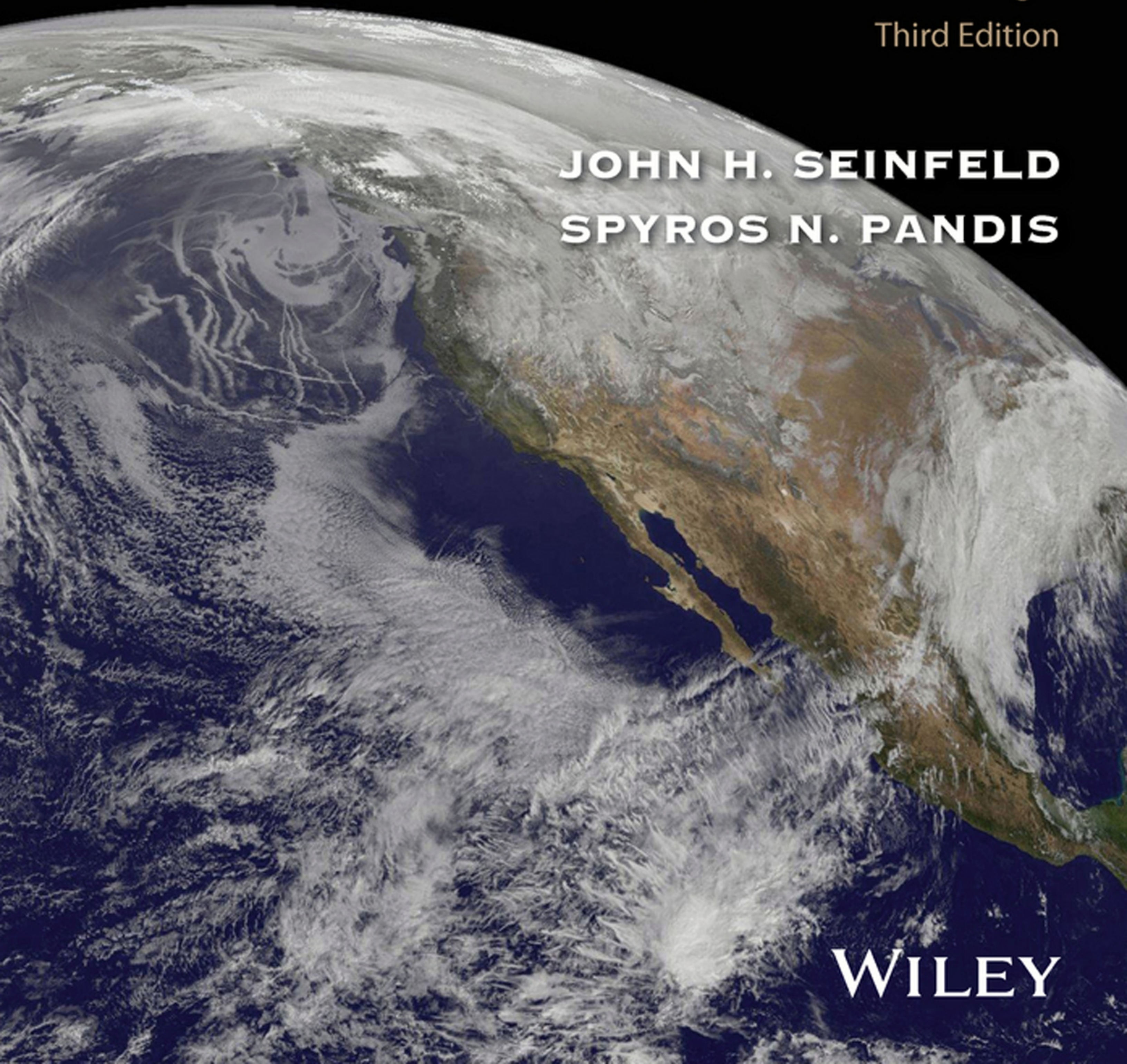
ATMOSPHERIC CHEMISTRY AND PHYSICS

From Air Pollution to Climate Change

Third Edition

JOHN H. SEINFELD
SPYROS N. PANDIS



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To
Benjamin and Elizabeth
and
Angeliki and Nikos

Contents

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 $\left(SO_4^{2-}\right)$, 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 or 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., $\mathbf{1.1}_A$ 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.

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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 strato-cumulus 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.

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PART I

The Atmosphere and Its Constituents