

## CHAPTER 1

### GENERAL PROPERTIES OF THE ATMOSPHERE OF THE EARTH AND OTHER PLANETS

To understand the effects of pollutants on the Earth's atmosphere we must first understand the chemical and physical processes that take place in the absence of pollutants. This will be the focus of the first two chapters of this book. In this chapter we present information on the general chemical and physical properties of the atmosphere. In the next chapter we go into a more detailed discussion of the chemical processes occurring in the lower atmosphere under clean conditions. At this point we will be in a position to discuss air pollution and its effects on air quality and the environment.

We begin this chapter with a discussion of the composition of the Earth's atmosphere and the implications this has for atmospheric chemistry. Since there are eight other planets in our solar system, we next discuss the composition of planetary atmospheres, with an emphasis on what this tells us about the formation and evolution of our own atmosphere. We conclude by touching on two additional topics of interest, the structure of the atmosphere and dynamical processes in the atmosphere.

#### 1.1 COMPOSITION OF THE EARTH'S ATMOSPHERE

Table 1.1 presents information on the composition of the Earth's atmosphere, along with related information concerning the atmosphere. Data are given for a dry sample of gas taken from the troposphere, or lower atmosphere. We may divide the observed gases into four general categories:

Major components - The diatomic molecules nitrogen ( $N_2$ ) and oxygen ( $O_2$ ) represent the two major components of the Earth's atmosphere. In rough terms, the lower atmosphere consists of an approximately 4:1 mixture of nitrogen and oxygen (the exact percentages are given in Table 1.1), with other atmospheric gases present in much smaller amounts.

Minor components - These represent gases present at concentrations greater than  $\sim 0.1$  ppm (see Table 1.2 for a discussion of ppm and related units of concentration), excluding major components and the noble gases. There are six gases in this category, one of which (water) we will discuss separately below. The other five gases are carbon dioxide ( $CO_2$ , 400. ppm), methane ( $CH_4$ , 1.7 ppm), molecular hydrogen ( $H_2$ , 0.6 ppm), nitrous oxide ( $N_2O$ , 0.31 ppm), and carbon monoxide ( $C$ ), 0.09 ppm). The concentrations of both carbon dioxide and methane have been slowly increasing over the past few centuries as a consequence of man's activities.

Noble gases - Concentrations of the stable noble gases range from 9340 ppm (or 0.934%) for argon (Ar) to 0.09 ppm for xenon (Xe). Radon, a radioactive noble gas, is a trace gas in the atmosphere but can be an important indoor air pollutant under some conditions. While the noble gases are chemically unreactive, their relative concentrations provide information about the evolution of the Earth's atmosphere, as discussed below.

Trace gases - There are literally thousands of additional species that have been identified in the atmosphere, all at concentrations smaller than 0.1 ppm. Important categories of trace gases include organic molecules (including hydrocarbons, aldehydes, ketones, and other molecules, along with species formed by the decomposition of these molecules), nitrogen oxides (excluding nitrous oxide, which is a minor component of the atmosphere), sulfur oxides, and oxidizing species such as ozone ( $O_3$ ), hydroxyl radical (OH), and hydroperoxyl radical ( $HO_2$ ).

The above discussion applies to dry samples of the lower atmosphere. One additional important component of the atmosphere is water vapor ( $H_2O$ ). Liquid and solid water cover approximately 75% of the surface of the Earth, but equilibrium between water in the solid, liquid, and vapor phases is not established. Instead, there is a large degree of variability in the concentration of water vapor in the lower atmosphere, from about 4% in humid air in the tropics to 0.1 ppm over central Antarctica. In general, the concentration of water vapor in the lower atmosphere decreases with increasing altitude (by altitude we mean vertical distance from sea level, for Earth, or average ground

level, for planets with solid surfaces), both because temperature generally decreases with increasing altitude and because of the sources of water vapor are at the Earth's surface. Atmospheric water vapor is commonly described in terms of relative humidity,  $H_{rel}$ , defined as follows

$$H_{rel} = [p(\text{H}_2\text{O, obsd})/p^\circ(\text{H}_2\text{O})] \times 100\% \quad (1.1)$$

where  $p(\text{H}_2\text{O, obsd})$  is the observed partial pressure of water in the air sample, and  $p^\circ(\text{H}_2\text{O})$  is the vapor pressure of water. Recall that vapor pressure is defined as the equilibrium partial pressure of vapor above a pure liquid, and that the value for vapor pressure increases as temperature increases. Table 1.3 gives the vapor pressure of water for a range of temperatures found in the lower atmosphere.

**TABLE 1.1 - COMPOSITION AND PROPERTIES OF THE EARTH'S ATMOSPHERE<sup>a,b</sup>**

Gas	Concentration	Gas	Concentration
N <sub>2</sub>	78.084 %	He	5.2 ppm
O <sub>2</sub>	20.946 %	Ne	18.2 ppm
		Ar	9340. ppm
CO <sub>2</sub>	365. ppm	Kr	1.14 ppm
CH <sub>4</sub>	1.7 ppm	Xe	0.09 ppm
H <sub>2</sub>	0.6 ppm		
N <sub>2</sub> O	0.31 ppm		+ many trace gases
CO	0.09 ppm		

total mass of atmosphere =  $5.14 \times 10^{18}$  kg

average molecular weight (dry sample, troposphere) =  $M_{ave} = 28.96$  g/mole

number density of molecules ( $p = 1.00$  atm,  $T = 288$ . K) =  $N/V = 2.55 \times 10^{19}$  molecule/cm<sup>3</sup>

average temperature of the atmosphere (sea level) = 288. K (15 °C)

<sup>a</sup> Data from R. P. Turco, Earth Under Siege, Oxford University Press, New York, 1997; NASA Goddard Space Flight Center, 2002. <sup>b</sup> Typical composition of a dry air sample of air in the lower troposphere. Percent and ppm values are by number of molecules. Tropospheric concentrations of water vapor range from 0 - 4%.

**TABLE 1.2 - CONCENTRATION UNITS FOR TRACE CONSTITUENTS**

1 ppm (part per million) = 1 in  $10^6$       ppm <sup>i</sup>th component =  $X_i \times 10^6$

1 ppb (part per billion) = 1 in  $10^9$       ppb <sup>i</sup>th component =  $X_i \times 10^9$

1 ppt (part per trillion) = 1 in  $10^{12}$       ppt <sup>i</sup>th component =  $X_i \times 10^{12}$

$X_i$  = mole fraction of <sup>i</sup>th component =  $n_i/n_{total} = p_i / p_{total}$ <sup>a</sup>

<sup>a</sup> Assumes the gas obeys the ideal gas law and Dalton's law of partial pressures.

We have assumed in the above discussion that the ideal gas law and Dalton's law of partial pressures can be used to describe the behavior of the Earth's atmosphere. The ideal gas law states that

$$pV = nRT \quad (1.2)$$

where  $p$  is the total pressure of gas,  $n$  is the total number of moles of gas molecules,  $V$  is the volume of gas being discussed, and  $T$  is the temperature of the gas in Kelvin. Recall that

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15 \quad (1.3)$$

allows us to convert between temperature in centigrade ( $^{\circ}\text{C}$ ) and temperature in Kelvin (K).  $R$ , the constant in the ideal gas law, is called the gas constant.

The ideal gas law may also be written in terms of number of molecules ( $N$ ). Since

$$n = N/N_A \quad (1.4)$$

where  $N_A$  is Avogadro's number, we can rewrite eq. 1.2 as

$$pV = NkT \quad (1.5)$$

where  $k = R/N_A$  is the Boltzmann constant. Values for the constants  $N_A$ ,  $R$ , and  $k$  are given at the end of this chapter.

We may also rewrite eq. 1.2 and 1.5 in such a way that we get expressions for the amount of gas per unit volume. The resulting equations are as follows

$$n/V = p/RT \quad (1.6)$$

and

$$N/V = pN_A/RT = p/kT \quad (1.7)$$

where  $n/V$  represents the moles of gas per unit volume (with mole/L being a common unit) and  $N/V$  represents the number of molecules per unit volume (with molecules/cm<sup>3</sup> being a common unit).

**TABLE 1.3 - VAPOR PRESSURE OF WATER AT SELECTED TEMPERATURES<sup>a</sup>**

Temperature ( $^{\circ}\text{C}$ )	Vapor pressure <sup>b</sup> (torr)	Temperature ( $^{\circ}\text{C}$ )	Vapor pressure <sup>b</sup> (torr)
- 80.	0.00040	5.	6.54
- 60.	0.00808	10.	9.21
- 40.	0.0966	15.	12.79
- 20.	0.776	20.	17.54
- 10.	1.95	30.	31.8
0.	4.58	40.	55.3

<sup>a</sup> Data from the CRC Handbook of Chemistry and Physics. <sup>b</sup> Vapor pressure with respect to H<sub>2</sub>O(s) for  $T < 0^{\circ}\text{C}$ , and with respect to H<sub>2</sub>O(l) for  $T \geq 0^{\circ}\text{C}$ .

For gas mixtures where each component in the mixture obeys the ideal gas law, Dalton's law of partial pressures will also apply. Dalton's law can be written in several ways. For the  $i^{\text{th}}$  component in a mixture of ideal gases we may say

$$p_i V = n_i R T \quad (1.8)$$

where  $p_i$  is the partial pressure of the  $i^{\text{th}}$  gas, and  $n_i$  is the number of moles of the  $i^{\text{th}}$  gas. It is easy to show that the following relationship follows

$$p_i = X_i p \quad (1.9)$$

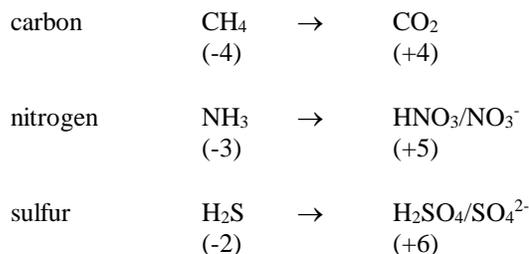
where  $p$  is the total pressure, and  $X_i$ , the mole fraction, is defined as  $X_i = n_i/n$ , where  $n$  is the total number of moles of gas.

For the conditions of pressure and temperature found in the Earth's atmosphere we expect the ideal gas law and Dalton's law to be correct to within  $\pm 0.2\%$ . For gases at higher pressures, such as near the surface of Venus or in the interiors of the outer planets, deviations from the ideal gas law will occur. In these cases, more complicated gas laws, such as van der Waals equation, may be used to improve accuracy.

Finally, there will also be suspended solid and liquid particles in samples of the atmosphere. The common way in which concentrations of suspended particles are reported is in units of  $\mu\text{g}/\text{m}^3$ , that is, mass of suspended particles (in micrograms) per cubic meter of air.

There are several general comments we can make concerning the Earth's atmosphere:

The Earth's atmosphere is a strongly oxidizing atmosphere. This is due to the large partial pressure of molecular oxygen present in the atmosphere. As a consequence of this, we expect the general tendency for atmospheric reactions is to produce more and more oxidized forms of elements. If we consider the three most important elements that cycle through the atmosphere, carbon, nitrogen, and sulfur, this means atmospheric reactions are expected to proceed in the following direction:



In the above schematic reaction scheme the oxidation number of the element (carbon, nitrogen, or sulfur) being cycled through the atmosphere has been given. The general tendency is for the oxidation number for elements other than hydrogen and oxygen to increase as chemical reactions proceed in the atmosphere.

The presence of significant amounts of reduced or partially reduced molecules in the Earth's atmosphere indicates that these molecules must continuously be introduced into the atmosphere. There is far more methane ( $\text{CH}_4$ ), ammonia ( $\text{NH}_3$ ), and hydrogen sulfide ( $\text{H}_2\text{S}$ ) present in the atmosphere than would be expected for equilibrium conditions. This indicates that new molecules of these gases must be continuously introduced into the atmosphere to replace the molecules that disappear via oxidation reactions. There are both biological and abiological processes that introduce reduced compounds into the atmosphere, as we will discuss later.

The most interesting chemical processes that occur in the Earth's atmosphere involve the minor and trace components. The covalent bond in nitrogen ( $\text{N}_2$ ) is a triple bond, while that in oxygen ( $\text{O}_2$ ) is a double bond. Both of these bonds are strong, making direct reaction of these molecules in the atmosphere usually a slow process. The

chemical reactions associated with the cycling of elements through the atmosphere and with air pollutants usually involve minor or trace gases.

In general, the lower the concentration of a gas in the atmosphere, the more the variability in the concentration of the gas that is observed. The percentage of nitrogen and oxygen in the lower atmosphere is essentially independent of factors such as altitude, geographic location, time of day, or time of year. Carbon dioxide and methane concentrations are weakly dependent on these factors, while concentrations of trace gases are often found to strongly depend on these factors. For example, Figure 1.1 shows the average concentration of ozone in the atmosphere as a function of altitude. Exceptions to this general rule are the noble gases and chemically unreactive trace species, including nitrous oxide ( $N_2O$ ), carbonyl sulfide (COS), and stable manmade compounds such as CFCs (chlorofluorocarbons). Because these molecules either do not participate in chemical reactions (the noble gases) or react only slowly in the lower atmosphere ( $N_2O$ , COS, and CFCs) they have a chance to mix well in the atmosphere and therefore are to a first approximation uniformly distributed in the lower atmosphere. Water, because of the competition between precipitation (which removes water vapor from the atmosphere) and evaporation and sublimation (which add water vapor to the atmosphere) exhibits a wider range of variability in concentration than the other trace gases.

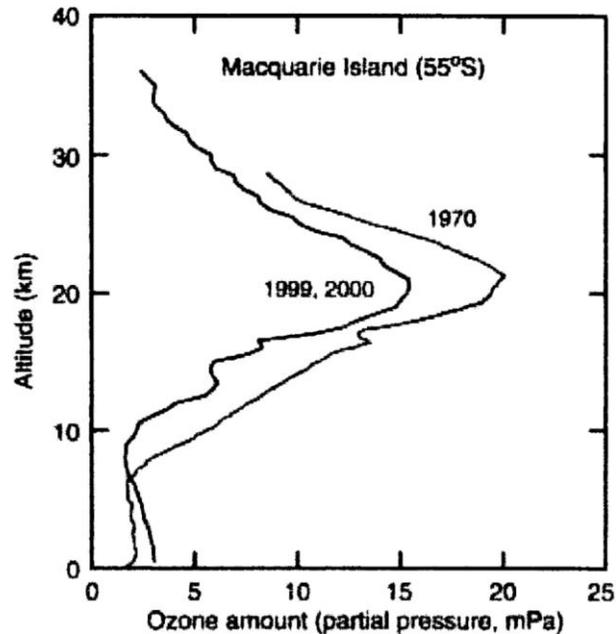


Figure 1.1. Ozone partial pressure vs altitude, Macquarie Island. This island is located south of Tasmania, Australia. Note the decrease in partial pressure of ozone over the past 20 years.

## 1.2 COMPOSITION OF PLANETARY ATMOSPHERES

We may gain insight into the formation and evolution of the Earth's atmosphere by comparing the atmosphere of the Earth to that observed for other planets. The planets in the solar system can be conveniently grouped into two categories:

Inner planets (Mercury, Venus, Earth, Mars). These planets are solid, with a relatively thin atmosphere.

Outer planets (Jupiter, Saturn, Uranus, Neptune). These planets are primarily or completely composed of gas, and are more massive than the inner planets. These planets are sometimes called the gas giants.

Table 1.4 lists general properties of the planets, including Earth, while Table 1.5 summarizes information concerning the surface pressure (for the inner planets) and composition of the planetary atmospheres. It is apparent from Table 1.5 that there are distinct differences between the inner and outer planets. The atmospheres of the outer planets are, to a first approximation, 9:1 mixtures of hydrogen (H<sub>2</sub>) and helium (He), with trace amounts of other gases. The presence of large amounts of free hydrogen in the atmospheres of the outer planets means that these planets have strongly reducing atmospheres. In fact, the trace gases found in the atmospheres of these planets are primarily reduced compounds such as methane and ammonia. In contrast, there are larger variations in the properties of the atmospheres of the inner planets. Venus and Mars, while differing by over four orders of magnitude in surface pressure, have similar atmospheric compositions (mainly carbon dioxide, with small amounts of nitrogen and argon). The presence of carbon primarily in the form of carbon dioxide instead of methane indicates that the atmospheres of Venus and Mars are oxidizing. However, because their atmospheres contain much smaller amounts of molecular oxygen than the atmosphere of the Earth, Venus and Mars are said to possess weakly oxidizing atmospheres, in contrast to the Earth, whose atmosphere is strongly oxidizing. Mercury, as a consequence of its small size and closeness to the sun, has virtually no atmosphere. Those gases that are present are either gases produced from outgassing from the crust (O<sub>2</sub>, Na) or captured gases from the solar wind (H<sub>2</sub>, He).

**TABLE 1.4 - GENERAL PROPERTIES OF THE PLANETS<sup>a</sup>**

Planet	M <sub>p</sub> <sup>b</sup> (kg)	r <sub>p</sub> <sup>b</sup> (km)	d <sub>sun</sub> <sup>b</sup> (km)	G <sub>s</sub> <sup>b,c</sup> (m/s <sup>2</sup> )	T <sub>s</sub> <sup>b,c</sup> (K)	Albedo
Mercury	3.30 x 10 <sup>23</sup>	2440	5.79 x 10 <sup>7</sup>	3.70	440	0.12
Venus	4.87 x 10 <sup>24</sup>	6050	1.08 x 10 <sup>8</sup>	8.87	730	0.59
Earth	5.97 x 10 <sup>24</sup>	6380	1.50 x 10 <sup>8</sup>	9.78	288	0.35
Mars	6.42 x 10 <sup>23</sup>	3400	2.28 x 10 <sup>8</sup>	3.73	218	0.15
Jupiter	1.90 x 10 <sup>27</sup>	71900	7.78 x 10 <sup>8</sup>	23.2	134	0.44
Saturn	5.68 x 10 <sup>26</sup>	60330	1.43 x 10 <sup>9</sup>	8.77	97	0.46
Uranus	8.68 x 10 <sup>25</sup>	25560	2.87 x 10 <sup>9</sup>	9.46	55	0.56
Neptune	1.02 x 10 <sup>26</sup>	24760	4.50 x 10 <sup>9</sup>	13.7	53	0.51

<sup>a</sup> Data from NASA Goddard Space Flight Center, 2002; CRC Handbook of Chemistry and Physics, 2002. <sup>b</sup> M<sub>p</sub> = mass of planet; r<sub>p</sub> = radius of planet; d<sub>sun</sub> = average distance between planet and sun; G<sub>s</sub> = surface gravity of planet; T<sub>s</sub> = surface temperature of planet. <sup>c</sup> For the outer planets (Jupiter, Saturn, Uranus, and Neptune) G<sub>s</sub> and T<sub>s</sub> are given at the cloud tops.

The observed differences between the composition of the atmospheres of the inner and outer planets, and in the composition of the Earth's atmosphere in comparison to that of Venus and Mars, suggest several questions that need to be answered concerning the origin and evolution of the atmosphere of the Earth and other planets.

Why are the atmospheres of the outer planets composed primarily of hydrogen and helium, while those of Venus and Mars are composed primarily of carbon dioxide, with trace amounts of nitrogen and argon?

Why do the surface pressures of Venus and Mars differ by over a factor of 10,000?

Why is the atmosphere of the Earth so different than that of Venus and Mars? In particular, why does the Earth's atmosphere contain so much oxygen and so little carbon dioxide? In addition, why is there so much water present on Earth compared to Venus and Mars?

Why is argon the most abundant noble gas in the atmospheres of the inner planets?

These and related questions are addressed in the next section of this chapter.

**TABLE 1.5 - TOTAL PRESSURE AND COMPOSITION OF PLANETARY ATMOSPHERES<sup>a</sup>**

Planet	P <sub>s</sub> (bar) <sup>b,c</sup>	Composition <sup>d</sup>
Mercury	~ 10 <sup>-15</sup>	O <sub>2</sub> (42%); Na(29%); H <sub>2</sub> (22%); He(6%)
Venus	92.	CO <sub>2</sub> (96.5%); N <sub>2</sub> (3.5%); SO <sub>2</sub> (150 ppm); Ar(70 ppm); H <sub>2</sub> O(20 ppm); CO(17 ppm)
Earth	1.0	N <sub>2</sub> (78.1%); O <sub>2</sub> (20.9%); Ar(9300 ppm); CO <sub>2</sub> (400 ppm)
Mars	0.006	CO <sub>2</sub> (95.3%); N <sub>2</sub> (2.7%); Ar(1.6%); O <sub>2</sub> (1300 ppm); CO(800 ppm); H <sub>2</sub> O(210 ppm)
Jupiter	0.2	H <sub>2</sub> (90%); He(10%); CH <sub>4</sub> (3000 ppm); NH <sub>3</sub> (260 ppm)
Saturn	0.1	H <sub>2</sub> (96%); He(3.2%); CH <sub>4</sub> (4500 ppm); NH <sub>3</sub> (125 ppm)
Uranus	0.1	H <sub>2</sub> (82%); He(15%); CH <sub>4</sub> (2.3%)
Neptune	0.1	H <sub>2</sub> (80%); He(19%); CH <sub>4</sub> (1.4%)

<sup>a</sup> Data from NASA Goddard Space Flight Center, 2002. <sup>b</sup> 1 bar = 0.987 atm. <sup>c</sup> P<sub>s</sub> = pressure at the surface of the planet. For the outer planets P<sub>s</sub> is given at the cloud tops. <sup>d</sup> Because of uncertainties and neglect of minor components, percentages may not add up to 100%.

### 1.3 EVOLUTION OF THE ATMOSPHERE OF THE EARTH AND OTHER PLANETS

Based on radioactive dating of ancient rocks on Earth, meteorites, and models of stellar evolution, the sun, Earth, and other solar bodies are believed to have formed approximately 4.5 billion years ago. There is no reason to believe that the composition of gases now observed in planetary atmospheres is the same as was originally present. In fact, we believe there has been substantial evolution in the atmospheres of the inner planets, particularly in the atmosphere of our own planet.

It is easiest to explain the composition of the atmospheres of the outer planets. All are approximately 9:1 mixtures of molecular hydrogen and helium, with only trace amounts of other elements. The sun, our galaxy, and the universe as a whole are also primarily composed of hydrogen and helium, at a ratio of approximately 9:1 hydrogen to helium. We therefore believe that the observed composition of the outer planets is essentially the same as was present when they first formed, with little or no subsequent evolution.

There is more uncertainty concerning the initial composition of the atmospheres of the inner planets. Up until the past decade or so the prevailing belief was that the inner planets had atmospheres that, like the outer planets, were composed primarily hydrogen and helium, and that these gases slowly disappeared by a process that will be described below. More recently, it has been suggested that the accretion processes responsible for the formation of the planets by collisions of smaller bodies may have stripped away most of the primordial atmosphere from the inner planets. The presence of large impact craters on the Earth's moon, Venus, and Mars is evidence of the large scale collision processes that occurred during the formation of the solar system (on Earth erosion has removed most of the evidence for these impact events). Outgassing from the interior of the inner planets would then produce an atmosphere enriched in carbon dioxide and nitrogen, as is now observed in the atmospheres of Venus and Mars.

Whether there were initially large amounts of hydrogen and helium present in the atmospheres of the inner planets or the smaller amounts expected if the initial atmospheres for these planets were stripped away by the collisional processes that formed them, one still must account for the fact that hydrogen and helium are now trace constituents in the atmospheres of Venus, Earth, and Mars.

The starting point in understanding the lack of low molecular weight gases in the atmospheres of the inner planets is the realization that gases can escape from a planetary atmosphere into space. The escape velocity ( $v_{esc}$ ), or

minimum speed required for a molecule to escape the gravitational attraction of a planet or moon, is given by the relationship

$$v_{\text{esc}} = (2M_p G/r_p)^{1/2} \quad (1.10)$$

where  $M_p$  is the mass of the planet,  $r_p$  is the radius of the planet, and  $G$  is the gravitational constant ( $G = 6.67 \times 10^{-11} \text{ N}\cdot\text{m}^2/\text{kg}^2$ , where  $1 \text{ N} = 1 \text{ Newton} = 1 \text{ kg}\cdot\text{m}/\text{s}^2$ ). Values for  $M_p$  and  $r_p$  are given in Table 1.4. A gas molecule moving away from the surface of a planet at a speed greater than the escape velocity will, if it does not collide with another gas molecule, leave the atmosphere and move into space.

For most regions of the atmosphere of the Earth and other planets the density of gas molecules is large enough that even if a molecule is moving at a speed greater than the escape velocity it will collide with other gas molecules, and therefore slow down, before escaping from the atmosphere. It is only at the top of a planetary atmosphere that gas molecules moving away from a planet at a speed greater than the escape velocity are likely to escape. The region of a planetary atmosphere where the density of gas is sufficiently low that molecular collisions are unlikely to occur is called the exosphere. For earth, the exosphere begins at an altitude of approximately 500 km.

To decide whether molecules of a particular gas are likely to escape into space we also need information about the distribution of molecular velocities. At equilibrium, the rms average speed of a gas molecule,  $v_{\text{rms}}$ , is given by the relationship

$$v_{\text{rms}} = (3RT/M)^{1/2} \quad (1.11)$$

where  $T$  is the temperature and  $M$  is the molecular weight of the gas. Note that in general the rms average velocity increases as temperature increases and as the molecular weight of the gas decreases.

However, the rms average velocity is somewhat misleading. There will in fact be a distribution of speeds observed for the molecules of a gas (called the Maxwell-Boltzmann distribution), as shown in Figure 1.2. What is important as far as the possible escape of molecules into space is the fraction of molecules that have a speed greater than that required to escape from the gravitational attraction of a planet. The fraction of molecules that have a speed  $v > n v_{\text{rms}}$  (which we will define as  $f(v > n v_{\text{rms}})$ ) can be calculated from the one dimensional distribution of molecular speeds. Table 1.6 gives values for  $f(v > n v_{\text{rms}})$  for several values of  $n$ .

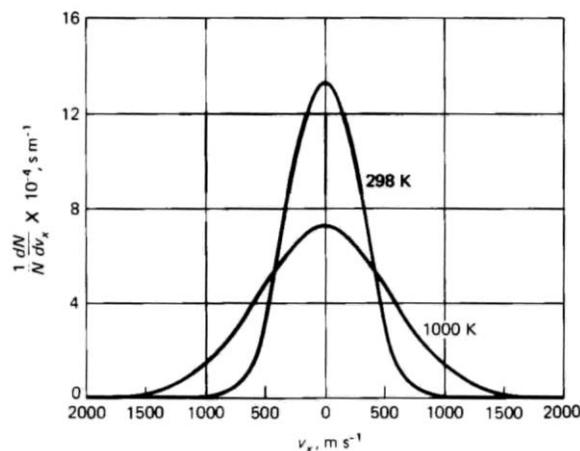


Figure 1.2. Distribution of molecular speeds in one dimension for  $\text{N}_2$  molecules at  $T = 298 \text{ K}$  and  $T = 1000 \text{ K}$ .

**TABLE 1.6 - VALUES FOR  $f(v > n v_{rms})$  FOR SEVERAL VALUES OF  $n^a$**

$n$	$f(v > n v_{rms})$	$n$	$f(v > n v_{rms})$
3.0	$1.05 \times 10^{-7}$	7.0	$3.95 \times 10^{-34}$
4.0	$2.17 \times 10^{-12}$	8.0	$5.84 \times 10^{-44}$
5.0	$2.38 \times 10^{-18}$	10.0	$1.65 \times 10^{-67}$
6.0	$1.36 \times 10^{-25}$		

<sup>a</sup> Calculated using the relationship  $f(v > n v_{rms}) \cong (1/2\pi x_0^2)^{1/2} \exp(-x_0^2/2)$ , where  $x_0 = 3^{1/2} n$ .

Examination of Table 1.6 shows that for all values in the table  $f(v > n v_{rms})$  is small. However, even if only a small fraction of molecules have a speed sufficient to escape from the gravitational attraction of a planet at any particular moment of time, a majority of molecules of a particular gas may escape over the 4.5 billion years that the planetary atmosphere has been in existence. As a general and approximate guide we may say the following:

if  $v_{esc}/v_{rms} < 5$  then almost all molecules of the gas will escape

if  $v_{esc}/v_{rms}$  is between 5 - 7.5 then some of the molecules of the gas will escape

if  $v_{esc}/v_{rms} > 7.5$  then virtually none of the molecules of the gas will escape

The above guidelines assume that gas molecules maintain an equilibrium distribution of molecular speeds, and that there are no other mechanisms by which molecules can escape from a planet. This will usually be the case. One exception is the escape of water molecules from the atmospheres of Venus and Mars, which is believed to have occurred in part by a photochemically assisted process, as discussed below.

As an example, let us apply the above process to the escape of hydrogen ( $H_2$ ) and nitrogen ( $N_2$ ) from the atmosphere of the Earth. Using the information in Table 1.4 we find that for Earth  $v_{esc} = 11170$  m/s. At the temperature of the Earth's exosphere ( $T \cong 600$ . K) the rms average velocities for  $H_2$  and  $N_2$  are  $v_{rms}(H_2) = 2740$ . m/s and  $v_{rms}(N_2) = 730$ . m/s. This gives  $v_{esc}/v_{rms} = 4.1$  for  $H_2$  and  $v_{esc}/v_{rms} = 15.3$  for  $N_2$ . We would therefore expect that any hydrogen initially present in the Earth's atmosphere will have escaped, while any nitrogen initially present will have remained trapped in the atmosphere. In fact, the small amounts of hydrogen (0.6 ppm) and helium (5.2 ppm) observed in the Earth's atmosphere are of recent origin, produced by chemical reaction ( $H_2$ ) or radioactive decay (He).

The above provides an explanation for the absence of low molecular weight gases in the atmospheres of the inner planets. Light gases such as hydrogen and helium have been able to slowly escape the gravitation attraction of the inner planets, while higher molecular weight gases have remained behind. For a small planet like Mars  $v_{esc}/v_{rms}$  is fairly small even for gases such as nitrogen, argon, and carbon dioxide, and so only a small fraction of those gases have been retained in the Martian atmosphere, accounting for the low surface pressure that is observed. For the gas giants,  $v_{esc}/v_{rms}$  is large even for hydrogen and helium, and so there has been almost no loss of atmospheric gases by these planets.

An additional unusual feature of the atmospheres of the inner planets is the large amount of argon that is observed relative to the amounts of other noble gases that are present. A clue to the origin of argon in the atmosphere of the inner planets lies in the relative abundance of argon isotopes that is observed. The vast majority of

argon in the atmospheres of the inner planets is the  $^{40}\text{Ar}$  isotope (for Earth, 99.60% of atmospheric argon is the  $^{40}\text{Ar}$  isotope, with the remainder the  $^{36}\text{Ar}$  or  $^{38}\text{Ar}$  isotopes). The  $^{40}\text{Ar}$  isotope can be produced by the radioactive decay of  $^{40}\text{K}$  by a process called electron capture. In this process, a core electron converts one of the protons in the nucleus of the potassium atom into a neutron.



The products formed from electron capture in  $^{40}\text{K}$  are a  $^{40}\text{Ar}$  nucleus and an electron neutrino ( $\nu_e$ ). About 10.7% of the radioactive decay of  $^{40}\text{K}$  nuclei decay occurs by this process, or by a rare second process that forms  $^{40}\text{Ar}$  by the emission of a positron and an electron neutrino. A third process, which forms a  $^{40}\text{Ca}$  nucleus by conversion of a neutron into a proton, electron, and electron antineutrino, accounts for the remainder of the radioactive decay of  $^{40}\text{K}$ . The half-life for the radioactive decay of  $^{40}\text{K}$  by all processes is  $t_{1/2} = 1.28$  billion years.

The Earth's crust is approximately 2.6% potassium by mass. The fraction of that potassium that is the  $^{40}\text{K}$  isotope is 11.8 ppm. Over the past several billion years  $^{40}\text{Ar}$  has formed from the radioactive decay of  $^{40}\text{K}$  and, due to its relatively high molecular weight, been retained in the Earth's atmosphere. This process also accounts for the observed amounts of argon found in the atmospheres of Venus and Mars. Interestingly enough, the above radioactive decay process is one way in which the age of some rocks and meteorites can be determined (this requires rocks that contain a significant fraction of potassium, and which trap the  $^{40}\text{Ar}$  produced by radioactive decay).

There are three differences between the atmosphere of the Earth and those of Venus and Mars that must still be explained: the relatively small fraction of carbon dioxide in the Earth's atmosphere, the large amounts of water in the biosphere of the Earth, and the large amount of molecular oxygen found in the Earth's atmosphere. These differences are accounted for as follows:

Absence of carbon dioxide. Although similar in size, Venus has approximately 200,000 times as much atmospheric carbon dioxide as the Earth. The presence of large amounts of carbonate minerals in the Earth's crust is the most likely explanation for this difference. Carbonates are a class of minerals formed by the reaction of carbon dioxide with metal oxides. For example, calcium carbonate is formed by the process



Carbonates can form by geological processes, but are formed even more efficiently by biological processes. For example, seashells are composed of calcium carbonate, along with smaller amounts of magnesium carbonate. As these shells are converted into sedimentary rock carbon dioxide is removed more or less permanently from the atmosphere. It has been estimated that if all of the carbon dioxide sequestered in the Earth's crust were released into the atmosphere the partial pressure of carbon dioxide that would result would be approximately 50 atm, comparable to the amount found on Venus. Carbonates are unlikely to form on Venus, both because of the absence of life and because at high temperatures metal carbonates decompose into metal oxides and carbon dioxide.

Presence of large amounts of water. Earth has abundant amounts of water in the biosphere, while both Venus and Mars have only trace amount of atmospheric water vapor, with little evidence of surface or subsurface water. Water is believed to have initially been present in significant amounts on all three planets. Because of the high temperatures found in the atmosphere of Venus water would have existed entirely in the gas phase. Over time, water is believed to have been removed by photodissociation (breaking apart of a molecule by light) in the upper atmosphere, by the process



with the hydrogen formed by the above process escaping into space, either directly as hydrogen atoms or as hydrogen molecules formed from the combination of hydrogen atoms (with the oxygen left behind playing a role in the formation of carbon dioxide). The same process would also be expected to occur on Mars, although the smaller mass of Mars means that direct escape of water molecules into space would also be possible. The lower temperature found on Earth means that the majority of water is present in liquid or solid form at the Earth's surface, limiting the amount

of water in the gas phase, and thus greatly slowing the removal of water by photodissociation in the upper atmosphere. (It is of interest to note that sedimentary rocks as old as 3.8 billion years have been found on Earth, providing evidence that liquid water has existed on the planet throughout most of its history.)

Partial support of this explanation is provided by the presence of features on the surface of Mars that suggest that liquid water may have once been present in significant amounts. These features include what appear to be river channels, deltas, and flood plains on the Martian surface. Recent satellite probes indicate that there may still be substantial quantities of water present beneath the surface of Mars, existing either as free water or as in hydrated minerals.

Presence of oxygen as a major component. Oxygen is a reactive gas, and its presence as a major component of the Earth's atmosphere might initially seem surprising. However, oxygen is a byproduct of photosynthesis, the process by which plants and some bacteria convert sunlight into chemical energy. Photosynthesis can be indicated schematically as follows:



where "CH<sub>2</sub>O" represents biomass produced via photosynthesis. Over time, plant photosynthesis would be expected to convert carbon dioxide into free oxygen (and would therefore play a minor role in reducing the concentration of carbon dioxide in the atmosphere).

If the above explanation is correct then there should have been significantly smaller amounts of oxygen in the Earth's atmosphere in the past than are observed today. There is geological evidence that this is in fact the case. For example, small particles of pyrites (minerals composed of a metal + sulfur, such as iron pyrite, FeS<sub>2</sub>) are often found in ancient rocks (rocks more than 3 billion years old), but are relatively rare in more recent rocks. Because metal oxides are thermodynamically more stable than pyrites, the latter compounds will only form under conditions of low partial pressures of oxygen. This suggests that initially there was little oxygen present in the atmosphere of the Earth. An estimate of how the concentration of oxygen in the Earth's atmosphere has changed over time, based on geological and fossil evidence, is given in Figure 1.3.

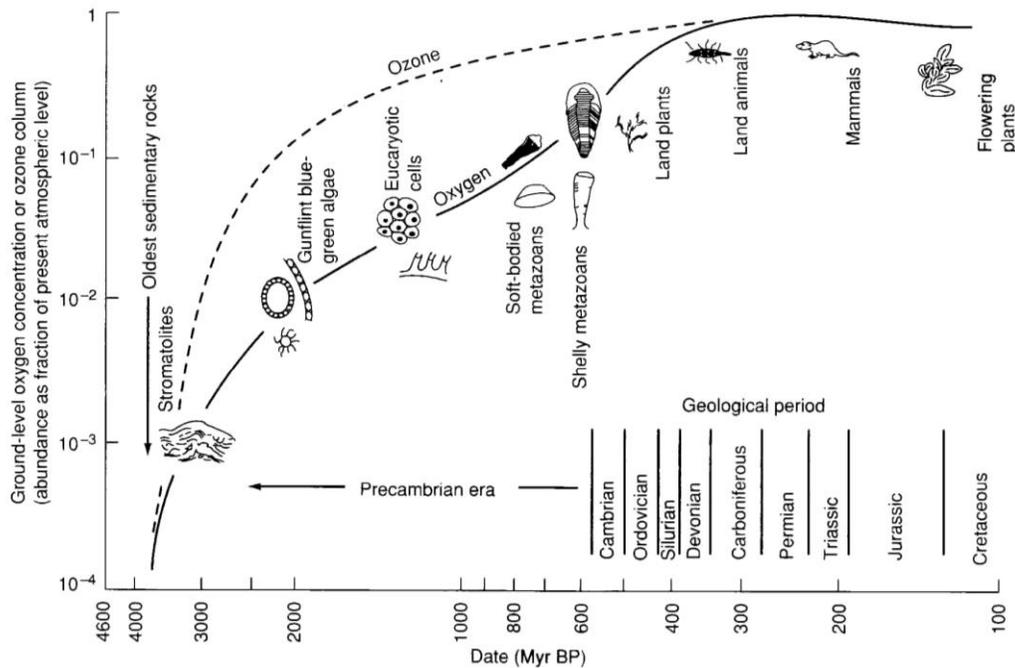


Figure 1.3. Estimated O<sub>2</sub> and O<sub>3</sub> concentrations vs time for the Earth. (Myr BP = millions of years before present.)

One important consequence of the buildup of oxygen in the Earth's atmosphere is the formation of an "ozone layer" in the lower stratosphere. Ozone absorbs high energy ultraviolet light, and thus prevents such light from reaching the surface of the Earth. The establishment of life on land approximately 500 million years ago (as opposed to life in seas and oceans, which has existed for at least 3.5 billion years) became possible only after this protective ozone layer had formed.

In summary, the discussion presented above provides a consistent and plausible explanation for the differences observed in the composition of the atmospheres of the inner and outer planets, the difference in atmospheric pressure on Venus and Mars, and the differences between the atmosphere of the Earth and that of Venus and Mars.

#### 1.4 STRUCTURE OF THE EARTH'S ATMOSPHERE

The average temperature at the surface of the Earth is about 15. °C (288. K). Since warming of the atmosphere by contact with the Earth's surface is the main process heating the atmosphere, it might be expected that the temperature of the atmosphere decreases with increasing altitude. However, the temperature vs altitude profile of the atmosphere is more complicated than this, as can be seen in Figure 1.4. There are in fact four distinct regions of the atmosphere:

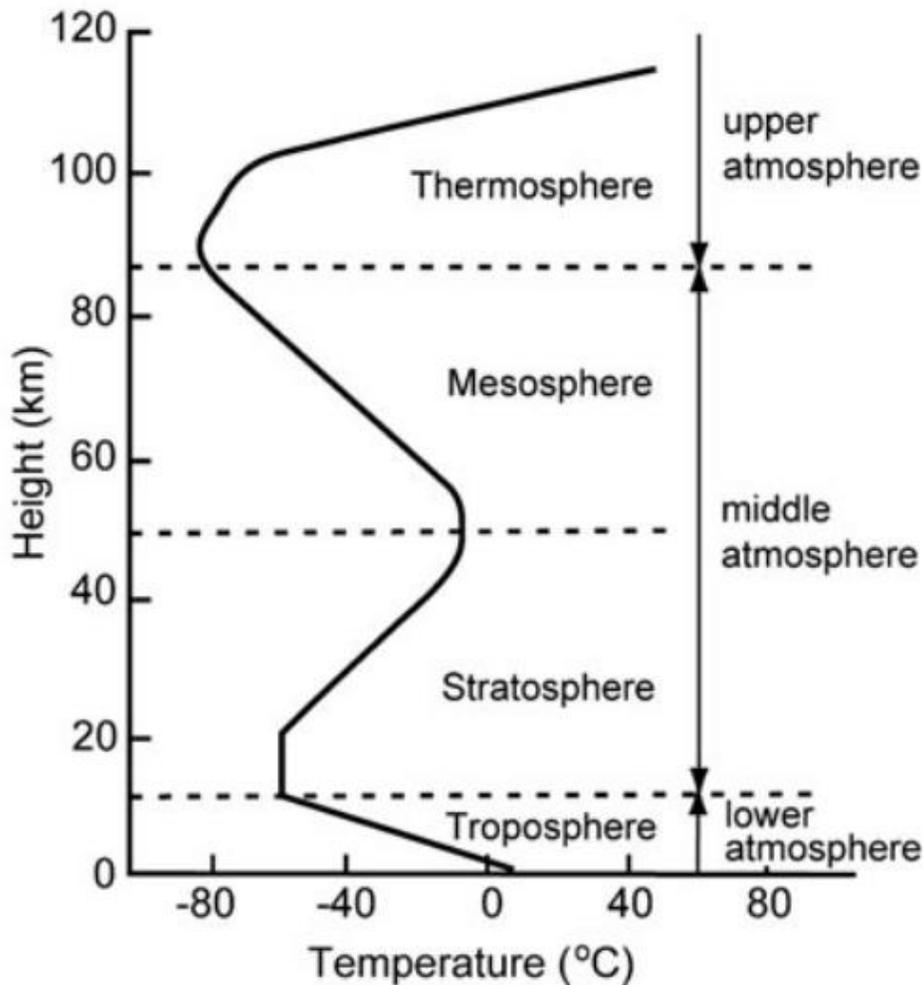


Figure 1.4. Structure of the Earth's atmosphere.

The troposphere is the region of the atmosphere extending from sea level to altitudes of 10 - 15 kilometers. This region of the atmosphere contains about 75% of the total mass of the atmosphere. This is the region of the atmosphere that we live in. Cloud formation and weather are for the most part confined to the troposphere.

In the stratosphere, the region of the atmosphere from the top of the troposphere to about 50 kilometers, temperature increases with increasing altitude. The lower stratosphere contains the "ozone layer", a region of relatively high concentration of ozone (maximum concentration of about 15 ppm at  $z = 25$  km). This layer of ozone is important because it filters out high energy UV light, preventing it from reaching the surface of the Earth. About 99% of the total mass of the atmosphere resides in either the troposphere or the stratosphere

The mesosphere, or middle atmosphere, extends from 50 - 85 kilometers in altitude. As is observed in the troposphere, temperature in the mesosphere generally decreases with increasing altitude.

Finally, the thermosphere represents the region of the atmosphere extending from an altitude of 85 kilometers out into space. There are two regions of the thermosphere that are of particular interest. In the ionosphere, the region between 90 - 110 km in altitude, the density of particles is sufficiently low that free electrons and ions, created by photoionization as discussed below, are stable. This layer of charged particles can reflect radio waves, making it possible for certain frequencies of light to propagate long distances by reflection back and forth off the ionosphere and the surface of the Earth. In the exosphere, at altitudes above about 500 km, the density of gas molecules becomes low enough that molecules moving away from the Earth at speeds greater than the escape velocity (11700 m/s) will escape into space.

The boundaries between the different regions of the atmosphere are not fixed, but are determined from the locations at which atmospheric temperatures reach either minimum or maximum values. These boundaries are named after the region of the atmosphere below the boundary. Thus the boundary between the troposphere and the stratosphere is called the tropopause. Similarly, the boundary between the stratosphere and mesosphere is called the stratopause, and that between the mesosphere and thermosphere is called the mesopause.

The thermal structure of the atmosphere is determined by a balance between heating and cooling processes. Except for a tiny amount of energy produced by the decay of radioactive elements in the Earth itself, the source of energy for the Earth is the sun. The intensity of sunlight as a function of wavelength ( $\lambda$ ) is given in Figure 1.5. Approximately 45% of solar energy appears in the visible region (400 - 700 nm), with 10% of the energy in the near UV region of the spectrum and 45% in the near IR region (UV = ultraviolet; IR = infrared). Figure 1.6 indicates the location of these and other regions of the electromagnetic spectrum.

The energy of a photon (particle) of light is given by the expression

$$E = hv = hc/\lambda \quad (1.16)$$

where  $c$  is the speed of light ( $c = 2.998 \times 10^8$  m/s),  $h$  is Planck's constant ( $h = 6.626 \times 10^{-34}$  J-s), and  $v$  (frequency) and  $\lambda$  (wavelength) are related by the expression

$$c = v\lambda \quad (1.17)$$

Because the UV region lies at shorter wavelengths than visible light, and the IR region lies at longer wavelengths, UV light is of higher energy than visible light, while IR light is of lower energy.

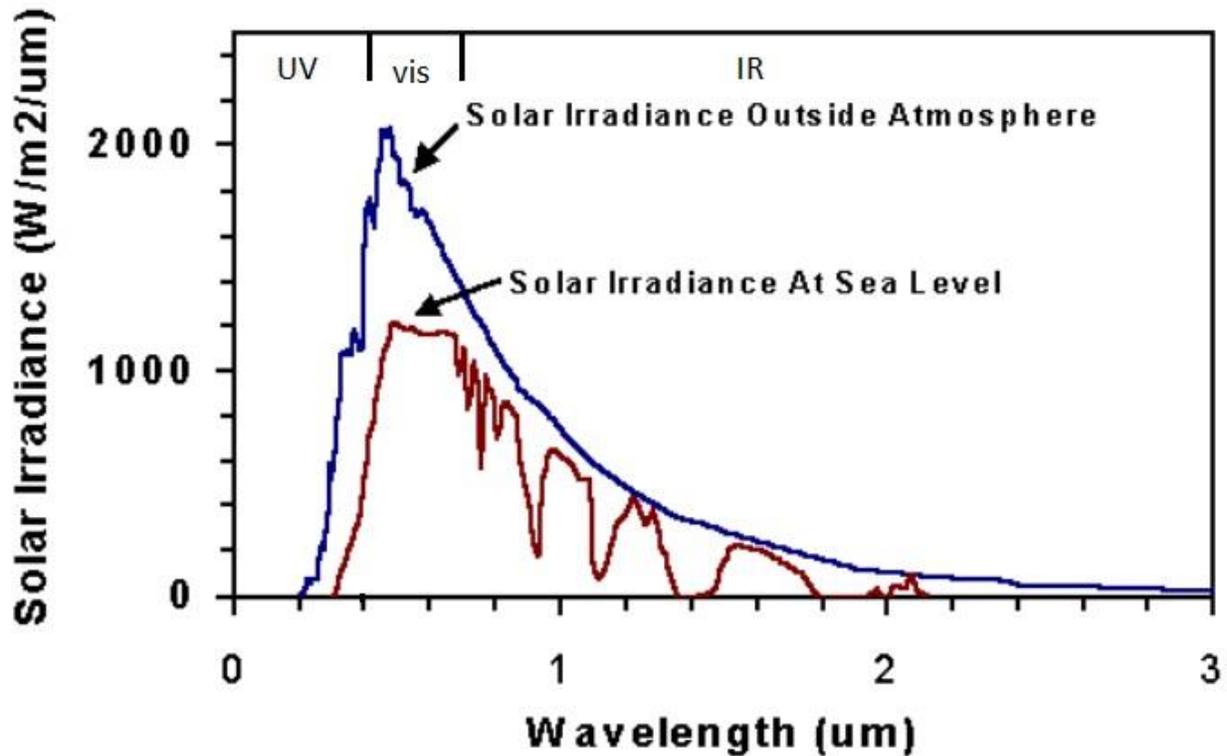


Figure 1.5. Intensity of sunlight vs wavelength. The visible region of the spectrum lies in the range 0.4 – 0.7  $\mu\text{m}$ .

## The Electromagnetic Spectrum

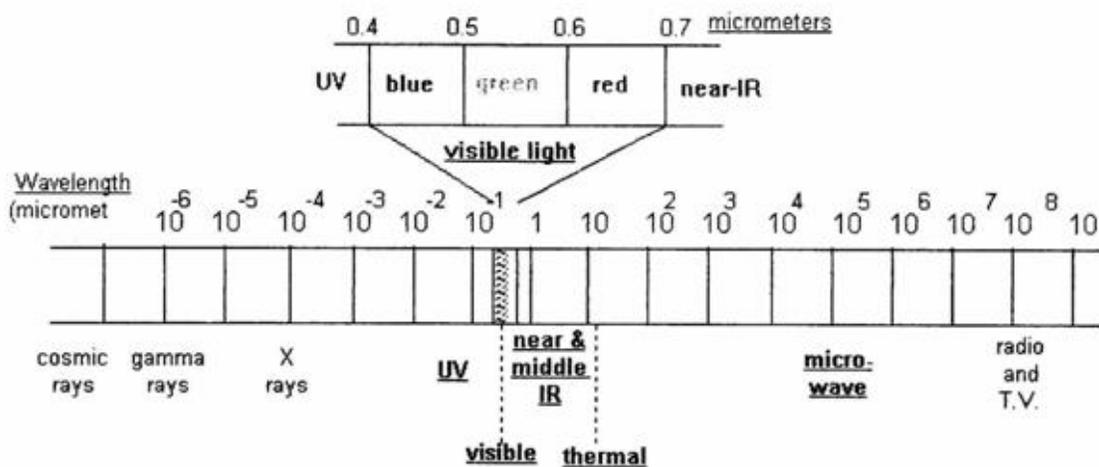


Figure 1.6. The electromagnetic spectrum. Wavelengths are given in  $\mu\text{m}$ .

We define the solar constant for the Earth ( $I_{\text{sol,Earth}}$ ) as the total amount of energy received by a unit surface area at a distance from the sun equal to the average Earth-sun distance per unit time. The solar constant can be measured directly by satellites in near Earth orbit, and has a value  $I_{\text{sol,Earth}} = 1367. \text{ J/m}^2\text{s}$ . This means that every

square meter of surface area above the Earth's atmosphere receives a little over 1 kilojoule of energy every second. Since the intensity of sunlight is inversely proportional to the square of the distance of an object from the sun's center, we may find the solar constant for other planets in terms of the solar constant for the Earth

$$I_{\text{sol,planet}} = I_{\text{sol,Earth}} (d_{\text{sun,Earth}}/d_{\text{sun,planet}})^2 \quad (1.18)$$

where  $d_{\text{sun,Earth}}$  and  $d_{\text{sun,planet}}$  are the average distance between the sun and the Earth or the sun and the planet respectively. Values for  $d_{\text{sun,Earth}}$  and  $d_{\text{sun,planet}}$  are given in Table 1.4.

There are a variety of things that can happen to sunlight when it interacts with the Earth. Sunlight can be reflected or scattered back into space by the atmosphere Earth's atmosphere (molecules, particles, or clouds) or reflected back into space by the Earth's surface. It can also be absorbed by the atmosphere or surface. We define the albedo ( $A$ ) of the Earth or other planet as the fraction of the total energy received from the sun that is reflected back into space. The average value for albedo for the Earth is  $A = 0.35$ , with some variations about this average value depending on time of year. Values for albedo for other planets are given in Table 1.4. Sunlight that is reflected back into space does not provide energy to the Earth. It is only sunlight that is absorbed in the atmosphere or the surface that adds energy to the Earth.

The temperature of the Earth is determined by the balance between energy received by the Earth from the sun and energy radiated away by the Earth, as will be discussed later. For now, we are concerned with the general processes that lead to the thermal structure observed in the atmosphere. Consider sunlight with an intensity distribution as given in Figure 1.5 as it enters the Earth's atmosphere. The first interaction of sunlight with the atmosphere will occur in the thermosphere. Oxygen and nitrogen molecules in this region of the atmosphere can absorb short wavelength UV radiation and photodissociate by the processes



Notice that it takes a higher energy photon to dissociate a nitrogen molecule than it does an oxygen molecule, as expected, since the chemical bond in  $\text{N}_2$  is a triple bond, while that in  $\text{O}_2$  is a double bond. The above photodissociation processes and the chemical reactions that reform  $\text{N}_2$  and  $\text{O}_2$  (along with  $\text{NO}$  and other molecules) by recombination deposit energy into the thermosphere, resulting in increased temperatures with increasing altitude in this region of the atmosphere.

The remaining sunlight passes through the thermosphere and mesosphere with little light absorption taking place. However, in the stratosphere there is a relatively high concentration of ozone molecules (see Figure 1.1). Ozone strongly absorbs sunlight in the region 200 - 300 nm, leading to photodissociation of ozone by the process



Ozone photodissociation, along with regeneration of ozone by recombination



deposits heat into the stratosphere, leading to increased temperatures with increasing altitude, just as is observed in the thermosphere.

Light with wavelengths longer than 300 nm passes through the entire bulk of the atmosphere with minimal absorption and strikes the surface of the Earth. Some of this light is absorbed by the ground (the fraction of light that is absorbed being determined by the nature of the surface), causing warming. Air in direct contact with the Earth's surface is warmed by contact, while air further away from the surface is warmed indirectly. Therefore, in the troposphere, temperature decreases as the distance from ground level increases.

We also know that atmospheric pressure decreases with increasing altitude. The dependence of pressure on altitude is described by the barometric equation

$$p_z = p_0 \exp(-z/H) \quad (1.23)$$

where  $p_z$  is the pressure at an altitude  $z$ ,  $p_0$  is the value for atmospheric pressure at sea level (1.00 atm for Earth), and  $H$  is a constant, called the scale height. For Earth, (and assuming an average atmospheric temperature  $T = 250$ . K) the value for scale height is  $H = 7.4$  km. Equation 1.23 is only approximately correct as it assumes that the temperature of the atmosphere is independent of altitude (it can however be modified to take the dependence of temperature on altitude into account). The barometric equation can also be used to describe the dependence of pressure on altitude for other planets, if we interpret  $p_0$  as the atmospheric pressure at some reference altitude and use the appropriate value for scale height, which is different for different planets.

As an example of the use of eq. 1.23 we can find the value for atmospheric pressure at  $z = 25$  km, the altitude where ozone concentration reaches its maximum value

$$p(z=25 \text{ km}) = (1.00 \text{ atm}) \exp(-25.0 \text{ km}/7.4 \text{ km}) = 0.034 \text{ atm} \quad (1.24)$$

We now have a reasonably complete picture of how pressure and temperature change with altitude in the atmosphere, as well as an understanding of the processes that establish the observed structure of the atmosphere. All that remains to be done is to discuss the dynamical processes that lead to mixing in the atmosphere.

## 1.5 DYNAMICAL PROCESSES IN THE EARTH'S ATMOSPHERE

As a final topic before discussing chemical reactions in the lower atmosphere we now consider the various types of mixing processes that occur in the atmosphere. Mixing is important because it both dilutes atmospheric pollutants and transports them from their point of origin to remote areas. We will be concerned with two general types of mixing processes: vertical mixing and horizontal mixing.

Vertical mixing refers to the up and down motion of air in the atmosphere. The main factor determining the occurrence and rate of vertical mixing is differences in density of parcels of air. Starting from the ideal gas law

$$pV = nRT \quad (1.25)$$

we can show that the density of a parcel of air,  $\rho$ , is given by the expression

$$\rho = pM_{\text{ave}}/RT \quad (1.26)$$

where  $\rho$  has units of mass/volume (g/L, for example) and  $M_{\text{ave}}$  is the average molecular weight of a molecule of air. Notice that density is inversely proportional to temperature, meaning that the density of air at a constant value for pressure will decrease as temperature increases.

In the troposphere the average temperature of the atmosphere decreases with increasing altitude at a rate of about  $-6.5$  °C/km. This is called the normal lapse rate of the troposphere (lapse rate is a general term referring to the change in temperature as a function of altitude). Consider what this implies for a parcel of hot air near the surface of the Earth. Since the air parcel has a higher temperature than the surrounding air it will have a lower density. Because of this, the air mass will begin to rise. As long as the parcel of air has a higher temperature than the surrounding atmosphere, it will have a lower density, and so tend to continue to rise in altitude. This in fact is the basis by which hot air balloons operate.

There is, however, another factor that must be taken into account in our discussion. As our air parcel increases in altitude it expands, due to the lower pressures present in the surrounding atmosphere. The energy for the expansion comes from the air parcel itself. The loss of energy due to expansion leads to a decrease in the temperature

of the air parcel. If we assume the expansion is adiabatic (no exchange of heat between the air parcel and the surrounding air) and that the parcel of air contains no water vapor, then the rate of cooling can be calculated. The rate of cooling of a dry parcel of air as it rises through the lower atmosphere, called the adiabatic lapse rate for dry air, is approximately  $-10.0\text{ }^{\circ}\text{C}/\text{km}$ .

While the normal lapse rate represents the average observed change in temperature with altitude, it is not surprising that the actual change in temperature for a specific location, time of day, and time of year may be far different from this average value. We define the environmental lapse rate as the actual rate of change of temperature with altitude that is observed at a particular time and location. In fact, the normal lapse rate is just the environmental lapse averaged over a large period of time and at several different geographic locations.

Figure 1.7 shows what happens when a parcel of dry air initially at a temperature  $5.0\text{ }^{\circ}\text{C}$  higher than the surrounding atmosphere forms at the Earth's surface. Since the temperature of the air parcel is higher than that of the surrounding air, the parcel will initially have a lower density than its surroundings, and will therefore begin to rise through the atmosphere. As the air parcel moves upwards it cools. If we assume that the environmental lapse rate at the location where the air parcel formed is equal to the normal lapse rate then the air parcel will continue to rise until the solid line in the figure (representing the environmental lapse rate) and the dashed line (representing the temperature of the air parcel as it rises through the atmosphere) cross. A simple calculation shows that this crossing point occurs at an altitude  $z \cong 1.4\text{ km}$ . At this altitude the temperature, and therefore the density, of the air parcel and the surrounding air are the same, and vertical motion of the air parcel ceases.

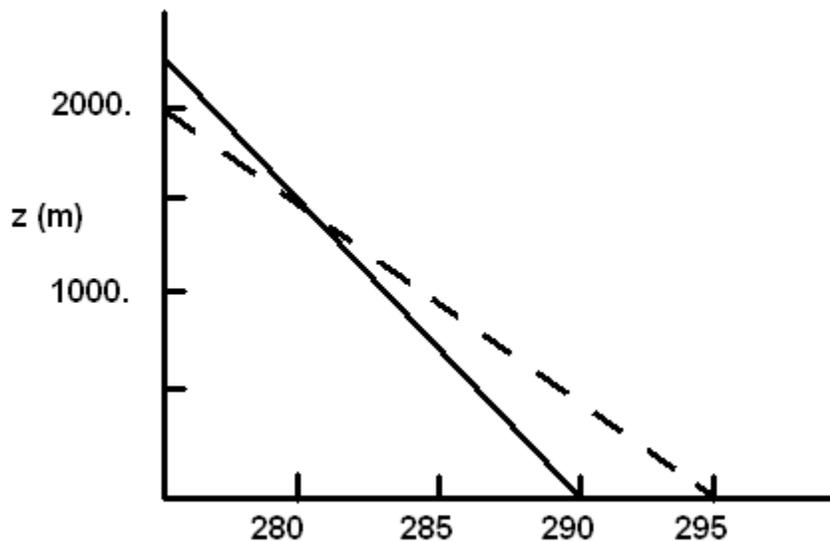


Figure 1.7. Environmental (solid line) and adiabatic (dashed line) lapse rate for an air parcel initially  $5.0\text{ }^{\circ}\text{C}$  warmer than the surrounding air. In this example the environmental lapse rate is equal to the normal lapse rate ( $-6.5\text{ }^{\circ}\text{C}/\text{km}$ ).

The conditions in the example shown in Figure 1.7 are typical for the vertical movement of air near the Earth's surface. Air near the surface warms due to contact with the ground, and then rises until expansion reduces the temperature of the air to that of the surrounding atmosphere. There will thus be a region near the Earth's surface where vertical mixing is usually extremely efficient. We define the maximum mixing height (MMH) as the height above the Earth's surface where rapid vertical mixing commonly occurs. Typical values for maximum mixing height

are from 1.0 - 2.5 km. Vertical mixing throughout the rest of the troposphere will also occur, but at a slower rate than mixing in the region within the maximum mixing height.

Under some conditions vertical mixing is a very inefficient process. For example, consider the situation in Figure 1.8. We again have a parcel of dry air that is initially at a temperature  $5.0\text{ }^{\circ}\text{C}$  higher than the surrounding air. However, in this example the environmental lapse rate is positive, that is, temperature (at least near the surface) is increasing with increasing altitude. For conditions where the environmental lapse rate is positive we say that there is a temperature inversion (the term thermal inversion is also used to describe this condition). In this particular example, where the environmental lapse rate is initially  $+6.5\text{ }^{\circ}\text{C}/\text{km}$ , the air parcel will only rise to an altitude  $z \cong 0.3\text{ km}$  before vertical mixing ceases to occur. This means that the air parcel (and any pollutants it might contain) will remain trapped near the surface. Temperature inversions occasionally occur at most locations, but in some places, such as the Los Angeles basin (United States) and Mexico City (Mexico) temperature inversions are the rule rather than the exception. The combination of a semi-permanent temperature inversion and large releases of air pollutants makes urban smog in cities such as these a serious problem.

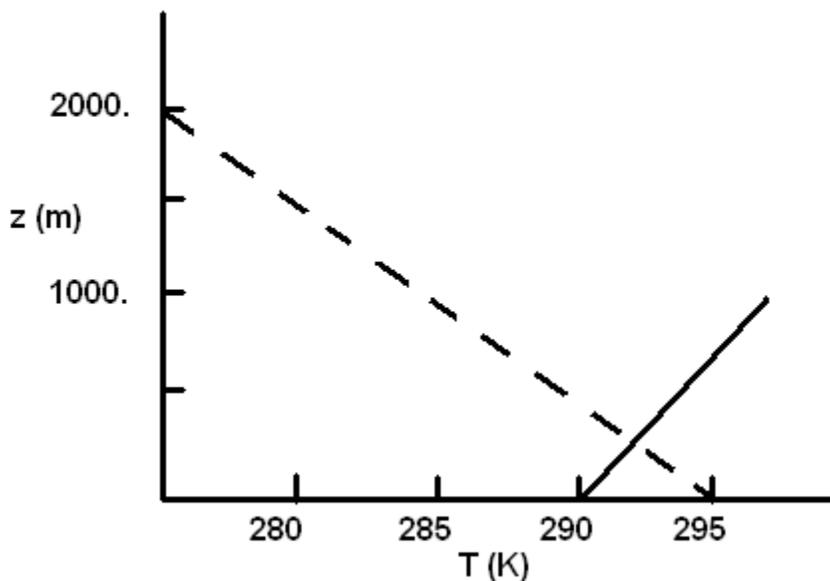


Figure 1.8. Environmental (solid line) and adiabatic (dashed line) lapse rate for an air parcel initially  $5.0\text{ }^{\circ}\text{C}$  warmer than the surrounding air. In this example there is a temperature inversion, with the environmental lapse rate initially equal to  $(+6.5\text{ }^{\circ}\text{C}/\text{km})$ .

The above discussion has focused on the cooling of a dry parcel of air as it rises through the atmosphere. If our air parcel contains a significant concentration of water vapor, the cooling that occurs will lead to an increase in the relative humidity of the air parcel as it increases in altitude. Once the relative humidity reaches 100%, additional cooling of the air will cause some of the water vapor to condense into droplets (or ice crystals, depending on temperature). Just as heat must be added to solid or liquid water to convert them into water vapor, the formation of droplets or ice crystals from the condensation of water vapor releases heat. Because of this, the rate of cooling of humid air as it rises through the atmosphere will be smaller in magnitude than that observed for dry air. One consequence of the condensation process is that humid air will generally rise higher into the troposphere than dry air. A second consequence is that once the water droplets or ice crystals formed by condensation become sufficiently large they will be pulled to the ground by the Earth's gravity, leading to precipitation (rain, sleet, or snow, depending on temperature).

In the stratosphere temperature normally increases with increasing altitude (see Figure 1.4). In a sense there is a permanent temperature inversion present in the stratosphere. Because of this, vertical mixing of gases in the stratosphere is extremely slow.

In addition to vertical mixing in the atmosphere, horizontal mixing (mixing in a direction parallel to the Earth's surface) will also occur. Horizontal mixing occurs due to differences in air pressure, which are most commonly caused by differences in temperature due to unequal heating of the atmosphere. This causes wind, or the horizontal flow of air from a region of higher pressure to a region of lower pressure.

A simple model for the global circulation of air was first proposed by George Hadley in 1735. He realized that the equatorial regions of the Earth receive a greater intensity of sunlight than the polar regions, and so air in the tropics will be significantly higher in temperature than air near the North and South Pole. Based on this observation Hadley proposed a global circulation model where warm air from the tropics rises through the atmosphere and is then transported to the polar regions, where it cools and descends back to the Earth's surface, as shown in Figure 1.9. These circulation patterns that would exist in the Northern and Southern hemisphere are termed Hadley cells.



Figure 1.9. Global circulation in the simple Hadley model.

The actual pattern of circulation of air in the lower atmosphere is far more complicated than in the above simple model. Several factors account for this. First of all, the rotation of the Earth about its axis tends to deflect the movement of air as it travels from the equator to the polar regions (in the Northern hemisphere the air movement is deflected to the east, while in the Southern hemisphere the air movement is deflected to the west). This tends to break the single Hadley cell predicted to occur in each hemisphere into three smaller Hadley cells, which are well defined in the tropical and polar regions and less well defined in the temperate zone in between these regions. This three zone circulation model is shown in Figure 1.10. The distribution of land and ocean, the presence of mountain ranges, and seasonal variations in the intensity of sunlight further affect the global circulation of air.

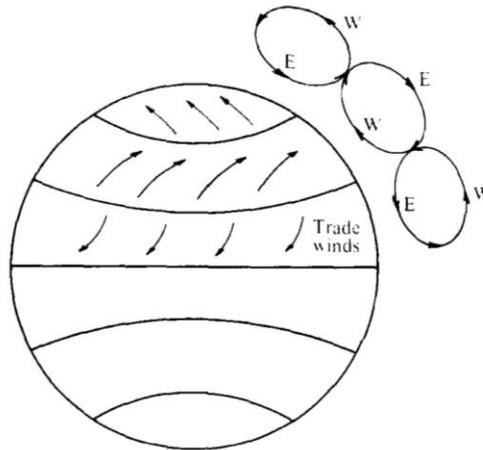


Figure 1.10. Three zone circulation model.

We conclude this general discussion of dynamical processes in the atmosphere by briefly discussing slow mixing processes in the atmosphere. We have already noted that vertical mixing in the stratosphere is slow due to the existence of a permanent temperature inversion in this region of the atmosphere. As a consequence of this, crossover of gases from the troposphere to the stratosphere (or from the stratosphere to the troposphere) is extremely slow, taking place on a time scale of several years. The movement of air in the tropics (vertical motion followed by movement towards the polar regions) tends to act as a barrier preventing mixing of gases between the Northern and Southern hemisphere. Movement of gases between the Northern and Southern hemisphere therefore also occurs on a time scale of years. In contrast to this, mixing within the troposphere within a hemisphere is relatively rapid, taking place on a time scale of weeks to a few months.

## 1.6 SUMMARY

The Earth's atmosphere is an approximately 4:1 mixture of nitrogen and oxygen, with much smaller amounts of other gases. The Earth's atmosphere differs from that found on other planets, and has evolved from the atmosphere that was present when the Earth was formed 4.5 billion years ago. The interaction of sunlight with the atmosphere establishes a structure to the atmosphere based on the temperature profile that occurs, while the gravitational attraction of the Earth leads to changes in pressure with altitude. Both vertical and horizontal mixing processes lead to large scale movement of air, with some mixing processes occurring significantly more slowly than other mixing processes.

Appendix 1 – Periodic table, miscellaneous relationships and constants

1A																				8A											
1 H 1.01	2A																2 He 4.00														
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18														
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95														
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80														
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc [98]	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3														
55 Cs 132.9	56 Ba 137.3	71 Lu 175.0	72 Hf 178.5	73 Ta 181.0	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po [209]	85 At [210]	86 Rn [222]														
87 Fr [223]	88 Ra [226]	103 Lr [262]	104 Rf [261]	105 Db [262]	106 Sg [266]																										
																		57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm [145]	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
																		89 Ac [227]	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]

Miscellaneous constants

$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$R = 0.08314 \text{ L}\cdot\text{bar/mol}\cdot\text{K}$$

$$R = 0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$$

$$1 \text{ atm} = 1.01325 \text{ bar}$$

$$1 \text{ atm} = 760. \text{ torr}$$

$$N_A = 6.022 \times 10^{23}$$

$$1 \text{ bar} = 10^5 \text{ Pa} = 10^5 \text{ N/m}^2$$

$$c = 2.998 \times 10^8 \text{ m/s}$$

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$k = 1.381 \times 10^{-23} \text{ J/K}$$

### Root mean square average velocity (3-dimensions)

$$v_{\text{rms}} = (3RT/M)^{1/2}$$

$$R = 8.314 \text{ J/mole}\cdot\text{K}$$

### Escape velocity

$$v_{\text{esc}} = (2M_p G/r_p)^{1/2}$$

$M_p$  = mass of planet

$$G = 6.67 \times 10^{-11} \text{ N}\cdot\text{m}^2/\text{kg}^2$$

$r_p$  = radius of planet

### Barometric equation

$$p_z = p_o \exp[-\int_o^z (M_{\text{ave}} G_z/RT) dz]$$

$$\cong p_o \exp[-(M_{\text{ave}} G_o/R) \int_o^z dz/T(z)]$$

$$\cong p_o \exp(-z/H) ; H = RT_o/M_{\text{ave}} G_o = \text{scale height}$$

$M_{\text{ave}}$  = average molecular mass

$p_o$  = pressure at reference altitude

$G_z$  = planetary gravitational attraction

### Relative humidity

$$H_{\text{rel}} = [p(\text{H}_2\text{O})/p^o(\text{H}_2\text{O})] \times 100\% ; p^o(\text{H}_2\text{O}) = \text{vapor pressure of H}_2\text{O}$$

### Diatomic molecules

#### Rotation (rigid rotor; $E_{\text{rot}}$ , $B$ in $\text{cm}^{-1}$ )

$$E_{\text{rot}} = J(J+1)B$$

$$B = h/8\pi^2 I c ; I = \mu r^2 ;$$

$$\mu_{AB} = m_A m_B / (m_A + m_B)$$

$$J = 0, 1, 2, \dots$$

$$M_J = 0, \pm 1, \pm 2, \dots, \pm J$$

$$g_J = 2J + 1$$

#### Vibration (harmonic oscillator; $E_{\text{vib}}$ , $\omega_e$ in $\text{cm}^{-1}$ )

$$E_{\text{vib}} = (v + 1/2)\omega_e$$

$$\omega_e = (1/2\pi c) (k/\mu)^{1/2}$$

$$v = 0, 1, 2, \dots$$

$$g_v = 1$$

### Black body relationships

$$M(\lambda, T) d\lambda = (2\pi hc^2/\lambda^5) [\exp(hc/\lambda kT) - 1]^{-1} d\lambda$$

$$M(T) = \sigma T^4 \text{ (total intensity)}$$

$$\lambda_{\text{max}} = C_w/T \text{ (wavelength maximum)}$$

$$k = 1.381 \times 10^{-23} \text{ J/K}$$

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$c = 2.998 \times 10^8 \text{ m/s}$$

$$\sigma = 5.67 \times 10^{-8} \text{ W/m}^2\cdot\text{K}^4$$

$$C_w = 0.290 \text{ cm}\cdot\text{K}$$

### Planetary solar constant

$$I_s(\text{planet})/I_s(\text{Earth}) = (d_E/d_p)^2$$

$$I_s(\text{Earth}) = 1367. \text{ W/m}^2$$

$d_p$  = mean planet-sun distance