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Basic Concepts of Environmental Chemistry, 2nd Edition
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The Role and Importance of Environmental Chemistry

1.1 ALCHEMY

Modern chemistry has its early beginnings in ancient Greece and Egypt. The Greeks were great philosophers and thinkers and debated the ultimate nature of the material world that surrounded them. On the other hand, the Egyptians were skilled in the practical arts of applied chemistry. They had an intimate knowledge of such matters as embalming of the dead, dyeing of clothing, and the isolation of some metals. In fact, the word alchemy is derived from the Arab word al-kimiya. This phrase was used to describe the art of transformation of materials and the practical use of chemicals in society. However, the lack of understanding of chemical processes led to alchemy being more of an art than a science. The art of alchemy was closely related to religion and involved the use of a set of hieroglyphics to represent the different metals. For example, gold was depicted as the sun, silver as the moon, copper as Venus, and so on. The occurrence of chemical changes was interpreted in a mysterious fashion and took on a mythological significance. The major area of concern of alchemy was not the development of a science, but the transmutation of metals, particularly the transmutation of base metals such as lead into gold.

The decline of alchemy was signaled by the works of such scientists as Agricola, in fact a German named Georg Bauer, who lived between 1494 and 1555. Agricola published a book titled De Re Metallica [Of Metallurgy], which took a practical approach and gathered together all of the knowledge available on metallurgy at the time. Also, the German scientist Andreas Libau (1540–1616), better known as Libavius, published Alchemia in 1597. Despite the name of this text, the book is written clearly and without resort to mysticism. The famous Swiss physician Paracelsus (1493–1541), although an alchemist, believed that the processes that occur in the human body are basically of a chemical nature and that chemical medicines could provide remedies to illness. So this marks the start of the development of chemotherapy, and doctors everywhere now use a vast array of chemicals to cure all kinds of illnesses.

Perhaps the end to alchemy occurred in 1661, when Robert Boyle, an Irishman, published his book The Sceptical Chymist. Boyle attacked the ideas and approach of the alchemists and advocated a rational scientific approach. To mark the change from alchemy, Boyle also advocated the use of the term chemistry to describe the science of materials. The well-known Boyle’s law was developed and amply illustrates the scientific approach to chemistry that he promoted.
It could be said that **environmental chemistry** had its beginning with one of the great pioneers of chemistry, Antoine Lavoisier, who was born in Paris in 1743. Lavoisier’s experiments on the atmosphere mark a great advance in chemistry and also a great advance in understanding the chemistry of the atmospheric environment. Not only did he discover fundamental information concerning the chemistry of air, but he also examined the use of air by animals and, by so doing, was investigating one of the major aspects of the chemistry of the environment. The use of oxygen by animals, and their consequent release of carbon dioxide, is a fundamental aspect of environmental chemistry. Lavoisier’s *Elementary Book of Chemistry*, published in 1789, effectively marks the start of the systematic development of the then new science of chemistry.

### 1.2 THE CHEMICAL AGE

In the first half of the 19th century, early chemists were endeavoring to describe the nature of molecules. They were taking the first steps in assembling the structures of organic chemicals, which we now take for granted as common scientific knowledge. As they were carrying out this early work, they were concerned with the reactions between organic chemicals and the nature of the products generated, thus embarking on the path to modern synthetic organic chemistry.

One of these early chemists, William Perkin (1838–1907), became aware that some of these synthetic organic chemical processes could possibly be turned to commercial advantage. Perkin left his academic studies at the university and used money obtained from his family to start a factory to manufacture synthetic dyes. One dye he produced, aniline purple, was extremely popular in the textile industry and in heavy demand with textile manufacturers in Europe. In fact, Perkin had founded the first chemical industry to be based on studies of the nature of organic compounds conducted in a research environment. Not only had he founded the synthetic chemical industry, but he was also able to retire a very wealthy man at an early age. This marks the start of the synthetic chemical industry, which, from this small beginning, was to expand to a size and extent where its products now dominate modern society. This development had important implications for the environment, since it resulted in the preparation and discharge of relatively large quantities of synthetic organic substances, previously unknown to occur in nature and with unknown environmental effects.

Of course, chemical processes such as the smelting of ores and the manufacture of soap had been carried out on a large commercial scale prior to this time. But these processes were developed as a result of trial and error and were more in the nature of trade practices rather than the products of scientific chemical research.

Another chemist whose activities were to have important environmental implications was on the scene about this time: German scientist Fritz Haber (1868–1934). Haber demonstrated in the laboratory how nitrogen and hydrogen could be combined to yield ammonia. He further developed this on a commercial scale so that commercial plants operating in Germany in the early part of this century were fixing nitrogen gas from the atmosphere and producing ammonia. This ammonia could be used as a fertilizer for the production of food crops, thereby eliminating the need to rely on
TABLE 1.1
Use of Synthetic Chemicals in Human Society

<table>
<thead>
<tr>
<th>Substance</th>
<th>Examples of Chemical Classification</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastics</td>
<td>Polystyrene, polyvinylchloride</td>
<td>Textiles, car tires, household goods, furniture, etc.</td>
</tr>
<tr>
<td></td>
<td>polyprene, nylon</td>
<td></td>
</tr>
<tr>
<td>Pesticides</td>
<td>DDT, 2,4-dichlorophenoxyacetic acid</td>
<td>Control of weeds, insects, and other pests</td>
</tr>
<tr>
<td></td>
<td>(2,4-D), malathion, glyphosate</td>
<td></td>
</tr>
<tr>
<td>Drugs</td>
<td>Aspirin, penicillin, Valium, sulfanilamide, barbiturates</td>
<td>Medicinal uses</td>
</tr>
<tr>
<td>Petroleum products</td>
<td>Hydrocarbons</td>
<td>Motor fuel, lubricant</td>
</tr>
<tr>
<td>Crop fertilizer</td>
<td>Ammonia, ammonium sulfate, ammonium nitrate, ammonium phosphate</td>
<td>Stimulate food crop production</td>
</tr>
</tbody>
</table>

the natural occurrence of nitrogen compounds in soil to stimulate plant growth. This process has continued to be used to the present day, thereby allowing the production of large quantities of plant fertilizer used to produce food crops and allowing rapid expansion of the world’s population. Without this process, the production of food would be limited by the availability of natural nitrogen compounds in soil for food plant growth. Thus, this chemical process has probably had the greatest impact on the environment through the rapid expansion of the human population with the subsequent environmental changes that have resulted.

It is traditional for human history to be divided into a series of ages, each building on and improving the technology of the previous. Thus, we have a sequence of ages going from the Stone Age to the Bronze Age to the Industrial Age and the Atomic Age. However, during the last approximately 100 years, the age in which we are living could very well be described as the Chemical Age. Table 1.1 indicates the wide range of synthetic chemicals now used in human society. The use of these substances permeates almost every aspect of our society, from life in the home to transport, food production, availability of medicines, and so on. The production and use of these many substances have improved human conditions and caused an enormous increase in the human population. These factors have many implications for the chemical processes that occur in the environment.

1.3 ENVIRONMENTAL CHEMISTRY

Environmental chemistry is not new, but the use of this term to describe a body of chemical knowledge has become accepted by scientists in recent years. This principally reflects the importance attached to the behavior and possible adverse effects of chemicals discharges to the environment.

There are many scientific events that could now be identified as the starting points of environmental chemistry. Some of these are in the area of fundamental chemistry, while others lie in applied chemistry. Also, the chemical aspects of other disciplines have played a major role. One of the starting points has been mentioned previously: the work of Lavoisier. His analysis of air and determination of the nature
of combustion are fundamental to the development of modern chemistry and atmospheric chemistry. Turning to the applications of chemistry, perhaps pollution of the Thames River during the 1800s can be identified as another starting point of environmental chemistry. The bad odors and diseases associated with the Thames were investigated by various British Royal Commissions, which weighed evidence on the chemistry of sewage treatment and water pollution. This culminated with the Royal Commission on Prevention of River Pollution, which reported in 1885 and recommended the use of the biochemical oxygen demand (BOD) test. This test is still extensively used today to evaluate the effects of sewage and other wastewaters on waterways.

The chemistry of the oceans, lakes, and freshwater areas also has a comparatively long history. In 1872, HMS Challenger commenced its historic voyages with many of the most noted men of science at that time aboard. They conducted many investigations of seawater composition and chemical processes in the oceans. Similarly in limnology, the key to understanding the ecology of freshwater areas lies in chemical transformations of carbon, oxygen, nitrogen, and phosphorus. This was recognized early in the development of this discipline, which has always had a strong emphasis on chemistry.

Since these early beginnings, environmental chemistry has expanded rapidly. Natural chemical processes in all sectors of the environment, particularly soil, water, and the atmosphere, have been subject to investigation, as well as the environmental behavior of contaminating chemicals. Not surprisingly, the management of chemicals discharged to the environment has become a major focus for environmental chemistry. Governmental agencies and industries employ large numbers of environmental chemists on a worldwide basis to monitor and manage the discharge of chemicals and their adverse effects.

Over recent years, a body of knowledge associated specifically with the behavior and effects of chemicals in the environment has been developing. A theoretical basis for understanding the distribution, transformation, toxicity, and other biological properties of chemicals in the environment is now becoming established. This means that environmental chemistry can be appropriately seen as a subbranch or subdiscipline of chemistry. This is reflected in the availability of excellent textbooks on the topic as illustrated by those by Manahan (2001) and Schwartzbach et al. (2002). The recent development of environmental chemistry was initiated during the 1960s. Rachel Carson's book *Silent Spring*, published in 1962, can be identified as a significant event stimulating worldwide interest and concern regarding chemical residues in the environment. This event was made possible by the development of analytical techniques capable of detecting chemicals at very low concentrations. In 1952, Richard Synge and Archer Martin were awarded the Nobel Prize for inventing the chromatography technique, which has a principal application to the analysis of organic compounds. Later, the technique was extended and improved such that trace amounts of xenobiotic organic chemicals could be quantified in environmental samples. The flame ionization detector extended the sensitivity of the method so that levels of a few parts per million of organic compounds could be detected in samples. In addition, with the chlorinated hydrocarbons, the development of the electron capture detector further extended the sensitivity of the technique. In 1967, only 15 years after the Nobel Prize for chromatography was
awarded, a considerable body of information was available on the concentrations of xenobiotic organic compounds in biota.

Environmental chemistry was dominated at this time by the collection of data on residues of synthetic compounds in biota, but there was little understanding of the mechanisms, how the residues accumulated, or their biological effects. Determination of residue levels remains an important aspect of chemical behavior in the environment, but now there is considerable interest in placing residues in a broader context of environmental effects. There have been major advances in understanding the distribution, transport, and transformation of contaminants, as well as exposure and uptake by biota. But human health effects as well as the responses of natural ecosystems require further expansion of knowledge (Boethling and Mackay, 2000; Lyman et al., 1990).

Over the last 15 years, some theoretical concepts have emerged that provide a sound conceptual basis for important aspects of environmental chemistry. Drawing on ideas already established in other fields, the introduction of partition and fugacity theory to explain environmental distribution of chemicals has occurred. In addition, the use of properties measured in the laboratory to assess behavior and effects in the environment has allowed the development of a clear understanding of many environmental processes. Theoretical methods to predict environmental properties of chemicals have been placed on a sound footing and provide a basis for expansion of knowledge in the future.

The global problem of the greenhouse effect now occupies the center stage of environmental management. The environmental chemistry of the processes leading to this problem provides the starting point in its resolution. A range of different scientists have pointed out the importance of developing a mechanistic chemical model of the cycles of carbon and other elements and their interaction with the land and sea in devising strategies for management of this global problem.

1.4 THE SCOPE OF ENVIRONMENTAL CHEMISTRY

It is difficult to precisely define environmental chemistry since the topic has not yet reached a stage where there is universal accord in the chemical community on its scope. However, this is developing and the following definition provides a reasonably acceptable statement at this stage:

**Environmental chemistry** is the study of sources, reactions, transport, and fate of chemical entities in the air, water, and soil environments, as well as their effects on human health and the natural environment.

Environmental chemistry is probably the most interdisciplinary of the many branches of chemistry. It contains aspects of related branches of chemistry, such as organic chemistry, analytical chemistry, physical chemistry, and inorganic chemistry, as well as more diverse areas, such as biology, toxicology, biochemistry, public health, and epidemiology. Figure 1.1 represents a diagrammatic illustration of some of the major aspects of these relationships. To place the area in some perspective, a set of topics that fall wholly or partially within environmental chemistry are listed in Table 1.2. Many of these topics are concerned with chemical pollutants in the environment,
but environmental chemistry is not only concerned with pollution, but also with the behavior of natural chemicals in natural systems. This is exemplified by topics such as oceanic and limnological chemistry, which are primarily concerned with natural systems.

Investigations within the scope of environmental chemistry provide a possible explanation for our very existence. The primitive Earth’s atmosphere contained simple gases that, on equilibration, followed by subsequent complex reaction sequences, have led to the formation of proteins, carbohydrates, fats, and other substances that are the basic molecules needed for life to develop. Later processes in this sequence may have led to the formation of cells and then on to more complex life-forms. The mechanisms of these processes draw heavily on our present understanding of the fundamental properties of molecules and reaction mechanisms.

Environmental chemistry is basically concerned with developing an understanding of the chemistry of the world in which we live. Such investigations and knowledge have an intrinsic value of their own. Our world, with all of its many complex chemical processes, is a worthy topic for a well-rounded education and research. The chemical processes in soil, water, and the atmosphere are central to our existence, and through them we can better understand ourselves and our role in the environment. Thus, it could be argued that environmental chemistry should be a part


<table>
<thead>
<tr>
<th>Aspect of the Environment</th>
<th>Area within or Relevant to Environmental Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evolution</td>
<td>Chemical evolution</td>
</tr>
<tr>
<td>Chemical processes in sectors of the abiotic natural environment</td>
<td>Oceanic, atmospheric, soil, and limnological chemistry, global chemical systems</td>
</tr>
<tr>
<td>Chemical influences in natural ecosystems</td>
<td>Chemical ecology, pheromones, allelochemistry</td>
</tr>
<tr>
<td>Behavior of hazardous chemicals in the environment</td>
<td>Mathematical modeling of environmental distribution, degradation processes, waste disposal</td>
</tr>
<tr>
<td>Effects of toxic chemicals on individuals, populations, and ecosystems</td>
<td>Environmental toxicology, ecotoxicology, quantitative structure-activity relationships (QSARs), environmental analysis</td>
</tr>
<tr>
<td>Effects of chemicals on human populations</td>
<td>Environmental health, safety, occupational health, epidemiology</td>
</tr>
</tbody>
</table>

of the chemistry curriculum wherever chemistry is taught. At a tertiary level, graduates in chemistry are in fact now expected to be familiar with many aspects of environmental chemistry. They are being asked by management in industry and within government to advise on the environmental and health effects of chemicals, management and safety of chemicals, and so on.

1.5 CHEMISTRY IN ENVIRONMENTAL MANAGEMENT

There is little doubt that the principal applications of environmental chemistry are in the development of an understanding of the behavior and effects of discharged chemicals on human health and the natural environment. When chemical use results in environmental contamination, it is necessary to set standards for acceptable concentrations in water, air, soil, and biota. Monitoring of these concentrations, and the resultant effects, must then be undertaken to ensure that the discharge standards are realistic and provide protection from adverse effects. Also, considerable attention is now being focused on regulation of the use of new chemicals and prevention of chemicals that may have adverse effects from entering the marketplace and environment. Most of these actions are undertaken by government and industry, for example, the disposal of chemical wastes generated in highly concentrated form, as well as occurring as trace contaminants in discharges. These chemical management issues involve political, social, and economic problems as well as technical problems, and many new approaches to management will be needed. On the other hand, new industrial processes that generate less chemical waste will be required. Some of the activities undertaken in government agencies and industry, within the scope of environmental chemistry, are outlined in Table 1.3. In addition, there is a considerable
TABLE 1.3
Some Activities of Government and Industry Related to Environmental Chemistry

<table>
<thead>
<tr>
<th>Objective</th>
<th>Some Actions Taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>Management of industrial emissions</td>
<td>Setting emission standards, monitoring ambient concentrations, disposal of waste, modeling distribution of chemicals</td>
</tr>
<tr>
<td>Protection of workers' health</td>
<td>Biochemical and physiological testing, epidemiology, monitoring ambient concentrations, evaluation of adverse effects</td>
</tr>
<tr>
<td>Protection of the natural environment</td>
<td>Monitoring contaminants in water, air, soil, and biota, evaluation of adverse effects</td>
</tr>
<tr>
<td>Testing and evaluation of new chemicals</td>
<td>Modeling of potential distributions, testing toxicity and other effects</td>
</tr>
</tbody>
</table>

volume of research in environmental chemistry being undertaken. A number of well-established research institutions specializing in environmental chemistry are operating in countries throughout the world.

Environmental chemistry activities in government, industry, and education are growing, to some extent in concert with the concerns expressed regarding chemicals in the environment by the community. At present, despite the enormous benefits that accrue from the many uses of chemicals, the community often sees chemicals as having a negative impact. A negative impact has occurred in many situations, but many of these have been eliminated and increased knowledge has provided a basis for enlightened future management and control. The further development of environmental chemistry will provide access to chemical products that will enhance the lives of people without resulting in detrimental effects. In this way, environmental chemistry will have a significant effect on the future of chemistry, chemists, and the chemical industry, as well as the community in general.

1.6 BASIC CONCEPT OF THIS BOOK

In the early 1970s, a new approach to explaining the environmental effects of chemicals was initiated. Hamelink and coworkers (1971) proposed that the bioaccumulation of organic compounds by biota was governed by the properties of the chemical rather than ecological factors, as was previously thought. Since that time, this concept has been extended considerably, and now it is clear that the distribution of chemicals in the environment relates to the properties of the chemical as well as characteristics of the environment (see Mackay et al., 1992).

The relationship of biological effects, particularly toxicity, to properties of a chemical, such as the olive oil–water partition coefficient, was well established by Ernest Overton in the early 1900s and extended by Covin Hansch during a later
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CHARACTERISTICS OF THE MOLECULE
(eg. surface area, molecular weight, functional groups, chemical bonds etc.)

PHYSICAL CHEMICAL PROPERTIES OF THE COMPOUND
(eg. aqueous solubility, vapour pressure, melting point, octanol/water partition coefficient etc.)

TRANSFORMATION & DISTRIBUTION IN THE ENVIRONMENT
(eg. persistence, bioaccumulation etc.)

BIOLOGICAL EFFECTS
(eg. lethal toxicity, reduction in growth, reduction in reproduction etc.)

FIGURE 1.2 The environmental chemistry of a chemical can be seen as an interrelated set of characteristics, as shown.

toxicity and other effects of chemicals in the environment. In addition, the influence of characteristics of the molecule itself, such as molecular surface area, was found to be of considerable significance.

A concept of an interdependent set of properties of a chemical has now developed, as shown in Figure 1.2. This has been used as the basic underlying concept of this book. The basic characteristics of the molecule itself are the starting point for understanding the environmental chemistry of chemicals. These characteristics govern the physical-chemical properties of the compound, such as its aqueous solubility and vapor pressure, which in turn control transformation and distribution in the environment. Biological effects relate to the chemical in its transformed and dispersed state. This set of interrelationships also provides a basis for predicting the environmental properties of a chemical. The distribution, transformation, and some biological properties can be predicted in many situations utilizing physical-chemical properties.

This concept provides a framework into which aspects of the environmental characteristics of a chemical can be logically placed. It allows these many diverse environmental characteristics to be rationalized into a set of relationships, rather than be seen as a disorganized collection of facts.
1.7 KEY POINTS

1. The alchemists were the earliest practitioners of applied chemistry, but alchemy was more of an art than a science. Many alchemists were concerned with mysticism and the transmutation of base metals such as lead into gold.

2. Environmental chemistry had an early beginning with Antoine Lavoisier, a French scientist born in Paris in 1743. Lavoisier combined classical experiments on the composition of air and its use by animals to investigate the chemical nature of the atmosphere.

3. The commercial application of chemical knowledge derived from laboratory experiments was commenced by William Perkin in the late 1800s. Perkin founded the synthetic dye industry, which was the forerunner of the large and diverse synthetic chemical industry of today.

4. Perhaps one of the most important environmental applications of chemical knowledge has been the development, by Fritz Haber in the early 1900s, of a commercial process to combine atmospheric nitrogen with hydrogen to produce ammonia. This allowed the manufacture of artificial fertilizers to enhance food crop production and the expansion of the human population.

5. The term environmental chemistry has become common only in recent times, although environmental aspects of chemistry have been investigated since the beginning of chemistry itself.

6. Environmental chemistry is the study of the sources, reactions, transport, and fate of chemical entities in air, water, and soil environments, as well as their effects on human health and the natural environment.

7. Over the last 15 years, theoretical concepts of the distribution, behavior, and effects of chemicals in the environment have been developed that provide a fundamental understanding of these processes.

8. Environmental chemistry plays a major role in government and industry in relation to many areas, including management of industrial emissions, protection of workers’ health, protection of the natural environment, and testing and evaluation of new chemicals.

9. The environmental properties of a chemical can be seen as an interrelated set of properties based on the characteristics of the molecule. These characteristics govern the physical-chemical properties of the compound, which in turn control transformation, distribution, and biological effects in the environment.

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QUESTIONS

1. The terms Stone Age, Bronze Age, Industrial Age, and Atomic Age are
   used to describe phases of knowledge and technology that human civil-
   izations have passed through. Why is the term Chemical Age appropriate
   for today’s society?
2. The applications of chemistry in industry have had a major effect on
   human society. Which chemical applications have had the greatest impact
   on the human and natural environment?
3. Environmental chemistry has developed from a diverse field of investiga-
   tions conducted in relation to the environment. Which of these areas of
   investigation have been the most important in influencing the scope of
   environmental chemistry as it is perceived today?