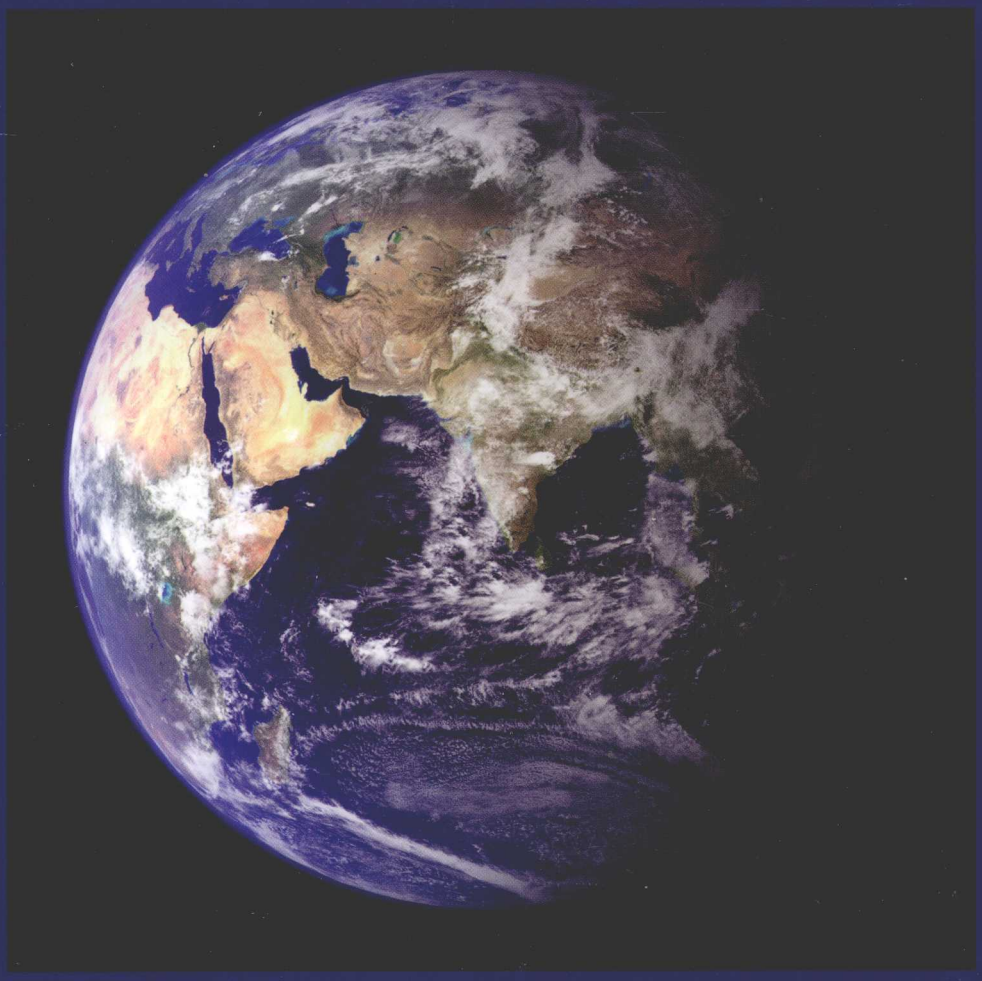
CHEMISTRY OF THE ENVIRONMENT

THIRD EDITION



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Dedicated to our children and grandchildren, and their generations.

FOREWORD

Chemistry of the Environment by Spiro, Purvis-Roberts, and Stigliani fills a critical need by providing a coherent chemical account of the environmental issues we face. From air pollution and climate change, to acid rain and oil spills, to food security and genetically modified plants, to carcinogens and lead poisoning, *Chemistry of the Environment* puts the environmental story in chemical context, showing how the problems arise and pointing ways to their solutions.

I am particularly pleased that the authors have devoted an entire part of their book to Energy and Materials, as I firmly believe that energy production and utilization are key to human welfare as well as the source of most environmental problems. The Energy and Materials part sets out the challenges we face, and points to the many opportunities to develop new chemistry for efficient energy production and use. It will be especially helpful to young investigators entering the field.

Spiro, Purvis-Roberts, and Stigliani write in a clear and engaging style. They organize the material in a logical and compelling manner, emphasizing the many cross-connections among environmental topics.

The bottom line is that this is *the book on environmental chemistry that we all have been waiting for*! It is a must-read for young and old alike.

Harry Gray

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PREFACE

Environmental Chemistry Lessons

"Here's a short chemistry lesson," wrote Bill McKibben in a 1995 *New York Times Magazine* feature story.[a] "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 (CO_2). 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 one-half pounds of carbon as CO_2, and this rate cannot be decreased. The atmospheric concentration of CO_2 is increasing worldwide, and bringing global warming with it. 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. Carbon monoxide is a side product of combustion and is subject to emission controls, but CO_2 is the end product of combustion and is the inevitable accompaniment of our reliance on fossil fuels. "Carbon monoxide versus carbon dioxide," says McKibben, "one damn oxygen atom, and all the difference in the world."

McKibben's story 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. 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 effects, as the experience

[a] B. McKibben, "Not So Fast," *New York Times Magazine*, July 23, 1995, pp. 24–25.

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 made combustion hotter, thereby increasing the nitrogen oxide (NO_x) emissions. Only then was it discovered that nitrogen oxides and hydrocarbons are *both* key players 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 the language of chemicals. 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 parts of the book, Sustainability and Green Chemistry, Atmosphere, Energy and Materials, Hydrosphere and 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 Part II, Atmosphere, but it is also a major health hazard, as discussed in Part V, Biosphere.

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.

These interconnections provide a satisfying context for understanding the chemical world we live in and the environmental issues we face.

What This Book Is About

This book is about the natural chemical cycles that form our world, and how humans are altering these cycles. Our world contains many chemical elements, which combine into a much larger number of compounds. Under the influence of the energy flowing out of earth's molten core and from the sun, these compounds are continually transformed into one another and back. These transformations occur in earth's crust, in its waters, and in its atmosphere. The cycles are linked, one reaction depending on others, according to the laws of chemistry.

Life evolved in harmony with these cycles, and has also altered them substantially. The rise of human civilizations has magnified this impact, first through the spread of agriculture and then through the development of manufacturing technologies. The modern industrial era accelerated the pace of chemical change, and now we see evidence everywhere of chemical imbalances that threaten human well-being, and even the continued existence of entire ecosystems. Increasingly, we are concerned whether our practices are sustainable.

What are the key threats to our environment, and how can they be averted? How can chemistry contribute to the sustainablility of our world? These are the questions that animate this book. It is organized around the environmental story, and it brings science in as needed to illuminate that story. Some familiarity with chemistry is assumed, but freshman chemistry, or a good high school course should be sufficient.

The book considers the following topics:

- Sustainability, and the role of "green chemistry" in reducing human impacts.
- The chemistry of the atmosphere, and how it determines the issues of climate change, protection from ultraviolet (UV) radiation, and air pollution.
- Energy, and how we obtain and use it, with emphasis on how we can reduce its environmental impact, particularly on climate.
- The chemistry of the hydrosphere, and the problems of acidification of fresh and ocean waters, and of water overfertilization and pollution.
- The biosphere, focusing on the role of agriculture and the spread of toxic compounds, both organic and inorganic.

Through these chapters, readers will learn about the critical role of chemistry in the great environmental issues of our time. This understanding can help to inform their actions as participants in our human enterprise.

Acknowledgments

This book is a successor to *Chemistry of the Environment,* eds. 1 and 2, by Spiro and Stigliani (Prentice Hall, 1996, 2003). The material has been extensively revised, reflecting the rapid evolution of all areas of environmental science and of environmental concerns. Much of the text has been rewritten for clarity, and the organization has been simplified for smoother flow. Additional worked and end-of-chapter problems have been provided, and the lists of additional readings have been updated.

We are indebted to a number of individuals who helped us improve the book. Douglas Fox, John Perona, and Richard Treptow read parts or all of the book, and provided extensive suggestions. Keith Kuwata tested several sections of the book in class, and provided thoughtful feedback from his students.

Special thanks go to Kirk Smith, Jim Purvis, Alexandra Soldatova, and Robert Socolow, for help with the Air Pollution, Nuclear Energy, Renewable Energy, and Energy Utilization chapters, and to Bruce Ames and Lois Gold for a helpful critique of the material on carcinogens in Chapter 19, Toxicity of Chemicals.

We are especially grateful to Helen Spiro and Jon Roberts for reading and helping revise some of the material, and for their patient and loving support and advice during the long and arduous process of crafting the book.

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