## **Radiation:**

Heat can be transferred from a hotter body to a cold body even when the two bodies are separated in vacuum. Heat in this case is transferred by the process of radiation. The radiant energy, however, does not exhibit itself unless it falls on matter. When radiation falls on a matter, it is absorbed by matter and is converted into heat energy.

The radiant energy is electromagnetic nature, similar to light. They travel in straight lines with the same velocity as light  $(3x10^8 \text{ m/sec})$ . They exhibit reflection, refraction, diffraction and polarization. They carry energy with themselves and exert pressure.

The radiant energy or radiation can be of any wavelength from 0 to  $\infty$ . Thermal radiation from bodies depends on the temperature of the body and its surface.

## Radiant energy and matter:

When radiation falls on matter, it may be partly reflected, partly transmitted and partly absorbed. If r be the fraction of total energy reflected – reflectance, a the fraction absorbed - absorbance and t the fraction that transmitted – transmittance, then

$$r + t + a = 1$$

The values of r, a, t may be different for different wavelengths. We thus use  $r_{\lambda}$ ,  $t_{\lambda}$ ,  $a_{\lambda}$  to denote the reflectance, transmittance and absorbance of the substance for wavelength  $\lambda$ . Thus,

$$r_{\lambda} + t_{\lambda} + a_{\lambda} = 1$$

For bodies having a = 0, t = 0, we have r = 1. Such bodies are called perfectly white bodies. A piece of chalk approximately can be assumed to be a perfectly white body. However, perfectly white body is an idealized concept.

For bodies having r = 0, t = 0, we have a = 1. Such bodies are called the perfectly black bodies. A perfectly black body neither reflects, nor transmits; it absorbs the entire radiation incident on it. Lampblack approximately can be assumed to be a perfectly black body. However, perfectly black body is an idealized concept.

## Prevost's theory of exchange:

The idea of radiant energy was much confused prior to the Privost's theory of exchange in 1792. People talked about 'hot radiations' and 'cold radiations'. For instance, people used to believe that ice produces a sensation of cold because it emits cold radiations. It was Prevost who cleared all the confusions. According to his exchange theory, a substances at all finite temperature emit 'radiant energy' and the amount of radiant energy increases with the temperature of the substance and is not affected by the presence of surrounding bodies.

## Black body and its realization:

A perfectly black body is defined as the body that absorbs the entire radiations incident on it. Therefore, a black body neither reflects, nor transmits any radiation. When such a body is heated to high temperatures, it emits radiations of all wavelengths and such radiations are called the total radiation. Kirchhoff showed theoretically that an enclosure whose walls are impervious to any type of radiations and is maintained at a constant temperature behaves as a perfect black body and the quality of radiations emitted by it is that of total radiation, i.e., they depend on the temperature of the enclosure and are independent of the nature of the material of the wall of the enclosure. If any matter is placed inside the enclosure, a steady state will be reached and the matter will attain the temperature of the enclosure and will emit black radiation characteristic of that temperature.

## Kirchhoff's law:

## **Emissive power:**

The amount of energy emitted in the form of radiation of wavelengths between  $\lambda$  and  $\lambda + d\lambda$  by an isotropic body at a particular temperature T, per unit area of the body and per unit time is called the emissive power of the body at that temperature for the radiation of wavelength  $\lambda$ . It is denoted by  $e_{\lambda}$ .

## Absorptive power:

If a given amount of energy in the form of radiation of wavelengths between  $\lambda$  and  $\lambda + d\lambda$  is incident on an isotropic body at temperature T, then the fraction of this energy absorbed by the body is called the absorptive power of the body at the temperature T for the radiation of wavelength  $\lambda$ . It is denoted by  $a_{\lambda}$ .

# Kirchhoff's law:

Kirchhoff's law states that the ratio of the emissive power to the absorptive power for radiation of a given wavelength is the same (constant) for all bodies at the same temperature and is equal to the emissive power of a perfect black body at that temperature.

If  $e_{\lambda}$  and  $a_{\lambda}$  be the emissive power and the absorptive power of a body at temperature T for the radiation of wavelength  $\lambda$ , then

$$\frac{e_{\lambda}}{a_{\lambda}} = cons \tan t = E_{\lambda}$$

where  $E_{\lambda}$  is the emissive power of a perfect black body at temperature T for the radiation of wavelength  $\lambda$ .

## Pressure of radiation:

As radiation is identical with light, it also exerts small but finite pressure on the surfaces on which it is incident.

## Stefan-Boltzmann law:

The dependence of total radiation from a radiator on its temperature was first studied experimentally by Stefan. He concluded that the total radiation is proportional to the fourth power

of the absolute temperature of the body. As a black body is supposed to behave as a perfect gas, Boltzmann applied the law of thermodynamics to radiation and deduced the Stefan's law theoretically. Since then, the law is generally referred to as Stefan-Boltzmann law.

If a black body at absolute temperature T is surrounded by another black body at absolute temperature  $T_1$ , the amount of radiation emitted per second per unit area of the former body is

$$Q = \sigma(T^4 - T_1^4)$$

where  $\sigma$  is a constant and is known as the Stefan's constant. This is Stefan-Boltzmann law.

## Newton's law of cooling:

Newton's law of cooling states that the rate at which a body loses heat energy due to radiation is directly proportional to the excess temperature, i.e., the difference of temperature between the body and the surroundings, provided the difference of temperature is small.

Let T and  $T_0$  be the temperatures of the body and the surrounding respectively. Then by Stefan's law, the loss of heat energy due to radiation per unit area per unit time is given by

$$Q = \sigma(T^{4} - T_{0}^{4})$$
  

$$\therefore Q = \sigma(T^{2} - T_{0}^{2})(T^{2} + T_{0}^{2})$$
  

$$= \sigma(T - T_{0})(T + T_{0})(T^{2} + T_{0}^{2})$$
  

$$= \sigma(T - T_{0})(T^{3} + T_{0}^{2}T + T_{0}T^{2} + T_{0}^{3})$$
  
If  $(T - T_{0})$  be small,  $T \simeq T_{0}$ .

$$\therefore Q \simeq \sigma(T - T_0) \ge 4T_0^3 = \beta(T - T_0)$$

where  $\beta = 4\sigma T_0^3$  is a constant, since  $T_0$  is a constant.

$$\therefore Q \propto (T - T_0)$$

This is Newton's law of cooling.

Energy distribution in black body radiation:



An ideal black body can be realized in practice by heating a hollow enclosure with a very small orifice, to an arbitrary temperature. The inner surface of the enclosure is coated with lampblack. Any

radiation entering the cavity through the orifice is almost entirely absorbed after multiple reflections from the wall of the cavity and very little can come out of the cavity through the orifice as it is very small. Thus the cavity may be taken to have unit absorptive power and it behaves like a black body.

The inner wall of the heated cavity can also emit radiation. This radiation has the characteristics of black body radiation. The radiation spectrum can be analyzed by an infrared spectrometer.

The variation of the intensity of the emitted radiation  $E_{\lambda}$  as a function of the wavelength for different temperatures of the black body is shown in the figure below. For a given temperature as wavelength  $\lambda$  increases  $E_{\lambda}$  first increases with increasing  $\lambda$  at very short wavelengths, attains a maximum at some wavelength  $\lambda_m$  and then decreases again with further increase in  $\lambda$ . The value of  $\lambda_m$  depends on the temperature T of the black body and it decreases with increasing temperature. It is independent of the nature of the emitting body.  $E_{\lambda}$  vs  $\lambda$  curves have the same nature at different temperatures. However, at higher temperatures the intensity is higher at all wavelengths.



The wavelength  $\lambda_m$  at which the intensity distribution curve has the maximum and the temperature of the black body are found to obey the empirical relation

$$\lambda_m T = \text{constant}$$

This is known as the Wien's displacement law (1893).

The total power E radiated per unit area per unit time is found to depend on the temperature of the black body and found by integrating  $E_{\lambda}$  for all possible values of wavelength  $\lambda$ .

$$\therefore E = E(T) = \int_{\lambda=0}^{\infty} E_{\lambda} d\lambda$$

#### Wien's law:

From thermodynamical considerations Wien proposed an empirical relationship between the intensity of the emitted radiation  $E_{\lambda}$  and wavelength  $\lambda$  for a given temperature T. This is of the following form:

$$E_{\lambda}d\lambda = \frac{A}{\lambda^5}f(\lambda T)d\lambda$$

where A is a constant and  $f(\lambda T)$  is a function of the product  $\lambda T$  .

The functional form  $f(\lambda T)$  cannot be deduced from thermodynamics. It is necessary to assume a suitable model for the radiating system in order to determine it.

Wien himself proposed an expression for the functional form of  $f(\lambda T)$  on the basis of some arbitrary assumptions regarding the mechanism of emission and absorption of radiation. Based on these assumptions, Wien's law for the energy density of the black body radiation can be written as

$$u_{\lambda}d\lambda = \frac{a}{\lambda^5}e^{-\frac{b}{\lambda T}}d\lambda$$

The constants a and b were chosen arbitrarily so as to fit the experimental energy distribution curves. Since the theory was not based on any possible physical model, it proved to be unsatisfactory.

#### **Rayleigh-Jeans law:**

After the failure of Wien's law to explain the energy distribution curve at longer wavelength, Rayleigh and Jeans approached the problem in a different fashion.

They assumed that the radiating system is composed of a collection of charged linear harmonic oscillators which according to the electromagnetic theory of light radiate electromagnetic waves because of their accelerated motion. They can also absorb electromagnetic radiation. If we consider a cavity full of radiation, then the atomic oscillators in the walls of the cavity will continually exchange energy with the radiation in the cavity. Ultimately equilibrium will be reached when the energy density of e.m. radiation will assume an equilibrium value determined by the temperature T of the cavity walls.

When the temperature of the walls is increased, the amplitudes of the existing modes of vibration of the oscillators are increased. Also, new modes are excited for which the frequencies are higher. Thus radiant energy density in the cavity is increased until a new equilibrium is reached.

According to classical mechanics, the total energy of a linear harmonic oscillator of mass  $\,m$  oscillating along X-direction is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

It thus has two degrees of freedom. According to the law of equipartition of energy, the mean energy corresponding to each degree of freedom is  $\frac{1}{2}kT$  and hence the mean energy of the oscillator is

$$\langle \varepsilon \rangle = kT$$

Here k is the Boltzmann constant.

The cavity is filled with e.m. radiation of wavelength 0 to  $\infty$ . They are reflected time and again from the walls of the cavity and thus form stationary waves in the space of the cavity.

To calculate the energy density of radiation in the cavity for a given frequency  $v = \frac{c}{\lambda}$ , we have to find the number  $n_{\lambda}$  of oscillators per unit volume having frequency v and to multiply it by the mean energy  $\langle \varepsilon \rangle = kT$ .  $n_{\lambda}$  can be calculated by determining the number of modes of stationary vibrations which can be excited in the space of the cavity. For simplicity we assume cavity in the form of three dimensional box of cubical shape with sides a and radiation is incident normally on the walls.

Let the incident and the reflected wave trains be

$$y_1 = ASin \frac{2\pi}{\lambda} (ct - x), y_2 = ASin \frac{2\pi}{\lambda} (ct + x)$$

Here c and  $\lambda$  are the velocity and wavelength of the wave, and A is the amplitude.

... The resultant displacement is given by

$$y = y_1 + y_2 = 2ACos \frac{2\pi x}{\lambda} Sin \frac{2\pi ct}{\lambda} = CSin \frac{2\pi ct}{\lambda}$$

where  $C = 2ACos \frac{2\pi x}{\lambda}$  is the amplitude of the resultant vibration.

Nodes are formed at points where y = 0 for all time *t*, i.e.,  $Cos \frac{2\pi x}{\lambda} = 0$ .

Therefore, 
$$\frac{2\pi x}{\lambda} = (2p+1)\frac{\pi}{2}$$
, where  $p = 0, 1, 2, 3, ....$ 

$$\therefore x = (2p+1)\frac{\lambda}{4}$$

Thus, nodes are formed at distances  $\frac{\lambda}{4}, \frac{3\lambda}{4}, \frac{5\lambda}{4}, etc.$ 

Distance between two successive nodes is  $\frac{\lambda}{2}$ .

If  $n_1$  nodes are formed between the walls, then  $n_1 \cdot \frac{\lambda}{2} = a$ . If the wave meets the reflecting surface at an angle  $\theta_1$ , then

$$n_1 \cdot \frac{\lambda}{2} = a Cos \theta_1$$

If  $\theta_1, \theta_2, \theta_3$  be the angles which the normal to the plane wavefront makes with the normal to the three pairs of faces of the cube, then

$$n_1 \cdot \frac{\lambda}{2} = al$$
,  $n_2 \cdot \frac{\lambda}{2} = am$ ,  $n_3 \cdot \frac{\lambda}{2} = am$ 

where l, m, n are the direction cosines.

$$\therefore n_1^2 + n_2^2 + n_3^2 = \frac{4a^2}{\lambda^2} (l^2 + m^2 + n^2) = \frac{4a^2}{\lambda^2} \quad [\because l^2 + m^2 + n^2 = 1]$$

A set of values of  $n_1, n_2, n_3$  satisfying the above equation represents a particular mode of vibration. To calculate the number of modes of vibration in the frequency interval v and v + dv we represent  $n_1, n_2, n_3$  in a three dimensional diagram where  $n_1, n_2, n_3$  are along X-,Y-,Z-axes respectively. Each combination of  $n_1, n_2, n_3$  values is then represented by a point in this diagram whose coordinates are  $(n_1, n_2, n_3)$ .

In two dimensions, this will look like as shown in the figure below where each circle represents a particular mode of vibration. It is also evident that each unit square contains one circle. Thus, the number of modes of vibration in the frequency interval  $\nu$  and  $\nu + d\nu$  can be calculated by counting

the number of unit squares in the annular area between two circular arcs of radii  $r = \frac{2a}{\lambda} = \frac{2av}{c}$  and

 $r + dr = \frac{2a(v + dv)}{c}$  in the first quadrant.



In actual three dimensional case, the number of modes of vibration in the frequency interval  $\nu$  and  $\nu + d\nu$  can be calculated by counting the number of unit cubes in the first octant of the spherical

shell of radii 
$$r = \frac{2a}{\lambda} = \frac{2av}{c}$$
 and  $r + dr = \frac{2a(v + dv)}{c}$ .

Hence the number of modes of vibration in the frequency interval v and v + dv is given by

$$N_{v}dv = \frac{1}{8} \times 4\pi r^{2} dr = \frac{1}{8} \times 4\pi \left(\frac{2av}{c}\right)^{2} \left(\frac{2adv}{c}\right) = \frac{4\pi a^{3}}{c^{3}} v^{2} dv = \frac{4\pi V}{c^{3}} v^{2} dv$$

Here  $V = a^3$  is the volume of the cavity. Hence the number of modes of vibration per unit volume of the cavity for frequencies in the interval v and v + dv is given by

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

Since e.m. radiation is transverse in nature with two possible directions of polarization, the above expression should be multiplied by two.

$$\therefore n_{\nu}d\nu = \frac{8\pi}{c^3}\nu^2 d\nu$$

Number of oscillators per unit volume emitting radiation of wavelength in the interval  $\lambda$  and  $\lambda + d\lambda$ 

$$\therefore n_{\lambda} d\lambda = \frac{8\pi}{\lambda^4} d\lambda$$

Hence the energy density of the black body radiation of wavelength in the interval  $\lambda$  and  $\lambda + d\lambda$  is given by

$$u_{\lambda}d\lambda = n_{\lambda}d\lambda \left\langle \varepsilon \right\rangle = \frac{8\pi kT}{\lambda^4}d\lambda$$

This is known as the Rayleigh-Jeans law.

The intensity of the emitted radiation is given by

$$E_{\lambda}d\lambda = \frac{c}{4}u_{\lambda}d\lambda = \frac{2\pi ckT}{\lambda^4}d\lambda$$

This equation agrees well with the experimental results for longer wavelengths. However, for shorter wavelengths, it fails completely.  $u_{\lambda}$  and hence  $E_{\lambda}$  approaches infinity as  $\lambda \to 0$ , but experimental result shows that  $E_{\lambda} \to 0$  as  $\lambda \to 0$ . This serious disagreement between theory and experiment is known as the ultraviolet catastrophe. This indicates the limitations of classical mechanics on the basis of which the equipartition law is deduced and which is used in this deduction.

#### Planck's law of black body radiation: Quantum hypothesis

The failure of R-J distribution to explain the observed energy distribution law of black body radiation showed that there was something wrong with the equipartition law or with the classical electromagnetic theory or both.

German physicist Max Planck (1900) then put forward a bold new postulate regarding the nature of vibration of linear harmonic oscillators which are in equilibrium with the electromagnetic radiation

within the cavity. According to Planck, an oscillator can have a discrete set of energies which are integral multiples of a finite quantum of energy  $\varepsilon_0 = hv$ , where h is a constant known as the Planck's constant and v is the frequency of the oscillator. Thus the energy of the oscillator can only have values

$$\varepsilon_n = n\varepsilon_0 = nhv$$

where *n* is zero or an integer. n = 0 corresponds to the lowest energy state of the oscillator and is called the ground state and its energy is zero.

Planck further assumed that the change in energy of the oscillator due to the emission or absorption of radiation can take place by a discrete amount hv. By fitting his theory to the experimental data, Planck estimated the value of h. Planck's constant h is a universal constant and plays a crucial role in all quantum mechanical phenomena. Its value is  $h = 6.62618 \times 10^{-34}$  Joule.second (Js).

Since radiation is emitted by oscillators, and since according to Planck the change in energy of the oscillators can take place by discrete amount, the energy carried by emitted by radiation will be hv which is equal to the loss of energy of the oscillator. This is also the energy gained by the oscillator when it absorbs radiation. No absorption of energy by the oscillator can take place unless the energy of the radiation hv 'is equal to the possible energy change of oscillator hv, i.e., unless v' = v.

According to the postulates of Planck, the oscillator can exist in a set of discrete energy states 0, hv, 2hv, 3hv etc.



Energy levels of an oscillator according to Planck.

The number of oscillators in an energy state  $\mathcal{E}_n = nhv$  is given by the Maxwell-Boltzmann distribution function given by

$$\mathbf{N}_{n} = \mathbf{N}_{0} e^{-\frac{\varepsilon_{n}}{kT}} = \mathbf{N}_{0} e^{-\frac{nhv}{kT}}$$

For  $\mathcal{E}_n = 0$  ,  $N_n = N_0$  so that  $N_0$  is the number of oscillators in the ground state.

Since the energies of the oscillators can only have discrete values, the mean value of energy of the oscillator is given by

Here  $\hbar = \frac{h}{2\pi}$  and  $\omega = 2\pi v$  is the circular frequency.

[Note: If  $h\nu \ll kT$ , i.e.,  $\frac{h\nu}{kT} \ll 1$ , average energy  $\langle \varepsilon \rangle = \frac{h\nu}{(1 + \frac{h\nu}{kT}) - 1} = kT$  which is the classical limit.

This corresponds to the continuous variation of the oscillator energy.]

The number of modes of vibration per unit volume of the cavity for frequencies in the interval v and v + dv is given by

$$n_{\nu}d\nu = \frac{8\pi}{c^3}\nu^2 d\nu$$

Hence the energy density of the black body radiation of frequencies in the interval v and v + dv is given by

$$u_{v}dv = \frac{8\pi}{c^{3}}v^{2}dv \left\langle \varepsilon \right\rangle$$
  
Or,  $u_{v}dv = \frac{8\pi}{c^{3}}\frac{hv^{3}dv}{e^{\frac{hv}{kT}}-1}$   
Or,  $u_{\lambda}d\lambda = \frac{8\pi hc}{\lambda^{5}}\frac{d\lambda}{e^{\frac{hc}{\lambda kT}}-1}$ 

This is the Planck's formula for the distribution of energy of the black body. This agrees well with the experimental results both for the long wavelength and the short wavelength end of the spectrum.

Note:

(i)For shorter wavelengths (  $\lambda \rightarrow 0$  ), we have

$$e^{\frac{hc}{\lambda kT}} - 1 \approx e^{\frac{hc}{\lambda kT}}$$

Writing  $\frac{hc}{k} = b$  and  $8\pi hc = a$  , we have from the Planck's distribution law

$$\lim_{\lambda \to 0} u_{\lambda} d\lambda = \frac{a}{\lambda^5} e^{-\frac{b}{\lambda T}} d\lambda$$

This is Wien's distribution law. Thus, in the limit  $\lambda \to 0$ , Planck's distribution law reduces to the Wien's distribution law.

(ii)For very long wavelengths (  $\lambda \rightarrow \infty$  ),  $\frac{hc}{\lambda} \!\ll\! kT$  . Hence

$$e^{\frac{hv}{kT}} - 1 \approx 1 + \frac{hc}{\lambda kT} - 1 = \frac{hc}{\lambda kT}$$
$$\therefore \lim_{\lambda \to \infty} u_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{\frac{hc}{\lambda kT}} = \frac{8\pi kT}{\lambda^4} d\lambda$$

This is the Rayleigh-Jeans distribution law. Thus, in the limit  $\lambda \to \infty$ , Planck's distribution law reduces to the R-J distribution law.

#### Deduction of Wien's displacement law from Planck's law:

Planck's distribution law is given by

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

The distribution curve will have a maximum for  $\lambda = \lambda_m$  when the denominator becomes minimum.

Let 
$$z = \lambda^5 (e^{\frac{hc}{\lambda kT}} - 1)$$
  

$$\therefore \frac{dz}{d\lambda} = 5\lambda^4 (e^{\frac{hc}{\lambda kT}} - 1) + \lambda^5 e^{\frac{hc}{\lambda kT}} . (-\frac{hc}{\lambda^2 kT}) = 0 \text{ for } \lambda = \lambda_m .$$
Or,  $5\lambda (e^{\frac{hc}{\lambda kT}} - 1) = \frac{hc}{kT} e^{\frac{hc}{\lambda kT}}$ 
Or,  $1 - e^{-\frac{hc}{\lambda kT}} = \frac{hc}{5\lambda kT}$ 
Or,  $1 - e^{-x} = \frac{x}{5}$ , where  $x = \frac{hc}{\lambda kT}$ .

This equation cannot be solved analytically. It can be solved graphically. If we put  $y = 1 - e^{-x}$  and  $y = \frac{x}{5}$ , then the point of intersection of the two graphs given by these equations gives the solution and it is given by x = 4.9651.

$$\therefore \frac{hc}{\lambda_m kT} = x = 4.9651$$

 $\therefore \lambda_m T = \frac{hc}{4.9651k} = \text{constant}$ 

This is Wien's displacement law.

#### Deduction of Stefan-Boltzmann law from Planck's law:

Total energy density of the black body radiation is given by

$$u = \int_{v=0}^{\infty} u_v dv = \frac{8\pi h}{c^3} \int_{v=0}^{\infty} \frac{v^3}{e^{\frac{hv}{kT}} - 1} dv$$
  
Let  $\frac{hv}{kT} = x$   
 $\therefore dv = \frac{kT}{h} dx$   
 $\therefore u = \frac{8\pi h}{c^3} \left(\frac{kT}{h}\right)^4 \int_{x=0}^{\infty} \frac{x^3}{e^x - 1} dx$   
It can be shown that  $\int_{x=0}^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$ .  
 $\therefore u = \frac{8\pi h}{c^3} \left(\frac{kT}{h}\right)^4 \frac{\pi^4}{15} = aT^4$   
Here  $a = \frac{8\pi^5 k^4}{15c^3h^3}$  = constant  
The intensity of the black body radiation is given by

$$E = \frac{c}{4}u = \frac{ca}{4}T^4 = \sigma T^4$$

Here  $\sigma = \frac{ca}{4} = \frac{2\pi^5 k^4}{15c^2 h^3} = 5.67 \text{ x} 10^{-8}$  Joule/sec/m<sup>2</sup>/deg<sup>4</sup>, known as Stefan's constant.

This is Stefan-Boltzmann law.