



Chemistry of the Environment

Second Edition

Thomas G. Spiro • William M. Stigliani

CHEMISTRY OF THE ENVIRONMENT

SECOND EDITION

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Library of Congress Cataloging-in-Publication Data

Spiro, Thomas G.
Chemistry of the environment / Thomas G. Spiro, William M.
Stigliani. -- 2nd ed.
p. cm.
Includes bibliographical references and index.
ISBN 013-754896-6 (hardcover)
I. Environmental chemistry. I. Stigliani, William M. II. Title.
TD193 .S7 2003
540—dc21 2002022048

Editor in Chief, Physical Sciences: John Challice

Project Manager: Kristen Kaiser

Senior Marketing Manager: Steve Sartori

Editorial/Production Supervision: ICC

Assistant Manufacturing Manager: Michael Bell

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Copy Editor: Bob Cooper

Art Director: Jayne Conte

Cover Designer: Bruce Kenselaar

Cover Image: Photodisc

The image used on Part and Chapter starting pages is courtesy of Digital Imagery © Copyright 2001 PhotoDisc, Inc.



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Upper Saddle River, NJ 07458

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Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

ISBN 0-13-754896-6

Pearson Education LTD.

Pearson Education Australia PTY, Limited

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PREFACE

This book is about environmental issues and the chemistry behind them. It is not a methods book, nor is it a catalog of pollutants and remediation options. It aims to deepen knowledge of chemistry and of the environment and to show the power of chemistry as a tool to help us comprehend the changing world around us.

In the six years since the first edition of *Chemistry of the Environment* was published, the frontiers of environmental science have advanced rapidly, and the debates on environmental issues have shifted ground. In this new edition, we have updated the various strands of our environmental story by integrating new facts and figures in the text, tables, and diagrams. [Recognizing that no book on environmental themes can stay current for long, we plan to post further updates on our website <http://www.prenhall.com/spiro2>]. Some of the new material [e.g., ocean chemistry and the inorganic carbon cycle (pp. 284–288), or the evolution of the oxygen atmosphere (pp. 316–319)] might have been included earlier, but some topics had not surfaced six years ago. These include genetically modified crops (pp. 401–406), carbon sequestration as a strategy for reducing greenhouse gas emissions (pp. 42–43, 288), and contamination of drinking water by the gasoline additive MTBE (pp. 260, 271, 344).

Chemistry of the Environment can be used in a one- or two-term environmental chemistry course. The instructor in a one-term course will want to pick a limited set of the book's topics for special emphasis; in a two-term course there would be time to address other topics and to explore the underlying chemical principles in more detail. The new edition is also suitable for basic environmental science courses. Readers will find that the biggest change from the first edition is improved accessibility through reorganization and expansion of the basic chemistry. We have separated background material relevant to the understanding of the topic under discussion into boxes marked Fundamentals. We have also added additional basic material, to help those readers without exposure to college chemistry, and to refresh the memories of those who have had such exposure. In addition, we have included worked problems in other boxes, and have added more end-of-chapter problems. A periodic table is now included, as is an Appendix that gives a brief introduction to organic chemical structures. Some of the Fundamentals boxes contain non-chemical background information [e.g., how to relate reservoirs and flows in environmental chemical cycles, p. 285–286].

In addition, we have separated the more advanced or specialized technical information into other boxes called Strategies, which readers can read or skip at their discretion. In this way, the environmental story line is unimpeded by background or technical information. We hope that these changes will make the book easier to read, and also more useful as a textbook.

We are indebted to a number of colleagues for reviewing parts of the manuscript, and/or providing new material: Drs. Michael Bender, Andrew Bocarsly, Harold Feiveson, Robert Goldston, Peter Jaffe, Hiram Levy, Francois Morel, Steve Pacala, Lynn Russel, Jorge Sarmiento, Daniel Sigman, Robert Socolow, Valerie Thomas (all from Princeton University); Trace Jordan (New York University); Bibudhendra Sarkar (University of Toronto); David Walker (University of British Columbia); and Chris Weber (student assistant, University of Iowa). Helen Spiro provided encouragement throughout the writing, and key editorial advice. Thanks also to Marie Stigliani—her companionship on bicycle trails along the Cedar River provided balance to long days at the office.

Supplements

Instructor's Solutions Manual—(0-13-017843-8) Contains the full solution to all end-of-chapter problems and is available to instructors upon adoption.

Companion Website—<http://www.prenhall.com/spiro2> This on-line site brings you abstracts of relevant environmental chemistry articles in newspapers, magazines, and scientific journals.

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*Dedicated to
our wives Helen and Marie,
and to our children and their generation*

INTRODUCTION

“Here’s a short chemistry lesson,” wrote Bill McKibben in a *New York Times Magazine* feature story.* “Grasp it and you will grasp the reason the environmental era has barely begun. . . .” McKibben’s lesson is about the difference between two molecules, carbon monoxide (CO) and carbon dioxide (CO₂). Today’s automobiles release half a pound of carbon as CO per gallon of gasoline burned, around half as much as they did a generation ago, and the rate is going down with continuing improvements in technology. As a result, the air is now cleaner than it used to be in Los Angeles and in many other cities. But the same gallon of gasoline releases almost five and a half pounds of carbon as CO₂, and this rate cannot be decreased. The atmospheric concentration of CO₂ is increasing world-wide, and bringing global warming with it, according to a consensus of international scientific opinion. The two molecules capture two sides of the environmental coin, local versus global effects of human activity. Environmental quality has improved in many localities, thanks to environmental controls and new technologies, but the global problems are just beginning to be addressed, and they are much more difficult to solve. CO is a side-product of combustion, and is subject to emission controls, but CO₂ is the end-product of combustion and is the inevitable accompaniment of our reliance on fossil fuels. “CO versus CO₂,” says McKibben, “one damn oxygen atom, and all the difference in the world.”

To us this is a wonderful illustration of the power of chemistry to illuminate environmental issues. Chemistry is all around us, and it really does make a difference. The chemical cycles of the planet are increasingly disturbed by human activities, and these disturbances can degrade the quality of life, as when auto emissions overwhelm the atmosphere’s capacity to clean the air over our cities. We are capable of ameliorating these perturbations, as the experience of Los Angeles demonstrates. But first we must understand the chemistry. In the case of Los Angeles, initial attempts to alleviate smog back in the 1960s actually made things worse. Standards were imposed on CO and hydrocarbon levels in auto emissions, and auto makers met those standards by increasing the air/fuel ratio to burn the fuel more completely. But smog levels *increased* because higher air/fuel ratios

*Bill McKibben, “Not So Fast,” *New York Times Magazine*, July 23, 1995, pp. 24–25.

made combustion hotter, thereby increasing the nitrogen oxide emissions. Only then was it discovered that nitrogen oxides and hydrocarbons are *both* key actors in smog formation and that both have to be controlled. This kind of surprise is not unusual in environmental affairs. The world is a marvelously complex place, chemically, as in other ways. We are just beginning to understand how it works.

This book tells the environmental story in chemical language. It is grounded in the flows of chemicals and energy through nature on the one hand, and through our industrial civilization on the other. The units of the book, Energy, Atmosphere, Hydrosphere/Lithosphere, and Biosphere, reflect this holistic perspective. Environmental issues frequently cut across these divisions, and the resulting interconnections add richness to the story. For example, leaded gasoline is linked to the issue of auto emission controls, a subject that arises in the Atmosphere section, but it is also a major health hazard, as discussed in the Biosphere section.

Interconnections are even more numerous at the level of the underlying chemistry. For example, the reactivity of dioxygen, O_2 , is a leitmotif for all parts of the book. Thus energy flow through industrial civilization (as well as through the biosphere itself) depends on the oxygen-oxygen bond being relatively weak, so that energy is released when O_2 combines with organic molecules. Yet, because of its unusual electronic structure, O_2 is quite unreactive until it encounters a free radical or a transition metal ion. These O_2 activators determine most aspects of atmospheric chemistry, including how smog is formed. They are also vitally important for the biosphere, since O_2 metabolism gone awry is a threat to the integrity of biological molecules and has been implicated as a factor in cancer and aging.

We hope these interconnections fascinate the reader as much as they fascinate us, and we hope the tapestry we weave will provide a satisfying context for understanding the chemical world we live in and the environmental issues we face.

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PART I

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SUMMARY

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CHAPTER 1

ENERGY FLOWS AND SUPPLIES

The question of energy use underlies virtually all environmental issues. The harnessing of energy for the manifold needs of industrial civilization has driven economic development, and access to affordable energy has been the key to a better life for people around the world. At the same time the environmental costs of human energy consumption are becoming ever more apparent: oil spills, the scarring of land by mining, air and water pollution, and the threat of global warming from the accumulation of carbon dioxide and other greenhouse gases. Increasingly, maintaining an expanding supply of cheap energy seems to clash with concern for the environmental costs of such expansion. In this part of the book, we explore the background of energy production and energy consumption, and examine the prospects for meeting the energy needs of society while protecting the environment.

1.1 PROLOGUE ON ENERGY AND SUSTAINABILITY

Environmental discussions often revolve around *sustainability*, an evocative and much-debated idea. It arises from the perception that human activity is using up nature's resources at rates beyond the capacity of nature to restore them. Sustainability implies maintaining these resources for future generations.

The concept has many applications. *Sustainable logging*, for example, refers to extracting wood in ways that permit regeneration of forests. *Sustainable agriculture* would feed people without depleting the nutritive capacity of the soil or the biodiversity of natural habitats. A growing number of companies embrace sustainability by protecting the environment in ways that go beyond legal requirements. Examples include voluntarily