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Kirchhoff's law Q-1 (11) Paper II

In 1859, Kirchhoff deduced an important law which may be stated as follows: At any given temperature and for radiations of the same wavelength the ratio of the emissive power to the absorptive power is the same for all substances and is equal to the emissive power of a perfectly black body.

Let us consider a body placed inside a uniformly heated enclosure maintained at temperature T. The radiation within the enclosure will be independent of the nature of the walls of the enclosure and of the presence of the body.

Let dQ be the quantity of radiant energy lying between the wavelength λ and $\lambda + d\lambda$, falling on the body per unit area of its surface per second. Let $a\lambda$ be the absorptive power of the body; $a\lambda$ is the ratio of the radiant energy absorbed by the body to the total incident energy at the temperature T and for the wavelength λ. Then the amount of radiant energy absorbed by the body per unit area per second is $a\lambda\, dQ$. The remainder $(1 - a\lambda)\, dQ$ is reflected or transmitted.

If $e\lambda$ be the emissive power of the body, the amount of energy radiated per unit area per second under the same conditions of temperature and wavelength is $e\lambda\, d\lambda$. Hence the total energy given out by the body per unit area per second is

$(1-a\lambda)dQ + e\lambda d\lambda$.

Since the body is in temperature equilibirium with the enclosure, the radiant energy given out must be equal to that recieved.

$$\therefore \ dQ = (1-a\lambda)\, dQ + e\lambda d\lambda$$

or $$a\lambda\, dQ = e\lambda\, d\lambda \quad \text{— (i)}$$

For a perfectly black body, since $a\lambda = 1$ and $e\lambda$ has a maximum value, which we may denote by $E\lambda$,

$$dQ = E\lambda\, d\lambda. \quad \text{— (ii)}$$

Substituting this value of dQ in (i), we have

$$a\lambda E\lambda d\lambda = e\lambda d\lambda$$

or $$\frac{e\lambda}{a\lambda} = E_\lambda. \quad \text{— (iii)}$$

This relation (iii) shows that, at any given temperature T and for radiations of the same wavelength λ, the ratio of the emissive power to the absorptive power of a substance is constant and equal to the emissive power of a perfectly black body. This is Kirchhoff's law which is here proved for bodies inside a uniform temperature enclosure. Since, however, the emissive and absorptive powers depend only on the nature of the body and not on its surroundings, it follows that the law is general, holding good under all conditions for pure temp. radiation.

In the above relation, since $E\lambda$ is a constant, if $e\lambda$ is large, $a\lambda$ is also large & vice versa. This shows that good emitters are also good absorbers.

If, therefore the system passes from the state A to state B along the path C_1 and comes back to the state via the reversible path C_2, then the total change in entropy is,

$$\int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ}{T} = -\int_B^A \frac{dQ}{T} + \int_B^A \frac{dQ}{T} = 0$$

Thus we again find that the change in entropy for a reversible cycle is always zero.