CONTENTS

CHAPTER 1

THERMAL RADIATION

1–1 Introduction. Radiant-energy transfer is of fundamental importance in the solution of many problems in applied science. Examples of interesting practical applications are theoretical calculations of radiant-heat transfer, flame-temperature measurements, determinations of gas composition and excitation behind shock fronts, and spectroscopic analysis of isothermal multicomponent gas mixtures. Usually a satisfactory (theoretical) description of the phenomena involved is feasible only for equilibrium (thermal) radiation. For this reason it is appropriate to begin a course on applications of radiant-energy transfer with a survey of fundamental laws and a (qualitative) outline of the methods used for calculations of thermal radiation characteristics.

Although the Planck blackbody distribution formula and Kirchhoff's law are generally familiar from introductory surveys of physics,[1-5]† it is desirable to review briefly the origin and significance of these relations after first presenting a brief summary of nomenclature and definitions.

1–2 Definitions and symbols. Because of the large number of measurable parameters involved in quantitative studies of radiant-energy transfer, it is of the utmost importance to adopt a consistent set of definitions and symbols. A compilation of useful quantities appears in Table 1–1. Spectral parameters will be derived by appending to the parent symbol borrowed from Table 1–1 the subscripts λ, ν, or ω, which then identify observable quantities in the wavelength range between λ and $\lambda + d\lambda$, in the frequency range between ν and $\nu + d\nu$, and in the wave number range between ω and $\omega + d\omega$. The emitted radiant flux, radiant intensity, radiancy, and steradiancy characteristic of a blackbody (discussed later in this chapter) source will be identified by the superscript $^\circ$.

In our quantitative theoretical studies of gas emissivities we shall be largely concerned with attempts to calculate from first principles the total ($R = \int_0^\infty R_\lambda \, d\lambda$) and spectral ($R_\lambda \, d\lambda$) radiancies for uniformly distributed gaseous emitters.

† See the references at the end of the chapter.

Table 1–1. Definitions and symbols of several observable quantities used in radiant energy transfer studies. (After Worthing and Halliday.[5])

Symbol	Definition	Representative units	Numerical value for a spherical source with a diameter of 1 cm emitting 100 watts
$\mathcal{E}$	Radiant energy.	ergs, joules	—
$\rho = \dfrac{d\mathcal{E}}{dV}$	Radiant energy per unit volume = radiant energy density.	$ergs/cm^3$	—
$\mathfrak{F}_e = \dfrac{d\mathcal{E}}{dt}$	Emitted radiant flux = radiant energy emitted from a given source in unit time.	ergs/sec, watts	100 watts
$\mathfrak{F} = \dfrac{d\mathcal{E}}{dt}$	Radiant flux (not emitted from a specified source).	watts	—
$J = \dfrac{d}{d\Omega}(\mathfrak{F}_e)$	Radiant intensity = radiant flux emitted from a given source per unit of solid angle. The radiant intensity may vary with the direction of observation.	watts/str (str = steradian)	$100/4\pi$ watts/str $\doteq$ 7.96 watts/str
$R = \dfrac{d}{dAr}(\mathfrak{F}_e)$	Radiancy† = radiant flux emitted from a given source per unit area of emitter (into an angle of 2π steradians).	$watts/cm^2$	$100/\pi$ $watts/cm^2$ = 31.8 $watts/cm^2$
$W = \dfrac{d}{dAr}(\mathfrak{F})$	Radiant flux density (not of a source).	$watts/cm^2$	—

$B_{str} = \frac{1}{\cos\theta}\frac{d}{dAr}\frac{d\mathfrak{F}_e}{d\Omega} = \frac{1}{\cos\theta}\frac{dJ}{dAr} = \frac{1}{\cos\theta}\frac{dH}{d\Omega}$ (θ = angle measured relative to the direction of observation.)	Steradiancy† or specific intensity of a source = radiant flux emitted per unit of solid angle per unit area of the projection of the emitter surface on a plane which is perpendicular to the direction of observation = radiant intensity per unit of projected area = radiancy per unit of solid angle measured with respect to the projected area.	watts/cm^2 · str	$7.96/(\pi/4)$ watts/str·cm^2 = 10.13 watts/str·cm^2 or $31.8/\pi$ watts/cm^2·str = 10.13 watts/cm^2·str (*Note:* The effective solid angle subtended by the projected surface is π steradians.)
I or H or $R = \frac{d\mathfrak{F}_i}{dAr}$ (The subscript i here identifies incident radiation.)	Irradiancy† or incident flux of a surface = rate at which radiant energy is received by a given surface per unit area in unit time.	watts/cm^2	For a surface located at a distance L from a source with radiant intensity J, $H = \frac{1}{dAr}\left(J\frac{dAr\cos\theta}{L^2}\right) = \frac{J\cos\theta}{2}$, where θ is the angle between the normal to the emitting source and the line connecting the center of the receiving surface with the source. For $L = 200$ cm and $\theta = 20°$, $H = 1.87$ watts/m^2.

† Following Worthing,[5] the ending *-ancy* is used in this table to identify a property per unit surface area.

1-3 Equilibrium energy density of radiation in an enclosure.† Consider a vacuum in an enclosure ("Hohlraum") of arbitrary shape. At equilibrium the walls of the enclosure absorb and emit radiant energy in such a way that the evacuated space contains, at any given time, a definite equilibrium number of photons of specified frequency and energy. The entropy of the radiation field per unit volume must remain unchanged when new partitions made of material at the same temperature as the walls are first inserted reversibly into and then removed reversibly from the enclosure.[6] Therefore, because the entropy per unit volume must be a unique function of the energy per unit volume, it follows that the equilibrium energy density of radiation cannot depend either on the size of the enclosure or on the materials used for construction. The total energy of the radiation field is an extensive property and depends, at a given temperature, only on the volume of the enclosure.

We may apply the universal thermodynamic relation for the rate of change of entropy (S) with volume (V) at constant temperature (T) to the radiation field, which must then be assumed to exert on the walls of the enclosure a pressure (p_{rad}) that varies with temperature at constant volume, i.e.,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p_{\text{rad}}}{\partial T}\right)_V. \tag{1-1}$$

However, it is well known from the electromagnetic theory of radiation (compare Eq. 1-17) that

$$p_{\text{rad}} = \frac{1}{3}\,\frac{\mathcal{E}}{V}, \tag{1-2}$$

where $\mathcal{E}$ denotes the total (internal) energy in the radiation field. Application of another universal thermodynamic relation to the radiation field yields the expression

$$T\left(\frac{\partial p_{\text{rad}}}{\partial T}\right)_V = p_{\text{rad}} + \left(\frac{\partial \mathcal{E}}{\partial V}\right)_T, \tag{1-3}$$

where we may identify the last term with $3p_{\text{rad}}$ if we consider a constant-pressure process in which the volume of the enclosure and the total radiant energy $\mathcal{E}$ are increased from zero. Hence

$$T\left(\frac{\partial p_{\text{rad}}}{\partial T}\right)_V = 4p_{\text{rad}}$$

† Throughout the following exposition the aim is an efficient demonstration of useful relations. No attempt will be made to classify historical developments in their proper perspective. The reader interested in the evolution of the science concerned with radiant-transfer problems will find the discussion by Worthing and Halliday[5] particularly informative.

or

$$p_{\text{rad}} = \frac{1}{3}\frac{\mathcal{E}}{V} = \text{constant} \times T^4. \tag{1–4}$$

That is, the energy density of the radiation field ($\mathcal{E}/V$) increases as the fourth power of the temperature.

1–4 Kirchhoff's law and Planck's equation. To identify the constant multiplicative factor appearing in Eq. (1–4), it is necessary to utilize more detailed arguments. First we define the spectral volume density of radiant energy,

$$\rho_\nu(T) = \frac{\mathcal{E}_\nu(T)}{V}, \tag{1–5}$$

as the radiant energy per unit volume in the frequency range between ν and $\nu + d\nu$. That the spectral volume density of radiant energy must be a universal function of the temperature follows from the invariance of the entropy of the system when arbitrary partitions, which are at the same temperature as the walls, are first introduced into the system and then removed from the system. The following[3] is an alternative thermodynamic argument for demonstrating this important result as well as the universal dependence of ρ on ν. Consider an enclosure consisting of two surfaces and divided into two compartments by a screen that has the property of transmitting radiation in only the narrow frequency range between ν and $\nu + d\nu$. When the two walls are at the same temperature, no net interchange of radiant energy can occur, according to the second law of thermodynamics, without the expenditure of work. Hence, since the screen is not movable, the spectral volume density of radiation must be the same on the two sides of the partition at equilibrium, that is, $\rho_\nu(T)$ is a universal function of temperature and frequency.

The velocity of propagation of radiant energy equals the velocity of light c. Using the same arguments as are employed in the kinetic theory of gases, it follows then that the radiant energy incident in unit time on unit area of the wall, in the frequency range between ν and $\nu + d\nu$, is

$$\frac{c}{4}\rho_\nu(T)\,d\nu.$$

If this energy falls on a completely opaque surface with spectral reflectivity r_ν, then the fraction of the incident energy absorbed is

$$\frac{c}{4}\rho_\nu(T)(1 - r_\nu)\,d\nu.$$

But, at equilibrium, the energy absorbed by unit area in unit time must be equal to the energy emitted from unit area in unit time. That is,

$$\frac{c}{4}\rho_\nu(T)(1 - r)_\nu \, d\nu = \frac{c}{4}\rho_\nu(T)\epsilon_\nu \, d\nu, \tag{1-6}$$

where ϵ_ν is called the spectral emissivity. Reference to Eq. (1–6) yields Kirchhoff's law for the case of a completely opaque surface:

$$\epsilon_\nu = 1 - r_\nu. \tag{1-7}$$

A blackbody is defined as a substance that absorbs all the incident radiation. Thus, for a blackbody, $r_\nu = 0$ and $\epsilon_\nu = 1$ for all ν. The radiant energy emitted from unit area of a blackbody at a specified temperature in unit time, into a solid angle of 2π steradians, in the frequency range between ν and $\nu + d\nu$, is

$$R_\nu^\circ \, d\nu = \frac{c}{4}\rho_\nu(T)\, d\nu. \tag{1-8}$$

Evidently R_ν° represents the spectral radiancy for a blackbody emitter.

According to the principles of quantum statistics, we may determine the function $\rho_\nu(T)$ by computing the equilibrium distribution of photons for which the entropy of the radiation field is a maximum and noting that the energy of a photon of frequency ν is $h\nu$, where h is Planck's constant. If the radiation field is treated as an Einstein-Bose gas, Planck's equation for the volume density of radiation is obtained,(3) namely,

$$\rho_\nu(T)\, d\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{[\exp(h\nu/kT)] - 1}\, d\nu, \tag{1-9}$$

where k is the Boltzmann constant.

A heuristic derivation of Eq. (1–9) may be obtained by observing(3,4) that the number of characteristic electromagnetic frequencies $n_\nu \, d\nu$ per unit volume is

$$n_\nu \, d\nu = \frac{8\pi\nu^2}{c^3}\, d\nu \tag{1-10}$$

in the frequency interval between ν and $\nu + d\nu$. The mean energy associated with these vibrations is

$$\bar{E} = \frac{\sum_{n=0}^{\infty} nh\nu\,[\exp(-nh\nu/kT)]}{\sum_{n=0}^{\infty}[\exp(-nh\nu/kT)]} = \frac{h\nu}{[\exp(h\nu/kT)] - 1} \tag{1-11}$$

if the nth harmonic of frequency $nh\nu$ occurs with probability $\exp(-nh\nu/kT)$. If we now make the identification

$$\rho_\nu \, d\nu = n_\nu \bar{E}\, d\nu,$$

we obtain Eq. (1–9) from Eqs. (1–10) and (1–11). It is interesting to note that Eq. (1–11) is consistent with the simplest functional form expressing the entropy of a radiation field in terms of the energy of harmonic oscillators. It was originally obtained by Planck as an interpolation relation between the Wien and the Rayleigh-Jeans formulas (see Section 1–6), which were known to be valid for large and small values of $h\nu/kT$, respectively.[4]

1–5 The Stefan-Boltzmann law and the thermodynamic functions for the radiation field. By using Eq. (1–9) we may derive an explicit relation for the constant appearing in Eq. (1–4). Thus

$$\frac{\mathcal{E}}{V} = \int_0^\infty \rho_\nu \, d\nu = \frac{8\pi h}{c^3}\left(\frac{kT}{h}\right)^4 \int_0^\infty \frac{x^3}{(\exp x) - 1}\, dx.$$

The integral appearing in the preceding expression is evaluated most conveniently by using the following relations:

$$[(\exp x) - 1]^{-1} = \sum_{n=1}^{\infty} \exp(-nx),$$

$$\int_0^\infty x^3 [\exp(-nx)]\, dx = \frac{6}{n^4},$$

and

$$\sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{90}.$$

In this manner it is found that

$$\frac{\mathcal{E}}{V} = \frac{8k^4\pi^5}{15h^3c^3}\, T^4, \tag{1–12}$$

and the constant in Eq. (1–4) is seen to be

$$\frac{8k^4\pi^5}{45h^3c^3}.$$

The integral

$$\int_0^\infty R_\nu^\circ(T)\, d\nu = \frac{c}{4}\int_0^\infty \rho_\nu(T)\, d\nu = \frac{c}{4}\,\frac{\mathcal{E}}{V} = \sigma T^4 \tag{1–13}$$

gives the total intensity of radiation emitted from unit area of a blackbody according to the Stefan-Boltzmann law, and

$$\sigma = \frac{2k^4\pi^5}{15h^3c^2} \tag{1–14}$$

is known as the Stefan-Boltzmann constant.

In view of the general thermodynamic relation

$$\frac{1}{T} = \left(\frac{\partial S}{\partial \mathcal{E}}\right)_V,$$

it follows that

$$\frac{S}{V} = \frac{1}{V}\int_0^T \frac{1}{T}\,d\mathcal{E} = \frac{32k^4\pi^5}{45h^3c^3}\,T^3, \tag{1–15}$$

since the entropy density of radiation must vanish at zero temperature, by Nernst's theorem. Also, the Helmholtz free energy per unit volume is

$$\frac{G}{V} = \frac{\mathcal{E}}{V} - T\frac{S}{V} = -\frac{1}{3}\,\frac{\mathcal{E}}{V} = -\frac{8\pi^5k^4}{45h^3c^3}\,T^4, \tag{1–16}$$

whence it follows that the radiation pressure is

$$p_{\text{rad}} = -\left(\frac{\partial G}{\partial V}\right)_T = \frac{1}{3}\,\frac{\mathcal{E}}{V} = \frac{8\pi^5k^4}{45h^3c^3}\,T^4. \tag{1–17}$$

This last relation for the radiation pressure has been used previously in Eq. (1–2). Finally, we find that the Gibbs free energy F of the equilibrium radiation field vanishes, since

$$F = G + p_{\text{rad}}V = 0. \tag{1–18}$$

1–6 Blackbody radiation laws. In Section 1–4 we defined a blackbody as a substance with zero reflectivity. Actually we were considering an enclosure that does not transmit any radiant energy. The general definition of a blackbody is that of a substance which neither transmits nor reflects any radiation it receives; a blackbody absorbs all the incident radiation. From the thermodynamic considerations given in Sections 1–1 through 1–5 it follows that the equilibrium energy of radiation emitted from unit area of a blackbody in unit time at a fixed temperature represents an upper limit for the thermally emitted energy from unit area for any substance which is at the same temperature as the blackbody. This definition of a blackbody and the quantum-mechanical principle of equipartition of energy have been shown to be sufficient to establish the Planck blackbody distribution law, which expresses the equilibrium rate at which radiant energy is emitted from a blackbody as a function of frequency and temperature T. The Planck blackbody distribution law has been abundantly confirmed by experiment.[5,6,8]

According to Eqs. (1–8) and (1–9), the spectral (monochromatic) blackbody radiancy is given by the expression

$$R_\lambda^\circ\,d\lambda = \frac{c_1}{\lambda^5}\,\frac{d\lambda}{[\exp\,(c_2/\lambda T)] - 1}, \tag{1–19}$$

where c_1/π and c_2 are known as the first and second radiation constants. The quantities c_1 and c_2 may, of course, be expressed in terms of the fundamental physical constants c, h, and k. Thus $c_1 = 2\pi c^2 h \simeq 3.742 \times 10^{-5}$ erg·cm^2·sec^{-1} and $c_2 = hc/k \simeq 1.439$ cm·°K.

For $\lambda T \leq 0.3$ cm·°K, with an accuracy of better than 1%, $R_\lambda^\circ\, d\lambda$ is given by Wien's radiation law,

$$(R_\lambda^\circ)_{\text{Wien}}\, d\lambda = \frac{c_1}{\lambda^5}\left(\exp \frac{-c_2}{\lambda T}\right) d\lambda; \tag{1–20}$$

for $\lambda T \geq 77$ cm·°K, the Rayleigh-Jeans radiation formula,

$$(R_\lambda^\circ)_{\text{R-J}}\, d\lambda = \frac{c_1 T}{c_2 \lambda^4}\, d\lambda, \tag{1–21}$$

gives an accuracy of better than 1%.

For a given temperature, the maximum value of R_λ° is found from Eq. (1–19) to be

$$(R_\lambda^\circ)_{\max} = 21.20 c_1 \left(\frac{T}{c_2}\right)^5 \tag{1–22}$$

and is seen to occur at the wavelength $\lambda_{\max}$ determined by Wien's displacement law,

$$\lambda_{\max} T = \frac{c_2}{4.965} \simeq 0.2898 \text{ cm·°K}. \tag{1–23}$$

The total radiant energy emitted from unit area in unit time by a blackbody over all wavelengths into a solid angle of 2π steradians is

$$R^\circ = \int_0^\infty R_\lambda^\circ\, d\lambda = \sigma T^4, \tag{1–24}$$

where the Stefan-Boltzmann constant σ has the numerical value $\sigma \simeq 5.670 \times 10^{-5}$ erg·cm^{-2}·(°K)$^{-4}$·sec^{-1}. The quantity R° represents the integrated blackbody radiancy and is sometimes referred to also as the total emissive power of a blackbody.

The quantities

$$R_\lambda^\circ, \qquad (R_\lambda^\circ)_{\max}, \qquad \frac{R_\lambda^\circ}{(R_\lambda^\circ)_{\max}}, \qquad \int_0^\lambda R_{\lambda'}^\circ\, d\lambda', \qquad R^\circ,$$

and

$$\frac{1}{R^\circ}\int_0^\lambda R_{\lambda'}^\circ\, d\lambda'$$

have been tabulated for many of the wavelengths and/or temperatures that are likely to be encountered in practice.[7]

The relation $\nu = c/\lambda$, between frequency ν and wavelength λ, where c is the velocity of light ($c \simeq 2.998 \times 10^{10}$ cm·sec^{-1}) has already been used; the wave number ω is the reciprocal of the wavelength, that is, $\omega = 1/\lambda$. It is apparent that the spectral blackbody radiancy in the frequency range between ν and $\nu + d\nu$ at the temperature T is given by the expression

$$R_\nu^\circ \, d\nu = \frac{2\pi h\nu^3}{c^2} \frac{d\nu}{[\exp(h\nu/kT)] - 1}. \tag{1-25}$$

Similarly, $R_\omega^\circ \, d\omega$ is determined according to the equation

$$R_\omega^\circ \, d\omega = 2\pi hc^2\omega^3 \frac{d\omega}{[\exp(hc\omega/kT)] - 1}. \tag{1-26}$$

It is often helpful to note appropriate units for the various radiation functions: ρ may be expressed in ergs/cm^3, $c\rho$ and R in ergs/cm^2·sec, ρ_ν in ergs/cm^3·sec^{-1}, ρ_ω in ergs/cm^3·cm^{-1}, R_ω in ergs/cm^2·sec·cm^{-1}, R_λ in ergs/cm^2·sec·μ, etc. Thus we find, for example, that $R_\omega = (c/4)\rho_\omega = (c^2/4)\rho_\nu$, etc.

1–7 Nonblack radiators. Before describing some of the properties of (solid) nonblack radiators, it is desirable to restate Kirchhoff's law in a slightly different form from the one used in Section 1–4.

Consider two boxes that are at the same temperature, one made of a completely black material, the other of an opaque nonblack substance. Since the temperature is the same in the two enclosures, the volume density of radiant energy $\rho_\nu(T)$ and the irradiancy for the enclosures, H°, must be the same. The equilibrium requirement for the blackbody box shows immediately that $H^\circ = (c/4)\rho = R^\circ$. On the other hand, for the nonblack enclosure the equilibrium condition is expressed by the relation

$$H^\circ = rH^\circ + R, \tag{1-27}$$

where r represents the (total) reflectivity† of the nonblack surface. Since $H^\circ = R^\circ$, it follows from Eq. (1–27) that

$$R = (1 - r)R^\circ \equiv \epsilon R^\circ$$

† Worthing[(5)] uses the ending *-ivity* to identify a property that is independent of the shape or size for a given (pure) substance. The ending *-ance* is used for properties that are functions of the shape or size. When this nomenclature is employed, it is clearly necessary to speak of transmittance and absorbance, rather than of transmissivity and absorptivity, for nonopaque solids, liquids, and gases. However, following conventional terminology for gas radiation, we shall not make Worthing's differentiation and instead shall always use the terms *reflectivity*, *absorptivity*, and *emissivity* even when these parameters depend on the size and/or shape of the substance under consideration.