

ATMOSPHERIC CHEMISTRY AND PHYSICS

From Air Pollution to Climate Change

Third Edition

JOHN H. SEINFELD
SPYROS N. PANDIS

WILEY

A satellite image of Earth showing atmospheric circulation patterns. The image is a grayscale or high-contrast color image of the Earth's atmosphere, showing swirling cloud patterns and wind vectors. The Americas are visible on the right side of the frame, with the Atlantic Ocean to the left. The overall image is used as a background for the book cover.

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To
Benjamin and Elizabeth
and
Angeliki and Nikos

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Preface to the First Edition

The study of atmospheric chemistry as a scientific discipline goes back to the eighteenth century, when the principal issue was identifying the major chemical components of the atmosphere, nitrogen, oxygen, water, carbon dioxide, and the noble gases. In the late nineteenth and early twentieth centuries attention turned to the so-called trace gases, species present at less than 1 part per million parts of air by volume (1 μmol per mole). We now know that the atmosphere contains a myriad of trace species, some at levels as low as 1 part per trillion parts of air. The role of trace species is disproportionate to their atmospheric abundance; they are responsible for phenomena ranging from urban photochemical smog, to acid deposition, to stratospheric ozone depletion, to potential climate change. Moreover, the composition of the atmosphere is changing; analysis of air trapped in ice cores reveals a record of striking increases in the longlived so-called greenhouse gases, carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Within the last century, concentrations of tropospheric ozone (O_3), sulfate (SO_4^{2-}), and carbonaceous aerosols in the Northern Hemisphere have increased significantly. There is evidence that all these changes are altering the basic chemistry of the atmosphere.

Atmospheric chemistry occurs within a fabric of profoundly complicated atmospheric dynamics. The results of this coupling of dynamics and chemistry are often unexpected. Witness the unique combination of dynamical forces that lead to a wintertime polar vortex over Antarctica, with the concomitant formation of polar stratospheric clouds that serve as sites for heterogeneous chemical reactions involving chlorine compounds resulting from anthropogenic chlorofluorocarbons—all leading to the near total depletion of stratospheric ozone over the South Pole each spring; witness the nonlinear, and counterintuitive, dependence of the amount of ozone generated by reactions involving hydrocarbons and oxides of nitrogen (NO_x) at the urban and regional scales—although both hydrocarbons and NO_x are ozone precursors, situations exist where continuous emission of more and more NO_x actually leads to less ozone.

The chemical constituents of the atmosphere do not go through their lifecycles independently; the cycles of the various species are linked together in a complex way. Thus a perturbation of one component can lead to significant, and nonlinear, changes to other components and to feedbacks that can amplify or damp the original perturbation.

In many respects, at once both the most important and the most paradoxical trace gas in the atmosphere is ozone (O_3). High in the stratosphere, ozone screens living organisms from biologically harmful solar ultraviolet radiation; ozone at the surface, in the troposphere, can produce adverse effects on human health and plants when present at levels elevated above natural. At the urban and regional scales, significant policy issues concern how to decrease ozone levels by controlling the ozone precursors—volatile organic compounds and oxides of nitrogen. At the global scale, understanding both the natural ozone chemistry of the troposphere and the causes of continually increasing background tropospheric ozone levels is a major goal.

Aerosols are particles suspended in the atmosphere. They arise directly from emissions of particles and from the conversion of volatile organic compounds to particles in the atmosphere. At elevated levels they inhibit visibility and are a human health hazard. There is a growing body of epidemiological data suggesting that increasing levels of aerosols may cause a significant increase in human mortality. For many years it was assumed that atmospheric aerosols did not interact in any appreciable way with the cycles of trace gases. We now know that particles in the air affect climate and interact chemically in heretofore unrecognized ways with atmospheric gases. Volcanic aerosols in the stratosphere, for example, participate in the catalytic destruction of ozone by chlorine compounds, not directly, but

through the intermediary of NO_x chemistry. Aerosols reflect solar radiation back to space and, in so doing, cool the planet Earth. Aerosols are also the nuclei around which clouds droplets form—no aerosols, no clouds. Clouds are one of the most important elements of our climate system, so the effect of increasing global aerosol levels on Earth's cloudiness is a key problem in climate.

Historically the study of urban air pollution and its effects occurred more or less separately from that of the chemistry of Earth's atmosphere as a whole. Similarly, in its early stages, climate research focused exclusively on CO_2 , without reference to effects on the underlying chemistry of the atmosphere and their feedbacks on climate itself. It is now recognized, in quantitative scientific terms, that Earth's atmosphere is a continuum of spatial scales in which the urban atmosphere, the remote troposphere, the marine boundary layer, and the stratosphere are merely points from the smallest turbulent eddies and the fastest timescales of free-radical chemistry to global circulations and the decadal timescales of the longest-lived trace gases.

The object of this book is to provide a rigorous, comprehensive treatment of the chemistry of the atmosphere, including the formation, growth, dynamics, and properties of aerosols; the meteorology of air pollution; the transport, diffusion, and removal of species in the atmosphere; the formation and chemistry of clouds; the interaction of atmospheric chemistry and climate; the radiative and climatic effects of gases and particles; and the formulation of mathematical chemical/transport models of the atmosphere. Each of these elements is covered in detail in the present volume. In each area the central results are developed from first principles. In this way, the reader will gain a significant understanding of the science underlying the description of atmospheric processes and will be able to extend theories and results beyond those for which we have space here.

The book assumes that the reader has completed introductory courses in thermodynamics, transport phenomena (fluid mechanics and heat and mass transfer), and engineering mathematics (differential equations). Thus the treatment is aimed at the senior or first-year graduate level in typical engineering curricula as well as in meteorology and atmospheric science programs.

The book is intended to serve as a textbook for a course in atmospheric science that might vary in length from one quarter or semester to a full academic year. Aside from its use as a course textbook, the book will serve as a comprehensive reference book for professionals as well as for those from traditional engineering and science disciplines. Two types of appendixes are given: those of a general nature appear at the end of the book and are designated by letters; those of a nature specific to a certain chapter appear with that chapter and are numbered according to the associated chapter.

Numerous problems are provided to enable readers to evaluate their understanding of the material. In many cases the problems have been chosen to extend the results given in the chapter to new situations. The problems are coded with a "degree of difficulty" for the benefit of the student and the instructor. The subscript designation "A" (e.g., 1.1_A in the "Problems" section of Chapter 1) indicates a problem that involves a straightforward application of material in the text. Those problems denoted "B" require some extension of the ideas in the text. Problems designated "C" encourage the reader to apply concepts from the book to current problems in atmospheric science and go somewhat beyond the level of "B" problems. Finally, those problems denoted "D" are of a degree of difficulty corresponding to "C" but generally require development of a computer program for their solution.

JOHN H. SEINFELD
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Preface to the Third Edition

The Third Edition contains a number of significant changes since the Second Edition. The treatment of tropospheric chemistry (Chapter 6) has been expanded and updated. A major section on the atmospheric chemistry of biogenic hydrocarbons has been added, including a detailed treatment of isoprene chemistry. Sections on amine chemistry and the atmospheric chemistry of mercury have been added. An expanded and updated treatment of atmospheric new-particle formation (nucleation) has been added to Chapter 11. Chapter 14, "Atmospheric Organic Aerosols," has been completely rewritten, reflecting the major advances in our understanding of how organic aerosols form and evolve that have emerged since the publication of the Second Edition. This includes new understanding of the nature of primary organic aerosols, of particle-phase chemistry, and of secondary organic aerosol formation in the aqueous phase. This Third Edition contains a major expansion of physical and dynamic meteorology (Chapter 16), including a rigorous, self-contained treatment of atmospheric temperature profiles, atmospheric stability, and moist atmospheric thermodynamics. Treatment of the global carbon cycle (Chapter 22) has been updated and expanded. Chapter 23, "Global Climate," is an entirely new chapter with a self-contained comprehensive treatment of radiative forcing of climate by greenhouse gases, solar output changes, and a development of Earth's climate sensitivity and climate feedbacks, including water vapor, clouds, and atmospheric lapse rate. A significantly expanded and updated treatment of aerosol-cloud relationships in climate has been added to Chapter 24, "Aerosols and Climate." Using stratocumulus clouds as the basis, the theory of the effect of aerosol perturbations on cloud properties is developed and illustrated. More examples, offset by vertical bars, have been added to the chapters to illustrate the concepts and show numerical calculations. Chapter 26 includes a new, self-contained treatment of positive matrix factorization, a widely used statistical method for analysis of aerosol data. New problems have been added in many of the chapters. A revised *Problem Solution Manual* is available for instructors.

In order to help the reader navigate the major areas covered in the book, the chapters in this edition are grouped according to major themes:

Part I: The Atmosphere and its Constituents

Chapters 1 and 2

Part II: Atmospheric Chemistry

Chapters 3–7

Part III: Aerosols

Chapters 8–15

Part IV: Physical and Dynamic Meteorology, Cloud Physics, and Atmospheric Diffusion

Chapters 16–18

Part V: Dry and Wet Deposition

Chapters 19 and 20

Part VI: The Global Atmosphere, Biogeochemical Cycles, and Climate

Chapters 21–24

Part VII: Chemical Transport Models and Statistical Models

Chapters 25 and 26

As in the First and Second Editions, many colleagues have provided important inputs. We want to especially acknowledge Kelvin Bates, Yi-Chun Chen, Neil Donahue, Christos Fountoukis, Daniel Jacob, Jesse Kroll, Mark Lawrence, Renee McVay, Sally Ng, Tran Nguyen, Allen Robinson, Rebecca Schwantes, Manabu Shiraiwa, Rainer Volkamer, Paul Wennberg, Xuan Zhang, and Andreas Zuend.

Finally, we are indebted to Martha Hepworth and Yvette Grant for skillful preparation of the manuscript for the Third Edition.

JOHN H. SEINFELD
SPYROS N. PANDIS

PART I

***The Atmosphere and
Its Constituents***

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 (CO₂), nitrogen (N₂), and water vapor (H₂O), with trace amounts of hydrogen (H₂), 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 CO₂ that outgassed formed sedimentary carbonate rocks after dissolution in the ocean. It is estimated that for each molecule of CO₂ presently in the atmosphere, there are about 10⁵ CO₂ molecules incorporated as carbonates in sedimentary rocks. Since N₂ is chemically inert, non-water-soluble, and noncondensable, most of the outgassed N₂ 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 O₂ rise is now well established, what triggered the increase is still in question. There is agreement that O₂ was initially produced by cyanobacteria, the only prokaryotic organisms (*bacteria* and *archaea*) 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 O₂ is still an issue of debate. The atmosphere from 3000 to 2300 million years ago was rich in reduced gases such as H₂ and CH₄. Hydrogen can escape to space from such an atmosphere. Since the majority of Earth's hydrogen was in the form of water, H₂ escape would lead to a net accumulation of O₂. One possibility is that the O₂ left behind by the escaping H₂ was largely consumed by oxidation of continental crust. This oxidation might have sequestered enough O₂ 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 O₂ is maintained by a balance between production from photosynthesis and removal through respiration and decay of organic carbon (Walker 1977).

Earth's atmosphere is composed primarily of the gases N₂ (78%), O₂ (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, N₂, O₂, water vapor, CO₂, 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 CO₂ and CH₄, 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 CO₂ and CH₄, polar ice core samples reveal global average concentrations of previous eras. Analyses of bubbles in ice cores show that CO₂ and CH₄ 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 CO₂, CH₄, and N₂O 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 SO₂, 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 N₂, 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.

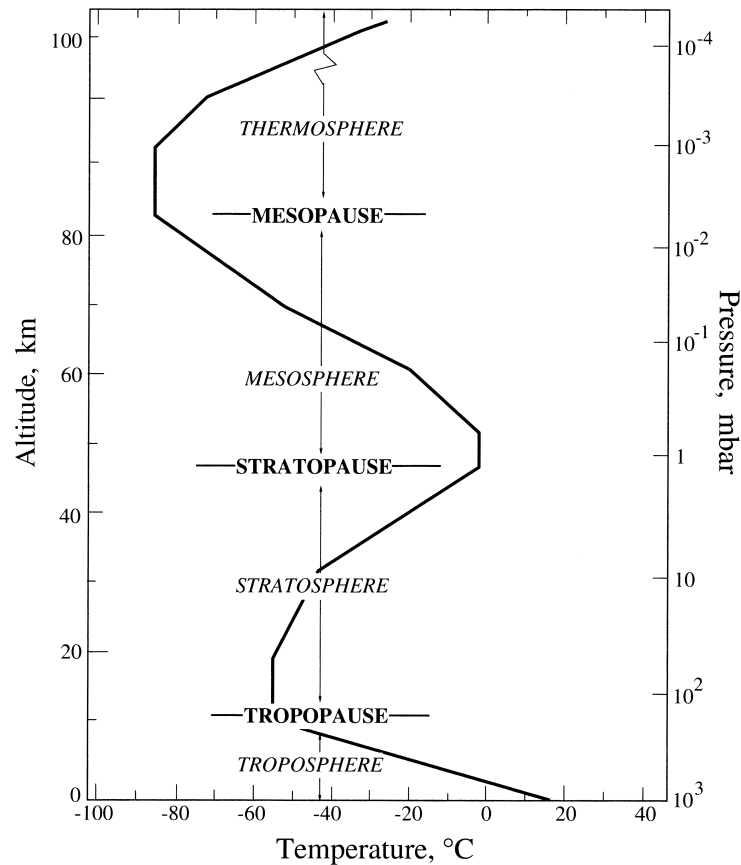


FIGURE 1.1 Layers of the atmosphere.

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 $\leq 2 \text{ K km}^{-1}$ (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 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 (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:

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

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

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 $dz \rightarrow 0$ produce

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

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

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

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

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

which we can rewrite as

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

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

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

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 $H = 7.4 \text{ km}$.

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 ($6.022 \times 10^{23} \text{ molecules mol}^{-1}$) and p_0 is the standard atmospheric pressure ($1.013 \times 10^5 \text{ Pa}$). 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:

z (km)	n_{air} (molecules cm^{-3})	
	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}

^aSee Table A.8.

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

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

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

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