2.8: A Thermodynamical Argument

I have pointed out that Wien's and Stefan's laws can be derived by differentiation and integration respectively of Planck's equation. Readers should try that for themselves if only to convince themselves that neither is particularly easy, nor indeed is the derivation of Planck's equation to begin with. Those who succeed may justifiably congratulate themselves. Those who fail may console themselves with the thought that Stefan's law was derived from a simple thermodynamical argument long before the derivation of Planck's equation, and it is not necessary to know Planck's equation, let alone how to differentiate it or integrate it, in order to arrive at Stefan's law. You do, however, have to know a little thermodynamics.

Among the plethora of thermodynamical relations is to be found one that reads:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{2.8.1}$$

The derivation is usually started by writing entropy as a function of volume and temperature, and the derivation is commonly found as a preliminary to the derivation of the Joule effect for a nonideal gas. When Equation 2.8.1 is applied to the equation of state of a non-ideal gas (for example a van der Waals gas), it can be used to calculate the drop in temperature during a Joule expansion. We wish to apply it, however, to radiation in an enclosure.

We assume that the radiation is isotropic and in a steady state. Under such conditions, photons will presumably bounce rather than stick at the walls, otherwise they would rapidly become depleted - or, if they are absorbed, others are being emitted at the same rate. Either way, the radiation pressure is given by Equation 1.18.3, i.e. $P = u/3$. The energy density depends only on the temperature and not on the volume; therefore the term $(\partial U/\partial V)_T$ on the left hand side of equation 2.9.1 is just the energy density u. And since the pressure is $u/3$, the term $(\partial P/\partial T)_V$ is $\frac{1}{3}(du/dT)_V$.

Equation 2.8.1 therefore becomes

$$u = \frac{T}{3}\left(\frac{du}{dT}\right) - \frac{u}{3} \tag{2.8.2}$$

or

$$4u = T\frac{du}{dT}, \tag{2.8.3}$$

which yields Stefan's law upon integration.