/E_0}, e^{-2\varepsilon/E_0}, e^{-3\varepsilon/E_0} \text{...... etc.}$$

where E_0 is an arbitrary constant.

Let N = number of resonators with zero quantum energy

M = total number of modes of vibration,

then
$$M = N + Ne^{-\varepsilon/E_0} + Ne^{-2\varepsilon/E_0} + ...$$

$$= N\left[1 + e^{-\varepsilon/E_0} + e^{-2\varepsilon/E_0 + ...}\right] \qquad \text{...(8)}$$

$$= \frac{N}{1 - e^{-\varepsilon/E_0}}$$

since $\left[1 + e^{-\varepsilon/E_0} + e^{-2\varepsilon/E_0} ....\right]$ represents an infinite geometric progression.

Total energy E of all the M modes will be

$$E = N \times 0 + \varepsilon \times Ne^{-\varepsilon/E_0} + 2\varepsilon \times Ne^{-2\varepsilon/E_0} + 3\varepsilon \times Ne^{-3\varepsilon/E_0} + ...$$

$$= N\varepsilon e^{-\varepsilon/E_0}[1 + 2e^{-\varepsilon/E_0} + 3e^{-2\varepsilon/E_0} + ... + \infty]$$

$$= N\varepsilon e^{-\varepsilon/E_0}\left[\frac{1}{\left(1 - e^{-\varepsilon/E_0}\right)^2}\right]. \qquad \text{...(9)}$$

Putting the value of N in terms of M from equation (8), we have

$$E = \frac{M\,[1 - e^{-\varepsilon/E_0}]\,\varepsilon e^{-\varepsilon/E_0}}{(1 - e^{-e/E_0})^2} = \frac{M\varepsilon e^{-\varepsilon/E_0}}{(1 - e^{-\varepsilon/E_0})} \qquad \text{...(10)}$$

The mean energy of the resonator is given by

$$\overline{U} = \frac{E}{M} = \frac{\varepsilon e^{-e/E_0}}{\left(1 - e^{-\varepsilon/E_0}\right)} \qquad \text{[from equation (10)]}$$

$$= \frac{\varepsilon}{\left(e^{\varepsilon/E_0} - 1\right)}. \qquad \text{...(11)}$$

According to kinetic theory $E_0 = kT$. Then eq. (11) is

$$\overline{U} = \frac{\varepsilon}{e^{\varepsilon/kT} - 1} \qquad \text{...(12)}$$

Comparing expression (12) with Wien's displacement law, we see that E must be proportional to ν; we write $\varepsilon = h\nu$ where h is called the Planck's constant, giving

$$\overline{U} = \frac{h\nu}{\left(e^{h\nu/kT} - 1\right)}$$

Using the classical statistics, he deduced that

$$u_\nu \, d\nu = \frac{8\pi\nu^2}{c^3} d\nu \, \overline{U}_\nu .$$

where u_ν is density of ν radiation, and $\overline{U}_\nu$ is mean energy of resonator emitting ν radiation.

Therefore
$$u_\nu d\nu = \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{\left(e^{h\nu/kT} - 1\right)} d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{\left(e^{h\nu/kT} - 1\right)} \cdot \qquad \text{...(13)}$$

We know that

$$\nu = \frac{c}{\lambda} \qquad \text{or} \qquad d\nu = -\frac{c}{\lambda^2} d\lambda$$

so that
$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{ch/\lambda kT} - 1}, \qquad \text{...(14)}$$

which is Planck's law.

For short wavelengths $e^{hc/\lambda kT}$ becomes large compared to unity so that Planck's formula reduces to

$$\begin{aligned} u_\lambda d\lambda &= \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{ch/kT\lambda}} \\ &= 8\pi hc\lambda^{-5} e^{-ch/kT\lambda} \times d\lambda \\ &= A\lambda^{-5} e^{-a/\lambda T} . d\lambda \end{aligned}$$

where A and a are constants.

$$u_\lambda d\lambda = A\lambda^{-5} e^{-a/\lambda T} . d\lambda$$

which is Wien displacement law.

Ex. 1. *Calculate the average energy of an oscillator of frequency* 5.6×10^{12} *second at* $T = 330$ K, *treating it as (i) classical oscillator, (ii) Planck's oscillator.*

The average energy of a classical oscillator is given by

$$\begin{aligned} kT &= (1.380 \times 10^{-23}) \times 330 \\ &= \mathbf{4.554 \times 10^{-21}} \textbf{ joule.} \end{aligned}$$

The average energy of Planck's oscillator is given by $\dfrac{h\nu}{\left(e^{h\nu/kT} - 1\right)}$

$$= \frac{(6.626 \times 10^{-34}) \times (5.6 \times 10^{12})}{\left\{ \exp. \left(\dfrac{6.626 \times 10^{-34}}{1.380 \times 10^{-23} \times 330} \right) - 1 \right\}}$$

$$= \mathbf{2.9450 \times 10^{-21}} \textbf{ joule.}$$

B–9. RAYLEIGH JEAN'S LAW :

The deduction of Rayleigh's formula for the distribution of energy in the normal spectrum has been done by assuming that the energy is equally divided among all the possible modes of

CHAPTER

9

IDEAL FERMI DIRAC GAS

In Fermi-Dirac distribution, we consider a system of *identical, independent, non-interacting particles* sharing a common volume and obeying antisymmetrical statistics so that the spin is *half-integral* (**fermions**) and then according to the Pauli principle, the *total wave function is antisymmetrical* on interchange of any two particles.

9•0. ENERGY AND PRESSURE OF THE GAS :

Particles with half-integral spin like electrons, protons and neutrons are fermions that obey Fermi-Dirac Statisitcs. The general expression for the most probable distribution-in-energy for the Fermi-Dirac gas is,

$$n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}+1}, \text{ (Eq. 12 art 6.3)}$$

which, on putting $D = e^{\alpha}$, is of the form

$$n_i = \frac{g_i}{De^{\beta\varepsilon_i}+1} \qquad \dots (1)$$

Since in the denominator factor +1 occurs, α need not be restricted to positive value only but may assume negative value as well *unlike* Bose Einstein gas.

The number of one particle states lying between momentum p and $(p + dp)$ is determined from

$$g_p = g_s \frac{(4\pi/3).p^3}{h^3/V}, \text{ (Eq. 1 art 6.10)}$$

giving

$$g_p dp = g_s \frac{4\pi V p^2 dp}{h^3}, \qquad \dots (2)$$

where $g_s = (2s+1)$ is the spin degeneracy factor (arising due to the spin, s, of the fermions).

Since $\varepsilon = p^2/2m$ and $dp = \frac{1}{2}\sqrt{(2m/\varepsilon)}\,.\,d\varepsilon$, the number of states in the energy range between ε and $(\varepsilon + d\varepsilon)$ will be, on using equation (2),

$$g(\varepsilon)\,d\varepsilon = g_s \frac{4\pi V}{h^3}.2m\varepsilon\,.\,\sqrt{(m/2\varepsilon)}\,.\,d\varepsilon, \qquad \dots (3)$$

where $g(\varepsilon)$ is termed as *density of states function*.

From equations (1) and (3) we get the number of particles in the energy range between ε and $(\varepsilon + d\varepsilon)$, as

$$dn(\varepsilon) = g_s \frac{4\pi m V}{h^3}.\sqrt{(2m)}.\frac{\varepsilon^{1/2} d\varepsilon}{De^{\varepsilon/kT}+1} \qquad \ldots (4)$$

where we have substituted $\beta = \dfrac{1}{kT}$.

Let us put $x = \varepsilon / kT$,

and $dx = d\varepsilon / kT$.

equation (4) then becomes

$$dn = g_s.\frac{4\pi m V}{h^3}.\sqrt{(2m)}.\frac{x^{1/2} dx\,(kT)^{3/2}}{De^x+1}$$

$$= g_s.\frac{2}{\sqrt{\pi}}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V.\frac{x^{1/2}dx}{De^x+1}$$

From the thermodynamic properties of diatomic molecules, we note that translational partition function is

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

It follows then

$$dn = \frac{2g_s Z_t}{\sqrt{\pi}}\frac{x^{1/2}dx}{De^x+1}.$$

Therefore total number of particles

$$n = \int dn = \frac{2g_s Z_t}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}dx}{De^x+1}. \qquad \ldots (5)$$

and energy

$$E = \int \varepsilon\, dn = kT \int x\, dx.$$

$$= kT.\frac{2g_s Z_t}{\sqrt{\pi}}\int_0^\infty \frac{x^{3/2}dx}{De^x+1}. \qquad \ldots (6)$$

We shall evaluate the integrals in equations (5) and (6) for both values of α, *i.e.*, when α is positive and again when it is negative. When α is positive, D is greater than one and the condition so obtained is referred to as slight or *weak degeneracy*. Condition corresponding to α negative *i.e.*, D less than one is referred to as *strong degeneracy*.

(A) Case of Slight Degeneracy :

For this case, integral in equation (5) can be expressed as

$$\int_0^\infty \frac{x^{1/2}dx}{De^x+1} = \int_0^\infty x^{1/2}dx.\frac{e^{-x}}{D}\left(1+\frac{e^{-x}}{D}\right)^{-1}$$

$$= \int_0^\infty x^{1/2}dx.\frac{e^{-x}}{D}\left[1-\frac{e^{-x}}{D}+\frac{e^{-2x}}{D^2}-\ldots\right]$$

$$= \frac{1}{D}\int_0^\infty x^{1/2}e^{-x}dx - \frac{1}{D^2}\int_0^\infty x^{1/2}e^{-2x}dx + \frac{1}{D^3}\int_0^\infty x^{1/2}e^{-3x}dx - \ldots$$

$$= \frac{\sqrt{\pi}}{2D}\left[1 - \frac{1}{2^{3/2}D} + \frac{1}{3^{3/2}D^2} - \dots\right],$$

so that total number of particles is given by

$$n = \frac{g_s Z_t}{D}\left(1 - \frac{1}{2^{3/2}D} + \frac{1}{3^{3/2}D^2} - \dots\right). \qquad \dots (7)$$

Further, the integral in equation (6) can be solved as follows :

$$\int_0^\infty \frac{x^{3/2}dx}{De^x + 1} = \frac{1}{D}\int_0^\infty x^{3/2}e^{-x}dx - \frac{1}{D^2}\int_0^\infty x^{3/2}e^{-2x}dx + \dots$$

$$= \frac{3\sqrt{\pi}}{4D}\left(1 - \frac{1}{2^{5/2}D} + \frac{1}{3^{5/2}D^2} - \dots\right)$$

so that the total energy is given by

$$E = \frac{3g_s Z_t}{4D}.kT\left(1 - \frac{1}{2^{5/2}D} + \frac{1}{3^{5/2}D^2} - \dots\right) \qquad \dots (8)$$

Putting the value of $g_s Z_t$ from equation (7) into equation (8), we get

$$E = \frac{3}{2}nkT\left(1 - \frac{1}{2^{5/2}D} + \frac{1}{3^{5/2}D^2} - \dots\right)\left(1 - \frac{1}{2^{3/2}D} + \frac{1}{3^{3/2}D^2}\right)^{-1}$$

$$= \frac{3}{2}nkT\left(1 + \frac{1}{2^{5/2}D} - \frac{1}{3^{5/2}D^2} + \dots\right),$$

which assumes the form

$$E = \frac{3}{2}nkT\left[1 + \frac{1}{2^{5/2}}\left(\frac{n}{g_s Z_t}\right) - \frac{1}{3^{5/2}}\left(\frac{n}{g_s Z_t}\right)^2 + \dots\right], \qquad \dots (9)$$

after putting $D = \frac{g_s Z_t}{n}$ from equation (7) which has been approximated only upon the first term of the expansion.

The pressure of the ideal Fermi gas can now be obtained by the relation

$$P = -\left(\frac{\partial E}{\partial V}\right)_{T,\,S}$$

$$= \frac{2E}{V}$$

$$= \frac{nkT}{V}\left[1 + \frac{1}{2^{5/2}}\left(\frac{n}{g_s Z_t}\right) - \frac{1}{3^{5/2}}\left(\frac{n}{g_s Z_t}\right)^2 + \dots\right], \qquad \dots (10)$$

in which $nk = R$, for one mole of the ideal Fermi gas.

We infer from equations (9) and (10), that ideal Fermi gas deviates from perfect gas behaviour and this deviation, as we know, is called *degeneracy*. Obviously, degeneracy is a function of $\frac{1}{D}$ or e^{-x}. Smaller is the value of D or greater the value of $\frac{1}{D}$, more marked will be the degeneracy.

(B) Case of Strong Degeneracy :

When α is large and negative, $e^{-\alpha} >> 1$ or D is much less than one. This increases the value of $\frac{1}{D}$ and hence the degeneracy will become more prominent. Further

$$\frac{1}{D} \simeq \frac{n}{g_s Z_t}, \text{ from equation (7),}$$

$$= \frac{n}{g_s} \cdot \frac{h^3}{(2\pi m\, kT)^{3/2} V}, \qquad \text{... (11)}$$

which shows that a gas will be highly degenerate at low temperature and high density $\left(\frac{n}{V}\right)$. We shall discuss this case of strong degeneracy at two temperature ranges : firstly when $T = 0$, *i.e.*, at absolute zero and secondly when temperature is above absolute zero but degeneracy is still considerably high *i.e.*, D is still less than unity.

(i) **At T = 0** : From equation (11) we note that when $T = 0$, $D = 0$ so that equation (5) assumes the form

$$n = \frac{2g_s Z_t}{\sqrt{\pi}} \int_0^{\infty} x^{1/2} dx$$

Since $D = 0$, we can replace the upper limit by $1/D$. Therefore

$$n = \frac{2g_s Z_t}{\sqrt{\pi}} \int_0^{1/D} x^{1/2} dx = \frac{2g_s Z_t}{\sqrt{\pi}} \cdot \frac{2}{3D^{3/2}} \qquad \text{... (12)}$$

which gives

$$\frac{1}{D} = \left(\frac{3n\, \pi^{1/2}}{4g_s Z_t}\right)^{2/3}$$

with

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

we find that

$$\frac{1}{D} = \frac{h^2}{2mkT}\left(\frac{3n}{4\pi V g_s}\right)^{2/3}, \qquad \text{... (13)}$$

which is a measure of degeneracy of the ideal Fermi gas at $T = 0$.

From equation (6) we can obtain the energy of the Fermi gas at absolute zero. Putting E as E_0 and $D = 0$ in equation (6), we get

$$E_0 = kT . \frac{2g_s Z_t}{\sqrt{\pi}} \int_0^{\infty} x^{3/2} dx,$$

where E_0 is termed as *zero point energy* of a highly degenerate Fermi gas. Replacing again the upper limit by $1/D$ and solving the integral, we arrive at

$$E_0 = kT . \frac{2g_s Z_t}{\sqrt{\pi}} \frac{2}{5D^{5/2}},$$

which, on using equation (13), becomes

$$E_0 = kT.\frac{2g_s.Z_t}{\sqrt{\pi}}.\frac{2}{5}\left[\frac{h^2}{2mkT}\left(\frac{3n}{4\pi V\, g_s}\right)^{2/3}\right]^{5/2}$$

$$= kT.\frac{2g_s}{\sqrt{\pi}}\left(\frac{2\pi m\, kT}{h^2}\right)^{3/2} V\times\frac{2}{3}\left[\frac{h^2}{2mkT}\left(\frac{3n}{4\pi Vg_s}\right)^{2/3}\right]^{5/2}$$

$$= \frac{3nh^2}{10m}\left(\frac{3n}{4\pi g_s V}\right)^{2/3} \qquad \dots (14)$$

and the corresponding zero point pressure will be

$$P_0 = \frac{2}{3}\frac{E_0}{V}$$

$$= \frac{n}{V}\frac{h^2}{5m}\left(\frac{3n}{4\pi g_s V}\right)^{2/3} \qquad \dots (15)$$

From equations (14) and (15) we find that a highly degenerate *Fermi Dirac gas would have a residual zero point energy and pressure*—the so called zero point pressure—*even at the absolute zero of the temperature, quite unlike a Bose Einstein gas where all the particles are condensed to the ground state with $\varepsilon = 0$ at $T = 0$.*

Expression of E and P in terms of Fermi Energy ε_f :

From equation (3), the total number of energy states lying between 0 and specified value ε_f can be obtained as

$$g_f = g_s\frac{2\pi V}{h^3}(2m^3)^{1/2}\int_0^{\varepsilon_f} \varepsilon^{1/2} d\varepsilon.$$

or

$$g_f = \frac{4\pi V g_s}{3h^3}(2m\,\varepsilon_f)^{3/2} \qquad \dots (15a)$$

Further, in Fermi Dirac distribution, not more than one particle is to be occupied by a given cell which is also obvious from

$$n_i = \frac{g_i}{De^{\varepsilon_f/kT}+1},$$

which gives $n_i = g_i$, since at $T = 0$, $D = 0$.

Therefore taking $g_f = n$, we write

$$n = \frac{4\pi\, Vg_s}{3h^3}(2m\varepsilon_f)^{3/2}$$

or

$$\varepsilon_f = \frac{h^2}{2m}\left(\frac{3n}{4\pi\, Vg_s}\right)^{2/3} \qquad \dots (16)$$

where the quantity ε_f is called the Fermi energy *and it represents the energy of the highest level filled at* $T = 0K$ *for the given assembly.*

From equations (13) and (16), we find that

$$\frac{1}{D} = \frac{\varepsilon_f}{kT}, \qquad \dots (17)$$

and from equations (14) and (16), zero point energy is

$$E_0 = \frac{3nh^2}{10m} \cdot \frac{2m\varepsilon_f}{h^2}$$

$$= \frac{3}{5} n\, \varepsilon_f . \qquad \dots (18)$$

and finally from equations (15) and (16), we arrive at

$$P_0 = \frac{n}{V} \cdot \frac{h^2}{5m} \cdot \frac{2m\varepsilon_f}{h^2}$$

$$= \frac{2}{5} \cdot \frac{n\varepsilon_f}{V} \qquad \dots (19)$$

If we define the Fermi temperature as

$$kT_f = \varepsilon_f$$

equation (17) becomes

$$\frac{1}{D} = \frac{T_f}{T},$$

from which we conclude that gas is degenerate when $T << T_f$.

(ii) At T above absolute zero but $D << 1$: From eq. (4), the number of particles lying in the energy range between ε and $(\varepsilon + d\varepsilon)$ is

$$dn(\varepsilon) = g_s \frac{4\pi\, mV}{h^3} \sqrt{(2m)} \frac{\varepsilon^{1/2} d\varepsilon}{De^{\varepsilon/kT} + 1}$$

We have seen in chapter 6 Art. 6.10, that

$$D = e^{\alpha} = -e^{-\mu/kT}$$

$$dn(\varepsilon) = 3n . \left(\frac{4\pi V g_s}{3n}\right)\left(\frac{2m^3}{h^6}\right)^{1/2} \cdot \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon-\mu)/kT} + 1} .$$

But from equation (16),

$$\varepsilon_f = \frac{h^2}{2m}\left(\frac{3n}{4\pi V g_s}\right)^{2/3},$$

giving

$$\left(\frac{4\pi V g_s}{3n}\right) = \left(\frac{2m\varepsilon_f}{h^2}\right)^{-3/2},$$

so that

$$dn(\varepsilon) = 3n.\left(\frac{2m\varepsilon_f}{h^2}\right)^{-3/2} \cdot \left\{\frac{2m^3}{h^6}\right\}^{1/2} \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon-\mu)/kT}+1}$$

$$= \frac{3n}{2\varepsilon_f^{3/2}} \cdot \frac{\varepsilon^{1/2}\, d\varepsilon}{e^{(\varepsilon-\mu)/kT}+1}, \qquad \dots (20)$$

which gives the total number of particles, as

$$n(\varepsilon) = \frac{3n}{2\varepsilon_f^{3/2}} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon-\mu)/kT}+1}, \qquad \dots (21)$$

and the energy

$$E = \frac{3n}{2\varepsilon_f^{3/2}} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon-\mu)/kT}+1}. \qquad \dots (22)$$

To evaluate the integrals of equations (21) and (22) we should solve the integral of the type

$$I = \int_0^\infty \frac{\phi(\varepsilon)\, d\varepsilon}{e^{(\varepsilon-\mu)/kT}+1},$$

where $\phi(\varepsilon)$ is a simple function of ε such that $\phi(\varepsilon) = 0$ if $\varepsilon = 0$. Such integrals can be expanded using the method of Taylor's series expansion, *i.e.*,

$$I = \int_0^\infty \frac{\phi(\varepsilon)\, d\varepsilon}{e^{(\varepsilon-\mu)/kT}+1} = \int_0^\mu \phi(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(kT)^2(\phi')_{\varepsilon=\mu} + \frac{7\pi^4}{360}(kT)^4(\phi''')_{\varepsilon=\mu} + \dots, \qquad \dots (23)$$

where ϕ', ϕ''', etc. denote the first, third, ... differentials of the function ϕ. We shall confine ourselves only to the first two terms of the expansion (23).

Observing equation (21), we write

$$\left.\begin{aligned} \phi(\varepsilon) &= \varepsilon^{1/2} \\ \text{so that} \qquad \int_0^\mu \phi(\varepsilon)\, d\varepsilon &= \frac{2}{3}\mu^{3/2} \\ \text{and} \qquad \phi'(\varepsilon)\Big|_{\varepsilon=\mu} &= \frac{1}{2}\mu^{-1/2} \end{aligned}\right\}$$

Therefore we write equation (20) as

$$n = \frac{3n}{2\varepsilon_f^{3/2}}\left[\int_0^\mu \phi(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}\cdot(kT)^2\phi'\Big|_{\varepsilon=\mu} + \dots\right]$$

$$n = \frac{3n}{2\varepsilon_f^{3/2}}\left[\frac{2}{3}\mu^{3/2} + \frac{\pi^2}{6}(kT)^2 \times \frac{1}{2}\mu^{-1/2} + \dots\right]$$

or

$$\varepsilon_f^{3/2} = \frac{3}{2}\left[\frac{2}{3}\mu^{3/2} + \frac{\pi^2}{12}\cdot \mu^{3/2}\left(\frac{kT}{\mu}\right) + \dots\right]$$

$$= \mu^{3/2}\left[1 + \frac{1}{8}\left(\frac{\pi kT}{\mu}\right)^2 + \dots\right]^{-2/3}$$

giving
$$\frac{\mu}{\varepsilon_f} = \left[1 + \frac{1}{8}\left(\frac{\pi kT}{\mu}\right)^2 + \ldots\right]^{-2/3}$$

$$= 1 - \frac{1}{12}\left(\frac{\pi kT}{\mu}\right)^2 + \ldots \qquad \ldots (24)$$

Taking into consideration only the first two terms of the expansion. We can write

$$\mu^2 = \varepsilon_f^2\left[1 - \frac{1}{12}\left(\frac{\pi kT}{\mu}\right)^2\right]^2$$

$$\approx \varepsilon_f^2\left[1 - \frac{1}{6}\left(\frac{\pi kT}{\mu}\right)^2\right],$$

neglecting higher order terms.

Thus
$$\frac{1}{\mu^2} \approx \frac{1}{\varepsilon_f^2}\left[1 + \frac{1}{6}\left(\frac{\pi kT}{\mu}\right)^2\right].$$

We make here a crude approximation by putting $\mu = \varepsilon_f$ in the second term on right side of above equation

$$\frac{1}{\mu^2} = \frac{1}{\varepsilon_f^2}\left[1 + \frac{1}{6}\left(\frac{\pi kT}{\varepsilon_f}\right)^2\right] \qquad \ldots (25)$$

Now putting equation (25) in equation (24), we get

$$\mu = \varepsilon_f\left[1 - \frac{1}{12}(\pi kT)^2 . \frac{1}{\varepsilon_f^2}\left\{1 + \frac{1}{6}\left(\frac{\pi kT}{\varepsilon_f}\right)^2\right\} + \ldots\right]$$

$$= \varepsilon_f\left[1 - \frac{1}{12}\left(\frac{\pi kT}{\varepsilon_f}\right)^2 - \ldots\right] \qquad \ldots (26)$$

neglecting the higher order terms.

Since equation (22) involves the integral of the same type, we write, using the expansion (23), as

$$E = \frac{3n}{2\varepsilon_f^{3/2}}\left[\int_0^{\mu} \phi(\varepsilon)\, d\varepsilon + \frac{1}{6}(\pi kT)^2 \phi'(\varepsilon)\Big|_{\varepsilon=\mu} + \ldots\right]$$

Now compressibility is given by

$$-\frac{1}{V}\cdot\frac{\partial V}{\partial P_0}=\frac{3}{5}\left[\frac{5m}{3^{2/3}\pi^{4/3}\hbar^2}\left(\frac{n}{V}\right)^{-5/3}\right]$$

$$=\frac{3^{1/3}m}{\pi^{4/3}\hbar^2}\left(\frac{n}{V}\right)^{-5/3}$$

It has been observed that the compressibility of alkali metals is close to the compressibility of an electron gas.

9•3. ELECTRON GAS :

A metal can be considered to be composed of a system of fixed positive nuclei and a number of mobile electrons referred to as electron gas.

To study the properties of an electron gas at low temperatures in the region $T \to 0$ we shall revise the earlier discussion. For electrons $s=\frac{1}{2}$ so that $g_z = 2s+1 = 2,$ and therefore from equation (16) art. 9.0, we get

$$\varepsilon_f=\frac{h^2}{2m}\left(\frac{3n}{4\pi V.2}\right)^{2/3}$$

$$=\frac{h^2}{8m}\left(\frac{3n}{\pi V}\right)^{2/3} \qquad \text{... (1)}$$

and from equation (18) art. 9.0,

$$E_0=\frac{3}{5}n\varepsilon_f \qquad \text{... (2)}$$

Further, from equations (15a) and (16) of art. 9.0, we get $g_f = n,$ which means that in the limit $T \to 0$ each one of the states is occupied fully upto the energy level ε_f whereas all the states above this energy level are empty.

From equation (13) art. 9.0, we can calculate the degeneracy factor for an electron gas. For electrons $m = 9.1\times10^{-28}$ gm. and $g = 2$, we get

$$\frac{1}{D}=\frac{h^2}{2\times9.1\times10^{-28}kT}\left(\frac{3n}{8\pi V}\right)^{2/3}$$

Taking a typical metal of atomic weight 100 and density 10 so that volume of gm. atom be 10 c.c. and the number of electrons, assuming one free electron per atom, is 6.02×10^{23}. Then,

$$\frac{1}{D}=\frac{(6.62\times10^{-27})^2}{2\times9.1\times10^{-28}\times1.38\times10^{-16}\times T}\left(\frac{3\times6.02\times10^{23}}{8\times3.14\times10}\right)^{2/3}$$

$$=\frac{10^5}{1.5T},$$

which means *degeneracy is sufficiently high.* It shows clearly that for electron gas, the classical statistics is not valid and can be applied only at temperatures of the order of 10^5 K (because only then D will approach unity). Therefore at low and other ordinary working temperatures, it is necessary to use Fermi-Dirac statistics to study the electron gas in the metals. At low temperatures electronic contribution to the specific heat of metals is given by equation (1) art. 9.1 which is

$$C_V = \frac{1}{2} nk\, \pi^2 \left(\frac{kT}{\varepsilon_f} \right).$$

But from equation (17) art. 9.0, we have

$$D = \frac{kT}{\varepsilon_f}.$$

so that
$$C_V = \frac{1}{2} nk\, \pi^2 D.$$

Using the above value of $1/D$, we find that

$$C_V = \frac{1}{2} nk\pi^2 \times 1.5 \times 10^{-5} \times T.$$

Putting
$$nk = R, \text{ gas constant}$$
$$= 1.978 \text{ cal deg}^{-1} \text{ mol}^{-1}$$
$$= 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$$
$$\pi^2 = 10,$$

we get electronic specific heat

$$C_V = \frac{1}{2} \times 1.5 \times 10^{-5} \times 2 \times 10 \times T$$
$$= 1.5 \times 10^{-4} \times T \text{ cal/gm. atom.}$$

Pressure of the electron gas can be obtained from equation (19) art. 9.0 as

$$P_0 = \frac{2}{5} \frac{n\varepsilon_f}{V}$$
$$= \frac{2n}{5V} \frac{h^2}{2m} \left(\frac{3n}{4\pi V g_s} \right)^{2/3}$$
$$= \frac{nh^2}{20mV} \left(\frac{3n}{\pi V} \right)^{2/3}, \text{ using } g_s = 2.$$

For a metal of atomic weight 100 and density 10 ($= n/V$)

$$P_0 \sim 10^5 \text{ atoms.}$$

which means at *normal temperature, the pressure of the gas is sufficiently high.*

Example 1. *Calculate the Fermi energy in electron volt for sodium assuming that it has one free electron per atom. Given : density of sodium* =0.97 gm./cm^3, *atomic weight of sodium* = 23.

From eq. (1) art. 9.3, we find that Fermi energy is given by escape must come from x component of the electron's motion. Only those electrons will come out which have got energy greater than $(E_a - \varepsilon_f)$, the work function. Therefore, number of electrons arriving per second per unit area of the metal surface will be

$$n_x = \int_{\sqrt{(E_a/m)}}^{\infty} n(v_x)\, v_x\, dv_x$$

$$= 2\left(\frac{m}{h}\right)^3 e^{\varepsilon_f/kT} \int_{\sqrt{(2E_a/m)}}^{\infty} v_x\, e^{-\frac{1}{2}mv_x^2/kT} dv_x \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2}m(v_y^2+v_z^2)} dv_y\, dv_z$$

$$= \frac{4\pi mk^2}{h^3} T^2 e^{-(E_a-\varepsilon_f)/kT}$$

Therefore emission current density per unit area

$$J = en_x = \frac{4\pi m\, ek^2}{h^3} T^2 e^{-(E_a-\varepsilon_f)/kT}$$

Putting $$A = \frac{4\pi m\, ek^2}{h^3}$$

and $$e\phi = (E_a - \varepsilon_f),$$

we get $$J = AT^2 e^{-\varepsilon\phi/kT}.$$

This equation is called *Richardson-Dushman equation of thermionic emission*. It was first derived classically upon the assumption that the electrons obey Maxwell-Boltzmann statistics. Its classical form is

$$J = \frac{ne}{(2\pi m)^{1/2}} (kT)^{1/2} e^{-e\phi/kT}$$

which differs from quantum equation in constant coefficient and in the power of T which multiplies the exponential term.

9•5. PAULI'S THEORY OF PARAMAGNETISM :

In metals free conduction electrons are present. As each electron is endowed with an intrinsic magnetic moment μ, it acts as an elementary magnet. Thus all free electrons, acting as elementary magnets, can orient themselves in the direction of an applied magnetic field $\vec{B}$ and make metals highly paramagnetic.

Let us consider an assembly of N free fermions of spin $\frac{1}{2}\hbar$ each of which is described by a single particle Hamiltonian,

$$H = \frac{p^2}{2m} - \vec{\mu}.\vec{B}$$

and the single particle energy levels

$$\varepsilon_{i,s} = \frac{p^2}{2m} - \mu SB$$

where $S = \pm 1$. Therefore for the assembly of N free fermions labelled by the occupation numbers $n_{i,s}$ of the single particle levels, $\varepsilon_{i,s}$ can be written as

$$E_n = \sum_i \sum_s \varepsilon_{i,s}\, n_{i,s}$$

$$= \sum_i \left[\left(\frac{p^2}{2m} - \mu B\right) n_{i,+1} + \left(\frac{p^2}{2m} + \mu B\right) n_{i,-1}\right] \qquad \dots (1)$$

where

$$n_{i,s} = 0, 1 \qquad \dots (2)$$

$$\sum_i \sum_s n_{i,s} = N$$

If we write it for particles with spin ±, then

$$\sum_i n_{i,+1} = N_+$$

$$\sum_i n_{i,-1} = N_- = N - N_+$$

then eq. (1) can be written as

$$E_n = \sum_i (n_{i,+1} + n_{i,-1}) \frac{p^2}{2m} - \mu B(N_+ - N_-)$$

$$= \sum_i (n_{i,+1} + n_{i,-1}) \frac{p^2}{2m} - \mu B\,(2N_+ - N) \qquad \dots (3)$$

The partition function is given by

$$Z_N = \sum_{n_{i,+1};\, n_{i,-1}}{}' \quad e^{-\beta E_n}$$

$$= \sum_{n_{i,+1};\, n_{i,-1}} e^{\beta\mu B(2N_+ - N)}\, e^{-\beta \sum_i \frac{p^2}{2m} n_{i,+1}}\, e^{-\beta \sum_i \frac{p^2}{2m} n_{i,-1}} \qquad \dots (4)$$

where prime over summation implies that restrictions imposed by eq. (2) must be followed while carrying out the summation, *i.e.*,

$$Z_N = \sum_{N_+ = 0}^{N}{}' \; e^{\beta\,\mu B(2N_+ - N)} \sum_{n_{i,+1}}{}'' \; e^{-\beta \sum_i \frac{p^2}{2m} n_{i,+1}} \sum_{n_{i,-1}}{}''' \; e^{-\beta \sum_i \frac{p^2}{2m} n_{i,-1}} \qquad \dots (5)$$

where an arbitrary value for integer, N_+, has been selected and Σ'' is subjected to restriction

$$\sum_i n_{i,+1} = N_+$$

and Σ''' is subjected to restriction

$$\sum_i n_{i,-1} = N_- = N - N_+$$

so that eq. (5) can be written as

$$Z_N = e^{-\beta\mu BN} \sum_{N_+=0}^{N} e^{2\,\beta\mu BN_+} \sum_{N_+=0}^{N} e^{-\beta\frac{p^2}{2m}N_+} \sum_{N-N_+}^{N} e^{-\beta\frac{p^2}{2m}(N-N_+)} \quad \dots (6)$$

If the partition function of an ideal Fermi gas of N spineless particles of mass m be denoted by Z_N^0 then

$$Z_N^0 = \sum_{\sum_i n_i = N}^{N} e^{-\beta\sum_i \frac{p^2}{2m}n_i} = e^{-\beta y(N)} \quad \dots (7)$$

then eq. (6) can be written as

$$Z_N = e^{-\beta\mu BN} \sum_{N_i=0}^{N} e^{2\beta\mu BN_+}\, Z_{N_+}^0\, Z_{N-N_+}^0 \quad \dots (8)$$

or

$$\frac{1}{N}\log Z_N = -\beta\mu B + \frac{1}{N}\log \sum_{N_+=0}^{N} e^{2\beta\mu\, BN_+ - \beta y(N_+) - \beta y(N-N_+)} \quad \dots (9)$$

Summation in eq. (9) contains $(N + 1)$ positive terms (0 to N); the logarithm of this sum is equal to the logarithm of the largest term in the sum plus a contribution of the order of $\log N$. Therefore, we neglect the term of order $\frac{1}{N}\log N$ and write

$$\frac{1}{N}\log Z_N = \beta f(\bar{N}_+),$$

where

$$f(\bar{N}_+) = \text{max.}\,[f(N_+]$$

$$f(\bar{N}_+) = \mu B\left(\frac{2N_+}{N} - 1\right) - \frac{1}{N}[y(N_+) + y(N-N_+)] \quad \dots (10)$$

$\bar{N}_+$ gives the average number of particles with spin up. We proceed to find its value. For maximum $f(N_+)$ we write the condition

$$\frac{\partial f(N_+)}{\partial N_+} = 0 \qquad \text{at} \quad N_+ = \bar{N}_+$$

or

$$\frac{\partial}{\partial N_+}\left\{\mu B\left(\frac{2N_+}{N} - 1\right) - \frac{1}{N}[y(N_+) + y(N-N_+)]\right\} = 0$$

or

$$\frac{2\mu B}{N} - \frac{1}{N}\frac{\partial[y(N_+)]}{\partial N_+} - \frac{1}{N}\frac{\partial[y(N-N_+)]}{\partial N_+} = 0$$

or

$$2\mu B - \left[\frac{\partial y(N_+)}{\partial N_+}\right]_{N_+=\bar{N}_+} - \left[\frac{\partial y(N-N_+)}{\partial N_+}\right]_{N_+=\bar{N}_+} = 0 \quad \dots (11)$$

Refer to eq. (4) art. 3.2–2 (a), free energy per particle, *i.e.*, chemical potential is given by

$$= -\tau\log\left(\frac{f}{\bar{n}}\right) = \tau\log\left(\frac{\bar{n}}{f}\right)$$

Applying it to particles with spin up, N_+, we have

$$\tau \log\left(\frac{\bar{N}_+}{f}\right) = \frac{\partial y(N_+)}{\partial N_+} = \frac{\partial}{\partial N_+}\left(\frac{p^2 N_+}{2m}\right) = \frac{p^2}{2m} \qquad \text{(see eqs. 7 and 9)}$$

and to particles with spin down, N_-, we have

$$\tau \log\left(\frac{\bar{N}_-}{f}\right) = -\frac{\partial y(N_-)}{\partial N_-} = -\frac{\partial y(N - N_+)}{\partial (N - N_+)} = -\frac{p^2}{2m} \qquad \text{(see eqs. 7 and 9)}$$

Therefore putting above equations in (11), we get

$$2\mu B - \tau \log\left(\frac{\bar{N}_+}{f}\right) + \tau \log\left(\frac{\bar{N}_-}{f}\right) = 0$$

or
$$\log\left(\frac{\bar{N}_+}{f}\right) - \log\left(\frac{\bar{N}_-}{f}\right) = \frac{2\mu B}{\tau} = \frac{2\mu B}{kT}$$

or
$$\log\left(\frac{\bar{N}_+}{\bar{N}_-}\right) = \frac{2\mu B}{kT}$$

or
$$\bar{N}_+ = \bar{N}_- \, e^{2\mu B/kT}$$

At $B = 0$,
$$\bar{N}_+ = \bar{N}_- = \frac{N}{2}$$

that is, when $B = 0$, half the particles have spin up and the other half spin down. At low temperature and for $B > 0$, $e^{2\mu B/kT} > 1$ and consequently $\bar{N}_+ > \bar{N}_-$, *i.e.*, balance $(\bar{N}_+ + \bar{N}_-)$ shifts in favour of spin up and a net magnetisation will result. The magnetisation per unit volume will be given by

$$I = \frac{\text{total magnetic moment}}{\text{volume}}$$

Since μ is the magnetic moment of a particle, net magnetisation will be

$$= \mu(\bar{N}_+ - \bar{N}_-)$$

so that
$$I = \frac{\mu(\bar{N}_+ - \bar{N}_-)}{V}$$

easily gives the value of magnetic susceptibility.

9•6. WHITE DWARFS :

A plot of brightness of stars against the predominant wavelength emitted is shown in fig. (2). This plot is Hertz sprung – Russel diagram. It is obvious from the figure that most of the stars fall within a linear strip (shown by dotted lines in the figure), indicating that the brightness is proportional to λ. However, there are two glaring exceptions to this rule : (i) the red giant stars which are huge and abnormally bright and (ii) the white dwarf stars which are highly under-luminous. The

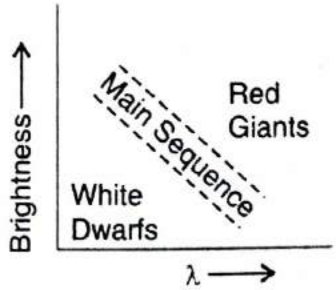

Fig. 2.

$$S = (S)_{T=T_0} + \frac{3}{2}nk\left[\log\frac{T}{T_0} + \frac{2}{3}\times 0.231\times\left\{1-\left(\frac{T_0}{T}\right)^{3/2}\right\}+\ldots\right] \qquad \ldots(10)$$

integrating upto second term only.

We note that

$$(S)_{T<T_0} = \frac{2}{3}(C_V)_{T<T_0}$$

and from figure 2 we find that C_V shows a sudden drop for the temperature below T_0 and consequently, entropy will also decrease suddenly. A decrease in entropy means *decrease in disorder* or *increase in order*. We have seen earlier that at $T < T_0$, a large number of particles *condense* into the ground state $(\varepsilon = 0)$ which is attributed to zero entropy (entropy $k\log_e 1 = 0$, since statistical weight of ground state is one). Since $\varepsilon = p^2/2m, \varepsilon = 0$, implies $p = 0$ and therefore we can say equivalently, that *condensed particles condense in the momentum space.* They acquire the same momentum $p = 0$ and, thereby, create an 'order in momentum space'. Therefore decrease in entropy implies that some sort of condensation is taking place–greater is the decrease in entropy more is the acquisition of orderly state *i.e.,* greater is the condensation. *For ground state, for which entropy is zero, it means, condensation is maximum* or, in otherwords a large number of particles will rapidly fall into the ground state. As the ground state is also characterised by $p = 0$, Bose Einstein condensation is sometimes described as a '*condensation in momentum space*'.

8•4. LIQUID HELIUM

As an application of Bose Einstein statistics, we may investigate the qualitative nature of the superfluid transition of liquid helium at 2.2K. Ordinary helium consists almost entirely of neutral atoms of the isotope ${}_2\text{He}^4$. As the total angular momentum of these atoms is zero, their discussion must fall under the jurisdiction of Bose Einstein statistics.

Helium exhibits peculiar properties at low temperatures. It is found that

(i) helium gas at atmospheric pressure condenses at 4.3K (its critical temperature being 5.2K) into a liquid of very low density, about 0.124 gm./cm^3.

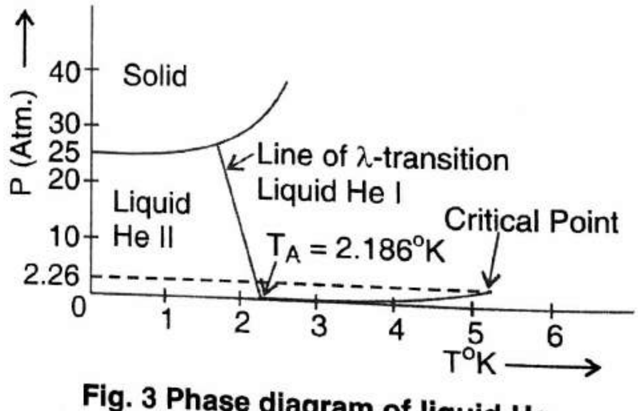

Fig. 3 Phase diagram of liquid He.

(ii) further cooling to about 0.82K does not freeze it and it is believed that it remains liquid all the way down to absolute zero. The solid state of helium does not form unless it is subjected to an external pressure of atleast 23 atmosphere. The phase diagaram is shown in figure 3.

(iii) for He^4 in liquid phase, there is another phase transition, called λ-transition, which divides the liquid state into two phases He *I* and *II*. K. Onnes, while liquefying helium, noted that at about 2.2K, density appeared to pass through an abrupt maximum and then decreasing slightly thereafter. Investigations also revealed that critical temperature is at 2.186K, and that it represents a transition to a new state of matter known as liquid He *II*. In liquid He *II* state, it was found that

(a) heat conductivity is very large of the order of 3.10^6 times greater,

(b) coefficient of viscosity gradually diminishes as the temperature is lowered, and appears to be approaching zero at absolute zero temperature, and

(c) specific heat measurements by Keesom show that specific heat curve, fig. 4, is discontinuous at 2.186K. The shape of the specific heat curve resembles the shape of letter λ and therefore this peculiar transition is called *λ-transition* and the discontinuity temperature 2.186K, is called '*λ-point*' Since experimentally it was found that at '*λ-point*' liquid He *II* state has no latent heat, Keesom concluded that transition He $I \rightarrow \text{He}\,II$ at T_λ is a second order transition. The transition temperature decreases as the pressure is increased, tracking out λ-line in figure 3.

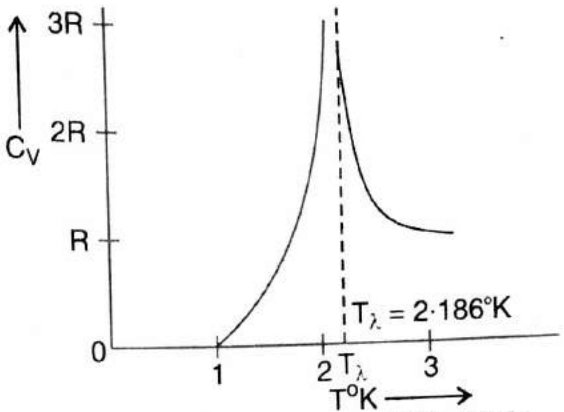

Fig. 4 Specific heat curve of liquid He

Explanation based on Bose Einstein condensation model : London's Theory :

Explanation of these pecularities of liquid He at low temperatures, based on *B-E* statistics, was given by London who suggested that He *II* is a liquid analogous to *B-E* gas and that λ-transition in liquid helium is the counter part of Bose Einstein condensation in the ideal gas. In Bose Einstein gas, degeneracy is

$$\frac{1}{D} = \frac{n}{g_s V}\left(\frac{2\pi m kT}{h^2}\right)^{3/2} . \quad \text{(see equation 11 art 8.1)}$$

London suggested that helium atoms are light enough and though the density (n/V) of the liquid is sufficiently high for the right hand side to be large and degeneracy to be well marked but is low enough for the liquid to behave as a gas. He concluded this λ-transition as a result of Bose Einstein condensation and gave an analogy between 'λ-point' and Bose Einstein condensation temperature T_0 defined by equation (4) art 8.2, giving

$$g_s\left(\frac{2\pi mk\,T_0}{h^2}\right)^{3/2} V = \frac{n}{F_{3/2}(0)} = \frac{n}{2.612}$$

or

$$T_0 = \frac{h^2}{2\pi mk}\left(\frac{n}{2.612\,Vg_s}\right)^{2/3}$$

In this expression, when we put $V = 27.4\,\text{cm}^3$ for a gram molecule of helium in liquid state, we get $T_0 = 3.12\,\text{K}$ which is quite close to the observed value $T_\lambda = 2.186\text{K}$ for the λ-point This agreement in the value T_0 and T_λ favours the London explanation.

Further, for the discontinuity in specific heat curve at λ-point, London suggested that similar discontinuity occurs in the specific heat and hence the existence of two liquid components He *I* and He *II* is automatically explained.

Again, the decrease in entropy below T_λ, being zero at 0.5K, is very well explained by Bose Einstein condensation because, in the latter, we have shown that at $T < T_0$ most of the particles rapidly fall into the ground state which is characterised by zero entropy.

Though London approximated the properties of liquid helium so as to resemble with those of Bose Einstein gas yet there is no reason to expect that liquid helium, with mutual interaction between the particles, should resemble with perfect Bose-Einstein gas in any important respect. Later on, Tisza introduced the two fluid hypothesis.

8•4. 1 SUPERFLUIDITY, TI EL AND SECOND SOUND :