

## 4

# Interactions of solar and terrestrial radiation with atmospheric trace gases and aerosols

This chapter is concerned with the attenuation by atmospheric gases and aerosols of the incoming shortwave radiation from the Sun (*solar radiation*), and the emission and absorption of outgoing longwave radiation (also called *infrared*, *terrestrial*, or *thermal radiation*) from the Earth and its atmosphere. These interactions play important roles in determining the energy balances, and therefore the temperatures, of the Earth's surface and the atmosphere. Also, the absorption of solar radiation by some atmospheric constituents can lead to photochemical reactions, which play crucial roles in atmospheric chemistry.

Figure 4.1 shows current best estimates of the annual global energy balance of the Earth-atmosphere system expressed in terms of 100 units of incoming solar radiation at the top of the Earth's atmosphere (TOA). About 22 of these units are reflected back into space by clouds, aerosols, and gases, about 20 units are absorbed by the atmosphere, 9 units are reflected from the Earth's surface, and the remaining 49 units are absorbed at the Earth's surface. Measured in the same units, the Earth receives an additional 95 units due to longwave radiation from the atmosphere. Therefore, the total energy received by the Earth is 144 units. Thermal equilibrium at the surface of the Earth is achieved by these 144 units being transferred back to the atmosphere: 114 of them are radiated to the atmosphere as longwave radiation, 23 units as evapotranspiration (which is ultimately released to the atmosphere as latent heat in precipitation), and 7 units are transferred to the atmosphere by heat fluxes associated with turbulence, convection, and so on.

The atmosphere itself must also be in thermal equilibrium. In terms of our units the atmosphere absorbs about 20 from solar radiation and 102 from longwave radiation from the Earth's surface (the other 12 units pass through the atmosphere unattenuated through the so-

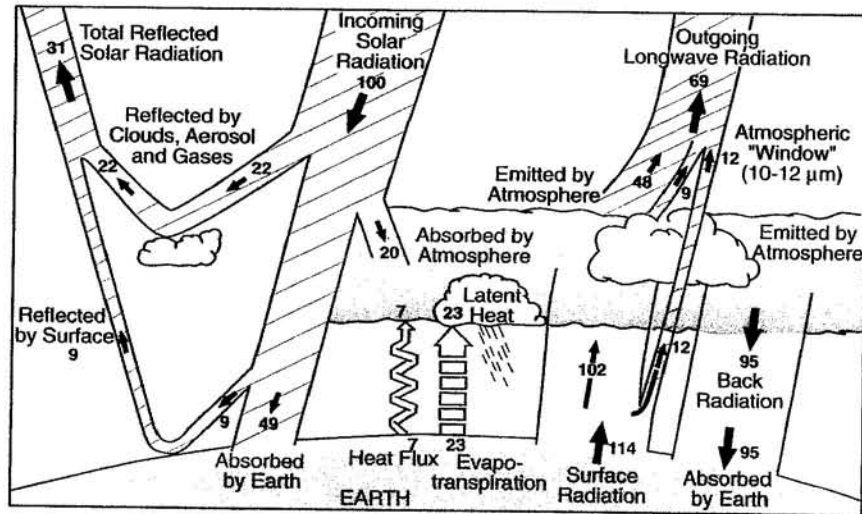


Figure 4.1. The annual mean global energy balance of the Earth-atmosphere system. Numbers are given as percentages of the globally averaged solar energy incident upon the top of the atmosphere (TOA). The 100 units of incoming solar radiation at the TOA represents  $342 \text{ W m}^{-2}$  (see text).

called infrared window), and 30 from latent heat and thermals, for a total receipt of 152 units. The atmosphere "loses" 95 units through longwave radiation to the Earth's surface and 57 to space from longwave radiation from gases, aerosols, and clouds. Note that at the TOA 100 units of energy are incoming and 100 (69 from outgoing longwave radiation and 31 from reflected solar radiation) are outgoing (Figure 4.1), which ensures thermal equilibrium for the Earth-atmosphere system as a whole.

Note that whereas the disposition of solar radiation is dominated by absorption and scattering, thermal radiation is dominated by emission and absorption.

#### 4.1 Some basic concepts and definitions<sup>1</sup>

The rate of transfer of energy by electromagnetic (em) radiation is called *radiant flux* (units are joules per second,  $\text{J s}^{-1}$ , or watts, W). The radiant flux incident on a unit area is called the *irradiance* ( $\text{W m}^{-2}$ ), denoted by  $E$ . The irradiance per unit wavelength interval, centered on wavelength  $\lambda$ , is denoted by  $E_\lambda$  ( $\text{W m}^{-2} \mu\text{m}^{-1}$ ).

$E$   
Wh  
whic  
the  
(t  
out  
(c  
perp  
the  
ener  
surfa  
pare  
 $S_0$   
Sinc  
outw  
wher  
radi  
the in  
= 6.3  
(b)  
the t  
perfe  
amou  
wave  
law  
  
wher  
5.67  
(in K  
visibl  
outer  
  
or  
  
(c)  
incide  
dicula

*Exercise 4.1.* (a) The radiant flux from the Sun is  $3.90 \times 10^{26}$  W. What is the irradiance at the outermost visible layer of the Sun, which is located at a distance of  $7 \times 10^8$  m from the center of the Sun?

(b) Calculate the *equivalent blackbody temperature* of the outermost visible layer of the Sun.

(c) If the average irradiance from the Sun incident on a surface perpendicular to the direction of propagation of the solar beam at the TOA is  $1,368 \text{ W m}^{-2}$  (called the *solar constant*), what is the solar energy (in  $\text{W m}^{-2}$ ) at the TOA when averaged over the whole surface of the globe? (Ignore the thickness of the atmosphere compared to the radius of the Earth.)

*Solution.* (a) Irradiance is the radiant flux passing through  $1 \text{ m}^2$ . Since the Sun's radiation can be considered to propagate radially outward in all directions from the center of the Sun, it will everywhere be normal to a sphere centered on the Sun. A sphere of radius  $7 \times 10^8$  m has a surface area of  $4\pi (7 \times 10^8)^2 \text{ m}^2$ . Therefore, the irradiance passing through this sphere is  $3.90 \times 10^{26} / 4\pi (7 \times 10^8)^2 = 6.34 \times 10^7 \text{ W m}^{-2}$ .

(b) The equivalent blackbody temperature ( $T_E$ ) of an object is the temperature that a blackbody (i.e., a perfect radiator and a perfect absorber) would have to have in order to emit the same amount of radiation as the object. The total irradiance (over all wavelengths) from a blackbody is given by the *Stefan-Boltzmann law*

$$E^* = \sigma T^4 \quad (4.1)$$

where  $\sigma$  is the Stefan-Boltzmann constant, which has a value of  $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ deg}^{-4}$ , and  $T$  is the temperature of the blackbody (in K). When  $T$  in Eq. (4.1) is equal to  $T_E$  for the Sun's outermost visible layer,  $E^*$  given by Eq. (4.1) is equal to the irradiance of the outermost visible layer of the Sun calculated in (a). Therefore,

$$(5.67 \times 10^{-8}) T_E^4 = 6.34 \times 10^7$$

or

$$T_E = 5,780 \text{ K}$$

(c) If the solar irradiance at the TOA is  $1,368 \text{ W m}^{-2}$ ,  $1,368 \text{ W}$  is incident on every square meter of surface that is oriented perpendicular to the Sun's rays at the TOA. If the Earth's radius is  $R_E$ , the

hemisphere of the Earth that faces the Sun at any given time has an area  $\pi R_E^2$  when projected onto a plane perpendicular to the Sun's rays. (Note: Because of its large distance from the Earth, the Sun's rays can be assumed to be parallel at the TOA.) Therefore, the total radiant flux incident on the Earth is  $1,368 \pi R_E^2$ . However, the total surface area of the Earth is  $4\pi R_E^2$ . Therefore, when averaged over the whole surface area of the Earth, the average solar energy at the TOA is  $1,368 \pi R_E^2 / 4\pi R_E^2$  or  $342 \text{ W m}^{-2}$ . (This means that in Figure 4.1, the 100 units of incoming solar radiation at the TOA represents  $342 \text{ W m}^{-2}$ . Therefore, the various percentages given in Figure 4.1 must be multiplied by 342 to convert them to  $\text{W m}^{-2}$ . For example, averaged over the globe the solar energy absorbed by the atmosphere is 20% of 342, or about  $68 \text{ W m}^{-2}$ .)

The wavelength ( $\lambda_m$ ) of peak radiant flux from a blackbody is given by the *Wien<sup>3</sup> displacement law*

$$\lambda_m = \frac{2,897}{T} \quad (4.2)$$

where  $T$  is the temperature (in K) of the blackbody and  $\lambda_m$  is in  $\mu\text{m}$ . Application of this law shows that the Sun (with its high value of  $T$ ) emits its peak radiant flux at a wavelength of  $0.5 \mu\text{m}$ , while the radiant flux emitted by the Earth and its atmosphere (which have much lower values of  $T$ ) is largely confined to infrared (IR) radiation (Figure 4.2).

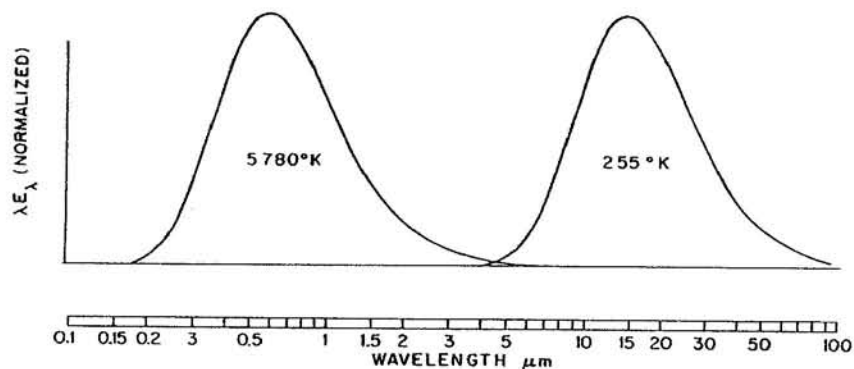


Figure 4.2. Normalized blackbody spectra representative of the Sun (left) and the Earth (right). The ordinate is multiplied by wavelength to make the area under each of the two curves proportional to irradiance, then each curve has been normalized.

The emiss

where  $E_\lambda$  is  
 ture  $T$  and  $I$   
 of a body is  
 at waveleng  
 (all of which  
 Materials  
 lengths are s  
 wavelength  
 they both a  
 summarized

Consider  
 downward th  
 $z + dz$  above  
 tively, and th  
 gases and ae  
 absorbing ra  
 ically) that a  
 wavelength  
 we can write

or

where

and  $b_{s\lambda}$ ,  $b_{a\lambda}$ ,  $\epsilon$   
 coefficients o  
 can be seen f  
 sions of inve  
 Earth's surfac  
 Scattering,  
 gases and aer

The *emissivity* ( $\epsilon_\lambda$ ) at wavelength  $\lambda$  of a body is defined as

$$\epsilon_\lambda \equiv \frac{E_\lambda}{E_\lambda^*} \quad (4.3)$$

where  $E_\lambda$  is the irradiance at wavelength  $\lambda$  from the body at temperature  $T$  and  $E_\lambda^*$  the irradiance from a blackbody at  $T$ . The *absorptivity*  $a_\lambda$  of a body is defined in a similar way, namely, the ratio of the irradiance at wavelength  $\lambda$  absorbed by a body to the irradiance incident upon it (all of which is absorbed by a blackbody).

Materials that are strong absorbers of em radiation at particular wavelengths are strong emitters at those same wavelengths (because at these wavelength the molecules of the material readily vibrate or rotate, so they both absorb and emit radiation efficiently). This relationship is summarized by *Kirchhoff's<sup>A</sup> law*

$$a_\lambda = \epsilon_\lambda \quad (4.4)$$

Consider a parallel beam of solar radiation propagating vertically downward through the atmosphere. Let the irradiances at heights  $z$  and  $z + dz$  above the Earth's surface be  $E_\lambda(z)$  and  $E_\lambda(z) + dE_\lambda(z)$ , respectively, and the irradiance at the TOA be  $E_{\lambda\infty}$  (Fig. 4.3). Atmospheric gases and aerosols can remove energy from the beam by scattering and absorbing radiation. It can be shown (both experimentally and theoretically) that a thin section  $dz$  of air scatters and absorbs em radiation of wavelength  $\lambda$  in an amount proportional to  $dz$  and to  $E_\lambda(z)$ . Therefore, we can write

$$dE_\lambda(z) = (b_{s\lambda} + b_{a\lambda})E_\lambda(z) dz \quad (4.5)$$

or

$$dE_\lambda(z) = b_{e\lambda}E_\lambda(z) dz \quad (4.6)$$

where

$$b_{e\lambda} \equiv b_{s\lambda} + b_{a\lambda} \quad (4.7)$$

and  $b_{s\lambda}$ ,  $b_{a\lambda}$ , and  $b_{e\lambda}$  are called the *scattering*, *absorption*, and *extinction coefficients* of the air, respectively. From dimensional considerations, it can be seen from Eqs. (4.5) and (4.6) that  $b_{s\lambda}$ ,  $b_{a\lambda}$ , and  $b_{e\lambda}$  have dimensions of inverse meters ( $m^{-1}$ ). Note that since  $z$  is height above the Earth's surface,  $dz$  in Figure 4.3 is negative as is  $dE_\lambda(z)$ .

Scattering, absorption, and extinction coefficients can be defined for gases and aerosols individually. For aerosols,  $b_{s\lambda}$ ,  $b_{a\lambda}$ , and  $b_{e\lambda}$  vary greatly



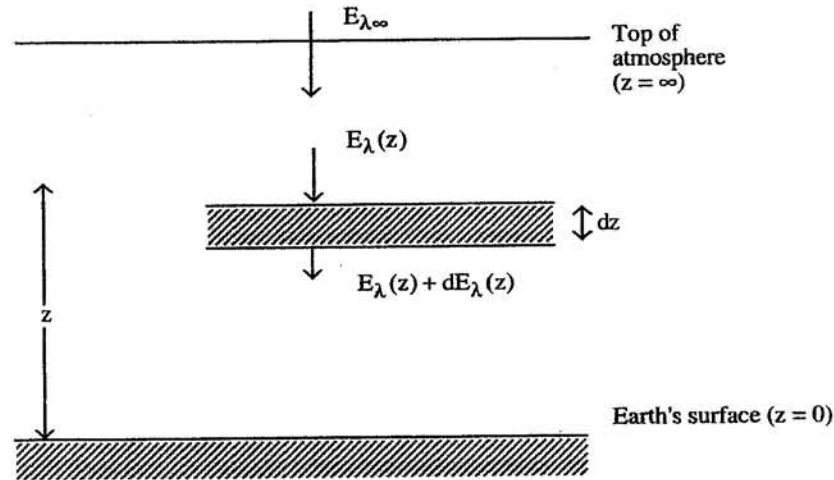


Figure 4.3. Schematic of a parallel beam of solar radiation propagating vertically downward through the atmosphere.

both with the concentration and the size of the particles (relative to  $\lambda$ ). For highly polluted urban air, the values of  $b_{s\lambda}$  near the surface and at mid-visible wavelengths are on the order  $2 \times 10^{-4} \text{ m}^{-1}$ . For clean rural air,  $b_{s\lambda}$  is  $\sim 3 \times 10^{-5} \text{ m}^{-1}$ . For aerosol-free air at sea level,  $b_{s\lambda}$  at midvisible wavelengths is  $\sim 1.3 \times 10^{-5} \text{ m}^{-1}$  (due to scattering by gaseous molecules).

The parameters  $b_{s\lambda}$ ,  $b_{a\lambda}$ , and  $b_{e\lambda}$  can be converted to *mass scattering*, *absorption*, and *extinction efficiencies* (represented by the symbol  $\alpha$  with an appropriate subscript) by dividing them by the mass concentration of the gas (or aerosol) being considered. For example, the absorption mass efficiency of air at wavelength  $\lambda$  is given by

$$\alpha_{a\lambda} = b_{a\lambda} / \rho \quad (4.8)$$

where  $b_{a\lambda}$  is the absorption coefficient for air, and  $\rho$  the density of the constituent. Since  $b_{a\lambda}$  has units of  $\text{m}^{-1}$  and  $\rho$  has units  $\text{kg m}^{-3}$ , the units of  $\alpha_{a\lambda}$  are  $\text{m}^2 \text{ kg}^{-1}$ . The most important absorbing aerosol for solar radiation is *black carbon*, which has an absorption mass efficiency of about  $10 \text{ m}^2 \text{ g}^{-1}$ .

Integration of Eq. (4.6) from height  $z$  above the Earth's surface to the TOA, where the irradiance is the solar spectral irradiance,  $E_{\lambda\infty}$ , gives

$$\int_{E_{\lambda}(z)}^{E_{\lambda\infty}} \frac{dE_{\lambda}(z)}{E_{\lambda}(z)} = \int_z^{\infty} b_{e\lambda} dz \quad (4.9)$$

The op  
and the

(Note t  
units of

or

Equatic

$E_{\lambda}$   
(i.e.,  
visib  
irrad  
 $S_{\lambda}$   
the

From

From  
irrad

If, a  
sola:

This  
visib  
aerc

We s  
the Ea  
irradia

The *optical depth* at wavelength  $\lambda$  of the atmosphere between height  $z$  and the TOA is defined as

$$\tau_\lambda \equiv \int_z^\infty b_{e\lambda} dz \quad (4.10)$$

(Note that, despite its name,  $\tau_\lambda$  is a dimensionless quantity since  $b_{e\lambda}$  has units of  $\text{m}^{-1}$ .) From Eqs. (4.9) and (4.10)

$$\ln E_{\lambda\infty} - \ln E_\lambda(z) = \tau_\lambda$$

or

$$E_\lambda(z) = E_{\lambda\infty} \exp(-\tau_\lambda) \quad (4.11)$$

Equation (4.11) is called *Beer's law*.

**Exercise 4.2.** If the *total column optical depth of the atmosphere* (i.e., the optical depth from the Earth's surface to the TOA) at mid-visible wavelengths is 0.4, what is the percentage reduction in solar irradiance between the TOA and sea level for a vertical Sun?

**Solution.** The percentage reduction is solar irradiance between the TOA ( $E_\infty$ ) and sea level is

$$\frac{E_\infty - E_{\text{sea level}}}{E_\infty} 100 \quad (4.12)$$

From Eq. (4.11)

$$E_{\text{sea level}} = E_\infty \exp(-\tau_\lambda) \quad (4.13)$$

From Eqs. (4.12) and (4.13), the percentage reduction in solar irradiance can be written as

$$[1 - \exp(-\tau_\lambda)]100$$

If, at midvisible wavelengths,  $\tau = 0.4$ , the percentage reduction in solar irradiance is

$$[1 - \exp(-0.4)]100 = 33\%$$

This reduction of about one-third in the solar intensity at mid-visible wavelengths in a polluted atmosphere is due primarily to aerosols.

We see from Eq. (4.11) that if  $\tau_\lambda = 1$  the irradiance at height  $z$  above the Earth's surface would be a factor  $\exp(-1)$ , or about one-third, of the irradiances at the TOA. Typical values of the total column optical depth

of the atmosphere at midvisible wavelengths are ~0.3 to 0.5 for urban air and ~0.2 for fairly clean air.

The *transmissivity* (or *transmittance*) of the atmosphere lying above height  $z$  is defined as

$$T_\lambda \equiv \frac{E_\lambda(z)}{E_{\lambda\infty}} = \exp(-\tau_\lambda) \quad (4.14)$$

The em energy that is scattered and absorbed between the TOA and height  $z$  is  $1 - T_\lambda$ . In the absence of scattering, the absorptivity (defined as the fraction of  $E_{\lambda\infty}$  that is absorbed between the TOA and height  $z$ ) is

$$a_\lambda = 1 - T_\lambda = 1 - \exp(-\tau_\lambda) \quad (4.15)$$

Equation (4.15) shows that  $a_\lambda$  approaches unity exponentially as the optical depth  $\tau_\lambda$  increases.

From Eq. (4.10), the optical depth of a layer of the atmosphere lying between heights  $z_1$  and  $z_2$  ( $z_2 > z_1$ ) is

$$\tau_\lambda = \int_{z_1}^{z_2} b_{e\lambda} dz$$

If  $b_{a\lambda} \gg b_{s\lambda}$ , and if  $b_{a\lambda}$  is independent of  $z$  between  $z_1$  and  $z_2$ ,

$$\tau_\lambda \approx b_{a\lambda}(z_2 - z_1)$$

where  $z_2 - z_1$  is the *path length* of the layer. At wavelengths close to the center of strong gaseous absorption lines  $b_{a\lambda}$  is large, so that very small path lengths can produce large values of  $\tau_\lambda$ , which absorb virtually all of the incident radiation. By contrast, at wavelengths away from absorption lines, very long path lengths are required to produce appreciable absorption.

The nonlinear relationship between  $a_\lambda$  and  $\tau_\lambda$ , given by Eq. (4.15), causes individual lines in the absorption spectrum of a gas (i.e., a plot of  $a_\lambda$  versus  $\lambda$ ) to broaden and merge into *absorption bands* as  $\tau_\lambda$  increases. For sufficiently short path lengths  $\tau_\lambda \ll 1$ , and Eq. (4.15) becomes

$$a_\lambda = 1 - T_\lambda \approx 1 - (1 - \tau_\lambda) = \tau_\lambda \approx b_{a\lambda}(z_2 - z_1)$$

In this case, there is a linear relationship between  $a_\lambda$  and the path length. As the path length increases the relationship between  $a_\lambda$  and  $(z_2 - z_1)$  becomes nonlinear, with  $a_\lambda$  asymptotically approaching unity (i.e., complete absorption) over an ever-widening span of wavelengths. This is depicted in Figure 4.4. As the individual absorption lines widen, adjacent

Figure  
lengths

lines b  
values  
fested  
a rang  
absorp

Figure  
upper  
aeroso  
solar i  
due to  
tion of  
by the  
tion by  
of sola  
Figure

The  
dimens  
molecu  
refract  
( $r/\lambda$ )<sup>4</sup>,  
em rad  
light ( $\lambda$   
size is



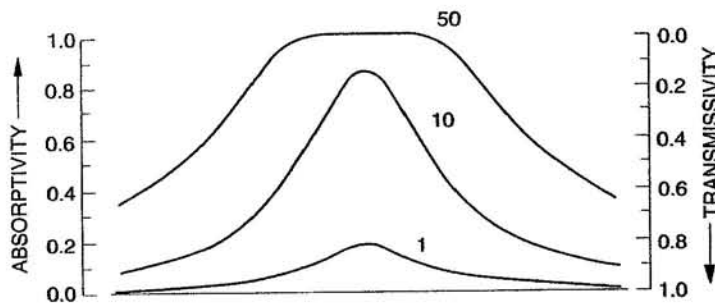


Figure 4.4. Absorption spectrum of an idealized spectral line for three path lengths with relative values indicated on the lines.

lines begin to progressively overlap. Consequently, for a certain range of values of the path length (or optical depth), line clusters become manifested as *absorption bands*, in which substantial absorption occurs over a range of wavelengths. The quasi-transparent regions that lie between absorption bands are called *windows*.

#### 4.2 Attenuation of solar radiation by gases

Figure 4.5 shows the spectrum of solar radiation at the TOA (thick upper curve) and at sea level (thick lower curve) for a hypothetical aerosol-free atmosphere. In the absence of aerosols, the reduction in solar irradiance between the top and the bottom of the atmosphere is due to scattering and absorption by gaseous molecules. The contribution of absorption to the attenuation of the solar radiation is indicated by the shaded region in Figure 4.5. Therefore, in the absence of absorption by gases (and attenuation by clouds and aerosols), the spectrum of solar radiation at sea level would be given by the thin curve in Figure 4.5.

The scattering of visible light by gaseous molecules (which have dimensions much smaller than the wavelength of visible light) is called *molecular or Rayleigh<sup>6</sup> scattering*. In this case, for a molecule with a given refractive index,<sup>7</sup> the fraction of light that is scattered is proportional to  $(r/\lambda)^4$ , where  $r$  is the radius of the molecule and  $\lambda$  the wavelength of the em radiation. For example, the relative amounts of em scattering of blue light ( $\lambda = 0.47 \mu\text{m}$ ) and red light ( $\lambda = 0.64 \mu\text{m}$ ) by a molecule of a given size is

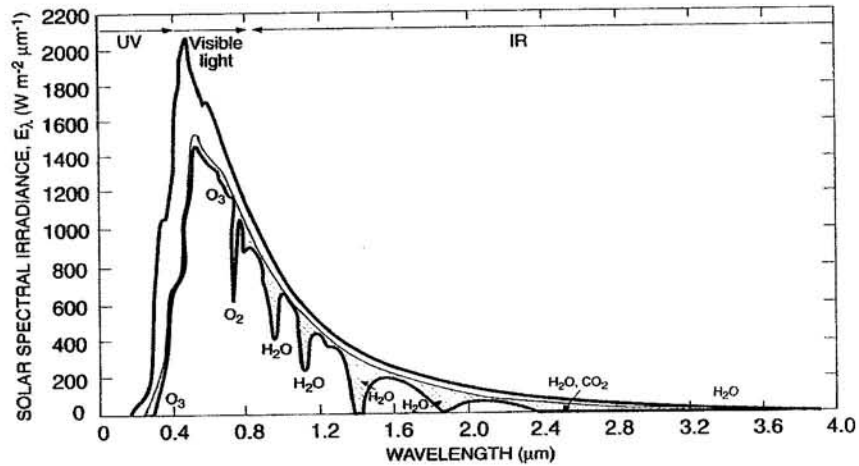


Figure 4.5. The upper thick curve shows the solar irradiance at the top of the atmosphere, and the lower thick curve the computed solar irradiance at sea level for the hypothetical case of an aerosol-free atmosphere. The thin curve represents the irradiance at sea-level if scattering by gaseous molecules alone attenuated solar radiation. The shaded area shows the contribution to the reduction in solar irradiance due to absorption by atmospheric gases, with the main gaseous absorbers indicated. [Adapted from *An Introduction to Atmospheric Radiation* by K.-N. Liou, Academic Press (1980).]

$$\frac{\text{scattering by blue light}}{\text{scattering by red light}} = \left( \frac{\lambda_{\text{red}}}{\lambda_{\text{blue}}} \right)^4 = \left( \frac{0.64}{0.47} \right)^4 = 3.5$$

The blueness of the sky is a consequence of the much greater amount of blue light, compared to red light, scattered by molecules in the air. The total column optical depth of the atmosphere due to Rayleigh scattering alone is about 0.1 at midvisible wavelengths. Rayleigh scattering is proportional to the density of the air, and therefore decreases with increasing altitude.

For Rayleigh scattering the radiation is evenly distributed between the forward and backward directions. For example, averaged over different Sun angles and wavelengths, atmospheric gases scatter about 6% of the incoming solar radiation back to space and about 6% reaches the Earth's surface as *diffuse* radiation.

In contrast to scattering, the absorption of solar radiation by atmospheric gases is quite variable with wavelength (the shaded areas in Fig. 4.5). This is because molecules can absorb em radiation by increasing

the  
the  
the  
Ch  
str  
are  
are  
S  
sol  
len  
the  
vid  
rad  
I  
is c  
will  
0.2  
T  
reg  
fro  
bar  
the  
cov  
V  
cen  
tion  
at 2  
1.6  
whi  
  
We  
of :  
a d  
(a :  
ove  
sca  
not

their *translational* kinetic energy (which increases the temperature of the gas), the *vibrational* energy of their atoms, the *rotational* energy of the molecules about their centers of mass, and their *electronic* energy. Changes in translational energy are not relevant in the troposphere or stratosphere. Changes in vibrational, rotational, and electronic energies are important, and these can change only by discrete amounts (i.e., they are *quantitized*).

Shown in Figure 4.5 are the main atmospheric gaseous absorbers of solar radiation from the near ultraviolet (UV), through visible wavelengths, to the near IR region of the em spectrum. The UV radiation from the Sun at  $\lambda < 0.3 \mu\text{m}$  is absorbed in the upper atmosphere, where it provides the main source of energy for the dynamics of that region. The UV radiation between 0.3 and  $0.4 \mu\text{m}$  reaches the Earth's surface.

In the near-UV ( $\lambda \approx 0.2\text{--}0.3 \mu\text{m}$ ), the absorption of solar radiation is due mainly to electronic transitions of  $\text{O}_3$  in the stratosphere, which will be discussed in Chapter 10. At shorter wavelengths in the UV ( $\lambda < 0.2 \mu\text{m}$ ),  $\text{O}_2$  and  $\text{N}_2$  also absorb solar radiation (not shown in Fig. 4.5).

There is relatively little absorption of solar radiation in the visible region (Fig. 4.5). Ozone absorbs weakly in the visible and near IR regions from about 0.44 to  $1.18 \mu\text{m}$ . Molecular oxygen has two weak absorption bands at red wavelengths. The  $\text{O}_2$  band at  $0.7 \mu\text{m}$  is important because of the large solar irradiance at this wavelength<sup>8</sup>; this band led to the discovery of the isotopes oxygen-18 and oxygen-17.

Water vapor has several important absorption bands in the near IR centered at 0.94, 1.1, 1.38, and  $1.87 \mu\text{m}$  (Fig. 4.5), which are due to vibrational and rotational energy transitions. There are also water vapor bands at 2.7 and  $3.2 \mu\text{m}$ . Carbon dioxide has very weak absorption bands at 1.4, 1.6, and  $2.0 \mu\text{m}$  (not resolved in Fig. 4.5); it also has a band at  $2.7 \mu\text{m}$ , which overlaps the water vapor band at this wavelength.

### 4.3 Vertical profile of absorption of solar radiation in the atmosphere<sup>9</sup>

We can illustrate some of the basic principles involved in the absorption of solar radiation as it passes through the atmosphere by considering a dry atmosphere in which the temperature does not vary with height (a so-called *isothermal atmosphere*), and by considering the case of an overhead Sun. Since we are interested in absorption, rather than scattering, we will assume that  $b_{e\lambda} = b_{a\lambda}$ . We will also assume that  $\alpha_{a\lambda}$  does not vary with height, which could be the case, for example, for absorp-

tion in a CO<sub>2</sub> band because CO<sub>2</sub> is well mixed in the atmosphere. (Note that since  $b_{a\lambda} = \rho\alpha_{a\lambda}$ ,  $b_{a\lambda}$  varies with height even when  $\alpha_{a\lambda}$  is constant.)

For an isothermal atmosphere at temperature  $T$ , the density of the air at height  $z$  above the Earth's surface is given by

$$\rho(z) = \rho_0 \exp\left(-\frac{z}{H}\right) \quad (4.16)$$

where  $\rho_0$  is the air density at the surface, and  $H$  is the scale height for air density which is given by

$$H = \frac{R_d T}{g} \quad (4.17)$$

Because we are assuming that the absorber is well mixed, its scale height is the same as that of the air.  $R_d$  is the gas constant for 1 kg of dry air, and  $g$  is the acceleration due to gravity (compare Eq. (4.16) with Eq. (3.2)). From Eqs. (4.8), (4.10), and (4.16), and using the assumptions stated earlier,

$$\tau_\lambda = \int_z^\infty b_{e\lambda} dz = \int_z^\infty b_{a\lambda} dz = \int_z^\infty \rho \alpha_{a\lambda} dz = \alpha_{a\lambda} \rho_0 \int_z^\infty \exp\left(-\frac{z}{H}\right) dz$$

or, carrying out the integration,

$$\tau_\lambda = H \alpha_{a\lambda} \rho_0 \exp\left(-\frac{z}{H}\right) \quad (4.18)$$

The incident radiation absorbed within any differential layer of the atmosphere is

$$-dE_\lambda = E_{\lambda\infty} T_\lambda da_\lambda \quad (4.19)$$

where  $T_\lambda$  is the transmissivity of the portion of the atmosphere that lies above the layer being considered. From the definition of  $a_\lambda$  and applying Eq. (4.6) for extinction due to absorption alone

$$da_\lambda \equiv -\frac{dE_\lambda}{E_\lambda} = -b_{a\lambda} dz = -\rho \alpha_{a\lambda} dz \quad (4.20)$$

Substituting for  $T_\lambda$  from Eq. (4.14) and  $da_\lambda$  from Eq. (4.20) into Eq. (4.19) yields

$$dE_\lambda = E_{\lambda\infty} \exp(-\tau_\lambda) \rho \alpha_{a\lambda} dz$$

Using Eq. (4.16) in this last expression

$$dE_\lambda = E_{\lambda\infty} \alpha_{a\lambda} \rho_0 \exp\left(-\frac{z}{H}\right) \exp(-\tau_\lambda) dz$$

Substituting for  $\exp(-z/H)$  from Eq. (4.18), we obtain an expression for the absorption per unit thickness of the layer as a function of optical depth

$$\frac{dE_\lambda}{dz} = \frac{E_{\lambda\infty}}{H} \tau_\lambda \exp(-\tau_\lambda) \quad (4.21)$$

Equation (4.21) is important because it represents the energy absorbed per unit volume of air, per unit time, and per unit wavelength.

The general shape of the curve  $dE_\lambda/dz$  versus  $z$  can be predicted as follows. If  $\alpha_{a\lambda}$  is constant with  $z$ , we see from Eqs. (4.8) and (4.20) that

$$\frac{dE_\lambda}{dz} \propto E_\lambda \rho$$

High in the atmosphere  $E_\lambda$  is large, but the density of the air  $\rho$  is small; low in the atmosphere  $E_\lambda$  is small, but  $\rho$  is large. Hence,  $dE_\lambda/dz$  should have a peak value at some intermediate height in the atmosphere. At the level in the atmosphere where  $dE_\lambda/dz$  has a maximum value,  $(d/dz)(dE_\lambda/dz) = 0$ . From Eq. (4.21) this level is given by

$$\frac{E_{\lambda\infty}}{H} \frac{d}{dz} [\tau_\lambda \exp(-\tau_\lambda)] = 0$$

which yields  $\tau_\lambda = 1$ . That is, the *strongest absorption per unit thickness occurs at a level in the atmosphere where the slant path optical depth is unity*. A schematic of the variation of  $dE_\lambda/dz$ ,  $E_\lambda$ , and  $\rho$  with height  $z$  is shown in Figure 4.6.

As we have seen, except in a very highly polluted atmosphere, the optical depth at visible wavelengths does not reach a value of unity even at the Earth's surface. However, at UV wavelengths, strong absorption by ozone results in an optical depth of unity in the stratosphere.

#### 4.4 Heating of the atmosphere due to gaseous absorption of solar radiation

The absorption of solar radiation by various trace gases results in heating of the air. The rate of this heating can be computed as follows.

Let the downward directed irradiances at wavelength  $\lambda$  at heights  $z + dz$  and  $z$  above the Earth's surface be  $E_\lambda^\downarrow(z + dz)$  and  $E_\lambda^\downarrow(z)$ , respectively,



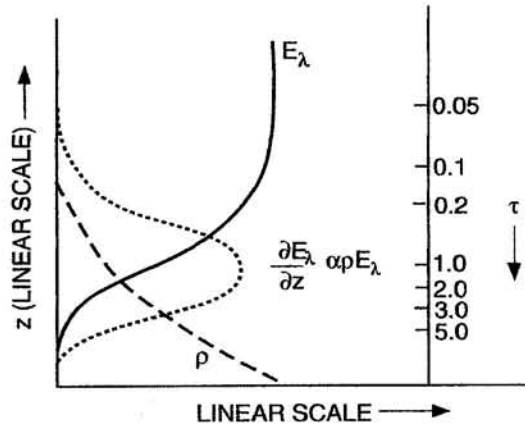


Figure 4.6. Schematic of the variations of  $E_\lambda$ ,  $\rho$ , and  $dE_\lambda/dz$  with height  $z$  in an isothermal and well mixed atmosphere.

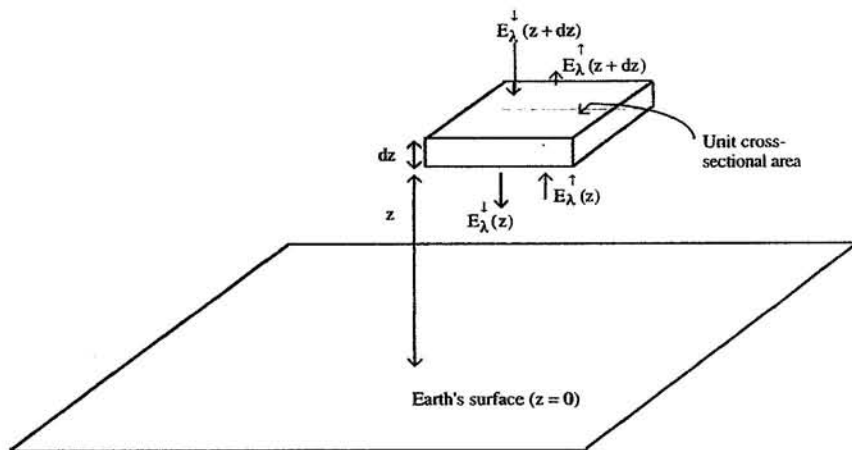


Figure 4.7. Flux divergence of radiation through an infinitesimal layer of air of thickness  $dz$  and unit cross-sectional area located at height  $z$  above the Earth's surface.

and the upward-directed irradiances at heights  $z + dz$  and  $z$  be  $E_\lambda^\uparrow(z + dz)$  and  $E_\lambda^\uparrow(z)$ , respectively (Fig. 4.7). Then the *net* irradiance in the downward direction at height  $z + dz$  is

$$E_\lambda(z + dz) = E_\lambda^\downarrow(z + dz) - E_\lambda^\uparrow(z + dz) \quad (4.22)$$

and the net irradiance in the downward direction at height  $z$  is

$$E_{\lambda}(z) = E_{\lambda}^{\downarrow}(z) - E_{\lambda}^{\uparrow}(z) \quad (4.23)$$

The difference between the net downward-directed irradiances at the bottom and at the top of the layer of thickness  $dz$  is

$$dE_{\lambda}(z) = E_{\lambda}(z) - E_{\lambda}(z + dz) \quad (4.24)$$

which is called the *flux divergence* at height  $z$ . If radiation is absorbed in the layer  $dz$ , the flux divergence  $dE_{\lambda}(z)$ , defined by Eq. (4.24), will be negative.

If we assume that there are no losses of radiant energy through the vertical walls of the layer and there is no upward scattering, it follows from the definition of the absorptivity  $a_{\lambda}$  of the layer  $dz$  that

$$dE_{\lambda}(z) = -E_{\lambda}^{\downarrow}(z + dz)a_{\lambda} \quad (4.25)$$

Since the absorbed energy given by Eq. (4.25) heats the layer of air, we can write

$$dE_{\lambda}(z) = -\rho dz c_p \frac{dT}{dt} \quad (4.26)$$

where  $\rho$  is now the density of the air in the layer of thickness  $dz$  (and therefore  $\rho dz$  is the mass of a unit horizontal area of this layer),  $c_p$  the specific heat at constant pressure of the air (units:  $\text{J kg}^{-1} \text{ deg}^{-1}$ ), and  $dT/dt$  the rate of temperature rise of the layer of air due to the absorption of em radiation. From Eqs. (4.25) and (4.26)

$$\frac{dT}{dt} = -\frac{1}{c_p \rho} \frac{dE_{\lambda}(z)}{dz} = \frac{a_{\lambda}}{c_p \rho} \frac{E_{\lambda}^{\downarrow}(z + dz)}{dz} \quad (4.27)$$

*Exercise 4.3.* Express  $dT/dt$  in terms of  $dE_{\lambda}(p)$ ,  $dp$ , and the *dry adiabatic temperate lapse rate*  $\Gamma_a$  [ $\equiv -(dT/dz)$  for dry parcels of air moving around in the atmosphere under adiabatic conditions], where  $p$  is the atmospheric pressure at height  $z$  above the Earth's surface.

*Solution.* The rate at which pressure changes with height in the atmosphere is given by the *hydrostatic equation*<sup>10</sup>

$$\frac{dp}{dz} = -g\rho \quad (4.28)$$

where  $g$  is the acceleration due to gravity, and  $\rho$  the density of the air at height  $z$ . From Eqs. (4.27) and (4.28),

$$\frac{dT}{dt} = \frac{g}{c_p} \frac{dE_\lambda(p)}{dp} \quad (4.29)$$

The dry adiabatic lapse rate is given by

$$\Gamma_d = \frac{g}{c_p} \quad (4.30)$$

Therefore, from Eqs. (4.29) and (4.30),

$$\frac{dT}{dt} = \Gamma_d \frac{dE_\lambda(p)}{dp} \quad (4.31)$$

Using Eq. (4.28), the quantity  $g/dp$  in Eq. (4.29) can be written as

$$\frac{g}{dp} = \frac{g}{-g\rho dz} = -\frac{1}{\rho dz} = -\frac{\rho_w/\rho}{\rho_w dz} = -\frac{q}{du} \quad (4.32)$$

where

$$q \equiv \frac{\rho_w}{\rho} = \frac{\text{density of water vapor}}{\text{density of air}}$$

is called the *specific humidity* of the air, and

$$du = \rho_w dz \quad (4.33)$$

is called the *density-weighted path length of water vapor* in the layer  $dz$ . Therefore, we can write Eq. (4.29) as

$$\frac{dT}{dt} = -\frac{q}{c_p} \frac{dE_\lambda(u)}{du} \quad (4.34)$$

If the solar spectrum is divided into  $n$  wavelength intervals, the total heating rate of a layer due to solar radiation can be written

$$\left(\frac{dT}{dt}\right)_{\text{tot}} = \sum_{i=1}^n \left(\frac{dT}{dt}\right)_i \quad (4.35)$$

Equations (4.34) and (4.35) can be used to compute the heating rate at various levels in the atmosphere due to the absorption of solar radiation by trace gases.

Fig  
ing  
mid  
surf  
[Ad  
dem

F  
a fu  
over  
abs  
and  
wat  
this  
heat  
abot  
trop

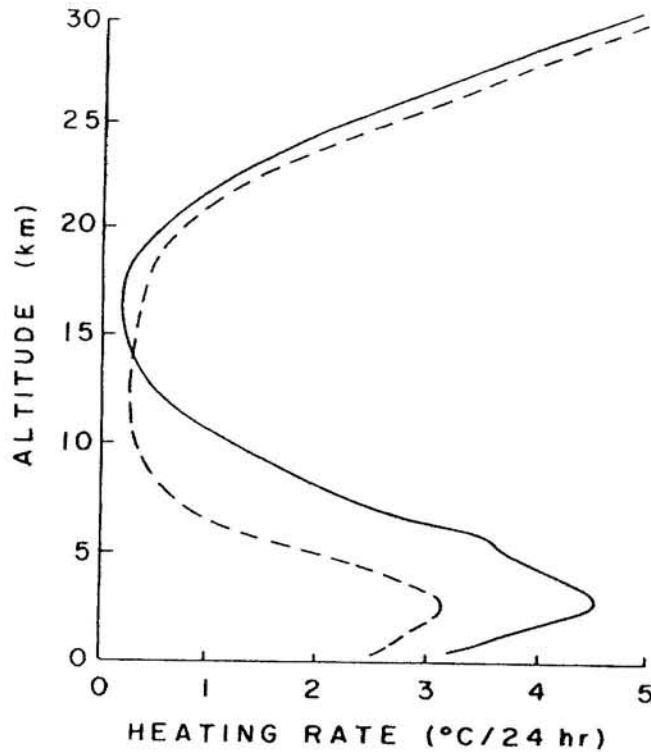


Figure 4.8. Calculated heating rates due to the absorption and multiple scattering of solar radiation by atmospheric gases in the tropics (solid line) and at middle latitudes (dashed line). The Sun is assumed to be overhead, and the surface of the Earth is assumed to reflect 15% of the incident solar radiation. [Adapted from *An Introduction to Atmospheric Radiation* by K.-N. Liou, Academic Press (1980).]

Figure 4.8 shows calculated solar heating rates of the atmosphere as a function of altitude for middle-latitudes and the tropics, assuming an overhead Sun for 24 hours. The calculations incorporate the effects of absorption by  $O_3$ ,  $H_2O$ ,  $O_2$ , and  $CO_2$ , scattering by gaseous molecules, and reflection from the Earth's surface. The higher concentrations of water vapor in the tropical troposphere cause greater heating rates in this region than in the troposphere at middle latitudes. Peaks in the heating rates, of about 3 to 4°C per 24 hours, occur at an altitude of about 3 km. The heating rate decreases sharply with height up to the tropopause (due primarily to the decrease in the amount of water vapor

with height); the heating rate then increases again in the stratosphere. Above the tropopause, the increase in the rate of solar heating is due to absorption by stratospheric  $O_3$ .

#### 4.5 Attenuation of solar radiation by aerosols

Aerosols, which derive from a variety of natural and anthropogenic sources (see Chapter 6), also scatter, and in some cases absorb, solar radiation. For example, it is estimated that the global mean optical depth due to aerosols at midvisible wavelength is  $\sim 0.1$ , with natural and anthropogenic aerosols contributing about equally. Unlike most gases in the atmosphere, aerosols are distributed very unevenly. In heavily polluted air the aerosol optical depth can be  $\sim 0.2$  to  $0.8$ , and in thick smoke (e.g., from biomass burning) it can be in excess of  $1$ . The main natural contributors to the attenuation of solar radiation by aerosols are soil dust, sulfates, and organics; the main anthropogenic contributors are sulfates (from  $SO_2$ ), possibly organics, and particles from biomass burning.

Because the most important aerosol scatterers have dimensions comparable to the wavelength of visible light, Rayleigh scattering does not apply in this case. Instead, the more complete theory of scattering for spherical particles developed by Mie<sup>11</sup> must be used. Shown in Figure 4.9 is the *scattering efficiency*  $K$  (namely, the ratio of the effective scattering cross section of a molecule or particle to its geometric cross section) versus the dimensionless quantity  $\alpha \equiv 2\pi r/\lambda$ , where  $r$  is the radius of the particle (assumed spherical) and  $\lambda$  the wavelength of the em radiation. As we have seen in Section 4.2, when  $\alpha \ll 1$  Rayleigh scattering applies and  $K$  is proportional to  $\alpha^4$ , which is represented by the first rapidly rising portion of the curve on the left-hand side of Figure 4.9. For the scattering of light by most aerosols, the values of  $\alpha$  are between about  $0.1$  and  $50$  (the *Mie regime*). In this regime the value of  $K$  oscillates with  $\alpha$  (Fig. 4.9), and forward scattering predominates over back scattering. If the particles are fairly uniform in size, the scattered sunlight is bluish or reddish in hue, depending on whether  $dK/d\alpha$  is positive or negative at visible wavelengths. If the particles have a size spectrum broad enough to span several of the maxima and minima in the curve shown in Figure 4.9, the scattered light will be whitish.

When  $\alpha > 50$ ,  $K \approx 2$  (the right-hand side of Fig. 4.9), and the angular distribution of the scattered radiation can then be described reasonably well by the theory of geometric optics. The scattering of visible radiation

K

Figure 4  
sorbing sby cloud  
produceThe r  
particle  
called  $e$   
which is  
aerosol  
tures of  
pogenicAbout  
through  
surface  
rium it  
from th  
transfer  
4.1. Mo  
in turn,  
relative  
Earth a  
lengths  
and ne



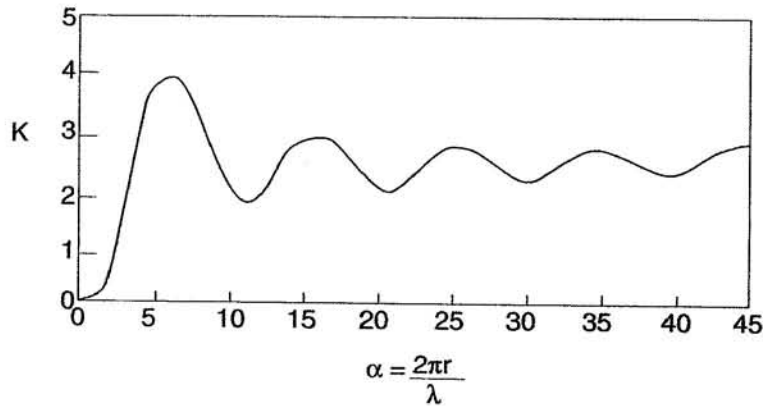


Figure 4.9. The scattering efficiency  $K$  versus the size parameter  $\alpha$  for nonabsorbing spheres with a refractive index of 1.33.

by cloud droplets, raindrops, and ice particles falls within this regime and produces such optical phenomena as rainbows and haloes.

The main absorbers of solar radiation are carbonaceous particles (i.e., particles containing carbon), which are of two types: black carbon (also called *elemental* or *graphitic* carbon) and organic carbon. Black carbon, which is produced by combustion, is the most abundant light-absorbing aerosol in the atmosphere. Organic carbon aerosols are complex mixtures of many compounds that derive from both natural and anthropogenic sources.

#### 4.6 Absorption and emission of longwave radiation

About 60% of the incoming solar radiation to the Earth is transmitted through the atmosphere, and about 40% is absorbed at the Earth's surface (Fig. 4.1). Since the Earth is approximately in thermal equilibrium it must, on average, lose the same amount of energy as it receives from the Sun. It does so by radiating energy upwards (as well as by the transfer of heat through evaporation and turbulent transfer) – see Figure 4.1. Most of the upward radiation is absorbed by the atmosphere which, in turn, emits radiation both upwards and downwards. Because of their relatively low temperatures (compared to the Sun), the surface of the Earth and the atmosphere emit most of their radiant energy at IR wavelengths, while most of the radiant energy from the Sun is in the visible and near IR portions of the em spectrum (see Fig. 4.2).

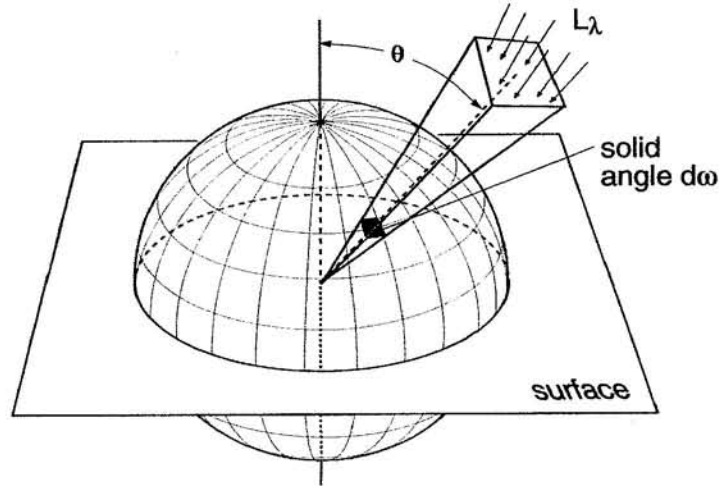


Figure 4.10. Relationship between radiance  $L_\lambda$  and irradiance  $E_\lambda$ . The irradiance of the surface is obtained by integrating the normal component of  $L^*$  to the surface over a hemisphere (see text).

There is another important difference between terrestrial and solar radiation. The solar radiation reaching the TOA can generally be considered as a parallel beam, whereas, terrestrial radiation within the Earth-atmosphere system can come from many different directions (so-called *diffuse radiation*). Consequently, calculations of terrestrial irradiances generally involve integrating IR radiation coming from all directions. To emphasize the processes that determine the emission and absorption of terrestrial radiation, we will set aside the geometrical problems associated with treating diffuse radiation. We can do this by using the various relationships we have derived for parallel beam solar radiation, provided we replace the irradiance  $E_\lambda$  by radiance  $L_\lambda$ . The radiance  $L_\lambda$  is defined as the irradiance (at wavelength  $\lambda$ ) per unit solid angle (units are  $\text{W m}^{-2}$  per steradian per  $\mu\text{m}$ ) reaching a surface from a specified infinitesimal arc of solid angle  $d\omega$  (Fig. 4.10). If the direction of  $L_\lambda$  is at angle  $\theta$  to the normal to the surface

$$E_\lambda = \int_0^{2\pi} L_\lambda \cos \theta d\omega \quad (4.36)$$

where the integration is carried out over a hemisphere (which subtends a solid angle  $2\pi$  steradian). Another important difference in treating solar and terrestrial radiation is that in the latter case we must consider

At

both the absorption and emissions of solar radiation are negligible (Fig. 4.10).

The absorption of solar radiation by the atmosphere is negligible, and the sign reverses.

where we have treated the path length along the surface as negligible. The gas can be treated as a parallel beam in the previous case, and the emission is

where  $\epsilon_\lambda$  is the emissivity (Kirchhoff's law) and  $T(z)$  is the temperature.

The net contribution to the energy balance at wavelength  $\lambda$  is the difference between emission and absorption (given by Eq. 4.36). Therefore,

or

where  $dz$  is the thickness of the layer. Equation (4.36) is the basis for computing the net atmospheric contribution to the energy balance yields

or, using Eqs. 4.36 and 4.37,

both the absorption and emission of longwave radiation, whereas emissions of shortwave radiation by the Earth and its atmosphere are negligible (Fig. 4.2).

The absorption of terrestrial radiation along an *upward* path through the atmosphere is described by a similar expression to Eq. (4.6) but with the sign reversed and with  $E_\lambda$  replaced by  $L_\lambda$

$$-dL_\lambda = L_\lambda \alpha_{a\lambda} \rho dz \quad (4.37)$$

where we have used Eq. (4.8) to substitute for  $b_{a\lambda}$  and  $dz$  is the path length along the line of the radiation. The emission of radiation from a gas can be treated in a similar manner to the way we treated absorption in the previous section. Thus, an analogous expression to Eq. (4.37) for emission is

$$dL_\lambda = L_\lambda^* d\epsilon_\lambda = L_\lambda^* da_\lambda = L_\lambda^* \alpha_{a\lambda} \rho dz \quad (4.38)$$

where  $\epsilon_\lambda$  is the emissivity of the gas, which is equal to its absorptivity  $a_\lambda$  (Kirchhoff's law), and  $L_\lambda^*$  is the blackbody radiance and temperature  $T(z)$ .

The net contribution of the layer of thickness  $dz$  to the radiance of wavelength  $\lambda$  passing upward through it is the difference between the emission (given by Eq. (4.38)) and the absorption (given by Eq. (4.37)). Therefore,

$$dL_\lambda(\text{net}) = L_\lambda^* \alpha_{a\lambda} \rho \sec \theta dz - L_\lambda \alpha_{a\lambda} \rho \sec \theta dz$$

or

$$dL_\lambda(\text{net}) = -\alpha_{a\lambda} (L_\lambda - L_\lambda^*) \rho \sec \theta dz \quad (4.39)$$

where  $dz$  is now the path length normal to the surface (see Fig. 4.10). Equation (4.39), which is known as *Schwarzschild's*<sup>12</sup> *equation*, is the basis for computing the transfer of longwave radiation. For an isothermal atmosphere,  $L_\lambda^*$  is constant. In this case, integration of Eq. (4.39) yields

$$\int_{L_{\lambda 0}}^{L_\lambda} \frac{dL_\lambda}{L_\lambda - L_\lambda^*} = -\int_0^z \alpha_{a\lambda} \rho \sec \theta dz$$

or, using Eqs. (4.8) and (4.10),

$$\ln \left( \frac{L_\lambda - L_\lambda^*}{L_{\lambda 0} - L_\lambda^*} \right) = -\tau_\lambda \sec \theta$$

where  $\tau_\lambda$  is the optical depth from the Earth's surface ( $z = 0$ ) to height  $z$ , and  $L_{\lambda 0}$  and  $L_\lambda$  and the upward radiances at  $z = 0$  and at  $z$ . Rearrangement of the last expression yields

$$L_\lambda - L_\lambda^* = (L_{\lambda 0} - L_\lambda^*) \exp(-\tau_\lambda \sec \theta) \quad (4.40)$$

Equation (4.40) shows that  $L_\lambda$  approaches  $L_\lambda^*$  as the optical depth  $\tau_\lambda$  increases. That is, a very deep atmosphere radiates like a blackbody.

#### 4.7 The greenhouse effect, radiative forcing, and global warming

As we have seen, about 50% of the solar radiation incident on the TOA reaches the surface of the Earth, where it is absorbed. Consequently, the Earth's surface is the principal source of heat for the atmosphere. The longwave radiation from the Earth's surface is largely absorbed by the atmosphere. The atmosphere, in turn, emits longwave radiation upward and downward in amounts that vary with the temperature of the air at the level of the emission. The downward flux of longwave radiation from the atmosphere causes the surface of the Earth to have a higher temperature than it would have in the absence of an absorbing atmosphere. This is called the *greenhouse effect*. The following exercise illustrates how this effect comes about for a simplified Earth-atmosphere system.

*Exercise 4.4.* (a) The *emission temperature*  $T_E$  of the Earth is defined as the temperature it would have to have to achieve radiative energy balance (i.e., solar radiation absorbed = terrestrial radiation emitted) assuming that the Earth radiates as a blackbody. Derive an expression for the emission temperature of the Earth, assuming that it does *not* have an atmosphere, in terms of the solar irradiance at the TOA ( $E_\infty$ ), the radius of the Earth ( $R_E$ ), and the fraction of the incoming solar radiation reflected back to space by the Earth ( $R$ , called the *albedo* of the Earth). If  $E_\infty = 1,368 \text{ W m}^{-2}$ ,  $R = 0.3$ , and  $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ deg}^{-4}$ , what is the value of  $T_E$  for this hypothetical Earth?

(b) Now consider a more realistic approximation to the Earth-atmosphere system, namely, an atmosphere that is blackbody (i.e., opaque) for terrestrial radiation but transparent for solar radiation. Show that in this case the surface temperature of the Earth ( $T_s$ ) is greater than  $T_E$  by about 20%.

*Solution.* (a) The radiant flux from the Sun incident on a surface oriented normal to the Sun's parallel rays and located at the same

Th

distan  
spher  
jected  
There  
the Su  
reflect  
that is  
For

There.

where  
fact th

Substi  
deg<sup>-4</sup> i  
the er  
hypotl  
the ac  
(15°C,  
(b)  
Eq. (4  
wave i  
to spa  
There)

We see  
the su  
see if  
(Fig. 4

or

distance from the Sun as the Earth is  $E_{\infty} \text{ W m}^{-2}$ . When the hemisphere of the Earth that is facing the Sun at any given time is projected onto a plane normal to the Sun's rays it has an area  $\pi R_E^2$ . Therefore, the total radiant energy incident on the Earth from the Sun is  $E_{\infty} \pi R_E^2$  watts. However, a fraction  $R$  of this energy is reflected back to space. Therefore, the radiant energy from the Sun that is absorbed by the Earth is  $E_{\infty} (1 - R) \pi R_E^2$  watts.

For the radiative energy balance of the Earth

solar radiation absorbed = terrestrial radiation emitted

Therefore, from the definition of  $T_E$ ,

$$E_{\infty} (1 - R) \pi R_E^2 = \sigma T_E^4 4 \pi R_E^2$$

where we have used the Stefan-Boltzmann law (Eq. 4.1), and the fact that the total surface area of the Earth is  $4 \pi R_E^2$ . Therefore,

$$\frac{E_{\infty}}{4} (1 - R) = \sigma T_E^4 \quad (4.41)$$

Substituting  $E_{\infty} = 1,368 \text{ W m}^{-2}$ ,  $R = 0.3$  and  $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ deg}^{-4}$  into this expression yields  $T_E = 255 \text{ K}$ , or  $-18^{\circ}\text{C}$ . Even though the emission temperature is not the actual temperature of this hypothetical Earth, the value of  $T_E$  we have calculated is far below the actual global mean surface temperature of the real Earth ( $15^{\circ}\text{C}$ ).

(b) In this case, the energy balance at the TOA is still given by Eq. (4.41). However, since the atmosphere absorbs all of the long-wave radiation from the Earth's surface, the only radiation emitted to space by the Earth-atmosphere system is from the atmosphere. Therefore, the energy balance at the TOA is now (Fig. 4.11)

$$\frac{E_{\infty}}{4} (1 - R) = \sigma T_A^4 = \sigma T_E^4 \quad (4.42)$$

We see from Eq. (4.42) that  $T_A = T_E$ . However, the temperature of the surface of the Earth ( $T_s$ ) is greater than  $T_A$  (or  $T_E$ ) as we can see if we write down the energy balance for the atmosphere itself (Fig. 4.11)

$$\sigma T_s^4 = 2 \sigma T_A^4$$

or

$$T_s = 1.19 T_A \quad (4.43)$$



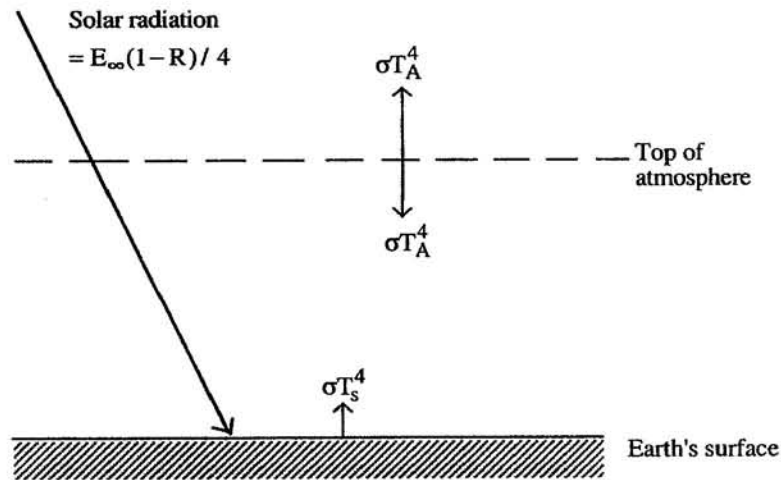


Figure 4.11. Irradiances for the Earth-atmosphere system assuming that the atmosphere is transparent to solar radiation but opaque to terrestrial radiation.

Changes in the concentrations of greenhouse gases (and aerosols) in the atmosphere have led to a perturbation in the radiation balance of the Earth-atmosphere system, which is referred to as a *radiative forcing*.<sup>13</sup> Radiative forcing can be defined as the perturbation to the net irradiance (in  $\text{W m}^{-2}$ ) at the TOA.<sup>14</sup> If the perturbation is positive (i.e., there is an increase in the net irradiance to the Earth-atmosphere system at the TOA), it will tend to increase the temperature of the Earth-atmosphere system; if the perturbation is negative, it will tend to lower the temperature of the Earth-atmosphere system.

The globally averaged radiative forcing due to changes in the concentrations of the well-mixed greenhouse gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and halocarbons) since preindustrial times is estimated to be  $+2.45 \pm 0.37 \text{ W m}^{-2}$ . Increases in the concentrations of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  of about 30%, 145%, and 15%, respectively, account for contributions of 64%, 19%, and 6%, respectively, to this radiative forcing. An increase in tropospheric  $\text{O}_3$  (not well mixed) is estimated to have caused an additional  $+0.2$  to  $+0.6 \text{ W m}^{-2}$  of radiative forcing. Since many greenhouse gases have long residence times in the atmosphere (e.g.,  $\text{CO}_2$  and  $\text{N}_2\text{O}$ ), they produce long-term radiative forcing.<sup>15</sup> The contribution to the direct radiative forcing by halocarbons (i.e., chlorofluorocarbons, CFC, and hydrochlorofluorocarbons, HCFC) is about  $+0.25 \text{ W m}^{-2}$ . However, the net radia-

tive  
the  
sph  
In  
cen  
sola  
and  
pog  
cen  
loc  
ave  
mo  
glo  
is c  
tive  
-0.4  
due  
tion  
inc  
neg  
qua  
F  
and  
trat  
to 1

Ph  
ph  
to  
asp  
rea  
A  
dep  
ene  
on  
wh  
are  
int

tive forcing due to halocarbons is reduced to about  $0.1 \text{ W m}^{-2}$  because they have caused reductions in the concentration of ozone in the stratosphere<sup>16</sup> (see Section 10.2).

In contrast to greenhouse gases, increases in atmospheric aerosol concentrations tend to cool the atmosphere by increasing the reflection of solar radiation back to space. However, also in contrast to the long-lived and well-mixed greenhouse gases, atmospheric aerosols from anthropogenic sources have short residence times, and they tend to be concentrated in industrialized/urban areas, where they produce large but local radiative forcing. For example, it has been estimated that the average radiative forcing in the Amazon Basin during the peak two months of the biomass burning season is  $-15 \pm 5 \text{ W m}^{-2}$ . However, the globally-averaged radiative forcing due to smoke from biomass burning is only about  $-0.3 \text{ W m}^{-2}$ . The total globally averaged direct radiative forcing due to anthropogenic aerosols is estimated to be about  $-0.5 \text{ W m}^{-2}$ . Aerosols may also have an important indirect radiative effect due to the fact that a component of the aerosol (called *cloud condensation nuclei*) can increase the concentration of cloud droplets and thereby increase the reflection of solar radiation by clouds. However, the negative radiative forcing due to this indirect effect of aerosols is poorly quantified.

Figure 4.12 summarizes and compares estimates of the globally and annually averaged radiative forcings due to changes in the concentrations of greenhouse gases and aerosols from preindustrial times to 1995.

#### 4.8 Photochemical reactions<sup>17</sup>

Photochemical reactions (i.e., reactions driven by the interaction of a photon of electromagnetic radiation and a molecule), which are referred to as *photolysis* if the molecule dissociates, play a key role in many aspects of atmospheric chemistry. Table 4.1 lists some examples of these reactions.

Whether a molecule can be involved in a photochemical reaction depends on the probability of it absorbing a photon with sufficient energy to cause dissociation of the molecule. This will depend, in part, on the radiant flux *from all directions* incident on a volume of the air, which is called the *actinic flux* ( $I$ ). The common (practical) units for  $I$  are photons  $\text{cm}^{-2} \text{s}^{-1}$  or, if we wish to specify a particular wavelength interval, photons  $\text{cm}^{-2} \text{s}^{-1} \mu\text{m}^{-1}$ . Comparing these definitions and units with

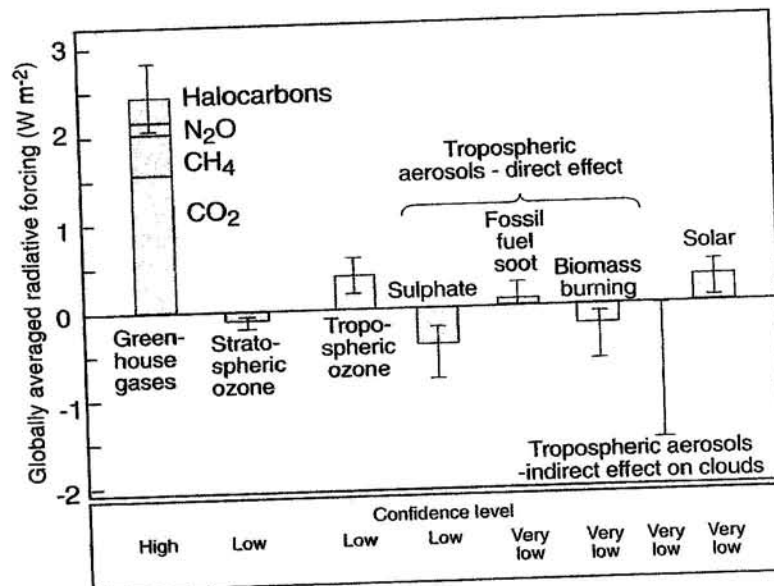


Figure 4.12. Estimate of the globally and annually averaged anthropogenic radiative forcings due to changes in the concentrations of greenhouse gases and aerosols from preindustrial times to 1995 and to natural changes in solar output from 1850. The height of the rectangular bar indicates a midrange estimate of the forcing, and the error bar shows an estimate of the uncertainty range. A subjective confidence that the actual forcing lies within the error bar is indicated by the "confidence level." [From *Climate Change 1995*, Ed. J. T. Houghton et al., Cambridge University Press (1996).]

those given in Section 4.1, we see that actinic flux is similar (but not identical) to irradiance.

For a photochemical reaction involving a species A, the rate of dissociation of A can be written

$$\frac{d[A]}{dt} = -j_A[A] \quad (4.44)$$

where  $[A]$  is the number concentration of the molecules of A and  $j_A$  is the *first-order photolysis rate coefficient* (units are  $s^{-1}$ ) for the reaction. The magnitude of  $j_A$  depends on the probability that a photon will be absorbed by a molecule of A (as measured by the *absorption cross section*  $\sigma_A$  ( $cm^2$ ) of a molecule of A), the probability that if absorption occurs the molecule A will dissociate (as measured by the *quantum yield*  $\phi_A$ ), and on the actinic flux  $I$ . Therefore, if we consider the wavelength

Table  
of in  
Reac  
6H<sub>2</sub>C

NO<sub>2</sub>

HOI

HCl

O<sub>2</sub>

O<sub>3</sub>

CF

=  
h

Table 4.1. *A few examples of the many photochemical reactions of importance in atmospheric chemistry*

Reaction <sup>a</sup>	Comments
$6\text{H}_2\text{O} + 6\text{CO}_2 + h\nu \rightarrow 6\text{O}_2 + \text{C}_6\text{H}_{12}\text{O}_6$	Photosynthesis by green plants (see Section 1.3).
$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$	Occurs for wavelengths from 0.400 to $0.625\ \mu\text{m}$ . The oxygen atom produced by this reaction leads to the only <i>in situ</i> chemical source of $\text{O}_3$ in the troposphere: $\text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M}$ (see Sections 5.2 and 9.2).
$\text{HONO} + h\nu \rightarrow \text{OH} + \text{NO}$	A source of the important hydroxyl (OH) radical. Occurs at relatively long wavelengths ( $<0.400\ \mu\text{m}$ ) that reach ground level.
$\text{HCHO} + h\nu \rightarrow \text{H} + \text{HCO}$	The photolysis of formaldehyde (HCHO) is a significant source of free radicals in the troposphere (see Section 5.2). Occurs at wavelengths $<0.340\ \mu\text{m}$ .
$\text{O}_2 + h\nu \rightarrow \text{O} + \text{O}$	The first of the Chapman reactions (see Section 10.1). Occurs in the stratosphere due to the absorption of solar radiation in the 0.2 to $0.22\ \mu\text{m}$ and 0.185 to $0.2\ \mu\text{m}$ wavelength regions.
$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}$	The third of the Chapman reactions (see Section 10.1). Occurs in the stratosphere (and troposphere) due to the absorption of solar radiation in the $\sim 0.305$ to $0.320\ \mu\text{m}$ wavelength range (see Section 5.2).
$\text{CFCl}_3 + h\nu \rightarrow \text{CFCl}_2 + \text{Cl}$	Example of photolysis of chlorofluorocarbons in the stratosphere. Occurs at wavelengths from 0.19 to $0.22\ \mu\text{m}$ (see Section 10.2).

<sup>a</sup> $h\nu$  represents 1 photon.

Table 4.2. Values of the quantum yields and absorption cross sections for Reaction (4.46) at 25°C for various wavelength bands between 0.295 μm and 0.410 μm; also listed is the actinic flux at the surface at solar noon at a latitude of 40°N on 1 March

Wavelength Interval (μm)	Quantum Yield	Absorption Cross Section (in units of 10 <sup>-19</sup> cm <sup>2</sup> )	Actinic Flux (photons cm <sup>-2</sup> s <sup>-1</sup> )
0.295-0.300	0.98	1.07	2.00 × 10 <sup>11</sup>
0.300-0.305	0.98	1.42	7.80 × 10 <sup>12</sup>
0.305-0.310	0.97	1.71	4.76 × 10 <sup>13</sup>
0.310-0.315	0.96	2.01	1.44 × 10 <sup>14</sup>
0.315-0.320	0.95	2.40	2.33 × 10 <sup>14</sup>
0.320-0.325	0.94	2.67	3.18 × 10 <sup>14</sup>
0.325-0.330	0.93	2.89	4.83 × 10 <sup>14</sup>
0.330-0.335	0.92	3.22	5.30 × 10 <sup>14</sup>
0.335-0.340	0.91	3.67	5.37 × 10 <sup>14</sup>
0.340-0.345	0.90	3.98	5.90 × 10 <sup>14</sup>
0.345-0.350	0.89	4.09	5.98 × 10 <sup>14</sup>
0.350-0.355	0.88	4.62	6.86 × 10 <sup>14</sup>
0.355-0.360	0.87	4.82	6.39 × 10 <sup>14</sup>
0.360-0.365	0.86	5.15	7.16 × 10 <sup>14</sup>
0.365-0.370	0.85	5.60	8.90 × 10 <sup>14</sup>
0.370-0.375	0.84	5.39	8.11 × 10 <sup>14</sup>
0.375-0.380	0.83	5.67	9.14 × 10 <sup>14</sup>
0.380-0.385	0.82	5.97	7.63 × 10 <sup>14</sup>
0.385-0.390	0.80	5.97	8.46 × 10 <sup>14</sup>
0.390-0.395	0.77	5.95	8.78 × 10 <sup>14</sup>
0.395-0.400	0.75	6.33	1.07 × 10 <sup>15</sup>
0.400-0.405	0.55	6.54	1.28 × 10 <sup>15</sup>
0.405-0.410	0.23	6.05	1.44 × 10 <sup>15</sup>

and temperature dependence of these various parameters, the value of  $j_A$  for wavelengths between  $\lambda_1$  and  $\lambda_2$  is

$$j_A = \int_{\lambda_1}^{\lambda_2} \sigma_A(\lambda, T) \phi_A(\lambda, T) I(\lambda) d\lambda \quad (4.45)$$

where the units of  $I$  are now photons cm<sup>-2</sup>s<sup>-1</sup> μm<sup>-1</sup>, if  $d\lambda$  is expressed in μm. Note that  $\sigma_A$  and  $\phi_A$  are fundamental properties of the molecule A, which can be determined from laboratory experiments.

Exer  
the val  
of 0.29

Assum  
Solu  
by sun  
exercis

where  
intervai  
Using  
mation  
value o  
conditic

See Exerci

- 1 For a mo  
reader is r  
by J. M. W
- 2 Josef Stefi  
versity of  
fundamen
- 3 Wilhelm V  
discovery  
(rough) de
- 4 Gustav Ki  
he made  
Bunsen) sj
- 5 August Be
- 6 Lord Rayl  
and physic  
light. Disc
- 7 The refract  
ensemble  
index of re



**Exercise 4.5.** Using the information given in Table 4.2, calculate the value of the photolysis rate coefficient  $j$  between wavelengths of 0.295 and 0.410  $\mu\text{m}$  for the reaction



Assume a cloud-free day and a surface albedo of zero.

**Solution.** The right-hand side of Eq. (4.45) can be approximated by summing over small wavelength intervals. Hence, for this exercise,

$$j = \sum_i \bar{\sigma}_A(\lambda_i, T) \bar{\phi}_A(\lambda_i, T) \bar{I}(\lambda_i) \quad (4.47)$$

where the overbars indicate average values over the wavelength interval  $\Delta\lambda_i$  centered on wavelength  $\lambda_i$ .

Using the values given in Table 4.2, and carrying out the summation of products on the right-hand side of Eq. (4.47), yields a value of  $j$  of  $5.50 \times 10^{-3} \text{s}^{-1}$  for Reaction (4.46) under the specified conditions.

### Exercises

See Exercises 1(j)–(n) and Exercises 14–17 in appendix I.

### Notes

- 1 For a more detailed discussion of the basic principles of atmospheric radiation, the reader is referred to Chapters 6 and 7 of *Atmospheric Science: An Introductory Survey* by J. M. Wallace and P. V. Hobbs (Academic Press, New York, 1977).
- 2 Josef Stefan (1835–1893). Austrian physicist. Became professor of physics at the University of Vienna at age 28. Originated the theory of diffusion of gases and carried out fundamental studies on radiation.
- 3 Wilhelm Wien (1864–1928). German physicist. Received the Nobel Prize in 1911 for the discovery (in 1893) of the displacement law named after him. Also made the first (rough) determination of the wavelength of x-rays.
- 4 Gustav Kirchhoff (1824–1887). German physicist. In addition to his work in radiation, he made fundamental discoveries in electricity and spectroscopy. Developed (with Bunsen) spectrum analysis. Discovered cesium and rubidium.
- 5 August Beer (1825–1863). German physicist, noted for his studies of optics.
- 6 Lord Rayleigh (John William Strutt, 3rd Baron) (1842–1919). English mathematician and physicist. Best known for his work on the theory of sound and the scattering of light. Discovered (with Ramsey) the presence of argon in the air, for which he won the Nobel Prize in 1904.
- 7 The refractive index is difficult to define for a molecule. The approach is to consider an ensemble of molecules, for which the scattering may be related to the macroscopic index of refraction of the gas.

- 8 Some of the more important absorption bands in the solar spectrum are given names. For example, the absorption bands due to  $O_3$  in the near-UV at wavelengths between 0.3 and  $0.36 \mu\text{m}$  (which can be seen on the left-hand side of Fig. 4.6) and a series of bands centered at  $0.255 \mu\text{m}$ , are called the *Huggins* and *Hartley* bands, respectively. Although the Hartley bands are quite weak, they appear in the solar spectrum when the Sun is low in the sky; they were responsible for the first positive identification of  $O_3$  in the atmosphere. The absorption band due to  $O_3$  at visible wavelengths is called the *Chappuis* band, and the  $O_2$  band at  $0.7 \mu\text{m}$  is called the *A-band*.
- 9 The less mathematically inclined reader may wish to skip Sections 4.3, 4.4, and the quantitative portions of Section 4.6.
- 10 For a derivation and discussion of the hydrostatic equation and the dry adiabatic lapse rate see Chapter 2 of *Atmospheric Science: An Introductory Survey* by J. M. Wallace and P. V. Hobbs (Academic Press, New York, 1977).
- 11 Gustav Mie (1868–1957). German physicist. Carried out fundamental studies on the theory of em scattering and kinetic theory.
- 12 Karl Schwarzschild (1873–1916). German astronomer skilled in both theoretical and experimental work, and also in popularizing astronomy. In 1960 the Berlin Academy referred to him as “the greatest German astronomer of the last hundred years.”
- 13 Radiative forcing provides a quantitative estimate of the potential impact of changes in the composition of the Earth’s atmosphere on the climate of the Earth. However, because the concept of “radiative forcing” does not account for feedbacks, general circulation models (GCM) of the atmosphere are needed to better estimate the many possible effects on climate of various types of radiative forcing.
- 14 A stricter definition of radiative forcing is the perturbation in the net irradiance (in  $\text{W m}^{-2}$ ) at the tropopause after allowing for stratospheric temperatures to adjust to radiative equilibrium (which takes a few months), but with surface and tropospheric temperatures and atmospheric moisture held constant.
- 15 If  $\text{CO}_2$  emissions remain at their levels at the end of the twentieth century, atmospheric  $\text{CO}_2$  concentrations will reach about 500 ppmv (i.e., about twice their preindustrial concentrations) by the end of the twenty-first century.
- 16 Radiative forcing due to changes in stratospheric  $O_3$  is difficult to calculate because such changes cause a significant change in both solar and terrestrial radiation. Also, the depletion of  $O_3$  causes changes in stratospheric temperatures, which significantly modify radiative forcing. Finally, radiative forcing is sensitive to the spatial (particularly the vertical) distribution of perturbations in  $O_3$ .
- 17 Some of the basic principles of photochemistry are discussed in Chapter 7 of *Basic Physical Chemistry for the Atmospheric Sciences* by P. V. Hobbs (Cambridge University Press, New York, 1995).

So  
siIn this c  
and sink  
on gasesThe pri  
sphere, t  
chemica  
subjectiEven th  
reservoi  
mining t  
The sme  
direct e  
biologic

- Photo  
tually
- Respi  
the ai  
declin  
during  
(Fig. 3  
dead