CHAPTER

1

Overview of the Chemistry of Polluted and Remote Atmospheres

Atmospheric chemistry is an exciting, relatively new field. It encompasses the chemistry of the globe, from polluted to "clean," remote regions and from the region closest to the earth's surface, the *troposphere* ($\lesssim$ 10–15 km), through the *tropopause* ($\sim$ 10–15 km) into the upper atmosphere—which, for the purposes of this book, we restrict to the *stratosphere* ($\sim$ 10–50 km). Chemical and physical processes occurring at the earth's surface—emissions, transport, lifetimes, and fates of certain anthropogenic and biogenic/geogenic chemicals—can impact the stratosphere—and vice versa. Thus, even though in some early studies the tropopause was perceived as being a "barrier" between the lower and upper atmospheres, it has become increasingly clear that the troposphere and stratosphere are intimately connected. Witness the vertical transport of long-lived ozone-destroying anthropogenic emissions of chlorofluorocarbons (CFCs) and conversely the downward transport of stratospheric ozone into the troposphere. Hence, even though we devote separate chapters to the chemistry of the troposphere and stratosphere, the emphasis throughout is on *one integrated "system" of global atmospheric chemistry*.

In this regard, there are several topics that fall outside the scope of this book, including the evolution of the earth's atmosphere. For reviews, the reader is referred to articles by Kasting (1993) and Allègre and Schneider (1994). Although we point out throughout this book the interconnectedness of the lower and upper atmospheres, practicality and length preclude extension to the obvious interrelationships and feedbacks with other components of the earth system, including the controversial *Gaia Hypothesis* (named after the Greek goddess of the earth). The reader is referred to articles by Lovelock (1989), Kirchner (1989), Schneider (1990), and Lenton (1998) for discussions of the latter.

Although atmospheric chemistry is sometimes viewed as an "applied" science, its foundations rest on *fundamental* research in diverse areas of chemistry. These include theoretical and experimental aspects of spectroscopy, photochemistry, and the kinetics and mechanisms of homogeneous and heterogeneous organic and inorganic reactions. We believe it is useful for today's students, researchers, and educators to be aware that major resources for Leighton's masterful 1961 treatment of the newly emerging field of atmospheric chemistry, *Photochemistry of Air Pollution*, were, in fact, pioneering, basic research monographs published years earlier. They include *Photochemistry of Gases* by W. A. Noyes, Jr., and P. A. Leighton (1939), two editions of *Atomic and Free Radical Reactions* by E. W. R. Steacie (1946, 1954), and G. Herzberg's classics *Atomic Spectra and Atomic Structure* (1944); *Molecular Spectra and Molecular Structure I*: *Spectra of Diatomic Molecules* (1950); and *Infrared and Raman Spectra of Polyatomic Molecules* (1945).

Throughout the body of this book, we address the basic chemistry driving key atmospheric processes in the natural and polluted troposphere and stratosphere and illustrate their critical interactions on local, regional, and global scales. In so doing, our treatment overall reflects the message that Sam sings so eloquently to Bogart and Bergman in the classic movie *Casablanca*, . . . "The fundamental things apply, as time goes by."

In this chapter we provide an overview of the chemistry of the lower and upper atmospheres. In Chapter 2, we illustrate how this chemistry plays a critical role in the concept of an *integrated* "atmospheric chemistry system"—a loop that starts with emissions (anthropogenic and natural) and ultimately closes with scientific health and environmental risk assessments and associated risk management decisions for the control of air pollutants.

Chapters 3–12 present a detailed examination and explanation of how one applies the theoretical and experimental *fundamentals* of photochemistry, spectroscopy, and kinetics and mechanisms (structure and reactivity) to the most important homogeneous and heterogeneous processes that take place in our natural and polluted atmosphere.

We conclude by illustrating how our understanding of these chemical processes in our clean and polluted troposphere and stratosphere plays a crucial role in generating the "*exposure*" portions of scientific health risk assessments. Such assessments provide the foundation for sound, health-protective and cost-effective strategies for the control of tropospheric ozone, particles, acids, and a spectrum of "hazardous air pollutants" (including carcinogens and pesticides)—as well as for the mitigation of stratospheric ozone depletion.

A. REGIONS AND CHARACTERISTICS OF THE ATMOSPHERE

Figure 1.1 shows the different regions of the atmosphere. (See also Appendix V for typical pressures and temperatures as a function of altitude.) In the troposphere, the temperature generally falls with increasing altitude (except in the presence of inversions; see Chapter 2.B.3). This is due to the strong heating effect at the surface from the absorption of radiation. Because hot air rises, this causes strong vertical mixing so that species emitted at the earth's surface can rise to the *tropopause*, the region separating the troposphere from the stratosphere, in a few days or less, depending on the meteorological conditions. Essentially all of the water vapor, clouds, and precipitation are found in the troposphere, which provides an important mechanism for scavenging pollutants from the atmosphere.

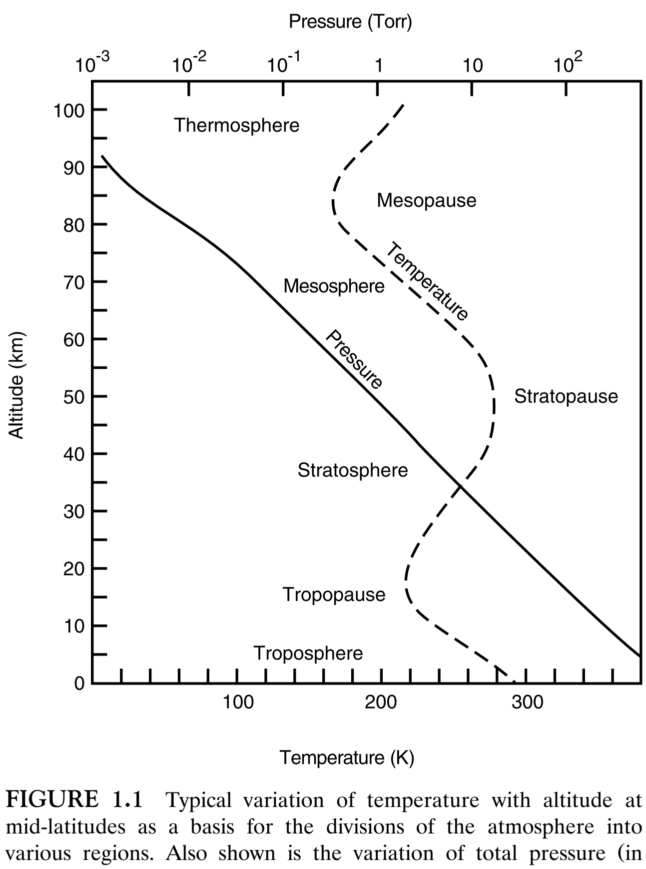

FIGURE 1.1 Typical variation of temperature with altitude at mid-latitudes as a basis for the divisions of the atmosphere into various regions. Also shown is the variation of total pressure (in Torr) with altitude (top scale, base 10 logarithms) where 1 standard atmosphere = 760 Torr.

However, at the tropopause the temperature profile changes, increasing with altitude throughout the stratosphere. The reason for this increase is a critical series of photochemical reactions involving ozone and molecular oxygen. The "Chapman cycle," reactions (1)–(4), hypothesized in the 1930's by Sir Sydney Chapman,

$$O_2 + h\nu \rightarrow 2O, \tag{1}$$

$$O + O_2 \xrightarrow{M} O_3, \tag{2}$$

$$O + O_3 \rightarrow 2O_2, \tag{3}$$

$$O_3 + h\nu \rightarrow O + O_2, \tag{4}$$

is responsible for generating a steady-state concentration of O_3 in the stratosphere.

Stratospheric ozone is essential for life on earth as we know it, because it strongly absorbs light of $\lambda < 290$ nm. As a result, sunlight reaching the troposphere, commonly referred to as *actinic radiation*, has wavelengths longer than 290 nm. This short-wavelength cutoff sets limits on tropospheric photochemistry; thus only those molecules that absorb radiation at wavelengths longer than 290 nm can undergo photodissociation and other primary photochemical processes.

Ozone absorbs light strongly between approximately 200 and 310 nm and weakly up into the visible. Dissociation to electronically excited O_2 $(^1\Delta_g)$ and $O(^1D)$ requires light energetically equivalent to 310 nm. Therefore, the excess energy available after absorption of light up to this threshold value is released as heat; energy is also released from the $O + O_2$ reaction (2). Both give rise to the increase in temperature in the stratosphere. Relatively little vertical mixing occurs in the stratosphere, and no precipitation scavenging occurs in this region. As a result, massive injections of particles, for example, from volcanic eruptions such as the Mt. Pinatubo eruption, often produce layers of particles in the stratosphere that persist for long periods of time (see Chapter 12).

In the *mesosphere*, from ~ 50 to ~ 85 km, the temperature again falls with altitude and vertical mixing within the region occurs. This temperature trend is due to the decrease in the O_3 concentration with altitude. At about 85 km the temperature starts to rise again because of increased absorption of solar radiation of wavelengths < 200 nm by O_2 and N_2 as well as by atomic species. This region is known as the *thermosphere*.

The transition zones between the various regions of the atmosphere are known as the *tropopause*, *stratopause*, and *mesopause*, respectively. Their locations, of course, are not fixed, but vary with latitude, season, and year. Thus Fig. 1.1 represents an average profile for mid-latitudes. Specific temperatures, pressures, densities, winds, and the concentrations of some atmospheric constituents as a function of altitude, geographic position, and time are incorporated into a NASA model, the *G*lobal *R*eference *A*tmosphere *M*odel (GRAM); information on obtaining this model and data is included in Appendix IV.

We shall see throughout this book that different chemical and physical processes occur in the troposphere and stratosphere, and we shall frequently refer to different regions in Fig. 1.1. However, it is important to put the atmosphere in perspective with respect to the size of the earth itself. The earth's average diameter is 12,742 km, yet the average distance from the earth's surface to the top of the stratosphere is only ~ 50 km, less than 0.4% of the earth's diameter! The space shuttle orbits outside the atmosphere, but at an altitude of only several hundred miles, which is less than the distance from Los Angeles to San Francisco. Clearly, the atmosphere is a very thin, and as we shall see, fragile shield upon which life as we know it on earth depends.

B. AIR POLLUTION AND THE CHEMISTRY OF OUR TROPOSPHERE

1. Historical Perspectives: Ancient and Medieval Times

Concern over air pollution has been well documented (Brimblecombe, 1978). The impacts of atmospheric chemistry on human health and the environment can be traced back many centuries, indeed some two thousand years. For example, the Mishnah Laws in Israel in the first and second centuries A.D. required that, because of the odors emitted, tanneries be located at least 30 m away from the town and only on the east side, due to prevailing westerly winds (Mamane, 1987).

In the twelfth century, the Hebrew philosopher, scientist, and jurist Moses Maimonides (1135–1204) wrote (Goodhill, 1971)

> "Comparing the air of cities to the air of deserts and arid lands is like comparing waters that are befouled and turbid to waters that are fine and pure. In the city, because of the height of its buildings, the narrowness of its streets, and all that pours forth from its inhabitants and their superfluities . . . the air becomes stagnant, turbid, thick, misty, and foggy . . . . If there is no choice in this matter, for we have grown up in the cities and have become accustomed to them, you should . . . select from the cities one of open horizons . . . endeavor at least to dwell at the outskirts of the city . . . .

> "If the air is altered ever so slightly, the state of the Psychic Spirit will be altered perceptibly. Therefore you find many men in whom you can notice defects in the actions of the psyche with the spoilage of the air, namely, that they develop dullness of understanding, failure of intelligence and defect of memory . . . ."

To this day, many of us can relate to his view of the health and psychological impacts of heavy smog episodes—whether they be of the London or Los Angeles variety.

2. "London" Smog: Sulfur Dioxide, Acidic Aerosols, and Soot

In the seventeenth century, John Evelyn published a major treatise on air pollution in London, caused by the widespread domestic use of high-sulfur coal. In it, he noted effects not only on materials:

> "It is this horrid Smoake which obscures our Church and makes our Palaces look old, which fouls our Cloth and corrupts the Waters, so as the very Rain, and refreshing Dews which fall in the several Seasons, precipitate to impure vapour, which, with its black and tenacious quality, spots and contaminates whatever is exposed to it."

but also on health:

> "But, without the use of Calculations it is evident to every one who looks on the yearly Bill of Mortality, that near half the children that are born and bred in London die under two years of age.[a] Some have attributed this amazing destruction to luxury and the abuse of Spirituous Liquors: These, no doubt, are powerful assistants; but the constant and unremitting Poison is communicated by the foul Air, which, as the Town still grows larger, has made regular and steady advances in its fatal influence."

> [a]"A child born in a Country Village has an even chance of living near 40 years . . . "

Evelyn's air pollution classic, and an article by Barr, *The Doom of London*, are reprinted in the book *The Smoake of London. Two Prophecies* (Lodge, 1969). They make interesting and useful reading and help place our present problems in perspective.