

CHEMISTRY
of the
*Natural
Atmosphere*

second edition

Peter Warneck



INTERNATIONAL GEOPHYSICS SERIES, VOLUME 71



Chemistry of the Natural Atmosphere

Second Edition

Peter Warneck

*Max-Planck-Institut für Chemie
Mainz, Germany*



ACADEMIC PRESS

A Harcourt Science and Technology Company

San Diego San Francisco New York Boston London Sydney Tokyo

Cover: Images © 1999 PhotoDisc.

This book is printed on acid-free paper. ∞

Copyright © 2000, 1988 by ACADEMIC PRESS

All Rights Reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording, or any information storage and retrieval system, without permission in writing from the publisher.

Requests for permission to make copies of any part of the work should be mailed to:
Permissions Department, Harcourt Inc., 6277 Sea Harbor Drive,
Orlando, Florida 32887-6777

Academic Press

A Harcourt Science and Technology Company

525 B Street, Suite 1900, San Diego, California 92101-4495, U.S.A.

<http://www.apnet.com>

Academic Press

24-28 Oval Road, London NW1 7DX, UK

<http://www.hbuk.co.uk/ap/>

Library of Congress Catalog Card Number: 99-64620

International Standard Book Number: 0-12-735632-0

PRINTED IN THE UNITED STATES OF AMERICA

99 00 01 02 03 04 MM 9 8 7 6 5 4 3 2 1

*Chemistry
of the
Natural
Atmosphere*

Second Edition

This is Volume 71 in the
INTERNATIONAL GEOPHYSICS SERIES
A series of monographs and textbooks
Edited by RENATA DMOWSKA, JAMES R. HOLTON, AND
H. THOMAS ROSSBY

A complete list of the books in this series appears at the end of this volume.

To the memory of
Christian E. Junge
(1912–1996)

a pioneer in the exploration of atmospheric trace substances

PREFACE TO THE SECOND EDITION

Our current knowledge and understanding of atmospheric chemistry are largely founded on scientific advances made in the 1970s. Work done during the past decade has consolidated many of the earlier results. In particular, reaction rate data and mechanisms have been refined, but new insight has also been obtained in several other areas. Examples are polar stratospheric chemistry and the chemistry in clouds. The preoccupation of atmospheric scientists in recent years with the problem of climate change and the role of radiatively active trace gases, such as methane and nitrous oxide, in the radiation balance of our planet has led to a reexamination and better description of their budgets. In preparing the second edition of this book I have tried to incorporate the most obvious advances that were made during the past decade. I have also noted, however, that comparatively little progress has been made in other areas that have received less attention. For example, our knowledge of the organic fraction of the atmospheric aerosol is still largely that of 10 years ago.

Although the text has been entirely rewritten, many sections have been left essentially unchanged, either because concepts based on the earlier data are still valid or because new data are scant. Some sections have been substantially revised to include new data, especially where they have changed the perception, even though final conclusions may still be out of reach. In such cases the treatment assumes the character of an abridged literature review. The ever-increasing rate of research publications makes it impossible, more so than ever before, to include a comprehensive list of literature citations. The reader is urged to consult the research papers cited to obtain additional information.

In this edition I have made an effort to use SI (Système International) units more consistently by following the recommendations of the IUPAC

Atmospheric Chemistry Commission, which appeared in *Pure and Applied Chemistry* (Vol. 67, pp. 1377–1406 (1995)). One of the recommendations was to replace the notation ppmv, ppbv, etc., for gas-phase mixing ratios with the unit mol mol^{-1} in combination with the appropriate SI prefix for submultiples; that is, ppmv should be replaced by $\mu\text{mol mol}^{-1}$, ppbv by nmol mol^{-1} , and so forth. Another suggestion was to retain molecule cm^{-3} as a unit of concentration despite the violation of the SI rule that a qualifying name should not be part of a unit, and the number of an entity such as a molecule has no dimension. (Note that in this unit *molecule* appears in the singular, although a great many molecules are present in 1 cm^3 of gas.)

As before, I have received much support from colleagues of the local science community, and I am grateful for their advice. I am also greatly indebted to I. Bambach and G. Feyerherd, who have prepared new illustrations and brought earlier ones up to date. Finally, I owe my thanks to the editor of this edition at Academic Press, David Packer, for his patience in bearing with me when, because of unforeseen circumstances, the preparation of the manuscript was delayed.

Peter Warneck

PREFACE TO THE FIRST EDITION

Atmospheric chemistry deals with chemical compounds in the atmosphere, their distribution, origin, chemical transformation into other compounds, and finally, their removal from the atmospheric domain. These substances may occur as gases, liquids, or solids. The composition of the atmosphere is dominated by the gases nitrogen and oxygen in proportions that have been found to be invariable in time and space at altitudes up to 100 km. All other compounds are minor ones, with many of them occurring only in traces. Atmospheric chemistry thus deals primarily with trace substances.

As an interdisciplinary field of science, atmospheric chemistry has its main roots in meteorology and chemistry, with additional ties to microbiology, plant physiology, oceanography, and geology. The full range of the subject was last treated by C. E. Junge in his 1963 monograph, "Air Chemistry and Radioactivity." The extraordinarily rapid development of the field in the past two decades has added much new knowledge and insight into atmospheric processes, so that an updated account is now called for. To some extent, the new knowledge has already been incorporated into the recent secondary literature. Most of these accounts, however, specifically address the problems of local air pollution, whereas the natural atmosphere has received only a fragmentary treatment, even though it provides the yardstick for any assessment of air pollution levels. The recognition that humanity has started to perturb the atmosphere on a global scale is now shifting attention away from local toward global conditions, and this viewpoint deserves a more comprehensive treatment.

Atmospheric chemistry is now being taught in specialty courses at departments of chemistry and meteorology of many universities. The purpose of this book is to provide a reference source to graduate students and other interested persons with some background in the physical sciences. In preparing the text, therefore, I have pursued two aims: one is to assemble and

review observational data on which our knowledge of atmospheric processes is founded; the second aim is to present concepts for the interpretation of the data in a manner suitable for classroom use. The major difficulty that I encountered in this ambitious approach was the condensation of an immense volume of material into a single book. As a consequence, I have had to compromise on many interesting details. Observational data and the conclusions drawn from them receive much emphasis, but measurement techniques cannot be discussed in detail. Likewise, in dealing with theoretical concepts I have kept the mathematics to a minimum. The reader is urged to work out the calculations and, if necessary, to consult other texts to which reference is made. As in any active field of research, atmospheric chemistry abounds with speculations. Repeatedly I have had to resist the temptation to discuss speculative ideas in favor of simply stating the inadequacy of our knowledge.

The first two chapters present background information on the physical behavior of the atmosphere and on photochemical reactions for the benefit of chemists and meteorologists, respectively. Chapter 3, which deals with observations and chemistry of the stratosphere, follows naturally from the discussion in Chapter 2 of the absorption of solar ultraviolet radiation in that atmospheric region. Chapter 4 develops basic concepts for treating tropospheric chemistry on a global scale. Methane, carbon monoxide, and hydrogen are then discussed. Subsequent chapters consider ozone, hydrocarbons, and halocarbons in the troposphere. Chapters 7 and 8 are devoted to the formation, chemistry, and removal of aerosol particles and to the interaction of trace substances with clouds and wet precipitation. These processes are essential for an understanding of the fate of nitrogen and sulfur compounds in the atmosphere, which are treated in Chapters 9 and 10. The last two chapters show the intimate connection of the atmosphere to other geochemical reservoirs. Chapter 11 introduces the underlying concepts in the case of carbon dioxide; Chapter 12 discusses the geochemical origin of the atmosphere and its major constituents.

A major problem confronting me, as it does many other authors, was the proper choice of units. Atmospheric scientists have not yet agreed on a standard system. Values often range over many orders of magnitude, and SI units are not always practical. I have used the SI system as far as possible, but have found it necessary to depart from it in several cases. One is the use of molecule per cubic centimeter as a measure of number density, since rate coefficients are given in these units. I have also retained moles per liter instead of moles per cubic decimeter, and mbar instead of hPa for simplicity and because of widespread usage, although the purist may disapprove of this.

Literature citations, although extensive, are by no means complete. A comprehensive coverage of the literature was neither possible nor intended. In keeping with the aim of reviewing established knowledge, the references

are to document statements made in the text and to provide sources of observational data and other quantitative information. On the whole, I have considered the literature up to 1984, although more recent publications were included in some sections.

Thanks are due to many colleagues of the local science community for advice and information. S. Dötsch and C. Wurzinger compiled the list of references. I. Bambach, G. Feyerherd, G. Huster, and P. Lehmann patiently prepared the illustrations. I am grateful to all of them for essential help in bringing this volume to completion.

Peter Warneck

CONTENTS

<i>Preface to the Second Edition</i>	xiii
<i>Preface to the First Edition</i>	xv
1 Bulk Composition, Structure, and Dynamics of the Atmosphere	
1.1 Observational Data and Averages	1
1.2 Temperature Structure and Atmospheric Regions	7
1.3 Pressure, Density, and Mixing Ratio	10
1.4 Global Circulation and Transport	15
1.4.1 Atmospheric Mean Motions	16
1.4.2 Eddy Diffusion	19
1.4.3 Molecular Diffusion	30
1.5 Air Mass Exchange between Principal Atmospheric Domains	31
1.6 The Planetary Boundary Layer	42
2 Photochemical Processes and Elementary Reactions	
2.1 Fundamentals of Reactions Kinetics	55
2.2 Properties of Rate Coefficients	60
2.3 Photochemical Processes	67
2.4 Attenuation of Solar Radiation in the Atmosphere	69
2.5 Photodissociation of Oxygen and Ozone	79
2.6 Photochemistry of Minor Atmospheric Constituents	85
3 Chemistry of the Stratosphere	
3.1 Historical Survey	100

3.2	Ozone Observations	104
3.2.1	Principal Features and Behavior of the Ozone Layer	104
3.2.2	Global Trends in Total Ozone	109
3.3	The Chapman Model	113
3.4	Trace Gases Other Than Ozone	118
3.4.1	Nitrogen Oxides	119
3.4.2	Water Vapor, Methane, and Hydrogen	126
3.4.3	Halocarbons	131
3.4.4	Carbonyl Sulfide and Sulfur Dioxide	136
3.5	Heterogeneous and Polar Stratospheric Chemistry	140
3.6	The Budget of Ozone in the Stratosphere	151
4	Chemistry of the Troposphere: The Methane Oxidation Cycle	
4.1	The Tropospheric Reservoir	158
4.2	Hydroxyl Radicals in the Troposphere	163
4.3	The Budget of Methane	174
4.4	Formaldehyde	189
4.5	Carbon Monoxide	192
4.6	Hydrogen	205
5	Ozone in the Troposphere	
5.1	Introduction	211
5.2	Photochemical Air Pollution	213
5.3	Distribution and Behavior of Tropospheric Ozone	230
5.3.1	Balloon Soundings	231
5.3.2	Aircraft Observations	236
5.3.3	Surface Measurements	238
5.4	A Minimum Tropospheric Ozone Budget	249
5.4.1	Influx of Ozone from the Stratosphere	249
5.4.2	Destruction of Ozone at the Ground Surface	252
5.5	Photochemical Production and Loss of Ozone in the Unperturbed Troposphere	255
5.5.1	Reaction Mechanism	255
5.5.2	Combined Tropospheric Ozone Budget	261
6	Hydrocarbons, Halocarbons, and Other Volatile Organic Compounds	
6.1	Hydrocarbons and Some Other Organic Volatiles	265
6.1.1	Hydrocarbon Lifetimes	265

6.1.2 Anthropogenic Sources of Atmospheric Hydrocarbons	270
6.1.3 Natural Sources of Hydrocarbons and Other Organic Compounds	275
6.1.4 Hydrocarbon Mixing Ratios over the Continents	283
6.1.5 Hydrocarbons in the Marine Atmosphere	292
6.1.6 Formic and Acetic Acid	300
6.2 Hydrocarbon Oxidation Mechanisms	309
6.2.1 Alkylperoxy Radicals	310
6.2.2 Alkoxy Radicals	314
6.2.3 Oxidation of Alkanes	318
6.2.4 Oxidation of Alkenes	321
6.2.5 Aromatic Compounds	330
6.3 Halocarbons	331
6.3.1 Methyl Chloride	334
6.3.2 Chlorofluorocarbons	336
6.3.3 Fully Fluorinated Compounds	339
6.3.4 Methyl Chloroform and Carbon Tetrachloride	340
6.3.5 Methyl Bromide and Methyl Iodide	342
7 The Atmospheric Aerosol	
7.1 Introduction	346
7.2 Particulate Size Distribution	348
7.3 The Physical Behavior of Particles	355
7.3.1 Coagulation and Condensation	355
7.3.2 Interaction of Aerosol Particles with Water Vapor	364
7.4 Aerosol Sources and Global Production Rates	373
7.4.1 Mineral Sources	373
7.4.2 Sea Salt	378
7.4.3 Gas-to-Particle Conversion	383
7.4.4 Miscellaneous Sources	397
7.4.5 Global Aerosol Production Rates	401
7.5 The Chemical Constitution of the Aerosol	405
7.5.1 The Inorganic Fraction, Soluble and Insoluble	408
7.5.2 The Organic Fraction	428
7.6 Global Distribution, Physical Removal, and Residence Time of the Tropospheric Aerosol	438
7.6.1 Vertical Aerosol Distribution and Global Budget	438
7.6.2 Residence Times of Aerosol Particles	441
7.6.2 Sedimentation and Dry Deposition	447
8 Chemistry of Clouds and Precipitation	
8.1 The Water Cycle	451

8.2	Cloud and Rain Formation	455
8.3	The Incorporation of Particulate Matter into Cloud and Raindrops	461
8.3.1	Nucleation Scavenging	461
8.3.2	Below Cloud Scavenging of Particles	463
8.4	The Scavenging of Gases by Cloud and Raindrops	468
8.4.1	Gas-Liquid Equilibria in Clouds	469
8.4.2	Time Constants for the Adjustment to Equilibrium	478
8.5	Inorganic Chemical Composition and pH of Cloud and Rain Water	484
8.6	Chemical Reactions in Cloud and Fog Waters	493
8.6.1	Basic Photochemistry in Clouds	494
8.6.2	Reactions of Nitrogen Compounds	496
8.6.3	The Role of Transition Metals	499
8.6.4	The Oxidation of Sulfur Dioxide in Aqueous Solution	503
9	Nitrogen Compounds in the Troposphere	
9.1	Biochemical Processes	511
9.2	Ammonia	515
9.2.1	Distribution in the Troposphere	516
9.2.2	Sources and Sinks of Atmospheric NH_3	520
9.3	Nitrous Oxide	530
9.4	Nitrogen Dioxide, NO_2 , and Related Nitrogen Compounds	541
9.4.1	Nitrogen Oxide Chemistry	542
9.4.2	The Tropospheric Distribution of NO_x	553
9.4.3	Peroxyacetyl Nitrate	561
9.4.4	Nitric Acid and Particulate Nitrate	566
9.4.5	Total Oxidized Nitrogen	572
9.4.6	Sources and Sinks of Oxidized Nitrogen in the Troposphere	574
10	Sulfur Compounds in the Atmosphere	
10.1	Introductory Remarks	587
10.2	Reduced Sulfur Compounds	589
10.2.1	Atmospheric Abundances, Behavior, Sources, and Sinks	589
10.2.2	Atmospheric Reactions and Life Times	598
10.2.3	Terrestrial Biosphere-Atmosphere Exchange	603
10.2.4	Summary of Natural Sources of Sulfur	610
10.3	Sulfur Dioxide, SO_2 , and Particulate Sulfate	611
10.3.1	Anthropogenic Emissions	611
10.3.2	Sulfur Emissions from Volcanoes	614
10.3.3	Chemical Conversion of SO_2 to Particulate Sulfate	618

Contents	xi
10.3.4 Distribution of SO_2 and SO_4^{2-} in the Troposphere	624
10.3.5 Wet and Dry Deposition of Sulfate	639
10.4 Tropospheric Sulfur Budgets	647
10.4.1 The Regionally Polluted Continental Atmosphere	647
10.4.2 The Circulation of Sulfur in the Unperturbed Marine Atmosphere	650
10.4.3 The Global Tropospheric Sulfur Budget	652
 11 Geochemistry of Carbon Dioxide	
11.1 Introduction	657
11.2 The Major Carbon Reservoirs	658
11.2.1 Carbon Dioxide in the Atmosphere	659
11.2.2 The Oceans	660
11.2.3 Carbon in Sedimentary Rocks	666
11.2.4 The Terrestrial Biosphere	672
11.3 The Global Carbon Cycles	675
11.3.1 The Geochemical Cycles	677
11.3.2 Exchange of CO_2 between Atmosphere and Ocean	686
11.3.3 Interaction between the Atmosphere and the Terrestrial Biosphere	694
11.3.4 Long-Term Atmosphere–Biosphere Interactions and Current CO_2 Budget	698
11.4 Summary	707
 12 The Evolution of the Atmosphere	
12.1 The Noble Gases	712
12.2 The Primitive Atmosphere	721
12.3 Nitrogen	730
12.4 Oxygen	734
12.4.1 Sources of Oxygen	734
12.4.2 The Budget and Cycles of Oxygen	736
12.4.3 The Rise of Atmospheric Oxygen	744
12.5 Atmospheric Gases: Cumulative versus Cyclic Behavior	750
 <i>Appendix</i>	
Supplementary Tables	755
 <i>References</i>	777
<i>Index</i>	905
<i>Volumes in Series</i>	925

Bulk Composition, Physical Structure, and Dynamics of the Atmosphere

1.1. OBSERVATIONAL DATA AND AVERAGES

Our knowledge about atmospheric phenomena derives largely from observations. In dealing with atmospheric data, one must make allowances for the mobility of the atmosphere and a tendency of all measurable quantities to undergo sizable fluctuations. The variability of meteorological observables such as temperature, wind speed, or wind direction is common knowledge from daily experience. Concentrations of atmospheric trace constituents are often found to exhibit similar fluctuations. These variations arise in part from temporal changes in the production mechanisms that we call sources and the removal processes that we call sinks. The irregularities of air motions responsible for the spreading of trace substances within the atmosphere impose additional random fluctuations on local concentrations. It is difficult to evaluate short-term, random variations except by statistical methods, so that for most purposes we are forced to work with mean values obtained by averaging over a suitable time interval. This situation is different from that in the laboratory, where it usually is possible to keep parameters influencing