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ACADEMIC PRESS **New York San Francisco London** **1978**
A Subsidiary of Harcourt Brace Jovanovich, Publishers

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Main entry under title:

Introduction to chemistry of the environment.

Includes bibliographies.
1. Environmental chemistry. I. Bailey, Ronald Albert, Date
QD31.2.I57 540 78-11293
ISBN 0-12-073050-2

PRINTED IN THE UNITED STATES OF AMERICA

78 79 80 81 82 9 8 7 6 5 4 3 2 1

PREFACE

This book was developed from the notes for a course in "Chemistry of the Environment" given by the authors over the past several years to juniors, seniors, and graduate students in Science and Engineering at Rensselaer Polytechnic Institute. While in its present form this book may serve as a text for a course of this sort, it also can be a valuable background source for those who wish to broaden their understanding of the chemical processes important in the environment, or who require a more thorough grounding in particular aspects of environmental chemistry. It should be useful to the chemist who finds that his or her conventional courses have not dealt adequately with environmental topics or to the nonchemist who needs to expand his knowledge in this area. The nonchemist, however, will need some knowledge of basic chemistry, including elementary organic chemistry, in order to profit from some areas of this book. The objective is to take the reader from a basic level of chemical knowledge to the point where he can deal with advanced monographs and the research literature in environmental chemistry.

The topics covered reflect to some extent the interests of the authors, but we have emphasized those subjects that seem to be of greatest environmental importance. Thus, we have dealt extensively with petroleum, chlorinated hydrocarbons, pesticides, heavy metals, nuclear chemistry, and atmospheric chemistry. We have also dealt with topics such as atmospheric circulation, which are important to understanding environmental processes. Both natural processes and technological processes that impinge on the environment are included. Obviously, not all important topics have been discussed, but the principles included here should be widely applicable to a general understanding of environmental problems. While specific environmental problems may vary, the basic chemistry of environment processes do not change. For example, the chemical and biochemical processes for the environmental degradation of crude oil or a plastic cup are the same. Knowledge of the chemistry as presented here will be applicable both to existing problems and to new problems as they arise.

A bibliography of items ranging from the very general to the very specific is given at the end of each chapter for those who wish to pursue a topic in depth. These references are not intended to provide complete coverage of a subject, but they will provide a significant introduction to the literature of many environmental problems.

Anyone dealing with the broad aspects of the environment must expand his or her knowledge into many fields of science and technology. One of the problems encountered while reading the literature in all these areas arises from the terminology and traditionally established units in each of the fields. We have chosen, as a practical matter, to use the units that are normally encountered in the literature of each field. In the interest of uniformity, however, we have very often expressed a given value for some property or process in both conventional and SI units.

We are indebted to many of our students for helpful suggestions during the development of this book. We also thank our colleagues, Professor Harry Herbrandson in particular, for valuable comments and suggestions.

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1
INTRODUCTION

1.1 GENERAL

Man evolved on earth with its atmosphere, land and water systems, and types of climate in such a way that he can cope reasonably well with this particular environment. Being intelligent and inquisitive, mankind has not only investigated the environment extensively, but has done many things to change it. Other living things also change their environment; the roots of large trees can crack rocks, the herds of elephants in present-day African game parks are uprooting the trees and turning forests into grasslands, but no other living thing can change its environment in so many ways or as rapidly as man. The possibility exists that man can change his environment into one that he cannot live in, just as the African elephant may be doing on a smaller scale. The elephants cannot learn to stop uprooting the trees they need for survival, but we should be capable of learning about our environment and about the problems we ourselves create.

One of the vital problems (among the many) that man must solve is how to continue his technologically based civilization without at the same time damaging irreversibly the environment in which he evolved and which supports his life. This environment is complex; the interrelations of its component parts are subtle and sometimes unexpected, and stress in one area may have far-reaching effects. This environment is also finite (hence, we have the expression "spaceship earth"). That being so, there is necessarily a limit to all things that can be tolerated before significant environmental changes take place. Modern society places extreme stress on the environment, and many environmental problems come from prior failure to understand what these limits are.

In this book, we shall use the term environment to refer to the atmosphere-water-earth surroundings that make life possible; basically this is a physicochemical system. Man's total environment consists also of cultural and esthetic components, which we shall not consider here. Neither shall we deal extensively with ecology--that is, with the interaction of living things with the environment--although some of the effects of the physiochemical system on life, and conversely, of living things on the physicochemical environment, will be included.

An immediate association with "environment" is "pollution." What constitutes a pollutant is not easily defined. One tends to associate the term with man-made materials entering the environment with harmful effects especially on living organisms--for example, SO_2 from combustion of sulfur-containing fuels, or hydrocarbons that contribute to smog. However, these and other "pollutants" would be present even in the absence of man, sometimes in considerable amounts. We shall consider a "pollutant" to be any substance not normally present, or which is present in larger concentrations than normal. Although any discussion of the environment must consider pollution, this will not be our primary aim. Rather, we shall be concerned with some of the more important chemical principles that govern the behavior of the physicochemical environment and the interactions of its various facets.

Two human activities that are strongly connected with environmental chemistry in general and pollution in particular are waste disposal and energy production. A few aspects of the chemistry of these activities will be considered later. Some general comments are given to serve as an introduction to the scope of the problem.

1.2 WASTE DISPOSAL

The environmental system represents a very large amount of material: 5×10^{18} kgm of air and 1.5×10^{18} m^3 of water. In principle, comparatively large amounts of other materials can be dispersed in these, and consequently both the atmosphere and water bodies have long been used for disposal of wastes. This is sometimes done directly, and sometimes after partial degradation such as by incineration. In part, such disposal is based on the principle of dilution; when the waste material is sufficiently dilute, it is not noticeable and perhaps not even detectable. A variety of chemical and biological reactions may also intervene to change such input into normal environmental constituents e.g., the chemical degradation of organic materials to CO_2 and H_2O.

Such disposal-by-dilution methods are not necessarily harmful in principle, but several factors must be considered in practice. The first is the problem of mixing. While the eventual dilution of a given material may be acceptable, local concentrations may be quite high since mixing is far from instantaneous. As the disposal of wastes from more and more sources becomes necessary because of population or industrial growth in a particular area, it becomes more difficult to avoid undesirable local excess either continuously or as natural mixing conditions go through inefficient periods. A second factor of long-term importance is the rate of degradation of waste material. It is obvious that if the rate of removal of any substance from a given sector of the environment remains slower than its rate of input, then the concentration of that material eventually will build up to an undesirable level. This is the case with many modern chemical products, including some pesticides and plastics that are only very slowly broken down into normal environmental components or rendered inaccessible by being trapped in sediments. Global contamination by such materials results from the dilution and mixing processes, and concentration levels increase while input continues. The examples of DDT and PCBs, discussed in Chapter 7, are well known. Other examples, such as the occurrence of pellets of plastics in significant amounts even in the open ocean, may ultimately be of equal concern.

A third problem in disposal by dilution is the question of what concentration is necessary before harmful effects are produced. This is often difficult to answer, both because effects may be slow to develop and noticeable only statistically on large samples, and because in many cases concentrations less than the part per million range have to be considered. This is very low indeed, and often methods of detection and measurement become limiting. However, various natural processes of reconcentrating materials may bring levels well above those expected on the basis of uniform mixing of even small portions of the environmental sink available (e.g., DDT and mercury in the food chain). Finally, synergistic effects may come into play--that is, two or more substances that exist at concentrations that separately present no problems, together may be much more deleterious.

Disposal by burying is a process that does not depend on dilution. In general, however, it ultimately depends either on degradation to harmless materials, or alternatively on the hope that the material stays where it is put. Such considerations are particularly important with highly toxic or radioactive waste materials. Leaching of harmful components from such disposal sites and consequent contamination of ground water or extraction from soils and concentration in plants are obvious concerns with such disposal methods.

Disposal of insoluble materials in the oceans also depends upon the principle of isolation of the waste. Solid materials may be attacked by sea water and harmful components leached out into the water. Barrels or other containers for liquid wastes may be corroded and leak. Contamination of the biological environment is a possible result. Ocean currents may play a role in distributing such wastes in unforeseen ways, as is the case with New York City sewage sludge that has been dumped in the Atlantic Ocean.

It is clear that understanding of a disposal problem involves knowledge of physical processes such as mixing, chemical processes that are involved in degradation reactions, chemical reactions of the waste and its products with various aspects of the environment, biological processes, meteorological processes, geology, oceanography, etc. Scientific understanding in all of these fields and the interactions among them are necessary to understand not only waste disposal but environmental problems generally. In this book we shall discuss some of the chemistry involved.

1.3 PROBLEMS ASSOCIATED WITH ENERGY PRODUCTION

Energy production is a major activity of modern man that gives rise to many environmental problems. Some of these problems are associated with the acquisition of the energy source itself (e.g., acid mine drainage, oil spills), others with the energy production step (e.g., combustion by-products such as CO, SO_2, partially burned hydrocarbons, nitrogen oxides), while still others arise from disposal of wastes (e.g., nuclear fission products). In any device depending on conversion of heat to mechanical energy, (e.g., a turbine) the fraction of the heat that can be so converted depends on the difference between the temperature at which the heat enters, and that at which it leaves the device. Practical restrictions on these temperatures limit efficiency, and also result in waste heat that must be dissipated, because it is not practical to make the exhaust temperature equal to ambient temperatures. This leads to the problem of thermal pollution. Such efficiency considerations also lead to the desire for ever higher input temperatures (i.e., the temperature in the combustion chamber). This in itself can produce secondary pollution problems, such as enhanced generation of nitrogen oxides. Some aspects of the energy problem are discussed in Chapter 2.

1.4 THE SCOPE OF CHEMISTRY OF THE ENVIRONMENT

Almost everything that happens in the world around us could come under the general heading "Chemistry of the Environment." Chemical reactions of all kinds occur continuously in the atmosphere, in oceans, lakes, and rivers, in all living things, and even underneath the earth's crust. These reactions take place quite independent of man's activities. The latter serve to complicate an already complex subject.

In order to understand environmental problems, we must have knowledge not only of what materials are being deliberately or inadvertently released into the environment, but also what processes they then undergo. More than this, we need to understand the general principles underlying these processes so that reasonable predictions can be made about the effects to be expected from new but related substances. We must also understand the principles that underlie natural environmental processes in order to anticipate interferences from man's activities. Since this book is chemistry-oriented, the chemical principles underlying environmental processes are emphasized. However, knowledge in biological, meteorological, oceanographic, and other fields is equally important to the overall understanding of the environment. Indeed, although it is convenient to segment topics for study purposes, Commoner's first law of the environment should always be kept in mind: "Everything is related to everything else."

2
ENERGY

2.1 INTRODUCTION

Figure 2.1 shows the annual energy flow pattern in the United States for a recent year. Changes in this picture have been relatively minor, except that our oil imports and our total energy consumption have increased. Many observations important to the discussion in this chapter can be made using Fig. 2.1. From the left-hand side, which shows the energy sources, the enormous preponderance of fossil fuels (oil, coal, and natural gas) in our energy picture is obvious. These energy sources are limited in amount and irreplaceable, except over huge stretches of geologic time. This alone makes it important for us to discover how to use these energy sources most efficiently. Furthermore, some of these energy sources, especially petroleum, are valuable sources of chemicals in addition to their value as fuels.

With regard to efficiency, it is apparent from the right-hand side of Fig. 2.1 that roughly 50% of the total energy input becomes "rejected energy." This rejected energy and its frequent inevitability will be considered below; it is a consequence of one of the major laws of science, specifically, of the second law of thermodynamics (Section 2.2.1). Whether this heat is used further, i.e., to heat a dwelling or work-place or to provide heat for a high-temperature chemical re-action, or whether it is discarded depends on circumstances. If we ever wish to use energy with efficiency, it will be necessary to find ways of turning much of the present rejected energy into useful heat. It has been suggested, for example, that the waste heat from nuclear power plants might be used to heat large enclosed areas in order to use them as greenhouses, i.e., in order to grow tropical fruits such as bananas in Vermont!

Present day use of electrical energy is particularly inefficient, because rejected or waste heat appears both during the generation of the electricity and during its use for residential, commercial, and industrial purposes. It should become possible to generate electrical energy with much lower heat losses in the future, but this will only be possible when more of our electrical energy is generated without the use of

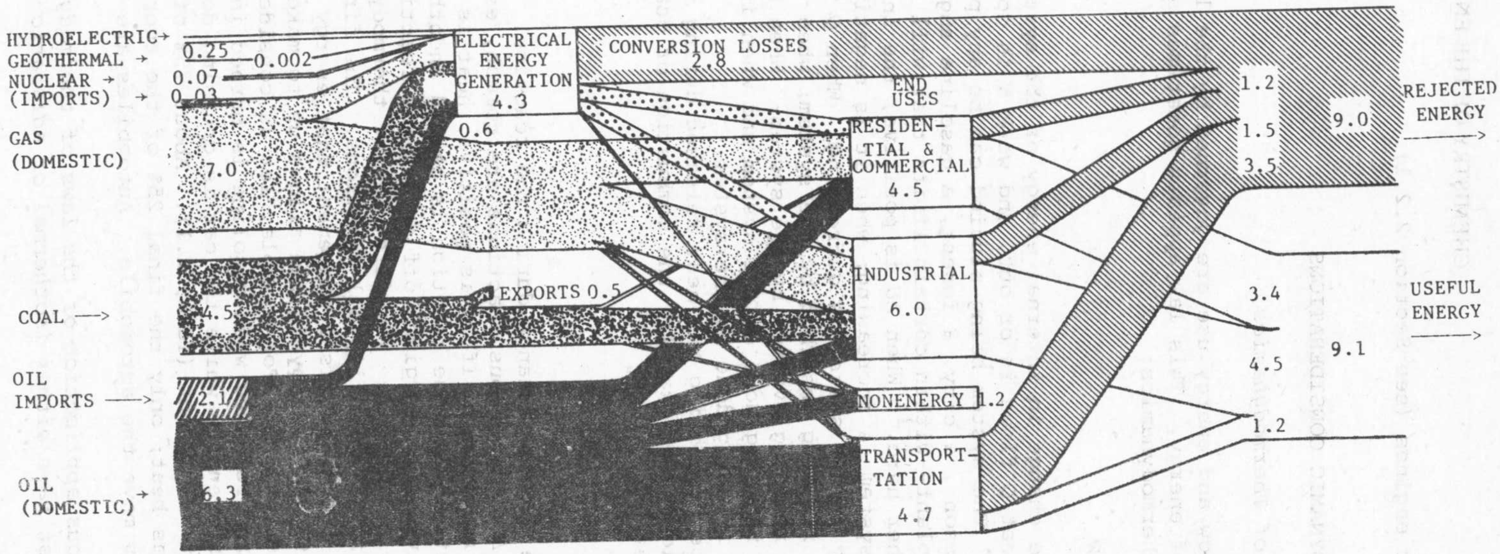

Fig. 2.1. The energy flow pattern in the U.S. in 1976. The units are in terms of Q (quads) (1Q = 10^{15} Btu = 1.055 × 10^{18} J). From W. J. Ramsey, U.S. Energy Flow in 1976, Lawrence Livermore Laboratory, March 24, 1977.

so-called heat engines (see Section 2.2.1).

2.2 THERMODYNAMIC CONSIDERATIONS

2.2.1 Laws of Thermodynamics

Energy flow and energy use are governed by the law of conservation of energy. This law appears sometimes as the first law of thermodynamics:

$$\Delta U = Q + W \tag{2.1}$$

where ΔU is the change in internal energy of the system being studied when heat Q flows in or out, and work W is done on or by the system. The system being studied can be any part of the universe--a person , a city, a forest, a gasoline engine, a nuclear power plant--within certain limits that will not be discussed further here.[1] When ΔU is positive, the internal energy of the system is increasing; when it is negative, the internal energy of the system is decreasing. When Q is positive, heat is being absorbed by the system; when it is negative, heat is being evolved by the system. When W is positive, work is being done *on* the system and when it is negative, work is being done *by* the system.

We shall be discussing the heat released during various chemical reactions, for example, the combustion of coal or oil. At constant pressure,

$$Q = \Delta H \tag{2.2}$$

where ΔH is the enthalpy change during the reaction. Tabulations of ΔH for various reactions are common, especially for combustion reactions. If ΔH is positive, heat is absorbed during the reaction, and the reaction is called endothermic; if ΔH is negative, heat is given off during the reaction, and the reaction is exothermic. The first law of thermodynamics [Eq. (2.1)] is followed during all reactions. The first law of thermodynamics, by itself, is a statement that energy can neither be created or destroyed, and allows us to make certain instructive calculations. For example, let us consider the fate of the energy released when gasoline is burned in an average automobile engine while the car is cruising down a highway at about 50 mi/hour (Table 2.1). About 75% of the energy appears as heat; only the final 25% of the energy in the table is used to move the automobile. Autombiles are thus a

[1] *For rigorous application of the laws of thermodynamics to a system, it must have either isothermal or adiabatic boundaries at any time.*