

Introduction to Atmospheric Chemistry is a concise, clear review of the fundamentals of atmospheric chemistry. In ten relatively brief chapters, it reviews our basic understanding of the chemistry of the Earth's atmosphere and some outstanding environmental issues, including air pollution, acid rain, the ozone hole, and global change.

Peter Hobbs is an eminent atmospheric chemistry teacher, researcher, and author of several well-known textbooks. This text and Hobbs' other Cambridge University Press book, *Basic Physical Chemistry for the Atmospheric Sciences* (second edition, 2000), form ideal companion volumes for a full course in atmospheric science. Subjects covered include evolution of the Earth's atmosphere; interactions between solar and terrestrial radiation and atmospheric chemical species; sources, transformations, transport, and sinks of chemicals in the atmosphere; atmospheric gases and particles; cloud and precipitation chemistry; biogeochemical cycling; air pollution; and stratospheric chemistry. Student exercises are provided at the end of each chapter.

The book is designed to be a primary textbook for a first university course (undergraduate or graduate) in atmospheric chemistry and will be adopted in departments of atmospheric science, meteorology, environmental science, geophysics, and chemistry. It is also eminently suitable for self-instruction.

**Professor Peter V. Hobbs** (University of Washington) is known internationally for his research on many aspects of the atmosphere: clouds, precipitation, aerosols, storms, atmospheric chemistry, and climate. He is the author of the definitive text *Ice Physics* (Oxford University Press), the author of *Basic Physical Chemistry for the Atmospheric Sciences* (Cambridge University Press), coauthor (with J. M. Wallace) of one of the most widely used textbooks in meteorology, *Atmospheric Sciences: An Introductory Survey* (Academic Press), and editor of several other books. He has authored more than 300 scientific papers. Professor Hobbs has served on many national and international committees, including the Scientific Steering Committee of the International Global Atmospheric Chemistry Program. He has been a visiting senior research scientist in England, France, Germany, and Italy.



## INTRODUCTION TO ATMOSPHERIC CHEMISTRY

A Companion Text to Basic Physical Chemistry for the Atmospheric Sciences

PETER V. HOBBS

University of Washington





## CAMBRIDGE UNIVERSITY PRESS

Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

Cambridge University Press
The Edinburgh Building, Cambridge CB2 2RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org

Information on this title: www.cambridge.org/9780521778008

© Cambridge University Press 2000

This publication is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published 2000

A catalogue record for this publication is available from the British Library

Library of Congress Cataloguing in Publication data

Hobbs, Peter Victor

Introduction to atmospheric chemistry / Peter V. Hobbs.

p. cm

Includes bibliographical references.

ISBN 0-521-77143-9 (hb)

1. Atmospheric chemistry. I. Title: Atmospheric chemistry. II. Title.

QC879.6 .H62 2000 551.51'1 – dc21

99-053320

ISBN-13 978-0-521-77800-8 paperback ISBN-10 0-521-77800-X paperback

Transferred to digital printing 2006

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for external or third-party Internet websites referred to in this publication, and does not guarantee that any content on such websites is, or will remain, accurate or appropriate.

The colour figures referred to within this publication have been removed for this digital reprinting. At the time of going to press the original images were available in colour for download from <a href="http://www.cambridge.org/9780521778008">http://www.cambridge.org/9780521778008</a>



## Contents

Pref	асе		page 1X	
1	Evolution of the Earth's atmosphere			
	1.1	The primitive atmosphere	2	
	1.2	Prebiotic atmosphere and the origins of life	3	
	1.3	Rise of oxygen and ozone	5	
	1.4	Oxygen and carbon budgets	6	
	1.5	Some other atmospheric constituents	9	
	1.6	The Gaia hypothesis	10	
	1.7	Summary	10	
2	Half-life, residence time, and renewal time of chemicals			
	in t	he atmosphere	13	
	2.1	Half-life	13	
	2.2	Residence time and renewal time	15	
	2.3	Spatial and temporal scales of variability	20	
3	Present chemical composition of the atmosphere			
	3.1	Units for chemical abundance	21	
	3.2	Composition of air close to the Earth's surface	23	
	3.3	Change in atmospheric composition with height	26	
4	Inte	eractions of solar and terrestrial radiation with		
	atmospheric trace gases and aerosols			
	4.1	Some basic concepts and definitions	34	
	4.2	Attenuation of solar radiation by gases	41	
	4.3	Vertical profile of absorption of solar radiation in		
		the atmosphere	43	



i		Contents	
	4.4	Heating of the atmosphere due to gaseous	
		absorption of solar radiation	45
	4.5	Attenuation of solar radiation by aerosols	50
	4.6	Absorption and emission of longwave radiation	51
	4.7	The greenhouse effect, radiative forcing, and	
		global warming	54
	4.8	Photochemical reactions	57
5	Sou	rces, transformations, transport, and sinks of	
	che	micals in the troposphere	63
		Sources	63
	5.2	Transformations by homogeneous gas-phase	
		reactions	72
		Transformations by other processes	78
	5.4	Transport and distributions of chemicals	79
	5.5	Sinks of chemicals	80
6	Atmospheric aerosols		
	6.1	Aerosol concentrations and size distributions	82
	6.2	Sources of aerosols	91
	6.3	Transformations of aerosols	95
	6.4	Chemical composition of aerosols	97
	6.5	Transport of aerosols	99
	6.6	Sinks of aerosols	100
	6.7	Residence times of aerosols	102
	6.8	Geographical distribution of aerosols	104
	6.9	Atmospheric effects of aerosols	104
7	Cloud and precipitation chemistry		
		Overview	111
	7.2	Cloud condensation nuclei and nucleation	
		scavenging	113
	7.3	Dissolution of gases in cloud droplets	121
	7.4	Aqueous-phase chemical reactions	125
	7.5	Precipitation scavenging	131
	7.6	Sources of sulfate in precipitation	134
	7.7	Chemical composition of rainwater	135
	7.8	Production of aerosols by clouds	137



		Contents	vii		
8	Tropospheric chemical cycles				
	8.1	Carbon cycle	143		
	8.2	Nitrogen cycle	149		
	8.3	Sulfur cycle	151		
9	Air pollution				
	9.1	Sources of anthropogenic pollutants	153		
	9.2	Some atmospheric effects of air pollution	156		
10	Stratospheric chemistry				
	10.1	Unperturbed stratospheric ozone	165		
	10.2	Anthropogenic perturbations to stratospheric ozone	171		
	10.3 Stratospheric aerosols; sulfur in the stratosphere				
App	endix .	Exercises	185		
Appendix II		I Answers to exercises in Appendix I and hints			
		and solutions to the more difficult exercises	206		
Appendix III		III Atomic weights	235		
Appendix IV		TV The International System of Units (SI)	238		
Appendix V		V Some useful numerical values	240		
Appendix VI			241		
Inde.	x		242		



## **Preface**

This short book is a companion volume and a natural extension to my textbook entitled *Basic Physical Chemistry for the Atmospheric Sciences* (Cambridge University Press, 1995; second edition published in 2000). Together these two books provide material for a first (undergraduate or graduate) course in atmospheric chemistry; they should also be suitable for self-study.

In *Basic Physical Chemistry for the Atmospheric Sciences* the groundwork was laid for courses in atmospheric chemistry and other areas of environmental chemistry. The present book provides a short introduction to the subject of atmospheric chemistry itself. Twenty years ago this subject was a minor branch of the atmospheric sciences, pursued by relatively few scientists. Today, atmospheric chemistry is one of the most active and important disciplines within meteorology, and one with which every geoscientist and environmental scientist should have some familiarity.

The emphasis of this book is on the basic principles of atmospheric chemistry, with applications to such important environmental problems as air pollution, acid rain, the ozone hole, and global change. In keeping with the pedagogical approach of its companion volume, model solutions are provided to a number of exercises within the text. In an appendix, readers are invited to test their skills on further exercises. Answers to all of the exercises and worked solutions to the more difficult ones, are provided.

Thanks are due to Halstead Harrison for allowing me to use some of his exercises, and to Richard Gammon, Dean Hegg, Daniel Jaffe, Robert Kotchenruther, Conway Leovy, Donald Stedman, and Stephen Warren for reviewing various portions of this book. I thank also the National Science Foundation and the National Aeronautics and Space Administration for their support of my own research on atmospheric chemistry.



x Preface

Comments on this book, which will be gratefully received, can be sent by e-mail to phobbs@atmos.washington.edu. Current information on the book, including any errata, can be found on http://cargsun2.atmos.washington.edu/~phobbs/IntroAtmosChem/Info.html.

Peter V. Hobbs Seattle