

ATMOSPHERIC CHEMISTRY AND PHYSICS

From Air Pollution to Climate Change

Second Edition

JOHN H. SEINFELD
SPYROS N. PANDIS

**ATMOSPHERIC
CHEMISTRY AND PHYSICS**

ATMOSPHERIC CHEMISTRY AND PHYSICS

From Air Pollution to Climate Change

SECOND EDITION

John H. Seinfeld

California Institute of Technology

Spyros N. Pandis

*University of Patras and
Carnegie Mellon University*



A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS, INC.

Copyright © 2006 by John Wiley & Sons, Inc. All rights reserved

Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

Seinfeld, John H.

Atmospheric chemistry and physics : from air pollution to climate change / John H. Seinfeld,
Spyros N. Pandis. – 2nd ed.

p. cm.

“A Wiley-Interscience publication.”

Includes bibliographical references and index.

ISBN-13: 978-0-471-72017-1 (cloth)

ISBN-10: 0-471-72017-8 (cloth)

ISBN-13: 978-0-471-72018-8 (paper)

ISBN-10: 0-471-72018-6 (paper)

1. Atmospheric chemistry. 2. Air–Pollution–Environmental aspects. 3. Environmental chemistry.

I. Pandis, Spyros N., 1963- II. Title.

QC879.6.S45 2006

660.6'2–dc22

2005056954

Printed in the United States of America

10 9 8 7

*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 ($1 \mu\text{mol}$ 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 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 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 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 of 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-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 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 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 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., 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

CONTENTS

Preface to the Second Edition	vii
Preface to the First Edition	ix
1 The Atmosphere	1
1.1 History and Evolution of the Earth's Atmosphere	1
1.2 Climate	4
1.3 The Layers of the Atmosphere	6
1.4 Pressure in the Atmosphere	8
1.4.1 Units of Pressure	8
1.4.2 Variation of Pressure with Height in the Atmosphere	9
1.5 Temperature in the Atmosphere	11
1.6 Expressing the Amount of a Substance in the Atmosphere	12
1.7 Spatial and Temporal Scales of Atmospheric Processes	16
Problems	19
References	20
2 Atmospheric Trace Constituents	21
2.1 Atmospheric Lifetime	22
2.2 Sulfur-Containing Compounds	27
2.2.1 Dimethyl Sulfide (CH ₃ SCH ₃)	31
2.2.2 Carbonyl Sulfide (OCS)	32
2.2.3 Sulfur Dioxide (SO ₂)	33
2.3 Nitrogen-Containing Compounds	33
2.3.1 Nitrous Oxide (N ₂ O)	35
2.3.2 Nitrogen Oxides (NO _x = NO + NO ₂)	36
2.3.3 Reactive Odd Nitrogen (NO _y)	37
2.3.4 Ammonia (NH ₃)	38
2.4 Carbon-Containing Compounds	38
2.4.1 Classification of Hydrocarbons	38
2.4.2 Methane	41
2.4.3 Volatile Organic Compounds	43
2.4.4 Biogenic Hydrocarbons	43
2.4.5 Carbon Monoxide	46
2.4.6 Carbon Dioxide	47
2.5 Halogen-Containing Compounds	47
2.5.1 Methyl Chloride (CH ₃ Cl)	50
2.5.2 Methyl Bromide (CH ₃ Br)	51

2.6	Atmospheric Ozone	52	
2.7	Particulate Matter (Aerosols)	55	
2.7.1	Stratospheric Aerosol	57	
2.7.2	Chemical Components of Tropospheric Aerosol	57	
2.7.3	Cloud Condensation Nuclei (CCN)	58	
2.7.4	Sizes of Atmospheric Particles	58	
2.7.5	Sources of Atmospheric Particulate Matter	60	
2.7.6	Carbonaceous Particles	60	
2.7.7	Mineral Dust	61	
2.8	Emission Inventories	62	
2.9	Biomass Burning	63	
Appendix 2.1	Air Pollution Legislation	63	
Appendix 2.2	Hazardous Air Pollutants (Air Toxics) Problems	69	
	References	70	
3	Chemical Kinetics		75
3.1	Order of Reaction	75	
3.2	Theories of Chemical Kinetics	77	
3.2.1	Collision Theory	77	
3.2.2	Transition State Theory	80	
3.2.3	Potential Energy Surface for a Bimolecular Reaction	82	
3.3	The Pseudo-Steady-State Approximation	83	
3.4	Reactions of Excited Species	84	
3.5	Termolecular Reactions	85	
3.6	Chemical Families	89	
3.7	Gas-Surface Reactions	91	
Appendix 3	Free Radicals	93	
	Problems	93	
	References	96	
4	Atmospheric Radiation and Photochemistry		98
4.1	Radiation	98	
4.1.1	Solar and Terrestrial Radiation	100	
4.1.2	Energy Balance for Earth and Atmosphere	101	
4.1.3	Solar Variability	105	
4.2	Radiative Flux in the Atmosphere	106	
4.3	Beer-Lambert Law and Optical Depth	108	
4.4	Actinic Flux	111	
4.5	Atmospheric Photochemistry	114	
4.6	Absorption of Radiation by Atmospheric Gases	117	
4.7	Absorption by O ₂ and O ₃	122	
4.8	Photolysis Rate as a Function of Altitude	126	
4.9	Photodissociation of O ₃ to Produce O and O(¹ D)	128	
4.10	Photodissociation of NO ₂	131	
	Problems	135	
	References	136	

5	Chemistry of the Stratosphere	138
5.1	Overview of Stratospheric Chemistry	138
5.2	Chapman Mechanism	142
5.3	Nitrogen Oxide Cycles	151
5.3.1	Stratospheric Source of NO_x from N_2O	151
5.3.2	NO_x Cycles	154
5.4	HO_x Cycles	156
5.5	Halogen Cycles	162
5.5.1	Chlorine Cycles	162
5.5.2	Bromine Cycles	166
5.6	Reservoir Species and Coupling of the Cycles	167
5.7	Ozone Hole	169
5.7.1	Polar Stratospheric Clouds	173
5.7.2	PSCs and the Ozone Hole	174
5.7.3	Arctic Ozone Hole	178
5.8	Heterogeneous (Nonpolar) Stratospheric Chemistry	179
5.8.1	The Stratospheric Aerosol Layer	179
5.8.2	Heterogeneous Hydrolysis of N_2O_5	180
5.8.3	Effect of Volcanoes on Stratospheric Ozone	185
5.9	Summary of Stratospheric Ozone Depletion	188
5.10	Transport and Mixing in the Stratosphere	191
5.11	Ozone Depletion Potential	193
	Problems	195
	References	200
6	Chemistry of the Troposphere	204
6.1	Production of Hydroxyl Radicals in the Troposphere	205
6.2	Basic Photochemical Cycle of NO_2 , NO , and O_3	209
6.3	Atmospheric Chemistry of Carbon Monoxide	211
6.3.1	Low NO_x Limit	214
6.3.2	High NO_x Limit	214
6.3.3	Ozone Production Efficiency	215
6.3.4	Theoretical Maximum Yield of Ozone from CO Oxidation	219
6.4	Atmospheric Chemistry of Methane	219
6.5	The NO_x and NO_y Families	224
6.5.1	Daytime Behavior	224
6.5.2	Nighttime Behavior	225
6.6	Ozone Budget of the Troposphere and Role of NO_x	227
6.6.1	Ozone Budget of the Troposphere	227
6.6.2	Role of NO_x	228
6.7	Tropospheric Reservoir Molecules	231
6.7.1	H_2O_2 , CH_3OOH , and HONO	231
6.7.2	Peroxyacyl Nitrates (PANs)	231

6.8	Relative Roles of VOC and NO _x in Ozone Formation	235
6.8.1	Importance of the VOC/NO _x Ratio	235
6.8.2	Ozone Isopleth Plot	236
6.9	Simplified Organic/NO _x Chemistry	239
6.10	Chemistry of Nonmethane Organic Compounds in the Troposphere	242
6.10.1	Alkanes	242
6.10.2	Alkenes	247
6.10.3	Aromatics	254
6.10.4	Aldehydes	258
6.10.5	Ketones	259
6.10.6	α, β-Unsaturated Carbonyls	260
6.10.7	Ethers	260
6.10.8	Alcohols	261
6.11	Atmospheric Chemistry of Biogenic Hydrocarbons	261
6.12	Atmospheric Chemistry of Reduced Nitrogen Compounds	265
6.12.1	Amines	265
6.12.2	Nitriles	266
6.12.3	Nitrites	266
6.13	Atmospheric Chemistry (Gas Phase) of Sulfur Compounds	266
6.13.1	Sulfur Oxides	266
6.13.2	Reduced Sulfur Compounds (Dimethyl Sulfide)	267
6.14	Tropospheric Chemistry of Halogen Compounds	270
6.14.1	Chemical Cycles of Halogen Species	270
6.14.2	Tropospheric Chemistry of CFC Replacements: Hydrofluorocarbons (HFCs) and Hydrochlorofluorocarbons (HCFCs)	272
	Problems	275
	References	279

7 Chemistry of the Atmospheric Aqueous Phase

284

7.1	Liquid Water in the Atmosphere	284
7.2	Absorption Equilibria and Henry's Law	286
7.3	Aqueous-Phase Chemical Equilibria	291
7.3.1	Water	291
7.3.2	Carbon Dioxide–Water Equilibrium	292
7.3.3	Sulfur Dioxide–Water Equilibrium	294
7.3.4	Ammonia–Water Equilibrium	299
7.3.5	Nitric Acid–Water Equilibrium	299
7.3.6	Equilibria of Other Important Atmospheric Gases	302
7.4	Aqueous-Phase Reaction Rates	306
7.5	S(IV)–S(VI) Transformation and Sulfur Chemistry	308
7.5.1	Oxidation of S(IV) by Dissolved O ₃	308
7.5.2	Oxidation of S(IV) by Hydrogen Peroxide	311
7.5.3	Oxidation of S(IV) by Organic Peroxides	312
7.5.4	Uncatalyzed Oxidation of S(IV) by O ₂	313

7.5.5	Oxidation of S(IV) by O ₂ Catalyzed by Iron and Manganese	314
7.5.6	Comparison of Aqueous-Phase S(IV) Oxidation Paths	316
7.6	Dynamic Behavior of Solutions with Aqueous-Phase Chemical Reactions	318
7.6.1	Closed System	319
7.6.2	Calculation of Concentration Changes in a Droplet with Aqueous-Phase Reactions	321
Appendix 7.1	Thermodynamic and Kinetic Data	325
Appendix 7.2	Additional Aqueous-Phase Sulfur Chemistry	328
7.A.1	S(IV) Oxidation by the OH Radical	328
7.A.2	Oxidation of S(IV) by Oxides of Nitrogen	334
7.A.3	Reaction of Dissolved SO ₂ with HCHO	334
Appendix 7.3	Aqueous-Phase Nitrite and Nitrate Chemistry	336
7.A.4	NO _x Oxidation	336
7.A.5	Nitrogen Radicals	337
Appendix 7.4	Aqueous-Phase Organic Chemistry	338
Appendix 7.5	Oxygen and Hydrogen Chemistry	339
	Problems	340
	References	343

8 Properties of the Atmospheric Aerosol

350

8.1	The Size Distribution Function	350
8.1.1	The Number Distribution $n_N(D_p)$	353
8.1.2	The Surface Area, Volume, and Mass Distributions	355
8.1.3	Distributions Based on $\ln D_p$ and $\log D_p$	358
8.1.4	Relating Size Distributions Based on Different Independent Variables	359
8.1.5	Properties of Size Distributions	360
8.1.6	The Lognormal Distribution	362
8.1.7	Plotting the Lognormal Distribution	365
8.1.8	Properties of the Lognormal Distribution	366
8.2	Ambient Aerosol Size Distributions	368
8.2.1	Urban Aerosols	370
8.2.2	Marine Aerosols	374
8.2.3	Rural Continental Aerosols	375
8.2.4	Remote Continental Aerosols	376
8.2.5	Free Tropospheric Aerosols	376
8.2.6	Polar Aerosols	378
8.2.7	Desert Aerosols	379
8.3	Aerosol Chemical Composition	381
8.4	Spatial and Temporal Variation	384
8.5	Vertical Variation	388
	Problems	389
	References	393

9	Dynamics of Single Aerosol Particles	396
9.1	Continuum and Noncontinuum Dynamics: The Mean Free Path	396
9.2	The Drag on a Single Particle: Stokes' Law	403
9.2.1	Corrections to Stokes' Law: The Drag Coefficient	405
9.2.2	Stokes' Law and Noncontinuum Effects: Slip Correction Factor	406
9.3	Gravitational Settling of an Aerosol Particle	407
9.4	Motion of an Aerosol Particle in an External Force Field	411
9.5	Brownian Motion of Aerosol Particles	412
9.5.1	Particle Diffusion	415
9.5.2	Aerosol Mobility and Drift Velocity	417
9.5.3	Mean Free Path of an Aerosol Particle	420
9.6	Aerosol and Fluid Motion	422
9.6.1	Motion of a Particle in an Idealized Flow (90° Corner)	423
9.6.2	Stop Distance and Stokes Number	425
9.7	Equivalent Particle Diameters	426
9.7.1	Volume Equivalent Diameter	426
9.7.2	Stokes Diameter	428
9.7.3	Classical Aerodynamic Diameter	429
9.7.4	Electrical Mobility Equivalent Diameter	431
	Problems	431
	References	432
10	Thermodynamics of Aerosols	434
10.1	Thermodynamic Principles	434
10.1.1	Internal Energy and Chemical Potential	434
10.1.2	The Gibbs Free Energy, G	436
10.1.3	Conditions for Chemical Equilibrium	438
10.1.4	Chemical Potentials of Ideal Gases and Ideal-Gas Mixtures	442
10.1.5	Chemical Potential of Solutions	443
10.1.6	The Equilibrium Constant	448
10.2	Aerosol Liquid Water Content	449
10.2.1	Chemical Potential of Water in Atmospheric Particles	452
10.2.2	Temperature Dependence of the DRH	453
10.2.3	Deliquescence of Multicomponent Aerosols	455
10.2.4	Crystallization of Single and Multicomponent Salts	460
10.3	Equilibrium Vapor Pressure over a Curved Surface: The Kelvin Effect	461
10.4	Thermodynamics of Atmospheric Aerosol Systems	464
10.4.1	The H_2SO_4 - H_2O System	464
10.4.2	The Sulfuric Acid-Ammonia-Water System	470
10.4.3	The Ammonia-Nitric Acid-Water System	472
10.4.4	The Ammonia-Nitric Acid-Sulfuric Acid-Water System	478

10.4.5	Other Inorganic Aerosol Species	483
10.4.6	Inorganic Aerosol Thermodynamic Models	484
	Problems	485
	References	486

11 Nucleation **489**

11.1	Classical Theory of Homogeneous Nucleation: Kinetic Approach	491
11.1.1	The Forward Rate Constant β_i	494
11.1.2	The Reverse Rate Constant γ_i	495
11.1.3	Derivation of the Nucleation Rate	496
11.2	Classical Homogeneous Nucleation Theory: Constrained Equilibrium Approach	500
11.2.1	Free Energy of <i>i</i> -mer Formation	500
11.2.2	Constrained Equilibrium Cluster Distribution	502
11.2.3	The Evaporation Coefficient γ_i	504
11.2.4	Nucleation Rate	505
11.3	Recapitulation of Classical Theory	508
11.4	Experimental Measurement of Nucleation Rates	509
11.4.1	Upward Thermal Diffusion Cloud Chamber	510
11.4.2	Fast Expansion Chamber	510
11.4.3	Turbulent Mixing Chambers	512
11.4.4	Experimental Evaluation of Classical Homogeneous Nucleation Theory	512
11.5	Modifications of the Classical Theory and More Rigorous Approaches	513
11.6	Binary Homogeneous Nucleation	514
11.7	Binary Nucleation in the H ₂ SO ₄ -H ₂ O System	520
11.8	Heterogeneous Nucleation	524
11.8.1	Nucleation on an Insoluble Foreign Surface	524
11.8.2	Ion-Induced Nucleation	526
11.9	Nucleation in the Atmosphere	529
	Appendix 11 The Law of Mass Action	531
	Problems	532
	References	533

12 Mass Transfer Aspects of Atmospheric Chemistry **537**

12.1	Mass and Heat Transfer to Atmospheric Particles	537
12.1.1	The Continuum Regime	537
12.1.2	The Kinetic Regime	541
12.1.3	The Transition Regime	542
12.1.4	The Accommodation Coefficient	546
12.2	Mass Transport Limitations in Aqueous-Phase Chemistry	547
12.2.1	Characteristic Time for Gas-Phase Diffusion to a Particle	549

12.2.2	Characteristic Time to Achieve Equilibrium in the Gas–Particle Interface	551
12.2.3	Characteristic Time of Aqueous Dissociation Reactions	554
12.2.4	Characteristic Time of Aqueous-Phase Diffusion in a Droplet	556
12.2.5	Characteristic Time for Aqueous-Phase Chemical Reactions	557
12.3	Mass Transport and Aqueous-Phase Chemistry	557
12.3.1	Gas-Phase Diffusion and Aqueous-Phase Reactions	558
12.3.2	Aqueous-Phase Diffusion and Reaction	560
12.3.3	Interfacial Mass Transport and Aqueous-Phase Reactions	561
12.3.4	Application to the S(IV)–Ozone Reaction	564
12.3.5	Application to the S(IV)–Hydrogen Peroxide Reaction	566
12.3.6	Calculation of Aqueous-Phase Reaction Rates	567
12.3.7	An Aqueous-Phase Chemistry/Mass Transport Model	573
12.4	Mass Transfer to Falling Drops	574
12.5	Characteristic Time for Atmospheric Aerosol Equilibrium	575
12.5.1	Solid Aerosol Particles	575
12.5.2	Aqueous Aerosol Particles	577
Appendix 12	Solution of the Transient Gas-Phase Diffusion Problem Equations (12.4)–(12.7)	580
	Problems	582
	References	584

13 Dynamics of Aerosol Populations

588

13.1	Mathematical Representations of Aerosol Size Distributions	588
13.1.1	Discrete Distribution	588
13.1.2	Continuous Distribution	589
13.2	Condensation	589
13.2.1	The Condensation Equation	589
13.2.2	Solution of the Condensation Equation	592
13.3	Coagulation	595
13.3.1	Brownian Coagulation	596
13.3.2	The Coagulation Equation	603
13.3.3	Solution of the Coagulation Equation	606
13.4	The Discrete General Dynamic Equation	610
13.5	The Continuous General Dynamic Equation	612
Appendix 13.1	Additional Mechanisms of Coagulation	613
13.A.1	Coagulation in Laminar Shear Flow	613
13.A.2	Coagulation in Turbulent Flow	614
13.A.3	Coagulation from Gravitational Settling	614
13.A.4	Brownian Coagulation and External Force Fields	615

Appendix 13.2	Solution of (13.73)	620
Problems		622
References		626

14 Organic Atmospheric Aerosols 628

14.1	Organic Aerosol Components	628
14.2	Elemental Carbon	628
14.2.1	Formation of Soot and Elemental Carbon	628
14.2.2	Emission Sources of Elemental Carbon	630
14.2.3	Ambient Elemental Carbon Concentrations	632
14.2.4	Ambient Elemental Carbon Size Distribution	633
14.3	Organic Carbon	634
14.3.1	Ambient Aerosol Organic Carbon Concentrations	635
14.3.2	Primary versus Secondary Organic Carbon	636
14.4	Primary Organic Carbon	640
14.4.1	Sources	640
14.4.2	Chemical Composition	642
14.4.3	Primary OC Size Distribution	645
14.5	Secondary Organic Carbon	647
14.5.1	Overview of Secondary Organic Aerosol Formation Pathways	647
14.5.2	Dissolution and Gas-Particle Partitioning of Organic Compounds	650
14.5.3	Adsorption and Gas-Particle Partitioning of Organic Compounds	658
14.5.4	Precursor Volatile Organic Compounds	661
14.5.5	SOA Yields	664
14.5.6	Chemical Composition	665
14.5.7	Physical Properties of SOA Components	666
14.5.8	Particle-Phase Chemistry	666
14.6	Polycyclic Aromatic Hydrocarbons (PAHs)	670
14.6.1	Emission Sources	671
14.6.2	Size Distributions	671
14.6.3	Atmospheric Chemistry	671
14.6.4	Partitioning between Gas and Aerosol Phases	672
Appendix 14	Measurement of Elemental and Organic Carbon	675
Problems		677
References		678

15 Interaction of Aerosols with Radiation 691

15.1	Scattering and Absorption of Light by Small Particles	691
15.1.1	Rayleigh Scattering Regime	696
15.1.2	Geometric Scattering Regime	698
15.1.3	Scattering Phase Function	700
15.1.4	Extinction by an Ensemble of Particles	700

15.2	Visibility	703	
15.3	Scattering, Absorption, and Extinction Coefficients from Mie Theory	707	
15.4	Calculated Visibility Reduction Based on Atmospheric Data	711	
Appendix 15	Calculation of Scattering and Extinction Coefficients by Mie Theory	715	
	Problems	716	
	References	718	
16	Meteorology of the Local Scale		720
16.1	Temperature in the Lower Atmosphere	722	
16.1.1	Temperature Variation in a Neutral Atmosphere	722	
16.1.2	Potential Temperature	726	
16.1.3	Buoyancy of a Rising (or Falling) Air Parcel in the Atmosphere	727	
16.2	Atmospheric Stability	729	
16.3	Micrometeorology	732	
16.3.1	Basic Equations of Atmospheric Fluid Mechanics	733	
16.3.2	Turbulence	736	
16.3.3	Equations for the Mean Quantities	737	
16.3.4	Mixing-Length Models for Turbulent Transport	739	
16.4	Variation of Wind with Height in the Atmosphere	742	
16.4.1	Mean Velocity in the Adiabatic Surface Layer over a Smooth Surface	743	
16.4.2	Mean Velocity in the Adiabatic Surface Layer over a Rough Surface	744	
16.4.3	Mean Velocity Profiles in the Nonadiabatic Surface Layer	746	
16.4.4	The Pasquill Stability Classes—Estimation of L	749	
16.4.5	Empirical Equation for the Mean Wind Speed	752	
Appendix 16	Derivation of the Basic Equations of Surface Layer Atmospheric Fluid Mechanics	752	
	Problems	756	
	References	759	
17	Cloud Physics		761
17.1	Properties of Water and Water Solutions	761	
17.1.1	Specific Heat of Water and Ice	762	
17.1.2	Latent Heats of Evaporation and of Melting for Water	762	
17.1.3	Water Surface Tension	762	
17.2	Water Equilibrium in the Atmosphere	763	
17.2.1	Equilibrium of a Flat Pure Water Surface with the Atmosphere	764	
17.2.2	Equilibrium of a Pure Water Droplet	765	
17.2.3	Equilibrium of a Flat Water Solution	766	

17.2.4	Atmospheric Equilibrium of an Aqueous Solution Drop	767
17.2.5	Atmospheric Equilibrium of an Aqueous Solution Drop Containing an Insoluble Substance	773
17.3	Cloud and Fog Formation	777
17.3.1	Isobaric Cooling	777
17.3.2	Adiabatic Cooling	778
17.3.3	Cooling with Entrainment	780
17.3.4	A Simplified Mathematical Description of Cloud Formation	781
17.4	Growth Rate of Individual Cloud Droplets	783
17.5	Growth of a Droplet Population	786
17.6	Cloud Condensation Nuclei	791
17.7	Cloud Processing of Aerosols	794
17.7.1	Nucleation Scavenging of Aerosols by Clouds	794
17.7.2	Chemical Composition of Cloud Droplets	795
17.7.3	Nonraining Cloud Effects on Aerosol Concentrations	797
17.7.4	Interstitial Aerosol Scavenging by Cloud Droplets	803
17.7.5	Aerosol Nucleation Near Clouds	804
17.8	Other Forms of Water in the Atmosphere	805
17.8.1	Ice Clouds	805
17.8.2	Rain	809
Appendix 17	Extended Köhler Theory	812
17.A.1	Modified Form of Köhler Theory for a Soluble Trace Gas	813
17.A.2	Modified Form of the Köhler Theory for a Slightly Soluble Substance	816
17.A.3	Modified Form of the Köhler Theory for a Surface-Active Solute	818
17.A.4	Examples	818
	Problems	822
	References	823

18 Atmospheric Diffusion

828

18.1	Eulerian Approach	828
18.2	Lagrangian Approach	831
18.3	Comparison of Eulerian and Lagrangian Approaches	832
18.4	Equations Governing the Mean Concentration of Species in Turbulence	833
18.4.1	Eulerian Approaches	833
18.4.2	Lagrangian Approaches	834
18.5	Solution of the Atmospheric Diffusion Equation for an Instantaneous Source	837
18.6	Mean Concentration from Continuous Sources	838
18.6.1	Lagrangian Approach	838

18.6.2	Eulerian Approach	843
18.6.3	Summary of Continuous Point Source Solutions	844
18.7	Statistical Theory of Turbulent Diffusion	845
18.7.1	Qualitative Features of Atmospheric Diffusion	845
18.7.2	Motion of a Single Particle Relative to a Fixed Axis	847
18.8	Summary of Atmospheric Diffusion Theories	851
18.9	Analytical Solutions for Atmospheric Diffusion: The Gaussian Plume Equation and Others	852
18.9.1	Gaussian Concentration Distributions	852
18.9.2	Derivation of the Gaussian Plume Equation as a Solution of the Atmospheric Diffusion Equation	854
18.9.3	Summary of Gaussian Point Source Diffusion Formulas	859
18.10	Dispersion Parameters in Gaussian Models	859
18.10.1	Correlations for σ_y and σ_z Based on Similarity Theory	862
18.10.2	Correlations for σ_y and σ_z Based on Pasquill Stability Classes	864
18.11	Plume Rise	867
18.12	Functional Forms of Mean Windspeed and Eddy Diffusivities	869
18.12.1	Mean Windspeed	869
18.12.2	Vertical Eddy Diffusion Coefficient K_{zz}	869
18.12.3	Horizontal Eddy Diffusion Coefficients K_{xx} and K_{yy}	873
18.13	Solutions of the Steady-State Atmospheric Diffusion Equation	873
18.13.1	Diffusion from a Point Source	874
18.13.2	Diffusion from a Line Source	875
Appendix 18.1	Further Solutions of Atmospheric Diffusion Problems	878
18.A.1	Solution of (18.29)–(18.31)	878
18.A.2	Solution of (18.50) and (18.51)	880
18.A.3	Solution of (18.59)–(18.61)	881
Appendix 18.2	Analytical Properties of the Gaussian Plume Equation Problems	882
	References	896

19 Dry Deposition

900

19.1	Deposition Velocity	900
19.2	Resistance Model for Dry Deposition	902
19.3	Aerodynamic Resistance	906
19.4	Quasi-Laminar Resistance	907
19.4.1	Gases	908
19.4.2	Particles	908

19.5	Surface Resistance	911
19.5.1	Surface Resistance for Dry Deposition of Gases to Water	914
19.5.2	Surface Resistance for Dry Deposition of Gases to Vegetation	918
19.6	Measurement of Dry Deposition	923
19.6.1	Direct Methods	923
19.6.2	Indirect Methods	925
19.6.3	Comparison of Methods	925
19.7	Some Comments on Modeling and Measurement of Dry Deposition	926
	Problems	927
	References	929
20	Wet Deposition	932
20.1	General Representation of Atmospheric Wet Removal Processes	932
20.2	Below-Cloud Scavenging of Gases	937
20.2.1	Below-Cloud Scavenging of an Irreversibly Soluble Gas	938
20.2.2	Below-Cloud Scavenging of a Reversibly Soluble Gas	942
20.3	Precipitation Scavenging of Particles	947
20.3.1	Raindrop–Aerosol Collision Efficiency	949
20.3.2	Scavenging Rates	951
20.4	In-Cloud Scavenging	953
20.5	Acid Deposition	954
20.5.1	Acid Rain Overview	954
20.5.2	Acid Rain Data and Trends	957
20.5.3	Effects of Acid Deposition	959
20.5.4	Cloudwater Deposition	963
20.5.5	Fogs and Wet Deposition	964
20.6	Acid Deposition Process Synthesis	965
20.6.1	Chemical Species Involved in Acid Deposition	965
20.6.2	Dry versus Wet Deposition	965
20.6.3	Chemical Pathways for Sulfate and Nitrate Production	966
20.6.4	Source–Receptor Relationships	968
20.6.5	Linearity	969
	Problems	971
	References	977
21	General Circulation of the Atmosphere	980
21.1	Hadley Cell	981
21.2	Ferrell Cell and Polar Cell	983
21.3	Coriolis Force	985

21.4	Geostrophic Windspeed	987	
21.4.1	Buys Ballot's Law	989	
21.4.2	Ekman Spiral	990	
21.5	The Thermal Wind Relation	993	
21.6	Stratospheric Dynamics	996	
21.7	The Hydrologic Cycle	997	
	Appendix 21 Ocean Circulation	998	
	Problems	1000	
	References	1002	
22	Global Cycles: Sulfur and Carbon		1003
22.1	The Atmospheric Sulfur Cycle	1003	
22.2	The Global Carbon Cycle	1007	
22.2.1	Carbon Dioxide	1007	
22.2.2	Compartmental Model of the Global Carbon Cycle	1009	
22.2.3	Atmospheric Lifetime of CO ₂	1014	
22.3	Analytical Solution for a Steady-State Four-Compartment Model of the Atmosphere	1018	
	Problems	1023	
	References	1024	
23	Climate and Chemical Composition of the Atmosphere		1026
23.1	The Global Temperature Record	1028	
23.2	Solar Variability	1032	
23.3	Radiative Forcing	1035	
23.4	Climate Sensitivity	1039	
23.5	Relative Radiative Forcing Indices	1042	
23.6	Unrealized Warming	1045	
23.7	Atmospheric Chemistry and Climate Change	1045	
23.7.1	Indirect Chemical Impacts	1046	
23.7.2	Atmospheric Lifetimes and Adjustment Times	1048	
23.8	Radiative Effects of Clouds	1049	
	Problems	1049	
	References	1052	
24	Aerosols and Climate		1054
24.1	Scattering–Absorbing Model of an Aerosol Layer	1057	
24.2	Cooling versus Heating of an Aerosol Layer	1060	
24.3	Scattering Model of an Aerosol Layer for a Nonabsorbing Aerosol	1062	
24.4	Upscatter Fraction	1064	
24.5	Optical Depth and Column Forcing	1067	
24.6	Internal and External Mixtures	1071	
24.7	Top-of-the-Atmosphere versus Surface Forcing	1074	
24.8	Indirect Effects of Aerosols on Climate	1078	
24.8.1	Radiative Model for a Cloudy Atmosphere	1080	

24.8.2	Sensitivity of Cloud Albedo to Cloud Droplet Number Concentration	1082
24.8.3	Relation of Cloud Droplet Number Concentration to Aerosol Concentrations	1084
	Problems	1087
	References	1088
25	Atmospheric Chemical Transport Models	1092
25.1	Introduction	1092
25.1.1	Model Types	1093
25.1.2	Types of Atmospheric Chemical Transport Models	1094
25.2	Box Models	1096
25.2.1	The Eulerian Box Model	1096
25.2.2	A Lagrangian Box Model	1099
25.3	Three-Dimensional Atmospheric Chemical Transport Models	1102
25.3.1	Coordinate System—Uneven Terrain	1102
25.3.2	Initial Conditions	1104
25.3.3	Boundary Conditions	1105
25.4	One-Dimensional Lagrangian Models	1106
25.5	Other Forms of Chemical Transport Models	1109
25.5.1	Atmospheric Diffusion Equation Expressed in Terms of Mixing Ratio	1109
25.5.2	Pressure-Based Coordinate System	1113
25.5.3	Spherical Coordinates	1114
25.6	Numerical Solution of Chemical Transport Models	1115
25.6.1	Coupling Problem—Operator Splitting	1116
25.6.2	Chemical Kinetics	1121
25.6.3	Diffusion	1126
25.6.4	Advection	1127
25.7	Model Evaluation	1131
	Problems	1133
	References	1135
26	Statistical Models	1136
26.1	Receptor Modeling Methods	1136
26.1.1	Chemical Mass Balance (CMB)	1139
26.1.2	Factor Analysis	1146
26.1.3	Empirical Orthogonal Function Receptor Models	1150
26.2	Probability Distributions for Air Pollutant Concentrations	1153
26.2.1	The Lognormal Distribution	1154
26.2.2	The Weibull Distribution	1154
26.3	Estimation of Parameters in the Distributions	1156
26.3.1	Method of Quantiles	1157
26.3.2	Method of Moments	1157

26.4	Order Statistics of Air Quality Data	1160
26.4.1	Basic Notions and Terminology of Order Statistics	1160
26.4.2	Extreme Values	1161
26.5	Exceedances of Critical Levels	1162
26.6	Alternative Forms of Air Quality Standards	1162
26.7	Relating Current and Future Air Pollutant Statistical Distributions	1167
	Problems	1169
	References	1172

Appendix A Units and Physical Constants **1175**

A.1	SI Base Units	1175
A.2	SI Derived Units	1175
A.3	Fundamental Physical Constants	1178
A.4	Properties of the Atmosphere and Water	1178
A.5	Units for Representing Chemical Reactions	1180
A.6	Concentrations in the Aqueous Phase	1180
A.7	Symbols for Concentration	1181
	References	1181

Appendix B Rate Constants of Atmospheric Chemical Reactions **1182**

	References	1190
--	------------	------

Index **1191**