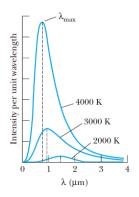
should be frequently repolished" to ensure reliable operation of the spark.<sup>2</sup> Apparently this result was initially quite mysterious to Hertz. In an effort to resolve the mystery, he later investigated this side effect and concluded that it was the ultraviolet light from the initial spark acting on a clean metal surface that caused current to flow more freely between the poles of the spark gap. In the process of verifying the electromagnetic wave theory of light, Hertz had discovered the photoelectric effect, a phenomenon that would undermine the priority of the wave theory of light and establish the particle theory of light on an equal footing.



**Figure 3.3** Emission from a glowing solid. Note that the amount of radiation emitted (the area under the curve) increases rapidly with increasing temperature.

## 3.2 BLACKBODY RADIATION

The tremendous success of Maxwell's theory of light emission immediately led to attempts to apply it to a long-standing puzzle about radiation—the so-called "blackbody" problem. The problem is to predict the radiation intensity at a given wavelength emitted by a hot glowing solid at a specific temperature. Instead of launching immediately into Planck's solution of this problem, let us develop a feeling for its importance to classical physics by a quick review of its history.

Thomas Wedgwood, Charles Darwin's relative and a renowned maker of china, seems to have been the first to note the universal character of all heated objects. In 1792, he observed that all the objects in his ovens, regardless of their chemical nature, size, or shape, became red at the same temperature. This crude observation was sharpened considerably by the advancing state of spectroscopy, so that by the mid-1800s it was known that glowing solids emit continuous spectra rather than the bands or lines emitted by heated gases. (See Fig. 3.3.) In 1859, Gustav Kirchhoff proved a theorem as important as his circuit loop theorem when he showed by arguments based on thermodynamics that for any body in thermal equilibrium with radiation<sup>3</sup> the emitted power is proportional to the power absorbed. More specifically,

$$e_f = J(f, T)A_f \tag{3.1}$$

where  $e_f$  is the power emitted per unit area per unit frequency by a particular heated object,  $A_f$  is the absorption power (fraction of the incident power absorbed per unit area per unit frequency by the heated object), and J(f, T) is a universal function (the same for all bodies) that depends only on f, the light frequency, and T, the absolute temperature of the body. A *blackbody* is defined as an object that absorbs all the electromagnetic radiation falling on it and consequently appears black. It has  $A_f = 1$  for all frequencies and so Kirchhoff's theorem for a blackbody becomes

Blackbody

$$e_f = J(f, T) \tag{3.2}$$

<sup>&</sup>lt;sup>2</sup>H. Hertz, Ann. Physik (Leipzig), 33:983, 1887.

<sup>&</sup>lt;sup>3</sup>An example of a body in equilibrium with radiation would be an oven with closed walls at a fixed temperature and the radiation within the oven cavity. To say that radiation is in thermal equilibrium with the oven walls means that the radiation has exchanged energy with the walls many times and is homogeneous, isotropic, and unpolarized. In fact, thermal equilibrium of radiation within a cavity can be considered to be quite similar to the thermal equilibrium of a fluid within a container held at constant temperature—both will cause a thermometer in the center of the cavity to achieve a final stationary temperature equal to that of the container.

Equation 3.2 shows that the power emitted per unit area per unit frequency by a blackbody depends only on temperature and light frequency and not on the physical and chemical makeup of the blackbody, in agreement with Wedgwood's early observation.

Because absorption and emission are connected by Kirchhoff's theorem, we see that a blackbody or perfect absorber is also an ideal radiator. In practice, a small opening in any heated cavity, such as a port in an oven, behaves like a blackbody because such an opening traps all incident radiation (Fig. 3.4). If the direction of the radiation is reversed in Figure 3.4, the light emitted by a small opening is in thermal equilibrium with the walls, because it has been absorbed and re-emitted many times.

The next important development in the quest to understand the universal character of the radiation emitted by glowing solids came from the Austrian physicist Josef Stefan (1835–1893) in 1879. He found experimentally that the total power per unit area emitted at all frequencies by a hot solid,  $e_{\rm total}$ , was proportional to the fourth power of its absolute temperature. Therefore, Stefan's law may be written as

$$e_{\text{total}} = \int_0^\infty e_f \, df = \sigma T^4 \tag{3.3}$$

where  $e_{\text{total}}$  is the power per unit area emitted at the surface of the blackbody at all frequencies,  $e_f$  is the power per unit area per unit frequency emitted by the blackbody, T is the absolute temperature of the body, and  $\sigma$  is the Stefan–Boltzmann constant, given by  $\sigma = 5.67 \times 10^{-8} \, \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$ . A body that is not an ideal radiator will obey the same general law but with a coefficient,  $a_i$  less than 1:

$$e_{\text{total}} = a\sigma T^4$$
 (3.4)

Only 5 years later another impressive confirmation of Maxwell's electromagnetic theory of light occurred when Boltzmann derived Stefan's law from a combination of thermodynamics and Maxwell's equations.

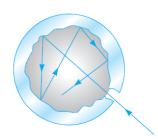


Figure 3.4 The opening to the cavity inside a body is a good approximation of a blackbody. Light entering the small opening strikes the far wall, where some of it is absorbed but some is reflected at a random angle. The light continues to be reflected, and at each reflection a portion of the light is absorbed by the cavity walls. After many reflections essentially all of the incident energy is absorbed.

Stefan's law

#### **EXAMPLE 3.1** Stefan's Law Applied to the Sun

Estimate the surface temperature of the Sun from the following information. The Sun's radius is given by  $R_{\rm s}=7.0\times10^8\,{\rm m}$ . The average Earth–Sun distance is  $R=1.5\times10^{11}\,{\rm m}$ . The power per unit area (at all frequencies) from the Sun is measured at the Earth to be  $1400\,{\rm W/m^2}$ . Assume that the Sun is a blackbody.

**Solution** For a black body, we take a = 1, so Equation 3.4 gives

$$e_{\text{total}}(R_{\text{s}}) = \sigma T^4$$
 (3.5)

where the notation  $e_{\mathrm{total}}(R_{\mathrm{s}})$  stands for the total power per unit area at the surface of the Sun. Because the problem gives the total power per unit area at the Earth,  $e_{\mathrm{total}}(R)$ , we need the connection between  $e_{\mathrm{total}}(R)$  and

 $e_{\text{total}}(R_{\text{s}})$ . This comes from the conservation of energy:

$$e_{\text{total}}(R_{\text{s}}) \cdot 4\pi R_{\text{s}}^2 = e_{\text{total}}(R) \cdot 4\pi R^2$$

or

$$e_{\text{total}}(R_s) = e_{\text{total}}(R) \cdot \frac{R^2}{R_s^2}$$

Using Equation 3.5, we have

$$T = \left[\frac{e_{\rm total}(R) \cdot R^2}{\sigma R_{\rm s}^2}\right]^{1/4}$$

or

$$T = \left[ \frac{(1400 \text{ W/m}^2)(1.5 \times 10^{11} \text{ m})^2}{(5.6 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4)(7.0 \times 10^8 \text{ m})^2} \right]^{1/4}$$
  
= 5800 K

As can be seen in Figure 3.3, the wavelength marking the maximum power emission of a blackbody,  $\lambda_{\rm max}$ , shifts toward shorter wavelengths as the blackbody gets hotter. This agrees with Wedgwood's general observation that objects in his kiln progressed from dull red to orange to white in color as the temperature was raised. This simple effect of  $\lambda_{\rm max} \propto T^{-1}$  was not definitely established, however, until about 20 years after Kirchhoff's seminal paper had started the search to find the form of the universal function J(f,T). In 1893, Wilhelm Wien proposed a general form for the blackbody distribution law J(f,T) that gave the correct experimental behavior of  $\lambda_{\rm max}$  with temperature. This law is called Wien's displacement law and may be written

$$\lambda_{\text{max}} T = 2.898 \times 10^{-3} \,\text{m} \cdot \text{K} \tag{3.6}$$

where  $\lambda_{max}$  is the wavelength in meters corresponding to the blackbody's maximum intensity and T is the absolute temperature of the surface of the object emitting the radiation. Assuming that the peak sensitivity of the human eye (which occurs at about 500 nm—blue-green light) coincides with  $\lambda_{max}$  for the Sun (a blackbody), we can check the consistency of Wien's displacement law with Stefan's law by recalculating the Sun's surface temperature:

$$T = \frac{2.898 \times 10^{-3} \text{ m} \cdot \text{K}}{500 \times 10^{-9} \text{ m}} = 5800 \text{ K}$$

Thus we have good agreement between measurements made at all wavelengths (Example 3.1) and at the maximum-intensity wavelength.

Exercise 1 How convenient that the Sun's emission peak is at the same wavelength as our eyes' sensitivity peak! Can you account for this?

# Spectral energy density of a blackbody

So far, the power radiated per unit area per unit frequency by the blackbody, J(f, T) has been discussed. However, it is more convenient to consider the spectral energy density, or energy per unit volume per unit frequency of the radiation within the blackbody cavity, u(f, T). For light in equilibrium with the walls, the power emitted per square centimeter of opening is simply proportional to the energy density of the light in the cavity. Because the cavity radiation is isotropic and unpolarized, one can average over direction to show that the constant of proportionality between J(f, T) and u(f, T) is c/4, where c is the speed of light. Therefore,

$$J(f, T) = u(f, T)c/4$$
 (3.7)

An important guess as to the form of the universal function u(f, T) was made in 1893 by Wien and had the form

$$u(f,T) = Af^3 e^{-\beta f/T} \tag{3.8}$$

where A and  $\beta$  are constants. This result was known as Wien's exponential law; it resembles and was loosely based on Maxwell's velocity distribution for gas molecules. Within a year the great German spectroscopist Friedrich Paschen

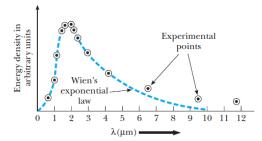


Figure 3.5 Discrepancy between Wien's law and experimental data for a blackbody at 1500 K.

had confirmed Wien's guess by working in the then difficult infrared range of 1 to 4  $\mu\rm m$  and at temperatures of 400 to 1600 K.<sup>4</sup>

As can be seen in Figure 3.5, Paschen had made most of his measurements in the maximum energy region of a body heated to 1500 K and had found good agreement with Wien's exponential law. In 1900, however, Lummer and Pringsheim extended the measurements to 18  $\mu$ m, and Rubens and Kurlbaum went even farther—to 60  $\mu$ m. Both teams concluded that Wien's law failed in this region (see Fig. 3.5). The experimental setup used by Rubens and Kurlbaum is shown in Figure 3.6. It is interesting to note that these historic

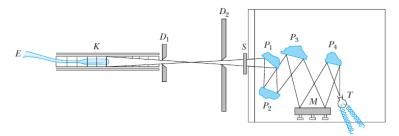


Figure 3.6 Apparatus for measuring blackbody radiation at a single wavelength in the far infrared region. The experimental technique that disproved Wien's law and was so crucial to the discovery of the quantum theory was the method of residual rays (*Restrahlen*). In this technique, one isolates a narrow band of far infrared radiation by causing white light to undergo multiple reflections from alkalide halide crystals ( $P_1-P_4$ ). Because each alkali halide has a maximum reflection at a characteristic wavelength, quite pure bands of far infrared radiation may be obtained with repeated reflections. These pure bands can then be directed onto a thermopile (T) to measure intensity. E is a thermocouple used to measure the temperature of the blackbody oven, K.

<sup>4</sup>We should point out the great difficulty in making blackbody radiation measurements and the singular advances made by German spectroscopists in the crucial areas of blackbody sources, sensitive detectors, and techniques for operating far into the infrared region. In fact, it is dubious whether Planck would have found the correct blackbody law as quickly without his close association with the experimentalists at the Physikalisch Technische Reichsanstalt of Berlin (a sort of German National Bureau of Standards)—Otto Lummer, Ernst Pringsheim, Heinrich Rubens, and Ferdinand Kurlbaum.

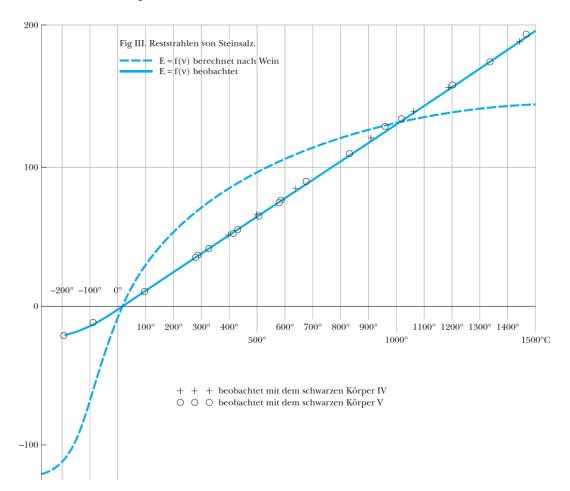


Figure 3.7 Comparison of theoretical and experimental blackbody emission curves at 51.2  $\mu$ m and over the temperature range of  $-188^{\circ}$  to  $1500^{\circ}$ C. The title of this modified figure is "Residual Rays from Rocksalt." *Berechnet nach* means "calculated according to," and *beobachtet* means "observed." The vertical axis is emission intensity in arbitrary units. (*From H. Rubens and S. Kurlbaum*, Ann. Physik, 4:649, 1901.)

experiments involved the measurement of blackbody radiation intensity at a fixed wavelength and variable temperature. Typical results measured at  $\lambda = 51.2~\mu \mathrm{m}$  and over the temperature range of  $-200^{\circ}$  to  $+1500^{\circ}\mathrm{C}$  are shown in Figure 3.7, from the paper by Rubens and Kurlbaum.

# **Enter Planck**

On a Sunday evening early in October of 1900, Max Planck discovered the famous blackbody formula, which truly ushered in the quantum theory. Planck's proximity to the Reichsanstalt experimentalists was extremely important for his discovery—earlier in the day he had heard from Rubens that his latest

measurements showed that u(f,T), the spectral energy density, was proportional to T for long wavelengths or low frequency. Planck knew that Wien's law agreed well with the data at high frequency and indeed had been working hard for several years to derive Wien's exponential law from the principles of statistical mechanics and Maxwell's laws. Interpolating between the two limiting forms (Wien's exponential law and an energy density proportional to temperature), he immediately found a general formula, which he sent to Rubens, on a postcard, the same evening. His formula was<sup>5</sup>

$$u(f, T) = \frac{8\pi h f^3}{c^3} \left( \frac{1}{e^{hf/k_{\rm B}T} - 1} \right)$$
(3.9)

where h is Planck's constant =  $6.626 \times 10^{-34} \,\mathrm{J} \cdot \mathrm{s}$ , and  $k_{\mathrm{B}}$  is Boltzmann's constant =  $1.380 \times 10^{-23} \,\mathrm{J/K}$ . We can see that Equation 3.9 has the correct limiting behavior at high and low frequencies with the help of a few approximations. At high frequencies, where  $hf/k_{\mathrm{B}}T \gg 1$ ,

$$\frac{1}{e^{hf/k_{\rm B}T}-1}\approx e^{-hf/k_{\rm B}T}$$

so that

$$u(f, T) = \frac{8\pi h f^3}{c^3} \left( \frac{1}{e^{hf/k_B T} - 1} \right) \approx \frac{8\pi h f^3}{c^3} e^{-hf/k_B T}$$

and we recover Wien's exponential law, Equation 3.8. At low frequencies, where  $hf/k_BT \ll 1$ ,

$$\frac{1}{e^{hf/k_{\rm B}T}-1} = \frac{1}{1 + \frac{hf}{k_{\rm B}T} + \cdots - 1} \approx \frac{k_{\rm B}T}{hf}$$

and

$$u(f, T) = \frac{8\pi h f^3}{c^3} \left( \frac{1}{e^{hf/k_B T} - 1} \right) \approx \frac{8\pi f^2}{c^3} k_B T$$

This result shows that the spectral energy density is proportional to T in the low-frequency or so-called classical region, as Rubens had found.

We should emphasize that Planck's work entailed much more than clever mathematical manipulation. For more than six years Planck (Fig. 3.8) labored to find a rigorous derivation of the blackbody distribution curve. He was driven, in his own words, by the fact that the emission problem "represents something absolute, and since I had always regarded the search for the absolute as the loftiest goal of all scientific activity, I eagerly set to work." This work was to occupy most of his life as he strove to give his formula an ever deeper physical interpretation and to reconcile discrete quantum energies with classical theory.

<sup>5</sup>Planck originally published his formula as  $u(\lambda,T)=\frac{C_1}{\lambda^5}\left(\frac{1}{e^{C_2/\lambda T}-1}\right)$ , where  $C_1=8\pi ch$  and  $C_2=hc/k_{\rm B}$ . He then found best-fit values to the experimental data for  $C_1$  and  $C_2$  and evaluated  $h=6.55\times 10^{-34}\,{\rm J}\cdot{\rm s}$  and  $k_{\rm B}=N_{\rm A}/R=1.345\times 10^{-23}\,{\rm J/K}$ . As R, the universal gas constant, was fairly well known at the time, this technique also resulted in another method for finding  $N_{\rm A}$ , Avogadro's number.

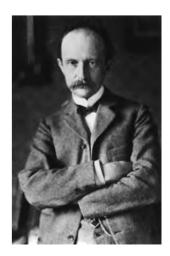


Figure 3.8 Max Planck (1858– 1947). The work leading to the "lucky" blackbody radiation formula was described by Planck in his Nobel prize acceptance speech (1920): "But even if the radiation formula proved to be perfectly correct, it would after all have been only an interpolation formula found by lucky guess-work and thus, would have left us rather unsatisfied. I therefore strived from the day of its discovery, to give it a real physical interpretation and this led me to consider the relations between entropy and probability according to Boltzmann's ideas. After some weeks of the most intense work of my life, light began to appear to me and unexpected views revealed themselves in the distance." (AIP Niels Bohr Library, W. F. Meggers Collection)

### The Quantum of Energy

Planck's original theoretical justification of Equation 3.9 is rather abstract because it involves arguments based on entropy, statistical mechanics, and several theorems proved earlier by Planck concerning matter and radiation in equilibrium. We shall give arguments that are easier to visualize physically yet attempt to convey the spirit and revolutionary impact of Planck's original work.

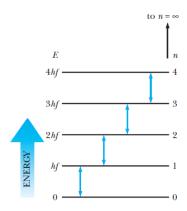
Planck was convinced that blackbody radiation was produced by vibrating submicroscopic electric charges, which he called resonators. He assumed that the walls of a glowing cavity were composed of literally billions of these resonators (whose exact nature was unknown at the time), all vibrating at different frequencies. Hence, according to Maxwell, each oscillator should emit radiation with a frequency corresponding to its vibration frequency. Also according to classical Maxwellian theory, an oscillator of frequency f could have any value of energy and could change its amplitude continuously as it radiated any fraction of its energy. This is where Planck made his revolutionary proposal. To secure agreement with experiment, Planck had to assume that the total energy of a resonator with mechanical frequency f could only be an integral multiple of hf or

$$E_{\text{resonator}} = nhf \qquad n = 1, 2, 3, \dots$$
 (3.10)

where h is a fundamental constant of quantum physics,  $h = 6.626 \times 10^{-34} \, \text{J} \cdot \text{s}$ , known as Planck's constant. In addition, he concluded that emission of radiation of frequency f occurred when a resonator dropped to the next lowest energy state. Thus the resonator can change its energy only by the difference  $\Delta E$  according to

$$\Delta E = hf \tag{3.11}$$

That is, it cannot lose just any amount of its total energy, but only a finite amount, hf, the so-called quantum of energy. Figure 3.9 shows the quantized energy levels and allowed transitions proposed by Planck.



**Figure 3.9** Allowed energy levels according to Planck's original hypothesis for an oscillator with frequency *f*. Allowed transitions are indicated by the double-headed arrows.

<sup>&</sup>lt;sup>6</sup>M. Planck, Ann. Physik, 4:553, 1901.