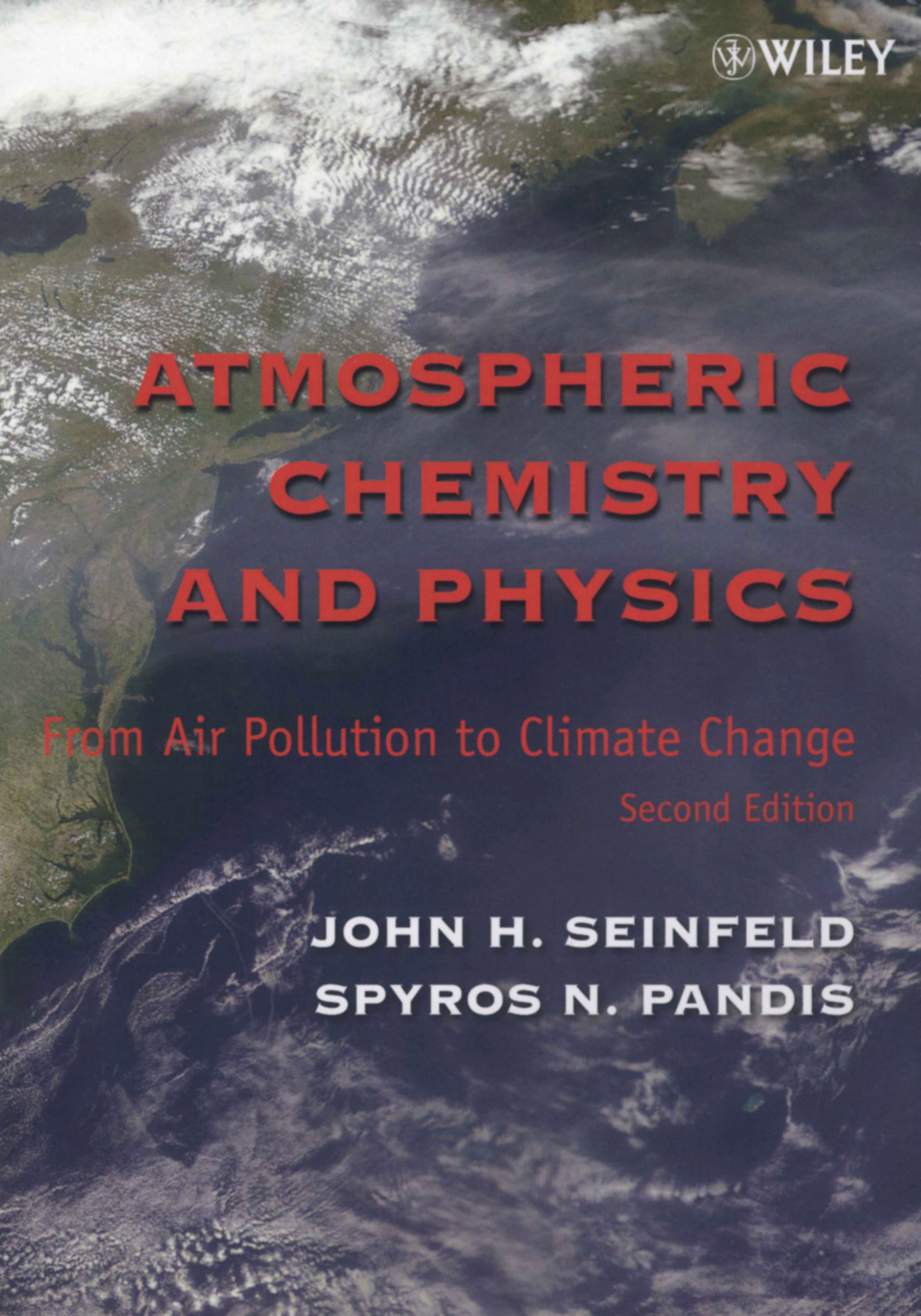

WILEY

ATMOSPHERIC CHEMISTRY AND PHYSICS

From Air Pollution to Climate Change

Second Edition

JOHN H. SEINFELD

SPYROS N. PANDIS

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SECOND EDITION

John H. Seinfeld
California Institute of Technology

Spyros N. Pandis
University of Patras and
Carnegie Mellon University

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To
Benjamin and Elizabeth
and
Angeliki and Nikos

PREFACE TO THE SECOND EDITION

Two considerations motivated us to undertake the Second Edition of this book. First, a number of important developments have occurred in atmospheric science since 1998, the year of the First Edition, and we wanted to update the treatments in several areas of the book to reflect these advances in understanding of atmospheric processes. New chapters have been added on chemical kinetics, atmospheric radiation and photochemistry, global circulation of the atmosphere, and global biogeochemical cycles. The chapters on stratospheric and tropospheric chemistry and organic atmospheric aerosols have been revised to reflect the current state of understanding in this area. The second consideration relates to the style of the book. Our goal in the First Edition was, and continues to be, in the Second Edition, both rigor and thoroughness. The First Edition has been widely used as a course textbook and reference text worldwide; feedback we have received from instructors and students is that additional examples would aid in illustrating the basic theory. The Second Edition contains numerous examples, delineated by vertical bars offsetting the material. In order to prevent an already lengthy book from becoming unwieldy with the new additions, some advanced material from the First Edition, generally of interest to specialists, has been omitted. Problems at the end of the chapters have been thoroughly reconsidered and updated. While many of the problems from the First Edition have been retained, in a number of chapters substantially new problems have been added. These problems have been used in courses at Caltech (California Institute of Technology), Carnegie Mellon, and the University of Patras.

Many colleagues have provided important material, as well as proofreading suggestions. Special appreciation is extended to Wei-Ting Chen, Cliff Davidson, Theodore Dibble, Mark Lawrence, Sally Ng, Tracey Rissman, Ross Salawitch, Charles Stanier, Jason Surratt, Satoshi Takahama, Varuntida Varutbangkul, Paul Wennberg, and Yang Zhang. Finally, Ann Hilgenfeldt and Yvette Grant skillfully prepared the manuscript for the Second Edition.

John H. Seinfeld

Spyros N. Pandis

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 atmostphere 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 long-lived 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 scale—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 life cycles 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 scale, significant policy issues concern how to decrease ozone levels by controlling the ozone precursors—hydrocarbons and oxides of nitrogen. At the global scale, understanding both the natural ozone chemistry of the troposphere and the causes of continually increasing background troposheric 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 certain gases 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 thought 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 Earth. Aerosols are also the nuclei around which clouds droplets form—no aerosols, no clouds. Clouds are one of the most important elements or our climate system, so the effect of increasing global aerosol levels on the 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 the 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 the 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-redical 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 propeties 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 had introductory courses in thermodynamics, transport phenomena (fluid mechanics and/or 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 meterology 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 scienc 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 the reader to evaluate his or her 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., $\mathbf{1.1}_A$ 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

SPYROS N. PANDIS

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