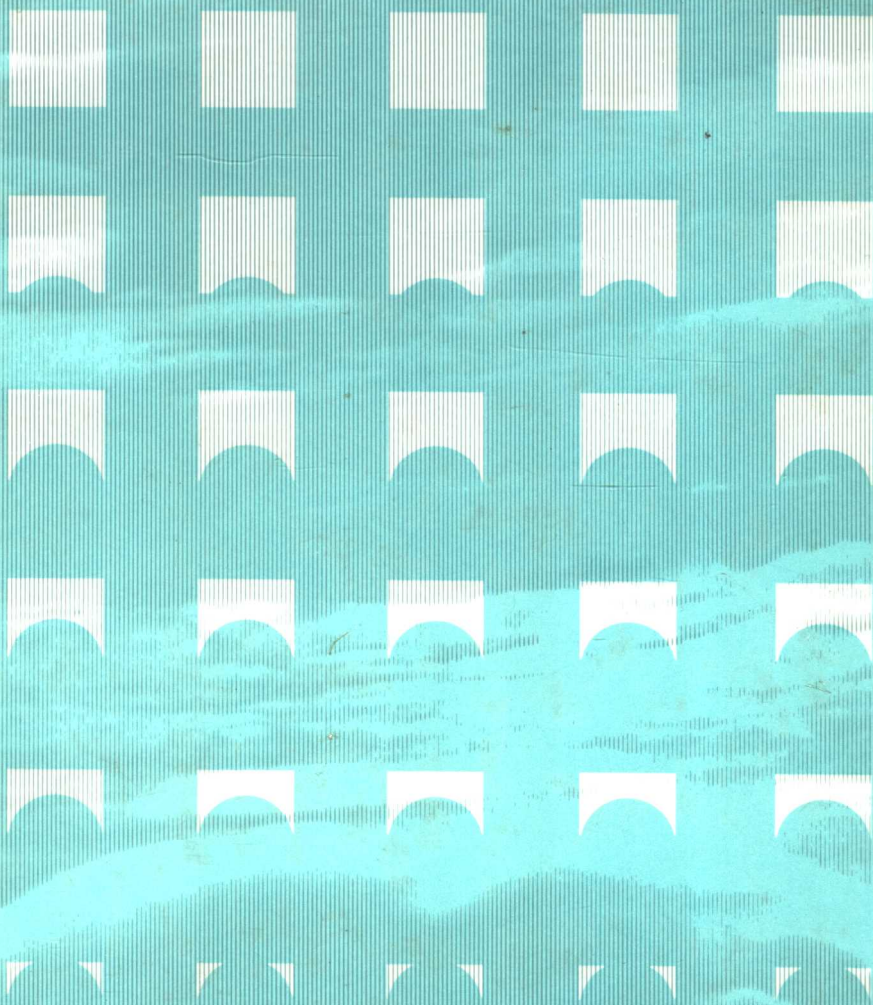


AIR QUALITY

SECOND EDITION



THAD GODISH



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PREFACE

The first edition of *Air Quality* was written to provide readers with a comprehensive overview of the air pollution problem and the practices involved in its control. It attempted to fill the need for thoroughness and readability (features that were missing from earlier air pollution texts and other treatises on the subject) while limiting the amount of quantitative information that characterized air pollution texts from that earlier period.

With any first effort, one inevitably finds errors in the finished product that were missed in the editing process. We hope that such errors have been caught and corrected in this edition of *Air Quality*. Additionally, as the field continues to advance, new knowledge is published. Regulatory policies continue to evolve. Though the principles remain unchanged, only periodic updating will keep the reader in the current context of things. That is what this second edition is about.

In this edition, Chapters 2, 4, 8, and 11 have been extensively revised. In Chapters 2 and 4, the chemistry of atmospheric pollution is treated in greater detail, reflecting the author's sense that readers need a more detailed understanding of atmospheric transformations of primary pollutants for the formation of secondary pollutants such as ozone (O_3), of atmospheric scavenging mechanisms, and of stratospheric reactions involving O_3 -depleting substances.

Chapter 4 has been almost completely revised. This reflects the significant advances made recently in the understanding of such problems as stratospheric O_3 depletion and global warming and the prominence they have achieved as public policy issues. This is also the case with indoor air pollution, the subject of Chapter 11.

The focus of Chapter 8 has been changed from regulatory approaches to air pollution control to regulation and public policy issues. In the first edition, the chapter emphasized the history of and practices involved in ambient air pollution control but did not address the major public policy concerns (such as nonattainment of air quality standards, acidic deposition, toxic air pollutants, stratospheric O_3 depletion, or global warming) in any major way. This edition shifts its focus to expanded treatments of major public policy issues, which further increases the comprehensiveness of the book, as does the addition of a section to Chapter 6 (Welfare Effects) on odor pollution.

The book is still designed as a text for advanced-level undergraduates and beginning-level graduate students in programs of environmental science, environmental health, industrial hygiene, and environmental engineering. It may also be used as a supplement in engineering courses where the primary focus is on design and operating principles of control equipment.

ACKNOWLEDGMENTS

The original *Air Quality* and this edition are products of a long-ago suggestion by my colleague, Clyde Hibbs, Professor of Natural Resources. They are also products of the typing, typesetting, graphic arts, and editing skills of a number of individuals, including Connie Tyner, Dave McClure, Eva Lantz, Stacey Wilcox, my daughters Aleta and Larissa, and my wife Diana.

The preparation of this edition is a tribute to my colleagues in the field who have selected it for use in their classes and those who have used it to acquire a broader understanding of the problems of ambient and indoor air pollution. To you I extend my gratitude. I hope that the second edition will provide for your needs even better than the first. As a faculty member who uses this book in the teaching of my own course, I am grateful for the opportunity to reach beyond the walls of my classroom to the many other classrooms where this book is used and to influence the many young minds who will be our future environmental scientists, engineers, and other environmental and public health practitioners.



THAD GODISH is the Director of the Indoor Air Quality Research Laboratory and Professor of Natural Resources at Ball State University in Muncie, Indiana. He received his doctorate at the Pennsylvania State University, where he was a predoctoral PHS Air Pollution Special Fellow. He was also affiliated with the Center for Air Environment Studies at Penn State as a postdoctoral scholar.

Dr. Godish has conducted research in a variety of air pollution-related areas, including plant toxicology, particulate matter sampling and indoor air pollution. The latter serves as the focal point of his responsibilities as Director of the Indoor Air Quality Research Laboratory at Ball State. Under his direction, the Laboratory conducts major programs of research and public service activities in the area of indoor air pollution, a problem rapidly being recognized for its public health significance. Dr. Godish is nationally known for his research and public service activities associated with formaldehyde contamination of buildings. In addition, he is the author of *Indoor Air Pollution Control*, published in 1989.

He is a member of Sigma Xi, the national honorary research society, and is a Fellow of the Indiana Academy of Science. He is a member of several professional societies, including the Air & Waste Management Association, the National Environmental Health Association, the American Industrial Hygiene Association and the American Association for the Advancement of Science. He has served as Chairman of the East Central Section and the Indiana Chapter of the Air Pollution Control Association.

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The planet on which we live is immersed in an invisible sea of gases held near to the earth's surface by the force of the earth's gravitational field. These gases and condensed droplets of water vapor comprise what we call our atmosphere. The earth's atmosphere is unique among the planets in our solar system, because it is the atmosphere that makes life as we know it possible.

CHEMICAL COMPOSITION

The atmosphere contains a variety of gaseous substances whose concentrations vary from trace levels to the levels of molecular nitrogen (N_2), which comprises 78% of the atmosphere's mass. The gaseous composition of the atmosphere can be described in terms of those constituents that remain constant over many millenia (Table 1.1) and those that vary (Table 1.2) within the time course of human experience.

Gases whose concentrations remain constant include nitrogen (N_2), oxygen (O_2), argon, neon, helium, krypton, hydrogen (H_2), and xenon. Nitrogen is the single most abundant gas in the atmosphere. Though abundant, N_2 has little direct significance relative to major atmospheric processes or to the nur-

Table 1.1 Atmospheric Constituents—Constant Concentrations¹

Constituent	Chemical Formula	Concentration (ppm)
Nitrogen	N_2	780,840.00
Oxygen	O_2	209,460.00
Argon	Ar	9,340.00
Neon	Ne	18.18
Helium	He	5.24
Krypton	Kr	1.14
Hydrogen	H_2	0.50
Xenon	Xe	0.09

turing of life forms. Gaseous N_2 , however, serves as a precursor for the formation of nitrate nitrogen (NO_3^-), which is required by plants to make the nitrogen-containing molecules (including proteins, nucleic acids, and chlorophyll) that are essential, directly or indirectly, to all living things. Life forms depend on a complex of biological and chemical processes (the nitrogen cycle) that convert N_2 to NO_3^- .

By means of biological and atmospheric processes, N_2 can react with O_2 , the second most abundant non-varying gas in the atmosphere, to produce substances known as nitrogen oxides (NO_x), which include nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O). These NO_x compounds, formed by oxidation of N_2 , are found in the atmosphere in trace levels (Table 1.2), and unlike their precursors (N_2 and O_2) they appear to vary with time. This is particularly the case for both NO and NO_2 . Until quite recently, N_2O was considered to exist in the atmosphere in constant concentrations. Changes have occurred as a consequence of the increasing use of chemically synthesized nitrogen fertilizers, which are denitrified by bacteria to produce N_2 and/or N_2O .

Molecular oxygen in the atmosphere comprises almost 21% of the atmosphere's mass. Its availability in sufficient concentrations has provided the opportunity for the evolution of oxidative metabolism, the series of energy-transferring biochemical reactions that sustain all higher life forms. Oxygen is, as a consequence, vital to almost all living things. Oxygen is also significant because its evolving presence in the atmosphere over billions of years has provided the precursor molecules for the formation of the stratospheric ozone layer, which protects organic molecules and living things from the destroying power of high-energy ultraviolet light that is incident on the earth's atmosphere. Ozone (O_3) concentrations at the earth's surface are relatively low (on the order of 0.02 ppm). But this changes dramatically with height, with maximum concentrations in the middle stratosphere (Figure 1.1).

In comparison to N_2 and O_2 , the amount of carbon dioxide (CO_2) in the atmosphere is relatively low, comprising only about 0.035% or 350 ppm.

Table 1.2 Atmospheric Constituents—Variable Concentrations¹

Constituent	Chemical Formula	Concentration (ppm)
Water vapor	H_2O	0.1–30,000.00
Carbon dioxide	CO_2	350.00
Methane	CH_4	1.67
Nitrous oxide	N_2O	0.30
Carbon monoxide	CO	0.19
Ozone	O_3	0.04
Ammonia	NH_3	0.004
Nitrogen dioxide	NO_2	0.001
Sulfur dioxide	SO_2	0.001
Nitric oxide	NO	0.0005
Hydrogen sulfide	H_2S	0.00005

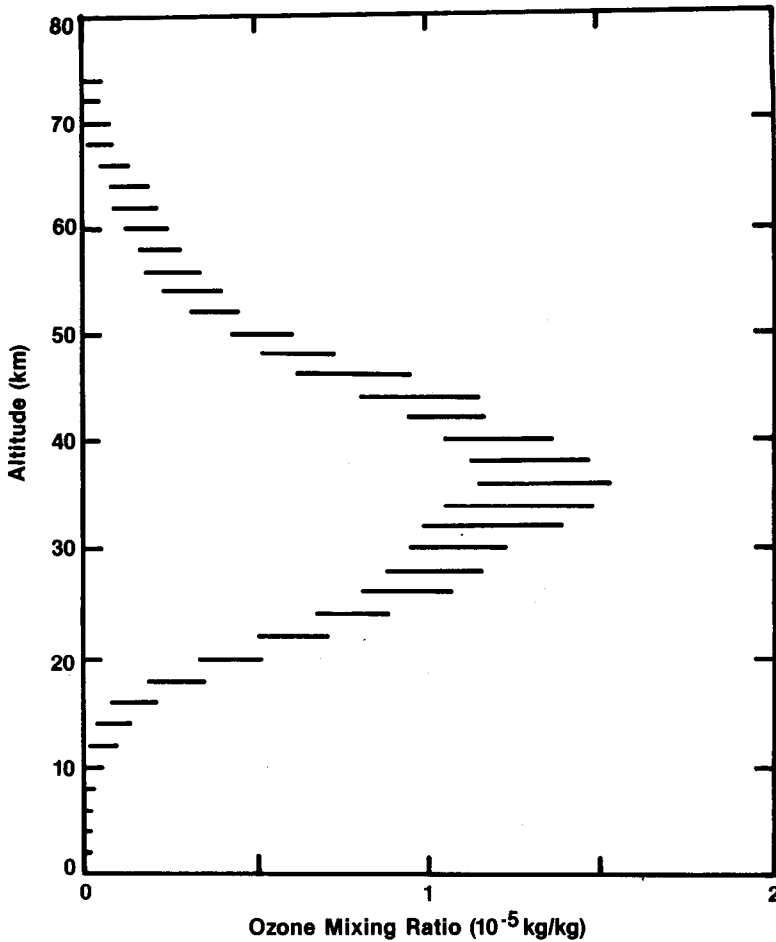


Figure 1.1 Distribution of ozone in the earth's atmosphere.¹

Despite this fact, CO_2 is of enormous importance. It is one of the two principal raw materials from which green plants in the process of photosynthesis make the food on which most living things depend. Life is carbon-based and CO_2 is the source of the carbon. Carbon dioxide is also a major greenhouse gas, and because of its thermal absorbancy it plays a significant role in maintaining a favorable global heat balance.

Water vapor is the atmospheric constituent whose concentration varies the most, from 0.1 to 30,000 ppm. Like CO_2 , it is also a major greenhouse gas, absorbing infrared energy being radiated back to space. Water vapor is also significant in the atmosphere because it readily changes phase. On cooling it condenses to form clouds, which are responsible for most of the earth's albedo

(the ability of the earth to radiate sunlight back to space). The albedo has an enormous effect on the amount of sunlight that reaches the earth's surface.

Hydrogen, helium, neon, krypton, and xenon are the so-called noble gases. They are inert and as consequence do not appear to have any major effect on, or role in, the atmosphere. Hydrogen and helium appear to be remnants of the primeval atmosphere. They are the lightest of all gases and are the most likely to escape the earth's gravity and be lost to space.

The atmosphere also contains trace gases produced by biological and/or geologic processes. These include ammonia (NH_3), methane (CH_4), hydrogen sulfide (H_2S), carbon monoxide (CO), and sulfur dioxide (SO_2). Ammonia, CH_4 , and H_2S are produced primarily by biological decomposition. Methane absorbs thermal energy and can serve as a greenhouse gas.

In addition to the gases listed in Tables 1.1 and 1.2 and described above, a variety of other gaseous substances can be found in the atmosphere. Such substances are often released by living things. During periods of active growth, plants release large quantities of volatile oils such as isoprenes and pinene. The presence of these substances in the atmosphere appears to be very transient; therefore, they cannot be described as being normal constituents of the atmosphere.

PHYSICAL CHARACTERISTICS

The atmosphere is a medium characterized by the mix of gases that comprise it. It is also characterized by the physical phenomena that act on and within it. These include solar radiation, heat, atmospheric pressure/density, gravity, water, and the movement of the atmosphere caused by the interaction of physical forces within and on it.

The Solar Spectrum

The sun emits energy in the form of electromagnetic waves. An electromagnetic spectrum is described in Figure 1.2. Of the electromagnetic energy received by the earth and its atmosphere, 99% is in the wavelength range of 0.15 to 4.0 μm (0.15 to 4.0×10^{-6} m). Of particular significance to living systems is the visible portion of this spectrum, the 0.40 to 0.70 μm region. This visible light accounts for 40% of all solar radiation received at the earth's surface. The solar energy spectrum peaks with a maximum of 0.5 μm , which is in the green portion of the visible region (Figure 1.3). Because of the domination of visible light in the solar spectrum, it is no coincidence that many life processes are promoted by specific wavelength bands in this spectral region.

The total amount of energy emitted from the sun is relatively constant. At the upper extremity of the earth's atmosphere approximately 1.92 cal/cm²/sec (the solar constant) is received. This value represents the incident energy on a unit area oriented perpendicular to the sun's rays.

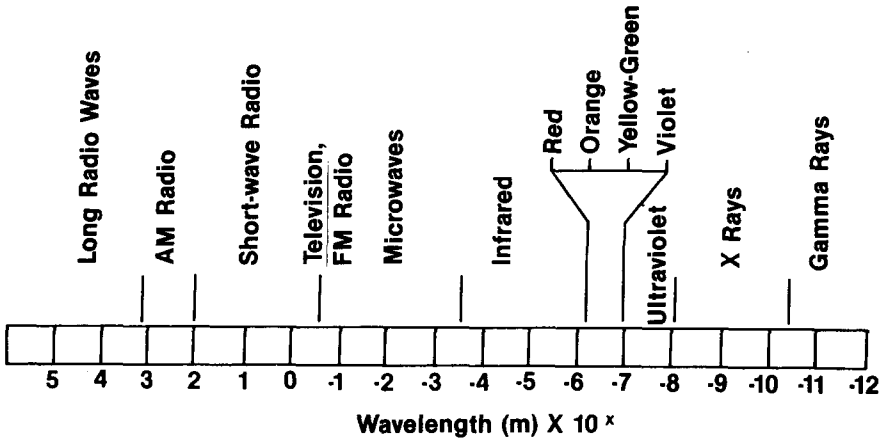


Figure 1.2 Electromagnetic spectrum.²

The amount of solar energy actually received at the earth's surface is far less than the solar constant. The differences between the extraterrestrial solar curve and the one near the earth's surface (Figure 1.3) are due to the absorption, scattering and reflection of the sun's energy by the atmosphere.

Molecular constituents such as water vapor, CO₂ and O₃ contain numerous absorption bands which absorb incoming solar radiation. Water vapor and

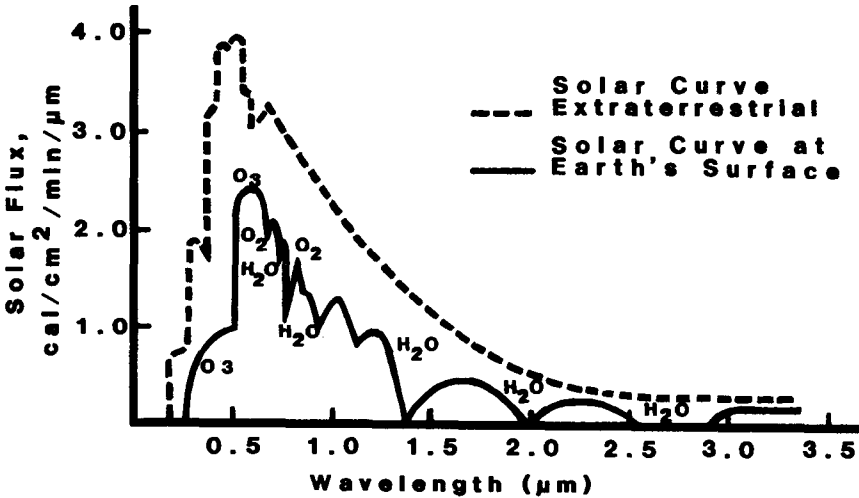


Figure 1.3 Solar spectra.³

CO₂ absorb in the infrared region; O₃ absorbs in both the ultraviolet and infrared regions.

The significant reduction in the quantity of solar energy entering the earth's atmosphere is due to reflection or back-scattering. The ability of the earth or any body to reflect light is called its albedo. It is this albedo, or reflected light, which allows us to see the moon and the planets of the solar system. The albedo of the earth varies over the course of the year from about 30 to 39%, with an average of 35%. The earth's albedo is due to both reflection from the surface and scattering by atmospheric aerosols and gases. Atmospheric scattering by the aerosols of clouds is responsible for approximately 85% of the earth's albedo.

Thermal Radiation

Solar energy incident on the earth's surface is ultimately converted to heat, which is radiated away from the earth in the infrared region of the electromagnetic spectrum. The atmosphere, acting as a greenhouse, traps infrared energy, preventing its radiation back to space (Figure 1.4). This phenomenon is due primarily to water vapor and CO₂, which absorb infrared or thermal energy in specific spectral bands. Note the strong infrared emissions in the spectral region from 7 to 13 μm and the weak emissions from the other spectral regions illustrated. The latter is due to the absorption of infrared energy by CO₂ and water vapor. The former is described as the "window." In the window range, the atmosphere is quite transparent to the flow of infrared energy.

Temperature Variation

Solar energy received at the earth's surface is distributed unequally, as the equatorial region receives significantly more energy than the polar regions. This unequal distribution of solar energy results in considerable spatial temperature variation, and consequently differences in climate. Changes in the

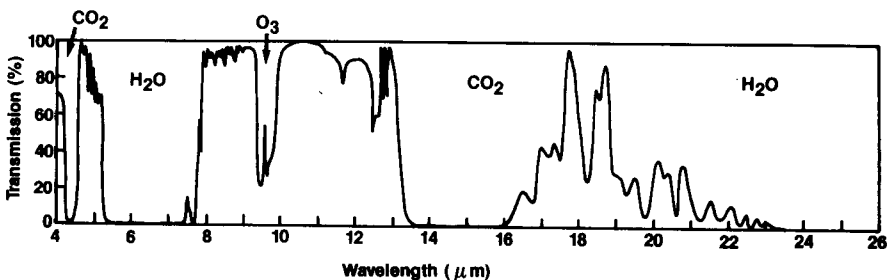


Figure 1.4 Nighttime thermal emission characteristics of the earth and its atmosphere.³

earth's inclination to the sun result in temporal temperature and climatic differences that we associate with the seasons.

Significant variations in temperature also occur in the vertical dimension. A vertical temperature profile of the atmosphere is described in Figure 1.5.

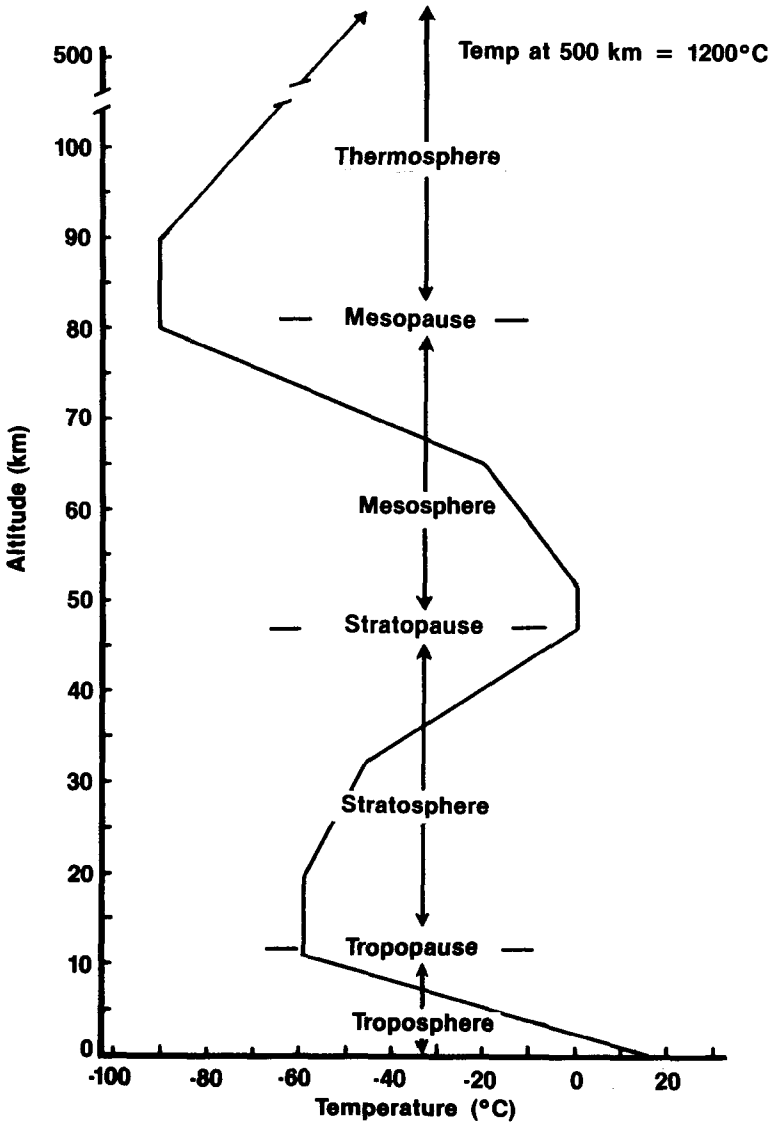


Figure 1.5 Vertical temperature profile of the earth's atmosphere.⁴

This temperature profile can be used to subdivide the atmosphere into zones or strata.

As described by temperature, the troposphere has an average depth of 10 km. It varies, however, from about 12 km over the equator to 8 km over the poles. In the troposphere temperature decreases with height at an average rate of $6.5^{\circ}\text{C}/\text{km}$. Because of the intense movement of thermal energy and significant temperature differences, the troposphere is a characteristically unstable part of the atmosphere. This is the atmospheric layer which produces our weather.

Near the top of the troposphere and the lower reaches of the stratosphere, temperature is isothermal. This is the tropopause. Similar isothermal regions are also found between layers of the upper atmosphere, including the stratosphere and the mesosphere, and the mesosphere and the thermosphere.

The stratosphere is approximately 30 km in depth. It is characterized by a temperature profile in which the temperature increases with height to about 0°C or 273°K . The stratosphere contains the ozone layer, which absorbs ultraviolet radiation. It is this UV absorption which is primarily responsible for the relatively elevated temperatures observed in the stratosphere. Maximum O_3 levels occur between 15 and 30 km. Although the concentration of O_3 begins to decrease above 30 km, these O_3 levels efficiently absorb ultraviolet light to account for the higher temperatures observed at the top of the stratosphere.

The stratosphere, in contrast to the troposphere, is a relatively stable region. It has very little manifestation of what we call weather. There are very few clouds, and winds are primarily horizontal.

The mesosphere begins above the stratosphere and the stratopause. It is characterized by decreasing temperatures up to an elevation of approximately 80 km. In some classifications of atmospheric zones or strata the mesosphere is described as the exosphere, as it is above here that light atmospheric molecules such as hydrogen and helium are lost to space.

The thermosphere extends from an altitude of approximately 90 to greater than 1000 km. The thermosphere, in fact, has no well-defined upper limit. It contains only a minute fraction of the atmosphere's mass. The relatively few molecules of N_2 and O_2 which are present absorb very-short-wave solar radiation. The high temperatures, which may exceed 1000°C , result from this absorption. Even though the air temperature may be very high, an object in the thermosphere is unlikely to become hot, as there are too few molecules present to transfer their energy to it.

In the thermosphere altitude range of 90–400 km, the atmosphere is electrically charged. This region is known as the ionosphere. Here atoms of O_2 and molecules of N_2 become photoionized, producing positive ions as electrons are set free to produce electric currents. It is the ionosphere which reflects AM radio signals back to earth during the nighttime. Following intense solar activity, the aurora borealis (northern lights) and aurora australis (southern lights) may occur. These phenomena are produced by solar storms containing protons and electrons which are captured by the earth's magnetic field. As they