PART I

The Atmosphere and Its Constituents

CHAPTER 1

The Atmosphere

1.1 HISTORY AND EVOLUTION OF EARTH'S ATMOSPHERE

It is generally believed that the solar system condensed out of an interstellar cloud of gas and dust, referred to as the *primordial solar nebula*, about 4.6 billion years ago. The atmospheres of Earth and the other terrestrial planets, Venus and Mars, are thought to have formed as a result of the release of trapped volatile compounds from the planet itself. The early atmosphere of Earth is believed to have been a mixture of carbon dioxide (CO_2), nitrogen (N_2), and water vapor (H_2O), with trace amounts of hydrogen (H_2), a mixture similar to that emitted by present-day volcanoes.

The composition of the present atmosphere bears little resemblance to the composition of the early atmosphere. Most of the water vapor that outgassed from Earth's interior condensed out of the atmosphere to form the oceans. The predominance of the CO_2 that outgassed formed sedimentary carbonate rocks after dissolution in the ocean. It is estimated that for each molecule of CO_2 presently in the atmosphere, there are about 10^5 CO_2 molecules incorporated as carbonates in sedimentary rocks. Since N_2 is chemically inert, non-water-soluble, and noncondensable, most of the outgassed N_2 accumulated in the atmosphere over geologic time to become the atmosphere's most abundant constituent.

The early atmosphere of Earth was a mildly reducing chemical mixture, whereas the present atmosphere is strongly oxidizing. Geochemical evidence points to the fact that atmospheric oxygen underwent a dramatic increase in concentration about 2300 million years ago (Kasting 2001). While the timing of the initial O_2 rise is now well established, what triggered the increase is still in question. There is agreement that O_2 was initially produced by cyanobacteria, the only prokaryotic organisms (*bacteria* and *archea*) capable of oxygenic photosynthesis. These bacteria emerged 2700 million years ago. The gap of 400 million years between the emergence of cyanobacteria and the rise of atmospheric O_2 is still an issue of debate. The atmosphere from 3000 to 2300 million years ago was rich in reduced gases such as H_2 and CH_4. Hydrogen can escape to space from such an atmosphere. Since the majority of Earth's hydrogen was in the form of water, H_2 escape would lead to a net accumulation of O_2. One possibility is that the O_2 left behind by the escaping H_2 was largely consumed by oxidation of continental crust. This oxidation might have sequestered enough O_2 to suppress atmospheric levels before 2300 million years ago, the point at which the flux of reduced gases fell below the net photosynthetic production rate of oxygen. The present level of O_2 is maintained by a balance between production from photosynthesis and removal through respiration and decay of organic carbon (Walker 1977).

Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Third Edition. John H. Seinfeld and Spyros N. Pandis.

Earth's atmosphere is composed primarily of the gases N_2 (78%), O_2 (21%), and Ar (1%), whose abundances are controlled over geologic timescales by the biosphere, uptake and release from crustal material, and degassing of the interior. Water vapor is the next most abundant constituent; it is found mainly in the lower atmosphere and its concentration is highly variable, reaching concentrations as high as 3%. Evaporation and precipitation control its abundance. The remaining gaseous constituents, the *trace gases*, represent less than 1% of the atmosphere. These trace gases play a crucial role in Earth's radiative balance and in the chemical properties of the atmosphere.

Aristotle was the first to propose in his book *Meteorologica* in 347 BC that the atmosphere was actually a mixture of gases and that water vapor should be present to balance the water precipitation to Earth's surface. The study of atmospheric chemistry can be traced back to the eighteenth century when chemists such as Joseph Priestley, Antoine-Laurent Lavoisier, and Henry Cavendish attempted to determine the chemical components of the atmosphere. Largely through their efforts, as well as those of a number of nineteenth-century chemists and physicists, the identity and major components of the atmosphere, N_2, O_2, water vapor, CO_2, and the rare gases, were established. In the late nineteenth–early twentieth century focus shifted from the major atmospheric constituents to trace constituents, that is, those having mole fractions below 10^{-6}, 1 part per million (ppm) by volume. We now know that the atmosphere contains a myriad of trace species. Spectacular innovations in instrumentation over the last several decades have enabled identification of atmospheric trace species down to levels of about 10^{-12} mole fraction, 1 part per trillion (ppt) by volume.

The extraordinary pace of the recent increases in atmospheric trace gases can be seen when current levels are compared with those of the distant past. Such comparisons can be made for CO_2 and CH_4, whose histories can be reconstructed from their concentrations in bubbles of air trapped in ice in such perpetually cold places as Antarctica and Greenland. With gases that are long-lived in the atmosphere and therefore distributed rather uniformly over the globe, such as CO_2 and CH_4, polar ice core samples reveal global average concentrations of previous eras. Analyses of bubbles in ice cores show that CO_2 and CH_4 concentrations remained essentially unchanged from the end of the last ice age some 10,000 years ago until roughly 300 years ago, at mole fractions close to 260 and 0.7 ppm by volume, respectively. Activities of humans account for most of the rapid changes in the trace gases over the past 200 years–combustion of fossil fuels (coal and oil) for energy and transportation, industrial and agricultural activities, biomass burning (the burning of vegetation), and deforestation.

These changes have led to the definition of a new era in Earth's history, the *Anthropocene* (Crutzen and Steffen 2003). Records of atmospheric CO_2, CH_4, and N_2O show a clear increase since the end of the eighteenth century, coinciding more or less with the invention of the steam engine in 1784. The global release of SO_2, from coal and oil burning, is at least twice that of all natural emissions. More nitrogen is now fixed synthetically and applied as fertilizers in agriculture than fixed naturally in all terrestrial ecosystems. The Haber–Bosch industrial process to produce ammonia from N_2, in many respects, made the human explosion possible.

The emergence of the Antarctic ozone hole in the 1980s provided unequivocal evidence of the ability of trace species to perturb the atmosphere. The essentially complete disappearance of ozone in the Antarctic stratosphere during the austral spring is now recovering, owing to a global ban on production of stratospheric ozone-depleting substances. Whereas stratospheric ozone levels eroded in response to human emissions, those at ground level have, over the past century, been increasing. Paradoxically, ozone in the stratosphere protects living organisms from harmful solar ultraviolet radiation, whereas increased ozone in the lower atmosphere has the potential to induce adverse effects on human health and plants.

Levels of airborne particles in industrialized regions of the Northern Hemisphere have increased markedly since the Industrial Revolution. Atmospheric particles (aerosols) arise both from direct emissions and from gas-to-particle conversion of vapor precursors. Aerosols can affect climate and have been implicated in human morbidity and mortality in urban areas.

Atmospheric chemistry comprises the study of the mechanisms by which molecules introduced into the atmosphere react and, in turn, how these alterations affect atmospheric composition and properties (Ravishankara 2003). The driving force for chemical changes in the atmosphere is sunlight. Sunlight directly interacts with many molecules and is also the source of most of the atmospheric free radicals. Despite their very small abundances, usually less than one part in a billion parts of air, free radicals act to transform most species in the atmosphere. The study of atmospheric chemical processes begins with determining basic chemical steps in the laboratory, then quantifying atmospheric emissions and removal processes, and incorporating all the relevant processes in computational models of transport and transformation, and finally comparing the predictions with atmospheric observations to assess the extent to which our basic understanding agrees with the actual atmosphere. Atmospheric chemistry occurs against the fabric of the physics of air motions and of temperature and phase changes. In this book we attempt to cover all aspects of atmospheric chemistry and physics that bear on air pollution and climate change.

1.2 CLIMATE

Viewed from space, Earth is a multicolored marble: clouds and snow-covered regions of white, blue oceans, and brown continents. The white areas make Earth a bright planet; about 30% of the sun's radiation is reflected immediately back to space. The surface emits infrared radiation back to space. The atmosphere absorbs much of the energy radiated by the surface and reemits its own energy, but at lower temperatures. In addition to gases in the atmosphere, clouds play a major climatic role. Some clouds cool the planet by reflecting solar radiation back to space; others warm the earth by trapping energy near the surface. On balance, clouds exert a significant cooling effect on Earth.

The temperature of the earth adjusts so that the net flow of solar energy reaching Earth is balanced by the net flow of infrared energy leaving the planet. Whereas the radiation budget must balance for the entire Earth, it does not balance at each particular point on the globe. Very little solar energy reaches the white, ice-covered polar regions, especially during the winter months. The earth absorbs most solar radiation near its equator. Over time, though, energy absorbed near the equator spreads to the colder regions of the globe, carried by winds in the atmosphere and by currents in the oceans. This global heat engine, in its attempt to equalize temperatures, generates the earth's climate. It pumps energy into storm fronts and powers hurricanes. In the colder seasons, low-pressure and high-pressure cells push each other back and forth every few days. Energy is also transported over the globe by masses of wet and dry air. Through evaporation, air over the warm oceans absorbs water vapor and then travels to colder regions and continental interiors where water vapor condenses as rain or snow, a process that releases heat into the atmosphere.

The condition of the atmosphere at a particular location and time is its *weather*; this includes winds, clouds, precipitation, temperature, and relative humidity. In contrast to weather, the *climate* of a region is the condition of the atmosphere over many years, as described by long-term averages of the same properties that determine weather.

1.3 LAYERS OF THE ATMOSPHERE

In the most general terms, the atmosphere is divided into lower and upper regions. The lower atmosphere is generally considered to extend to the top of the stratosphere, an altitude of about 50 kilometers (km). Study of the lower atmosphere is known as *meteorology*; study of the upper atmosphere is called *aeronomy*.

The earth's atmosphere is characterized by variations of temperature and pressure with height. In fact, the variation of the average temperature profile with altitude is the basis for distinguishing the layers of the atmosphere. The regions of the atmosphere are (Figure 1.1) as follows:

Troposphere. The lowest layer of the atmosphere, extending from Earth's surface up to the tropopause, which is at 10–15 km altitude depending on latitude and time of year; characterized by decreasing temperature with height and rapid vertical mixing.

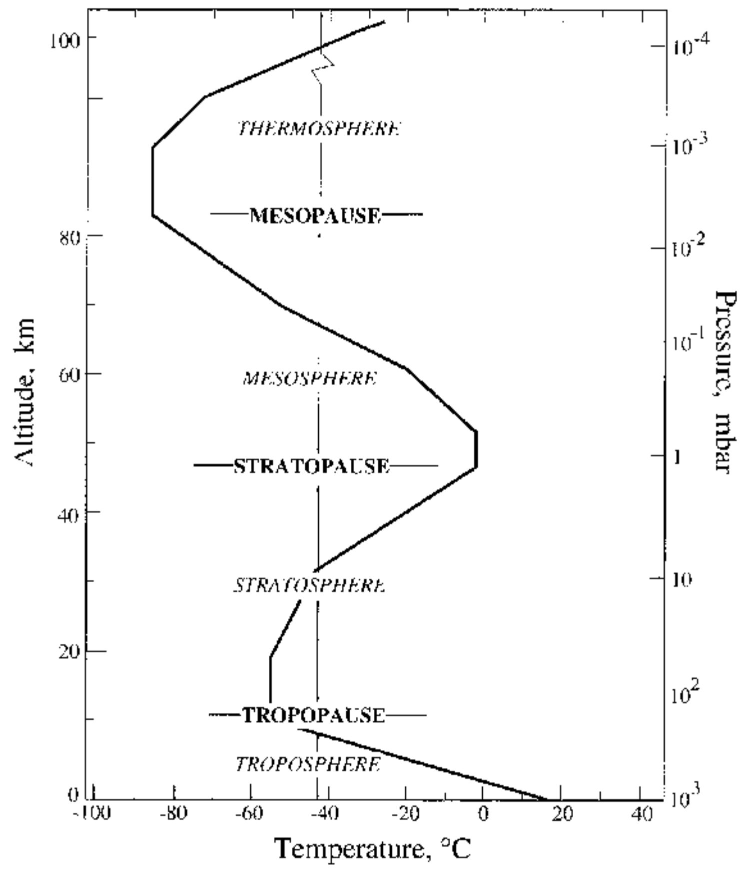

FIGURE 1.1 Layers of the atmosphere.

Stratosphere. Extends from the tropopause to the stratopause (from ~45 to 55 km altitude); temperature increases with altitude, leading to a layer in which vertical mixing is slow.

Mesosphere. Extends from the stratopause to the mesopause (from ~80 to 90 km altitude). Its temperature decreases with altitude to the mesopause, which is the coldest point in the atmosphere. It is characterized by rapid vertical mixing.

Thermosphere. The region above the mesopause characterized by high temperatures as a result of absorption of short-wavelength radiation by N_2 and O_2 and rapid vertical mixing. The *ionosphere* is a region of the upper mesosphere and lower thermosphere where ions are produced by photoionization.

Exosphere. The outermost region of the atmosphere (>500 km altitude) where gas molecules with sufficient energy can escape from Earth's gravitational attraction.

Over the equator the average height of the tropopause is about 16 km; over the poles, about 8 km. By convention of the World Meteorological Organization (WMO), the *tropopause* is defined as the lowest level at which the rate of decrease in temperature with height is sustained at $\leq 2\,\mathrm{K\,km^{-1}}$ (Holton et al. 1995). The tropopause is at a maximum height over the tropics, sloping downward moving toward the poles. The *troposphere*—a term coined by British meteorologist, Sir Napier Shaw, from the Greek word *tropi,* meaning turn—is a region of ceaseless turbulence and mixing. The caldron of all weather, the troposphere contains almost all of the atmosphere's water vapor. Although the troposphere accounts for only a small fraction of the atmosphere's total height, it contains about 80% of its total mass. In the troposphere, the temperature decreases almost linearly with height. In dry air the rate of decrease with increasing altitude is $9.7\,\mathrm{K\,km^{-1}}$. The reason for this decline in temperature is the increasing distance from the sun-warmed earth. At the tropopause, the temperature has fallen to an average of ~217 K (−56 °C). The troposphere can be divided into the *planetary boundary layer*, extending from Earth's surface up to ~1 km, and the *free troposphere*, extending from ~1 km to the tropopause.

The stratosphere, extending from approximately 11 km to ~50 km, was discovered at the turn of the twentieth century by the French meteorologist Léon Philippe Teisserenc de Bort. Sending up temperature-measuring devices in balloons, he found that, contrary to the popular belief of the day, the temperature in the atmosphere did not steadily decrease to absolute zero with increasing altitude, but stopped falling and remained constant after 11 km or so. He named the region the *stratosphere* from the Latin word *stratum*, meaning layer. Although an isothermal region does exist from approximately 11–20 km at midlatitudes, temperature progressively increases from 20 to 50 km, reaching 271 K at the stratopause, a temperature not much lower than the average of 288 K at Earth's surface. The vertical thermal structure of the stratosphere is a result of absorption of solar ultraviolet radiation by O_3.

1.4 PRESSURE IN THE ATMOSPHERE

1.4.1 Units of Pressure

The unit of pressure in the International System of Units (SI) is newtons per meter squared ($\mathrm{N\,m^{-2}}$), which is called the *pascal* (Pa). In terms of pascals, the atmospheric pressure at the surface of Earth, the so-called standard atmosphere, is 1.01325×10^5 Pa. Another commonly used unit of pressure in atmospheric science is the millibar (mbar), which is equivalent to the hectopascal (hPa) (see Tables A.5 and A.8). The standard atmosphere is 1013.25 mbar.

Because instruments for measuring pressure, such as the manometer, often contain mercury, commonly used units for pressure are based on the height of the mercury column (in millimeters) that the gas pressure can support. The unit mm Hg is often called the *torr* in honor of the scientist Evangelista Torricelli. A related unit for pressure is the standard atmosphere (abbreviated atm).

We summarize the various pressure units as follows:

$$
\begin{aligned}
1\ \mathrm{Pa} &= 1\ \mathrm{N\,m^{-2}} = 1\ \mathrm{kg\,m^{-1}\,s^{-2}}\\
1\ \mathrm{atm} &= 1.01325 \times 10^5\ \mathrm{Pa}\\
1\ \mathrm{bar} &= 10^5\ \mathrm{Pa}\\
1\ \mathrm{mbar} &= 1\ \mathrm{hPa} = 100\ \mathrm{Pa}\\
1\ \mathrm{torr} &= 1\ \mathrm{mm\ Hg} = 134\ \mathrm{Pa}
\end{aligned}
$$

$$\boxed{\text{Standard atmosphere:}\ 1.01325 \times 10^5\,\mathrm{Pa} = 1013.25\,\mathrm{hPa} = 1013.25\,\mathrm{mbar} = 760\,\mathrm{torr}}$$

The variation of pressure and temperature with altitude in the standard atmosphere is given in Table A.8. Because the millibar (mbar) is the unit most commonly used in the meteorological literature, we will use it when discussing pressure at various altitudes in the atmosphere. Mean surface pressure at sea level is 1013 mbar; global mean surface pressure, calculated over both land and ocean, is estimated as 985.5 mbar. The lower value reflects the effect of surface topography; over the highest mountains, which reach an altitude of over 8000 m, the pressure may be as low as 300 mbar. The 850 mbar level, which as we see from Table A.8, is at about 1.5 km altitude, is often used to represent atmospheric quantities, such as temperature, as the first standard meteorological level above much of the topography.

1.4.2 Variation of Pressure with Height in the Atmosphere

Let us derive the equation governing the pressure in the static atmosphere. Imagine a volume element of the atmosphere of horizontal area dA between two heights, z and $z + dz$. The pressures exerted on the top and bottom faces are $p(z + dz)$ and $p(z)$, respectively. The gravitational force on the mass of air in the volume $= \rho g\, dA\, dz$, with $p(z) > p(z + dz)$ due to the additional weight of air in the volume. The balance of forces on the volume gives

$$(p(z) - p(z + dz))\, dA = \rho g\, dA\, dz$$

Dividing by dz and letting $dz \to 0$ produce

$$\frac{dp(z)}{dz} = -\rho(z) g \tag{1.1}$$

where $\rho(z)$ is the mass density of air at height z and g is the acceleration due to gravity. From the ideal-gas law, we obtain

$$\rho(z) = \frac{M_{\text{air}} p(z)}{RT(z)} \tag{1.2}$$

where M_{air} is the average molecular weight of air (28.97 g mol^{-1}). Thus

$$\frac{dp(z)}{dz} = -\frac{M_{\text{air}} g p(z)}{RT(z)} \tag{1.3}$$

which we can rewrite as

$$\frac{d \ln p(z)}{dz} = -\frac{1}{H(z)} \tag{1.4}$$

where $H(z) = RT(z)/M_{\text{air}} g$ is a characteristic length scale for decrease of pressure with height.

The temperature in the atmosphere varies by a factor of <2, while the pressure changes by six orders of magnitude (see Table A.8). If the temperature can be taken to be approximately constant, just to obtain a simple approximate expression for $p(z)$, then the pressure decrease with height is approximately exponential

$$\boxed{\frac{p(z)}{p_0} = e^{-z/H}} \tag{1.5}$$

where $H = RT/M_{\text{air}}\, g$ is called the *pressure scale height*.

Since the temperature was assumed to be constant in deriving (1.5), a temperature at which to evaluate H must be selected. A reasonable choice is the mean temperature of the troposphere. Taking a surface temperature of 288 K (Table A.8) and a tropopause temperature of 217 K, the mean tropospheric temperature is 253 K and $H = 7.4$ km.

Number Concentration of Air at Sea Level and as a Function of Altitude

The number concentration of air at sea level is

$$n_{\text{air}}(0) = \frac{p_0 N_A}{RT}$$

where N_A is Avogadro's number (6.022×10^{23} molecules mol^{-1}) and p_0 is the standard atmospheric pressure (1.013×10^5 Pa). The surface temperature of the US Standard Atmosphere (Table A.8) is 288 K, so

$$\begin{aligned} n_{\text{air}}(0) &= \frac{(6.022 \times 10^{23}\ \text{molecules mol}^{-1})(1.013 \times 10^5\ \text{N m}^{-2})}{(8.314\ \text{N m mol}^{-1}\ \text{K}^{-1})(288\ \text{K})} \\ &= 2.55 \times 10^{25}\ \text{molecules m}^{-3} \\ &= 2.55 \times 10^{19}\ \text{molecules cm}^{-3} \end{aligned}$$

Throughout this book we will need to know the number concentration of air molecules as a function of altitude. We can estimate this using the average scale height $H = 7.4$ km and

$$n_{\text{air}}(z) = n_{\text{air}}(0)e^{-z/H}$$

where $n_{\text{air}}(0)$ is the number density at the surface. If we take the mean surface temperature as 288 K, then $n_{\text{air}}(0) = 2.55 \times 10^{19}$ molecules cm^{-3}. The table below gives the approximate number concentrations at various altitudes based on the average scale height of 7.4 km and the values from the US Standard Atmosphere:

	n_{air} (molecules cm^{-3})	
z (km)	Approximate	US Standard Atmosphere[a]
0	2.55×10^{19}	2.55×10^{19}
5	1.3×10^{19}	1.36×10^{19}
10	6.6×10^{18}	6.7×10^{18}
15	3.4×10^{18}	3.0×10^{18}
20	1.7×10^{18}	1.4×10^{18}
25	8.7×10^{17}	6.4×10^{17}

[a] See Table A.8.

Often we need to use the atmospheric number concentration at Earth's surface at 298 and 273 K:

$$\begin{aligned} n_{\text{air}} &= 2.46 \times 10^{19} \text{ molecules cm}^{-3} \quad 298\text{ K} \\ &= 2.69 \qquad\qquad\qquad\qquad\quad 273\text{ K} \end{aligned}$$

Total Mass, Moles, and Molecules of the Atmosphere

The total mass of the atmosphere m_{atm} is

$$m_{\text{atm}} = \int_0^\infty \rho(z) A_e dz$$

where $A_e = 4\pi R_e^2$, the total surface area of the earth. We can obtain an estimate of the total mass of the atmosphere using (1.5) as follows:

$$\begin{aligned} m_{\text{atm}} &= 4\pi R_e^2 \rho_0 \int_0^\infty e^{-z/H} dz \\ &= 4\pi R_e^2 \rho_0 H \end{aligned}$$

Using $R_e \cong 6400$ km, $H \cong 7.4$ km, and $\rho_0 \cong 1.23$ kg m^{-3} (Table A.8), we get the following rough estimate:

$$m_{\text{atm}} \cong 4.7 \times 10^{18} \text{ kg}$$

An estimate for the total number of moles of air in the atmosphere is total mass/M_{air}

$$\text{Total moles} \cong 1.62 \times 10^{20} \text{ mol}$$

and an estimate of the total number of molecules in the atmosphere is

$$\text{Total molecules} \cong 1.0 \times 10^{44} \text{ molecules}$$

An accurate estimate of the total mass of the atmosphere can be obtained by considering the global mean surface pressure (985.50 hPa) and the water vapor content of the atmosphere (Trenberth and Smith 2005). The total mean mass of the atmosphere is

$$m_{\text{atm}}\,(\text{accurate}) = 5.1480 \times 10^{18}\ \text{kg}$$

The mean mass of water vapor in the atmosphere is estimated as 1.27×10^{16} kg, and the dry air mass of the atmosphere is

$$\text{Total dry mass}\,(\text{accurate}) = 5.1352 \times 10^{18}\ \text{kg}$$

1.5 TEMPERATURE IN THE ATMOSPHERE

Figure 1.2 shows the global average temperature distribution for January over the period 1979–1998, as determined from satellite. The heavy dark line denotes the height of the tropopause; the tropopause is highest over the tropics (~14–15 km) and lowest over the poles (~8 km). The coldest region of the atmosphere is in the stratosphere just above the tropical tropopause, where temperatures are less than 200 K (−73 °C). Since Figure 1.2 presents climatology for the month of January, temperatures over the North Pole (90° latitude) are colder than those over the South Pole (−90° latitude); the reverse is true in July.

The US Standard Atmosphere (Table A.8) gives mean conditions at 45°N latitude. From Figure 1.2 we note that the change of temperature with altitude varies with latitude. Throughout this book we will need the variation of atmospheric properties as a function of altitude. For this we will generally use the US Standard Atmosphere.

1.6 EXPRESSING THE AMOUNT OF A SUBSTANCE IN THE ATMOSPHERE

The SI unit for the amount of a substance is the mole (mol). The number of atoms or molecules in 1 mol is Avogadro's number, $N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$. *Concentration* is the amount (or mass) of a substance in a

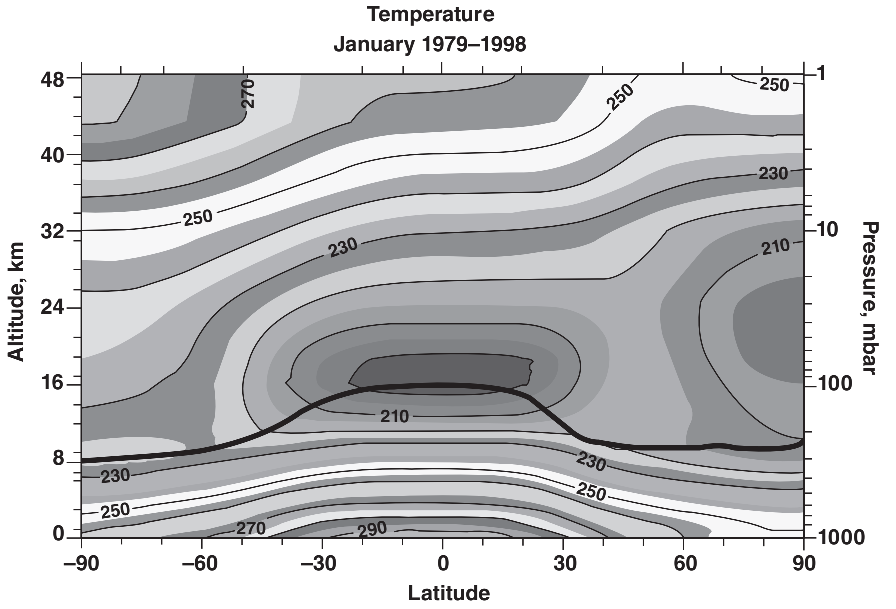

FIGURE 1.2 Global average temperature distribution for January over 1979–1998.

given volume divided by that volume. *Mixing ratio* in atmospheric science is defined as the ratio of the amount (or mass) of the substance in a given volume to the total amount (or mass) of all constituents in that volume. In this definition for a gaseous substance the sum of all constituents includes all gaseous substances, including water vapor, but *not* including particulate matter or condensed phase water.

The volume mixing ratio for a gaseous species i is simply its mole fraction

$$\boxed{\xi_i = \frac{c_i}{c_{\text{total}}} \qquad (1.6)}$$

where c_i is the molar concentration of i and c_{total} is the total molar concentration of air. From the ideal-gas law the total molar concentration at any point in the atmosphere is

$$c_{\text{total}} = \frac{N}{V} = \frac{p}{RT} \qquad (1.7)$$

Thus the mixing ratio ξ_i and the molar concentration are related by

$$\begin{aligned} \xi_i &= \frac{c_i}{p/RT} \\ &= \frac{p_i/RT}{p/RT} = \frac{p_i}{p} \end{aligned} \qquad (1.8)$$

where p_i is the partial pressure of i.

Concentration (mol m^{-3}) depends on pressure and temperature through the ideal-gas law. Mixing ratios, which are just mole fractions, are therefore better suited than concentrations to describe abundances of species in air, particularly when spatiotemporal variation is involved. The inclusion of water vapor in the totality of gaseous substances in a volume of air means that mixing ratio will vary with humidity. The variation can amount to several percent. Sometimes, as a result, mixing ratios are defined with respect to dry air.

It has become common use in atmospheric chemistry to describe mixing ratios by the following units:

parts per million (ppm)	10^{-6}	μmol mol^{-1}
parts per billion (ppb)	10^{-9}	nmol mol^{-1}
parts per trillion (ppt)	10^{-12}	pmol mol^{-1}

These quantities are sometimes distinguished by an added v (for volume) and m (for mass):

ppmv	parts per million by volume
ppmm	parts per million by mass

Unless noted otherwise, we will always use mixing ratios by volume and not use the added v. The parts per million, parts per billion, and parts per trillion measures are not SI units; the SI versions are, as given above, μmol mol^{-1}, nmol mol^{-1}, and pmol mol^{-1}.

Water vapor occupies an especially important role in atmospheric science. The water vapor content of the atmosphere is expressed in several ways:

1. Volume mixing ratio, ppm
2. Ratio of mass of water vapor to mass of dry air, g H_2O (kg dry air)$^{-1}$
3. Specific humidity – ratio of mass of water vapor to mass of total air, g H_2O (kg air)$^{-1}$
4. Mass concentration, g H_2O (m^3 air)$^{-1}$

5. Mass mixing ratio, g H_2O (g air)$^{-1}$
6. Relative humidity – ratio of partial pressure of H_2O vapor to the saturation vapor pressure of H_2O at that temperature, $p_{H_2O}/p^0_{H_2O}$

Relative humidity (RH) is usually expressed in percent:

$$\mathrm{RH} = 100\frac{p_{H_2O}}{p^0_{H_2O}} \tag{1.9}$$

Number Concentration of Water Vapor

The vapor pressure of pure water as a function of temperature can be calculated with the following correlation:

$$p^0_{H_2O}(T) = 1013.25\exp[13.3185\,a - 1.97\,a^2 - 0.6445\,a^3 - 0.1299\,a^4] \tag{1.10}$$

where

$$a = 1 - \frac{373.15}{T}$$

(An alternate correlation is given in Table 17.1.)

Let us calculate the number concentration of water vapor n_{H_2O} (molecules cm^{-3}) at RH = 50% and $T = 298$ K:

$$\begin{aligned}\mathrm{RH}\,(\text{in }\%) &= 100\frac{p_{H_2O}}{p^0_{H_2O}}\\ p_{H_2O} &= n_{H_2O}RT\end{aligned}$$

From the correlation above, at 298 K, we obtain

$$p^0_{H_2O} = 31.387\ \text{mbar}$$

Thus

$$n_{H_2O} = \frac{31.387\times 0.5\times 100\times 6.022\times 10^{23}}{8.314\times 298\times 10^{6}} = 3.81\times 10^{17}\ \text{molecules cm}^{-3}$$

Figure 1.3 shows the US Standard Atmosphere temperature profile at 45°N and that at the equator. Corresponding to each temperature profile is the vertical profile of $p^0_{H_2O}/p$, expressed as mixing ratio. Note that in the equatorial tropopause region, the saturation mixing ratio of water vapor drops to about 4–5 ppm, whereas at the surface it is several percent. Air enters the stratosphere from the troposphere, and this occurs primarily in the tropical tropopause region, where rising air in towering cumulus clouds is injected into the stratosphere. Because this region is so cold, water vapor is frozen out of the air entering the stratosphere. This process is often referred to as "freeze drying" of the atmosphere. As a result, air entering the stratosphere has a water vapor mixing ratio of only 4–5 ppm, and the stratosphere is an extremely dry region of the atmosphere.

Conversion from Mixing Ratio to μg m^{-3}

Atmospheric species mass concentrations are sometimes expressed in terms of mass per volume, most frequently as μg m^{-3}. Given a concentration m_i, in μg m^{-3}, the molar concentration of species i, in mol m^{-3}, is

$$c_i = \frac{10^{-6}\,m_i}{M_i}$$

where M_i is the molecular weight of species i.

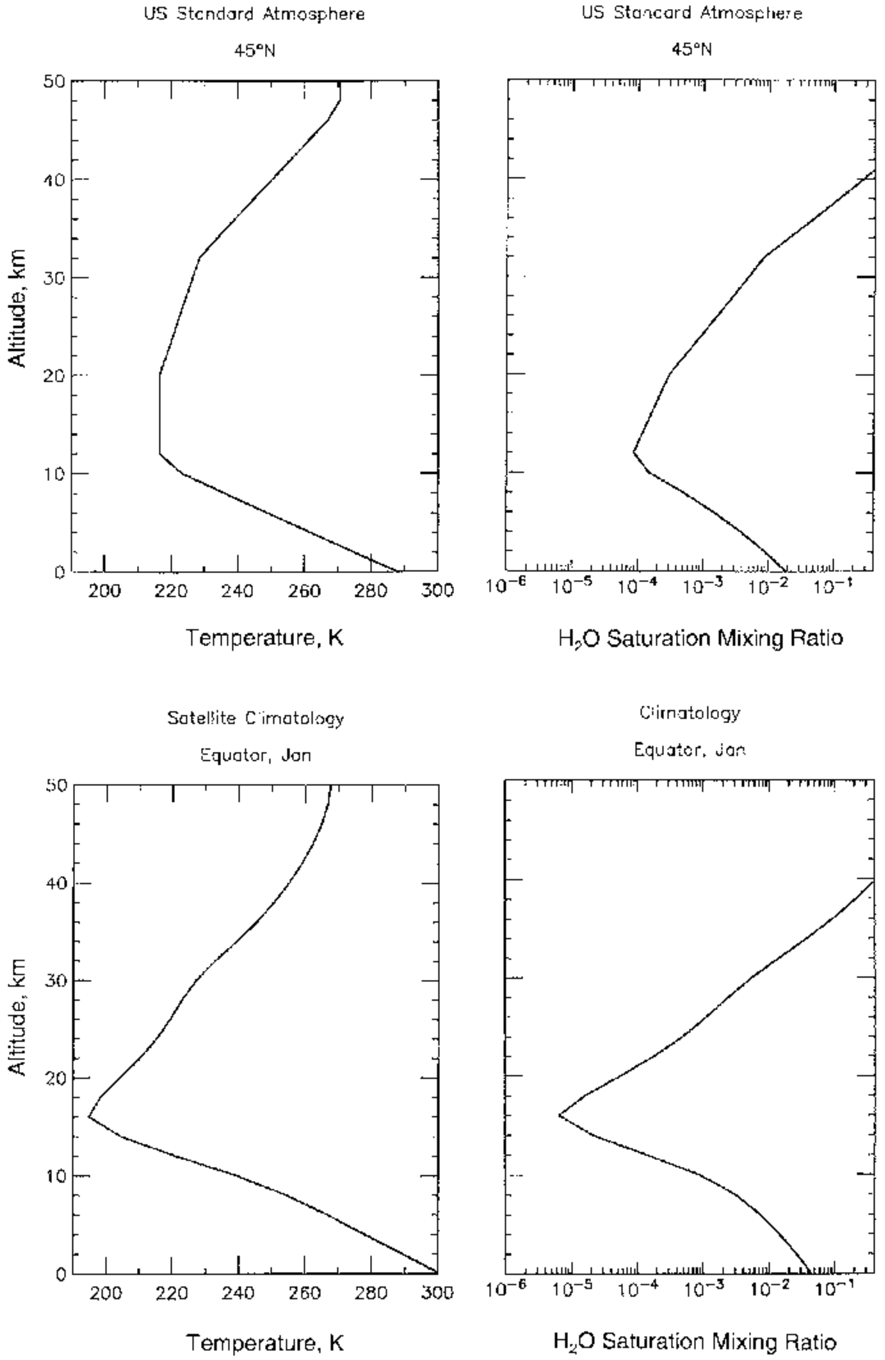

FIGURE 1.3 US Standard Atmosphere temperature and saturation water vapor mixing ratio at 45°N and at the equator.

Noting that the total molar concentration of air at pressure p and temperature T is $c = p/RT$, then

$$\text{Mixing ratio of } i \text{ in ppm} = \frac{RT}{p\,M_i} \times \text{concentration of } i \text{ in } \mu\text{g m}^{-3}$$

If T is in K and p in Pa (see Table A.6 for the value of the molar gas constant, R)

$$\boxed{\text{Mixing ratio of } i \text{ in ppm} = \frac{8.314\,T}{p\,M_i} \times \text{concentration of } i \text{ in } \mu\text{g m}^{-3}}$$

As an example, let us determine the concentration in μg m^{-3} for O_3 corresponding to a mixing ratio of 120 ppb at $p = 1$ atm and $T = 298$ K. The 120 ppb corresponds to 0.12 ppm. Then

$$\begin{aligned}\text{Concentration in } \mu\text{g m}^{-3} &= \frac{p\,M_i}{8.314\,T} \times \text{Mixing ratio in ppm}\\ &= \frac{(1.013 \times 10^5)(48)}{8.314(298)} \times 0.12\\ &= 235.6\ \mu\text{g m}^{-3}\end{aligned}$$

Now let us convert 365 μg m^{-3} of SO_2 to ppm at the same temperature and pressure:

$$\begin{aligned}\text{Mixing ratio in ppm} &= \frac{(8.314)(298)}{(1.013 \times 10^5)(64)} \times 365\\ &= 0.136\ \text{ppm}\end{aligned}$$

1.7 AIRBORNE PARTICLES

The atmosphere contains a myriad of microscopic particles. Virtually all of these are smaller than the diameter of a human hair, which can be considered to be $\sim 100 \times 10^{-6}$ m (100 μm). Diameters of airborne particles range from as small as 1×10^{-9} m (1 nm) to 10×10^{-6} m (10 μm). If we consider a single spherical 100-nm-diameter particle with mass density of 1.4 g cm^{-3} containing molecules of molecular weight 150 g mol^{-1}, then that particle will contain 2.94×10^6 molecules. The total surface area of all the particles in the atmosphere is $\sim 1 \times 10^{14}$ m^2; this is roughly equivalent to the total surface area of Earth, $\sim 1.25 \times 10^{14}$ m^2.

1.8 SPATIAL AND TEMPORAL SCALES OF ATMOSPHERIC PROCESSES

The atmosphere is a dynamic system, with its gaseous constituents continuously being exchanged with vegetation, the oceans, and biological organisms. Gases are produced by chemical processes within the atmosphere itself, by biological activity, volcanic exhalation, radioactive decay, and human industrial (anthropogenic) activities. Gases are removed from the atmosphere by chemical reactions in the atmosphere, by biological activity, by physical processes in the atmosphere (such as particle formation), and by deposition and uptake by the oceans and land. The average lifetime of a gas molecule introduced into the atmosphere can range from seconds to millions of years, depending on the effectiveness of the removal processes. Most of the species considered air pollutants (in a region in which their concentrations exceed substantially the normal background levels) have natural as well as anthropogenic sources. Therefore, in order to assess the potential effect of anthropogenic emissions on the atmosphere as a whole, it is essential to understand the atmospheric cycles of the trace gases, including natural and anthropogenic sources as well as predominant removal mechanisms.

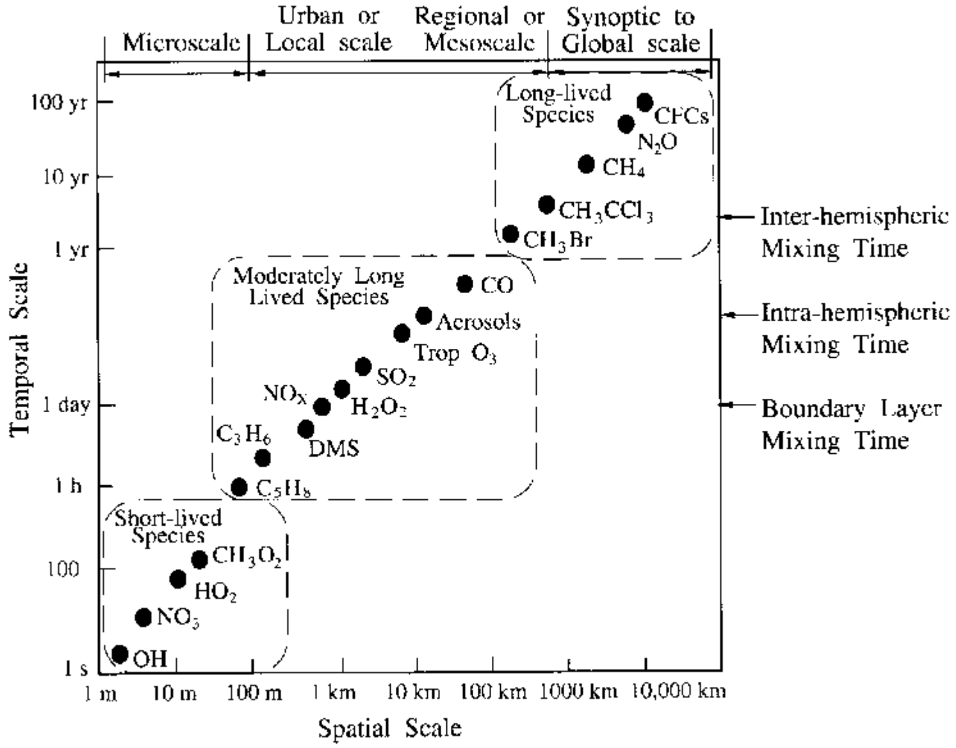

FIGURE 1.4 Spatial and temporal scales of variability for atmospheric constituents.

During transport through the atmosphere, all except the most inert substances are likely to participate in some form of chemical reaction. This process can transform a species from its original state, the physical (gas, liquid, or solid) and chemical form in which it first enters the atmosphere, to another state that may have either similar or very different characteristics. Transformation products can differ from their parent substance in their chemical properties and other characteristics. These products may be removed from the atmosphere in a manner very different from that for their precursors. For example, when a substance that was originally emitted as a gas is transformed into a particle, the overall removal is usually hastened since particles often tend to be removed from the air more rapidly than gases.

Since the atmosphere is an oxidizing medium, species, once emitted, are generally converted into substances characterized by higher chemical oxidation states than their parent substances. Frequently this oxidative transformation is accompanied by an increase in polarity (and hence water solubility) and a decrease in volatility. An example is the conversion of sulfur dioxide (SO_2) into sulfuric acid (H_2SO_4). Sulfur dioxide is moderately water-soluble, but its oxidation product, sulfuric acid, is so water-soluble that even single molecules of sulfuric acid in air immediately become associated with water molecules.

The atmosphere can be likened to an enormous chemical reactor in which a myriad of species are continually being introduced and removed over a vast array of spatial and temporal scales. The atmosphere itself presents a range of spatial scales that spans eight orders of magnitude (Figure 1.4), varying from tiny eddies of a centimeter or less in size to huge airmasses of continental dimensions. Four rough categories have proved convenient to classify atmospheric scales of motion:

1. *Microscale.* Phenomena occurring on scales of the order of 0–100 m, such as the meandering and dispersion of a chimney plume and the complicated flow regime in the wake of a large building.
2. *Mesoscale.* Phenomena occurring on scales of tens to hundreds of kilometers, such as land–sea breezes, mountain–valley winds, and migratory high- and low-pressure fronts.

TABLE 1.1 Spatial Scales of Atmospheric Chemical Phenomena

Phenomenon	Length scale (km)
Urban air pollution	1–100
Regional air pollution	10–1000
Acid rain/deposition	100–2000
Toxic air pollutants	0.1–100
Stratospheric ozone depletion	1000–40,000
Greenhouse gas increases	1000–40,000
Aerosol–climate interactions	100–40,000
Tropospheric transport and oxidation processes	1–40,000
Stratospheric–tropospheric exchange	0.1–100
Stratospheric transport and oxidation processes	1–40,000

3. *Synoptic Scale.* Motions of whole weather systems, on scales of hundreds to thousands of kilometers.
4. *Global Scale.* Phenomena occurring on scales exceeding 5×10^3 km.

Spatial scales characteristic of various atmospheric chemical phenomena are given in Table 1.1. The spatial scales of the various atmospheric chemical phenomena result from an intricate coupling between the chemical lifetimes of the principal species involved and the atmosphere's scales of motion. The *lifetime* of a species is defined as the average time that a molecule of that species resides in the atmosphere before removal (chemical transformation to another species counts as removal). Atmospheric lifetimes vary from less than a second for the most reactive free radicals to many years for the most stable molecules. Associated with each lifetime is a characteristic spatial transport scale; species with very short lifetimes have comparably small characteristic spatial scales while those with lifetimes of years have a characteristic spatial scale equal to that of the entire atmosphere. With a lifetime of less than 0.01 s, the hydroxyl radical (OH) has a spatial transport scale of only about 1 cm. Methane (CH_4), on the other hand, with its lifetime of about 10 years, becomes more or less uniformly mixed over the entire Earth.

Units of Atmospheric Emission Rates and Fluxes

Fluxes of species into the atmosphere are usually expressed on an annual basis, using the prefixes given in Table A.5. A common unit used is teragrams per year, $\mathrm{Tg\,yr^{-1}}$ ($1\,\mathrm{Tg} = 10^{12}\,\mathrm{g}$). An alternative is to employ the *metric ton* ($1\,\mathrm{t} = 10^6\,\mathrm{g} = 10^3\,\mathrm{kg}$). Carbon dioxide fluxes are often expressed as multiples of gigatons, Gt ($1\,\mathrm{Gt} = 10^9\,\mathrm{t} = 10^{15}\,\mathrm{g} = 1\,\mathrm{Pg}$).

PROBLEMS

1.1_A Calculate the concentration (in molecules $\mathrm{cm^{-3}}$) and the mixing ratio (in ppm) of water vapor at ground level at $T = 298\,\mathrm{K}$ at RH values of 50%, 60%, 70%, 80%, 90%, 95%, and 99%.

1.2_A Determine the concentration (in $\mu\mathrm{g\,m^{-3}}$) for N_2O at a mixing ratio of 311 ppb at $p = 1$ atm and $T = 298\,\mathrm{K}$.

1.3_A A typical global concentration of hydroxyl (OH) radicals is about 10^6 molecules $\mathrm{cm^{-3}}$. What is the mixing ratio corresponding to this concentration at sea level and 298 K?

1.4_A Measurements of dimethyl sulfide (CH_3SCH_3) during the Aerosol Characterization Experiment-1 (ACE-1) conducted November–December 1995 off Tasmania were in the range of 250–500 $\mathrm{ng\,m^{-3}}$. Convert these values to mixing ratios in ppt at 298 K at sea level.

1.5$_A$ Your car consumes 500 gallons (gal) of gasoline per year (1 gal = 3.7879 L). Assume that gasoline can be represented as consisting entirely of C_8H_{18}. Gasoline has a density of 0.85 g cm^{-3}. Assume that combustion of C_8H_{18} leads to CO_2 and H_2O. How many kilograms of CO_2 does your driving contribute to the atmosphere each year? (Problem suggested by T. S. Dibble.)

1.6$_A$ Show that 1 ppm CO_2 in the atmosphere corresponds to 2.1 Pg carbon and therefore that the current atmospheric level of 400 ppm corresponds to 841 Pg C.

1.7$_A$ **a.** Determine the scale heights for the atmospheres of Venus and Mars. The table below gives the relevant information for the two planets:

Planet	T_s (K)	g (m s^{-2})	M_{air} (g mol^{-1})	Composition
Venus	737	8.9	43.44	0.965 CO_2, 0.035 N_2
Mars	210	3.7	43.33	0.953 CO_2, 0.027 N_2, 0.016 Ar

Source: NASA Planetary Fact Sheet.

b. Why is the scale height of Mars greater than the scale height of Earth, even though Mars is colder than Earth?

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