Statistical Mechanics

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Unit:-

Quantum Theory of Radiation

Topic- 1. Planck's Quantum Postulates.

Planck's Mechanism of Emission and Absorption of Radiation :
Planck in 1900, introduced entirely new ideas to explain the distribution of energy among the various wavelengths of the cavity radiation. He assumed that ***the atoms of the walls of the cavity radiator behave as oscillators, each with a characteristic frequency of oscillation***. These oscillators emit electromagnetic radiant energy into the cavity and also absorb the same from it, and maintain an equilibrium state. Planck made two rather revolutionary assumptions regarding these atomic oscillators :

- **Planck consider that each oscillator have its own characteristic frequency .**
- **Oscillator can have discrete energy level.**
- **Oscillator do not emit or absorb the energy continuously but only in jumps**

Cont/..

(i) An oscillator can have only discrete energies given by

$$\epsilon = n h \nu,$$

where ν is the frequency of the oscillator, h is a constant known as 'Planck's constant', n is an integer known as 'quantum number'. This means that the oscillator can have only the energies $h\nu$, $2h\nu$, $3h\nu$, ... and not any energy in between. In other words, the energy of the oscillator is quantised.

(ii) The oscillators do not emit or absorb energy continuously but only in 'jumps'. That is, an oscillator emits or absorbs packets of energy, each packet carrying an amount of energy $h\nu$.

$$\Delta\epsilon = (\Delta n)\, h\nu, \quad \Delta n = 1, 2 \,........$$

Average Energy of Planck's Oscillator : Let us now calculate the average energy of a Planck's oscillator of frequency ν. The relative probability that an oscillator has the energy $h\nu$ at temperature T is given by the Boltzmann factor $e^{-h\nu/kT}$. Now, let $N_0, N_1, N_2 \,........ N_r \,........$ be the number of oscillators having the energies $0, h\nu, 2h\nu, ...r h\nu .....$ respectively. Then, we have $N_r = N_0\, e^{-rh\nu/kT}$.

The total number of oscillators is

$$N = N_0 + N_1 + N_2 + ...$$

$$= N_0 (1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + ...)$$

$$= \frac{N_0}{1 - e^{-h\nu/kT}}. \qquad ...(i)$$

The total energy of the oscillators is given by

$$\epsilon = (N_0 \times 0) + (N_1 \times h\nu) + (N_2 \times 2h\nu) + ...$$

$$= (N_0 \times 0) + (N_0\, e^{-h\nu/kT} \times h\nu) + (N_0\, e^{-2h\nu/kT} \times 2h\nu) + ...$$

$$= N_0\, e^{-h\nu/kT} h\nu\, (1 + 2e^{-h\nu/kT} + 3e^{-2h\nu/kT} + ...)$$

$$= N_0\, e^{-h\nu/kT} \frac{h\nu}{(1 - e^{-h\nu/kT})^{2}}{*}. \qquad ...(ii)$$

Dividing eq. (ii) by eq. (i), we obtain the *average* energy of an oscillator as given by

$$\bar{\epsilon} = \frac{\epsilon}{N} = \frac{e^{-h\nu/kT}(h\nu)}{1 - e^{-h\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1}. \qquad ...(iii)$$

This is the expression for the average energy of a Planck's oscillator.

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Meaning

$$* \; 1 + 2x + 3x^2 + ... = \frac{1}{(1-x)^2}.$$

Planck's Radiation formula :

Planck's Radiation Formula : We can now combine Planck's expression for the average energy of an oscillator with the number of oscillators (or standing waves) per unit volume of the radiation as computed by Rayleigh and Jeans. Thus, the energy-density of radiation, u_ν, in the frequency range ν to $\nu + d\nu$ is given by

$$u_\nu \, d\nu = \frac{8\pi\nu^2 \, d\nu}{c^3} \times \bar{\epsilon}.$$

The term $\frac{8\pi\nu^2 \, d\nu}{c^3}$ represents the number of electromagnetic standing waves per unit volume in the frequency range ν to $\nu + d\nu$ in the cavity radiation.

Substituting the value of $\bar{\epsilon}$ from eq. (iii), we have

$$u_\nu \, d\nu = \frac{8\pi\nu^2 \, d\nu}{c^3}\left(\frac{h\nu}{e^{h\nu/kT} - 1}\right)$$

or

$$\boxed{u_\nu \, d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1}.}$$

This is Planck's radiation formula in terms of frequency ν. To express it in terms of wavelength, we observe that, since $\nu = \frac{c}{\lambda}$,

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

and since an increase in frequency corresponds to a decrease in wavelength,

$$u_\lambda \, d\lambda = -u_\nu \, d\nu.$$

Therefore

$$u_\lambda \, d\lambda = \frac{8\pi h}{c^3} \frac{\left(\frac{c}{\lambda}\right)^3 \cdot \left(\frac{c}{\lambda^2} d\lambda\right)}{e^{hc/\lambda kT} - 1}$$

or

$$\boxed{u_\lambda \, d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda kT} - 1}.} \qquad \text{...(iv)}$$

This is Planck's formula in terms of wavelength.

Topic-2. Wien's Distribution and Rayleigh-Jeans Law from Planck's formula

Explanation of Energy Distribution by Planck's Formula : Wien's Law and Rayleigh-Jeans Law are Special Cases : The Planck's formula is found to be in complete agreement with experiment for the entire wavelength range at all temperatures. This can be seen in the following way :

(1) When λ is very small, then $e^{hc/\lambda kT} >> 1$, so that Planck's formula given by eq. (iv) can be written as

$$u_\lambda \, d\lambda = \frac{8 \pi h c}{\lambda^5} e^{-hc/\lambda kT} \, d\lambda .$$

Putting $8 \pi h c = A$ and $\frac{h c}{k} = B$, we have

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

This is Wien's law which agrees with experiment at short wavelengths.

(2) When λ is very large, then $e^{hc/\lambda kT} \approx 1 + \frac{h c}{\lambda k T}$, so that eq. (iv) can be written as

$$u_\lambda \, d\lambda = \frac{8 \pi h c}{\lambda^5 \left(1 + \frac{h c}{\lambda k T} - 1\right)} d\lambda = \frac{8 \pi k T}{\lambda^4} d\lambda .$$

This is Rayleigh-Jeans law which agrees with experiment at long wavelengths.

Further, both Wien's displacement law and Stefan's law can also be derived from the Planck's formula.

Topic- 3. Wien's Displacement law from Planck's law

Wien's Displacement Law from Planck's Formula : The Planck's radiation formula is

$$u_\lambda \, d\lambda = \frac{8\pi h c}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda k T} - 1}$$

or

$$u_\lambda = 8\pi h c \, (\lambda^{-5}) \, (e^{hc/\lambda k T} - 1)^{-1} .$$

To find the wavelength at which the spectral radiancy is maximum, we put

$$\frac{du_\lambda}{d\lambda} = 0$$

that is

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

or

$$\frac{5}{\lambda} = (e^{hc/\lambda k T} - 1)^{-1} \, e^{hc/\lambda k T} \, \frac{hc}{\lambda^2 k T}$$

or

$$5 = \frac{hc}{\lambda k T} \frac{e^{hc/\lambda k T}}{e^{hc/\lambda k T} - 1} .$$

Putting $\frac{hc}{\lambda k T} = x$, we get

$$5 = \frac{x e^x}{e^x - 1} = \frac{x}{1 - e^{-x}}$$

or

$$\frac{x}{5} + e^{-x} = 1 .$$

This equation has a single root given by $x = 4{\cdot}965$, and therefore x must be a constant. That is

$$\frac{hc}{\lambda k T} = 4{\cdot}965 .$$

Therefore, the wavelength λ_m at which the spectral radiancy per unit range of wavelength has its maximum value is given by

$$\lambda_m T = \frac{hc}{4{\cdot}965 \, k} = b \text{ (say)} .$$

This is Wien's diplacement law.

Topic- 4. Stefan Law from Planck's law

Stefan's Law from Planck's Formula : Let us write the Planck's radiation formula in terms of frequency :

$$u_\nu \, d\nu = \frac{8 \pi h}{c^3} \frac{\nu^3 \, d\nu}{e^{h\nu/kT} - 1}.$$

The spectral radiancy E_ν is related to the energy-density u_ν by

$$E_\nu = \frac{c}{4} u_\nu .$$

Thus

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

The total radiant energy over all frequencies is

$$E = \int_0^\infty E_\nu \, d\nu = \frac{2\pi h}{c^2} \int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1}.$$

Let us make the substitution $\frac{h\nu}{kT} = x$, so that $\nu = \frac{kT}{h} x$ and $d\nu = \frac{kT}{h} dx$.

Then

$$E = \frac{2 \pi k^4 T^4}{h^3 c^2} \int_0^\infty \frac{x^3 \, dx}{e^x - 1}.$$

The value of the integral $\int_0^\infty \frac{x^3 \, dx}{e^x - 1}$ is $\frac{\pi^4}{15}$. Thus

$$E = \frac{2 \pi^5 k^4}{15 h^3 c^2} T^4 .$$

Let us put $\frac{2 \pi^5 k^4}{15 h^3 c^2} = \sigma$ (a universal constant). Then

$$E = \sigma T^4$$

This is Stefan's law.

Let us calculate the value of Stefan's constant from above :

$$\sigma = \frac{2 \pi^5 k^4}{15 h^3 c^2}$$

$$= \frac{2 \times (3{\cdot}14)^5 \times (1{\cdot}38 \times 10^{-23} \text{ J/K})^4}{15 \times (6{\cdot}63 \times 10^{-34} \text{ J-s})^3 \times (3 \times 10^8 \text{ m/s})^2}$$

$$= 5{\cdot}64 \times 10^{-8} \text{ J/(m}^2\text{-s-K}^4\text{)}.$$

Topic- 5. Determination of sun Temperature

Determination of Temperature of the Sun :

The sun consists of a central hot part known as the "*photosphere*", which is surrounded by a comparatively cooler atmosphere, called "chromosphere." By the temperature of sun we mean temperature of the photosphere.

Let r be the radius and T the absolute temperature of the photosphere of the sun. If we treat it as a black body, then by Stefan's law, the heat radiated by it per unit time is

$$4\pi r^2 \times \sigma T^4,$$

where σ is the Stefan's constant. If R be the mean distance of the earth from the sun, then this radiated energy will be spread over a sphere of surface area $4\pi R^2$. Hence the energy received per unit time per unit surface area of the earth is

$$\frac{4\pi r^2 \times \sigma T^4}{4\pi R^2}.$$

But, this is defined as the solar constant S.

$$\therefore S = \frac{4\pi r^2 \times \sigma T^4}{4\pi R^2}$$

or

$$T^4 = \frac{S}{\sigma}\left(\frac{R}{r}\right)^2.$$

Thus, knowing the values of S, R, r and σ, the black-body temperature of the sun, T, can be found out.


Thank you