

NOTE ON THE DEDUCTION OF STEFAN'S LAW.

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BOLTZMANN'S thermodynamic deduction of Stefan's law, that the total temperature radiation of a black body is proportional to the fourth power of the absolute temperature, is very concise; and it seems to me that the same thing may be done a little more clearly, at least for those who are familiar with the free energy principle.

Starting with the two laws of thermodynamics,

$$(1) \quad \delta\varepsilon = \delta Q + \delta W,$$

$$(2) \quad \delta\eta = \frac{\delta Q}{\theta},$$

we have, for reversible processes,

$$(3) \quad \delta\varepsilon = \theta\delta\eta + \sum X\delta x,$$

where ε = internal energy, η = entropy, θ = absolute temperature, δQ = heat added to the system, δW = work done on the system, and $X_\kappa\delta x_\kappa$ = the part of the work due to the increase in the variable x_κ . If the system has only two degrees of freedom, and the only external force is a pressure, equation (3) takes the familiar form

$$(4) \quad \delta\varepsilon = \theta\delta\eta - p\delta v.$$

Let

$$(5) \quad \phi = \varepsilon - \theta\eta.$$

Then

$$(6) \quad \delta\phi = -\eta\delta\theta - p\delta v.$$

In any isothermal process, $\delta\theta = 0$, hence

$$(7) \quad \delta\phi = -p\delta v,$$

i. e., the work done on the system by the pressure p , during an increase of volume δv , is equal to the increase of ψ .

The function ψ is Helmholtz's "free energy," and equation (7) may be read: "The work done by a system during an isothermal, reversible change of state, is equal to the decrease of its free energy." This "free energy principle" is generally expressed simply by the equation which defines ψ , namely,

$$(8) \quad \psi = \varepsilon - \theta \eta,$$

which is then to be read: "The decrease of the free energy of any system during a reversible, isothermal change of state, is equal to the decrease of the total energy, minus its absolute temperature multiplied by the decrease in its entropy."

From equation (6) it is evident that

$$(9) \quad -\eta = \frac{\partial \psi}{\partial \theta},$$

so that (8) may be written in the familiar form

$$(10) \quad \psi = \varepsilon + \theta \frac{\partial \psi}{\partial \theta},$$

the interpretation in words being similar to that given above. So much for our thermodynamic tools.

The assumption to be made in the deduction of Stefan's law is one drawn from the electromagnetic theory of light; namely, that parallel rays falling on a black surface exert on it a pressure equal to φ , the volume density of energy in the incident beam. For an entirely unordered radiation inside a black enclosure of absolute temperature θ , the pressure at any point of the bounding surface will then be $\frac{1}{3}\varphi$; just as in the kinetic theory of gases we imagine our molecules, for simplicity, divided into three groups moving at right angles, each group having the sum total of the components in its direction of the momenta of all the molecules with their actual distribution of momentum, and then compute the pressure on that basis.

Consider a cylindrical enclosure formed of black surfaces, having a volume v , and provided with a frictionless black piston. Let the

uniform temperature of the walls be θ , and let the density of the unordered radiation inside be φ . Let the piston move out, reversibly and isothermally, so that the volume increases by δv . The work done by the system is

$$(11) \quad p\delta v = \frac{1}{3} \varphi \delta v,$$

which is, accordingly, the decrease in the free energy of the system, or the ψ of equation (10). We therefore have

$$(12) \quad \frac{\partial \psi}{\partial \theta} = \frac{1}{3} \frac{\partial \varphi}{\partial \theta} \delta v,$$

δv being arbitrary and independent of θ .

The temperature having been kept constant, the density of energy has not changed. Therefore, a quantity of energy $\varphi \delta v$ is now inside the enclosure, in addition to what was there at first. The internal energy of the system has, therefore, *decreased* by $(-\varphi \delta v)$, which is, therefore, the value of the second term in equation (10). Substituting these values in equation (10), we at once get the equation

$$\frac{1}{3} \varphi \delta v = -\varphi \delta v + \frac{1}{3} \theta \frac{\partial \varphi}{\partial \theta} \delta v,$$

or

$$(13) \quad 4\varphi = \theta \frac{\partial \varphi}{\partial \theta}.$$

From this we have, at once,

$$\frac{d\varphi}{\varphi} = 4 \frac{d\theta}{\theta},$$

and

$$(14) \quad \varphi = C\theta^4.$$

Those who do not like the free energy principle, may get the result by using the familiar thermodynamic relation

$$(15) \quad \left(\frac{\partial \eta}{\partial v} \right)_{\theta} = \left(\frac{\partial p}{\partial \theta} \right)_v,$$

which is evident from equation (6). The heat added to the system during the change of volume is equal to the increase of the internal energy $\varphi \delta v$, plus the work which the system has *given out*, namely

$p\delta v$, or $\frac{1}{3}\varphi\delta v$. Therefore, during the isothermal change, the total amount of heat added has been

$$\delta Q = \frac{4}{3}\varphi\delta v;$$

whence

$$\delta\eta = \frac{\delta Q}{\theta} = \frac{4}{3}\frac{\varphi}{\theta}\delta v,$$

and

$$(16) \quad \left(\frac{\partial\eta}{\partial v}\right)_\theta = \frac{4}{3}\frac{\varphi}{\theta}.$$

Also, since $p = \frac{1}{3}\varphi$, we have

$$(17) \quad \left(\frac{\partial p}{\partial\theta}\right)_v = \frac{1}{3}\left(\frac{\partial\varphi}{\partial\theta}\right)_v.$$

Substituting in (15) we have

$$(18) \quad \frac{1}{3}\frac{\partial\varphi}{\partial\theta} = \frac{4}{3}\frac{\varphi}{\theta},$$

whence

$$\frac{d\varphi}{\varphi} = 4\frac{d\theta}{\theta},$$

and

$$(19) \quad \varphi = C\theta^4,$$

as before.