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B.Sc. – III, Unit – I

Physical Chemistry

# Introductory Quantum Mechanics

# Black body radiation

Black body is a body that absorbs all the received radiation. In practice an isothermal cavity with a small aperature through which radiation from outside may be admitted is considered as black body. The cavity always contains radiation emitted by the walls. But in practice no body is absolutely black body.

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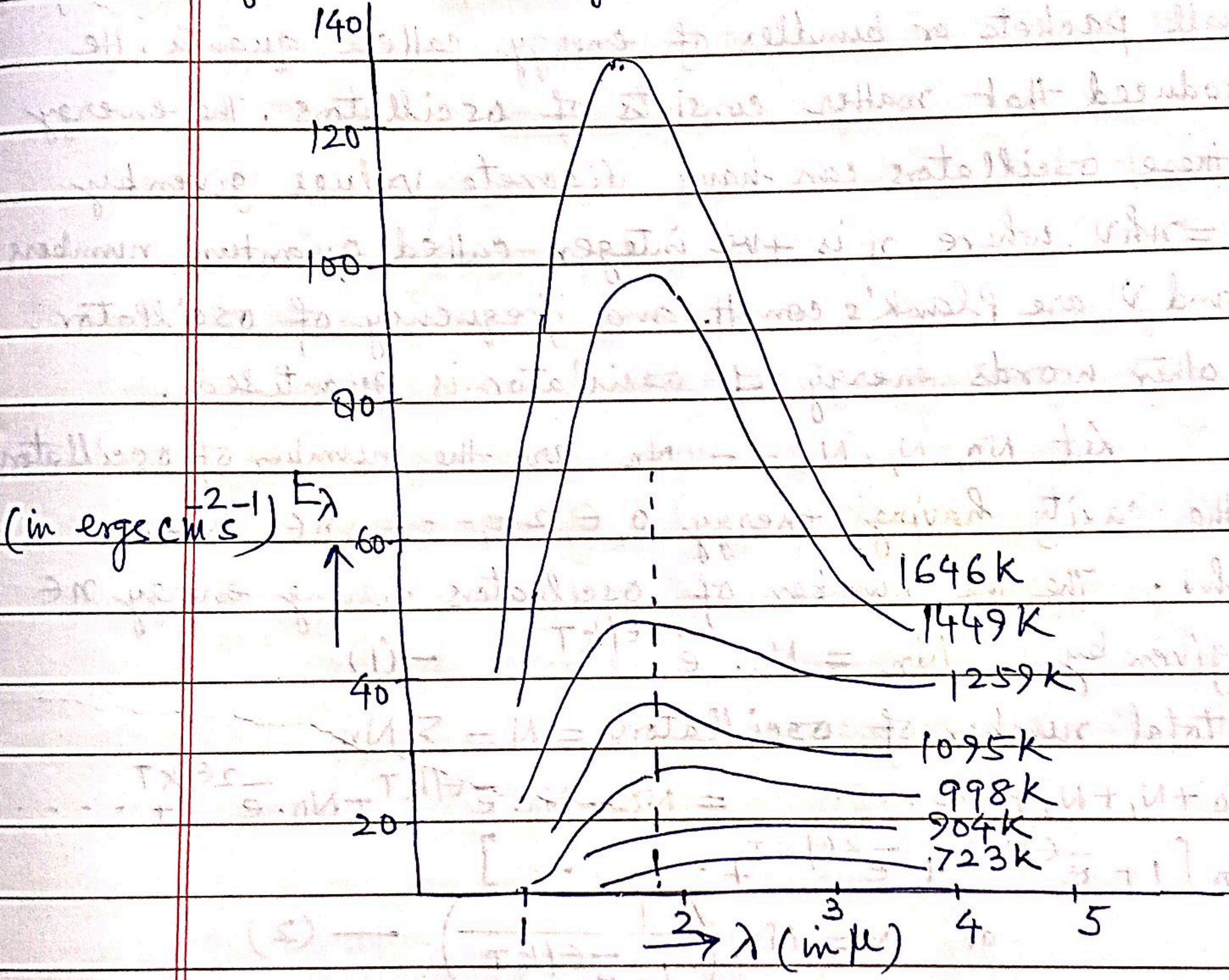
Characteristic of black body radiation — Lummer and Pringsheim obtained spectral distribution curve for black body corresponding to various temperature ranging from 621 to 1646 k. All the curves have similar shape. The characteristics are —

1. At a given T, energy is not radiated out at a single $\lambda$ instead it is distributed over a large range of $\lambda$.
2. At a given T, on increasing $\lambda$ the intensity of radiation first increases, reaches to maximum value at a certain wavelength ($\lambda m$) and then decreases.
3. On increasing T, the emissive power of surface increases for all $\lambda$. The emmissive power of the black body is proportional to the fifth power of absolute temperature. i.e. $E_\lambda \propto T^5$
4. with increase in T, the $\lambda m$ shifts towards shorter $\lambda$ and follows the law $\lambda m \times T = b$ (Wein's constt.). This is called Wein's displacement law. The height of the peak also rises very fast with increase of the temperature.
5. The area enclosed by the $E_\lambda$ V/s $\lambda$ curve gives the total amount of energy radiated at the given T (for all $\lambda$). The area $E = \int_0^\infty E_\lambda \cdot d\lambda$ is found to be proportional to the fourth power of absolute temperature of the body i.e. $E \propto T^4$ so that $E = \sigma . T^4$ where $\sigma$ is stephen Boltzmann constt. and $E \propto T^4$ is called Stephen's law.

6. From Wein's displacement law $\lambda_m \propto \frac{1}{T}$. This law explains why the colour of visible light radiation changes from red (greater $\lambda$) to yellow (lower $\lambda$) as the temperature of the hot body is increased.




Q. A body of temp 1500K radiates max. energy at $\lambda = 20000 \mathring{A}$. If Sun radiates out max. energy at $500 \mathring{A}$, calculate temperature of sun.

A. By Wein's law, $\lambda_m \times T = b$

for the body, $b = (20000 \times 10^{-10} m) \times 1500 k = 0.3 \times 10^{-2} mk$

For the Sun, $0.3 \times 10^{-2} = (500 \times 10^{-10} m) \times T \Rightarrow T = 6000K$

## Plank's Radiation Law

Contrary to classical ideas Plank assumed that emission or absorption of radiation by matter is not in the form of continuous wave but it takes place in the form of small packets or bundles of energy called quanta. He introduced that matter consists of oscillators. The energy of these oscillators can have discrete values given by $\epsilon_n = nh\nu$ where $n$ is +ve integer called quantum numbers, $h$ and $\nu$ are Plank's constt. and frequency of oscillator. In other words energy of oscillator is quantised.

Let $N_0, N_1, N_2 - - N_n$ are the number of oscillators in the cavity having energy $0, \epsilon, 2\epsilon, - - - , n\epsilon$ where $\epsilon = h\nu$. The the number of oscillators having energy $n\epsilon$ is given by $N_n = N_0 . e^{-n\epsilon/kT}$ —(1)

The total number of oscillators $= N = \sum N_n$

$= N_0 + N_1 + N_2 + - - - . . . .$ $= N_0 + N_0 . e^{-\epsilon/kT} + N_0 . e^{-2\epsilon/kT} + . . . .$

$= N_0 [1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT} + - - . . . . - -]$

or $N = N_0 . \left( \frac{1}{1 - e^{-\epsilon/kT}} \right)$ — (2)

Because if we put $e^{-\epsilon/kT} = x$, then $N = N_0 (1 + x + x^2 + - - - )$

and $1 + x + x^2 + - - - = \frac{1}{1-x}$ $\left( S_\infty = \frac{a}{1-r} \right)$

The total energy of these oscillators is given by

$E = \sum \epsilon_n . N_n = 0 . N_0 + \epsilon . N_1 + 2\epsilon . N_2 + - - -$

or $E = 0 + \epsilon . N_0 e^{-\epsilon/kT} + 2\epsilon . N_0 e^{-2\epsilon/kT} + - - - .$

$= \epsilon . N_0 . e^{-\epsilon/kT} \left( 1 + 2 e^{-\epsilon/kT} + 3 e^{-2\epsilon/kT} + - - - - \right)$

Put $e^{-\epsilon/kT} = x$, then $E = \epsilon \cdot N_0 \cdot e^{-x} (1+2x+3x^2+\cdots)$

but $1+2x+3x^2+\cdots = 1/(1-x)^2$

So $E = \epsilon \cdot N_0 \cdot \frac{e^{-x}}{(1-x)^2}$ or $E = \frac{\epsilon N_0 \cdot e^{-\epsilon/kT}}{(1-e^{-\epsilon/kT})^2}$ —— (3)

The average energy of the oscillator is given by,

$$\bar{\epsilon} = \frac{E}{N} = \frac{\epsilon \cdot e^{-\epsilon/kT}}{1-e^{-\epsilon/kT}} \Rightarrow \bar{\epsilon} = \frac{\epsilon}{e^{\epsilon/kT}-1}$$

or $\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT}-1}$ —— (4) (Since $\epsilon = h\nu$)

Hence the average ~~kinetic~~ energy of an oscillator is not $kT$ but given by equation (4).

The energy density belonging to range $\nu$ to $\nu+d\nu$ is obtained by multiplying the average energy of an oscillator ($\bar{\epsilon}$) and the number of resonators per unit volume ($= \frac{8\pi\nu^2}{c^3} d\nu$) in the frequency range $\nu$ to $\nu+d\nu$.

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

or $E_\nu \, d\nu = \frac{8\pi h}{c^3} \cdot \frac{\nu^3 d\nu}{e^{h\nu/kT}-1}$ —— (5)

The equation (5) is called Plank's radiation law.

Since $\lambda$ and $\nu$ are related by $\nu = \frac{c}{\lambda}$ hence $|d\nu| = |\frac{c}{\lambda^2} d\lambda|$

Hence from equation (5), $E_\lambda \, d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{hc/\lambda kT}-1}$

in the range $\lambda$ to $\lambda + d\lambda$

Case-1 For small T and short $\lambda$, the $\lambda T$ is small and hence $e^{hc/\lambda kT} \gtrsim 1$ so $E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \cdot e^{-hc/\lambda kT}$

or $E_\lambda d\lambda = \frac{A}{\lambda^5} \cdot e^{-B/\lambda T} d\lambda$ where $A = 8\pi hc$, $B = \frac{hc}{k}$

This is Wein's law

case-2 For large T and higher $\lambda$,
$e^{hc/\lambda kT} \simeq 1 + \frac{hc}{\lambda kT}$ so $E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} \cdot d\lambda$

If $A = 8\pi k$ then it is Rayleigh Jeans radiation law. So Plank's theory of radiation incorporates all that is valid from the older theories as the special cases. So it is conceptual advance while preserving much of the classical physics.

# Photoelectric Effect

when UV light, X-ray or even visible light strikes surface of a metal, the electrons are ejected from the metal. This is called photo-electric effect (PEE). The characteristics of PEE are as follows—

1. For each metal, a certain min. frequency called thresold freq ($\nu_0$) is needed to eject electron. If frequency of light is $< \nu_0$, no electron is ejected. No matter how long it falls on the surface or how much high its intensity is.
2. The K.E. of emitted electrons depends upon frequency $\nu$ of incident radiation and independent of its intensity.
3. The no. of electrons ejected from metal surface depends upon intensity of incident radiation ($\nu > \nu_0$)

Explanation— According to classical wave theory, the energy of light depends on its intensity. Therefore light of any frequency, if made sufficient intense will eject electron from metal surface. But this is not so. The quantum theory of radiation gives an easy explanation. According to quantum theory of radiation, light is made of bundles of energy called photons having energy $h\nu$ where $\nu$ is the frequency. A body can emitt or absorb energy in terms of $nh\nu$ where $n = 1, 2, 3 \ldots$ According to Einstein, when a photon of energy $h\nu$ strikes a metal surface, some of its energy W ($= h\nu_0$ called work function) is used to remove electron from the surface and rest part is given to electron as kinetic energy ($= \frac{1}{2}mv^2$). So we can write,

$h\nu = W + \frac{1}{2}mv^2$ or $h\nu = h\nu_0 + \frac{1}{2}mv^2$ — (1)

or $\frac{1}{2}mv^2 = h(\nu - \nu_0)$ — (2) This is called Einstein's photo-electric equation. The equation(2) explains all the facts. This shows that velocity of photo-electron increases with $\nu$. If $\nu < \nu_0$, no electron will be ejected.

Millikan tested equation(2) by determining the K.E. of emitted electrons for various frequencies by finding the opposing potential required to stop the photoelectric current. Knowing the frequencies $\nu$ and $\nu_0$, the value of $h$ was found to be $6.570 \times 10^{-34}$ J.S which is in excellant agreement with $6.626 \times 10^{-34}$ J.S obtained from experiment on black body radiation. Application of PEE is in the construction of photo electric cells eg Cesium which converts light energy into electrical energy.

## Heat capacity of solids

According to classical Physics, the heat capacity of all monatomic solids (metals) should be constt equal to 3R (Dulong and Petit Law). But this is true only at high T. At low T, the value is $< 3R$ and approaches zero as $T \to 0$. Einstein explained this using Plank theory of quantication.

Explanation — A monatomic solid can be considered as collection of oscillators having 3-vibrational deg. of freedom. So according to law of equipartition of energy each atom (oscillator) in solid state has mean vib. energy $= 3kT$. For one mole of monatomic solid $N_A(3kT) = 3RT$ and $C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R$ —(1)

Einstein suggested that all vibrators do not have the same vib. freq. (i energy) but have energy which is integral multiple of some minimum value $h\nu_0$. The mean energy of oscillator is given by,

$$\bar{E} = \frac{h\nu_0}{e^{h\nu_0/kT} - 1} \quad \text{—(2)}$$

So the molar energy of solid $E = N_A \times 3\bar{E} = \dfrac{3N_A \cdot h\nu_0}{e^{h\nu_0/kT} - 1}$

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$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3N_A \cdot k\left(\frac{h\nu_0}{kT}\right)^2 \cdot \frac{e^{h\nu_0/kT}}{(e^{h\nu_0/kT}-1)^2} \quad -(3)$$

At low T, $\frac{h\nu_0}{kT} >> 1$ so $e^{h\nu_0/kT} >> 1$

Hence $C_V = 3N_A \cdot k\left(\frac{h\nu_0}{kT}\right)^2 \cdot e^{-h\nu_0/kT}$ $-(4)$

So as temperature decreases, the exponential factor decreases more rapidly than corresponding increase in $\left(\frac{h\nu_0}{kT}\right)^2$. So $C_V$ decreases with decreasing T.

At high T, $\frac{h\nu_0}{kT}$ is very small and hence terms with power $\geq 2$ can be ignored. Thus,

$C_V = 3N_A \cdot k = 3R$ (classical value)

## Compton effect

If monochromatic X-rays are allowed to fall on carbon or some other light element, the scattered X-rays have larger wavelength than incident radiation. Since scattering is caused by electrons hence some interception between X-rays and electron have taken place. This decrease in energy after scattering from the surface of an object is called compton effect. Compton showed that increase in $\lambda$ is given by $\Delta\lambda = \left(\frac{2h}{mc}\right) \cdot \sin^2\left(\frac{\theta}{2}\right)$ where $\Delta\lambda$ is called compton shift, $m$ is the rest mass of electron, $\theta$ is the angle between incident and scattered X-rays. Value of $\Delta\lambda$ (calculated) and $\Delta\lambda$ (experimental) are close. From the equation value of $\Delta\lambda$ is independent of wavelength of incident X-rays.

This effect gives a good illustration of Heisenberg's uncertainty principle. Suppose X-rays are used to determine the position and momentum of an electron. Since frequency of X-rays decreases, this energy must have been transferred to electron. So momentum of electron must have changed during the process i.e. can not be determined with certainty. This effect provides corpuscular (or photon) nature of radiation also.

The equation $\Delta\lambda = \lambda' - \lambda = \frac{h}{mc}(1-\cos\theta)$ for the different cases –

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Case-1, If $\theta = 0^\circ$, $\cos\theta = 1$ so $\Delta\lambda = 0$

Case-2, If $\theta = 90^\circ$, $\cos\theta = 0$ so $\Delta\lambda = \frac{h}{mc}$

or $\Delta\lambda = \frac{6.626 \times 10^{-34}\ J.s}{9.1 \times 10^{-31}\,kg \times 3 \times 10^{8}\ ms^{-1}}$

$= 0.02422 \times 10^{-10}\,m = 0.02422\,A^\circ$

This is called compton wavelength.

Case-3, If $\theta = 180^\circ$, $\cos\theta = -1$ so $\Delta\lambda = \frac{2h}{mc}$

which is two times the compton wavelength.

## de Broglie Hypothesis

The phenomenon of Black body radiation and photo-electric effect can be explained if light is considered to have particle character. However interference and diffraction can be explained only if light is considered to have wave nature.

Newton had suggested that light is a stream of particles, called photons. de Broglie advanced the concept that like photons, all material particles have dual character. The wave associated with matter is called matter wave.

In case of photon energy $E = h\nu$ —(1) Plank q. theory and assuming wave character.

Further if we suppose photon to have particle character then $E = mc^2$ —(2) Einstein equation.

From (1) and (2), $mc^2 = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{h}{mc}$ —(3)

So for any particle having velocity v, $\lambda = \frac{h}{mv} = \frac{h}{p}$
where p is the momentum of the particle. The de Broglie equation has significance only in case of microscopic bodies. So it has no significance in everyday life. eg, A ball of mass 0.1 kg with a speed $60 ms^{-1}$

Here $\lambda = \frac{6.62 \times 10^{-34}}{0.1 \times 60} \simeq 10^{-34} m$ Too small for observation

Further electron $m = 9.1 \times 10^{-31}$ kg moving with speed $60 ms^{-1}$

Here $\lambda = \frac{6.62 \times 10^{-34}}{9.1 \times 10^{-31} \times 60} \simeq 10^{-5} m$ can be measured.

Experimentally wave character of electrons is verified by (a) Davisson and Germer experiment and (b) Thomson experiment. The particle character is proved by Miliken oil drop experiment (det^n of charge on electron), Black body radiation and photoelectric effect.

## Heisenberg Uncertainty Principle

According to this, it is not possible to determine precisely the position and momentum simultaneously of a microscopic body. All the observations are made by impact of light radiation (photons). For object of reasonable size, the position or velocity will not be altered by impact of light photons. The extremely minute particles as electron, will suffer a change in its velocity and path due to impact of even a single photon of light used to observe it. This is the physical significance of the principle. It is expressed as $\Delta x \cdot \Delta p \simeq h/4\pi$ where $\Delta x$ = uncertainty in position and $\Delta p$ = uncertainty in momentum.

In light of this principle, the concept of Bohr's fix orbit can't hold good. Instead it is possible only to predict the probability of locating an electron of a particular energy in a given region of space at a given time around the nucles. This is called orbital.

Ex.:- A body of mass 100 gm is to be located within 0.1 A°. Then uncertainty in velocity

$$\Delta V = \frac{\Delta P}{m} = \frac{h}{4\pi . \Delta x . m} = \frac{6.6 \times 10^{-34}\ Js}{4\pi (10^{-11} m)(0.1\ kg)}$$

$$= 0.527 \times 10^{-22}\ ms^{-1}$$

This uncertainty in velocity can be neglected.

For electron under same condition. ($m = 9.1 \times 10^{-31}$ kg)

$\Delta V = 0.579 \times 10^{7}\ ms^{-1}$ which is very large.

# Postulates of Qunatum mechanics

Quantum mechanics is used for wave-mechanical treatment of atom. It depends on some postulates. For a system moving in one direction (say x-direction) these postulates are –

First – The physical state of system at time t is described by wave function $\Psi(x,t)$

Second – $\Psi(x,t)$, $\frac{\partial \Psi}{\partial x}(x,t)$ and $\frac{\partial^2 \Psi}{\partial x^2}(x,t)$ are finite, continuous and single valued for all x. Further $\Psi(x,t)$ is normalised i.e. $\int_{-\infty}^{\infty} \Psi^*(x,t)\, \Psi(x,t)\, dx = 1$

where $\Psi^*$ is the complex conjugate of $\Psi$.

Third – A physically observable quantity can be represented by Hermitian operator. Operator $\hat{A}$ is Hermitian if,

$$\int \Psi_i^* \hat{A} \Psi_j \, dx = \int \Psi_j (\hat{A} \Psi_i)^* dx$$

Fourth – The allowed values of observable A are the eigenvalue $a_i$ in the operator equation $\hat{A}\Psi_i = a_i \Psi_i$. This is called Eigenvalue equation.

Fifth – The average value of $\langle A \rangle$ of observable A corresponding to operator A is given by,

$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi \, dx$ where $\Psi$ is assumed to be normalised.

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Sixth - The quantum mechanics operators corresponding to observables are constructed by writing classical expressions.

Seventh - $\Psi(x,t)$ is a solution of the equation.

$$\hat{H}\Psi(x,t) = i\hbar \frac{\partial}{\partial t}\Psi(x,t)$$

where $\hat{H}$ is called Hamiltonian operator of the system.