

2.3: Kirchhoff's Law

Kirchhoff's law, as well as his studies with Bunsen (who invented the Bunsen burner for the purpose) showing that every element has its characteristic spectrum, represents one of the most important achievements of mid-nineteenth century physics and chemistry. The principal results were published in 1859, the same year as Darwin's *The Origin of Species*, and it has been claimed that the publication of Kirchhoff's law was at least as influential in the advance of science as the Darwinian theory of evolution. It is therefore distressing that so few people can achieve the triple task of spelling his name, pronouncing it correctly, and properly stating his law. Kirchhoff and Bunsen laid the foundations of quantitative and qualitative spectroscopy.

Imagine an enclosure filled with radiation at some temperature such that the energy density per unit wavelength interval at wavelength λ is $u_\lambda(\lambda)$. Here I have used a subscript and parentheses, according to the convention described in Section 1.3, but, to avoid excessive pedantry, I shall henceforth omit the parentheses and write just u_λ . Imagine that there is some object, a football, perhaps, levitating in the middle of the enclosure and consequently being irradiated from all sides. The irradiance, in fact, per unit wavelength interval, is given by Equation 1.17.1

$$E_\lambda = u_\lambda c/4 \quad (2.4.1)$$

If the absorptance at wavelength λ is $a(\lambda)$, the body will absorb energy per unit area per unit wavelength interval at a rate $a(\lambda)E_\lambda$. The body will become warm, and it will radiate energy. Let the rate at which it radiates energy per unit area per unit wavelength interval (i.e. the exitance) be M_λ . When the body and the enclosure have reached an equilibrium state, the rates of absorption and emission of radiant energy will be equal:

$$M_\lambda = a(\lambda)E_\lambda. \quad (2.4.2)$$

But E and u are related through Equation 2.4.1, and u_λ is independent of the nature of the surface (of the walls of the enclosure or of any body within it), and so we see that the ratio of the exitance to the absorptance of any surface is independent of the nature of the surface. This is Kirchhoff's Law. (In popular parlance, "good emitters are good absorbers".) The ratio is a function only of temperature and wavelength. For a black body, the absorptance is unity, and the exitance is then the Planck function.

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