Undergraduate Semester – VI

MJC – 12 (T): Physical Chemistry: Quantum Chemistry & Spectroscopy (T)

Quantum Chemistry & Spectroscopy
Theory: 4 credits

Unit 1: Elementary Quantum Mechanics (contd. from the e-note of 06 – 02 – 2026)

The curves so obtained have the following characteristics.
The radiation emitted by a black body is not confined to a single wavelength but spread over a wide spectrum of wavelengths. The distribution of radiant energy over the different frequencies is described in terms of a function ρ (υ)dυ which denotes the radiant energy density (amount of radiation per unit volume of the black body chamber) in the frequency range υ and υ + dυ.

(i) For each temperature, there is a particular wavelength at which the energy radiated is maximum.

(ii) The position of maximum shift toward lower wavelength with increase in temperature.

(iii) The higher the temperature, the more pronounced is the maximum.

These curves are usually referred to the black body radiation curves. A perfect absorber is also a perfect emitter of radiation. Thus, of all bodies heated to a given temperature, maximum energy is radiated by black body.

According to Wien's displacement law, $\lambda_m T = b$, where λ_m is the wavelength corresponding to maximum in the curve the wein constant b = 0.0029 mK. Wein, the german physicist, was awarded the 1911 Physics Nobel prize for his discovery concerning the laws governing the heat radiation.

Quantum Hypothesis Used for Blackbody Radiation Law:

- To understand how energy is quantized in blackbody radiation.

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James

Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus, matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could not be explained by the theories available at the time.

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation (Figure 1). Attempts to explain or calculate this spectral distribution from classical theory were complete failures. A theory developed by Rayleigh and Jeans predicted that the intensity should go to infinity at short wavelengths. Since the intensity actually drops to zero at short wavelengths, the Rayleigh-Jeans result was called the ultraviolet catastrophe (Figure 1 dashed line). There was no agreement between theory and experiment in the ultraviolet region of the blackbody spectrum.

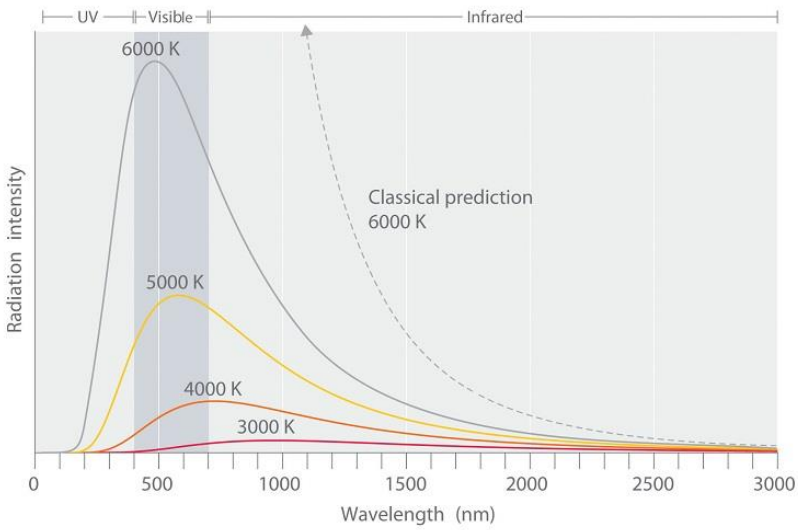

Figure 1: Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun. Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity.